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FACULTAD DE QUÍMICA

“Powder In-Mold Coatings with self-releasing properties for Class A Surface Finishing of Fibre Reinforced Plastics”

“Desarrollo de recubrimientos con propiedades autodesmoldantes para la consecución de acabados Clase A en materiales compuestos de matriz polimérica reforzados con fibras”

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Departamento de Ingeniería Química
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In collaboration with TIGER Coatings GmbH & Co KG

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CERTIFICAN:

Que Don Daniel López Valero ha realizado su Tesis Doctoral titulada "Desarrollo de recubrimientos con propiedades autodesmoldantes para la consecución de acabados Clase A en materiales compuestos de matriz polimérica reforzados con fibras utilizados en aviación y automoción" en esta Universidad y bajo la tutoría de los abajo firmantes.

Y para que conste a los efectos oportunos firma la presente en Murcia a 8 de mayo de 2015:

Fdo. Antonia Baeza Caracena
Fdo. José Manuel Palazón Espinosa

Mag. Christoph Mader, team leader of the Powder In Mould Coating-Team in the R&D Department of TIGER Austria and the direct supervisor of this project

CERTIFY:

That Daniel Lopez Valero; with ID 48630267-X has realized his Doctoral Thesis entitled "***Powder In-Mould Coatings with self-releasing properties for Class A Surface Finishing of Fibre Reinforced Plastics***" in this Department and under my supervision:

Wels; 29th of April, 2015.

Christoph Mader

Mag. Christoph Mader

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I want to start this section clarifying that during the journey towards the completion of this thesis, I am grateful for all the support and encouragement I have received from many important people.

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Para el final de este texto dejo a los que, sin ninguna, duda son las personas más importantes en mi vida: mi Familia. Dentro de estos me gustaría destacar a mi madre (quien más ha sufrido la distancia) y por supuesto a todos mis tíos, tías, primos y primas, sin por supuesto olvidar a la abuela. Una familia tan grande y unida es lo que nunca se olvida.

ABSTRACT

PiMC is a new technique that, in connection with RTM, SMC, BMC or pre-preg, is able to produce FRP with Class A surface finishing. This technique has many advantages, reason why is starting to be implanted industrially; however, it can be improved. In fact, the method requires the application of releasing agents on the metallic mould. These releasing agents are required to separate the FRP from the metallic mold where the composite is produced.

Along this study, are developed several formulations with self-detaching properties. This will be achieved through the modification of the production process and the successful additivation. The inclusion of these new additives in the formulations offers different and varied situations, as is explained in this thesis.

Keywords: PiMC, composites, FRP, coatings, powder coatings, thermosetting, additives, adhesion, RTM, SMC, BMC, pre-preg, internal releaser, VOC´s, polymers, surface treatment, Class A.

RESUMEN

La variada industria relacionada con el sector de los polímeros está en constante desarrollo; y de hecho, nuevas formulaciones con mejores prestaciones llegan prácticamente a diario al consumidor final en forma de viscoelásticos más resistentes, tintas inteligentes o bolsas biodegradables.

Con la optimización de las propiedades de estos productos; debido principalmente a una adecuada adición de aditivos y al desarrollo de las técnicas de procesado, no sólo se alcanzan artículos de mayor calidad, sino también ampliar el campo de sus aplicaciones. Y es en este punto donde la tesis doctoral se centra: desarrollar una nueva aplicación para recubrimientos (powder coatings).

En primer lugar, cabe destacar que esta pintura seca es tradicionalmente utilizada como recubrimiento de superficies. Este recubrimiento sirve para, o bien proporcionar un determinado aspecto físico (color/brillo), o bien para proteger de ataques medio ambientales, como puede ser la oxidación. Ambas aplicaciones pueden darse a la vez. De hecho; este tipo de formulaciones vienen a ser llamados los recubrimientos del futuro debido a sus múltiples cualidades, como son: óptimas propiedades estéticas, sostenibles para el medioambiente, económicos en grandes procesos productivos, gran facilidad de manipulación…

El trabajo desarrollado en esta tesis trata de mejorar las características de recubrimientos con poder autodesmoldante (Powder in Mold Coatings, -PiMC-). Esta tecnología reside en utilizar estos recubrimientos como agente de relleno en la producción de material compuesto polimérico (composites) obteniendo acabados de primera calidad (los denominados acabados de Clase A).

Actualmente, PiMC se utiliza para la producción de materiales plásticos de bajas calidades, sin embargo, ya está prevista su futura implantación para otro tipo de materiales más exclusivos. Empresas como BMW, Aston Martin, AUDI o FACC están mostrando un alto interés en esta tecnología. La reducción del tiempo necesario en la producción del producto si se utiliza esta tecnología está valorada en, al menos, un 70%. Este porcentaje se ve aumentado en caso de piezas con formatos especiales (piezas de carrocería de vehículos y aviones, etc…). Con esta nueva técnica no es necesario el proceso de pulido, limado, alisado y

perfilado en la superficie donde es aplicada, que en este caso se trata de materiales reforzados con fibras.

Hoy por hoy, hay formulaciones en el departamento de I+D+i de la empresa austriaca Tiger Coatings, lugar donde se desarrolla íntegramente la parte experimental de este trabajo, útiles para ser aplicados mediante PiMC junto a SMC, BMC, pre-preg y RTM. Sin embargo, estas formulaciones son susceptibles de mejora, pues hasta el momento, las mismas no poseían propiedades liberalizadoras de desmolde sobre el soporte metálico donde se fabrican los composites.

Esta dificultad puede ser solucionada con la aplicación de una serie de agentes liberalizadores (normalmente Compuestos Orgánicos Volátiles, -VOC’s-) sobre el molde de aluminio en el que el composite se fabrica. No obstante, esto implica que PiMC pueda perder parte de su atractivo para los grandes productores debido principalmente a que:

1. Hay que aplicar el agente liberalizador sobre el molde metálico y esto conlleva la ralentización del proceso de producción.
2. Es necesario una etapa posterior de tratamiento del composite tras su fabricación. Se debe limpiar para eliminar los restos de estos agentes liberalizadores de la superficie. En caso negativo no se podría aplicar el recubrimiento superficial (top coating), el cual consta de dos capas superpuestas; una para conseguir el color y otra para conseguir el brillo deseado en el producto final.
3. Deja de ser un proceso 100% sostenible para el medioambiente, dado que se produce la emisión de COV´s. Esto conlleva medidas extra de prevención sobre los trabajadores, pérdida de certificaciones medioambientales, mala imagen pública...

Por todos estos motivos, se consideró para este trabajo, desarrollar una formulación con propiedades desmoldantes que provoquen la liberación de la pieza plástica sin la necesidad de agentes liberadores externos. Este diseño con propiedades desmoldantes es de gran utilidad práctica para la producción vía SMC (Sheet Moulding Compound), BMC (Bulk Moulding Compound), pre-preg y RTM (Resin Transfer Moulding) y cabe destacar su transcendencia, dado que todavía no existe en el mercado una formulación con estas características.

Con esta investigación se cubre prácticamente la totalidad de los composites producidos en la industria aeronáutica y de automoción. Fueron estudiadas:

1. Cinco formulaciones de naturaleza muy distinta: una epoxi, una poliéster, una acrílica y dos epoxi self-curing. Desde el punto de vista práctico, resulta muy interesante (aunque no totalmente necesario) que el FRP producido y el powder coating aplicado mediante PiMC pertenezcan a la misma familia química.
2. Siete aditivos desmoldantes o liberalizadores de química bastante dispar: una sal metálica, un ácido orgánico sólido o una bio-cera entre ellos.

Se estudió también el rango de temperaturas de ensayo que intenta cubrir la mayor variedad de producción posible: 110 ºC y 160 ºC.

Una vez que estos factores fueron analizados, se pasó a considerar una metodología útil para poder comprobar si existía una posible reducción del nivel de adhesión logrado. Debido a la falta de normativa en el sector, pues esta técnica todavía no está en uso, se desarrolló una metodología de ensayo propia. En la misma se tuvo en cuenta las condiciones especiales que rodean la producción de estos recubrimientos (FRP).

Este método consistió en recubrir de powder coating un soporte metálico de aluminio de un grosor especial (para poder resistir el test de adhesión), fijar en la superficie unas sujeciones, aumentar la temperatura hasta el valor al cual se produce el composite y aplicarle el test anti adhesión (Pull-off test).

Tras definir todas estas variables que tiene en cuenta esta tesis, cabe centrarse en el desarrollo experimental: en primer lugar se analizó cada una de las cinco bases madre seleccionadas (esta selección se realizó en base a los estudios previos realizados por la empresa Tiger Coatings). Estas bases se denominaron en clave: AT 3.1, AT 3.2, AT 3.3, AT 3.4 y AT 3.5 (codificadas en este trabajo por ser material susceptible de patente y propiedad intelectual de Tiger Coatings pero cuya composición genérica se especifica más adelante). Esta última base, AT 3.5, tiene carácter acrílico, y fue escogida considerando que en un futuro próximo la aplicación de recubrimientos (top coating) no será necesaria gracias a esta técnica de imprimación (PiMC); hecho alcanzable a medio plazo.

Estos primeros ensayos con los cinco diseños nos han permitido observar las características necesarias para PiMC. Entre las propiedades examinadas destacaron las siguientes:

- fluidez
- distribución de tamaño de partículas
- parámetros de curado
- resistencia mecánica
- parámetros de impresión

Tras esta etapa, se ha desarrollado un total de 35 formulaciones diferentes combinando las 5 bases y los 7 aditivos. Todas estas formulaciones buscan las mejores propiedades desmoldantes o liberadoras. Para esto, se tuvo en cuenta de forma muy especial todos los parámetros relacionados con la premezcla o la extrusión específica que se precisa en el proceso de fabricación de estos materiales.

Entre estas formulaciones, como se comentará a continuación, hay todo tipo de resultados. Unos de gran aplicabilidad práctica y otros que descartan futuras investigaciones con esa combinación de materiales. Las formulaciones se presentan agrupadas en función de la formulación madre para un mejor entendimiento.

A continuación se presenta un resumen de los resultados obtenidos con las mismas.

AT 3.1 Y REFORMULACIONES:

En el límite inferior de temperatura (110 ºC) los resultados hallados para estas formulaciones epoxi son bastante negativos. En cinco de los siete casos, la adhesión, lejos de disminuir, aumenta. Además, no se produce un desmoldado limpio. Este hecho implica que no se pueda alcanzar un acabado de Clase A.

Respecto al límite superior, 160 ºC, los datos tampoco mejoran. Pese a que la adhesión es bastante baja, ninguna formulación consigue ser lo suficientemente desmoldante como para acabar con las pequeñas partículas que quedan sobre el molde metálico.

A temperatura ambiente se observa que cuatro de las formulaciones pierden parte de su estabilidad; hecho bastante negativo. Sin embargo, en tres de ellas, disminuye la adhesión de una forma limpia, es decir, la fuerza de unión con el molde metálico. Pese a esos últimos valores, a estas temperaturas tan bajas los clientes no están interesados en el producto. Se considera el ensayo no exitoso.

AT 3.2 Y REFORMULACIONES:

En estas creaciones de tipo poliéster se vuelve a observar una pérdida de estabilidad (en formulaciones codificadas como AT 4.11 y AT 4.12) debido a, en este caso, la aplicación de una sal metálica (codificada como IR 2). Además, se comprueba como en función de la temperatura dichos aditivos pueden variar su rendimiento. Pese a lo anterior, **particularmente positivo es el valor de AT 4.10 a 110ºC de temperatura (0,56 MPa de presión). Es un valor que puede ser llamativo para la industria; además, el desmolde es perfecto. Este diseño realizado con un ácido orgánico de fuerte carácter polar fue seleccionado para un minucioso examen al final del estudio.**

AT 3.3 Y REFORMULACIONES:

La mezcla de una resina “auto-entrecruzable” (self-crosslinking) y un catalizador puede provocar una polimerización desordenada y catastrófica; sin embargo, esta unión provoca el ensayo más exitoso de toda la investigación. **AT 4.17 y AT 4.18 presentan un interesante comportamiento a 110 ºC (0,50 MPa y 0,65 MPa respectivamente).** A mayores temperaturas estos valores mejoran hasta ser prácticamente cero. Realmente las probetas no pueden ser tratadas pues el recubrimiento se despega del soporte con gran facilidad. Además, el powder coating se comporta como una lámina. Esta, cuando comienza a despegarse, se libera por completo del soporte metálico; siendo este hecho muy útil para una futura automatización del producto. La superficie del powder coating es perfecta y copia exactamente las características del molde.

Como conclusión a este punto, se puede afirmar que compuestos tan diferentes como una sal de un ácido graso (IR1) o una sal metálica (IR2) dan resultados similares y bastante positivos. De este ensayo se seleccionaron las formulaciones AT 4.17 y AT 4.18 para ser estudiadas como posibles productos a comercializar.

AT 3.4 Y REFORMULACIONES:

En este caso se ha estudiado una resina epoxi de carácter self-crosslinking (distinta de las del apartado anterior) y es el primer caso en el que ninguna de las formulaciones pierde la estabilidad fisicoquímica. Los aditivos influyen sin romper el delicado equilibrio.

Sin embargo, en general, los valores de adhesión no parecen disminuir; incluso hay algunos casos donde aumentan a temperatura ambiente. Otros casos no pueden ser exactamente determinados debido a una mayor integración del recubrimiento con el soporte metálico que con los distintos pegamentos para fijar el soporte. Pese a esto, todos los valores son bastante altos por lo que se abandonó la idea de buscar su valor óptimo. De todos modos, la formulación AT 4.26 presentó valores medianamente buenos; por lo que se consideró conveniente analizarla en profundidad.

AT 3.5 Y REFORMULACIONES:

En este grupo se estudiaron formulaciones que contenían una base acrílica. Casi todos los resultados obtenidos han sido bastante negativos. Todos excepto en **el diseño AT 4.33**. Esta fórmula, además de ofrecer una mínima adhesión, se comporta de forma auto desmoldante. Es decir, **se separa del soporte metálico de una forma excepcional**: una vez comienza la separación, esta no se puede parar hasta que la pieza queda liberalizada por completo. Este suceso es similar al ofrecido por las formulaciones AT 4.17 y AT 4.18. Destacar que este diseño tiene un valor especial debido a que se realizó pensando que, gracias a un desarrollo extra y futuro, se podrá reemplazar por el top coating. Por todos estos motivos, AT 4.33 se seleccionó para un análisis más exhaustivo.

Una vez se conocen los valores de adhesión de todos los ensayos, se distinguen las mejores formulaciones de las 35 desarrolladas con propiedades desmoldantes: AT 4.10, AT 4.17, AT 4,18; AT 4.26 y AT 4.33. Estas has sido analizadas en profundidad y todas las características halladas han sido bastante buenas. En ninguna de ellas se ha apreciado una variación en los parámetros de curado o de resistencia química; al menos no lo suficientemente importante como para descartarlas. Cabe destacar que de los siete aditivos analizados, sólo dos han llegado a esta fase final: los denominados IR 1 e IR 2.

Un hecho bastante positivo de estas cinco formulaciones es que cubren un amplio rango del sector: temperatura de trabajo bastante amplia (110 ºC-160 ºC), útiles para SMC, BMC, pre-preg y RTM y, por supuesto, diversidad de sustratos en donde ser aplicadas: polyesters, resinas epoxy y materiales compuestos acrílicos. Estos tres factores provocan una ampliación del mercado bastante importante.

Por todo lo anterior, estas formulaciones serán ofrecidas a potenciales clientes con la idea de ser comercializadas a nivel industrial en un futuro inmediato; siendo este el principal objetivo práctico de este trabajo.

Keywords: PiMC, composites, FRP, recubrimientos, Clase A powder coatings, aditivos termoestables, adhesión, RTM, SMC, BMC, pre-preg, liberalizadores internos, polímeros, tratamiento de superficies.

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µm: micrometers

1k: 1 component

2k: 2 components

AS/NZS: Australian/New Zealand Standard

ASTM: American Society for Testing and Materials

AT: Adhesion test

BMC: Bulk moulding compound or bulk molding composite

GFC: Glas Fiber Composite

DIN: Deutsches Institut für Normung

DSC: Differential scanning calorimetric

FRP: Fibre-reinforced plastic or fibre-reinforced polymer

FWHM: Full Width at Half Maximum

HAPs: Hazardous air pollutants

IMC: in mould coating

IR: Internal releaser

ISO: International Organization for Standardization

JIS: Japanese Industrial Standards

Mc: Molecular weights between the cross-links

MDF: Medium-Density Fiberboard

MPa: Mega Pascal

PiMC: Powder in-Mold Coating process or Powder in-Mold coatings

Psd: Particle size distribution

Psi: pounds per square inch

R&d: Research & Development

RTM: Resin Transfer Moulding or Resin Transfer Molding,

SMC: Sheet Moulding Compound

T: Temperature

t: time

T_g: Glass transition temperature

TGIG: Triglycidyl Isocyanurate

VA-RTM: Vacuum Assisted Resin Transfer Molding

VIP: Vacuum Infusion Processing

VOC´s: Volatile Organic Compounds

WPC: Wood-Plastic-Composite

I. INTRODUCTION

I. INTRODUCTION

Nowadays, polymers in the market appear in a wide range of formulations and properties achieved through the meticulous selection of a polymeric base (such as elastomers, thermosetting and thermoplastics) and additives. These mixtures polymer-additive are ultimately reached by the consumer in ways as diverse as plastic bags, paint, glue or mattresses.

Despite that only a handful of polymers are used in its pure form and they practically always require chemical modification to acquire optimum properties and to be able to obtain the varied characteristics required by the demanding society. Some of these include improving resistance to oxidation, high temperatures, flammability, impact loads or ultraviolet radiation. Among those modifications of an extensive range of properties, this project is focus on removing adhesion properties.

Regarding thermosetting, the properties depend on numerous factors such as chemical structure and crosslink density of the resin, type of curing agent, type and amount of filler, pigment content and additives (L.W. Hill. 1992). In fact, these elements are combined to improve their properties by companies over the entire planet. However, the inclusion of an additive in an organic polymer matrix can produce the opposite fact; it is the deterioration of their physical and chemical properties.

Moreover, production process may selectively degrade different additives. It is required that processes are developed and validated by functional testing of the final compound. Mixing methods must be very carefully controlled to assure consistent quality. Variations in compound quality can have an adverse and varying impact on components prepared from the compound.

In conclusion, it is essential that all ingredients added to a polymer, in this case a powder coating formulation; remain in the compound in a manner that assures functionality.

I.1. BASIC FEATURES OF THE PROJECT

To understand the importance of this project, it is noted that Global demand on powder coatings was valued at approximately US$5.8 billion in 2010 and is expected to grow by 6% in the coming years (acmite. 2011). In fact, there are innumerable everyday uses for powder coated products, and, thanks to development of that, powder coatings can have more applications and be more useful for the general public.

Indeed, in this project, it seeks to achieve a new application: ***Powder coatings with self-releasing properties, which are applied as in-Mould-Coatings primers for class A automotive composites or aeronautics composites.***

In this study we will try to find the best combination of internal releaser and its concentration for different powder chemistry bases. The tests will be performed at 110°C and 160°C to illustrate the environment apparent during various production technologies. These temperatures cover the main range of manufacturing temperatures of the production of composites for which the project is carried out.

Firstly is necessary to know that PiMC is still not used industrially to manufacture Class A finished surfaces; however, it is a future reality. The inclusion of a property related to demolding favors the characteristics of this technology; a technology with a big future.

Advantages of Powder coating, in general, are quite numerous, including:

- They are the most environmentally “friendly” coatings that currently exist in the business. They do not contain solvents that could release hazardous air pollutants (HAPs). In fact, powder coatings release very low amounts of volatile organic compounds (VOCs) and contain very few harmful chemicals. Moreover, they produce practically no waste material.

- Powder coating overspray can be recycled and thus it is possible to achieve nearly 100% use of the coating.

- Fewer storage spaces are required for powder if they are compared to other kind of paints (liquid paints).

- Great resistant to abrasion, scratching and chipping. They are high quality products with enjoyable properties of toughness, durability and hardness. In addition, they are robust mechanical and chemical performing - worthy at resisting abrasion, acids, solvents, etc.

- Owing to viscosity adjustments are not necessary, powder coatings are very useful for continuous and automatic processes.

- Really good turnaround times, a fact truly useful in manufacturing.

- Clean working conditions for workers, simple clean-up and maintenance.

- Thick coatings are easily achievable, without problems related to sap or drip.

- Few variations to produce consistent color and appearance of the final product for allowing homogenization of manufacturing.

- The number of colors available is practically infinite. Powder suppliers offer a huge variety of brightness, texture and irradiancy which produces a large variety of optical effects.

- Exceptional gloss and color preservation.

- Complete coverage ensured credit to the electrostatic powder application process, including complex shapes, and possibility of choice of finishes with different textured like metallic, smooth, clear…

The continuing success of powder coatings is not only due to their known ecological and economic (among others) advantages but also to their improved performance and the variety of substrates on which can be applied (E.G. Belder, H.J.J. Rutten, D.Y. Perera. 2001). In fact; in this R&D project is considered a non-usual substrate: an organic composite necessary in the automotive and aeronautic industry; a FRP (Fibre Reinforced Plastic or Fibre Reinforced Polymer).

All these features, shown above, are the reasons why this product is so keen for the industry. However, *this project will not seek to improve these properties, but is aiming to offer new properties*.

I.2. GOAL OF THE PROJECT

The goal of the research in this thesis is to obtain a powder coating formulation with further requirements:

1. Useful for PiMC.
2. Coating thickness between 50 to 800µm adjustable.
3. Powder fills crudity (pores, uneven woven fiber surfaces, other defects).
4. Chemical bonding between powder system & composite matrix.
5. Very good adhesion between the powder coat and the composite resin.
6. Good releasing or self-detaching properties from the mold when the press is opened.

The five first steps are already succeeded by the viable R&D team of the company, so this thesis will focus in the sixth point, trying not to take apart the delicate balance of the first five points. This kind of product is still far from reaching by customers; therefore the possibility of Technology Watch is not valid.(Just the companies Adapta Color, Raschig GmbH and Protech/Oxyplast Group owns “crop” in the field; however, it is not focus in automotive and aeronautic business).

In PiMC technology, powder coatings are used to fill up the surface of high-quality composites and that way avoid the expensive steps of brushing, scraping, chipping or sanding the surface. Just a slow sanding and a quickly surface cleaning is necessary due to the external releaser; sometimes not even that sanding.

In case of achieving this landmark, the time required in the whole process (in production of composites class A surface finishing) can be reduced **up to *70%,*** and consequently the costs.

This point will be explained deeply in chapter II; but, in conclusion, TIGER Coatings GmbH & Co KG has obtained some formulations useful for PiMC technology. These formulations will be introduced in the market during the next years; but there is an extra property that can make more attractive this tool: loss of adhesion between composite and mold where it is produced. And this project is involved in getting this formulation; still lacking (non-existent) and with wide applicability.

I.3. OUTLINE

This thesis memory is divided into 7 Chapters and 5 Annexes. Firstly appears a basic introduction in order to familiarize the reader with the context. Here will be explained basic characteristics and also will be listed all the steps development during the project.

In chapter II, the reason why this project is realized has been clarified. It discusses the pros and cons of PiMC technology with releaser properties and the reasons why several aeronautical and automotive companies as Aston Martin, AUDI, BMW or FACC are interested in the same.

In chapter III a deep review on the knowledge related al project is exposed. On the same is discussed about Class A surface finishing, powder coatings production, PiMC technology and adhesion; among other essential topics related to the project.

Subsequently, in chapter IV, the material used is specified and the experimental method development for checking adhesion properties is described. This method was specially developed for this project (there are no regulations related; neither standardization in the market). This test took into account all knowledge of Tiger Coatings GmbH and customer requirements. Remember that the real purpose of this work is the attainment of an attractive product for the consumers.

Continue with the project, the chapter V called “Results and discussion”; which is subdivided in three parts: selection of base formulation, re-formulation with mold release properties and checking the suitability of the best creations.

Chapter VI deals with the most relevant conclusions of the project and the work is put into a broader perspective.

Finally, is placed the Bibliography and the five Annexes.

I.4. GRAPHICAL REPRESENTATION OF WORKING PACKAGES (WP’S)

In order to achieve the projects objectives, the work has been structured into Work Packages (WP’s) which are subdivided into Tasks (T).

WP 1: Literature review

- Powder coatings
- SMC/ BMC and others composites
- Surface modifications
- Adhesion
- Internal Release Agent
- PiMC

WP 2: Definitions of requirements/ specifications

- Industrial characteristics assessment
- General physical properties required (durability, toughness…)
- Demould properties required
- PiMC properties required
- Valorization for industrial application

WP 3: Selection of Materials, Pre-treatment Techniques, Test and Methods

- Selection of internal releasers
- Characterization techniques, Test and Methods
- Regulations

WP 4: Evaluation of different powder chemistry bases

- Polyester resin/ Epoxy resin/ Acrylic resin
- Preparation of first benchmark powders (without internal releasers)
- Estimating its suitability at process temperatures (110°C – 160°C)

WP 5: Preparation of the different base systems with highest recommended concentration of 7 internal releasers

- Conducting first adhesion tests
- Stability Analysis (with internal release agents)
- Acquiring the results and defining a minimum release improvement for Powder samples next step

WP 6: Optimization of the best results obtained during the previous step

- Repetition of the best adhesion essays with different concentrations
- Exhaustive Quality Control of the physic-chemical properties

II. OBJECTIVES

II. OBJECTIVES

The main objective of this doctoral thesis called **“Powder In-Mold Coatings with self-releasing properties for Class A Surface Finishing of Fibre Reinforced Plastics”** or **“Desarrollo de recubrimientos con propiedades autodesmoldantes para la consecución de acabados Clase A en materiales compuestos de matriz polimérica reforzados con fibras utilizados en aviación y automoción”** is to achieve a PiMC formulation which is capable of having mold release properties by itself, and, this way, eliminating the necessity of external release agents on the metallic mold in the production of composites.

Major producers in different sectors, such as automobile, aeronautics, toys or furniture business like AUDI, BMW or FACC are very interested in pursuing these powders coating owing to it can offer great benefits in theirs productions, which will be listed at the end of that chapter.

PiMC technology is still in an experimental step. Although there are many benefits for his application; at this time can be found two topics still for improve:

- Important initial financial investment for establishing the process. There is still no engineering design created to development a production process. This is solved by saving production costs in finishing surfaces A manufacturing in a fairly rapid way.
- Necessity of external releaser agents, whose disadvantages are set forth below in the next paragraphs:

The utilization of internal releaser on the metallic mold means, at least, the total elimination of a cleaning treatment in the production of Class A surface finishing. It is because of rests of external demold agents remain on the FRP surface and it incites wetting problems. These wetting problems mean a bad top coating impression; and with that; the desired surface finishing coating cannot be reached due to colorimetric complications.

Moreover, these external releaser agents may be able to raise small spots on the surface (it depends on the case); reason enough to be necessary a slow sanding or powerful washing.

In addition, the use of external releaser causes another extra step in the production. It is, obviously, its application on the metallic mold. This translates directly into loss of time, and time is always related to production efficiency and money. (These processes are slowed because it is necessary to apply external mold release on the metal –mainly aluminum or iron-mold where the composite part is going to be synthesized).

The consequences of getting this type of releaser properties in a powder coating formulation can be really beneficial in PiMC technology. Despite these problems, do not forget that PiMC is the future and, with or without demold properties, it saves processing steps associated with the post surface treatment: brushing, scraping, chipping and sanding; and it can be the 70% of the time in the production of FRP.

II.1. ADVANTAGES

To summarize the entire chapter, benefits of obtaining a powder coating formulation with mold release properties will be listed in two potential groups, Economic and Environmental factors:

II.1.1. Economic advantages

- Deleting the step or stage of placing an external releaser on the mould in the production of high quality composites.
- The elimination of a step related with the post treatment surface. The post cleaning step is for sure removed due to there is no place for wetting problems. Moreover, is probably necessary other post treatment step; a slow sanding of the surface. (The total elimination of post surface treatments, which means more than 70% of the time required to produce this kind of material suppose an important saving).

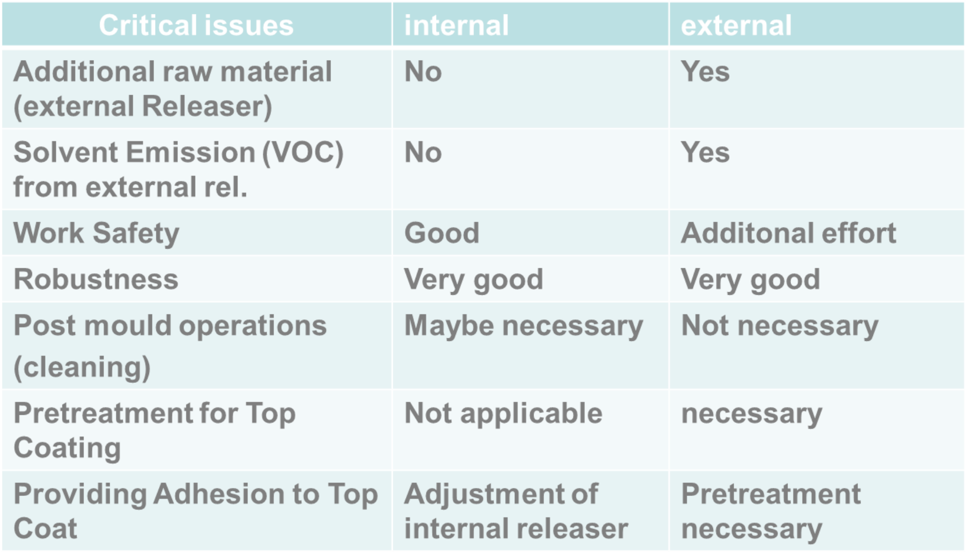
Achieving these release properties in powder coatings convert technology PiMC in a rather advantageous position over other composites production systems that currently exist in the market, ideally complementing SMC, BMC, pre-preg or RTM.

II.1.2. Environmental advantages

- External release agents, besides being unhealthy, are corrosive to the environment. Considering this improvement, PiMC can be considered a process really environmentally friendly.
- Reduce of waste of energy owing the surface post treatment is not required.
- Stop using external release agents, which are usually associated with organic compounds harmful to health, which is why these regulations force companies to spend large amounts of money in protecting their workers.

In conclusion to this section, this R&D project will be based in adding organic and inorganic ingredients to thermoset polymers to achieve a powder coating formulation with mold release properties which can be used in PiMC technology. Avoidance of external releaser application will give great advantage to Powder In Mould Coating Technology and will increase its competitiveness. The results of this project will be a ground for final product formulations. The Table II.1 resumes the critical issues that can be reached with this project.

Table II.1 Internal releaser vs external releaser.



Critical issues	internal	external
Additional raw material (external Releaser)	No	Yes
Solvent Emission (VOC) from external rel.	No	Yes
Work Safety	Good	Additonal effort
Robustness	Very good	Very good
Post mould operations (cleaning)	Maybe necessary	Not necessary
Pretreatment for Top Coating	Not applicable	necessary
Providing Adhesion to Top Coat	Adjustment of internal releaser	Pretreatment necessary

III. BASIC AND FUNDAMENTALS

III.1. ADHESION

Adhesion is the property of materials to "stick together" across an interface and is affected by a wide range of forces and stresses resulting from many types of bonding, interfacial chemistries and complex loading conditions. (Gerberich W.W. et cols, 2006)

Three different levels of adhesion are usually distinguished (Mittal K.L., 1995) and perfectly summarized by Olavio Dos Santos Ferreira in his literary work "Adherence of nickel films to inorganic materials":

- The fundamental adhesion: it corresponds to the sum of all molecular interactions between the two materials in contact, and is collectively represented by the work of adhesion W_{adh}.
- The practical adhesion (experimentally determined): related to a force or a work required to separate the two materials studied. It is delivered in the form of stress. This description includes both the work of adhesion as well as the effect of energy dissipative mechanisms acting during the separation of both materials.
- The thermodynamic adhesion: it is defined as the change of Helmholtz energy when an interface is made (or broken). The Young-Dupré equation is usually used to calculate the reversible work of adhesion W_{adh}:

$$W_{adh} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad \textit{(Eq III.1)}$$

Where γ_i is the surface Helmholtz energy of material i at vacuum conditions, and γ_{12} is the Helmholtz energy associated with the interface between materials 1 and 2.

For a good adhesion or union between two different materials is necessary to fulfill two conditions:

1. The fluid which should be deposited onto the surface has to wet the surface for a good contact.
2. A good adaptation between the fluid and the surface material is needed to get an effective chemical link. (Eckert W., 2004)

Additionally, this adhesion properties can be modified thanks to heat accelerates polymerization reactions (Frihart C. R., 2005) and an appropriate cleanness of the surface (Ammar M. R. et cols, 2008). Moreover, higher molecular weight and more crosslinked polymers are generally good properties to improve adhesion. (Frihart C. R., 2005).

III.1.1. Adhesion in Powder Coating- Aluminum surface

Factors affecting coating adhesion can be grouped in five points (Vaca-Cortés E. et cols, 1998):

- *Powder Coating Formulation:* the formulation determines the properties of the product: viscosity, hardener, flexibility, colorimetry, brightness…
- *Coating Process:* under heating will trigger a bad mechanical interlock and overheating degrades the powder and reduces the electrochemical bond by producing new oxide layers in the surface that will not react with hydroxyl groups in the resin.(Kenneth C. et cols,1995)
- *Moisture:* Coatings lose adhesion when they are subjected to moist environments. (Sagüés A.A.,1991) (Kenneth C. et cols, 1995)
- *Temperature*: High temperatures cause temporary losses of adhesion.
- *Coating Damage:* chemical substances can lodge between powder coating-substrate couple through coating discontinuities (pinholes, scratches…).

Regarding aluminum surfaces, facts like increasing roughness, complete removal of organic layers and reduction of inorganic magnesium oxide layers (Anagreh N.et cols, 2010) improve the adhesion in this type of surfaces.

On Figure III.1 it can be observed how the same material, in this case an epoxy resin, have different contact angle depending on the surface.

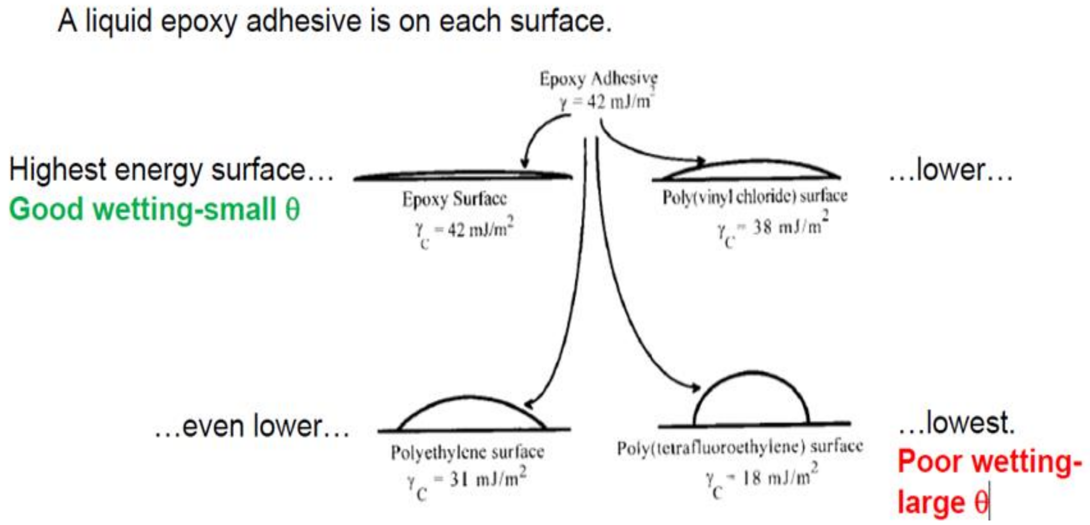


Figure III.1. Influence of the substrate in the surface tension. Source: The Joint Advanced Materials and Structures Center of Excellence. (University of Washington)

A great variety of compounds have adhesive characteristics, natural and synthetic materials, and, between the last one, powder coatings.

Once explained what adhesion is, is necessary to be remembered that the aim of this thesis and the general content is obtain a powder coating where adhesion properties disappear, or at least, be as small as possible. In short it can be said that the adhesion is the great enemy or obstacle to the objective.

III.2. POWDER COATINGS (introduction)

Powder coating is a dry paint composed of a polymer resin (or various), pigments, additives such as degassing agents or flow agents, and habitually, a cross-linking agent. The chemistry of powder coatings is not very different from that of liquid coatings (Waelde L. R., 2006); however, each powder particle contains exactly the same amount of resin, pigments and all the additives used in the formulation; fact that does not occur in solvent coatings.

It is a product that is increasing its applications and sales, as is indicated by Global Industrial Coatings Markets 2010-2020 on Figure III.2.

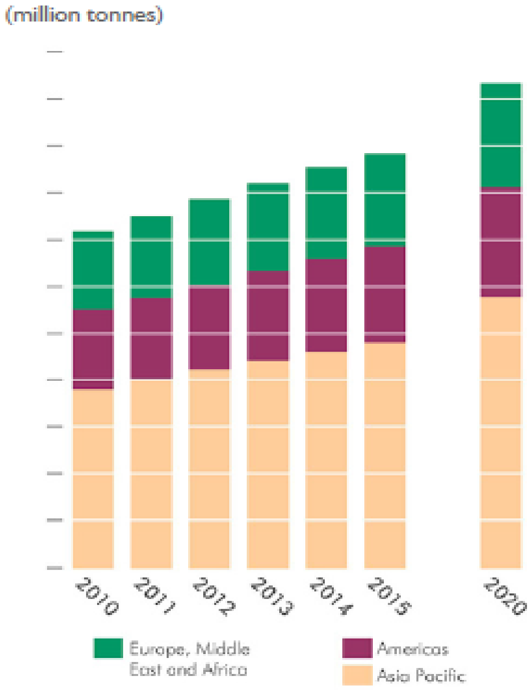


Figure III.2.Forecast powder coatings demand by region. (PRA, 2011)

Among all his benefits, explained previously in Chapter I, is remarkable that powder coatings are arguably the most environmentally “friendly” coatings. They do not contain solvents that release HAPs and, moreover, powder coatings release very low amounts of VOCs during the baking cycle.

The fact they contain very little hazardous chemicals and produce almost no waste material is related to a promising future.

III.3. POWDER COATINGS CLASSIFICATION

Powder coating business is very wide, and there is a huge variety of products with different properties and qualities. Furniture, architecture or automotive business are among their applications and can be observed on Figure III.3.

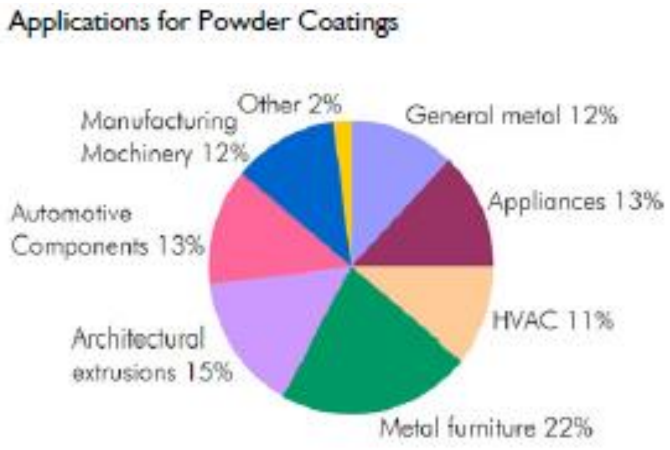


Figure III.3. Global Industrial Coatings Markets 2010-2020. (PRA, 2011).

However, a chemical classification containing all this product utilities can be made in the following way:

- Thermosetting powder coating.
- Thermoplastic powder coating.

III.3.1. Thermosetting Powder coatings

Thermoset powder coatings are able to cross-link chemically within themselves or with other reactive components, called hardener or catalyst and accelerator.

The cross linking of powder coatings enables a three-dimensional network to be formed (Spyrou E., 2012) how is described in the Figure III.4 obtained from Thermal Characterization of Polymeric Materials (Prime R. B., 1997).

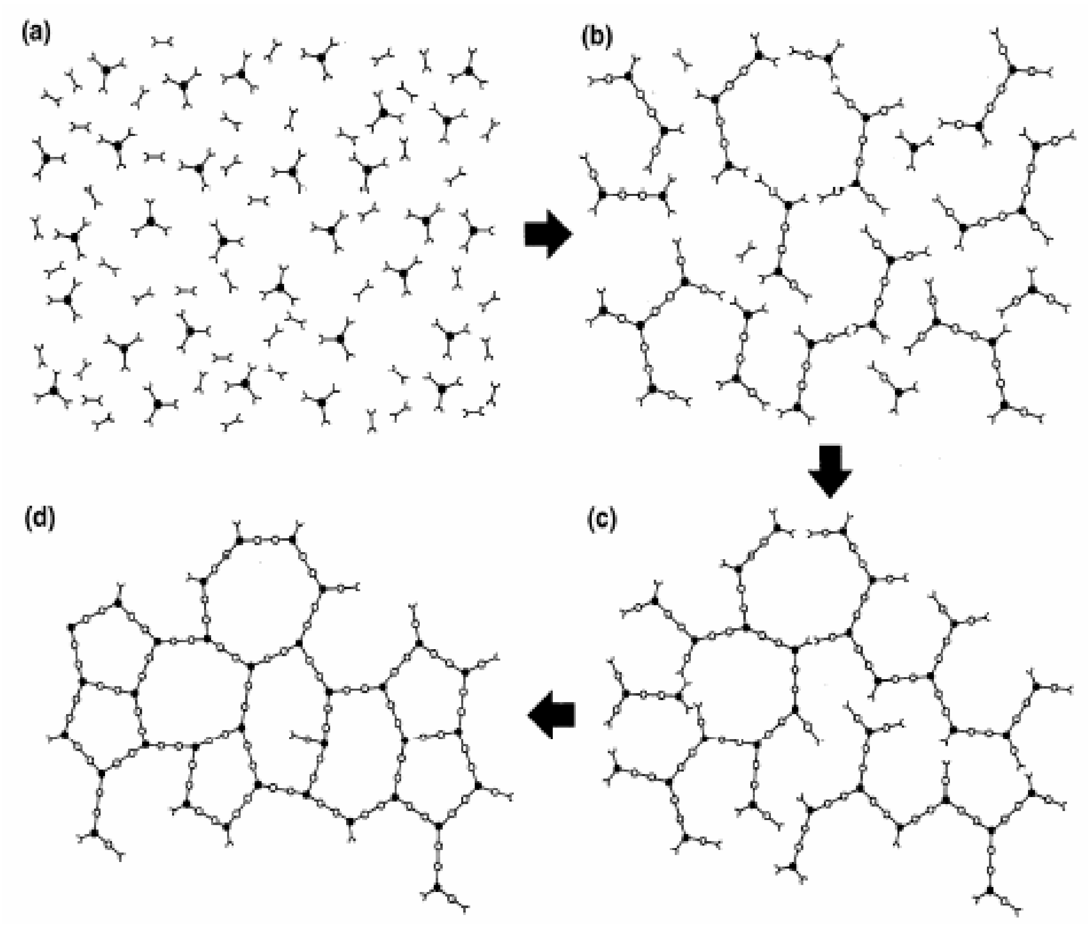


Figure III.4.Schematic of thermoset cure. Source: R. B. Prime, Chapter 6 “Thermosets” in Thermal Characterization of Polymeric Materials. E. A. Turied, Academic Press, San Diego.1997.

Initially, application of heat on the polymeric sample is necessary, in order to outset the polymerization or curative process. As the reaction proceeds, the increase in molecular weight accelerates, causing an increase in viscosity (Winter H. H., 1997) and the reduction in the total number of molecules. (Prime R. B., 2009).

At the end of the process (d), the material is totally cured and can offer their physico-chemical features. Among this features, thermosetting powder coatings own diverse and various characteristics, including advantages and disadvantages (Wallace P. D., 2013):

- High strength properties
- Very fast cure
- Usually water based
- Non-flexible, hard
- Storage restrictions

    - Limited storage life
    - Limited temperature storage
    - Need high temperature curing

Thanks to these features, a huge variety of thermoset powder coatings are produced, mainly with three kind of primary resins:

- Polyester
- Epoxy
- Acrylic

Although there are other that can be found in the market:

- Phenolic
- Polyurethane
- Dicyanate
- Bismaleimide
- Hybrids (Acrylic–Isocyanate, Epoxy–Polyester…)

The most common bases (Polyester, epoxy and acrylic) will be discussed in the next lines:

Polyester

Polyester powder coatings are the most common and versatile chemistry used in powder coatings because they can be formulated for indoor or outdoor applications. (Global Industrial Coatings Markets 2010-2020. PRA 2011.)

The raw materials used for the production of polyester resins are oil based and to develop a polyester of this type there are generally three chemical components required:

- saturated acid (e.g. phthalic anhydride)
- unsaturated acid (e.g. maleic anhydride)
- dihydric alcohol (e.g. propylene glycol)

In a warm environmental, these compounds combine to form a resin which is a viscous liquid when hot, but a brittle solid when cold. In the presence of a catalyst and accelerator, although in the case of self-curing resins these kinds of additives are not necessary, the chains crosslinks can form a solid three dimensional network. This means that the polymerization process is happening or occurring. On Figures III.5 and III.6, it can be observed examples of resin polyester and how this 3D complex is built:

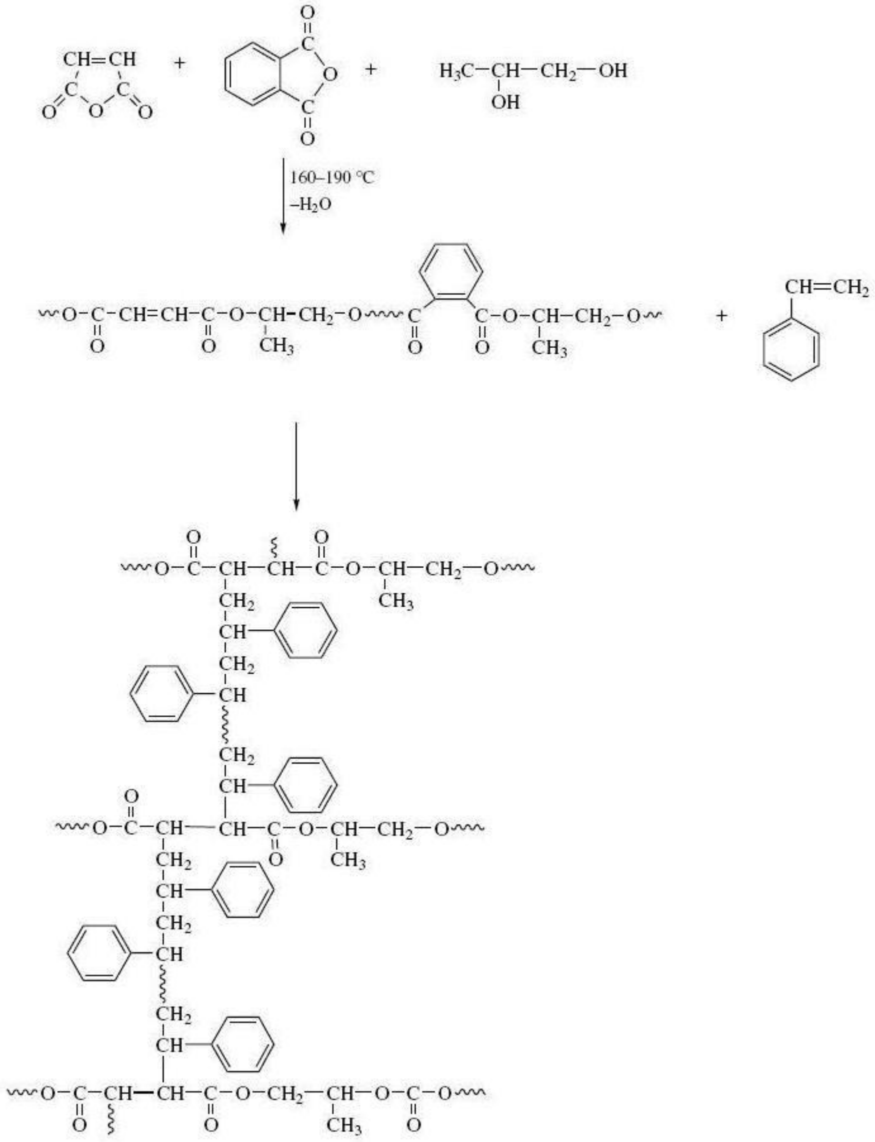


Figure III.5. Image of a Polyester Resin: Scheme with Cross linking.
Source: Bharat Dholakiya. 2012.

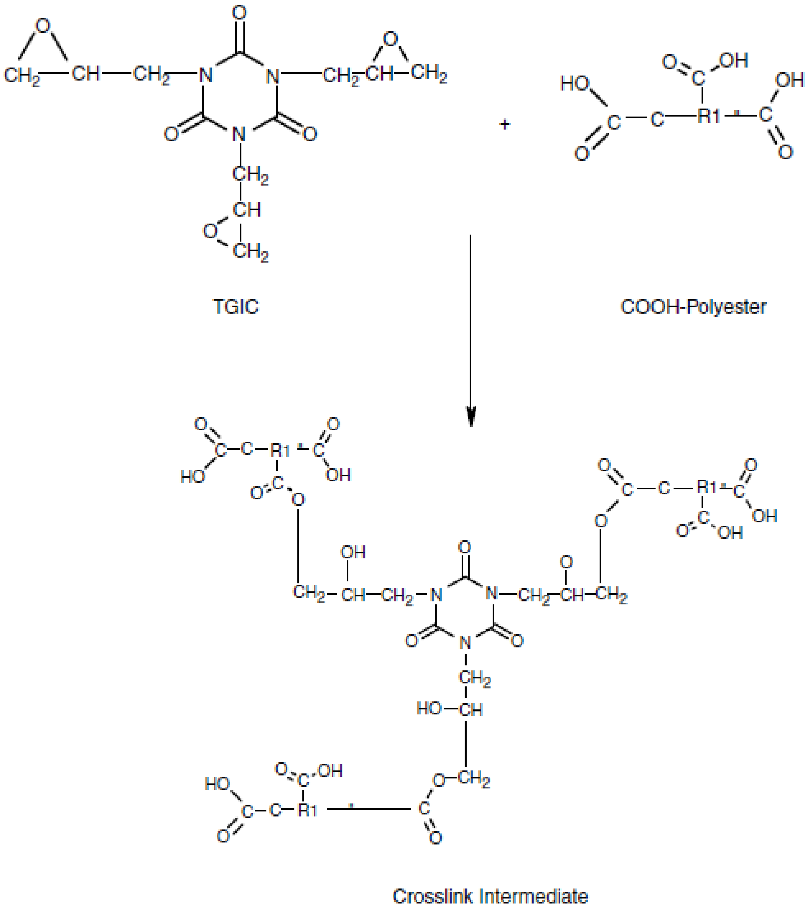


Figure III.6. Image of a polyester resin cured with TGIG. Source: Lawrence R. Waelde. 2006. Coatings Technology Handbook, Third Edition.

Regarding their properties, the matrix toughness plays an important role in the fracture behaviour of composites (Davallo M. et cols. 2010), although for manufacturing the main criteria are (Baley C. et cols. 2006):

- The amount of styrene emission in the workshop during impregnation and cure.

- Ease of impregnation of the fibers (wetting, compaction).

- Reactivity (gel time, maximum exotherm).

- Degree of cross-linking under industrial conditions.

- Influence of the manufacturing environment (temperature, relative humidity).

- Viscosity (impregnation of vertical surfaces).

- Delivery reliability.

Moreover, there are other properties quite important for the sector, like environmentally friendly or cost.

Epoxy:

Epoxy resins are polyether resins containing more than one epoxy group capable of being converted into the thermoset form (Bhatnagar M. S., 1996) which cures, once the process starts, by internally generated heat. Maybe one of the main advantages of epoxy thermosets is that the starting monomers have low viscosity so that complex geometries can be easily shaped and fixed after curing the monomers. (González González M. et cols, 2012)

They are especially valued in the automotive and aerospace industries for joining composite and aluminum parts (Petrie E. M., 2007); among their features:

- Low level of creep under sustained load.
- Good tolerance to elevated temperatures.
- Good chemical resistance.
- Good gap filling properties.
- Good adhesion to a number of materials of construction.
- Low level of shrinkage on cure.

However, one problem with early epoxy formulations is that they cured to a relatively brittle material (Petrie E.M., 2008). The strength and toughness of epoxy resins below the glass transition temperature Tg depend on the mechanism of the movement of short segments in the solid state, and above Tg mechanical properties are influenced by cross-linking density (Bhatnagar M. S., 1996).

The most common epoxy resins in use today are diglycidyl ethers of bisphenol A made from reaction of epichlorohydrin with bisphenol A (Waelde L. R., 2006), which is illustrated in Figure III.7. The formulation can be modified, and consequently the properties: if the proportion of epichlorohydrin is reduced, the molecular weight of the resin is increased (Singla M.et cols, 2010), among an infinite number of modifications.

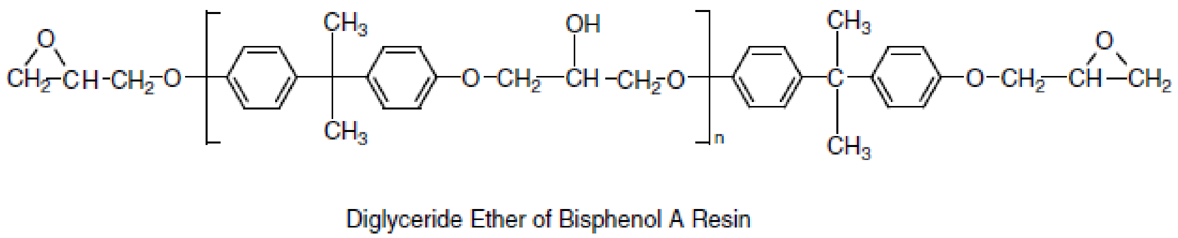


Figure III.7. Epoxy resin. Source: Coatings Technology Handbook, Third Edition. Lawrence R. Waelde. 2006.

__Acrylic:__

There are two primary acrylic systems: those based on hydroxy-functional acrylic resins and those using epoxy- or glycidyl-functional polymers (Waelde. L. R., 2006) and both can be formulated to bond many substrates and to operate over an extensive temperature range. Very short cure times are achievable with this class of polymers, thus allowing fast turn-round times. Moreover, they are characterized by worthy gloss and colour retention on exterior exposure as well as heat and alkali resistance.

III.3.2. Thermoplastic Powder coatings

A thermoplastic coating is manufactured in a similar way as thermoset coatings, with the main difference that a curing agent is not included. Instead of forming a cross-linked polymer network, the thermoplastic coating is melted on to the substrate and no chemical changes occur.

Thermoplastics can be processed into a desired shape through many processes, the most common of which are injection molding and extrusion. Blow molding, transfer molding, calendaring, casting, and other forming operations are all possible with thermoplastics. (Bolgar M. et cols, 2008.). In fact, thermoplastic powder coatings offer simple methods of manufacturing and application; however, problems like poor solvent resistance, poor pigmentation level and weaknesses at high temperature (Spyrou E., 2012) decreases the attraction of the product, how is detailed out in the next section called Thermoplastic VS Thermosetting.

Simply highlight, the thermoplastic powder coatings can be removed chemically or by heating the substrate and have inferior adhesion properties and mechanical properties compared to thermoset powders. Therefore, thermoset powder coatings are the prime choice when any of these properties are important. This can also be seen in the market where thermoset powders have a total dominance. (Ståhlberg D., 2006).

Connecting powder coating based in thermoplastic, first to exist in the market, can be highlighted the next bases:

- Polyethylene (PE)
- Polypropylene (PP)
- Nylon
- Polyvinyl chloride (PVC)
- Polyvinyledene flurides / fluorocarbons
- Ethylene terephthalate (PET)
- Polycarbonate

III.3.3. Thermoplastic VS Thermosetting

Thermosetting powder coatings own some properties that thermoplastic powders do not have, for instance:

- Excellent resistance to solvents and corrosives.
- Brilliant resistance to heat and high temperature.
- Fatigue strength.
- Tailored elasticity.
- Excellent adhesion.
- Color Strength
- Excellent finishing (polishing, painting, etc.).

These are some of the reasons why, nowadays, the use of thermosetting bases are more widespread used in the production of powder coatings. However, the main reason is that thermosetting coatings are heat-stable and, unlike thermoplastic powders, will not soften back to liquid phase when re-heated.

III. 4. PROCESSING

The process of producing a powder coating is more complex that for other types of coatings. Furthermore, time production is longer and the amount of apparatus needs is superior to liquid coatings. However, for large production of powder coating is economically right profitable.

In this section, it will be described superficially each of the necessary steps or stages during the process of making a powder coating.

This process of production can be continuous or discontinuous, depending on the plant capacity, and is mainly composed of the following steps:

- Premixture
- Extrusion
- Grilling or Grinding

III.4.1. Premixture

The first stage in the manufacture of a powder coating is the premixing. This is a really a crucial phase of production. Insufficient premixing of ingredients, especially of those which are employed in small concentrations such as additives and coloring pigments cannot be compensated for later on in the second stage by the hot melt extrusion process (Spyrou E., 2012) and this can be revealed with the results of bad mechanical properties, surface defects or reduced gloss.

Regarding the extrusion (next part of the process), it is a simple melt mixer, and not a very efficient disperser; is unmanageable to correct an unfortunate premixing by extruding. The premix step has to allow a good dispersion of all ingredients (resin, pigments, fillers, degassing agents…) in the final product. Consequently, premixture is performed in equipment with sufficient ability to break down and triturate the large resin flakes, thoroughly blend any liquid components, and disperse the smaller quantity ingredients, it means, the additives.

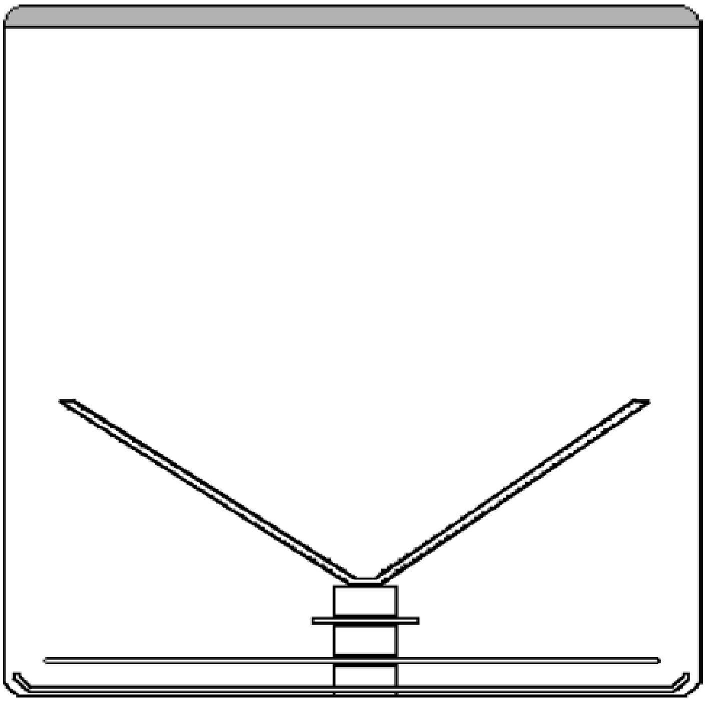


Figure III.8.Schematic of premix equipment. (Waelde L. R., 2006).

The variety of machinery that can be used in this step is amazing and exceptionally wide, among them are:

- Tumbler Mixers
- Horizontal Mixers
- Conical Mixers
- Double Cone Blenders
- High-Speed Blenders

The choice depends on the requirements of the process and especially on the powder coating formulation. Ideally, the binder should have a particle size of 2 to 4 mm when the mixing is completed. (Gillis de Lange P., 2004)

III.4.2. Extrusion

The second phase of powder coating production, called extrusion or hot melt compounding, consists on the extrusion of the premix. There are, mainly, three types of extruder that can be used for performing the extrusion, but just one of them is used in powder coating production:

This type of extruder, used in the thermosetting powder coatings industry, is composed of two screws placed side-by-side and turning in the identical directions. The screws, made of stainless steel, turn and move the premix forward through heated "mixing zones". The mixing zones have special attachments, called mixing paddles or blades. The paddles knead the melted premix and blend the various ingredients. This greatly increases throughput and decreases residence time.

In the Figure III.9 can be observed a scheme of a basic extruder, where the raw material enter in the installation by the hopper, and, after the extrusion, is obtained the powder coating.

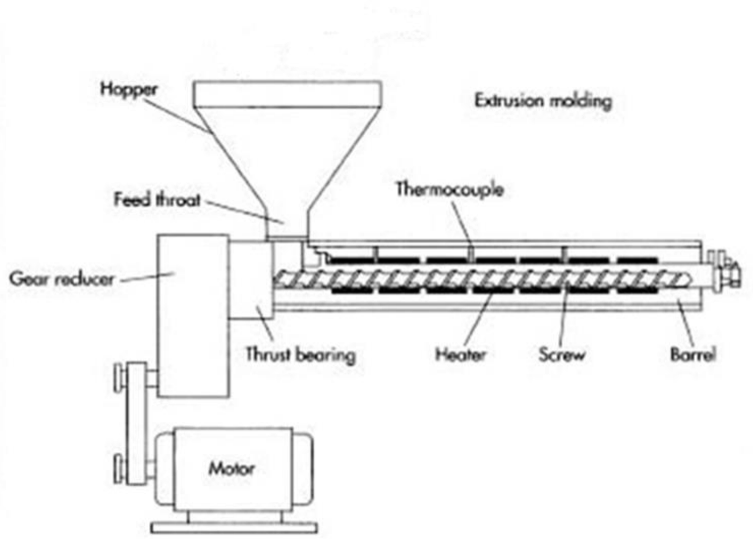


Figure III.9. Basic elements of an extruder for powder production Source: http://www.gsmindustries.co.in/pages/products/plastic-extruder-machinery.html

Reduced residence time is important in thermoset coatings, especially in the most reactive systems with short gel times (Waelde L. R., 2006), and this kind of extrude moves material forward rapidly. This is important in preventing of reaction in the barrel and gel prematurely inside of the equipment. To modify the hostility of the process in reactive formulations, the screw mechanism can be adapted.

This step in the powder coating production cannot be used to dispersing the “condiments” owing to insufficient time to be dispersed suitably. However, due to the threaded nature of the screws and their proximity in an enclosed heated barrel, the ingredients are subjected to high shear as they melt. The thread pitch causes the compound to travel down the barrel, where mixing time increases and viscosity drops as the compound heats. (Bolgar M.et cols. 2008). These details are needed to know in order to perform a high quality formulation.

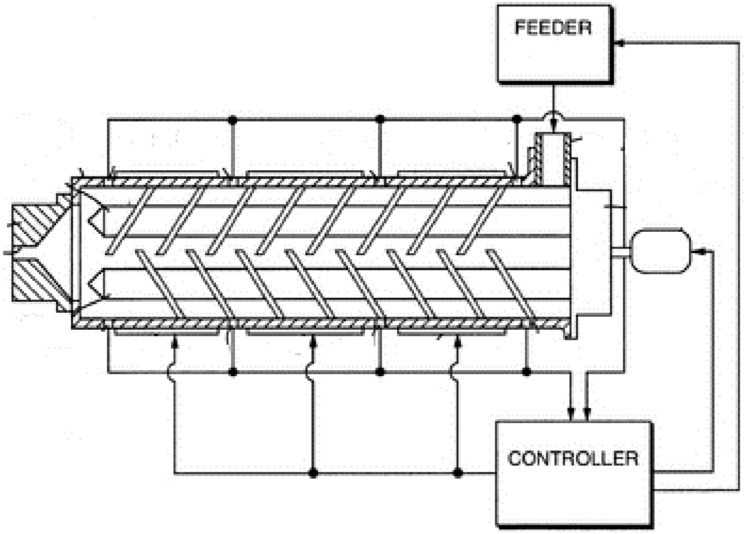


Figure III.10. Screw extruder and method of controlling the same. Source: United States Patent 6790023. Collins, Thomas Robert and Corby, Nelson R..

At the end of this stage, chips or pastes are produced. Once cooled, they are used in the grilling step.

III.4.3. Milling or Grinding

The third step consists of the micron zing of the chip into the final powder which will be marketed; however, it may be necessary breaking the extruded coating material into flakes.

The mills themselves have evolved in size, power draw and durability for over a century but the technology has remained basically the same (Barkhuysen N. J., 2009), in point of fact, the size reduction of the chip is always the result of impact of the grinding surface with the solid granules or the fragments.

The average particle size and distribution are important in the application properties and final surface appearance of the coating. Once a powder coating has been extruded, it passes through one or more stages to prepare it for grinding. The molten material is dropped onto chilled metal rollers, where it is pressed flat and cooled. The coating is then broken into flakes or granulated and fed to the grinder (Waelde L. R., 2006). At this point is when the material cools and reverts to low temperature, towards an ambient temperature.

Finally, the powder is carried through a classifier into a collection system via a regulated air flow.

With the aim of achieve the optimal psd, auxiliary treatment can be needed which can consist of cycloning, classifying, separation, filtering or sieving, between other techniques.

Figure III.11, obtained from the website of the company TIGER Coatings GmbH, represents the complete process in the production of powder coatings, from the initial mixture of additives, like resin, hardener or pigments, until obtaining the final product, which will be packaged and marketed.

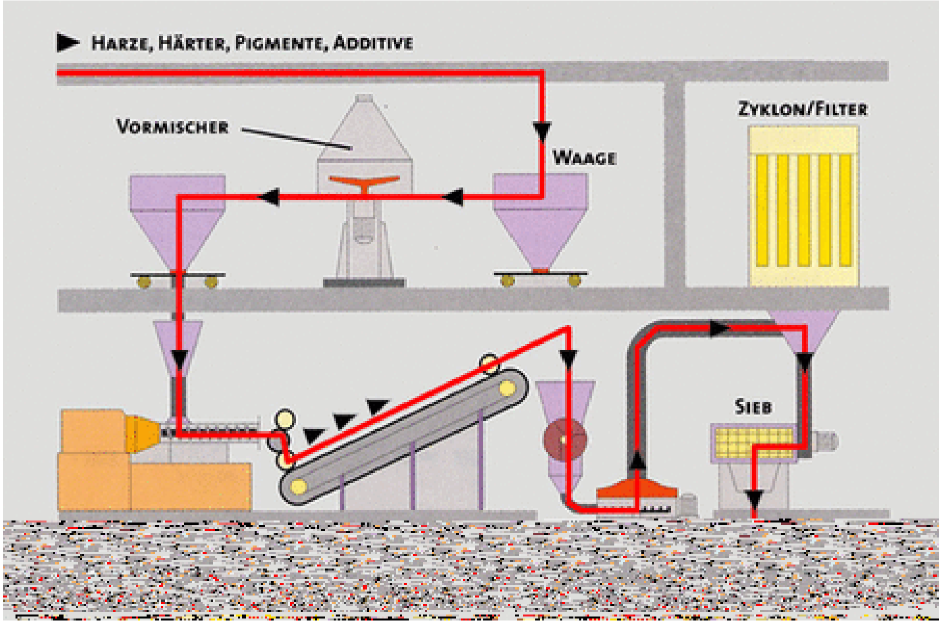


Figure III.11. Powder coatings process from www.tigercoatings.com

III.5. METHODS OF POWER CHARACTERIZATION

It is mandatory to characterize the powder prior to applying on a surface; for this reason, there are several methods of powder characterization as well as the techniques used, including (Krepski R., 1993) (Davis J.R., 2004):

- Particle size (Mechanical sieve analysis, X-ray absorption)
- Chemical composition (X-ray florescence, XRF spectroscopy)
- Shape of the grain (SEM or Optical microscopy OM)
- Density and flowability (ASTM B 329-76).

Among the techniques used in this thesis for the characterization of the different formulations of powder coatings are:

III.5.1. Particle size

The size (and shape) of powders have an important influence in flow and compaction properties. Larger, more spherical particles will typically flow more easily than smaller or high aspect ratio particles. Smaller particles dissolve more quickly and lead to higher suspension viscosities than larger ones. Smaller droplet sizes and higher surface charge (zeta potential) will typically improve suspension and emulsion stability. The ideal particle size is between 20 and 80 µm.

Powder or droplets in the range of 2-5µm aerosolize better and will penetrate into lungs deeper than larger sizes. For these and many other reasons it is important to measure and control the particle size distribution of many products.

Particle size is usually expressed in micrometers (µm), although it can also be presented in mesh screen.

Particle Size Distribution Calculations.

The measurement of Particle Size Distribution is one of the most widely methods used in the industry, and especially useful is its graphical representation. In the Figure III.12 is represented the typical graphic of a particle size distribution.

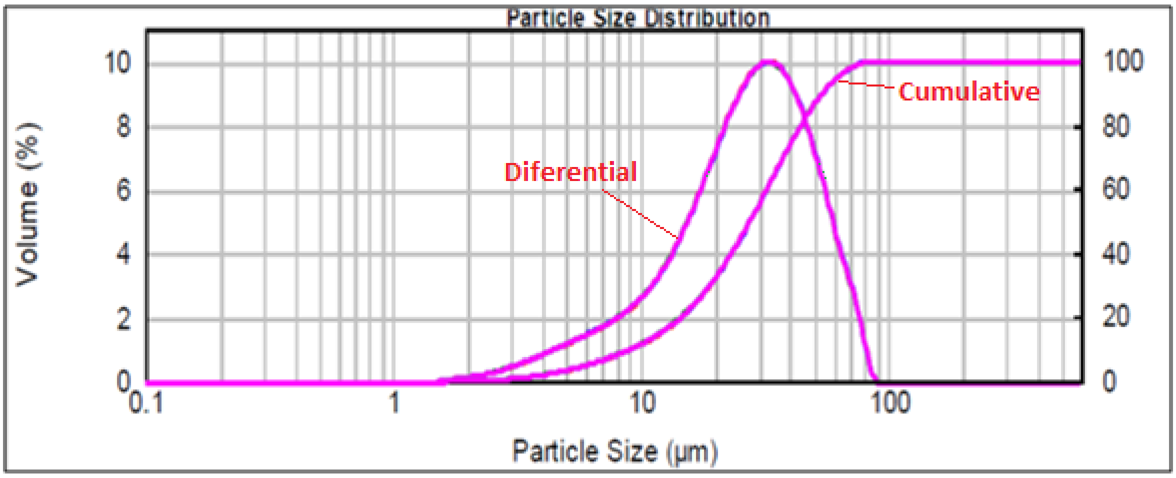


Figure III.12.Particule size distribution (psd).

In the same figure can be observed two different graphics: with differential and cumulative values.

- Differential Size Distribution: is the probability that the particle have a diameter with the value x.

$$f(x) = \Pr[X=x] \qquad \textit{Eq. III. 2}$$

On Figure III.13 the scheme of the normal probability density function is represented. On this figure, it can be distinguished the Modal (the most frequent value), Mean (arithmetical average) and Full Width At Half Maximum (FWHM is an expression of the extent of a function, given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value).

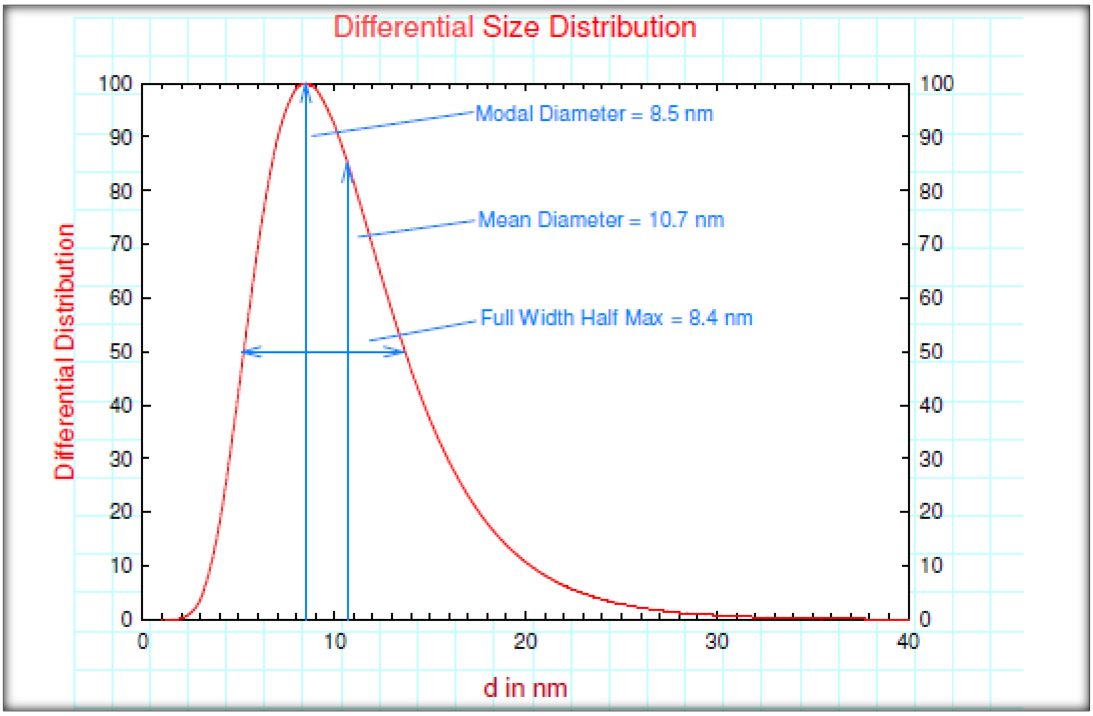


Figure III.13.Differential Size Distribution. Source: What is a Continuous Particle Size Distribution?.(Weiner B. B., 2011).

- *Cumulative Undersize Distribution*: The cumulative undersize distribution function or cdf is the probability that the particle has a diameter less than or equal to x. That is

$$F(x) = \Pr[X <= x] = \alpha \qquad \text{(Eq. III. 3)}$$

That function is represented on the Figure III.14.

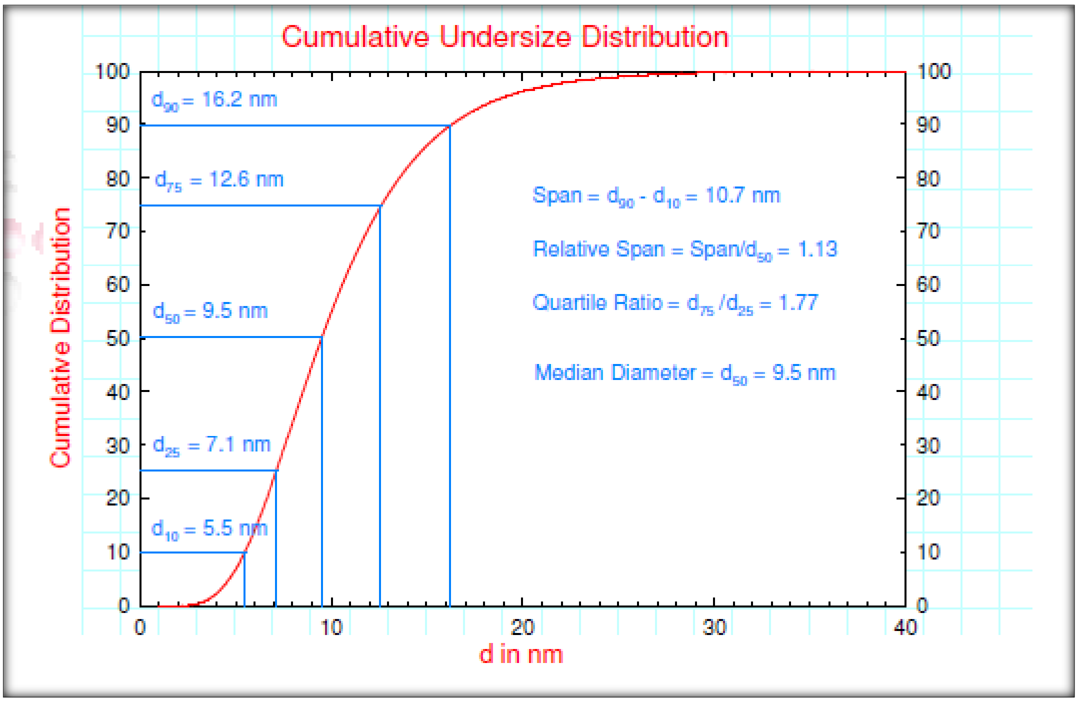


Figure III.14.Cumulative Undersize Distribution. Source: What is a Continuous Particle Size Distribution?.(Weiner B. B. 2011).

In the statistic representation, the next values acquire importance: Span, Relative Span, Quartile Ratio (all of them measures of the width of a distribution) and Median (average value of all particles in the sample).

III.5.2. Differential Scanning Calorimetry (DSC).

Differential Scanning Calorimetry, or DSC, is a thermal analysis technique where the difference in heat flow to the sample and a reference at the same temperature is recorded as a function of temperature. That looks at how a material’s heat capacity (Cp) is changed by temperature. In this test, a sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow.

This technique allows the detection of transitions like melts, glass transitions, phase changes and curing.

III.5.3. Viscosity

Viscosity is a quantitative measure related to the resistance to flow: it describes the internal friction of a moving fluid. The main factors that affecting this physical force are: temperature, pressure and composition.

There are various simulations or equations to predict the viscosity, but in a “perfect” world, the **Newton's law of viscosity** is highlighted**:** it states that the shearing stress and the rate of deformation are directly proportional through a constant of proportionality called viscosity.

That law is represented with the equation III.4:

$$\tau = \mu \frac{du}{dy} \qquad \textbf{(}\textit{Eq. III. 4)}$$

Viscosity can be divided into two categories: dynamic viscosity (cP, Pa.s, N.s/m² or kg/ms) and Kinematic viscosity (St or m/s²).

III.5.4. Gel time

Gel time is the interval of time that is required for a powder coating to become a solid or semisolid gel or jelly, it means, the quantity of time it takes for solidify into a gel. It is reached when crosslinking begins to act over the resin and the curing process is happening. This value is generally expressed in seconds. This property is determined through a Gel time device; which is explained in the chapter IV.1.2 (Specific Equipment).

III.5.5. Thickness

The thickness of an object is the dimension between two surfaces thereof. It is usually the dimension of smallest measure. The most common units used are µm or mm and that values can be easily acquired with a Thickness gauge (Analyzed in section IV.1.2.)

III.5.6. Adhesion

This property is explained extensively in the section III.1; into this chapter. Moreover, in section IV.1.2, there is a subdivision called “Pull-Off Test Machine (adhesion test)” where is analyzed the equipment used to obtain this property. Finally, throughoutIV.3, the special methology developed in that project is deeply exposed and the using of that machine is clarified.

III.5.7. Surface tension

Surface tension is a physical principle in which the surface of a fluid, where the fluid is in contact with gas, acts like a thin elastic sheet. This property is due to intermolecular forces (such as Van der Waals) between the liquid's molecules at the liquid's external limits.

Surface tension has the units of force/length or equivalently energy/area, and so may be thought of as a negative surface pressure.

III. 6. POWDER COATING APPLICATION METHODS

There are a wide variety of substrates where powder coating can be applied although aluminium and steel are the main substrates today (Schmidt T., 2012). Among these substrates, nowadays less significant but increasing in influence, are materials as different as ceramic, glass, natural fiber composites (for instance, MDF) or synthetic polymers (nylon, polycarbonate…).

Figure III.15. Examples of substrates for powder coatings.

Unlike metals, non-conventional carrier materials show low temperature stability, much rougher and more irregular surface texture, large dependence of their dimensional stability on the moisture content of the surrounding environment and significantly less electrical conductivity. (Schmidt T. W. et cols, 2011)

It is one of the reasons whereby the method of applying the powder has to be adapted to each product. The choice of technique used to spread over this dry paint depends on a diversity of variables, like the kind of material impregnated (commented in the two preceding paragraphs) or the next properties:

- The geometry of piece that is to be coated. Rounded shapes with holes are more difficult to treat than smooth surfaces. Size, height, width, length…are variables decisive for the choice of an application technique.
- Quality required for the final product. Aerospace or automotive requires qualities far superior to other sectors.
- Automatic or manual process. Automated processes are related to large mass production.

Emmanouil Spyrou, stated in his book "Powder Coatings Chemistry and Technology. 3rd Revised Edition" all the techniques used in the application of powder coatings:

- Electrostatic Spraying Technique
    - Corona Charging guns
    - Tribo charging guns
- Fluidized Bed Process
- Electrostatic Fluidized Bed
- Flame- Spray Technique
- Electromagnetic Brush (EMB) Technology
- Electrostatic Spraying with "Kompstat" Technology

Although each process has its own characteristics, which sets it apart from the rest, formulations of powder coatings are not categorically different from one technique to another, so that is the reason the same formulation is valid for using, for instance, in Electrostatic Spraying Technique or Fluidized Bed Process.

There are some properties common to all the techniques, and the most remarkable for companies is a high degree of transfer efficiency (Noonan J.R., 2000) in all the procedures.

Surface pretreatment.

Concerning recommendations or care that the process should have before starting, can be highlighted a surface preparation.

The cleaning of the surface is an essential requisite, and at least, water, solvent (acetone, trichloroethylene…) or a chemical cleaning pretreatment has to be carried out. Cleaning pretreatment also can be accomplished by physical-mechanical technology, for instance, airless centrifugal wheel blast or air blasting (sandblasting), where sand is used to abrasive the surface.

Moreover, it is confirmed that pre-heating proves to be an efficient method to improve the powder application onto non-conventional substrates. (Schmidt T. W. et cols, 2011).

III.6.1. Electrostatic Spraying Technique

Regarding all the existing techniques, entitled previously in this section, will be explained the Electrostatic Spraying Technique, due to being the most widespread technique in the industry.

The electrostatic application of powder coating over a surface initiates with fluidization. This process consists on spray the powder mixed with compressed air, and that way it is driven from a container to the spray guns. The control of the air supplied allows the variation of the powder flow. Then, the powder is charged using, generally, a corona or tribocharging gun.

As soon as the powder elements come into contact with the fragment will be coated, an electrostatic attraction between the charged powder particles and the grounded part adheres powder to the part (K. Kreeger. 1994). A field is created, as shown in the Figure III.16. According to several studies, the electrostatic field is predicted by solving the Laplace equation (Z. Li, J. Zhu, and C. Zhang. 2005)

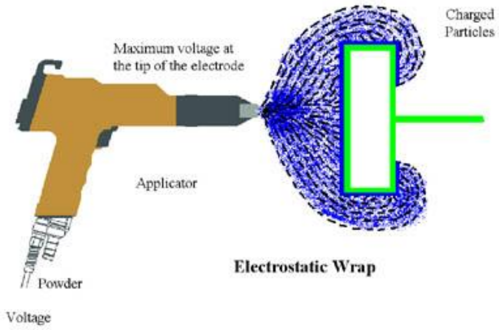


Figure III.16. Electrostatic Spraying Technique.Source: http://www.professionalcoatings.co.uk

The potential at the surface of a layer of the powder after it has been deposited on a flat surface depends on the kind of materials, the coating thickness or the application distance, among other variables. Increasing the coating thickness, the potential gradient increases linearly as long as it reaches the dielectric strength of the powder layer (Spyrou E., 2012) and sets the variables that affect it.

Process:

Once the product is lying on the surface, the coated support is subjected or exposed to high temperatures, from 130°C/20min until 180°C/3min (Skjelby B., 2012) in an oven and this way is cured, although that value depends on the formulation. In fact, there are some kinds of powder coatings, commonly used for heat sensitive substrates like MDF and plastics (Knoblauch M.et cols, 2012) that require UV radiation to be cured.

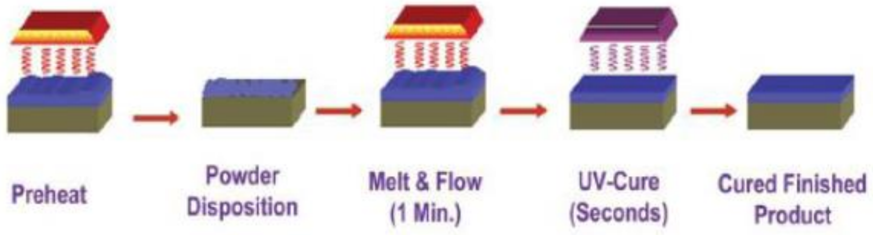


Figure III.17. Plastics decoration 2012 July/August: UV-Cured Powder Coating Developments.

III.7. PIMC (introduction)

PiMC or Powder in-Mould coatings is a process of production of high quality composites, really Class A Surface Finishing, which is destined to be the future of the sector thanks to its multiple benefits and the wide range of processes where can be used.

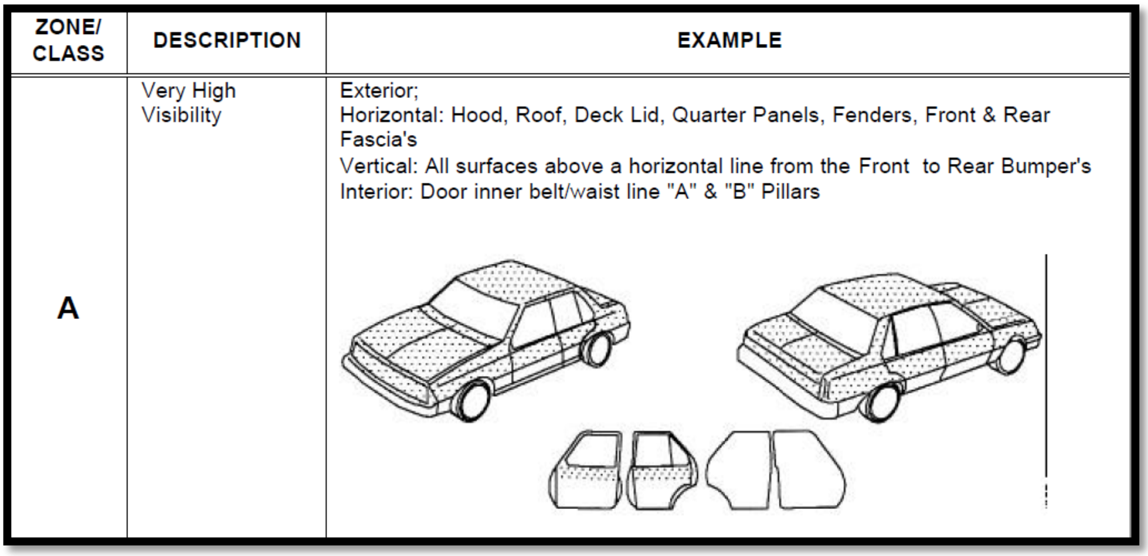
This technology is used close to SMC, RTM or VA-RTM.; however, before giving more details of this technology, is necessary an explanation of the goal: What is a Class A Surface Finishing?

III.7.1. Class A Surface Finishing

Surface finishing can be described as the degree of smoothness of a surface once it has been synthesized or manufactured. It is the result of the surface roughness, waviness, and flaws remaining on the part.

The standard AS-100-1 contains four different grades for surface finishing: A (related with very high visibility parts), B (High visibility) C (Moderate visibility) and D (Low visibility). In the automotive industry, the surface appearance is, along with the design of the exterior body, the first impression that can bring a desire in one mind to own a vehicle (Hsakou R., 2006). This reason alone is enough for companies to focus its efforts in accomplishment of really good surfaces finishing, it means, Class A surface finishing.

Of course, Class A is the most difficult grade to reach. The Figure III.18 shows which parts of a vehicle needs this type of finished.



ZONE/ CLASS	DESCRIPTION	EXAMPLE
A	Very High Visibility	Exterior; Horizontal: Hood, Roof, Deck Lid, Quarter Panels, Fenders, Front & Rear Fascia's Vertical: All surfaces above a horizontal line from the Front to Rear Bumper's Interior: Door inner belt/waist line "A" & "B" Pillars

Figure III.18. AS-100-1 Paint Appearance Standard (Roush).

All the requirements to obtain a Class A surface are related with the aesthetics of the product, although a good design of the curvature is decisive. In fact, the product must achieve some Mathematical Requirements when is designed. Then is when it takes into account other factors called Visual Characteristics:

- Aesthetic requirements.
- Reflection, smoothness.
- Style features as intended by Designer/Stylist.

The reflection of light plays a major role in surface appearance. If a surface does not possess certain described characteristics, Visual appearance of the product will get affected.

Concerning problems that prejudice obtaining Class A surface finishing in plastic composites can be highlighted:

- Shrinkage marks
- Molding direction
- Undercuts
- Seen parting lines
- Insufficient draft angle for given textures
- Inadequate coating
- Warping

III.7.2.PiMC and manufacturing

In SMC and BMC process, there is the problem that the composite need to be brushed, scraped and sanded after being produced; and that high effort of the finishing of the FRP to Class A surfaces increases the cost of production considerably (Mader C., 2013). In fact, it is about the 70% of the total cost of production, in some cases more, depending on the shape of the good. That is the reason of the promising future of this technology.

In the next picture can be appreciated little defects in the surface of the composite that need to be homogenous. This kind of FRP are used for aeronautic and automotive activities so they have to own optimal properties, it required to be class A.

Figure III.19. Composite with surface defects.

PiMC is used close to SMC, BMC, RTM or VA-RTM. In fact; it is an optimization of these production practices. Other methods less suitable for In-Mould Coating are Filament Winding, Pultrusion, Braiding or Spray up.

In actual business, it is still impossible to build composite with PiMC technology. However, the company where that R&D project was developed owns some formulations that can be useful for that procedure.

III.7.3. Process.

Powder-In-Mold-Coating (PIMC) process starts with the application of powder coating on the preheated RTM or press mold (Figure III.20).

Figure III.20. Coated mold by powder coatings.

The powder coating melts and cures in the heated mold. Subsequently the FRP is built up in the mold and cured after closing the press. Then the primed FRP part is removed. After a washing step it is ready for top coating.

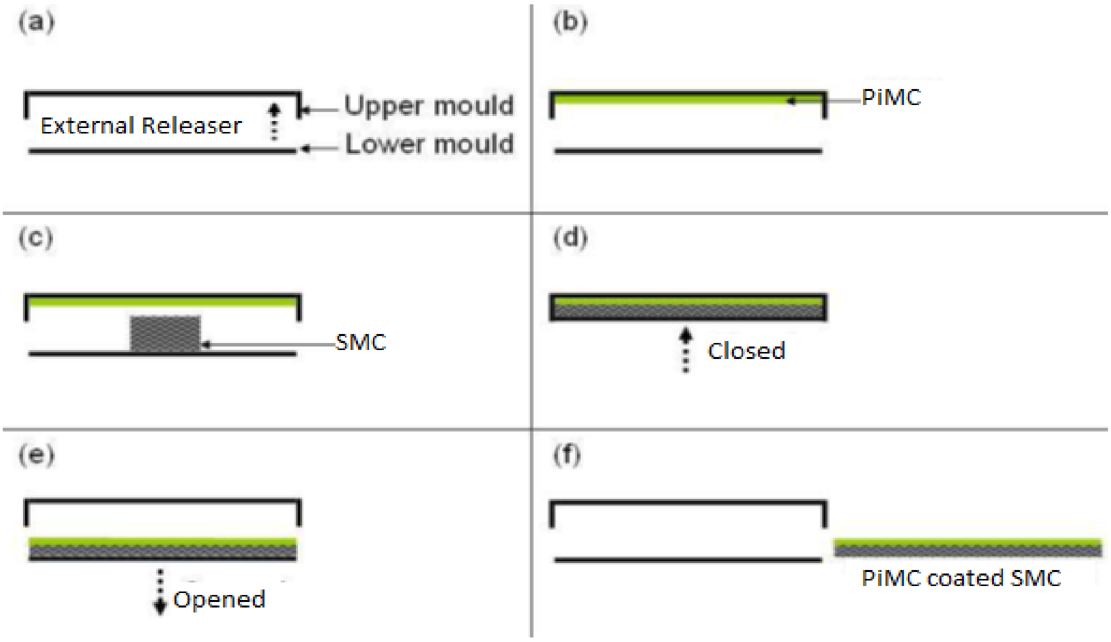


Figure III.21. PiMC process. Source: Renkema H. et cols, 2011.

In the previous image, adapted from “New powder in-mould coating for SMC in automotive applications”, is described the process in 6 diagrams. In the first (a), the external releaser, normally organic solution water based, is applied on the preheated mould (step to remove in this project). In (b), powder coating is applied and starts to curing. The curing process finishes at diagram (e), where the composite is produced. In (c), is introduced the FRP and in the next stage (d) the press close during the composite time production. The functions of the external releaser agent are valuable in the diagram (f) and Figure III.22, where the coated composite can be separated smoothly and the mold is immaculate. The main problem of these releaser agents is that it slows the process.

Figure III.22. Example of SMC mould.

As a conclusion for this chapter, it can be said that a powder coating is applied to a preheated mould to pre-gel. Subsequently, SMC (or other technology like RTM) is placed into the mould and pressed as one with the PIMC to cure together inside the mould. When the SMC is removed from the mould it comes out coated with a highly durable, super smooth powder coating layer which has a strong adhesion to the SMC. (Renkema H.et cols, 2011), thus obtaining a composite with special surface properties.

III.8. TIGER Coatings GmbH & Co. KG

TIGER Coatings GmbH, or also known as Tiger Lacke, is an Austrian Company founded in 1930 by Theodor Berghofer and his brother Gustav. Actually it has become the sixth largest powder coatings manufacturers in the world (Chemie Report: Austrian Life Sciences. 2008).

Originally, the company started producing only liquid coatings (oil-based paints and plaster), but in 1968 Theodor Berghofer, helped by his son Kurt, decided to enter in the previously unknown field of powder coating technology, factor that made possible years later his great expansion around the world. In fact, in 1985 the time for an international expansion had come for the Austrian organization and a sales organization was founded in Los Angeles (USA), followed by Canada.

Figure III.23. TIGER Coatings GmbH & Co KG. Wels (Austria).

At that time, a constant expansion of worldwide sales of TIGER Drylac® Coating began. TIGER opened any new production plants in countries as different as Egypt, Mexico, Brazil or China (Tiger Coatings, 2012) and for this reason the company can sells its products throughout the whole world.

Figure III.24. Actual TIGER Coatings GmbH in the world.

For the company, R&D is the one of the main forces, and in 2003 was completed a new R&D department located in Wels, location where this thesis was gestated. In these facilities the company has a variety of equipment to development a wide range of thermoset powder coatings; among other kind of coatings. The main applications, ordered by importance, are:

1. Architecture
2. Automotive
3. Stores
4. Furniture
5. Agricultural & Construction Equipment
6. Transportation Industry (e.g. Aviation, Railroad, Aeronautics…)
7. Machinery
8. Sport Equipment
9. Electronics
10. Wind Energy

In fact, Tiger produces powder coatings for various surfaces, such as aluminum, steel, wood (specifically: MDF), plastic and glass, which can be used indoors and outdoors. The properties and qualities of each powder coating is certainly diverse, therefore, weathering, chemical resistance, metallic effects, impact, shock, adhesion, abrasion and scratch resistance, among other characteristics, are the typical properties measure daily in that R&D Centre.

The company has an assured good future due to its powerful investment in R&D, investigating and developing new products that do not exist yet on the market. This project based on PiMC technology for obtain surfaces Class A surface finishing is a clear example.

IV. MATERIALS AND METHODS

IV.1. EQUIPMENT DESCRIPTION

IV.1.1. Basic Equipment

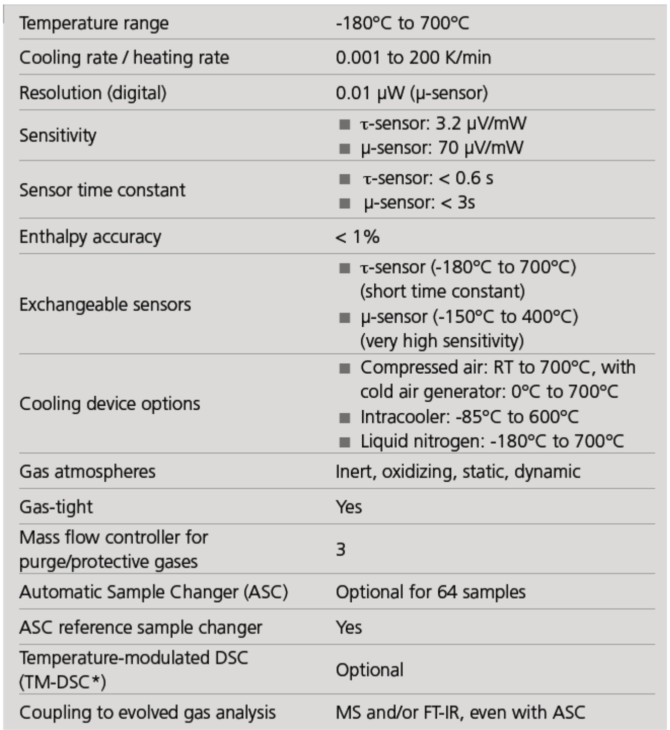
- Differential Scanning Calorimetric Device (NETZSCH DSC 204).

This system is based on a homogeneous heating of a disc-sensor system for stable and reproducible baselines. Peak performance is achieved with effective, low-consumption cooling system, and long product lifespan is ensured with high mechanical and chemical resistance. This is achieved by incorporating the sensor into a cylindrical silver furnace with embedded heating oil and silver lids above and below the sensor, ensuring a good coupling of different cooling systems (intracooler, liquid nitrogen and compressor), reducing the inertia of the furnace, and using resistant metals for furnace bodies and heat flow sensors. The highly efficient insulation and protective gas flow allow continuous process at low temperatures without frost or ice accumulation in the main body of the measuring cell. The gas-tight construction of the DSC cell enables measurements under very pure and defined gas atmospheres. Precise control and automated switching of gases processes are provided by the integrated and calibrated mass flow controllers. The DSC sensors are exchangeable, allowing one to optimize around current needs, or future application requirements.

Figure IV.1. DSC Machine: NETZSCH DSC 204.

Technical Key Data for the DSC 204 F1 Phoenix®:

Table IV.1. Technical specifications.



Temperature range	-180°C to 700°C
Cooling rate / heating rate	0.001 to 200 K/min
Resolution (digital)	0.01 μW (μ-sensor)
Sensitivity	■ τ-sensor: 3.2 μV/mW ■ μ-sensor: 70 μV/mW
Sensor time constant	■ τ-sensor: < 0.6 s ■ μ-sensor: < 3s
Enthalpy accuracy	< 1%
Exchangeable sensors	■ τ-sensor (-180°C to 700°C) (short time constant) ■ μ-sensor (-150°C to 400°C) (very high sensitivity)
Cooling device options	■ Compressed air: RT to 700°C, with cold air generator: 0°C to 700°C ■ Intracooler: -85°C to 600°C ■ Liquid nitrogen: -180°C to 700°C
Gas atmospheres	Inert, oxidizing, static, dynamic
Gas-tight	Yes
Mass flow controller for purge/protective gases	3
Automatic Sample Changer (ASC)	Optional for 64 samples
ASC reference sample changer	Yes
Temperature-modulated DSC (TM-DSC*)	Optional
Coupling to evolved gas analysis	MS and/or FT-IR, even with ASC

- Balance (Sartorius).

The use of this high precision equipment is critical for the entire project; in the case of inaccurate measurements, the study will be invalid as each measurement is brought forward to the subsequent process. For this reason, the balances were calibrated.

Technical data (details):

- Balance from Sartorius, type LP5200P
- Weighing capacity: auto scaling / 5000 g.
- Readability: 5,200. accuracy: 0.1
- Dimensions pan size (W) x (D): 21,5 x 20 cm.
- Housing (W) x (D) x (H): 23,5 x 38 x 9 cm.

- Hot air oven (Thermo Scientific Heraeus UT 12).

The hot air oven is necessary for the perfect curing of powder coating on aluminum plates. If the complete curing of the resin does not occur, there will not be good gluing properties. The equipment specifications are highlighted in the following list:

Equipment Specifications:

- Model: UT 12
- Serial Number: 40835260
- Capacity Size: 2.32 Kw
- Temperature Range: 250° C
- Length: 700 MM
- Width: 600 MM
- Height: 840 MM
- Voltage: 230 VOLTS

- Grinding Mill: Hosokawa MikroPul Köln ACM 2L.

The grinding mill is used to break solid materials into smaller pieces which are useful for determinate applications. Although there are a great variety of ways to power a mill, (wind, water, animal force…) the most common mill used is actually powered by electricity.

The Figure IV.2 shows the mill room the company own and the mill was used in this R&D project.

Figure IV.2. Grinding Mill: Hosokawa Mikro Pul Köln ACM 2L.

Technical data (details):

- Rotor diameter: 177 mm
- 3600 rpm
- 480V
- Serial #B0180K
- Control panel

- Logger 177. T4 testo (control temperature)

This apparatus permits to know how the temperature of an object changes with time, and in that way, one can determine how the environment is being influenced. The device has sensors attached to the object to scan and thus allows the identification of the temperature with high accuracy in each moment.

Technical Data:

- Dimensions: 103 x 64 x 33 mm
- Weight: 129 g
- Memory: 48000
- Power supply: 110 to 240 VAC
- Probe type Typ T (Cu-CuNi): Meas. range -200 to +400 °C
- Material/Housing: ABS

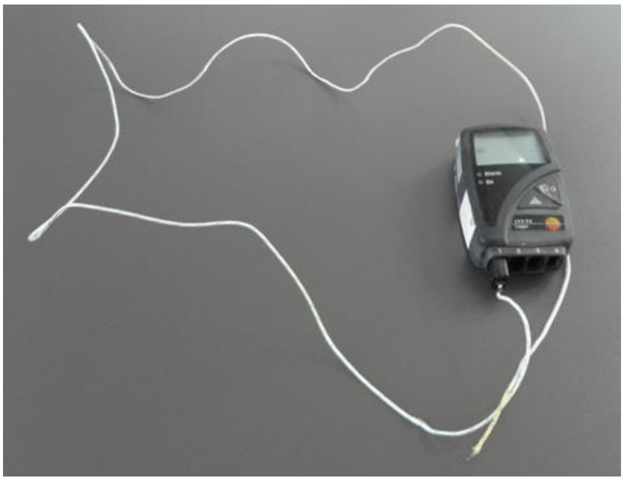


Figure IV.3. Logger 177. T4 testo: temperature controller.

IV.1.2. Specific Equipment

- Pull-Off Test Machine (adhesion test)

PosiTest Adhesion Tester, which is shown in Figure IV.4, is a reliable machine to determine the adhesion that occurs between a powder coating and a substrate (such as wood, plastic or, in this case, in a metallic support).

Figure IV.4. Pull-off test machine: PosiTest®.

It is a quantitative method where a dolly or stub is affixed to a coating. Then, apply a load that increase gradually until the dolly or stub is moved off. At that point, the value of the force necessary to separate the coating from the surface can be obtained in the units of MPa or psi. Figure IV.5.represents a diagram of the basic principle of the mechanism.

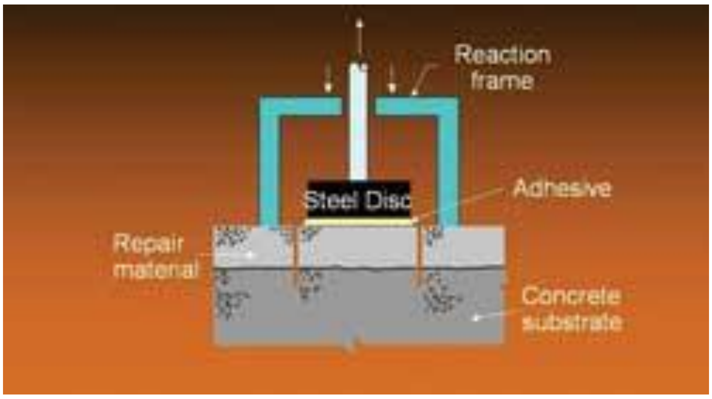


Figure IV.5. Adhesion test mechanism. Source: http://www.concrete.org

The machine is useful to check the standards ASTM D4541/D7234, ISO 4624/16276-1 or AS/NZS 1580.408.5, among others international standards.

In case the connection surface-coating is extreme, the test can be adapted in function of the dolly or stub:

Table IV.2. Maximum strength in function of size of dolly.

Dolly Size (mm)	Adhesion (psi)	Adhesion (MPa)
10	10000	70
14	6000	40
20	3000	20
50	500	3,5

About the substrate, the only requirement for it, is to support the force without deformation, otherwise the results would be incorrect.

Technical data (details):

- Kit Weight (with case): 13 lbs / 6 kg
- Carrying Case Dimensions: L – 17 in / 43 cm x W – 13 in / 33 cm x H – 6 in / 15 cm
- Maximum working temperature: 200°C
- Availability of different dolly size (mm): 10, 14, 20 and 50mm
- For 20mm dolly (used in the project):
  - Resolution: 1 psi (0.01 MPa)
  - Accuracy: ± 1% Full Scale
  - Adhesion Strength: 0 – 3000 psi (0 – 20 MPa)

- Krüss DSA 100E (surface tension/ contact angle measuring)

The value of contact angle/surface energy measurements is really useful to the repellence or attraction determination of a liquid, like water or acetone on a surface. This tool can be a clear indicator of the Lotus effect (water or other liquids droplets tend to minimize their surface by trying to achieve a spherical shape the apparent).

Equipment Specifications: Technical Data of the DSA100E

- Max. sample size (WxDxH): 300 x ∞ x 150 mm (500 x ∞ x 150 mm for the long frame version)
- Dimension of sample (LxW): 105 x 105 mm (Ø 300 mm) (500 x 500 mm for the long frame version)

- Range of contact angle measurements: 0 to 180° (0.1° resolution)
- Range of surface tension measurements: 1x10-2 to 1000mN/m (0.01mN/m resolution).
- Temperature range: -60 to 400°C
- Dimensions (WxDxH): 620 × 380 × 610mm (954 x 380 x 610 for the long frame version)
- Weight: 25 to 45 kg
- Power supply: 110 to 240 VAC

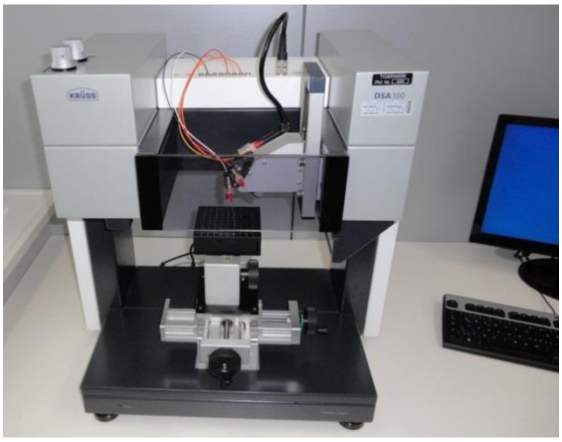


Figure IV.6. Contact Angle Measuring System: Krüss DSA 100E.

- BYK-Gardner Cupping Tester.

BYK-Gardner cupping tester calculates the elongation and deformability of a layer, like paints, inks or powder coating, on metal substrates. With this mechanism (Figure IV.7), the Erichsen Cupping test can be realized (fast and cost-effective testing method). This test gives a reliable first impression of the quality of a coating. Also, it permits checking the quality conform to the international standards ISO 1520.

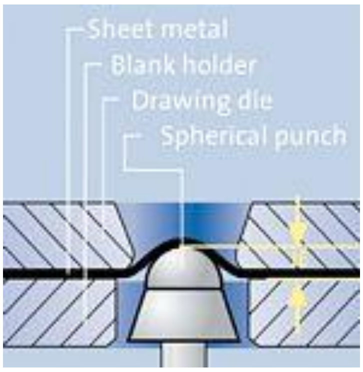


Figure IV.7. Erichsen Cupping test scheme. Source: http://www.erichsen.de

This tool owns a stereo microscope with illumination and brightness control, useful to detect the paint surface breaking during the test, as seen in the image Figure IV.8.

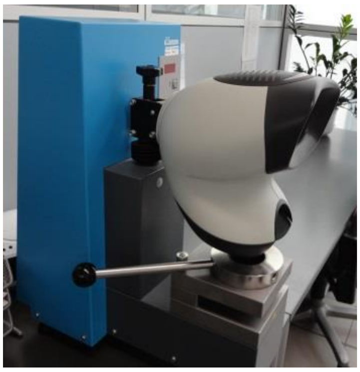
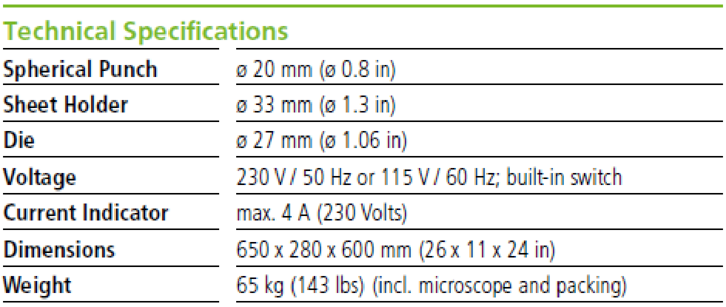


Figure IV.8. Erichsen Cupping test machine: BYK-Gardner Cupping Tester.

The basic characteristics of this apparatus are detailed in Table IV.3.:

Table IV.3.Technical Specifications for BYK-Gardner Cupping Tester.



Technical Specifications

Spherical Punch	ø 20 mm (ø 0.8 in)
Sheet Holder	ø 33 mm (ø 1.3 in)
Die	ø 27 mm (ø 1.06 in)
Voltage	230 V / 50 Hz or 115 V / 60 Hz; built-in switch
Current Indicator	max. 4 A (230 Volts)
Dimensions	650 x 280 x 600 mm (26 x 11 x 24 in)
Weight	65 kg (143 lbs) (incl. microscope and packing)

- Gel time device (Gel Instrumente AG, Heizblock PL).

For determining the gel time of powder coatings (time required to melt a specimen at a laid down temperature and to achieve a gel) this device has been used (Figure IV.9.):

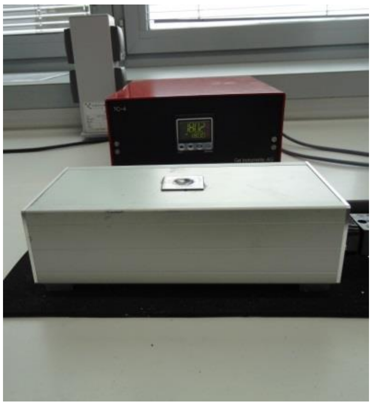


Figure IV.9. Gel time device: Gel Instrument AG, Heizblock PL.

In this trial, a metallic block is pre-heated up to a determinate temperature (110°C and 160°C) and a little amount of the specimen material (powder), about 10 grams, is placed into the depression of the heating block. Simultaneously, a timer is started and the sample is stirred steadily until a gel-like consistency is achieved. The end point is reached when by sudden withdrawal of a glass rod (approx. 20 mm upwards), the "string" of material that is picked up, or when it breaks away from the surface of the mould. Right after that the timer is stopped and time is recorded in minutes and seconds.

Calibration of the mould in the Heating Block GT is performed by melting salts (e.g. temperature indicators of MERCK).

Its dimensions and characteristics, displayed below, are in accordance with the Standard EN ISO 8130-6.

Technical data:

- Heating Block PL acc. DIN 55 990 Ref. 30.45 incl. Pt100-Sensor
- Temperature range 30,0 °C … 200,0 °C
- Main power supply 230 V / 50 Hz or 115 V / 60 Hz, ± 10 %
- Heating power 550 W
- Temperature Controller TC-4 Ref. 70.06
- Melting Salts Various e.g.140 – 180 °C

- Thickness gauge (BYK Gardner, Byko-test 4500).

The project requires that all aluminum sheets have the same thickness of powder coating; for this reason is necessary to use Byko-test 4500 (Figure IV.10.). This equipment is valid to be utilized on different surfaces which can be iron, steel, aluminum, copper, brass, zinc or stainless steel. It is an easy, economic and Non-destructive technique.

Figure IV.10. Thickness gauge (BYK Gardner, Byko-test 4500).

Technical data:

The following list highlights the Technical specifications:

- Measuring Range Fe: 0 - 3000 μm (0 - 120 mils).
- NFe: 0 - 3000 μm (0 - 120 mils).
- Accuracy: ± (2μm + 3 %*), from 0 - 999 μm (0 - 39 mils).
- Minimum Curvature: 5 mm (0.2 in) convex; 30 mm (1.2 in) concave.
- Minimum Substrate Thickness: Fe= 0.2 mm (0.01 in), NFe= 0,05 mm (0,002 in).
- Minimum Area of Measurement: 10 x 102 mm (0.4 x 0.4 in).
- Operating Temperature: 0 - 60 °C (32 - 140 °F).
- Dimensions: 100 x 62 x 27 mm (4 x 2.5 x 1.1 in).
- Weight approximate: 130 g with battery.

- Particle size analyzer (Malvern Instruments).

A Particle Size Analyzer measures particle size using a laser light scattering, uphold by the classic Mie theory. Size plays an important role in determining the end use application of materials. This kind of machines provides an easy way to measure several variables at the same moment:

- size distribution in volume
- size distribution in number
- distribution surface area

An external element is necessary to create homogeneous dispersions and obtainer reproducible values: Scirocco 2000. Below listed are the main features:

Technical data (Mastersizer 2000):

- Principle: Laser light scattering
- Analysis: Mie and Fraunhofer scattering
- Data acquisition rate:1 kHz
- Size range:0.02 - 2000 µm
- Accuracy: Better than 1% (polydisperse standard)
- Reproducibility: Better than 1% variation (polydisperse standard)
- Dimensions: 1293mm x 255mm x 375mm (LxWxH)
- Mass: 31 kg
- Supply voltage: 100/240 v, 50/60 Hz

Technical data (Scirocco 2000):

- Sample feed: Variable feed-rate vibrating tray
- Sample dispersion: Compressed air venture with particle and wall collision
- Pressure range: 0-4 bar

Figure IV.11. Particle size analyzer: Mastersizer 2000/ Scirocco 2000.

- Gradient-oven (BYK, gradient-oven PT-2610):

It is an evaluator of curing temperature. With this special oven, a production baking process can be simulated (with different temperature profiles)and in that manner, able to determine the baking temperature and time for a perfect curing.

Technical data (Gradient-oven PT-2610):

- Voltage 230 V, 50/60 Hz
- Power Consumption: 3400 VA
- Heating Surface 520 x 100 mm (20.4 x 3.9 in)
- Test Surface 500 x 70 mm (19.6 x 2.7 in)
- Linear Gradient max. temp. difference between: 30 and 250 (320) °C: 100 °C; 86 and 482 (608) °F: 180 °F
- Step Gradient with 2, 3 or 4 steps: max temp. difference between. 2 steps: 50 °C (90 °F)
- Heat-Up-Speed 2 °C to 30 °C/min, programmable (3.6 °F/min to 54 °F/min)
- Baking Time in sec. and min.
- Dimensions 465 x 720 x 595 mm (18 x 28 x 23 in)
- Weight 50 kg (110 lbs)
- Accuracy control accuracy of the heating elements: < ± 2 °C(< 3.6 °F) surface temperatures on 0.8 mm test panels from element 3 to 43:
    - to 200 ° ± 2 °C (to 392 ° ± 3.6 °F)
    - to 250 ° ± 3 °C (to 482 ° ± 5.4 °F)
    - to 320 ° ± 5 °C (to 608 ° ± 9.0 °F)

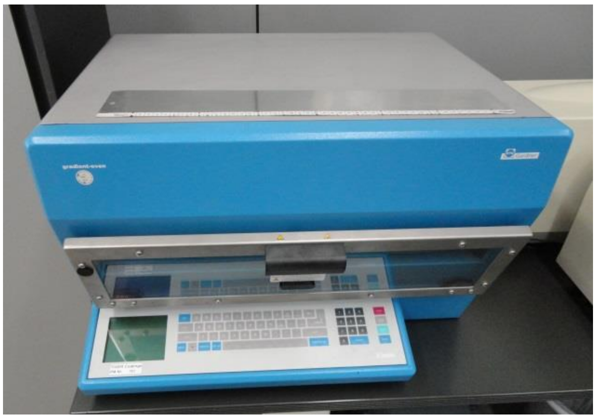


Figure IV.12. Gradient-oven: BYK, PT-2610.

- Dry mixer (Thermo PRISM Pilot 3).

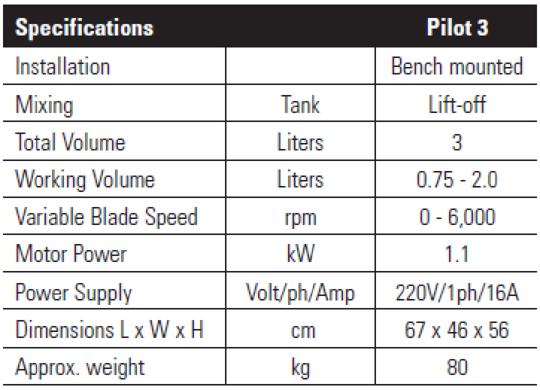
Pilot 3 (Figure IV.13) is designed for mixing different additives in a quick, easy and safe way. Firstly, the tank is locked to the mixer and then premixing is performed. In this system, impellor speeds can be adjusted for optimum mixing of powder coatings, and the modular impellor can be configured for different materials owing to additives can have different properties. Mixing cycles can be preset for repeatable batches.

Figure IV.13. Dry mixer: Thermo PRISM Pilot 3.

High-speed premixing ensures efficient distribution of the many ingredients in a powder coatings formulation, with the added benefit of breaking down resin flakes to give a uniform pre-blend. Trials have shown that high speed premixing improves color development and allows the same color strength to be obtained with lower pigment concentrations.

Technical Data:

Table IV.4. Technical Data: Thermo PRISM Pilot 3.



Specifications		Pilot 3
Installation		Bench mounted
Mixing	Tank	Lift-off
Total Volume	Liters	3
Working Volume	Liters	0.75 - 2.0
Variable Blade Speed	rpm	0 - 6,000
Motor Power	kW	1.1
Power Supply	Volt/ph/Amp	220V/1ph/16A
Dimensions L x W x H	cm	67 x 46 x 56
Approx. weight	kg	80

- Extruder (Theysohn PCE 20/24D).

Basic equipment in the production of powder coatings, PCE 20/24D offers processing equipment on an extremely small scale (in fact, is possible to produce just 100 grams), and thereby, develop rapid and cost-effective investigation of materials, all the way to pilot production systems that permit reliable scale-up to production scale.

The control panel of Theysohn PCE 20/24D consists of a control terminal with touch screen feature which is the heart of the system. Malfunctions and alarm messages are indicated via text in case of any type of necessity; in addition, the control offers a general overview of the current production status.

The Figure IV.14 shows two of the eight pilot extruders that the R&D Department owns.

Figure IV.14. Extruder: Theysohn PCE 20/24D.

<u>Technical data of the process part:</u>

- Power supply 400 V AC / 3ph / 50 Hz
- Frequency 50 Hz
- Device supply voltage 400 V
- Heaters 240 V AC

- Solenoid valve voltage 24 V AC
- Control voltage 24 V DC / 240 V AC
- Processing section length: 24xD = 480 mm
- Number of screws: 2
- Screw diameter: 20 mm
- Screw trim length: 25 × D = 500 mm
- Screw rotation: counterclockwise in the same direction, in the direction seen
- Operating speed of the screw: 600 min-1
- Power: 4 kW
- Eff. Output torque: max. 2x 40Nm
- Efficiency: 97%

- Gloss meter: Micro-TRI-gloss (BYK).

This simple utensil is used to measure gloss of materials such as paper, paint or plastics. There are three measurement angles (20°, 60°, 85°) based on a gloss range. Measuring principles are according to the following standards: ISO 2813/7668, ASTM D 523/D 2457, DIN 67530 and JIS Z8741.

Technical Values:

- Auto range:
    - 0-2000 GU (20°)
    - 0-1000 GU (60°)
    - 0-160 GU (85°)
- Measuring time: 0.5 seconds / geometry
- Dimensions: 155 x 73 x 48 mm (6.1 x 2.9 x 1.9 in)
- Weight: 0.4 kg (0.9 lbs)
- Measuring time: 0.5 seconds / geometry
- Statistics: number of readings per sample are selectable from 2 to 99
- Difference and Pass/Fail: memory for 50 standards with limits
- Power supply one 1.5V AA Alkaline Battery 10,000 readings or via USB-port
- Operating temperature 15 – 40 °C (60 – 104 °F)
- Relative humidity up to 85 %, non-condensing

Figure IV.15. Glossmetter: Micro-TRI-gloss.

- Electrostatic powder gun: ITW Gema Powder Coating Gun.

There are mainly two kinds of electrostatic guns: tribocharging and corona charging (the difference is the method by which the powder is charged). In this R&D project, corona system was used where 80 KV are generated in the gun and released at the gun tip; and at that moment, a flow of free ions created in the field rush towards an object to be coated. To complete the process it is also requires a compressed gas stream to propel the powder thought the piece.

In this delicate process is given the Faraday Effect, making it very difficult to reach certain geometric shapes. Simply put, it is problematic to deposit the powder in very complex objects. Due to that, an object without recesses is chosen to be coated.

In reference to the morphology of the gun, with clear parallels similarity to a real gun, the Figure IV.16.illustrates the parts of that electrostatic gun with pictures and labels.

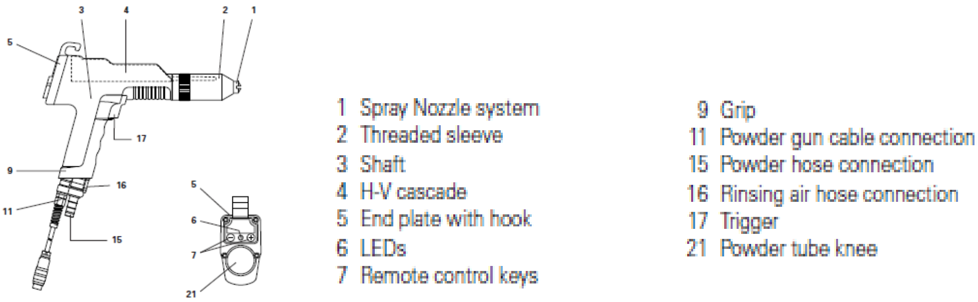


Figure IV.16. Schema of a standard powder gun. Source: Figure Operating Instructions and Spare parts list: Easy Select Manual Powder Gun (ITWGema).

The electrostatic gun is used inside a metallic cabin where coating materials that are unable to reach the objective (piece to be coated) can be collected for recycling or simply for cleaning purposes.

Figure IV.17. Powder gun: Easy Select ITWGEMA.

Equipment Specifications:

- Series n°: 130107554
- Nominal input voltage: 0–12 V DC
- Nominal output voltage: 80 kV
- Polarity: Negative (Option - Positive)
- Max. Output current: 150 μA
- High-voltage display: 2 Light emitting diodes– LEDs

- Spectrophotometer: Bench-top Spectrophotometer CM-3600A.

All the colorimetric values have been determined thought that equipment (Figure IV.18) according to CIELab System.

Figure IV.18. Colorimeter: Bench-top Spectrophotometer CM-3600A.

CIELab system determinates all the colors visible to the human eye and is a reference where three coordinates indicate an exclusive color. These three coordinates or numbers are:

- L (0 is related to black colors and 100 is related to white)
- a (negative values indicate green while positive values indicate magenta)
- b (negative values indicate blue and positive values indicate yellow)

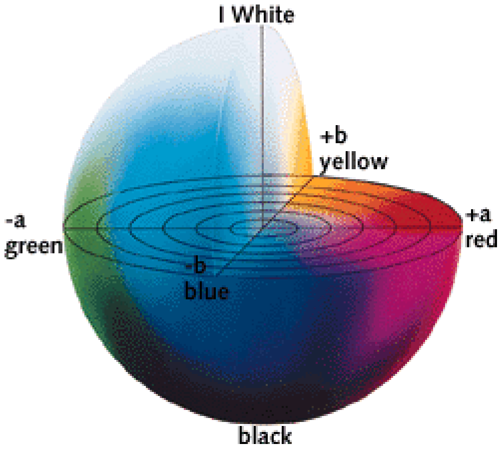


Figure IV.19.CIELab model representation.

Moreover, the parameter E determinates the position of a color in the previous sphere.

$$E= \left((L)^2+(a)^2+(b)^2\right)^{1/2} \qquad (Eq\ V.1)$$

Equipment Specifications:

- Illumination/observation system: Reflectance; di:8°, de:8° (diffused illumination, 8-degree viewing), equipped with simultaneous measurement of SCI (specular component included) / SCE (specular component excluded).
- Light-receiving element: Silicon photodiode array (dual 40 elements)
- Wavelength range: 360 to 740 nm
- Wavelength pitch: 10 nm
- Reflectance range: 0 to 200%; Resolution: 0.01%
- Minimum interval between measurements: Normal SCI/ SCE measurement: 4sec. UV-cut / UV-adjusted measurement: 5 sec. Transmittance measurement: 3 sec.
- Transmittance chamber: Width: 133 mm, Depth: Approx. 50 mm; Measurement diameter: Approx. 17 mm Transmission sample holder (optional accessory): Sample holder for both plate-shaped and liquid samples (removable); Liquid samples not measurable with CM-3610A.
- Size (W × H × D): 244 × 205 × 378 mm

IV.2. DESCRIPTION OF RAW MATERIALS

Almost all the compounds used in the study are standard materials that TIGER Coatings GmbH uses for his production, saving:

Table IV.5. Special compounds used in formulations.

Compound	Main Characteristic	Utility reason
Wax 11…3581	Polyolefin wax coated with PTFE	Necessary in PiMC
Epoxy resin D 671	Self-crosslink resin	Necessary in PiMC
Internal Releaser 1	Fatty Acid Salt	Releaser properties
Internal Releaser 2	Organic Acid	Releaser properties
Internal Releaser 3	Organic Enhancer	Releaser properties
Internal Releaser 4	Metallic salt	Releaser properties
Internal Releaser 5	Mixture of surface-active polymers adsorbed on silicon dioxide	Releaser properties
Internal Releaser 6	Micronized polyethylene wax	Releaser properties
Internal Releaser 7	Bio wax	Releaser properties

Analytical studies were conducted on each compound and their formulation thoroughly examined and tested. Due to confidentially reasons, all the mentioned compounds in Table IV.5cannot be further elaborated as the company wish to hide their formulations.

IV.3. EXPERIMENTAL METHODS

Initially, it was selected and produced 5 powder coatings bases of different nature:

- 3 epoxy (AT 3.1, AT 3.3 and AT 3.4).
- 1 polyester (AT 3.2).
- 1 acrylic (AT 3.5).

The production conditions are presented on Table IV.6

Table IV.6. Production conditions.

Formulation	Par motor (%)	Moment (rpm)	T extrusion (°C)
AT 3.1	35	300	50/90/100/100/100
AT 3.2	35	300	50/80/90/90/90
AT 3.3	35	300	50/80/90/90/90
AT 3.4	35	400	50/90/115/115/105
AT 3.5	30	600	60/80/100/100/100

The development of these five bases uses the technology and knowledge of “Tiger” which still do not exist in the market. The reason of this development of the five bases is to conduct a series of tests to verify this support were in line with reality. The reason why they were selected as bases so different formulations is to know where can behave better this series of additives, and in the future, improve these formulations.

These formulations need to fulfill a number of requirements (low curing temperatures and times, chemical stability, elasticity, fluency...) to be usable for IMC technology. For those reasons, these formulations were deeply analyzed:

- Gel time
- Temperature stability
- Curing parameters
- Mechanical properties (Erichsen Cupping test)
- Chemical properties (acetone test)
- Surface tension
- Size particle distribution
- Viscosity
- Pull-off test

At this point, it is important to note that only four of the five bases were analyzed because one of them (AT 3.5, of acrylic nature) was directly selected from the formulations that the company preserves in his database and intends to market in the coming months.

Although with different characteristic, all of them were considered like acceptable owing to different companies(who are interested on this product) are looking for special and different features.

Once the “mother formulation” was analyzed and studied (is known its time curing, temperature curing…); it was proceeded to add the additives with releaser properties that had been found in a previous research. These additives were found through personal supplier from TIGER Coatings GmbH & Co KG and also via internet.

Each additive was added at its maximum recommended concentration, considering that in a later stage, this can optimize the concentration. In this step, 35 extra bases were produced. (5 mother bases per 7 additives). The production of these bases is one of the hardest points of the project; it requires a laborious work to create each: premix, extrusion, grinding...and for sure, checking their properties.

In the study of these 35 bases highlights the gel time test, basic and essential test in Powder coating business. In all the cases the values of those properties were inside the provisions, saving some formulations which were discarded as they will be displayed in the next chapter.

As soon as the powder was ready to use (thanks to analyzing the stability for curing), it was coated on an aluminum surface (Figure IV.20). These metal supports were performed in the installations of the company because no producer is able to have this type of product for sale with these special dimensions: 17*7,9*0,8cm. (Special thickness because a smaller can deform the support during the adhesion test and distort the values).

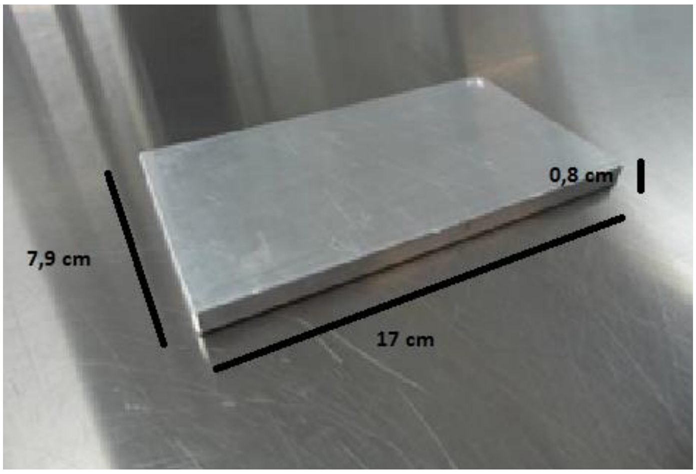


Figure IV.20.Support made of aluminum.

At that point, the sample is introduced in the curing oven, where the powder melts and cross-links to form a hard film to complete the process. Then, dollies are glued on the surface.

This is one of the most important steps because there are difficulties to paste the dolly on the support in some cases (actually the best; it means the internal releaser works).

Once the glue is cured (24h), it is necessary to cut off the powder coating around the dolly and be sure in all the trials are testing the same amount of surface.

Figure IV.21. Dolly glued on powder coatings.

At that moment, it is necessary to record the behavior of powder coatings against the temperature to harvest the optimal temperature/which will be used in production. For this reason, an example will be heated up to 110 °C and another to 160 °C, upper and lower limits of production (it depends on the product, process and company so there are absolute values).

To achieve these temperatures, it is observed that the residence time in the oven was too long, which could harm the sample, and also not so correctly arrived at the desired temperature.

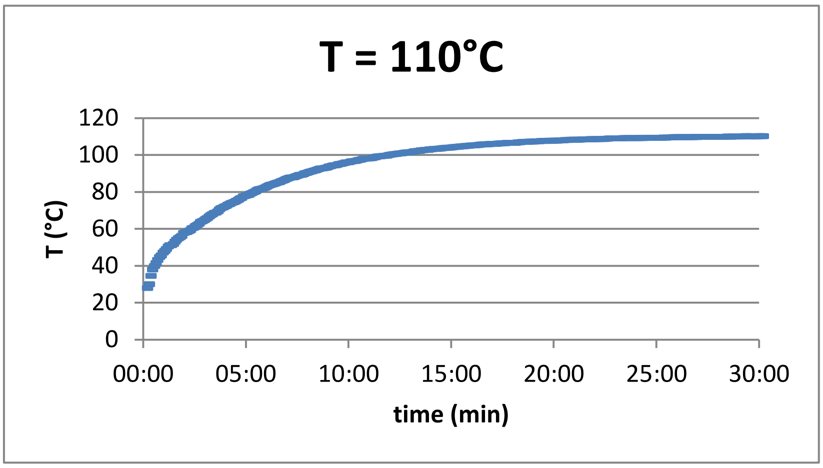
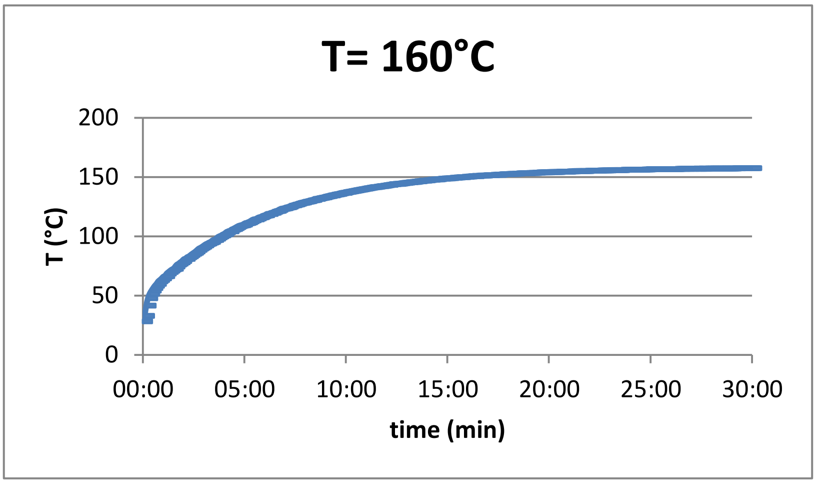


Figure IV.22.T vs t (T_{oven} = 110°C).



FigureIV.23. T vs t (T_{oven} = 160°C).

For this reason, it was decided to bring the samples under a temperature of 200 °C and thus and when they reach the desired temperature, take them to another oven where the temperature is around 110 °C and 160 °C in each case.

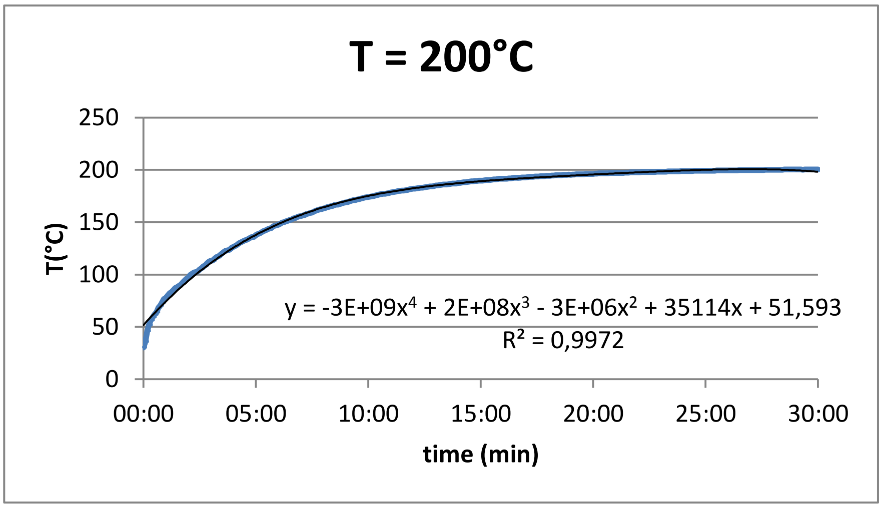


Figure IV.24. T vs t (T_{oven} = 200 °C).

The residence time at 200°C to reach a determinate temperature is given by the equation:

$$T= -3*10^{9*}t^4 + 2*10^8*t^3 - 3*10^6*t2 + 35114*t + 51,593 \qquad (Eq\ V.2)$$

T= Temperature (°C)

t= time (minutes)

So the procedure is as follows:

For T= 110°C: 2 minutes and 48 seconds at 200°C and change to a second oven at 110°C.

For T= 160°C: 7minutes and 34 seconds at 200°C and change to a second oven at 160°C.

This test was also conducted at 240° C, but was suppressed because these temperatures could cause slight deterioration to sample.

When the models are in the second oven, it is necessary to wait 2-3 minutes to reach again the stability, the correct temperature. At that moment, the head of the Pull-off test machine is quickly introduced in the oven and fitted to the dolly, the door is closed and the measure can be taken.

IV.3.1. Quality test

In Section V there are several "quality test" developed to check whether the new formulations are losing properties or not. Though this subsection, the methods of the most important test will be explained.

IV.3.1.1. Viscosity (viscosity tablet test)

The viscosity test method needs to be explained due his generic name. In that test fluidity isdetermined.

Fluidity is a physic-chemical property of a liquid that helps to cover greater surfaces. In PiMC projects, this characteristic is really important. It expects that powder coatings gain access inside the cavities of the damage, the imperfections, leaving with a Class A surface, like is shown in the next Figure.

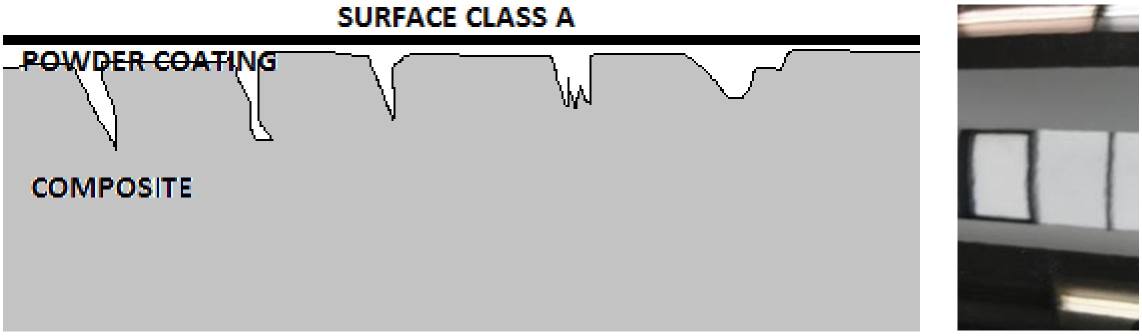


Figure IV.25. Scheme of PiMC technology and example of Class A brightness.

The material (powder coatings) can reach the recesses or holes just in a precious moment: at the beginning of the process. When powder coating starts to polymerizing, it becomes liquid, and in that accurate instant, when is producing the phase change (solid to liquid), the material can flow and fill the gaps or fissures that the composite owns. For this previous reason, a low viscosity is necessary.

This test consists in the production with "raw powder coating" of a round tablet of around 0.7 grams. Once it is ready, it is introduced on an aluminum support into the pre-heat oven (horizontally) for one minute. In that moment starts the phase change, from solid to liquid. During that time, the pill or tablet fits close to the surface support. After this first minute, it will be changed the position of the support, now it must stay vertically, and then the test can carry on.

Test conditions depend on each sample and it is exposed in Table V. in this case were:

Table IV.7. Viscosity tablet test conditions.

Base	**AT 3.1**	**AT 3.2**	**AT 3.3**	**AT 3.4**	**AT 3.5**
Temperature(°C)	120	140	120	120	170
Time (min)	20	20	20	20	30

These conditions are adapted to the resin with which each formulation is composed. The characteristics of the resins are:

Table IV.8. Basic properties of the resin.

Formulation (resin)	**Melt point resin (°C)**	**Viscosity 150° (mPa*s)**
AT 3.1	89-97	1900-3300
AT 3.2	70-72	1200-4000
AT 3.3	75-85	400-950
AT 3.4	100-110	5500-10200
AT 3.5	42-46	200-240

Once the test in finished, it will be able to measure the elongation achieved by the pill with a simple ruler. A high value will be related to a big fluency and a low viscosity. In this test include other factors such as cure time, but not taken into account because the assay conditions. These must ensure a sufficient time for displacement.

IV.3.1.2. Chemical resistance

Once a powder coating is cured, the coated material is very resistant to chemical attack. Moreover, in our special case (PiMC technology), these special powder coatings, will be covered by two layers: one which provides the desired color, and another of varnish that provides the desired gloss (matt, gloss, off…).

These two layers, also known in the business as top coatings, act like a protective film. However, chemical stability due to attack other products can be a serious problem.

The assay was performed by testing different samples which have been cured at different temperatures. In that test, a coated sample is cured in a Gradient-oven (BYK, gradient-oven PT-2610; section) under different conditions:

Formulations: AT 3.1, AT 3.2, AT 3.3, AT 3.4.
    Curing time= 10 minutes
    Temperature range= 80°-180°C
Formulations: AT 3.5.
    Curing time= 20 minutes
    Temperature range= 110°-210°C

Once the sample is cured, it is introduced into acetone during one minute and checked the stability and quality of the coating.

IV.3.1.3. Physical resistance

Testing of the resistance of the coated surface to mechanical damage, especially the measurement of scratch or graze resistance and abrasion resistance, have become essential for many applications. In PiMC technology, the powder coating is located between the good (FRP) and the top coating. For that reason it is not necessary to check the abrasion; but the resistance testing is always a must. Erichsen test is a good method of checking physical properties related to elasticity, hardness or flexibility.

It is developed thank the BYK-Gardner Cupping Tester; previously explained in Section IV.1.

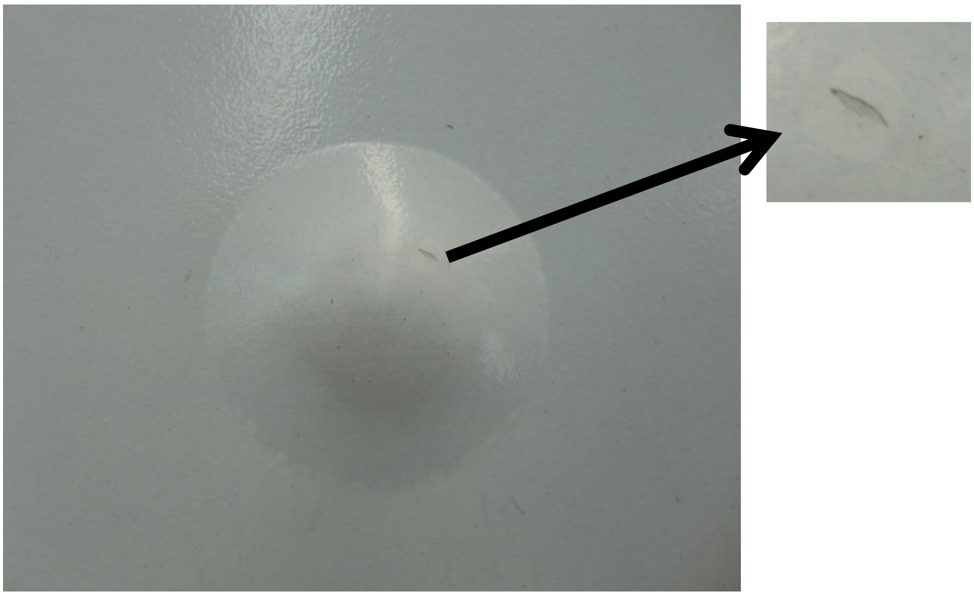


Figure IV.26. Coating breakage.

As can be appreciated in Figure V.27, gradient test is performed with each formulation in order to identify the resistance value at different temperatures.

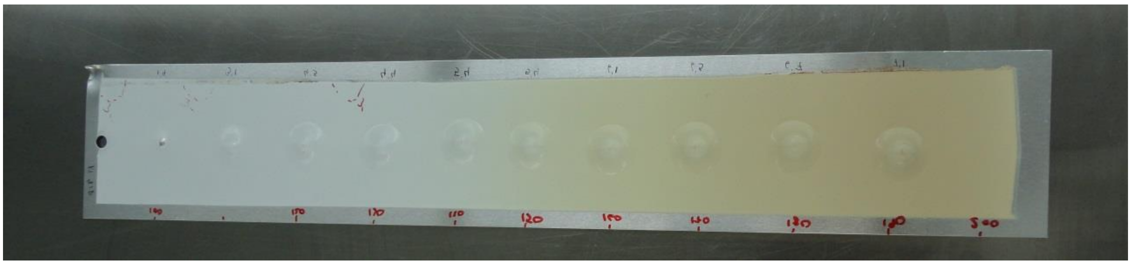


Figure IV.27. Gradient sheet example.

IV.3.1.4. Surface Energy. (Owens-Wendt method)

The contact angle is decisive to the manufacturing of composite materials reinforced with fibers, which play a more and more significant role in such areas as the aviation or automotive industries.

Measurement of contact angles on solids yields data that reflect the thermodynamics of a liquid/solid interaction. These data can be used to estimate the surface tension of the solid. For this purpose, drops of a series of liquids are formed on the solid surface and their angles of contact are measured. In that case, these angles of contact are determined using the equipment Krüss DSA 100E (previously explained) and Owens-Wendt method.

This method proposed the division of the total surface energy of a solid or liquid in two components: dispersion force and hydrogen bonding. The values indicate the surface energy or the surface free energy. The values are achieved through the analysis of various liquid drop placed on a polymer surface; in our case, powder coating. As the measuring liquids; water, acetone, ethanol and diiodomethane are used.

V. EXPERIMENTAL

V.1. INTRODUCTION

This chapter presents the explication of the experimental tests performed and the reasons why these trials have been realized. Moreover, the necessity and basic characteristic for each experiment is commented next to them. A logical explanation for each outcome is offered at the end of each case. The main sections are the following:

Highlighting that, in this section, the exigencies of the customers who are interested in the innovative product have been always considered. Due to each company is interested in different properties, there are diverse test completed for each formulation (depending on the goal). All these exigencies are summarized in the following list:

- Chemical stability and chemically familiar: Is necessary, or at least recommended, a chemical similarity between the FRP and powder coatings. This will promote a good bond between powder coating- FRP.
- Low viscosity: this property allows the filling of recesses and setbacks. (Fluidity to fill the gaps).
- Appropriate energy surface: It depends on the top coatings, but there are some general indications established in the industry.
- Useful to be coated: particle size must be appropriate to charge electronically. An inadequate size offers multiple problems, as is discussed along the text.
- Physicochemical resistance: the final product must withstand a series attacks during its life cycle.
- Low curing temperature and curing time. PiMC needs to be adapted to the production of the conglomerate. (Usually time and temperature curing values for powder coatings are higher than for FRP manufacturing. For instance, a standard powder coating can require 250°C and 15 minutes to be cured; values too high for FRP).

- Useful for PiMC technology: Physical appearance/ influence on top coatings.

However, all the chemical formulations have a common goal:

- **Removing adhesion properties in couple metallic mold-FRP**.

V.2. DESIGNING THE "MOTHER FORMULATIONS"

As previously discussed, the use of the R&D database of the private company was absolutely necessary to develop these initial formulations. In this section, the preliminary work is realized in order to check the quality of the 5 mother formulations used. These mother formulations are really useful in section V.3. As in that part, the materialization of 35 formulations with releasing properties is developed.

These 5 powder coatings formulations (described in Annex V) own really different nature: three of them are epoxy based (AT 3.1, AT 3.3 and AT 3.4; moreover, the latter two are cross linking), another is polyester based (AT 3.2) and the last one (AT 3.5); an acrylic based. All of differences are theoretically explained in Chapter III.3.1., called "Thermosetting Powder coatings". Thermoplastic powder coatings are not considered for the reasons detailed in III.3.2.

The development of the formulations is carried out in conjunction with different tests. As a direct result of that; quality of formulations, properties and future internal releaser influences can be related.

V. 2.1. Analysis of physicochemical properties

V.2.1.1. Fluidity

This method is explained properly in Section V.3.1;including their conditions. Anyway, to acquire a better idea about the test, trials for the formulations AT 3.4 and AT 3.5 are shown in Figure V.1.

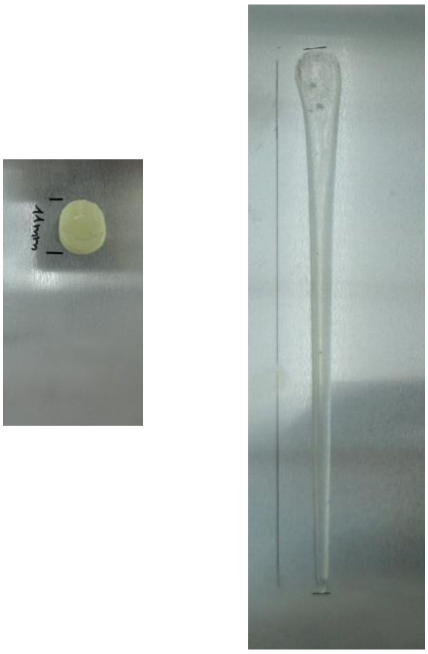


Figure V.1. Viscosity Tablet test. (Formulations AT 3.4 and AT 3.5)

Remember also that, greater elongation is related to a lower viscosity, and in turn, a greater flowability. It is a property that we require for a good composite-powder coating connection. The experimental values can be observed in Figure V.2.

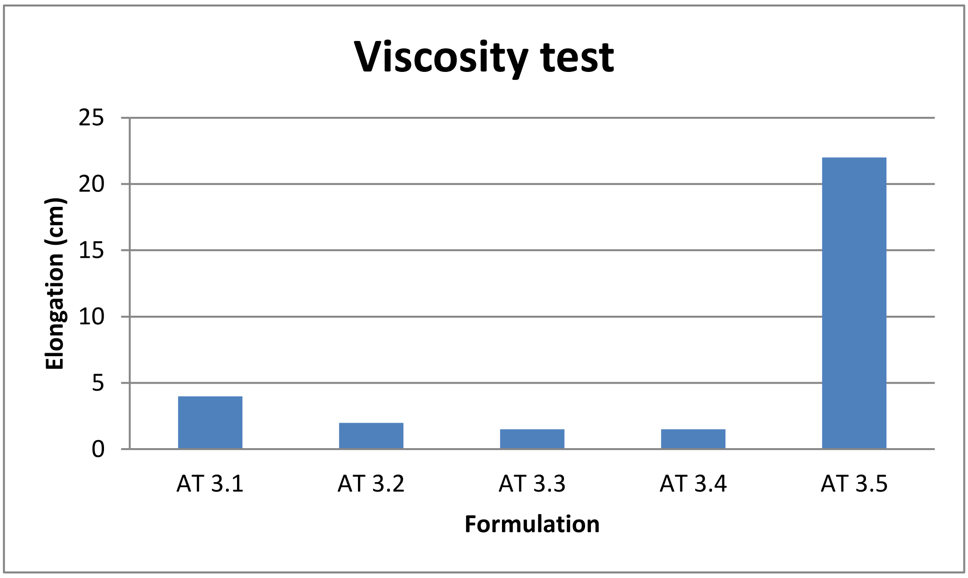


Figure V.2. Viscosity tablet test results.

The powder coating (mother base) called AT 3.5, based mainly on an acrylic type and whose formulation is in Annex V, provides exceptional flow properties. This extraordinary flow property of AT 3.5 is useful to cover all the holes that a fiber reinforced composite owns.

Although formulation AT 3.3. and AT 3.4 own bad viscosity properties, trial be continued because this can be solved with the inclusion of certain fluidizing additives. In addition, the internal releaser may modify this trend.

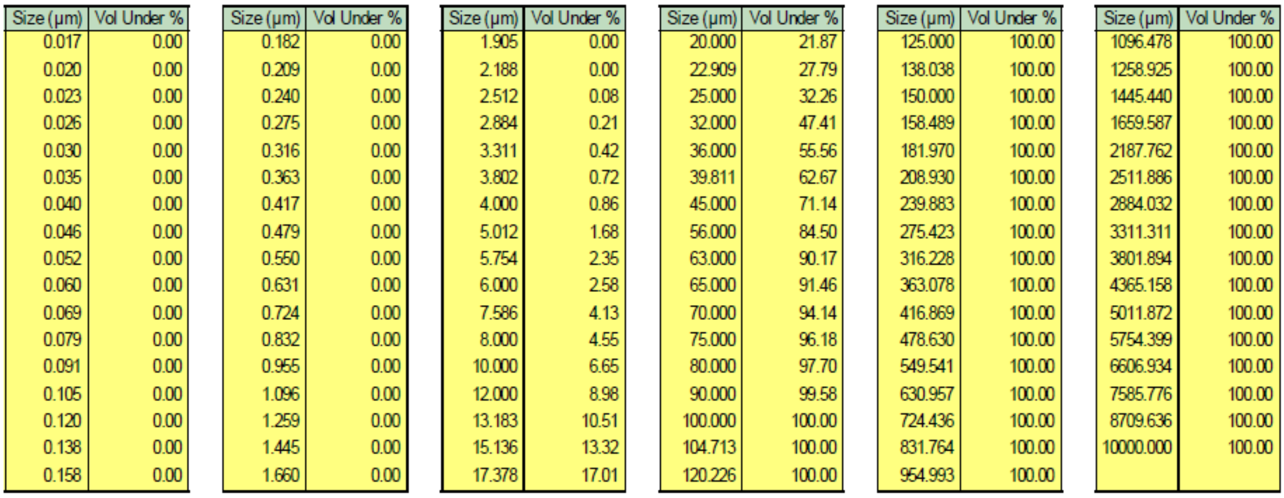
V.2.1.2. Size Particle Analysis

In this subsection, the size of particle of the mother base is evaluated. An inadequate particle size causes a wrong coating.

High particles are related to pinholes, orange peel, and shrinkage during curing. Moreover, because of the Faraday cage effect, the smaller particles will penetrate less into the opening on the article to be coated, thus causing non-uniform distribution of the particles across the coated surface. The accepted range in powder coatings business is about 20-80 µm.

With Particle Size Analyzer, described in Section IV.1.1.2, is obtained the amount of particle depending on the particle size values. For instance for base AT 3.1:

Table V.1.Particle Size Distribution (Psd) of the formulation AT 3.1.



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	21.87	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	27.79	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.08	25.000	32.26	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.21	32.000	47.41	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.42	36.000	55.56	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.72	39.811	62.67	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.86	45.000	71.14	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.68	56.000	84.50	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.35	63.000	90.17	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.58	65.000	91.46	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.13	70.000	94.14	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.55	75.000	96.18	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.65	80.000	97.70	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	8.98	90.000	99.58	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.51	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	13.32	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	17.01	120.226	100.00	954.993	100.00		

And also is obtained a fine representation with Cumulative Undersize Distribution and Differential Size Distribution:

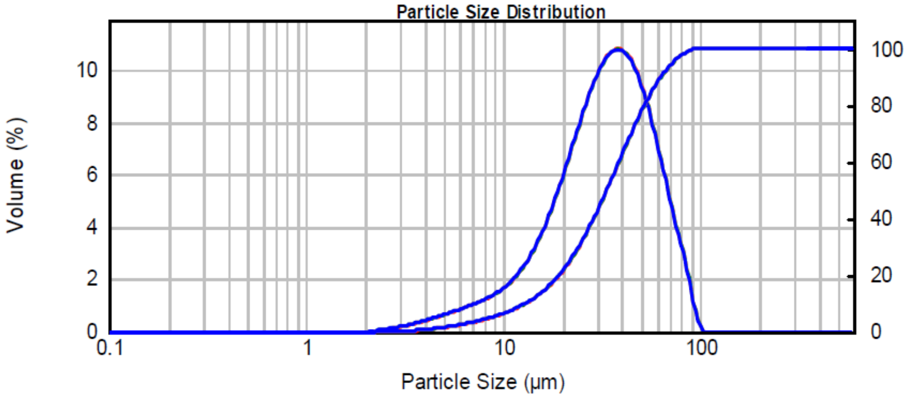


Figure V.3. Particle Size Distribution for Formulation AT 3.1.

Figure V.3 is very useful to appreciate where most particle sizes are concentrated. Due to there are 40 different formulated different powder coatings, it is enough to just consider d(0,1), d(0,5) and d(0,9) values. They are fair representative of the others, and, in any case, Annex 1 shows all these values in a more detailed way.

Table V.2.Psd of the formulation mothers.

Base	d(0,1) (μm)	d(0,5) (μm)	d(0,9) (μm)
AT 3.1	12,8	33,239	62,756
AT 3.2	14,582	39,754	74,213
AT 3.3	9,532	28,09	54,589
AT 3.4	19,255	46,758	87,41
AT 3.5	9,426	28,415	61,123

In following sections, the range between AT 3.4 (upper limit) and AT 3.3 (low limit) will be accepted as the particle size distribution required.

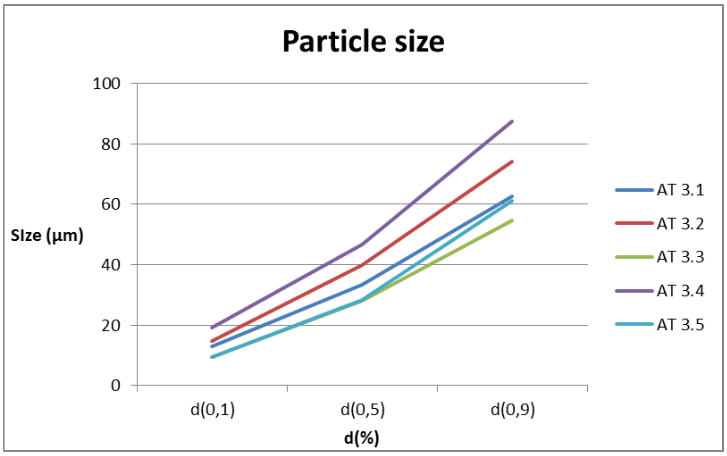


Figure V.4. Acceptable range of particle size.

In case any of the formulations offer an inadequate value of particle size, the problem can be solved easily.

There are two possibilities:

- Changing the conditions of the mill and get the desired particle size. (The conditions in that mill are: rotor 10, sichter 75)
- Sifting the powder coatings. Lower and upper limits can be achieved.

Finally, remark that the particle size depends mainly on the resin to be used (it is about the 90% of the final product), although additives may modify this. The influence of the additives is an undeniable fact, as many researchers have verified. This will be also evident across this work.

V.2.1.3. Curing parameters

In general the study of cure kinetics is of great importance in polymer products for the analysis and design of processing operations. Differential Scanning Calorimetry (DSC) is the main technique used in this kind of works to study the curing reactions. It is usually applied on raw materials.

Notwithstanding, in that kind of material that will be used for really expensive products; like airplanes or automobiles, the consumer and producer must be completely sure of a perfect curing or polymerization. In fact, extra treatment could be accepted or even more expensive production processes. (Just to guarantee a high quality).

For that reason, DSC test of “raw powder coatings” was not the only technique used for measuring curing parameters. This section can be divided into the following points:

- Gel time (initial analysis).
- DSC (standard cure analysis).
- DSC and Gradient-oven (Post-cure analysis).

These analyzes are explicated below for all the mother formulations studied; excepting for AT 3.5. This formulation is not yet optimized. Curing temperatures are too high in that design which means it is not ready for PiMC. Anyway, there is a parallel investigation line to this project that works on reduce this value. Data from this study will be transferred to the parallel line.

Gel time:

The values obtained from this technique, previously explained in Chapter III.5.4, can be appreciated in Table V.3.

Table V.3. Gel time values at 110°C and 160°C.(*)

	Gel time 110°C (s)	**Gel time 160°C (s)**	**Ratio(110/160)**
AT 3.1	67,01	29,72	2,25
AT 3.2	180,23	95,1	1,90
AT 3.3	166,05	24,65	6,74
AT 3.4	125,41	19,84	6,32

(*) It has been decided to use the temperatures of 110°C and 160°C, as are the limits of our project, although this test is performed usually at 170-180°C in the powder coatings industry.

The values indicate that high temperature always offer faster curing. That is nothing new, but taking into account the ratio (t_{110}/t_{160}) other conclusion can be obtained: formulations with larger radius (AT 3.3 and AT 3.4) are better for using at high temperatures (catalysts and accelerators act potently activate for the temperature).

In cases where the ratio is smaller (AT 3.1 and AT 3.2), the formulation are less influenced by the temperature, so it would be more useful in processes where high amount of heat are not required.

Resins used in AT 3.3 and AT 3.4 are the only ones with self-crosslinking character, which indicates that self-crosslinking resins are more influenced by high temperatures. Moreover, note that the influences on the resin used in each formulation are quite clear.

Table V.4. Melt point resin.

Resin	Melt point resin (T°)	Gel time 110°C (s)	Gel time 160°C (s)
Resin epoxy H312 (AT 3.1)	89-97	67,01	29,72
Polyester resin H 6055 (AT 3.2)	70-72	180,23	95,1
Epoxy resin D 671 (self crosslink) (AT 3.3)	75-85	166,05	24,65
Epoxy resin D 664 (self crosslink) (AT 3.4)	100-110	125,41	19,84

Furthermore, a first knowledge of the stability can be achieved:

Table V.5. Physical characteristic. Gel time.

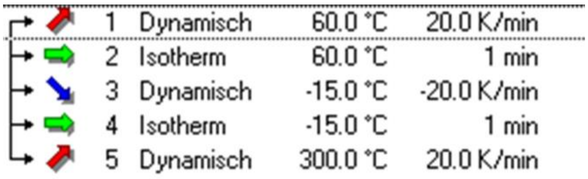
	Gel time 110°C (s)	Gel time 160°C (s)
AT 3.1	Hard	Minimally gum
AT 3.2	Hard	Little elastic but quite hard
AT 3.3	Really hard	Really hard
AT 3.4	Hard	Little smothy

AT 3.1 shows a slight loss of stability. However, when the material is cooled, the powder coating formulation always demonstrates fairly good hardness properties, recovering all the stability needed for the project. All the bases are seemed to be useful for PiMC technology.

DSC (standard cure analysis): Raw formulation

Dynamic and isothermal cure experiments on the powder coating formulation are carried out in order to model its cure mechanism. The T_g signifies a transition of the polymer from a solid to a rubbery state. As the temperature of a polymer is raised above its Tg, the effective distance between molecular segments is increased. The conditions that are brought under are listed in the Table V.6.

Table V.6. Test conditions.



↗	1	Dynamisch	60.0 °C	20.0 K/min
➡	2	Isotherm	60.0 °C	1 min
↘	3	Dynamisch	-15.0 °C	-20.0 K/min
➡	4	Isotherm	-15.0 °C	1 min
↗	5	Dynamisch	300.0 °C	20.0 K/min

The next figures are obtained from this essay.

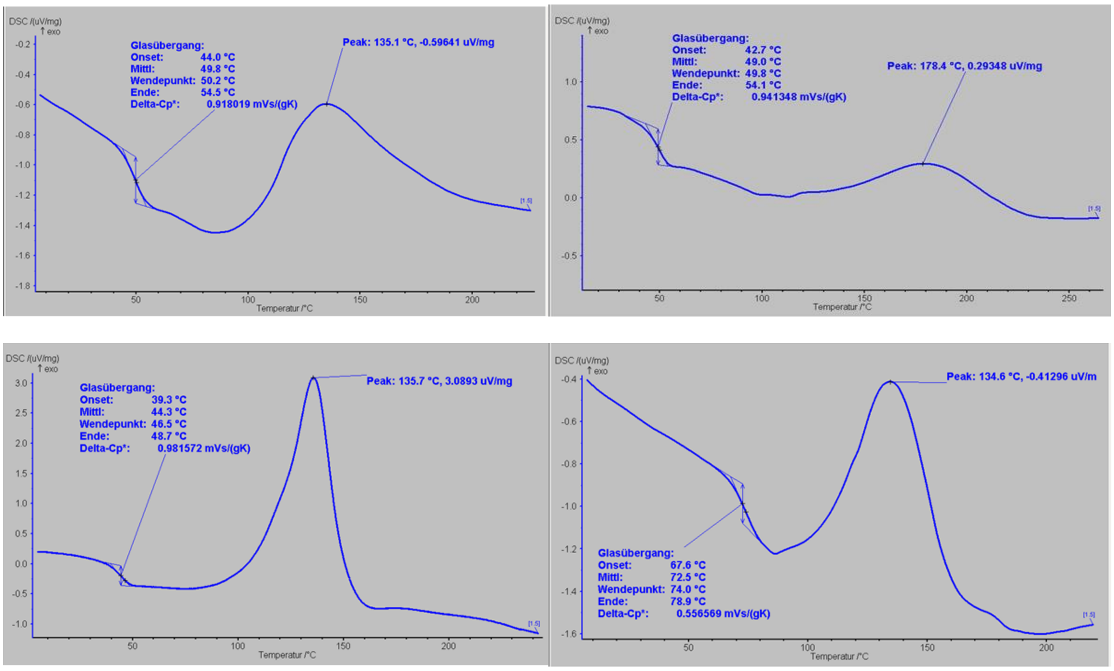


Figure V.5. DSC of “raw” formulations.

With the tests, the values are obtained from the Table V.7, which also indicate initial values curing.

Table V.7. DSC values of raw material.

Powder	Melt point (°C)	DSC Curing starting point (°C)	DSC Peak (°C)
AT3.1	50,2	88	135,1
AT3.2	49,8	100	178,4
AT3.3	46,5	82	135,7
AT3.4	74	83	134,6

These values suggest that the formulation AT 3.2 probably requires more time to be cured. It starts to cure later, and the peak is quite high.

This test is supposed to be sufficient to determinate the curing parameters. However, as mentioned earlier, due to the high value of the product, some extra tests are carried.

DSC and Gradient-oven (Post-cure analysis)

In this section, a DSC test of the cured samples is done. A little amount of each material cured at different temperatures (110 °C, 120 °C, 130 °C...) is used as specimen. Curing times for each example are as follows:

- AT 3.1, AT 3.3 and AT 3.4: 10 minutes
- AT 3.2: 15 minutes

This sample is analyzed until a complete polymerization is achieved. For simplify of the assay; are considered intervals of 10 °C. (Smaller intervals do not show clear differences).

AT 3.1. 120°C

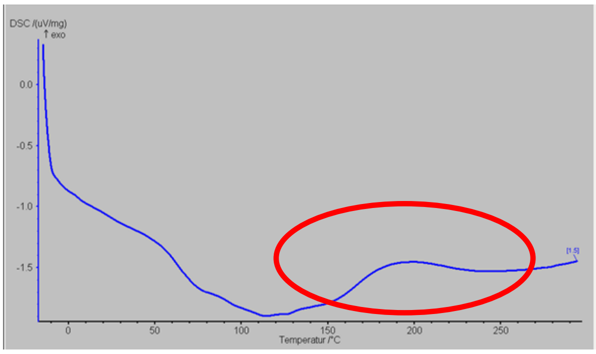


Figure V.6. DSC. Formulation AT 3.1. (10 min- 120°C)

AT 3.1 130°C

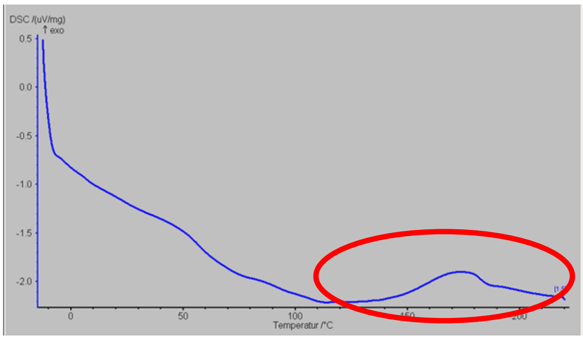


Figure V.7. DSC. Formulation AT 3.1. (10 min- 130°C)

AT 3.1 140°C

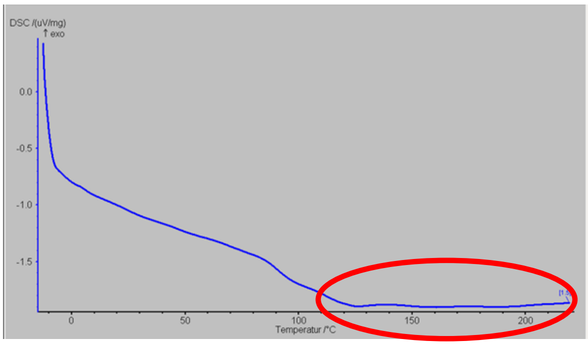


Figure V.8.DSC.Formulation AT 3.1. (10 min- 140°C)

By increasing the curing temperature, is noted how the variation of the line is reduced (from 150°C until 200°C).In the last of the figures can be seen as there is no variation in the display, indicating that the curing process had already reached. (Circled in red)

These same tests are conducted for the other bases. The results are shown in Table V.8. The graphics can be observed in Annex II.

Table V.8. Total curing temperatures.

Formulation	T complete cured (°C)
AT 3.2	140
AT 3.3	140
AT 3.4	140

With the increasing of time applied on AT 3.2, is achieved a homogenization of the temperatures.

V.2.1.4. Chemical resistance

Once a powder coating is cured, the coated material is very resistant to chemical attack. Moreover, in our special case (PiMC technology), these special powder coatings, will be covered by two layers: one which provides the desired color, and another of varnish that provides the desired gloss (matt, gloss, off…). These two layers, also known in the business as top coatings, act like a protective film.

The previous paragraph indicates that this test is not necessary; however, chemical stability due to attack other products can be a serious problem. For that reason, this assay, explained in subsection IV.3.1, is carried out. The values are exposed in Table V.9.

Table V.9.Temperature of chemical stability. (Mother formulations)

Formulation	**T $_{\text{Chemical stability}}$ (°C)**
AT 3.1	120
AT 3.2	134
AT 3.3	102
AT 3.4	105
AT 3.5	165

The fact that the solvent did not affect the coating indicates that chemical stability is pretty good; although it is not a 100% cured. (as is explained in the previous section). Special attention to the formulation AT 3.5 owing has a higher value of chemical stability (165°C). It is because the formulation is not properly optimized. It needs a higher temperature to cure correctly.

AT 3.3 and AT 3.4, both epoxy self-crosslinking bases, offers the best results. The stability is reached at really low temperatures.

V.2.1.5. Printing parameters

It is important to identify if the top coating shall fit properly on the surface of the composite or not. This depends directly on the nature of top coating, but can be taken into account the following consideration: high surface tension of the substrate and low tension of inks facilitate the coating process.

Certainly, the best situation for the coating of a substrate occurs when the surface tension of the substrate is much greater than the liquid that will be coated on the substrate. It stands to reason that is interesting to attain a low surface tension value in powder coating manufacturing.

However, in this particular case, the substrate is the powder coating. At this point everything is different from what is supposed for a standard powder coating. The surface tension should be as great as possible. Whichever type of surfactant in the formulation is quite negative and, as is mentioned previously, it can trigger a problem related to the optical defects.

There are various tests to check the surface tension. In the project this test is performed in accordance with Owens- Method (explained in Section IV.3).

The results of the formulation AT 3.1 are shown in Figure V.9 and Tables V.10/V.11. The detailed values for the rest of the bases can be found in Annex III.

Table V.10. Solvent test: Owens-Wendt Method. AT 3.1.

No.	Theta [°]	Liquid Name	IFT [mN/m]	Disperse Part	Polar Part
0	110,8	Water (Ström)	72.80	21.80	51.00
1	101,2	Glycerol (Ström)	63.40	37.00	26.40
2	88,1	Ethylene glycol (Ström)	47.70	30.90	16.80
3	30,1	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table V.11. Surface tension results. AT 3.1.

Calculation Results [Method: Owens-Wendt]
Disperse Part = 23.77 [mN/m]
Total Surface Energy = 23.77 [mN/m]
Polar Part = 0.00 [mN/m]

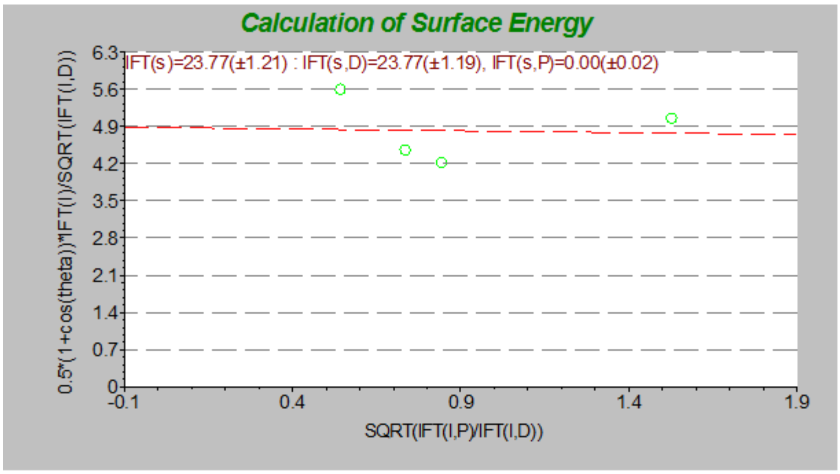


Figure V.9. Calculation of Surface Energy. AT 3.1.

The Figure V.9 provides a representation where each solvent provides information to obtain the surface energy.

The Table V.12 offers a resume with the most important values:

Table V.12. Surface tension (basic formulations).

Formulation	**Disperse part (mN/m)**	**Polar part (mN/m)**	**Total Surface Energy (mN/m)**
AT 3.1	23,77	0	23,77
AT 3.2	22,26	2,13	24,39
AT 3.3	16,94	3,63	20,57
AT 3.4	9,70	20,48	30,18
AT 3.5	13,39	17,07	30,46

In this section, it is interesting to get a large value of at least 2mN/m for the polar part. All formulations are within the minimum specifications, except formulation AT 3.1. However, AT 3.1 is not discarded, foreknowing that mold release additives are able to influence this property. (Although not really knowing yet)

Despite all the trials, with this physicochemical property, is necessary to verify that the process works while the applying of a top coating.

V.2.1.6. Physical Resistance.

The values of Erichsen test are represented on Figure V.10.

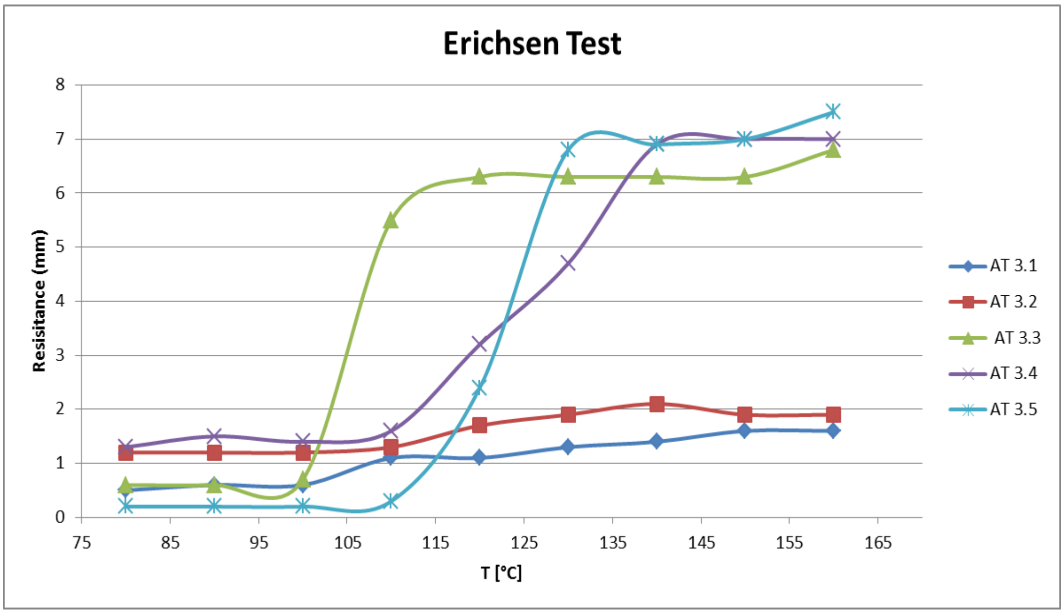


Figure V.10. Erichsen Test values for mother formulations.

As shown in Figure V.10; values increase when the curing process is occurring. It is stabilized when is reached (or exceeded) the polymerization. The results can be divided into two groups: formulations with very good properties (AT 3.3, AT 3.4 and AT 3.5), which resist 7mm of deformation, and formulations with bad properties (AT 3.1 and AT 3.2). The lowest value will be studied with caution in the following section. It must be taken into account that the "special" additives which modify such properties have not yet been introduced.

V.2.1.7. Physical Appearance

Maybe it can be thought that physical appearance (color and brightness) to this project is not essential because this material will be covered by a top coating. However, the colorimetry of the top coating can be influenced because this owns a minimum thickness. For this reason, this section is required.

Additionally, at this moment, this product is so little progress in the market that it is impossible to develop the color and gloss that the customer desire. However, this idea saves the top coating process: printing of a top layer of color paint and other one with a clear coating. This clear coating is used for improve the gloss; like a varnish.

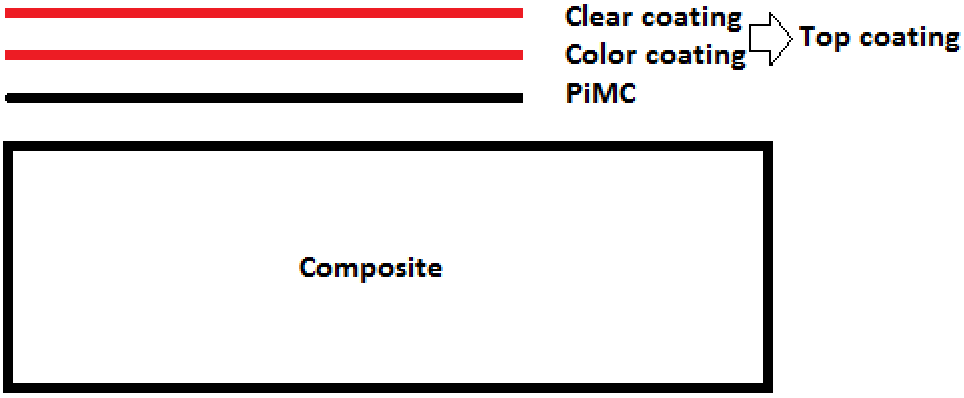


Figure V.11. Scheme of top coating.

It is perfectly conceivable that once the technique is in a most advanced development, it will be able to eliminate the color application step, and maybe the clear coating. This is one of the reasons because formulation AT 3.5 is developed.

Colorimetry

In the event that the customer would be interested, these are the colorimetry values of the mother bases:

Table V.13. Colorimetry of the mother bases.

Formulation	L	a	b	E
AT 3.1	92,59	-1,13	0,26	92,60
AT 3.2	90,49	-0,92	0,77	90,50
AT 3.3	90,87	-1,03	-0,94	90,88
AT 3.4	90,58	-0,61	1,09	90,59
AT 3.5	84,07	-0,28	1,2	84,08

Four of the bases possess a colorimetry clearly white, positive as we can assume that only with the addition of pigments, it can obtained the desire color. In addition, there are uncertainties about a strong color (such as black, dark gray...) like a PiMC. It can influence the top coating, and, for sure the final color product.

The mother formulation called AT 3.5 is a clear coating. The observed color really belongs to the metallic substrate.

Brightness

Like is previously discussed; if deemed a further step in PiMC technology, why not also get the desired brightness? It is, nowadays, a fact unthinkable in the automotive and aeronautic industry.

This is not the main reason for the project because it would be a goal that will be reached in many more years to come, maybe decades, but it is the reason to consider the AT 3.5 formulation.

TableV.14. Brightness of the mother bases.

Comment	Gloss (GU)*
AT 3.1	1,1
AT 3.2	4,5
AT 3.3	22,5
AT 3.4	3,7
AT 3.5	127,3

* Formulation AT 3.1.-AT 3.4. With measurement angle 20°/Formulation AT 3.5 with measurement angle 60°.

The values of the formulation AT 3.1, AT 3.2, AT 3.3 and AT 3.4 are quite matt, in contrast to the formulation AT3.5, which is formulated with the purpose of having a high gloss. The main reason of that differences are caused by the acrylic resin (7610) and the additive 548; an optical brightener, among others.

In the section V.3.5.2, the brightness values for all formulations arising from the formulation 3.5 will be analyzed, because glitter loss starring by mold releasing additive is a reason of worthlessness in the formula.

V.2.2 Conclusion

At this point, five formulations have been obtained which are useful for change his mold release characteristics: real innovation in the market. Currently, almost everything is within expectations, but out of the horizon results are to be seen on next section.

V.3. DESIGNING THE POWDER COATINGS FORMULATION WITH RELEASER PROPERTIES.

Once all the “mother bases” have surpassed the initial tests and have been properly characterized (resistance, curing parameters, surface tension…); now it proceeds with the inclusion of the “special” additives. These additives are supposed to offer mold release properties. On the other hand, this can lead to the destabilization of the chemical formulation.

First note that these formulations are produced mainly with resin (polyester, acrylic or epoxy); and these same resins are used to produce adhesives or glue. This indicates that the success of the project can be doubted. It seeks to remove a property (adherence) that is intrinsic of the resins.

At this point is necessary to re-formulate, prepare, extruding and grinding 35 different formulations. These steps have been explained on Section III. 4.

1. From AT 3.1 are obtained the next formulations: AT 4.1, AT 4.2, AT 4.3, AT 4.4, AT 4.5, AT 4.6 and AT 4.7.
2. From AT 3.2 are obtained the next formulations AT 4.9, AT 4.10, AT 4.11, AT 4.12, AT 4.13, AT 4.14 and AT 4.15.
3. From AT 3.3are obtained the next formulations: AT 4.17, AT 4.18, AT 4.19, AT 4.20, AT 4.21, AT 4.22 and AT 4.23.
4. From AT 3.4are obtained the next formulations: AT 4.25, AT 4.26, AT 4.27, AT 4.28, AT 4.29, AT 4.30 and AT 4.31.
5. From AT 3.5are obtained the next formulations: AT 4.33, AT 4.34, AT 4.35, AT 4.36, AT 4.37, AT 4.38 and AT 4.39.

The formulations 4.8, 4.16, 4.24 and 4.32 are not included owing to the additive considered for that formulation was declared as forbidden during the development of the project.

All the formulations are exposed in Annex V; although of course, hiding the original name of the products used. The mission of each component will be reported for give sense to the formulation.

About these new formulations, each releaser compound is used at the highest recommended concentration. These “highest recommended concentrations” is determined thought the advice of some suppliers of the company.

Due to each base having different characteristics, properties and requirements, it will be considered separately in function of the “mother base”. The tests performed on each formulation (depending on the mother formulation) are listed below:

For AT 3.1, AT 3.2, AT 3.3 and AT 3.4 “reformulations”:

- Gel time
- Particle size distribution
- Pull-off Test.

For AT 3.5 “reformulations”:

- Gel time
- Particle size distribution
- Aesthetic test
- Pull-off Test

In AT 3.5 is considered an aesthetic test due to this product is designed with a clear intention: eliminating the top coating.

The best values are deeper discussed in the section V.4 (Analysis of the best results). This is the last step before submitting the final product to the customer.

V.3.1. Formulation AT 3.1

This formulation is mainly based on an epoxy resin and a high concentration of hardener. The hardener (H866) is added to the formulation once the powder has been extruded; it mean, with the cool chips. Otherwise, the pre-reactions would occur inside the extruder and the coating material would not be valid.

V.3.1.1. Gel time

This test will inform us about the incompatibility of the additive with the chemical base. A disorder in the curing process or instability in the final product can be checked (although it is a primary test and should be verified by other analytical techniques, as clarified in section V.2.1.3):

Table V.15. Gel time values. Reformulations AT 3.1.

Formulation	Gel time 110°C (s)	Gel time 160°C (s)	Time Influence at 110°C (s)	Time Influence at 160°C (s)
AT 3.1	67,01	29,72	-	-
AT 4.1	69,25	32,41	2,24	2,69
AT 4.2	69,02	33,12	2,01	3,40
AT 4.3	68,21	31,82	1,20	2,10
AT 4.4	65,92	29,13	-1,09	-0,59
AT 4.5	76,01	34,08	9,00	4,36
AT 4.6	68,53	29,79	1,52	0,07
AT 4.7	66,84	29,58	-0,17	-0,14

The influences of each additive in the polymerization can be observed in Table V.14. All the variations are perfectly acceptable. The additive AR 5 included in AT 4.5, a mixture of surface-active polymers adsorbed on silicon dioxide, could slow down the process. It shall not be taken into account and is just considered that the influence on the design is a reality.

Regarding physical stability, in no case seems loss. The formulations at high temperature (160°C) are slightly rubbery; practically inappreciable. However, with the decreasing of the temperature, the hardness and physical properties are exceptional. It can be considered that all formulations pass this first screening.

V.3.1.2. Particle size distribution

The inclusion of an additive in a powder coating formulation, as mentioned above, can bring its destabilization. In the best case, the variation of their mechanical properties, like gloss or hardness. With the change of hardness emerge a different resistance to be milled. This section examines the resistance to be grounded.

As explained previously; psd is always a necessary test (as it proves a worthy coating, and thus, the absence of holes or orange peel, among others problems).

Here it is exposed only d (0, 1), d (0, 5) and d (0, 9) values for reasons of space. Annex I contains further details. For the next psd studies, it is also necessary to resort to the same Annex for additional specifications.

Table V.16. Psd values. Reformulations AT 3.1.

Formulation	d (0,1)(µm)	d (0,5)(µm)	d (0,9)(µm)
AT 3.1	**12,800**	**33,239**	**62,756**
AT 4.1	13,648	34,223	64,004
AT 4.2	13,153	34,24	63,623
AT 4.3	12,543	35,964	69,659
AT 4.4	12,656	36,429	70,566
AT 4.5	13,781	34,916	64,981
AT 4.6	12,913	33,992	63,812
AT 4.7	12,656	36,219	70,059

Although there are some visible differences (for example AT 3.1 and AT 4.4), everything is inside of the standard the project requires.

For second time, the additives do not seem to influence seriously.

V.3.1.3. Pull-off Test

This test is the most important owing it is informing us about the adhesion the coating owns. A loss of adhesion between the metallic substrate and the coating is the desired goal. These tests are discussed in deeper. The values of the formulations based on the “mother formulation” AT 3.1 are in the Table V.17.

Table V.17. Adhesion tests. Reformulations AT 3.1.

	Pressure at Room Temperature: 22°C (Mpa)					**Pressure at 110°C (Mpa)**					**Pressure at 160°C (Mpa)**				
				Average	**Comment**				**Average**	**Comment**				**Average**	**Comment**
AT 3.1	4,56	3,89	4,23	***4,23***	Perfect separation	0,08	0,11	0,11	***0,10***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.1	0,85	0,89	0,79	***0,84***	Perfect separation	0,19	0,14	0,10	***0,14***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.2	1,59	1,82	1,65	***1,69***	Powder breaks	0,13	0,10	0,09	***0,11***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.3	1,26	1,1	1,11	***1,16***	Perfect separation	0,08	0,11	0,07	***0,09***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.4	1,00	0,71	0,74	***0,82***	Perfect separation	0,15	0,18	0,15	***0,16***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.5	4,64	5,00	4,84	***4,83***	Powder breaks	0,05	0,06	0,13	***0,08***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.6	5,17	6,14	5,84	***5,72***	Powder breaks	0,38	0,44	0,37	***0,40***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface
AT 4.7	2,86	3,06	2,68	***2,87***	Powder breaks a little	0,12	0,13	0,13	***0,13***	Small particles on the surface	<0,05	<0,05	<0,05	***<0,05***	Small particles on the surface

The values obtained in this section are quite disappointing. The formulation called AT 3.1 is a combination that offers tiny adhesion at high temperatures. For this reason, was considered that the inclusion of the special additive, in a very simple manner, would allow obtaining the desired self-detaching product. However, it does not occur.

Close to the average value of the each test, there is a mild comment indicating the quality of the releasing: perfect, the powder breaks...

In order to consider the results, the analysis is performed in function of the temperature.

Lower limit (Temperature = 110°C)

The influence of each additive can be mildly perceived in each case, although, in no case there is a "clean demolding". Powder coating particles remaining on the metallic support, as is shown in Figure V.12. This is a serious problem: Class A surface finishing disappears.

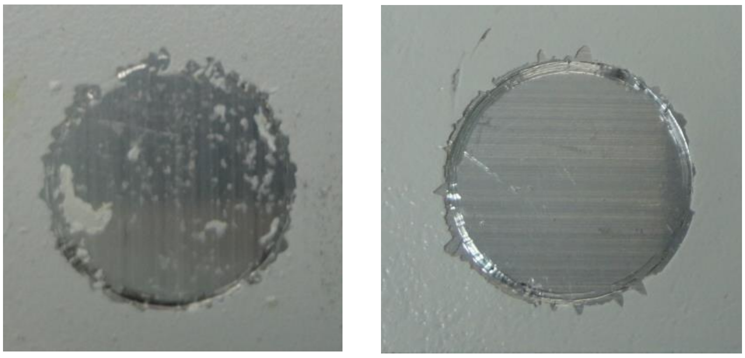


Figure V.12. Comparison: bad vs good releasing.

Moreover, in contraposition of what is pursued, in 5 of the 7 cases (AT 4.1, AT 4.2, AT 4.4, AT 4.6 and AT 4.7) the adhesion increases. Particularly striking is the case AT 4.6, where a micronized polyethylene wax marketed to reduce adhesion on plastic materials produces a heavy increase (from 0,10MPa till 0,40MPa or from 31,4N to 125,66N considering the diameter of the doll: 20mm).

All these formulations will be deleted to its use at that temperature conditions (110°C).

Upper limit (Temperature = 160°C)

Although adhesion is minimal (<0,05MPa) in all the cases, the same problem appears: the detaching is not cleaning. Moreover, the influence of the “special” additives at these temperatures is questionable. In no case there is a difference that the machine PosiTest® (Pull-Off Adhesion Tester) is able to detect. No formulation is valid for the project.

Room Temperature (22°C)

Based on the obtained data, it is considered to analyzing the adhesive properties at room temperature; around 22°C. In that conditions, the formulation AT 4.1 and 4.4 offer really good results.

The reduction in each case is described in Figure V.13:

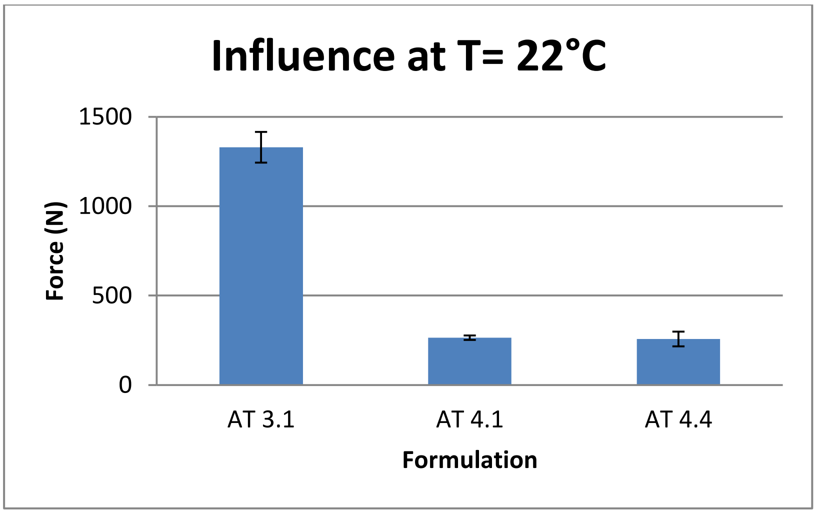


Figure V.13. Adhesion of reformulations AT 3.1 at room temperature. (22°C).

The force required to peel the coating decreases due to additives addition: from 1328,85 N till 263, 89N (AT 4.1) or 364,41N (AT 4.4). Responsible are a fatty acid salt (AT 4.1) and a metallic salt powered by an organic enhancer.

On the other hand, AT 4.5, AT 4.6 and AT 4.7 lost the stability and are not useful for PiMC technology. Under pressure it breaks. Moreover, AT 4.5 and AT 4.6 show bad behavior: adherence increases. Throughout the project will be checked that some additives, especially IR 6, a micronized polyethylene wax, increase the connection between the metallic mold and the powder coating.

Despite of At 4.1 and AT 4.2 brought hope to the project's viability; neither of them are not useful for customers. They require obtaining the FRP at high temperatures. No client company wants to produce high performance composite, cool the mold (with the expenditure of energy and time that this entails) and remove the piece.

In spite of the reduction of the adhesive properties at room temperature is obvious in some designs, the test is declared unsuccessful.

V.3.2. Formulation AT 3.2

This formulation is based on a polyester resin cured by the action of an organic hardener. It is also a really reactive formulation.

V.3.2.1. Gel time

Table V.18. Gel time values. Reformulations AT 3.2.

Formulation	Gel time 110°C (s)	Gel time 160°C (s)	Time Influence at 110°C (s)	Time Influence at 160°C (s)
AT 3.2	**180,23**	**95,10**	**-**	**-**
AT 4.9	185,99	95,58	5,76	0,48
AT 4.10	184,50	104,61	4,27	9,51
AT 4.11	182,73	99,06	2,50	3,96
AT 4.12	180,09	94,22	-0,14	-0,88
AT 4.13	182,32	95,05	2,09	-0,05
AT 4.14	181,65	95,48	1,42	0,38
AT 4.15	180,44	95,29	0,21	0,19

Values fall within the specifications: the formulations present no problem curing. Nonetheless, the delay in AT 4.9 at 110°C or AT 4.10 indicates a clear modification in their characters. It will be else obvious in the test related to adhesion. The reduction of curing time is negligible.

V.3.2.2. Particle size distribution

Table V.19. Psd values Reformulations AT 3.2.

Formulation	d (0,1)(µm)	d (0,5)(µm)	d (0,9)(µm)
AT 3.2	**14,582**	**39,754**	**74,213**
AT 4.9	14,778	40,371	74,933
AT 4.10	14,823	40,462	75,172
AT 4.11	14,760	40,248	74,898
AT 4.12	14,860	40,335	74,839
AT 4.13	14,873	40,394	74,919
AT 4.14	14,677	40,201	74,790
AT 4.15	14,812	40,228	74,726

No noticeable differences: in any case appear differences greater than 1 µm. It is considered to comply with the limits.

V.3.2.3. Pull-off Test

Table V.19 collects these of the formulations (AT 3.2. and AT 4.9.-4.15).

Table V.20. Adhesion tests. Reformulations AT 3.2.

	Pressure at Room Temperature: 22°C (Mpa)					**Pressure at 110°C (Mpa)**					**Pressure at 160°C (Mpa)**				
				Average	**Comment**				**Average**	**Comment**				**Average**	**Comment**
AT 3.2	14,25	13,25	13,78	***13,76***	Glue-powder	1,47	1,54	1,54	***1,52***	Glue-powder	15,25	15,30	15,14	***15,23***	Perfect separation
AT 4.9	8,32	7,48	7,90	***7,90***	Glue-powder	0,9	0,78	1,10	***0,93***	Glue-powder	0,19	0,24	0,24	***0,22***	Glue-powder. Slight break.
AT 4.10	4,84	4,93	4,87	***4,88***	Glue-powder	0,51	0,59	0,59	***0,56***	Perfect separation	0,73	0,69	0,83	***0,75***	Glue-powder. Powder is a little elastic and does not stick a lot.
AT 4.11	4,93	7,01	6,98	***6,31***	Glue-powder and powder breaks a little	2,06	2,01	1,90	***1,99***	Bad stability. Powder breaks	<0,05	<0,05	<0,05	***<0,05***	Bad stability. Lots of particles on the surface.
AT 4.12	5,59	6,74	6,52	***6,28***	Glue-powder and powder breaks a little	0,56	0,46	0,54	***0,52***	Bad stability. Powder breaks	0,08	0,10	0,09	***0,09***	Bad stability. Lots of particles on the surface.
AT 4.13	5,74	12,67	11,62	***10,01***	Powder breaks	0,90	0,96	0,098	***0,65***	Glue-powder	0,35	0,30	0,48	***0,38***	Glue-powder
AT 4.14	5,99	5,65	12,46	***8,03***	Glue-powder	1,37	1,17	1,29	***1,28***	Perfect separation	1,50	1,42	1,48	***1,47***	Glue break a little
AT 4.15	14,55	15,25	17,00	***15,60***	Glue-powder	0,83	0,94	0,81	***0,86***	Glue-powder	0,58	0,59	0,61	***0,59***	Glue-powder

For a second time, the data are analyzed depending on the temperature. This pattern will be repeated along the thesis. The values obtained at 22°C are discussed at the end of each section. In the industry these temperatures for detaching are not useful. However, they help us to understand the behavior of each additive. Moreover, we report on the stability of the formulation at room temperature (at which it is assumed that the material is, more or less, for most of the time of his lifecycle).

Lower limit (Temperature = 110°C)

In this case appears a new variable: detachment between the glue and powder. This was not foreseen when the project commence. Different glues useful at high temperatures, as J-B Weld or Scotch Weld 2214, were used and in all the cases the same problem remains. This suggested:

1. Formulation is “quite comfortable” attached to metal. This is fairly negative as can indicate a separation between FRP and powder coating is, virtually impossible, but feasible. This would destroy the product.
2. The force (or pressure) required to perform the separation FRP metal mold is, at least, the value indicated in the table. A high value also allows rejecting the formulation.

Respect the values, striking positive results values for AT 4.10; with the addition of an Organic Acid with a strong polar nature. The formulation AT 4.10 offers really good values at low temperatures (110°C). However, at high temperatures the additive loses its properties. Denaturing occurs possibly. Anyway, formulation AT 4.10 is selected to be studied in depth in the following section called V.4. It is considered "possibly valid" for production of FRP at low temperatures.

Formulations AT 4.11 and AT 4.12 lost the stability and the powder breaks; like is shown in Figure V.18. Both compositions share the additive IR 4.

Figure V.14.Formulation AT 4.11 at 110°C.

Upper limit (Temperature = 160°C)

Owing the increasing of the temperature the additive effects IR4, a metallic salt used in AT 4.11 and AT 4.12 are magnified. The Figure shows this problem, where part of the powder coatings remain in the metalic surface. It is owing an important loss of stability.

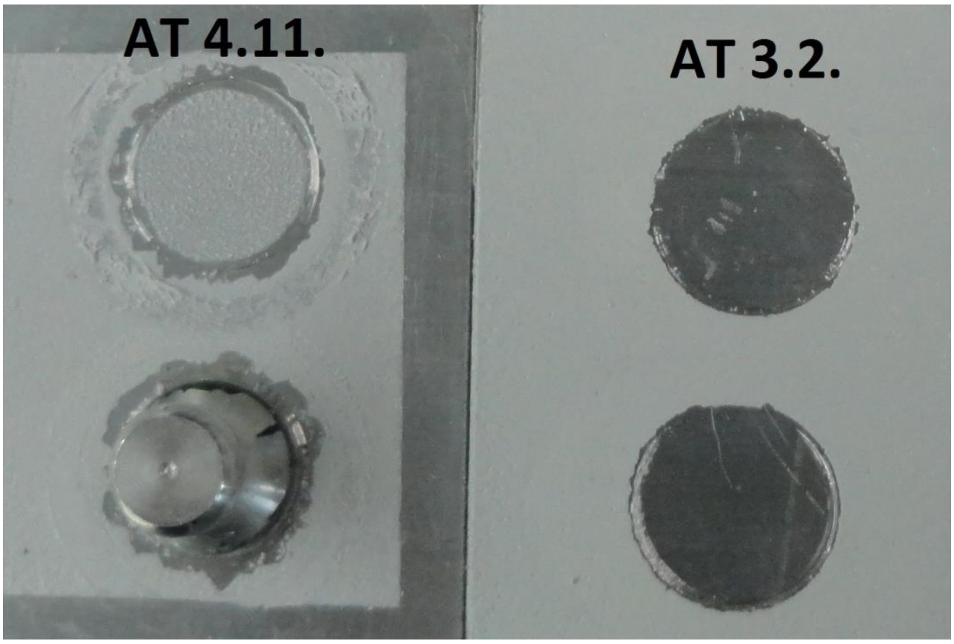


Figure V.15. Example of good and bad test.

Instability at high temperatures (from 110°C to 160°C) is a reality. Moreover, AT 4.9 manifests, at these conditions, a slight break. It is reason enough for it to be discarded.

Room Temperature (22°C)

There are three formulations that lost stability: AT 4.11, AT 4.12 and 4.13. These automatically become invalid.

In conclusion to this subsection, the formulation named AT 4.10 passes this screening because of its potential usefulness for "low temperatures" (110°C). However, if a customer requires higher temperatures for its production, it will be not recommended.

V.3.3. Formulation AT 3.3

This formulation is composed for a self-crosslinking epoxy resin. Despite these self-crosslinking properties, the mix has a catalyst. It transforms the mix into a very reactive preparation. As can be appreciated, there are different methods, as deleting the hardener in the extrusion process or decreasing the temperature during the production procedure, to develop reactively active formulations.

V.3.3.1. Gel time

Table V.21. Gel time values. Reformulations AT 3.3.

Formulation	Gel time 110°C (s)	Gel time 160°C (s)	Time Influence at 110°C (s)	Time Influence at 160°C (s)
AT 3.3	**166,05**	**24,65**	**-**	**-**
AT 4.17	173,12	30,08	7,07	5,43
AT 4.18	178,51	29,53	12,46	4,88
AT 4.19	165,12	22,85	-0,93	-1,80
AT 4.20	159,41	19,26	-6,64	-5,39
AT 4.21	179,59	29,10	13,54	4,45
AT 4.22	167,38	26,21	1,33	1,56
AT 4.23	165,64	25,10	-0,41	0,45

Compliance with the company specifications. For third occasion, IR2 (present in AT 4.2 AT, 4.10 and AT 4.18) shows an increase of time required for curing. This organic acid has a small but clear influence. Generally, all the additives slow the polymerization, except IR3 and IR4 that are found in AT 4.19 and AT 4.20. There is virtually variation in the use of IR7 (AT 23). Anyway, all the re-formulations are slightly influenced by the additives.

V.3.3.2. Particle size distribution

Table V.22. Psd values. Reformulations AT 3.3.

Formulation	d (0,1)(µm)	d (0,5)(µm)	d (0,9)(µm)
AT 3.3	**9,532**	**28,09**	**54,589**
AT 4.17	8,988	27,536	54,307
AT 4.18	8,273	26,917	53,795
AT 4.19	9,043	27,448	54,058
AT 4.20	9,744	28,254	54,810
AT 4.21	9,543	28,505	55,168
AT 4.22	8,954	27,072	53,689
AT 4.23	8,953	27,332	54,029

The results are as expected: variations are minimal.

V.3.3.3. Pull-off Test

On Table V.23 adhesion values for AT 3.3 are shown.

Table V.23. Adhesion tests. Reformulations AT 3.3.

	Pressure at Room Temperature: 22°C (Mpa)					**Pressure at 110°C (Mpa)**					**Pressure at 160°C (Mpa)**				
				Average	**Comment**				**Average**	**Comment**				**Average**	**Comment**
AT3.3	3,80	2,75	2,64	***3,06***	Perfect separation	1,35	1,48	1,47	***1,43***	Perfect separation	1,25	1,32	1,25	***1,27***	Glue-powder
AT 4.17	0,21	0,25	0,24	***0,23***	Perfect separation	0,54	0,45	0,51	***0,50***	Perfect separation (like a sheet)	<0,05	<0,05	<0,05	***<0,05***	Perfect separation (like a sheet)
AT 4.18	0,28	0,33	0,31	***0,31***	Perfect separation	0,64	0,64	0,67	***0,65***	Perfect separation (like a sheet)	<0,05	<0,05	<0,05	***<0,05***	Perfect separation (like a sheet)
AT 4.19	0,41	0,42	0,45	***0,43***	Perfect separation	0,74	0,75	0,74	***0,74***	Perfect separation (like a sheet)	0,22	0,21	0,24	***0,22***	Perfect separation (like a sheet)
AT 4.20	0,88	0,84	0,87	***0,86***	Perfect separation	1,09	1,17	1,12	***1,13***	Perfect separation	0,84	0,54	0,47	***0,62***	Perfect separation
AT 4.21	4,00	3,87	3,98	***3,95***	Perfect separation	0,96	0,97	0,97	***0,97***	Perfect separation	2,06	2,10	2,14	***2,10***	Glue-powder Stick little
AT 4.22	4,19	4,10	4,15	***4,15***	Perfect separation	1,09	1,12	1,18	***1,13***	Perfect separation	1,64	1,36		***1,50***	Glue-powder
AT 4.23	2,18	3,03	2,98	***2,73***	Perfect separation	1,66	1,48	1,51	***1,55***	Perfect separation	1,12	1,21	1,15	***1,16***	Good separation; however small particles on the surface.

These formulations are among the most successful creations. Before examining by temperature values, it is interesting check the preparations AT 4.17 and AT 4.18. AT 4.19 is also an interesting formulation; however the study focuses on the two best formulations: AT 4.17 and AT 4.18.

Lower limit (Temperature = 110°C)

All formulations appear to be physically stable. One of the most positive properties of AT 3.3 is that it does not own a large adhesion, so the goal is easier to achieve.

There is a widespread reduction in adhesion, although, as is indicated previously, most interesting formulations are AT 4.17 and AT 4.18. The force applied is represented in Figure V.16.

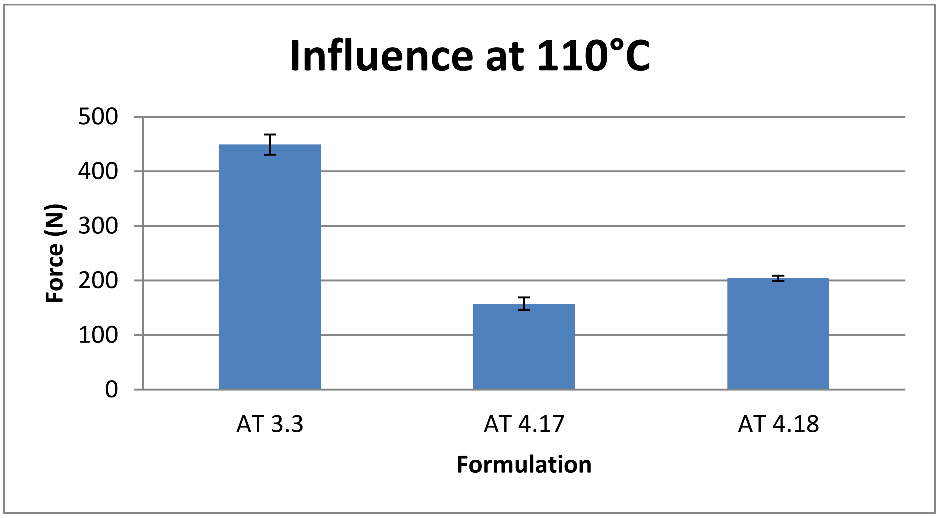


Figure V.16. Adhesion of reformulations AT 3.3 at room temperature. (110°C).

Considering AT 3.3 as 100%; the reduction is:

Table V.24. Decreased adhesion. (110°C)

Formulation	Additive	Chemical nature	Reduction (%)
AT 4.17	IR 1	Fatty Acid Salt	65,63
AT 4.18	IR 2	Organic Acid	54,54

Moreover, three of the formulations present a behavior pro mold release. This means, they are like sheet (check Figure V.17). When it begin to separate from de metallic support, normally on the corner of the FRP, the good is easily rip out, offering virtually no resistance.

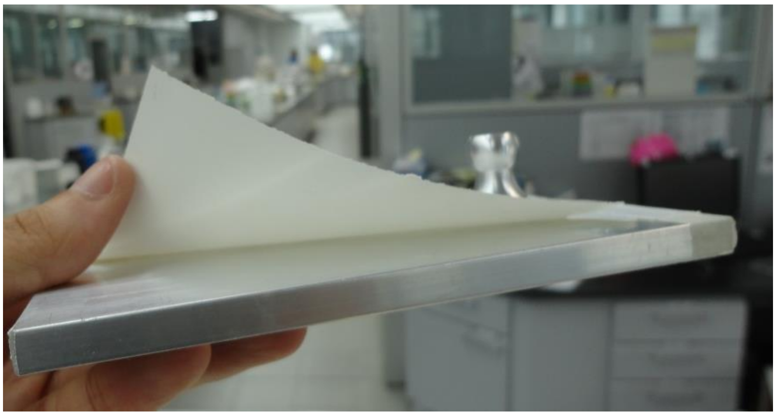


Figure V.17. Example of self-detaching.

On the other hand, one of the formulations appears to worsen its behavior. It is AT 4.23 and is prepared with AR 7; same additive that gives more of a problem in other cases.

Upper limit (Temperature = 160°C)

At higher temperatures there are multitude and variety of cases:

There is a great improving in the behavior in AT 4.17, AT 4.18 and AT 4.19 designs. In fact, in the first two examples, the adhesion is so low that it can not be measured with the equipment (Pull-off test machine). The problem is that when the specimen is trataded (explained in section IV.3), it does not endure it and the powder coating is removed from the support. For this reason, Table V.22 shows a value of<0,05. This can be considered practically nil.

AT 4.20 offers also a good separation; although does not behave as a sheet and a greater adhesion value.

Regarding AT 4.21 and AT 4.22, the precise value cannot be determined due to the problem of stability of the glue at high temperatures. However, the additives seem to denature and lose its mission. In fact, the bond is strengthened.

About AT 4.23, produced with IR 7 (a bio wax), it lost the stability. This additive shows several complications throughout the project. As discussed in the conclusions

Room Temperature (22°C)

With these last test atnormal temperature, the previously observedis confirmed: formulations AT 4.17 and AT 4.19 show a remarkable performance.

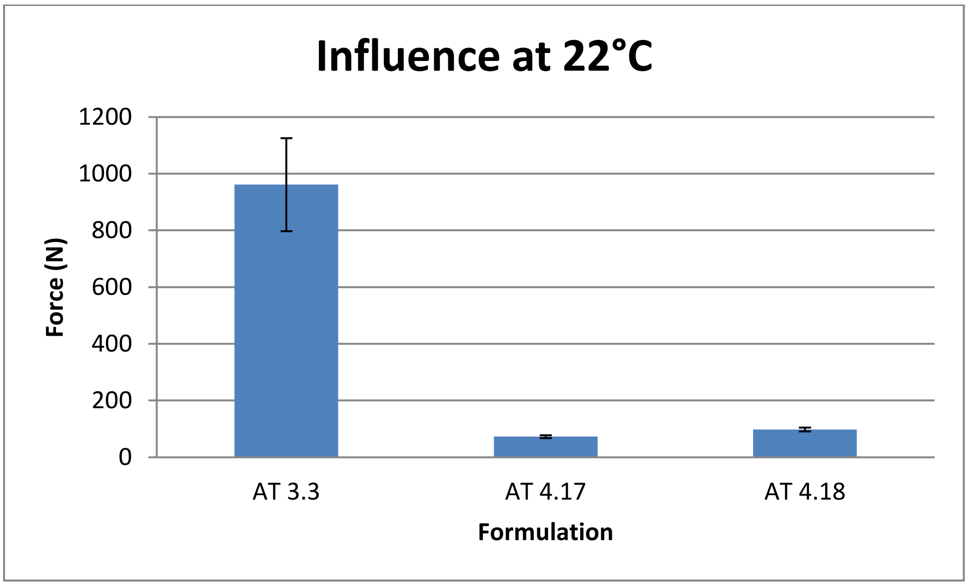


Figure V.18. Adhesion of reformulations AT 3.1 at room temperature. (22°C).

Percentages of improvements are even better:

Table V.25. Decreased adhesion (22 °C).

Formulation	Additive	Chemical nature	Reduction (%)
AT 4.17	IR 1	Fatty Acid Salt	90,91
AT 4.18	IR 2	Organic Acid	88,26

Also, consider that the release in all cases is fairly clean. This allows achieving a Class A Surface Finishing.

Figure V.19.Example of perfect separation in AT 4.17.

In conclusion, for all the previously described above, the formulations AT 4.17 and AT 4.18 are selected. It means that they are deeply analyzed in section V.4; where just the best formulations are accepted. AT 4.19 is not chose because of its chemical similarity to the previous two formulations and the slight underperformance.

V.3.4. Formulation AT 3.4

This design keeps several similarities with AT 3.3. Although different materials are used in each situation; both designs seek or pursue the same idea: catalyze an epoxy resin with self-crosslinking character. (Indeed this addition is not necessary to reach the curing, but increases the reactivity).

V.3.4.1. Gel time

Table V.26. Gel time values. Reformulations AT 3.4.

Formulation	Gel time 110°C (s)	Gel time 160°C (s)	Time Influence at 110°C (s)	Time Influence at 160°C (s)
AT 3.4	**125,41**	**19,84**	**-**	**-**
AT 4.25	121,23	23,21	-4,18	3,37
AT 4.26	132,44	19,41	7,03	-0,43
AT 4.27	124,21	18,24	-1,20	-1,60
AT 4.28	124,38	18,75	-1,03	-1,09
AT 4.29	136,85	27,85	11,44	8,01
AT 4.30	130,50	20,65	5,09	0,81
AT 4.31	125,15	19,23	-0,26	-0,61

There is a fairly significant change in AT 4.29. In relation to the other trials, all can be considered within certain consistent limits.

V.3.4.2. Particle Size Distribution

Table V.27. Psd values. Reformulations AT 3.4.

Formulation	d (0,1)(µm)	d (0,5)(µm)	d (0,9)(µm)
AT 3.4	**19,255**	**46,758**	**87,410**
AT 4.25	20,367	47,999	88,956
AT 4.26	20,411	47,996	88,958
AT 4.27	20,248	47,865	88,740
AT 4.28	19,994	47,459	88,269
AT 4.29	19,869	47,491	88,309
AT 4.30	19,890	47,423	88,229
AT 4.31	19,805	47,272	88,077

The reformulations from AT 3.4 do not provide significant differences in psd.

In point of fact, the previous table shows that the additives do not affect the hardness or mechanic properties in the chip, material useful for production of powder coatings. Once more, the mother formulation continues being the main culprit of the mechanic properties.

V.3.4.3. Pull-off Test

Table V.28 lists the adhesion values for AT reformulations 3.4:

Table V.28. Adhesion tests. Reformulations AT 3.4.

	Pressure at Room Temperature: 22°C (Mpa)					**Pressure at 110°C (Mpa)**					**Pressure at 160°C (Mpa)**				
				Average	**Comment**				**Average**	**Comment**				**Average**	**Comment**
AT 3.4	6,17	6,15	6,54	***6,29***	Glue-powder	4,55	4,68	4,70	***4,64***	Perfect separation	7,47	7,50	7,57	***7,51***	Perfect separation
AT 4.25	8,25	8,24	8,3	***8,26***	Perfect separation	2,72	2,46	2,50	***2,56***	Perfect separation	1,25	1,27	1,20	***1,24***	Glue-powder
AT 4.26	4,77	4,84	4,78	***4,80***	Perfect separation (a little glue-powder trouble)	1,02	1,14	1,00	***1,05***	Perfect separation	0,36	0,38	0,37	***0,37***	Glue- powder
AT 4.27	5,5	4,41	5,6	***5,17***	Glue-powder	2,01	1,98	1,98	***1,99***	Glue-powder	0,95	1,11	1,03	***1,03***	Glue-powder
AT 4.28	7,52	7,59	7,65	***7,59***	Perfect separation	2,66	2,28	2,32	***2,42***	Perfect separation	1,25	1,32	1,33	***1,30***	Glue-powder
AT 4.29	6,05	6,12	6,14	***6,10***	Glue-powder	2,12	2,30	1,94	***2,12***	Perfect separation	1,52	1,45	1,44	***1,47***	Glue-powder
AT 4.30	4,37	4,86	4,62	***4,62***	Perfect separation	1,52	1,52	1,26	***1,43***	Perfect separation	1,19	1,19	1,25	***1,21***	Glue-powder
AT 4.31	5,56	5,61	5,49	***5,55***	Perfect separation	1,59	1,96	1,82	***1,79***	Perfect separation	1,47	1,36	1,39	***1,41***	Glue-powder

Here unfavorably striking a formulation (AT 4.27), which appears to be particularly useless and there is not a good separation among the metal surface and the powder coating. However, at low temperatures there are some good results. It is clarified in the next points.

Lower limit (Temperature = 110°C)

There is a general reduction in the adhesive properties; however, all values are quite high. Exerting a pressure of 800-600N over a FRP to be obtained can be too high. Furthermore, depending on the physical characteristics of the object, this could be damaged.

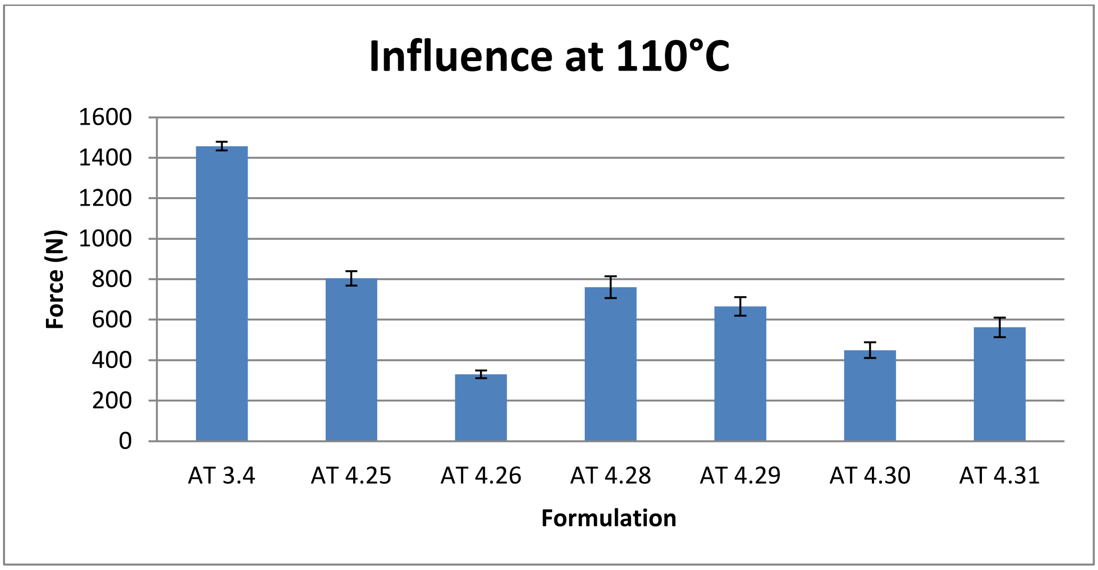


Figure V.20. Adhesion of reformulations AT 3.4 (110°C).

The formulation AT 4.26 is the best value offered in this temperature limit (329,9N). This formulation will be selected for further testing. The reasons:

- Chemical family: Is recommended a chemical similarity between the FRP and PiMC. This promotes a good bond between powder coating- FRP. With a wider range of different powder coatings families, may cover a wider market.
- For large pieces, such as part of the wings of an airplane, applying a force of about 30 kg may be within logical limits.

NOTE: AT 4.27 is not represented in Figure V.24 due to the date obtained is a minimum value which will be higher. (there is a bigger connection metal-powder than glue-powder)

Upper limit (Temperature = 160°C)

Similarly as the above test, there is no design that shines over others at 160°C; maybe AT 4.26. Again the Organic Acid (IR 2) may offerspecial results.This is not a certainty, but the good result at 110°C can encourage us to think about that. Furthermore, if it is correct (or almost), the benefits are quite clear. (Figure V.25)

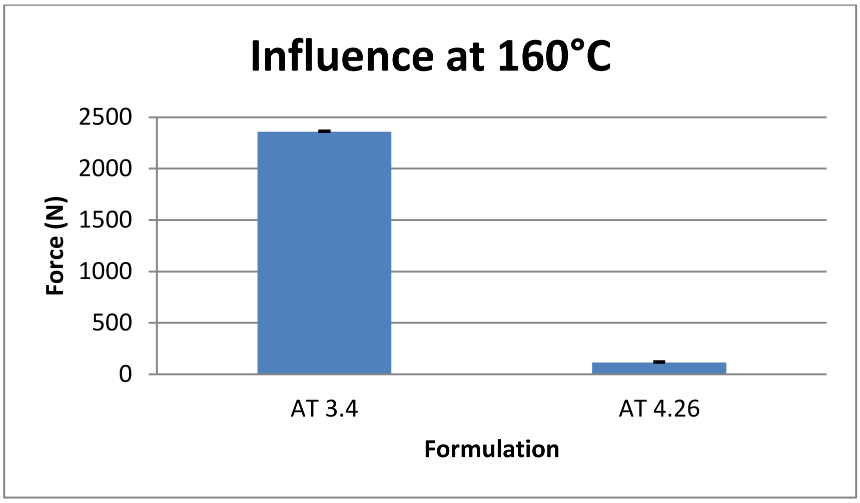


Figure V.21. Adhesion test. AT 3.4 vs AT 4.26.

Room Temperature (22°C)

All values are really high, which indicates that none of the formulations is really successful. The lowest value recorded on test is 4,62 MPa (AT 4.30). Perhaps too high, although is positive the fact that it offers a clean and neat segregation.

Anyway, as already mentioned before, these data are not interesting for customers, so long shall not be taken into account.

In conclusion at this section, AT 4.26 is carefully chosen and analyzed in depth in V.4.

V. 3.5. Formulation AT 3.5

These last formulations are a special case. As discussed previously, these mixes have been developed considering the elimination of a necessary manufacturing step: top coating. Aesthetic skills are of primary importance. The design is composed by an acrylic resin, a catalyst, some chemical stabilizer and several additives pro-aesthetic.

Regarding gel time values, they are not offered for the same reason that is explained in section V.2.1.3; although everything is inside the specifications.

V.3.5.1. Gel time

Table V.29. Gel time values. Reformulations AT 3.5.

Formulation	Gel time 110°C (s)	Gel time 160°C (s)	Time Influence at 110°C (s)	Time Influence at 160°C (s)
AT 3.5	**210,01**	**45,36**	-	-
AT 4.33	212,41	45,54	2,40	0,18
AT 4.34	215,84	43,78	5,83	-1,58
AT 4.35	210,93	49,06	0,92	3,70
AT 4.36	214,66	49,26	4,65	3,90
AT 4.37	210,21	49,10	0,20	3,74
AT 4.38	214,29	47,41	4,28	2,05
AT 4.39	214,64	47,28	4,63	1,92

V.3.5.2. Particle Size Distribution

Table V.30. Particle Size Distribution of reformulations AT 3.5.

Formulation	d (0,1)(μm)	d (0,5)(μm)	d (0,9)(μm)
AT 3.5	**9,426**	**28,415**	**61,123**
AT 4.33	9,459	82,264	316,902
AT 4.34	9,376	79,981	310,864
AT 4.35	9,299	60,137	263,980
AT 4.36	9,153	57,932	242,385
AT 4.37	10,162	71,297	286,456
AT 4.38	9,964	75,076	298,891
AT 4.39	9,476	59,105	246,669

In this exceptional case, the psd traced for each formulation is quite different. These materials are not useful to be coated properly and offer a nice finishing. The solution, in a laboratory scale, is related to sieve. Formulations need to be sieved and then, it is obtained a particle size distribution within the limits developed previously (between 20-80 microns).

For scaling up (migration of the process to a commercial scale), it is necessary to proceed in extreme caution. In the case the change of configuration of the mill is not enough, several cyclones in series can solve this issue.

V.3.5.3. Physical Appearance

Firstly, it is checked the brightness loss due the influence of the additives. Among the additives to achieve a nice physical appearance have been used: Gloss Enhancer 542 DG, UV absorber 622 SF, UV absorber 405, antioxidant 126, antioxidant 1076 or optical brighteners 548. They help to achieve a beautiful aesthetic which should be one of the main reasons because the final customer is interested in the product. However, these compounds can develop several problems when they are mixed with external releaser at high temperatures during the extrusion process.

Reminder that these physical properties are measured just in that case because, in the future, is desired to removing the top coating layer in the production of automotive and aeronautic composites.

Brightness

Relating parameters brightness:

Table V.31. Brightness test. Reformulations AT 3.5.

Formulation	Brightness (60°) GU	Average Brightness (60°) GU
AT 3.5	127,0	127,3
	127,3	
	127,5	
AT 4.33	132,6	132,3
	131,8	
	132,6	
AT 4.34	49,9	49,7
	49,6	
	49,7	
AT 4.35	122,9	123,0
	122,5	
	123,5	
AT 4.36	128,6	128,6
	128,4	
	128,9	
AT 4.37	116,1	116,6
	117,0	
	116,8	
AT 4.38	81,2	81,2
	81,6	
	80,9	
AT 4.39	124,6	125,0
	125,8	
	124,7	

In this test, formulation AT 4.34 and AT 4.38 are removed due the decreasing of gloss. It is not acceptable for such large decrease of gloss property (from 127.3 GU to 49.7 GU in formulation AT 4.34). Neither till 81.2 GU (formulation AT 4.38). This second case is surprising. AT 4.38 contains a micronized polyethylene wax (additive IR6) into its composition. This additive belongs to a family of compounds that are used to increase the brightness. A probable explanation may be because of a secondary reaction in the process of extrusion.

Colorimetry

All of them are transparent formulations, and in no case there is a strong variation of color. It is show in Table V.32.

Table V.32. Colorimetry test. Reformulations AT 3.5.

	L	**A**	**B**	**E**
AT 3.5	84,07	-0,28	1,2	84,08
AT 4.33	87,51	-0,24	1,41	87,52
AT 4.35	82,07	2,85	2,73	82,16
AT 4.36	85,13	-0,19	1,91	85,15
AT 4.37	86,81	-0,19	1,56	86,82
AT 4.39	84,12	-0,25	1,11	84,13

All are within specification, therefore not discussed in depth. Moreover, due it is a transparent coating; it is really measured the color of the metallic support. For a future development would consider adding pigments on these designs. These pigments will offer the colors that the customer desires.

V.3.5.4. Pull off Test

On Table V.33 values of adhesion are shown only for AT 3.5 reformulations. AT 4.34 and AT 4.38 have not been included because of their loss of gloss; how is explained on previous section.

Table V.33. Adhesion tests. Reformulations AT 3.5.

	Pressure at Room Temperature: 22°C(Mpa)					**Pressure at 110°C (Mpa)**					**Pressure at 160°C (Mpa)**				
				Average	**Comment**				**Average**	**Comment**				**Average**	**Comment**
AT 3.5	18,67	9,21	10,93	***12,94***	Glue-powder	2,75	2,19	2,52	***2,49***	Perfect separation	1,37	1,52	1,42	***1,44***	Perfect separation
AT 4.33	0,46	0,54	0,49	***0,50***	Perfect separation	1,35	1,30	1,22	***1,29***	Perfect separation (like a sheet)	0,32	0,14	0,21	***0,22***	Perfect separation
AT 4.34	-	-	-	**-**	Hue variations	-	-	-	**-**	Hue variations	-	-	-	**-**	Hue variations
AT 4.35	11,25	15,19	12,59	***13,01***	Glue-powder	1,22	1,31	1,27	***1,27***	Glue-powder	1,17	1,01	1,12	***1,10***	Glue-powder
AT 4.36	10,41	10,7	11,16	***10,76***	Glue-powder	1,37	1,41	1,42	***1,40***	Glue-powder	1,18	1,08	1,17	***1,14***	Glue-powder
AT 4.37	20,4	20,42	19,99	***20,27***	Glue-powder	3,30	3,24	2,97	***3,17***	Almost perfect (glue-powder)	1,36	1,22	1,22	***1,27***	Almost perfect (powder breaks a few)
AT 4.38	-	-	-	**-**	Hue variations	-	-	-	**-**	Hue variations	-	-	-	**-**	Hue variations
AT 4.39	17,45	19,52	16,91	***17,96***	Glue-powder	2,48	2,59	2,00	***2,36***	glue-powder	1,72	1,64	1,62	***1,66***	almost perfect (powder-glue)

The formulation AT 4.33 offers special properties which are analyzed in the following lines:

Lower limit (Temperature = 110°C)

At this temperature there are various cases (AT 4.35, AT 4.36, AT 4.37 and AT 4.39) where the exact value of adhesion cannot be determined. However, all of them have a good rate. In AT 4.37; instead of decreasing the adhesion with the metallic substrate, this property is increased. This is possibly due to some sort of secondary reaction between IR6 and "trim" additives. These elements hold together at high temperatures during the extrusion process.

On other hand, how advanced in the previous line, AT 4.33 features are quite good. Although perhaps, the necessary value to demold is a bit high (1,29 MPa); this formulation offers a special feature: once demold process begins, the whole piece comes off without offering any resistance. It means than, in a manufactured piece, once a corner of the piece is off (easiest part), the composite will suffer a great stripping. Moreover, the sheet of powder coating provides high hardness values, necessary feature for FRP.

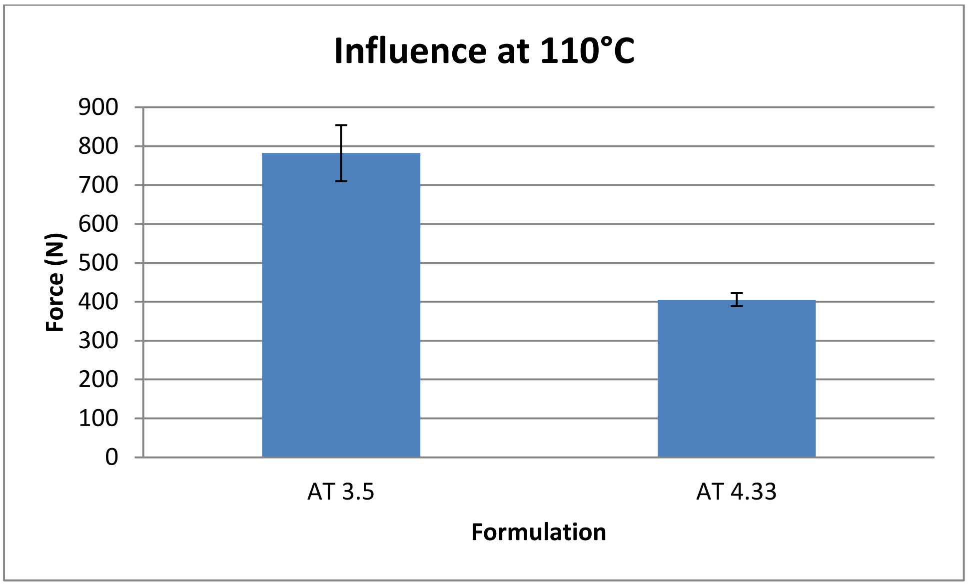


Figure V.22. Adhesion test. AT 3.5 vs AT 4.33.(110°C).

Upper limit (Temperature = 160°C)

At high temperatures all the designs behave in a similar way than at lower temperatures. Likeexception: AT 4.37; using of this mixture of surface-active polymers adsorbed on silicon dioxide causes a mild desestabilization. Probably stricter check on this formulation could declare it as null. Moreover, remember that at 110°C offers really poor results.

The best formulation, AT 4.33, provides great facility to be separated from the metallic mold. Furthermore, exactly the same fact ocurrs: when the stripping begins, it can not be stopped. This feature is pretty positive, futhermore, allows full automation of the production process.

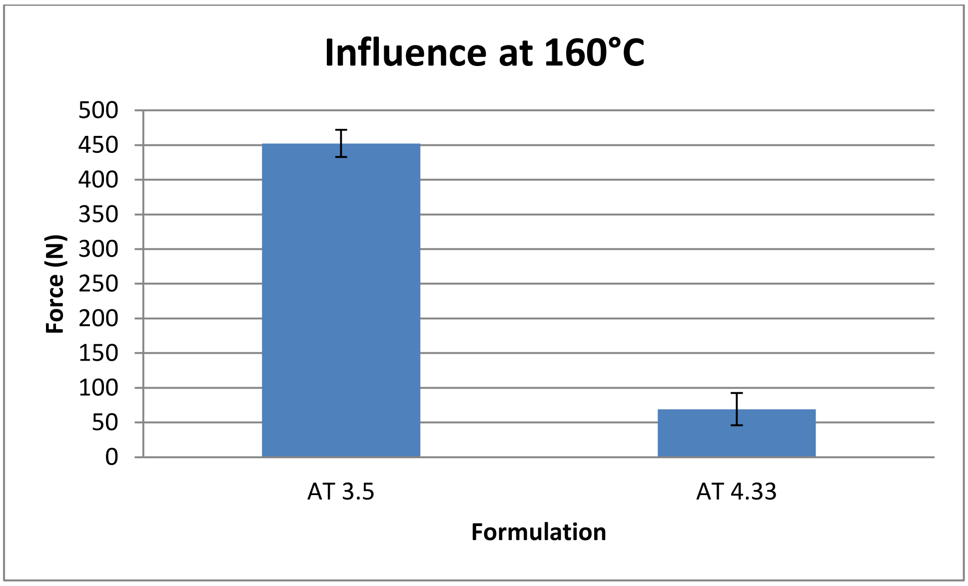


Figure V.23. Adhesion test. AT 3.5 vs AT 4.33. (160°C).

Room Temperature (22°C)

Draws attention that, even at low temperatures, the mold release in formulation AT 4.33 occurs quite easily. Just has to be an applied pressure of 0,50 MPa. Without that additive, at least, 12.94 MPa are necessary (really more, because 12.94 MPa is an indicative value due to there is a separation glue-powder coating).

Anyway, the true success lies in getting these features in the range of 110ºC and 160ºC, where most of the FRP for aerospace and automotive are produced. Respect the stability, in all the cases seem to be good.

In this area, AT 4.33 is chose owing to his good behavior at 110°C and 160°C, especially at high temperatures.

V.4. SELECTION OF THE BEST RESULTS

Once known adhesion levels, the next step is checking whether such formulations meet certain requirements or quality criteria. Although, in each case is the customer who "own the last word", and HE (the client) imposes its conditions; there are a standard of quality.

The best "re-formulations" chosen in the previous section have been the next: **AT.4.10, AT 4.17, AT 4.18, AT 4.26** and finally **AT 4.33**. Just two of the seven releaser additives are present in this formulation: AR 1; a fatty acid salt and IR 2, an organic acid. All others have been discarded: IR 3 (Organic Enhancer), IR 4 (Metallic salt)…until IR 7 (Bio wax)

The results are compared with the formulations mother (AT 3.1, AT 3.2, AT 3.3, AT 3.4 and AT 3.5) depending on the case where each re-formulation comes from. This is because it is significant knowing the behavior of each additive in each base; with each resin. This may allow future product development.

Tests performed are the following:

- Flowability
- Curing parameters
- Chemical resistance
- Printing parameters
- Resistance

Another test of main importance, as gel time or Particle Size Distribution has been shown on Section V.3.

V.4.1. Flowability

At this point, the values will be separated into two groups. So it can be perceived better of its characteristics:

In the first group, variations are quite small. In general, the viscosity decreases with the additives. Mother bases are shown in red bars, and close it, the re-formulation with releaser properties.

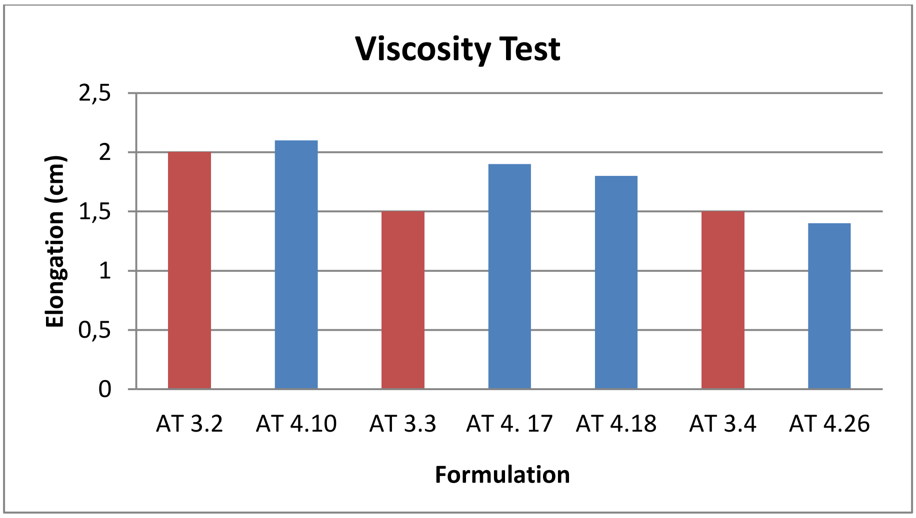


Figure V.24. Viscosity test. Best formulations. Part 1.

The flowability offered is not particularly good in any case; the maximum value of elongation is 2.1 cm. However, all of them are considered as “enough”. It is thanks to, during the PiMC process, the application of powder coating is realized over the entire mold metal.

Regarding the rest of the formulations analyzed, the flowability presented is quite worthy. AT 4.33 reaches an elongation of 24.2 cm, which indicates a fairly low viscosity. This is favored by IR 1.

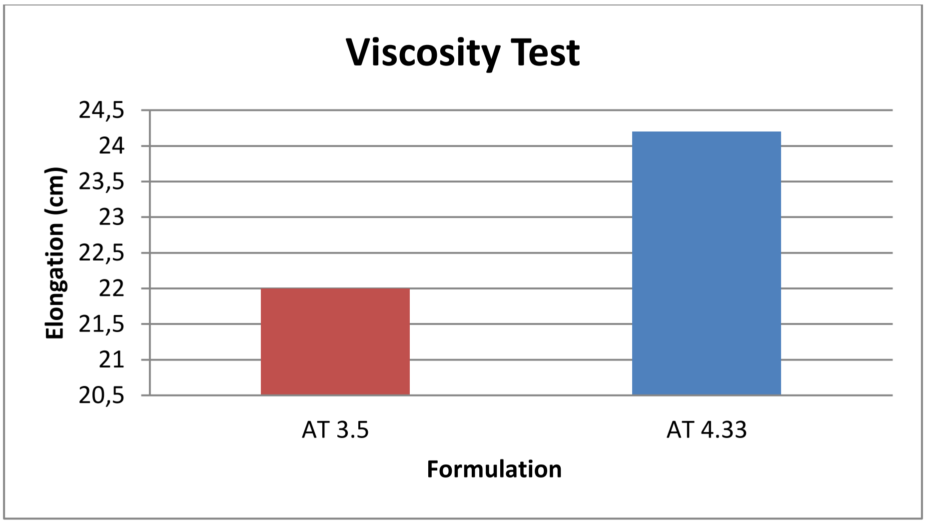


Figure V.25.Viscosity test. Best formulations. Part 2.

The formulation AT 4.33 is remarkable due to it further enhancement of its features. It is still better, as shown in Figure V.25. This design does not own any problem to cover all the gaps created in the FRP processing. It is capable of reaching virtually anywhere. This splendid trial is presented in Figure V.26.

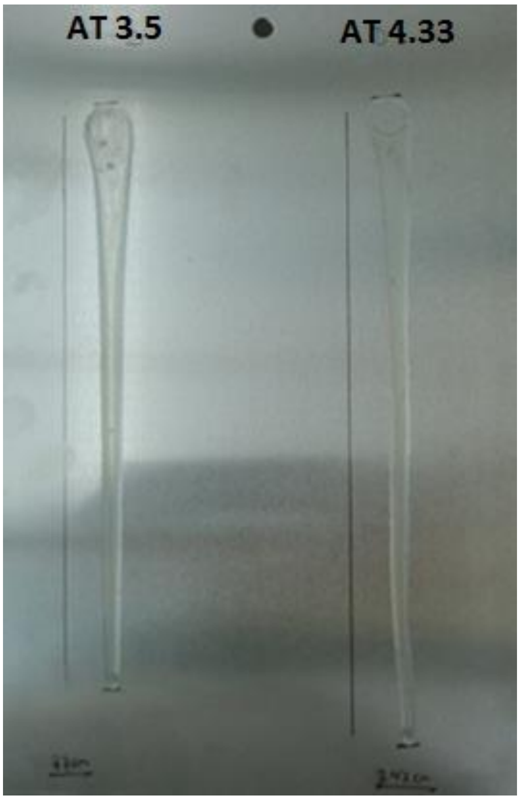


Figure V.26. Viscosity Tablet test. AT 3.5 and At 4.33.

This preparation ensures reach the 100% of the gaps during the composite manufacturing. In the other cases, is necessary to ensure a perfect application on the mold.

V.4.2. Curing parameters

Gel time values are ignored because it is already realized in the previous section. One more time, AT 3.5 is not treated for the reasons explained previously.

DSC (standard cure analysis): Raw formulation

Test conditions are exactly the same than in section V.2.1.3. The values are collected in Table V.34.

Table V.34. Curing parameters. Mother formulations VS best releaser formulations.

Powder	**Melt point (°C)**	**DSC Curing starting point (°C)**	**DSC Peak (°C)**
AT 3.2	49,8	100	178,4
AT 4.10	51,1	107	173,6
AT 3.3	46,5	82	135,7
AT 4.17	56,3	89	138,2
AT 4.18	51,0	80	134,8
AT 3.4	74	83	134,6
AT 4.26	51,7	77	134,5

The main difference is found between AT 4.26 and AT 3.4. This is because the IR 2 owns a low Tg; about 50 °C; and this is reflected in the test. This indicates that there is not reaction during the extrusion process. The additive conserves their properties. It is also observed in AT 4.10 and AT 4.18 (both add with IR 2), although in that cases, the peak is overlapped by the resin.

DSC and Gradient-oven (Post-cure analysis)

Table V.35. Mother formulations VS best releaser formulations.

Formulation	T cured 100% (°C)
AT 3.2	140
AT 4.10	140
AT 3.3	140
AT 4.17	140
AT 4.18	140
AT 3.4	140
AT 4.26	140

According to the Table V.35, these two additives (IR 1 and IR 2) do not have strong influences on curing parameters. It was already observed in gel time test: this test indicated that the variations in time are about 3-4%; sometimes less (Rarely variations are considerable).

In conclusion, the influence of these additives in curing parameters is completely acceptable.

V.4.3. Chemical resistance

Chemical resistance values obtained, using the same test as in the previous chapter, are reported in Figure V.27.

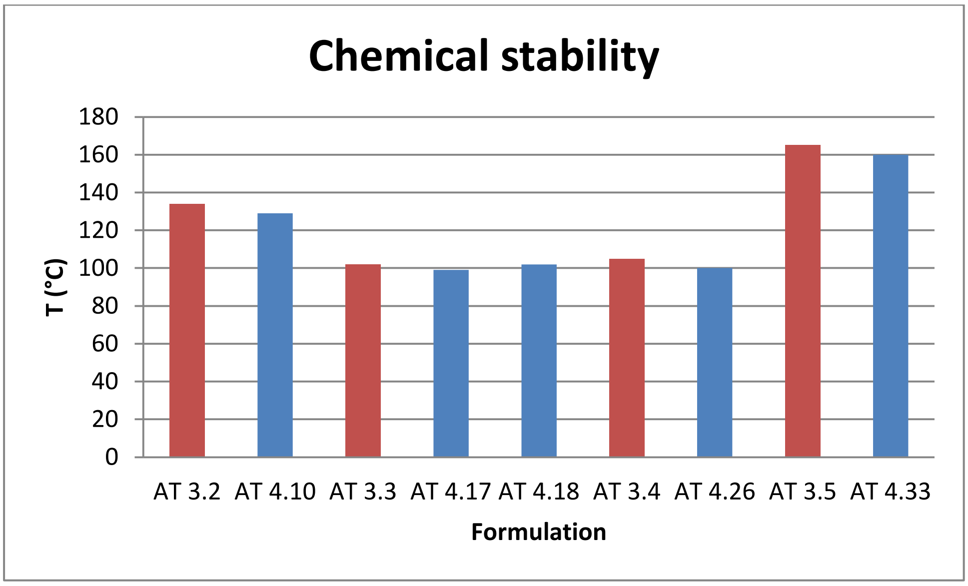


Figure V.27. Chemical Stability of mother formulations and best releaser formulations.

As it can be observed, the chemical stability is not damaged; in point of fact, it looks even improved in some cases. For instance, AT 4.10 and AT 4.33 register lower temperatures to achieve the desired stability. Although there are variations, these are very small; practically negligible in a production process.

It is expected that all the values were good because of all these formulations have passed the Pull-off-test without breaking. This indicates a physical stability, and also, a chemical stability. (It is remarkable that many formulations were previously rejected because powder coatings do not support the pull-off test)

Once again, no significant deviations occur. In consequence, none of the formulations is discarded.

V.4.4.Printing parameters

Poor surface tension in the substrate may lead to the misapplication of top coating. This fact implies a heterogeneous colorimetry and, even the manifestation of bubbles on the surface. These kinds of troubles do away with the Class A surface finishing.

Printing parameters for “mother formulations” and releasing formulations are exposed in Table V.36.

Table V.36. Mother formulations and the best releaser formulations printing parameters.

Formulation	Disperse part (mN/m)	Polar part (mN/m)	Total Surface Energy (mN/m)
AT 3.2	22,26	2,13	24,39
AT 4.10	20,10	0,40	20,50
AT 3.3	16,94	3,63	20,57
AT 4.17	20,18	2,23	22,41
AT 4.18	21,19	0,11	21,30
AT 3.4	9,70	20,48	30,18
AT 4.26	21,19	0,34	21,53
AT 3.5	13,39	17,07	30,46
AT 4.33	22,02	4,63	26,65

In all these cases, the values evidence that the polar part diminishes with the releaser additives. This fact is quite negative.

Although the best value is found in formulation AT 4.33; it is one of the designs that suffer more loss in surface tension. The reduction of the polar part is right clear: from 17.07 mN/m to 4.63mN/m. It is 72.8% of reduction.

It is quite likely that the formulation AT 4.17 does not present any problems in front of its coat (part polar= 2,23mN/m); however, it is expected that AT 4.18 may offer some resistance to the impression.

To be able to give a good quality impression; inks used in top coating require low polar parts. In function of the characteristics of the top coating, it can be given problems or not, but it would be quite positive that the materials used to print this material containing surfactants. Surfactants reduce the surface tension of the ink.

In conclusion, the surface tension of the coating is decisive. Our supports do not allow any type of top coatings; just top coating with low surface tension. This fact is not a mandatory an impediment; however, it is required to notify the customer.

V.4.5. Resistance

Foremost, this test brought a pretty good surprise. At some temperatures and in more than one sample; is observed a detachment or separation of powder coating. It takes place at the point of measurement. Figure V.32 represents this situation. This image was processed to enhance color differences due to separation.

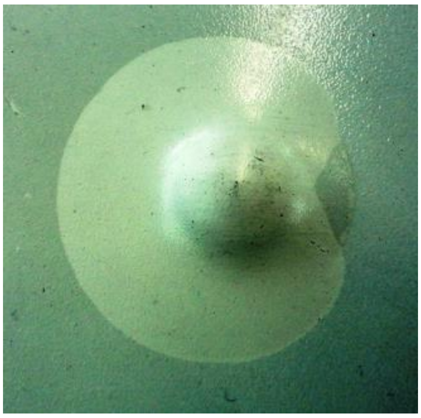


Figure V.28. AT 4.26 (120°C).

This test positive as produced that, separated, the powder coating is broken, and with it a false value resistance. Much more under-reported.

On Figure V.29 to V.33, the reformulation is compared with its formulation mother:

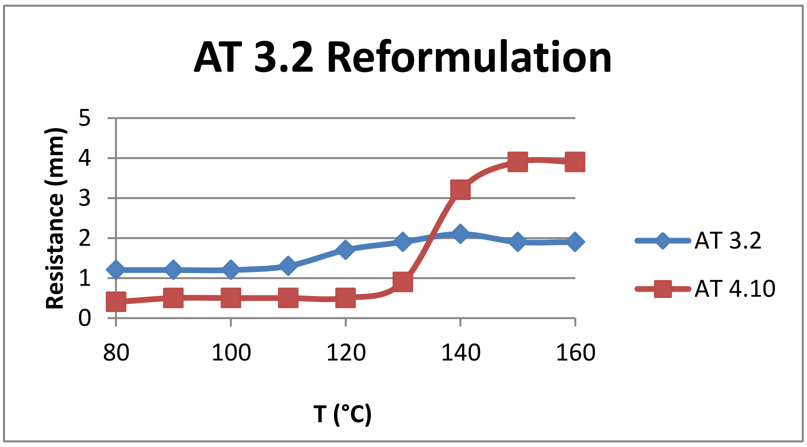


Figure V.29. Resistance of AT 3.2 and AT 4.10 reformulations.

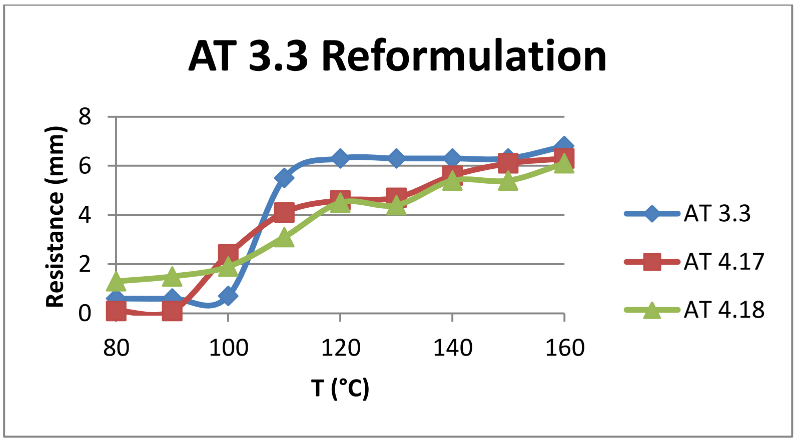


Figure V.30. Resistance of AT 3.3, AT 4.17 and AT 4.18 reformulations.

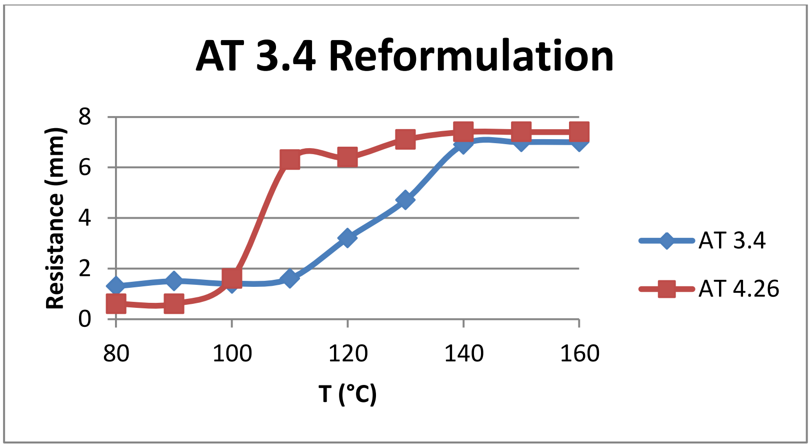


Figure V.31. Resistance of AT 3.3,AT 4.17 and AT 4.18 reformulations.

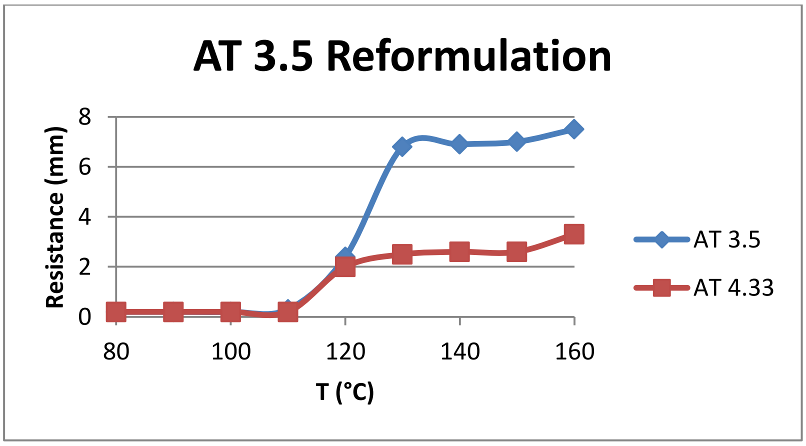


Figure V.32. Resistance of AT 3.3, AT 4.17 and AT 4.18 reformulations.

In general, the additives provide elasticity; and with that property, the resistance increases in most of the cases. Despite, in case AT 3.5 reformulation, the resistance of AT 4.33

is lower than the value acquired by AT 3.5. However, none of the self-detaching formulations is rejected by lack of resistance.

V.4.6. Physical Appearance

This section is providing some useful insights for future developments. As already is explained, these powder coatings are design to be covered by top coat process (except AT 4.33; whose values are in V.3.5.2.).

Brightness

Table V.37. Brightness. Mother formulations VS best releaser formulations.

Comment	Gloss (GU)*
AT 3.2	4,5
AT 4.10	4,9
AT 3.3	22,5
AT 4.17	56,7
AT 4.18	9,9
AT 3.4	3,7
AT 4.26	4,3
AT 3.5	127,3
AT 4.33	132,3

*All the measures are realized with geometry of 20° saving AT 3.5 and AT 4.33 where the brightness is considerably larger.

The only formulation that seems to be altered, and in quite different ways, is AT 3.3. With IR 1 the gloss increases; however, with IR 2, it decreases. Respect AT 4.10 and AT 4.26, both additived with IR 2, the brightness rises slightly. Anyway, none of these formulations has been designed to be used outdoors. For that reason, UV stabilizers or optical enhancers cannot be found in these formulations (Annex 5).

Colorimetry

Possible variations are analyzed to not affect the top coating:

Table V.38. Colorimetry. Mother formulations VS best releaser formulations.

Formulation	L	a	b	E
AT 3.2	90,49	-0,92	0,77	90,50
AT 4.10	90,21	-0,14	0,2	90,21
AT 3.3	90,87	-1,03	-0,94	90,88
AT 4.17	91,24	-2,31	-1,22	91,28
AT 4.18	90,98	-1,29	-1,32	91,00
AT 3.4	90,58	-0,61	1,09	90,59
AT 4.26	90,12	-1,2	0,54	90,13

Fortunately, the color variations are quite low. The top coating process will not be affected in future steps. They are practically close to nil, undetectable by the human eye

V.4.7. Conclusions

AT 4.10, AT 4.17, AT 4.18, AT 4.26 and AT 4.33 meet all the requirements demanded for PiMC. In addition, they offer a clear self-detaching behavior. For these reasons, these five formulations can be offered to customers. The next step will be testing them (complementing SMC, BMC, pre-preg or RTM) in an authentic composite production.

V.5. PERFORMANCE OF EACH ADDITIVE

If in the future, the company considers looking for other releasing additives, (due to problems such as high price or strategy change), it is interesting to examine into the same chemical family of studied additives. Thus, each additive will be discussed separately.

In many cases, compounds with similar structures have similar properties, although this rule is not always a reality.

1. **IR 1, this fatty acid salt is one of the best additives chosen**. Although it can destabilize the polyester bases, **with epoxy self-crosslink and acrylic resins**, **the performance is greatly improved.** Their presence **at high temperatures** is not crippled, in fact, **is when it best behaves**. IR 1 is present in two of the five best formulations (AT 4.17 and AT 4.33).
2. **IR 2 can be selected, in general, as the best option**. It is present in three out of the five reformulations picked up. Formulation AT 4.18 does not own adhesion at high temperatures (exceptional fact). Moreover, AT 4.10 and AT 4.26 decrease his adhesion values clearly. In the other hand, this additive has a disappointment: in all cases, especially with acrylic resin, there has been a decrease in brightness rather important. However, as mentioned before, this is not a problem for the current state of art.
3. About **IR 3**, its usefulness is not clear. It is assumed the compound was to "strengthen" IR 4, but nothing is further from reality. In all trials, this organic "enhancer", deteriorates the features of IR 4. **Its use in future developments should be dismissed**.
4. Respecting **IR 4**, this metallic salt was one with better expectations before starting the study. Unfortunately, **the results are not as good as expected**.
5. With regard to **IR 5,** in general, this mixture of surface-active polymers adsorbed on silicon dioxide, an additive highly pretreated **does not offer a good behavior.**
6. In the case of **IR 6**, **at low temperatures has a good performance**; however, other additives show better characteristics. Moreover, **loss of gloss is a generalized behavior**. **Its use in future developments will be slightly taken into account**.
7. Finally, **IR 7** is one of the worst additives selected. This bio-wax, far from facilitating the release, increases the adhesion. Cannot be considered that the concentration used is too high, because it has been just 0,4%. This type of bio compounds **can be completely rejected**.

In conclusion, future developments should be executed with IR 1 and IR2 families.

VI. CONCLUSION

VI. CONCLUSIONS

This project demonstrates that the applications of powder coatings have yet an extensive development and a promising future. The attainment of new applications is entirely feasible. Among them, and in which the project focuses, the improvement of PiMC process. Thanks to the advances established during this research, it has managed to turn this technology into a position even more advantageous.

How is explained previously in the work, a factor that can reduce the alluring of this technology is the application of external releasers. Well, this duty has been removed along the study.

1. Five of the designs, conceived during the work**, own self-detaching properties (AT 4.10, AT 4.17, AT 4.18, AT 4.26 and AT 4.33)**. In other words, are capable of liberalize a FRP piece from the production mold without practically resistance. The necessity of external release disappears.
2. Moreover, **three of these formulations (AT 4.17, AT 4.18 and AT 4.33)** behave like a sheet where, once starts the releasing process, **the piece is completely liberalized**.
3. **All these formulations are useful for use in PiMC** alongside SMC, BMC, pre-preg or RTM and in a big range of temperatures. It has succeeded in providing a product applicable to a wide variety of markets. For instance; aerospace, wind power or architecture (not just automotive and aeronautic).
4. If in the future the company considers looking for other releasing additives, **future developments should be executed with IR 1** (a Fatty Acid Salt) **and IR 2** (an Organic Acid) **families**.

VI.1. FUTURE OF PiMC

PiMC is almost a reality. The following image shows the first prototype realized by Porsche thought this technology.

Figure VI.1. First prototype produced thought PiMC technology.

It has been manufactured manually due the process is not yet automated. However, it is a first sign that this process is useful. In this prototype, external releasers were used; but thanks to the improvements achieved on this project, automation will be easier and cheaper.

These kinds of developments drive to the implantation of PiMC. Table VI.1 shows part of a contract between Tiger Coatings GmbH and a German automotive company (not Porsche Automobile Holding SE). It collects the commitment of both to produce a certain number of vehicles per year. Therein describe the minimum amount of cars that are to be produced by this technique.

Table VI.1. Planned units on maturity.

Year	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027
Units	97	956	809	751	688	619	564	501	464	400	248

These minimum amounts are supposed to be increased after 2019. In case the process works, which seems quite feasible, it will be extended. It is a minimal agreement where these developments are very worth.

VI.1.1. Future Research lines

Although PiMC is offering enough positive features as to be implemented on large scale; it can be considered some further improvements:

- Diversification of valid basis: amines, polyurethane, phenolic or hybrid resins, among others.
- Eliminating the necessity of top coatings. (This is not yet a reality in the field of powder coatings; so for PiMC can be harder. However, it can be a possible goal to achieve).
- Extension of range of temperatures where PiMC is valid: some composites require less than 110°C to be cured, like some kind of windmills used to generate energy.
- Reduction of curing cycle times (< 2 min).
- Increase the variety of techniques where PiMC technology is useful: currently these formulations are useful for SMC, BMC, pre-preg or RTM; leaving out other techniques such as GFC or WPC.

Although these features seem ideals, it must to be recognized that there is still a lot of work and development of the art necessary to attain all that features. This work finishes with an image that shows the integration between FRP and powder coating.

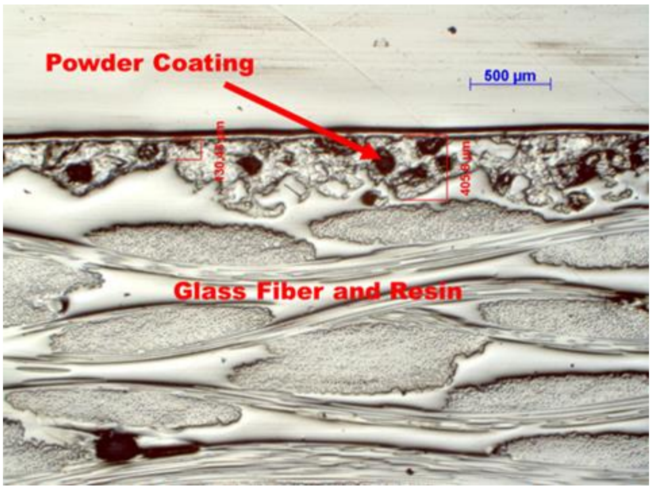


Figure VI.2. Goal of PiMC.

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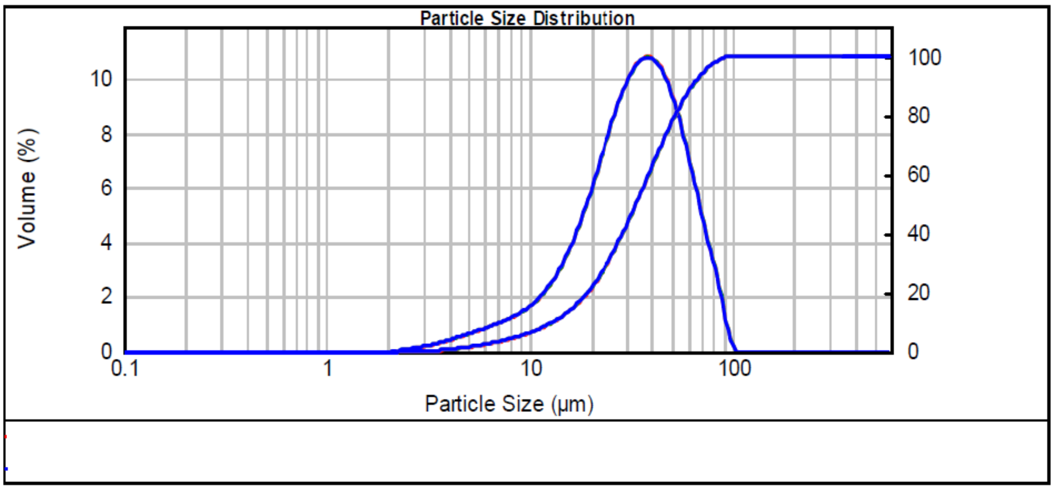
ANNEXES

ANNEX I

Table AI.1 and Figure AI.1. Particle size distribution: Formulation AT 3.1.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.15 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.469 %	**Result Emulation:** Off
Concentration: 0.0016 %Vol	**Span :** 1.503	**Uniformity:** 0.461	**Result units:** Volume
Specific Surface Area: 0.257 m²/g	**Surface Weighted Mean D[3,2]:** 23.369 um	**Vol. Weighted Mean D[4,3]:** 35.850 um	

d(0.1): 12.800 um **d(0.5):** 33.239 um **d(0.9):** 62.756 um



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	21.87	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	27.79	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.08	25.000	32.26	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.21	32.000	47.41	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.42	36.000	55.56	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.72	39.811	62.67	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.86	45.000	71.14	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.68	56.000	84.50	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.35	63.000	90.17	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.58	65.000	91.46	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.13	70.000	94.14	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.55	75.000	96.18	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.65	80.000	97.70	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	8.98	90.000	99.58	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.51	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	13.32	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	17.01	120.226	100.00	954.993	100.00		

Table AI.2 and Figure AI.2. Particle size distribution: Formulation AT 3.2

Particle Name:
Default

Particle RI:
1.520

Dispersant Name:

Accessory Name:
Scirocco 2000

Absorption:
0.1

Dispersant RI:
1.000

Analysis model:
General purpose (fine)

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.413 %

Sensitivity:
Normal

Obscuration:
0.76 %

Result Emulation:
Off

Concentration:
0.0007 %Vol

Specific Surface Area:
0.205 m²/g

Span :
1.434

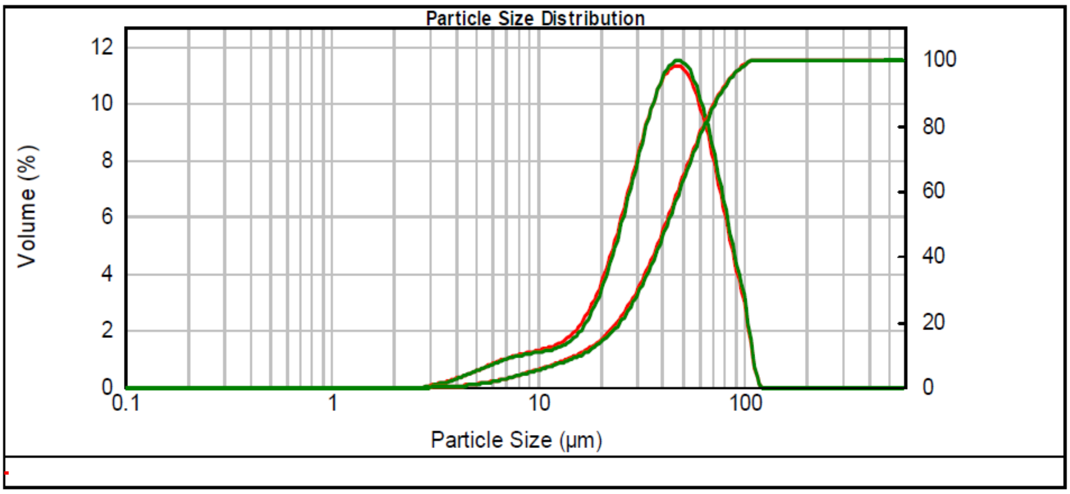
Surface Weighted Mean D[3,2]:
29.335 um

Uniformity:
0.432

Vol. Weighted Mean D[4,3]:
45.020 um

Result units:
Volume

d(0.1): 16.299 um **d(0.5): 42.476 um** **d(0.9): 77.203 um**



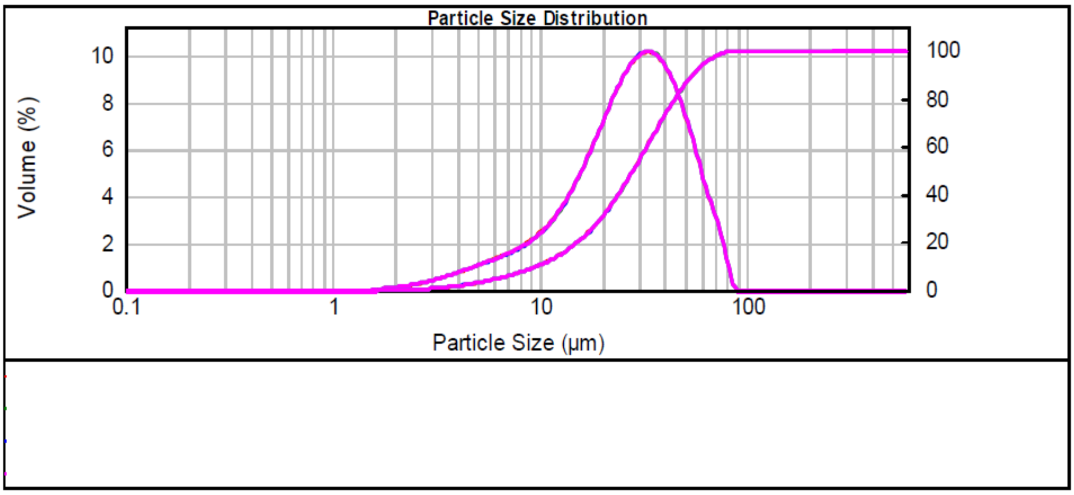
Size (μm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.00
2.512	0.00
2.884	0.00
3.311	0.06
3.802	0.21
4.000	0.30
5.012	0.92
5.754	1.51
6.000	1.72
7.586	3.17
8.000	3.55
10.000	5.26
12.000	6.78
13.183	7.64
15.136	9.08
17.378	10.92
20.000	13.48
22.909	16.95
25.000	19.83
32.000	31.26
36.000	38.44
39.811	45.31
45.000	54.29
56.000	70.59
63.000	78.66
65.000	80.63
70.000	85.01
75.000	88.62
80.000	91.56
90.000	95.79
100.000	98.48
104.713	99.35
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.3 and Figure AI.3. Particle size distribution: Formulation AT 3.3.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.37 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.512 %	**Result Emulation:** Off

Concentration: 0.0008 %Vol	**Span :** 1.604	**Uniformity:** 0.489	**Result units:** Volume
Specific Surface Area: 0.323 m²/g	**Surface Weighted Mean D[3,2]:** 18.588 um	**Vol. Weighted Mean D[4,3]:** 30.426 um	

d(0.1): 9.532 um **d(0.5): 28.090 um** **d(0.9): 54.589 um**



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.09	20.000	30.84	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.22	22.909	37.77	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.42	25.000	42.77	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.72	32.000	58.57	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	1.14	36.000	66.44	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	1.70	39.811	72.97	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	1.94	45.000	80.36	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	3.30	56.000	91.05	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	4.36	63.000	95.10	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	4.72	65.000	95.95	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	7.05	70.000	97.67	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	7.67	75.000	98.98	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	10.74	80.000	99.80	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	14.07	90.000	100.00	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	16.21	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	20.04	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.01	17.378	24.82	120.226	100.00	954.993	100.00		

Table AI.4 and Figure AI.4. Particle size distribution: Formulation AT 3.4.

Particle Name:
Default

Particle RI:
1.520

Dispersant Name:

Accessory Name:
Scirocco 2000

Absorption:
0.1

Dispersant RI:
1.000

Analysis model:
General purpose (fine)

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.330 %

Sensitivity:
Normal

Obscuration:
1.74 %

Result Emulation:
Off

Concentration:
0.0019 %Vol

Specific Surface Area:
0.177 m²/g

Span :
1.458

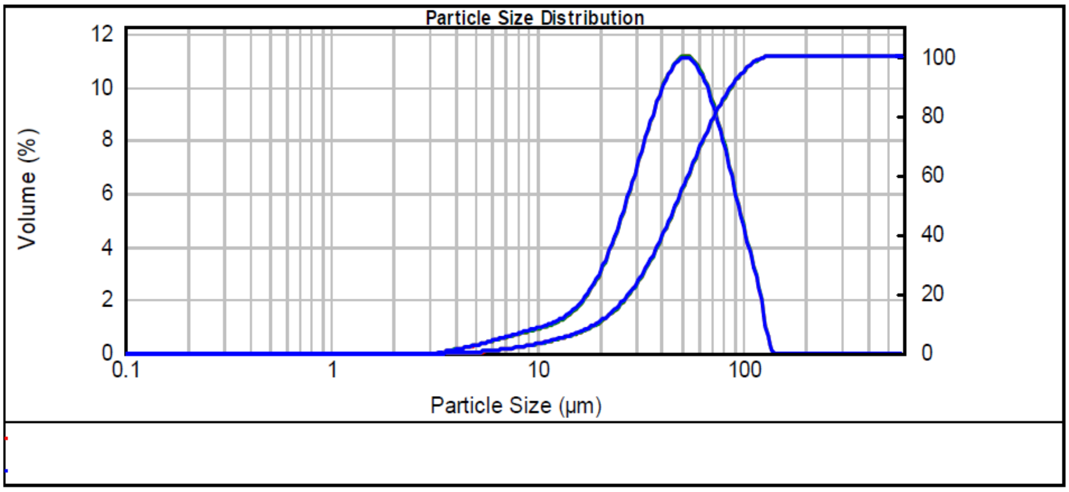
Surface Weighted Mean D[3,2]:
33.935 um

Uniformity:
0.447

Vol. Weighted Mean D[4,3]:
50.433 um

Result units:
Volume

d(0.1): **19.255** **um** **d(0.5):** **46.758** **um** **d(0.9):** **87.410** **um**

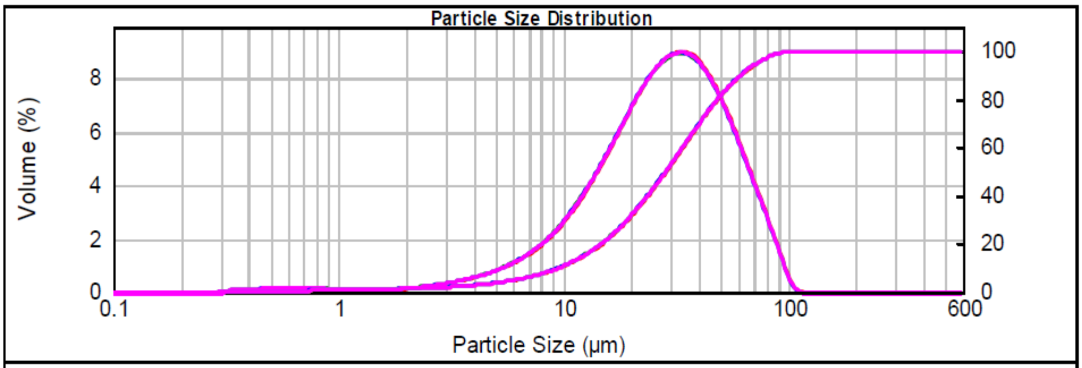


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	10.72	125.000	99.73	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	13.85	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	16.41	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	26.46	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	32.83	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.06	39.811	39.02	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.10	45.000	47.29	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.42	56.000	63.04	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.75	63.000	71.33	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.87	65.000	73.43	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.76	70.000	78.20	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	2.01	75.000	82.30	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	3.25	80.000	85.79	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	4.50	90.000	91.23	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	5.27	100.000	94.97	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	6.61	104.713	96.28	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	8.34	120.226	99.23	954.993	100.00		

Table AI.5 and Figure AI.5. Particle size distribution: Formulation AT 3.5.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.15 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.126 %	**Result Emulation:** Off
Concentration: 0.0009 %Vol	**Span :** 1.819	**Uniformity:** 0.559	**Result units:** Volume
Specific Surface Area: 0.432 m²/g	**Surface Weighted Mean D[3,2]:** 13.894 um	**Vol. Weighted Mean D[4,3]:** 32.258 um	

d(0.1): 9.426 um **d(0.5): 28.415 um** **d(0.9): 61.123 um**



Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	1.50	20.000	31.81	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	1.64	22.909	38.32	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	1.83	25.000	42.88	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	2.07	32.000	56.89	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.01	3.311	2.39	36.000	63.80	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.09	3.802	2.80	39.811	69.59	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.19	4.000	2.98	45.000	76.29	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.31	5.012	3.98	56.000	86.62	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.44	5.754	4.81	63.000	91.06	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.58	6.000	5.10	65.000	92.08	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.72	7.586	7.18	70.000	94.26	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.85	8.000	7.78	75.000	95.98	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.98	10.000	10.96	80.000	97.31	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	1.08	12.000	14.61	90.000	99.10	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	1.18	13.183	16.94	100.000	99.87	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	1.28	15.136	21.01	104.713	99.98	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	1.38	17.378	25.92	120.226	100.00	954.993	100.00		

Table AI.6 and Figure AI.6. Particle size distribution: Formulation AT 4.1.

Particle Name:
Default

Accessory Name:
Scirocco 2000

Analysis model:
General purpose (fine)

Sensitivity:
Normal

Particle RI:
1.520

Absorption:
0.1

Size range:
0.020 to 2000.000 um

Obscuration:
2.50 %

Dispersant Name:

Dispersant RI:
1.000

Weighted Residual:
0.393 %

Result Emulation:
Off

Concentration:
0.0019 %Vol

Span :
1.585

Uniformity:
0.481

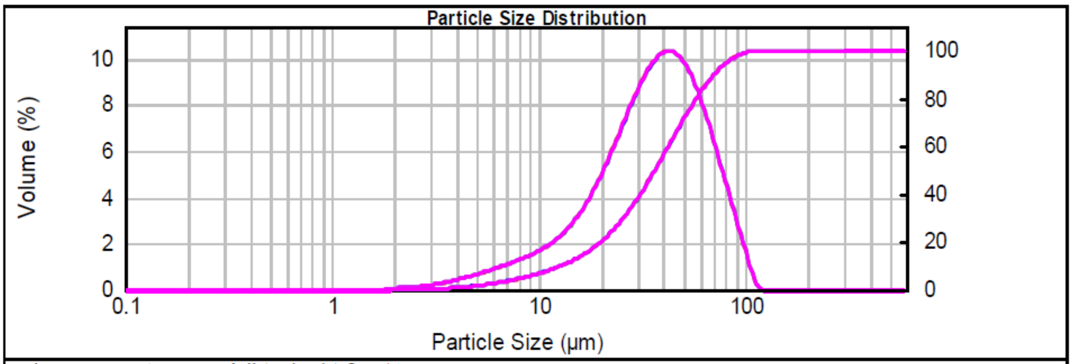
Result units:
Volume

Specific Surface Area:
0.249 m²/g

Surface Weighted Mean D[3,2]:
24.140 um

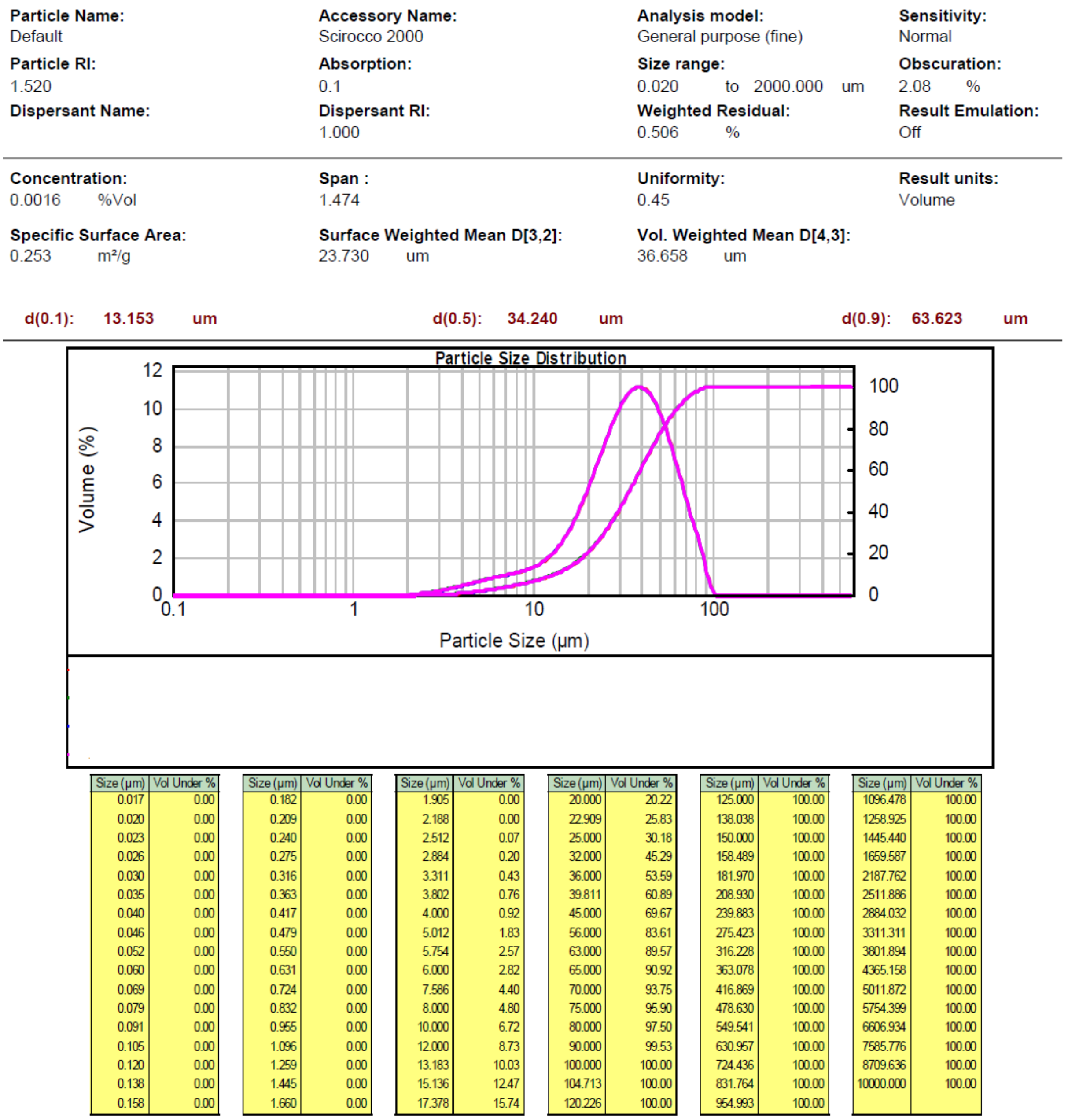
Vol. Weighted Mean D[4,3]:
39.241 um

d(0.1): 12.656 um **d(0.5): 36.219 um** **d(0.9): 70.059 um**



Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	20.37	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.06	22.909	25.32	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.16	25.000	29.08	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.30	32.000	42.22	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.51	36.000	49.61	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.81	39.811	56.27	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.95	45.000	64.55	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.77	56.000	78.55	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.46	63.000	85.06	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.70	65.000	86.61	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.33	70.000	89.97	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.77	75.000	92.65	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.94	80.000	94.78	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	9.22	90.000	97.74	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.64	100.000	99.34	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	13.14	104.713	99.74	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	16.30	120.226	100.00	954.993	100.00		

Table AI.7 and Figure AI.7. Particle size distribution: Formulation AT 4.2.



Particle Name: Default

Accessory Name: Scirocco 2000

Analysis model: General purpose (fine)

Sensitivity: Normal

Particle RI: 1.520

Absorption: 0.1

Size range: 0.020 to 2000.000 um

Obscuration: 2.08 %

Dispersant Name:

Dispersant RI: 1.000

Weighted Residual: 0.506 %

Result Emulation: Off

Concentration: 0.0016 %Vol

Span : 1.474

Uniformity: 0.45

Result units: Volume

Specific Surface Area: 0.253 m²/g

Surface Weighted Mean D[3,2]: 23.730 um

Vol. Weighted Mean D[4,3]: 36.658 um

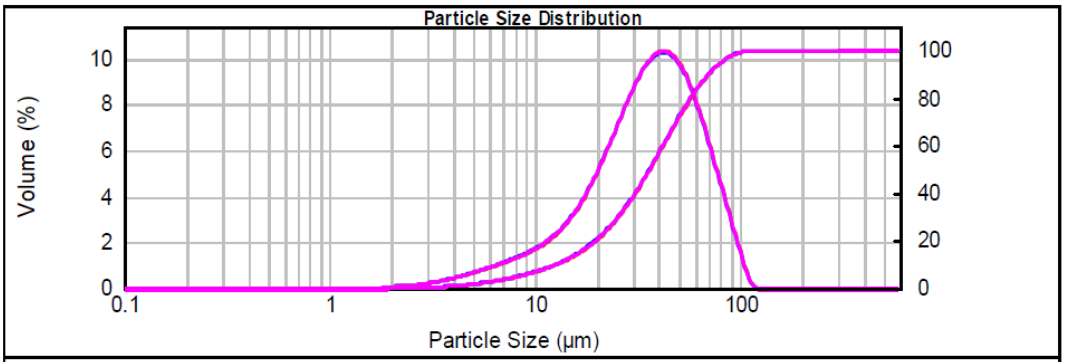
d(0.1): 13.153 um **d(0.5): 34.240 um** **d(0.9): 63.623 um**

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	20.22	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	25.83	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.07	25.000	30.18	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.20	32.000	45.29	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.43	36.000	53.59	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.76	39.811	60.89	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.92	45.000	69.67	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.83	56.000	83.61	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.57	63.000	89.57	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.82	65.000	90.92	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.40	70.000	93.75	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.80	75.000	95.90	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.72	80.000	97.50	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	8.73	90.000	99.53	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.03	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	12.47	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	15.74	120.226	100.00	954.993	100.00		

Table AI.8 and Figure AI.8. Particle size distribution: Formulation AT 4.3.

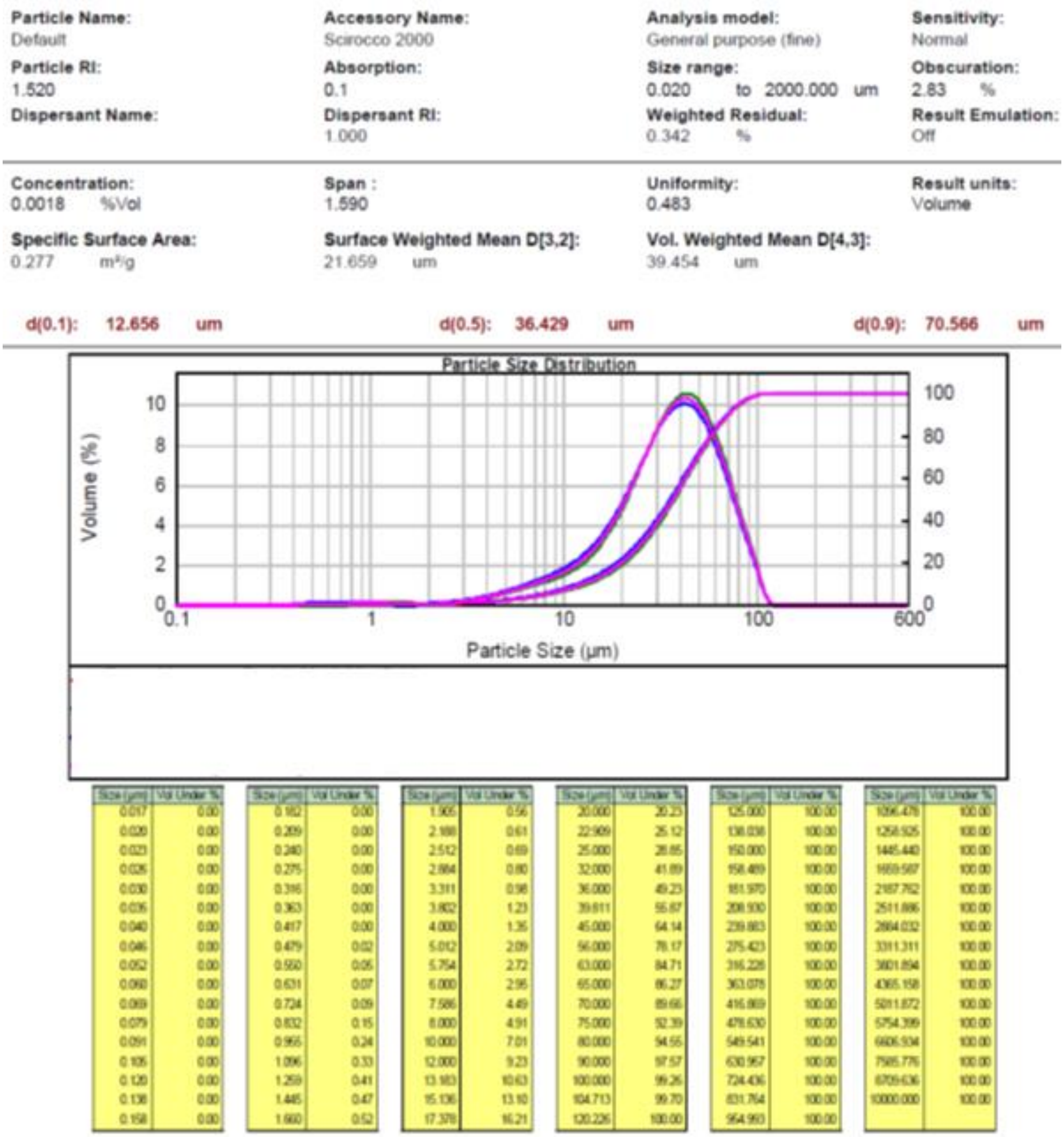
Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.78 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.394 %	**Result Emulation:** Off
Concentration: 0.0021 %Vol	**Span :** 1.588	**Uniformity:** 0.482	**Result units:** Volume
Specific Surface Area: 0.251 m²/g	**Surface Weighted Mean D[3,2]:** 23.943 um	**Vol. Weighted Mean D[4,3]:** 38.984 um	

d(0.1): 12.543 um **d(0.5): 35.964 um** **d(0.9): 69.659 um**



Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.07
2.512	0.17
2.884	0.31
3.311	0.53
3.802	0.84
4.000	0.98
5.012	1.81
5.754	2.51
6.000	2.76
7.586	4.40
8.000	4.84
10.000	7.04
12.000	9.35
13.183	10.79
15.136	13.34
17.378	16.54
20.000	20.67
22.909	25.67
25.000	29.46
32.000	42.67
36.000	50.07
39.811	56.73
45.000	64.98
56.000	78.91
63.000	85.35
65.000	86.89
70.000	90.20
75.000	92.85
80.000	94.95
90.000	97.85
100.000	99.39
104.713	99.77
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.9 and Figure AI.9. Particle size distribution: Formulation AT 4.4.



Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.83 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.342 %	**Result Emulation:** Off
Concentration: 0.0018 %Vol	**Span :** 1.590	**Uniformity:** 0.483	**Result units:** Volume
Specific Surface Area: 0.277 m²/g	**Surface Weighted Mean D[3,2]:** 21.659 um	**Vol. Weighted Mean D[4,3]:** 39.454 um	

d(0.1): 12.656 um **d(0.5):** 36.429 um **d(0.9):** 70.566 um

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.56	20.000	20.23	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.61	22.909	25.12	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.69	25.000	28.85	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.80	32.000	41.89	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.98	36.000	49.23	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	1.23	39.811	55.87	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	1.35	45.000	64.14	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.02	5.012	2.09	56.000	78.17	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.05	5.754	2.72	63.000	84.71	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.07	6.000	2.95	65.000	86.27	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.09	7.586	4.49	70.000	89.66	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.15	8.000	4.91	75.000	92.39	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.24	10.000	7.01	80.000	94.55	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.33	12.000	9.23	90.000	97.57	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.41	13.183	10.63	100.000	99.26	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.47	15.136	13.10	104.713	99.70	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.52	17.378	16.21	120.226	100.00	954.993	100.00		

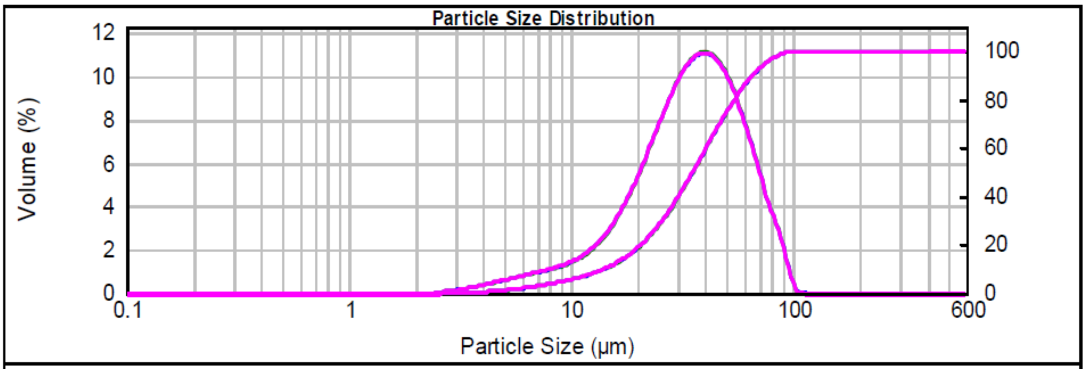
Table AI.10 and Figure AI.10. Particle size distribution: Formulation AT 4.5.

Particle Name: Default
Accessory Name: Scirocco 2000
Analysis model: General purpose (fine)
Sensitivity: Normal
Particle RI: 1.520
Absorption: 0.1
Size range: 0.020 to 2000.000 um
Obscuration: 2.42 %
Dispersant Name:
Dispersant RI: 1.000
Weighted Residual: 0.470 %
Result Emulation: Off

Concentration: 0.0019 %Vol
Span : 1.466
Uniformity: 0.448
Result units: Volume

Specific Surface Area: 0.241 m²/g
Surface Weighted Mean D[3,2]: 24.852 um
Vol. Weighted Mean D[4,3]: 37.489 um

d(0.1): 13.781 um
d(0.5): 34.916 um
d(0.9): 64.981 um

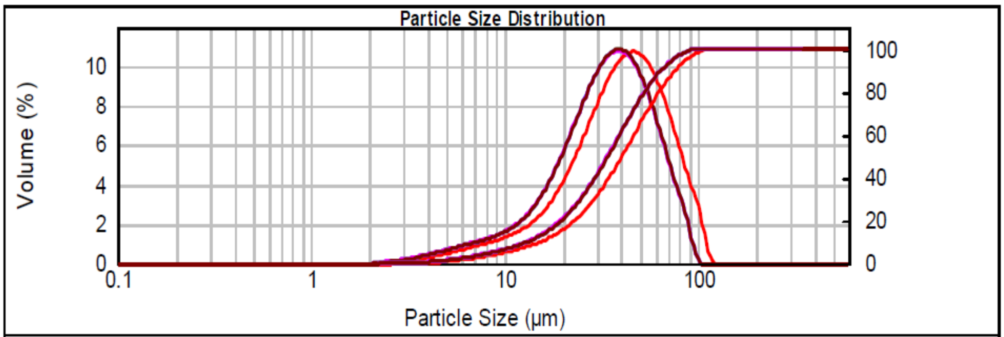


Size (μm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.00
2.512	0.00
2.884	0.08
3.311	0.24
3.802	0.50
4.000	0.62
5.012	1.37
5.754	2.01
6.000	2.23
7.586	3.69
8.000	4.07
10.000	5.95
12.000	7.97
13.183	9.29
15.136	11.73
17.378	14.98
20.000	19.39
22.909	24.90
25.000	29.14
32.000	43.97
36.000	52.17
39.811	59.44
45.000	68.24
56.000	82.42
63.000	88.59
65.000	90.01
70.000	93.00
75.000	95.25
80.000	96.95
90.000	99.28
100.000	99.98
104.713	100.00
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.11 and Figure AI.11. Particle size distribution: Formulation AT 4.11.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.18 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.476 %	**Result Emulation:** Off
Concentration: 0.0016 %Vol	**Span :** 1.497	**Uniformity:** 0.457	**Result units:** Volume
Specific Surface Area: 0.253 m²/g	**Surface Weighted Mean D[3,2]:** 23.733 um	**Vol. Weighted Mean D[4,3]:** 36.530 um	

d(0.1): 12.913 um **d(0.5): 33.992 um** **d(0.9): 63.812 um**

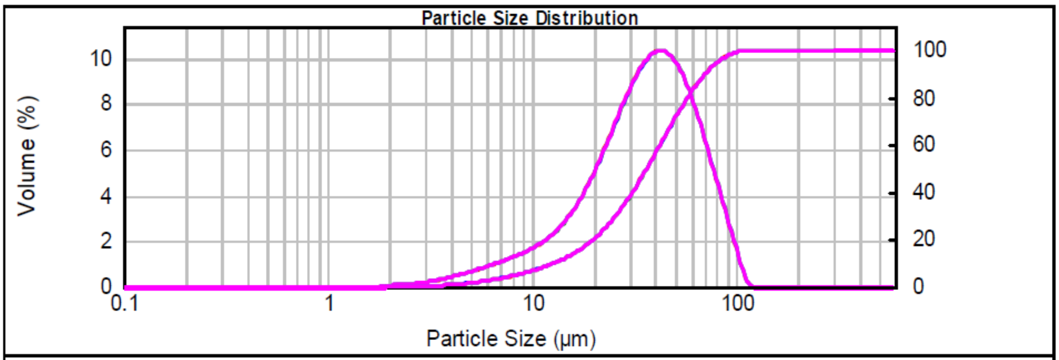


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	20.96	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	26.62	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.06	25.000	30.95	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.17	32.000	45.87	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.37	36.000	54.02	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.66	39.811	61.20	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.80	45.000	69.82	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.64	56.000	83.55	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.35	63.000	89.44	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.60	65.000	90.79	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.20	70.000	93.60	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.63	75.000	95.75	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.70	80.000	97.38	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	8.91	90.000	99.49	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.33	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	12.95	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	16.38	120.226	100.00	954.993	100.00		

Table AI.12 and Figure AI.12. Particle size distribution: Formulation AT 4.7.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.50 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.393 %	**Result Emulation:** Off
Concentration: 0.0019 %Vol	**Span :** 1.585	**Uniformity:** 0.481	**Result units:** Volume
Specific Surface Area: 0.249 m²/g	**Surface Weighted Mean D[3,2]:** 24.140 um	**Vol. Weighted Mean D[4,3]:** 39.241 um	

d(0.1): 12.656 um **d(0.5): 36.219 um** **d(0.9): 70.059 um**

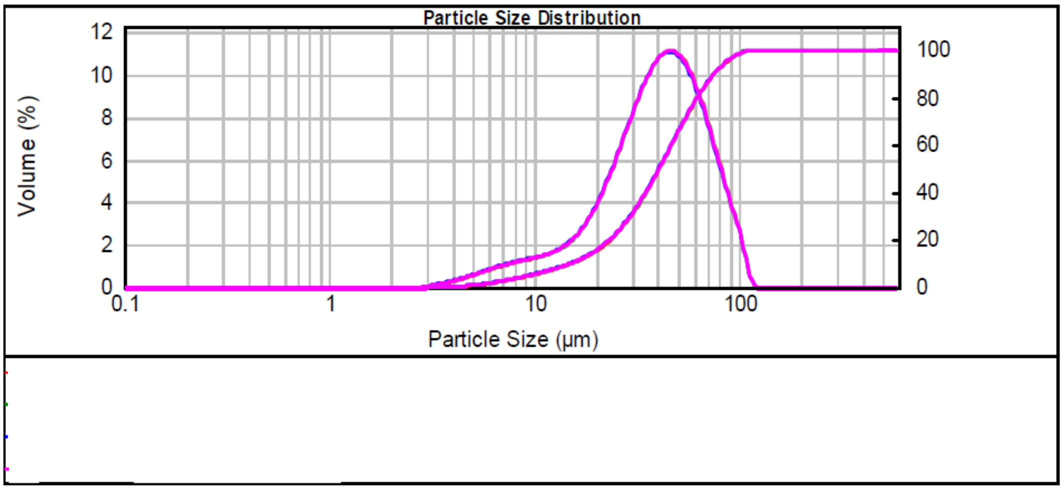


Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	20.37	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.06	22.909	25.32	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.16	25.000	29.08	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.30	32.000	42.22	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.51	36.000	49.61	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.81	39.811	56.27	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.95	45.000	64.55	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.77	56.000	78.55	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	2.46	63.000	85.06	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	2.70	65.000	86.61	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	4.33	70.000	89.97	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	4.77	75.000	92.65	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	6.94	80.000	94.78	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	9.22	90.000	97.74	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	10.64	100.000	99.34	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	13.14	104.713	99.74	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	16.30	120.226	100.00	954.993	100.00		

Table AI.13 and Figure AI.13. Particle size distribution: Formulation AT 4.9.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.16 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.397 %	**Result Emulation:** Off
Concentration: 0.0019 %Vol	**Span :** 1.490	**Uniformity:** 0.451	**Result units:** Volume
Specific Surface Area: 0.216 m²/g	**Surface Weighted Mean D[3,2]:** 27.756 um	**Vol. Weighted Mean D[4,3]:** 43.082 um	

d(0.1): **14.778** **um** **d(0.5):** **40.371** **um** **d(0.9):** **74.933** **um**



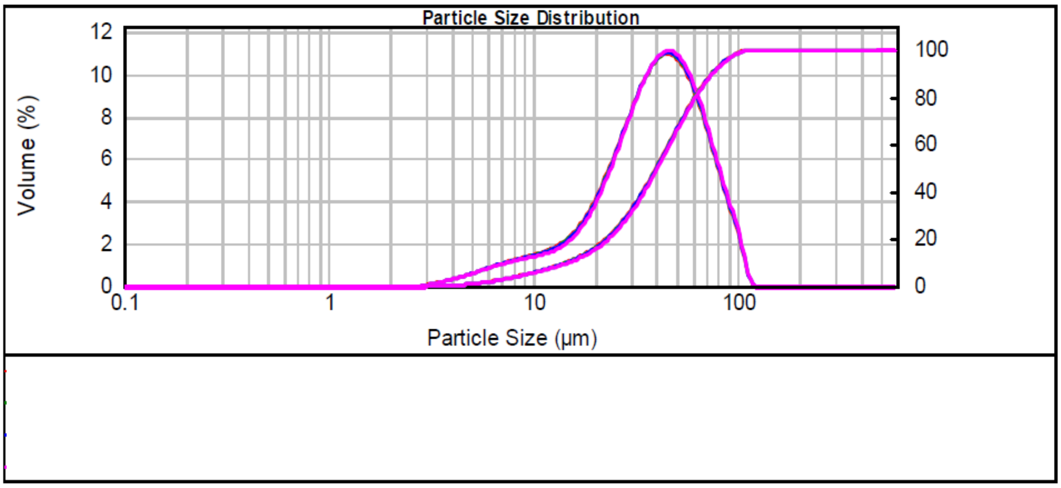
Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.66	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.61	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.80	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	34.87	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.08	36.000	42.17	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.25	39.811	49.01	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.35	45.000	57.81	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.02	56.000	73.39	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.64	63.000	80.92	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.87	65.000	82.75	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.40	70.000	86.76	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.81	75.000	90.04	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.71	80.000	92.68	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.50	90.000	96.44	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.55	100.000	98.77	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.34	104.713	99.48	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.60	120.226	100.00	954.993	100.00		

Table AI.14 and Figure AI.14. Particle size distribution: Formulation AT 4.10.

Particle Name:	**Accessory Name:**	**Analysis model:**	**Sensitivity:**
Default	Scirocco 2000	General purpose (fine)	Normal
Particle RI:	**Absorption:**	**Size range:**	**Obscuration:**
1.520	0.1	0.020 to 2000.000 um	2.46 %
Dispersant Name:	**Dispersant RI:**	**Weighted Residual:**	**Result Emulation:**
	1.000	0.426 %	Off

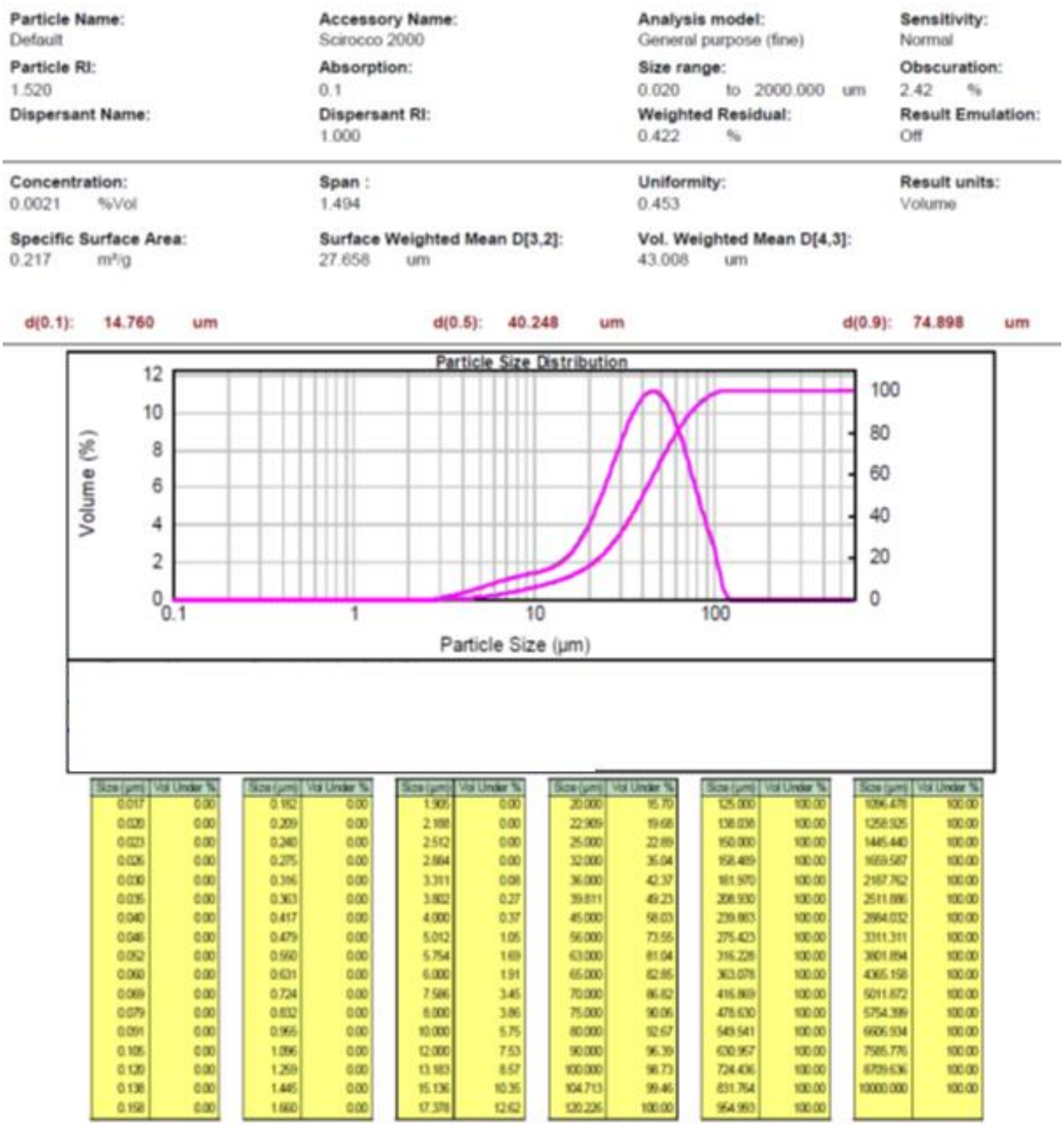
Concentration:	**Span :**	**Uniformity:**	**Result units:**
0.0022 %Vol	1.491	0.451	Volume
Specific Surface Area:	**Surface Weighted Mean D[3,2]:**	**Vol. Weighted Mean D[4,3]:**	
0.216 m²/g	27.772 um	43.202 um	

d(0.1): 14.823 um **d(0.5): 40.462 um** **d(0.9): 75.172 um**



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.54	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.47	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.64	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	34.69	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.08	36.000	42.00	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.26	39.811	48.85	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.36	45.000	57.66	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.04	56.000	73.26	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.68	63.000	80.79	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.90	65.000	82.62	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.44	70.000	86.63	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.85	75.000	89.90	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.74	80.000	92.53	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.51	90.000	96.30	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.53	100.000	98.69	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.29	104.713	99.44	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.52	120.226	100.00	954.993	100.00		

Table AI.15 and Figure AI.15. Particle size distribution: Formulation AT 4.11.



Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.42 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.422 %	**Result Emulation:** Off
Concentration: 0.0021 %Vol	**Span :** 1.494	**Uniformity:** 0.453	**Result units:** Volume
Specific Surface Area: 0.217 m²/g	**Surface Weighted Mean D[3,2]:** 27.658 um	**Vol. Weighted Mean D[4,3]:** 43.008 um	

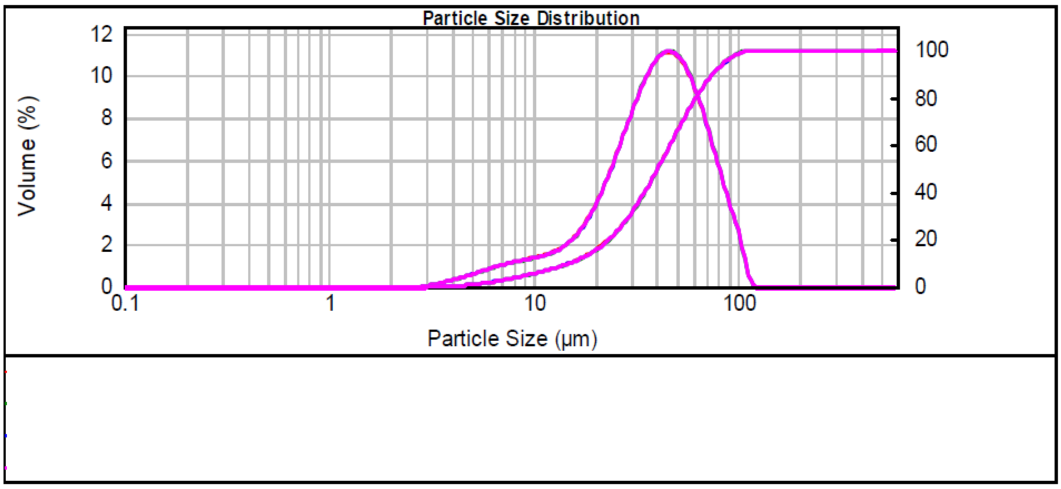
d(0.1): 14.760 um   d(0.5): 40.248 um   d(0.9): 74.898 um

Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.70	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.68	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.89	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	35.04	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.08	36.000	42.37	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.27	39.811	49.23	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.37	45.000	58.03	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.05	56.000	73.55	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.69	63.000	81.04	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.91	65.000	82.85	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.45	70.000	86.82	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.86	75.000	90.06	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.75	80.000	92.67	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.53	90.000	96.39	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.57	100.000	98.73	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.35	104.713	99.46	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.62	120.226	100.00	954.993	100.00		

Table AI.16 and Figure AI.16. Particle size distribution: Formulation AT 4.12.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.11 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.414 %	**Result Emulation:** Off
Concentration: 0.0019 %Vol	**Span :** 1.487	**Uniformity:** 0.451	**Result units:** Volume
Specific Surface Area: 0.216 m²/g	**Surface Weighted Mean D[3,2]:** 27.736 um	**Vol. Weighted Mean D[4,3]:** 43.058 um	

d(0.1): 14.860 um **d(0.5): 40.335 um** **d(0.9): 74.839 um**



Size (μm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.00
2.512	0.00
2.884	0.00
3.311	0.08
3.802	0.26
4.000	0.36
5.012	1.05
5.754	1.68
6.000	1.91
7.586	3.45
8.000	3.85
10.000	5.73
12.000	7.48
13.183	8.50
15.136	10.26
17.378	12.49
20.000	15.53
22.909	19.49
25.000	22.70
32.000	34.84
36.000	42.19
39.811	49.07
45.000	57.91
56.000	73.50
63.000	81.03
65.000	82.85
70.000	86.84
75.000	90.10
80.000	92.72
90.000	96.45
100.000	98.77
104.713	99.47
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.17 and Figure AI.17. Particle size distribution: Formulation AT 4.13.

Particle Name:
Default

Accessory Name:
Scirocco 2000

Analysis model:
General purpose (fine)

Sensitivity:
Normal

Particle RI:
1.520

Absorption:
0.1

Size range:
0.020 to 2000.000 um

Obscuration:
2.27 %

Dispersant Name:

Dispersant RI:
1.000

Weighted Residual:
0.411 %

Result Emulation:
Off

Concentration:
0.0020 %Vol

Span :
1.487

Uniformity:
0.45

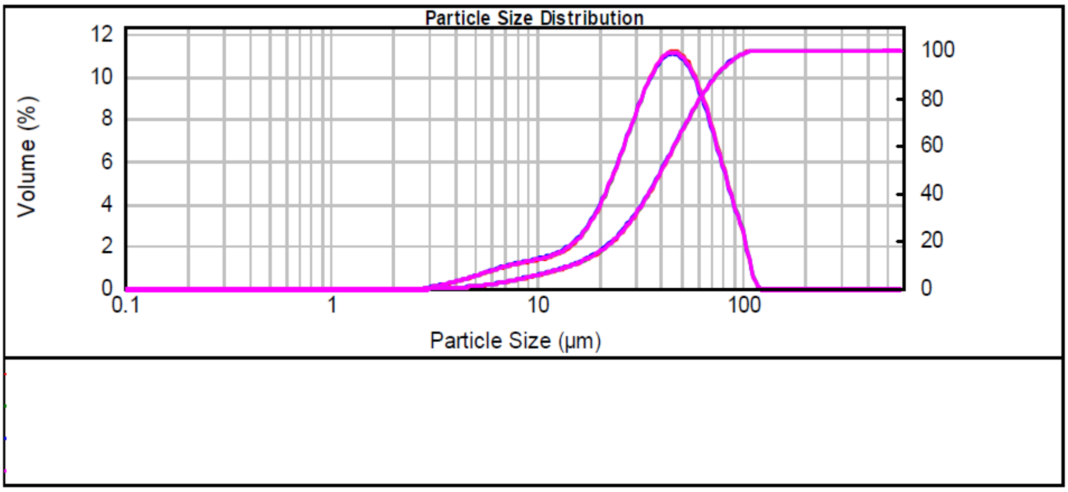
Result units:
Volume

Specific Surface Area:
0.216 m²/g

Surface Weighted Mean D[3,2]:
27.757 um

Vol. Weighted Mean D[4,3]:
43.110 um

d(0.1): 14.873 um **d(0.5): 40.394 um** **d(0.9): 74.919 um**



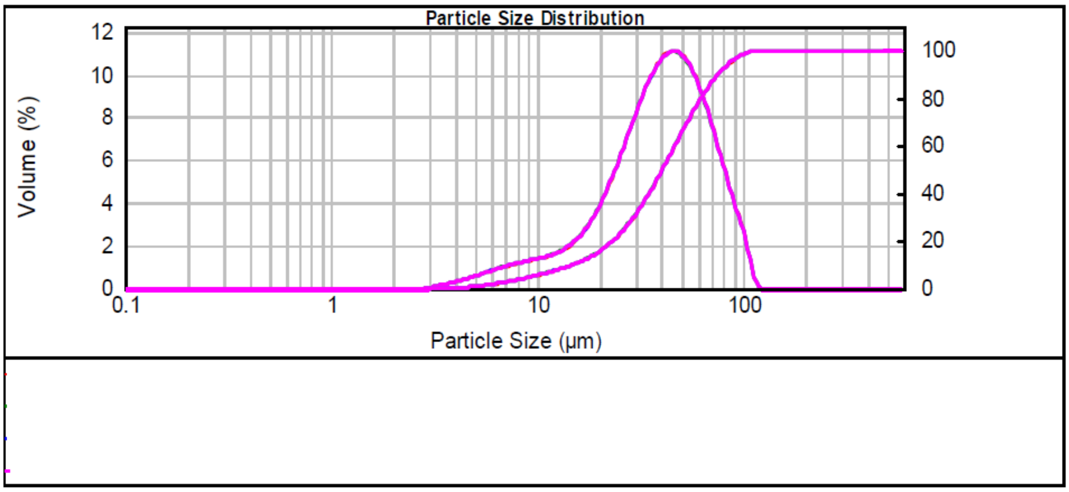
Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.50	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.45	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.64	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	34.76	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.08	36.000	42.09	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.27	39.811	48.97	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.37	45.000	57.80	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.05	56.000	73.42	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.69	63.000	80.95	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.91	65.000	82.78	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.45	70.000	86.78	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.85	75.000	90.05	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.73	80.000	92.68	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.48	90.000	96.43	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.49	100.000	98.76	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.24	104.713	99.47	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.47	120.226	100.00	954.993	100.00		

Table AI.18 and Figure AI.18. Particle size distribution: Formulation AT 4.14.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.51 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.420 %	**Result Emulation:** Off

Concentration: 0.0022 %Vol	**Span :** 1.495	**Uniformity:** 0.453	**Result units:** Volume
Specific Surface Area: 0.218 m²/g	**Surface Weighted Mean D[3,2]:** 27.582 um	**Vol. Weighted Mean D[4,3]:** 42.942 um	

d(0.1): 14.677 um **d(0.5): 40.201 um** **d(0.9): 74.790 um**

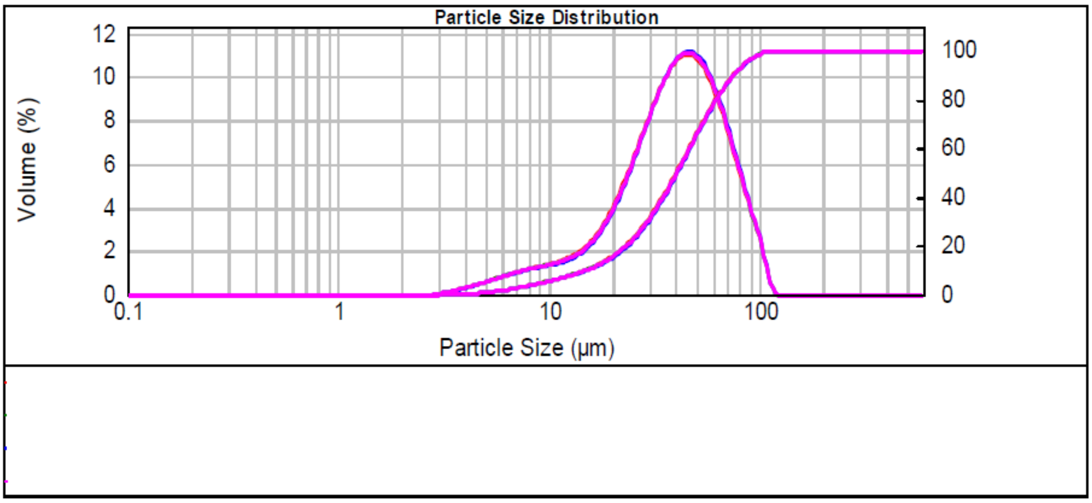


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.78	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.77	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.98	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	35.12	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.09	36.000	42.45	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.27	39.811	49.31	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.37	45.000	58.11	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.06	56.000	73.64	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.70	63.000	81.11	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.93	65.000	82.93	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.48	70.000	86.89	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.89	75.000	90.12	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.80	80.000	92.72	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.59	90.000	96.43	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.64	100.000	98.75	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.43	104.713	99.47	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.71	120.226	100.00	954.993	100.00		

Table AI.19 and Figure AI.19. Particle size distribution: Formulation AT 4.15.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.95 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.411 %	**Result Emulation** Off
Concentration: 0.0017 %Vol	**Span :** 1.489	**Uniformity:** 0.452	**Result units:** Volume
Specific Surface Area: 0.217 m²/g	**Surface Weighted Mean D[3,2]:** 27.682 um	**Vol. Weighted Mean D[4,3]:** 42.959 um	

d(0.1): **14.812** **um** **d(0.5):** **40.228** **um** **d(0.9):** **74.726** **um**

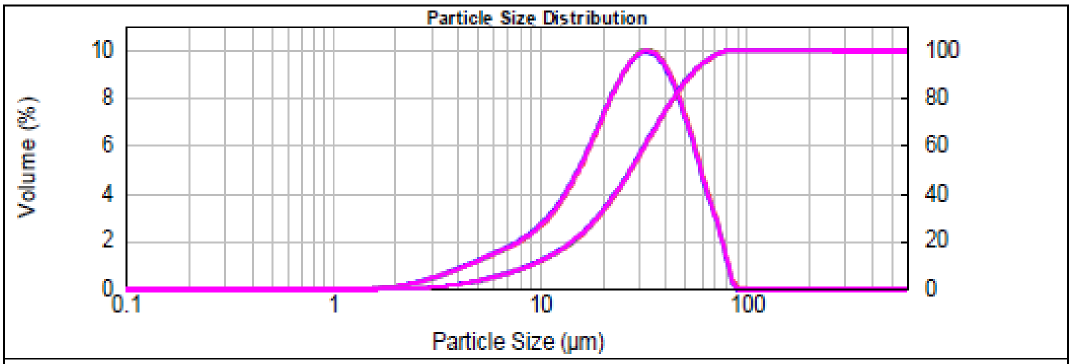


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	15.66	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	19.66	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	22.88	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	35.06	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.08	36.000	42.40	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.27	39.811	49.26	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.37	45.000	58.07	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	1.05	56.000	73.61	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	1.68	63.000	81.11	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	1.90	65.000	82.93	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	3.43	70.000	86.91	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	3.83	75.000	90.16	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	5.71	80.000	92.78	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	7.49	90.000	96.51	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	8.52	100.000	98.80	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	10.31	104.713	99.49	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	12.58	120.226	100.00	954.993	100.00		

Table AI.20 and Figure AI.20. Particle size distribution: Formulation 4.17.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.41 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.508 %	**Result Emulation:** Off
Concentration: 0.0008 %Vol	**Span :** 1.646	**Uniformity:** 0.501	**Result units:** Volume
Specific Surface Area: 0.333 m²/g	**Surface Weighted Mean D[3,2]:** 18.044 um	**Vol. Weighted Mean D[4,3]:** 29.960 um	

d(0.1): 8.988 um **d(0.5):** 27.536 um **d(0.9):** 54.307 um

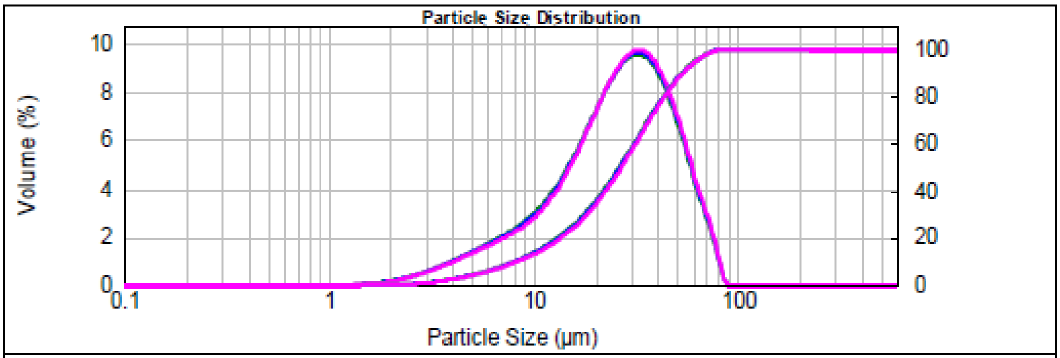


Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.08	20.000	32.35	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.21	22.909	39.22	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.41	25.000	44.15	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.72	32.000	59.62	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	1.17	36.000	67.29	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	1.78	39.811	73.65	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	2.04	45.000	80.84	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	3.54	56.000	91.23	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	4.71	63.000	95.18	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	5.10	65.000	96.01	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	7.68	70.000	97.69	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	8.36	75.000	98.94	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	11.71	80.000	99.74	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	15.28	90.000	100.00	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	17.52	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	21.46	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.01	17.378	26.32	120.226	100.00	954.993	100.00		

Table AI.21 and Figure AI.21. Particle size distribution: Formulation 4.18.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.48 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.482 %	**Result Emulation:** Off
Concentration: 0.0008 %Vol	**Span :** 1.691	**Uniformity:** 0.513	**Result units:** Volume
Specific Surface Area: 0.352 m²/g	**Surface Weighted Mean D[3,2]:** 17.063 um	**Vol. Weighted Mean D[4,3]:** 29.350 um	

d(0.1): 8.273 um **d(0.5):** 26.917 um **d(0.9):** 53.795 um



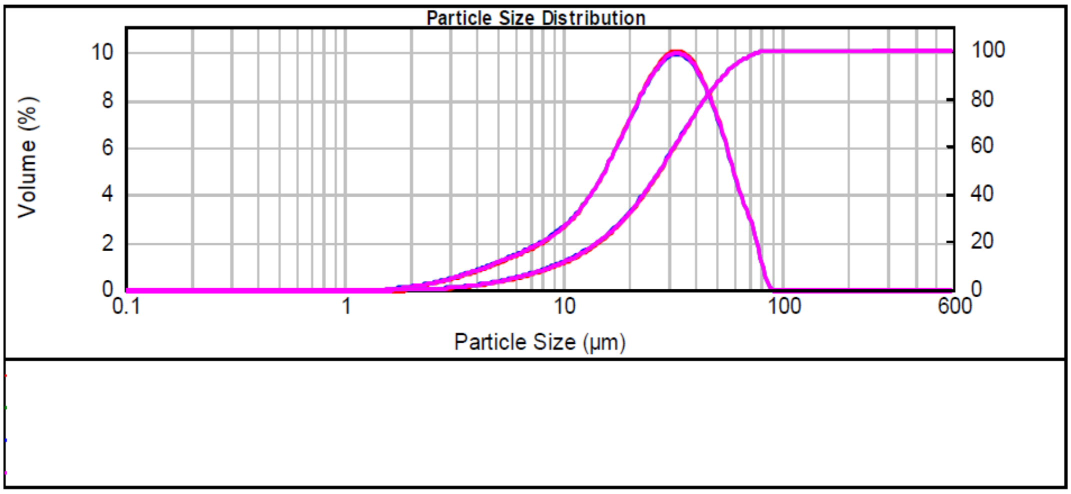
Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.18	20.000	33.96	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.35	22.909	40.76	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.61	25.000	45.63	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.99	32.000	60.82	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	1.52	36.000	68.31	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	2.22	39.811	74.51	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	2.53	45.000	81.50	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	4.22	56.000	91.58	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	5.53	63.000	95.39	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	5.96	65.000	96.18	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	8.78	70.000	97.81	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	9.52	75.000	99.04	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	13.08	80.000	99.81	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	16.78	90.000	100.00	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	19.07	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.01	15.136	23.08	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.08	17.378	27.96	120.226	100.00	954.993	100.00		

Table AI.22 and Figure AI.22. Particle size distribution: Formulation 4.19.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.90 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.467 %	**Result Emulation:** Off

Concentration: 0.0017 %Vol	**Span :** 1.640	**Uniformity:** 0.499	**Result units:** Volume
Specific Surface Area: 0.332 m²/g	**Surface Weighted Mean D[3,2]:** 18.073 um	**Vol. Weighted Mean D[4,3]:** 29.858 um	

d(0.1): 9.043 um **d(0.5): 27.448 um** **d(0.9): 54.058 um**



Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.06
2.188	0.19
2.512	0.40
2.884	0.71
3.311	1.15
3.802	1.75
4.000	2.01
5.012	3.47
5.754	4.62
6.000	5.01
7.586	7.58
8.000	8.26
10.000	11.64
12.000	15.25
13.183	17.51
15.136	21.50
17.378	26.41
20.000	32.47
22.909	39.38
25.000	44.33
32.000	59.85
36.000	67.53
39.811	73.89
45.000	81.08
56.000	91.41
63.000	95.31
65.000	96.12
70.000	97.77
75.000	99.03
80.000	99.81
90.000	100.00
100.000	100.00
104.713	100.00
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.23 and Figure AI.23. Particle size distribution: Formulation AT 4.20.

Particle Name:
Default
Particle RI:
1.520
Dispersant Name:

Accessory Name:
Scirocco 2000
Absorption:
0.1
Dispersant RI:
1.000

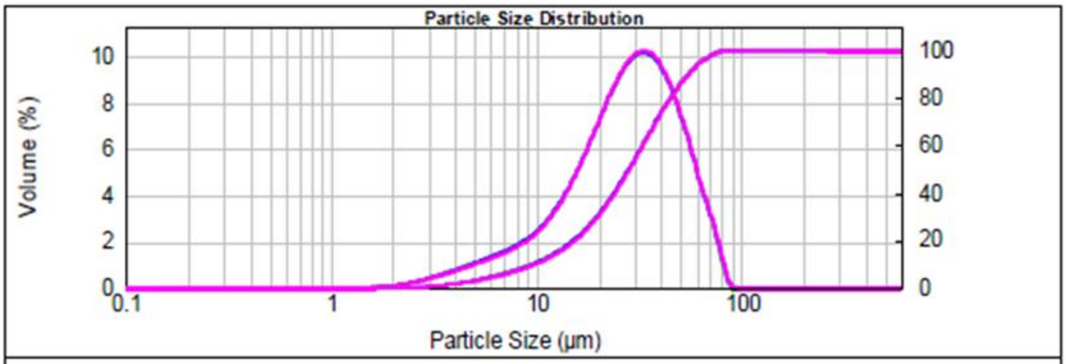
Analysis model:
General purpose (fine)
Size range:
0.020 to 2000.000 um
Weighted Residual:
0.517 %

Sensitivity:
Normal
Obscuration:
1.49 %
Result Emulation:
Off

Concentration:
0.0009 %Vol
Span :
1.595
Uniformity:
0.487
Result units:
Volume

Specific Surface Area:
0.319 m²/g
Surface Weighted Mean D[3,2]:
18.814 um
Vol. Weighted Mean D[4,3]:
30.619 um

d(0.1): **9.744** **um** **d(0.5):** **28.254** **um** **d(0.9):** **54.810** **um**

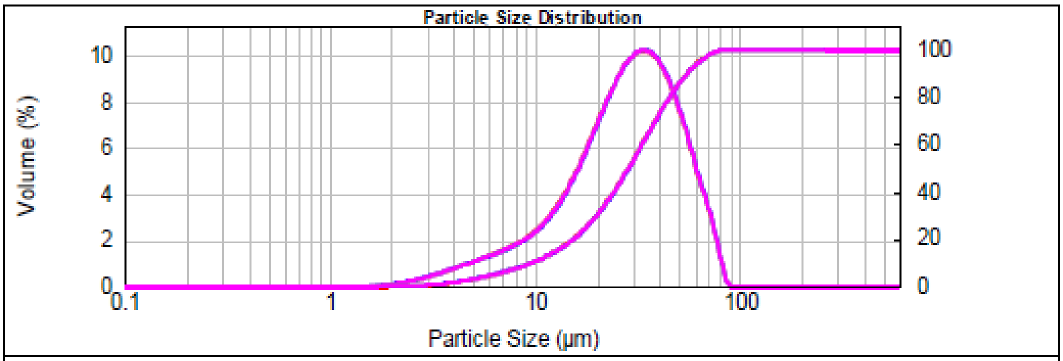


Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.08	20.000	30.40	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.21	22.909	37.35	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.40	25.000	42.37	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.69	32.000	58.23	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	1.10	36.000	66.13	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	1.64	39.811	72.70	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	1.87	45.000	80.14	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	3.19	56.000	90.88	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	4.21	63.000	94.97	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	4.55	65.000	95.83	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	6.80	70.000	97.57	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	7.40	75.000	98.87	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	10.40	80.000	99.70	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	13.68	90.000	100.00	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	15.80	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	19.61	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.01	17.378	24.39	120.226	100.00	954.993	100.00		

Table AI.24 and Figure AI.24. Particle size distribution: Formulation AT4.21.

Particle Name:	**Accessory Name:**	**Analysis model:**	**Sensitivity:**
Default	Scirocco 2000	General purpose (fine)	Normal
Particle RI:	**Absorption:**	**Size range:**	**Obscuration:**
1.520	0.1	0.020 to 2000.000 um	1.88 %
Dispersant Name:	**Dispersant RI:**	**Weighted Residual:**	**Result Emulation:**
	1.000	0.446 %	Off
Concentration:	**Span :**	**Uniformity:**	**Result units:**
0.0011 %Vol	1.601	0.487	Volume
Specific Surface Area:	**Surface Weighted Mean D[3,2]:**	**Vol. Weighted Mean D[4,3]:**	
0.32 m²/g	18.769 um	30.774 um	

d(0.1): 9.543 um **d(0.5):** 28.505 um **d(0.9):** 55.168 um

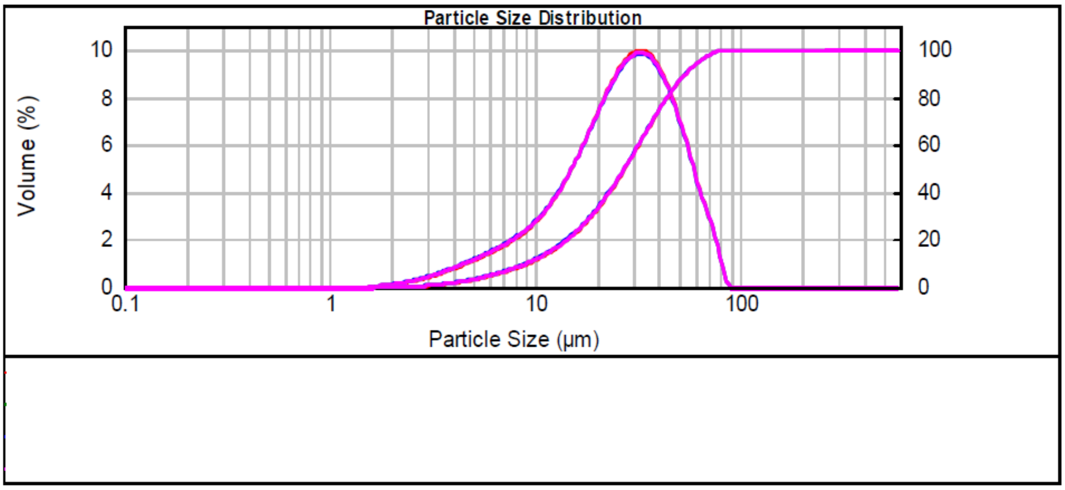


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.05	20.000	30.20	125.000	100.00	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.17	22.909	36.98	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.37	25.000	41.91	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.67	32.000	57.60	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	1.10	36.000	65.50	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	1.67	39.811	72.10	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	1.92	45.000	79.63	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	3.31	56.000	90.63	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	4.38	63.000	94.88	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	4.74	65.000	95.78	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	7.07	70.000	97.61	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	7.68	75.000	98.97	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	10.70	80.000	99.80	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	13.95	90.000	100.00	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	16.02	100.000	100.00	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	19.72	104.713	100.00	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	24.35	120.226	100.00	954.993	100.00		

Table AI.25 and Figure AI.25. Particle size distribution: Formulation AT 4.22.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.69 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.463 %	**Result Emulation:** Off
Concentration: 0.0015 %Vol	**Span :** 1.652	**Uniformity:** 0.503	**Result units:** Volume
Specific Surface Area: 0.335 m²/g	**Surface Weighted Mean D[3,2]:** 17.892 um	**Vol. Weighted Mean D[4,3]:** 29.551 um	

d(0.1): 8.954 um **d(0.5): 27.072 um** **d(0.9): 53.684 um**



Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.01
1.905	0.08
2.188	0.21
2.512	0.41
2.884	0.72
3.311	1.15
3.802	1.75
4.000	2.01
5.012	3.47
5.754	4.63
6.000	5.03
7.586	7.65
8.000	8.35
10.000	11.85
12.000	15.60
13.183	17.95
15.136	22.06
17.378	27.09
20.000	33.25
22.909	40.22
25.000	45.19
32.000	60.64
36.000	68.24
39.811	74.50
45.000	81.56
56.000	91.66
63.000	95.46
65.000	96.25
70.000	97.85
75.000	99.06
80.000	99.81
90.000	100.00
100.000	100.00
104.713	100.00
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.26 and Figure AI.26. Particle size distribution: Formulation AT 4.23

Particle Name:
Default

Accessory Name:
Scirocco 2000

Analysis model:
General purpose (fine)

Sensitivity:
Normal

Particle RI:
1.520

Absorption:
0.1

Size range:
0.020 to 2000.000 um

Obscuration:
2.61 %

Dispersant Name:

Dispersant RI:
1.000

Weighted Residual:
0.470 %

Result Emulation:
Off

Concentration:
0.0015 %Vol

Span :
1.649

Uniformity:
0.502

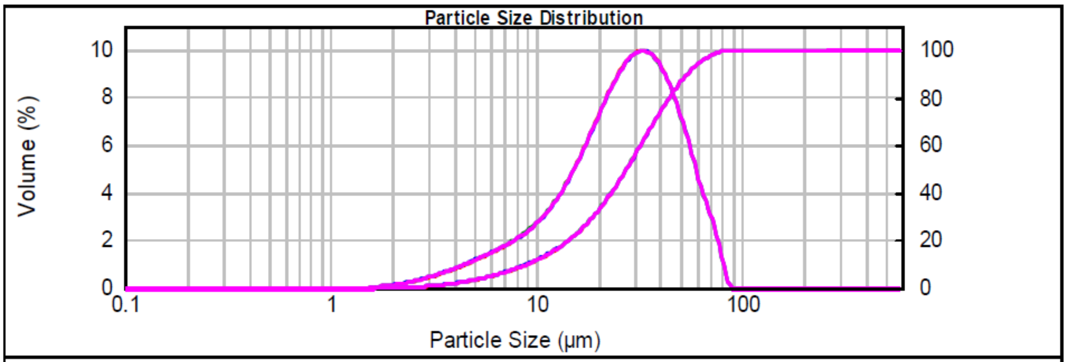
Result units:
Volume

Specific Surface Area:
0.334 m²/g

Surface Weighted Mean D[3,2]:
17.941 um

Vol. Weighted Mean D[4,3]:
29.769 um

d(0.1): 8.953 um **d(0.5): 27.332 um** **d(0.9): 54.029 um**



Size (μm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.01
1.905	0.09
2.188	0.22
2.512	0.43
2.884	0.74
3.311	1.19
3.802	1.79
4.000	2.05
5.012	3.52
5.754	4.69
6.000	5.08
7.586	7.69
8.000	8.38
10.000	11.82
12.000	15.48
13.183	17.77
15.136	21.79
17.378	26.71
20.000	32.78
22.909	39.68
25.000	44.62
32.000	60.06
36.000	67.69
39.811	74.01
45.000	81.15
56.000	91.43
63.000	95.31
65.000	96.12
70.000	97.77
75.000	99.02
80.000	99.80
90.000	100.00
100.000	100.00
104.713	100.00
120.226	100.00
125.000	100.00
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.27 and Figure AI.27. Particle size distribution: Formulation AT 4.25

Particle Name:
Default

Particle RI:
1.520

Dispersant Name:

Accessory Name:
Scirocco 2000

Absorption:
0.1

Dispersant RI:
1.000

Analysis model:
General purpose (fine)

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.311 %

Sensitivity:
Normal

Obscuration:
0.87 %

Result Emulation:
Off

Concentration:
0.0010 %Vol

Specific Surface Area:
0.17 m²/g

Span :
1.429

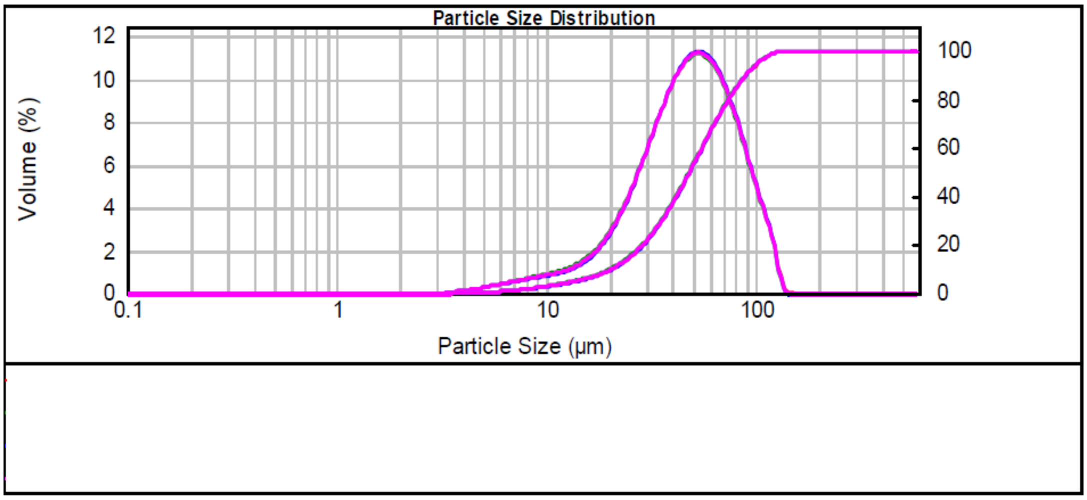
Surface Weighted Mean D[3,2]:
35.215 um

Uniformity:
0.437

Vol. Weighted Mean D[4,3]:
51.668 um

Result units:
Volume

d(0.1): 20.367 um **d(0.5): 47.999 um** **d(0.9): 88.956 um**

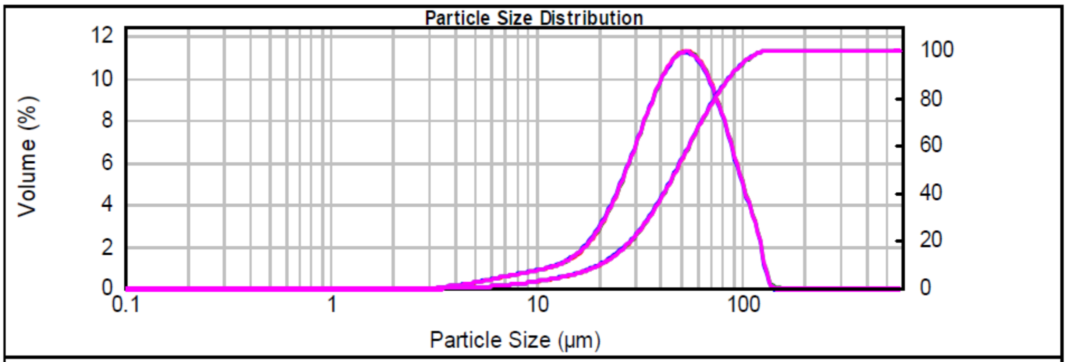


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	9.66	125.000	99.63	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	12.59	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	15.02	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	24.74	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	31.00	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.05	39.811	37.13	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.08	45.000	45.39	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.37	56.000	61.32	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.66	63.000	69.80	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.78	65.000	71.96	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.59	70.000	76.89	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	1.81	75.000	81.15	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	2.92	80.000	84.79	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	4.04	90.000	90.51	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	4.72	100.000	94.49	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	5.91	104.713	95.89	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	7.48	120.226	99.07	954.993	100.00		

Table AI.28 and Figure AI.28. Particle size distribution: Formulation AT 4.26.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.13 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.318 %	**Result Emulation:** Off
Concentration: 0.0013 %Vol	**Span :** 1.428	**Uniformity:** 0.437	**Result units:** Volume
Specific Surface Area: 0.17 m²/g	**Surface Weighted Mean D[3,2]:** 35.281 um	**Vol. Weighted Mean D[4,3]:** 51.680 um	

d(0.1): 20.411 um **d(0.5): 47.996 um** **d(0.9): 88.958 um**



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	9.62	125.000	99.62	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	12.55	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	14.99	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	24.72	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	30.99	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.05	39.811	37.12	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.08	45.000	45.39	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.36	56.000	61.32	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.65	63.000	69.81	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.76	65.000	71.97	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.56	70.000	76.90	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	1.78	75.000	81.15	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	2.88	80.000	84.80	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	3.99	90.000	90.51	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	4.67	100.000	94.48	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	5.86	104.713	95.89	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	7.43	120.226	99.06	954.993	100.00		

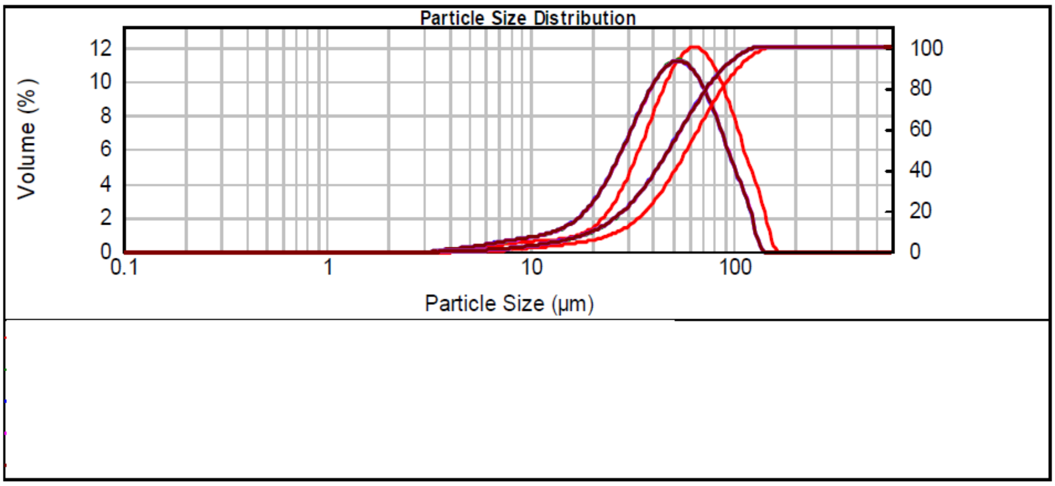
Table AI.29 and Figure AI.29. Particle size distribution: Formulation AT 4.27.

Particle Name: Default
Accessory Name: Scirocco 2000
Analysis model: General purpose (fine)
Sensitivity: Normal
Particle RI: 1.520
Absorption: 0.1
Size range: 0.020 to 2000.000 um
Obscuration: 1.32 %
Dispersant Name:
Dispersant RI: 1.000
Weighted Residual: 0.320 %
Result Emulation: Off

Concentration: 0.0015 %Vol
Span : 1.431
Uniformity: 0.438
Result units: Volume

Specific Surface Area: 0.171 m²/g
Surface Weighted Mean D[3,2]: 35.058 um
Vol. Weighted Mean D[4,3]: 51.517 um

d(0.1): 20.248 um **d(0.5): 47.865 um** **d(0.9): 88.740 um**

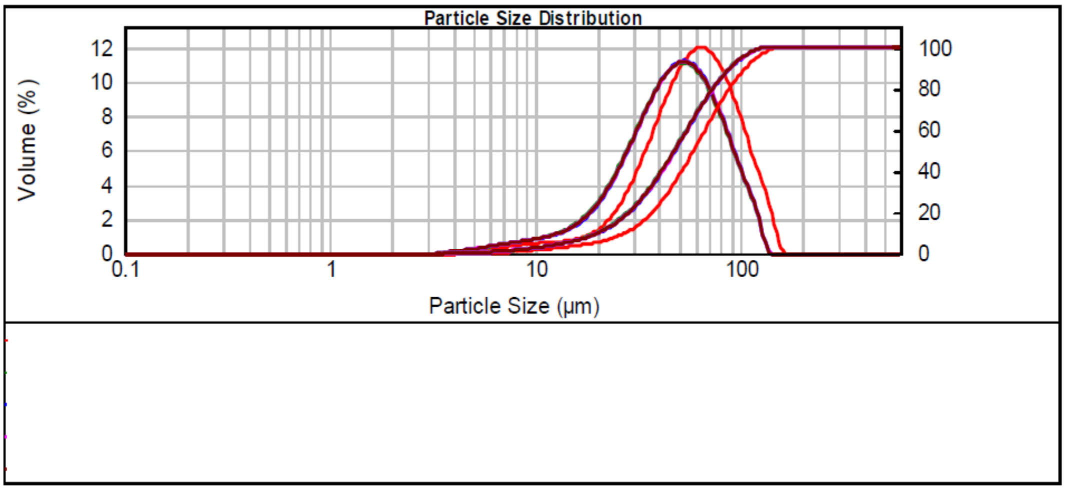


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	9.77	125.000	99.69	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	12.72	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	15.17	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	24.93	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	31.20	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.05	39.811	37.33	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.09	45.000	45.60	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.39	56.000	61.50	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.69	63.000	69.97	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.80	65.000	72.13	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.61	70.000	77.05	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	1.84	75.000	81.29	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	2.95	80.000	84.92	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	4.07	90.000	90.62	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	4.76	100.000	94.56	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	5.97	104.713	95.95	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	7.56	120.226	99.14	954.993	100.00		

Table AI.30 and Figure AI.30. Particle size distribution: Formulation AT 4.28.

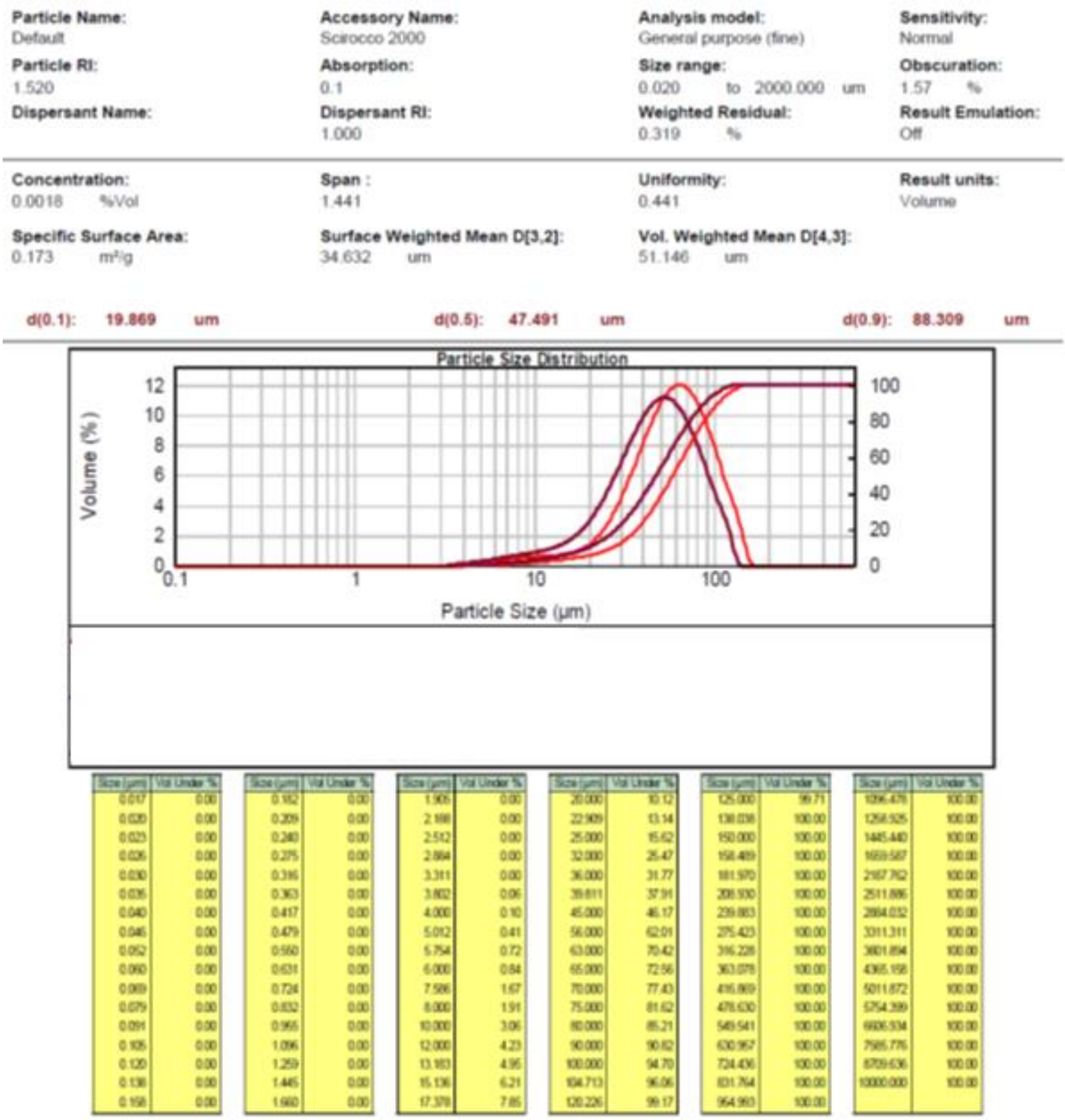
Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.43 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.313 %	**Result Emulation:** Off
Concentration: 0.0016 %Vol	**Span :** 1.439	**Uniformity:** 0.44	**Result units:** Volume
Specific Surface Area: 0.173 m²/g	**Surface Weighted Mean D[3,2]:** 34.759 um	**Vol. Weighted Mean D[4,3]:** 51.146 um	

d(0.1): 19.994 um **d(0.5): 47.459 um** **d(0.9): 88.269 um**



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	10.01	125.000	99.71	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	13.03	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	15.53	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	25.44	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	31.76	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.05	39.811	37.93	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.09	45.000	46.21	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.39	56.000	62.07	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.70	63.000	70.47	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.81	65.000	72.61	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.63	70.000	77.47	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	1.86	75.000	81.66	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	2.99	80.000	85.24	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	4.14	90.000	90.84	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	4.84	100.000	94.70	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	6.09	104.713	96.07	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	7.73	120.226	99.17	954.993	100.00		

Table AI.31 and Figure AI.31. Particle size distribution: Formulation AT 4.29.



Particle Name: Default
Accessory Name: Scirocco 2000
Analysis model: General purpose (fine)
Sensitivity: Normal
Particle RI: 1.520
Absorption: 0.1
Size range: 0.020 to 2000.000 um
Obscuration: 1.57 %
Dispersant Name:
Dispersant RI: 1.000
Weighted Residual: 0.319 %
Result Emulation: Off

Concentration: 0.0018 %Vol
Span : 1.441
Uniformity: 0.441
Result units: Volume
Specific Surface Area: 0.173 m²/g
Surface Weighted Mean D[3,2]: 34.632 um
Vol. Weighted Mean D[4,3]: 51.146 um

d(0.1): 19.869 um
d(0.5): 47.491 um
d(0.9): 88.309 um

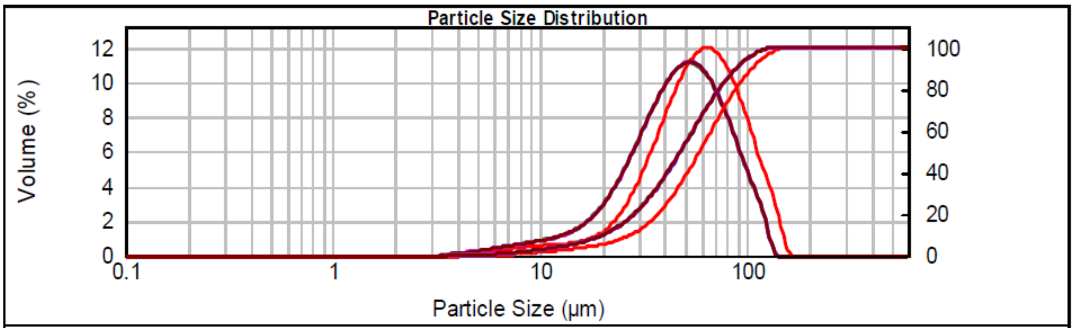
Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.00
2.512	0.00
2.884	0.00
3.311	0.00
3.802	0.06
4.000	0.10
5.012	0.41
5.754	0.72
6.000	0.84
7.586	1.67
8.000	1.91
10.000	3.06
12.000	4.23
13.183	4.95
15.136	6.21
17.378	7.85
20.000	10.12
22.909	13.14
25.000	15.62
32.000	25.47
36.000	31.77
39.811	37.91
45.000	46.17
56.000	62.01
63.000	70.42
65.000	72.56
70.000	77.43
75.000	81.62
80.000	85.21
90.000	90.82
100.000	94.70
104.713	96.06
120.226	99.17
125.000	99.71
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.32 and Figure AI.32. Particle size distribution: Formulation AT 4.30.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.71 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.319 %	**Result Emulation:** Off

Concentration: 0.0019 %Vol	**Span :** 1.441	**Uniformity:** 0.441	**Result units:** Volume
Specific Surface Area: 0.173 m²/g	**Surface Weighted Mean D[3,2]:** 34.644 um	**Vol. Weighted Mean D[4,3]:** 51.097 um	

d(0.1): 19.890 um **d(0.5): 47.423 um** **d(0.9): 88.229 um**

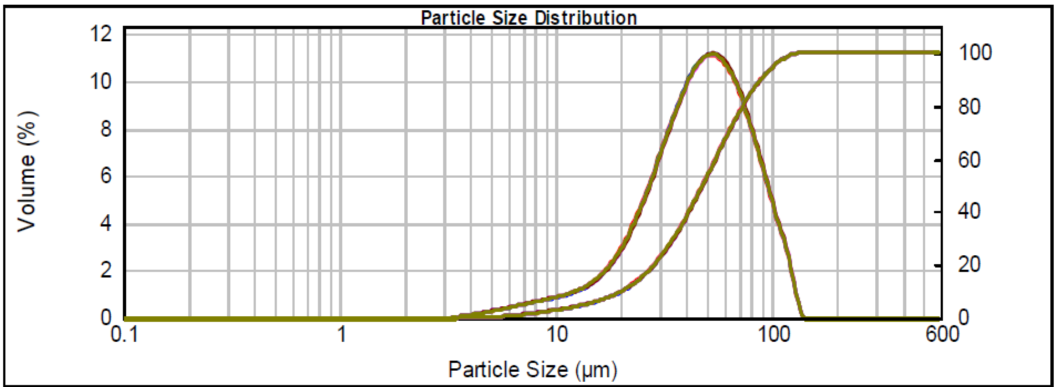


Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	0.00
1.259	0.00
1.445	0.00
1.660	0.00
1.905	0.00
2.188	0.00
2.512	0.00
2.884	0.00
3.311	0.00
3.802	0.06
4.000	0.10
5.012	0.41
5.754	0.72
6.000	0.83
7.586	1.66
8.000	1.89
10.000	3.03
12.000	4.20
13.183	4.91
15.136	6.17
17.378	7.82
20.000	10.10
22.909	13.13
25.000	15.63
32.000	25.52
36.000	31.84
39.811	38.00
45.000	46.27
56.000	62.12
63.000	70.51
65.000	72.65
70.000	77.51
75.000	81.69
80.000	85.27
90.000	90.86
100.000	94.72
104.713	96.08
120.226	99.17
125.000	99.71
138.038	100.00
150.000	100.00
158.489	100.00
181.970	100.00
208.930	100.00
239.883	100.00
275.423	100.00
316.228	100.00
363.078	100.00
416.869	100.00
478.630	100.00
549.541	100.00
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.33 and Figure AI.33. Particle size distribution: Formulation AT 4.31.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 1.64 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.314 %	**Result Emulation:** Off
Concentration: 0.0018 %Vol	**Span :** 1.444	**Uniformity:** 0.442	**Result units:** Volume
Specific Surface Area: 0.174 m²/g	**Surface Weighted Mean D[3,2]:** 34.577 um	**Vol. Weighted Mean D[4,3]:** 50.967 um	

d(0.1): 19.805 um **d(0.5): 47.272 um** **d(0.9): 88.077 um**

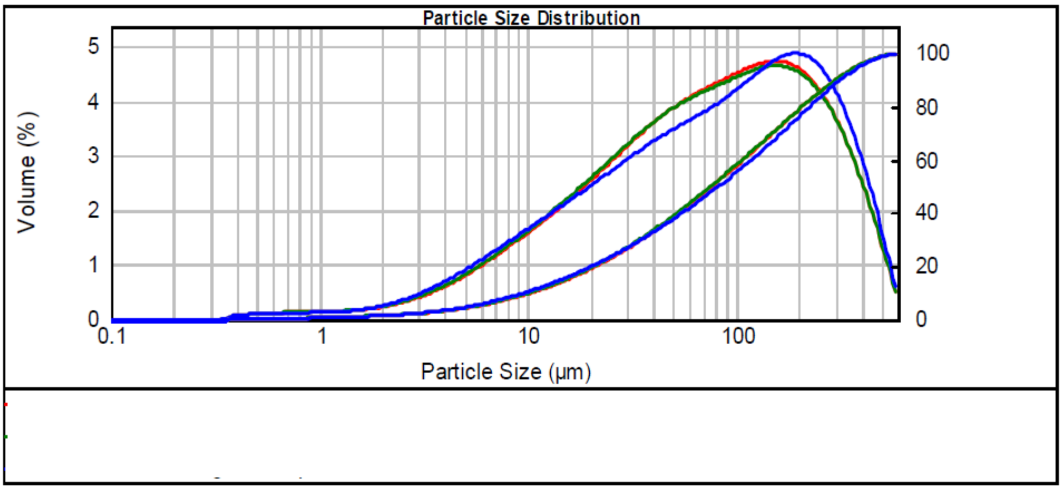


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	0.00	20.000	10.19	125.000	99.71	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	0.00	22.909	13.25	138.038	100.00	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	0.00	25.000	15.78	150.000	100.00	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	0.00	32.000	25.73	158.489	100.00	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	0.00	36.000	32.06	181.970	100.00	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	0.05	39.811	38.23	208.930	100.00	2511.886	100.00
0.040	0.00	0.417	0.00	4.000	0.09	45.000	46.50	239.883	100.00	2884.032	100.00
0.046	0.00	0.479	0.00	5.012	0.40	56.000	62.32	275.423	100.00	3311.311	100.00
0.052	0.00	0.550	0.00	5.754	0.70	63.000	70.69	316.228	100.00	3801.894	100.00
0.060	0.00	0.631	0.00	6.000	0.82	65.000	72.81	363.078	100.00	4365.158	100.00
0.069	0.00	0.724	0.00	7.586	1.64	70.000	77.65	416.869	100.00	5011.872	100.00
0.079	0.00	0.832	0.00	8.000	1.87	75.000	81.81	478.630	100.00	5754.399	100.00
0.091	0.00	0.955	0.00	10.000	3.02	80.000	85.37	549.541	100.00	6606.934	100.00
0.105	0.00	1.096	0.00	12.000	4.20	90.000	90.92	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.00	13.183	4.92	100.000	94.76	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	0.00	15.136	6.20	104.713	96.11	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	0.00	17.378	7.87	120.226	99.18	954.993	100.00		

Table AI.34 and Figure AI.34. Particle size distribution: Formulation AT 4.33.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.74 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.114 %	**Result Emulation:** Off
Concentration: 0.0015 %Vol	**Span :** 3.737	**Uniformity:** 1.16	**Result units:** Volume
Specific Surface Area: 0.317 m²/g	**Surface Weighted Mean D[3,2]:** 18.921 um	**Vol. Weighted Mean D[4,3]:** 126.805 um	

d(0.1): **9.459** **um** **d(0.5):** **82.264** **um** **d(0.9):** **316.902** **um**



Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	1.47	20.000	19.92	125.000	61.58	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	1.71	22.909	22.17	138.038	64.55	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	2.00	25.000	23.69	150.000	67.10	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	2.37	32.000	28.33	158.489	68.81	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	2.81	36.000	30.71	181.970	73.18	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	3.36	39.811	32.82	208.930	77.59	2511.886	100.00
0.040	0.00	0.417	0.08	4.000	3.59	45.000	35.49	239.883	81.94	2884.032	100.00
0.046	0.00	0.479	0.16	5.012	4.78	56.000	40.50	275.423	86.10	3311.311	100.00
0.052	0.00	0.550	0.26	5.754	5.67	63.000	43.31	316.228	89.94	3801.894	100.00
0.060	0.00	0.631	0.37	6.000	5.97	65.000	44.07	363.078	93.33	4365.158	100.00
0.069	0.00	0.724	0.48	7.586	7.86	70.000	45.90	416.869	96.13	5011.872	100.00
0.079	0.00	0.832	0.60	8.000	8.34	75.000	47.63	478.630	98.26	5754.399	100.00
0.091	0.00	0.955	0.72	10.000	10.60	80.000	49.28	549.541	99.55	6606.934	100.00
0.105	0.00	1.096	0.84	12.000	12.71	90.000	52.36	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	0.97	13.183	13.89	100.000	55.22	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	1.11	15.136	15.74	104.713	56.49	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	1.27	17.378	17.74	120.226	60.43	954.993	100.00		

Table AI.35 and Figure AI.35. Particle size distribution: Formulation AT 4.34.

Particle Name:
Default

Particle RI:
1.520

Dispersant Name:

Accessory Name:
Scirocco 2000

Absorption:
0.1

Dispersant RI:
1.000

Analysis model:
General purpose (fine)

Size range:
0.020 to 2000.000 um

Weighted Residual:
0.100 %

Sensitivity:
Normal

Obscuration:
3.54 %

Result Emulation:
Off

Concentration:
0.0019 %Vol

Specific Surface Area:
0.322 m²/g

Span :
3.770

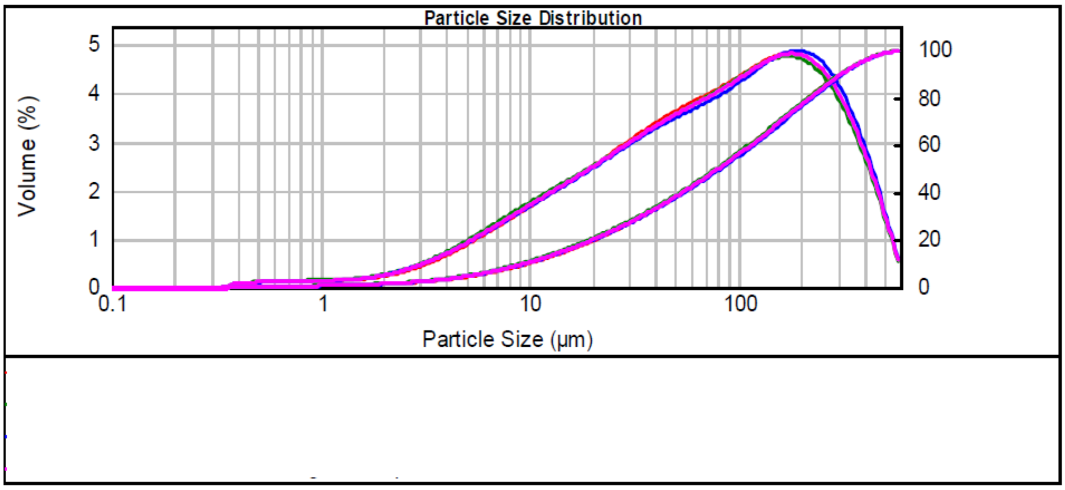
Surface Weighted Mean D[3,2]:
18.618 um

Uniformity:
1.16

Vol. Weighted Mean D[4,3]:
124.099 um

Result units:
Volume

d(0.1): 9.376 um **d(0.5):** 79.981 um **d(0.9):** 310.864 um



Size (μm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.08
0.479	0.17
0.550	0.27
0.631	0.38
0.724	0.50
0.832	0.62
0.955	0.75
1.096	0.87
1.259	1.01
1.445	1.15
1.660	1.32
1.905	1.51
2.188	1.75
2.512	2.04
2.884	2.40
3.311	2.84
3.802	3.39
4.000	3.61
5.012	4.81
5.754	5.71
6.000	6.01
7.586	7.92
8.000	8.41
10.000	10.70
12.000	12.84
13.183	14.04
15.136	15.92
17.378	17.94
20.000	20.15
22.909	22.42
25.000	23.96
32.000	28.65
36.000	31.07
39.811	33.21
45.000	35.93
56.000	41.03
63.000	43.90
65.000	44.68
70.000	46.55
75.000	48.32
80.000	50.01
90.000	53.16
100.000	56.07
104.713	57.37
120.226	61.37
125.000	62.52
138.038	65.52
150.000	68.07
158.489	69.79
181.970	74.13
208.930	78.47
239.883	82.72
275.423	86.74
316.228	90.44
363.078	93.67
416.869	96.33
478.630	98.35
549.541	99.57
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.36 and Figure AI.36. Particle size distribution: Formulation AT 4.35.

Particle Name:
Default

Accessory Name:
Scirocco 2000

Analysis model:
General purpose (fine)

Sensitivity:
Normal

Particle RI:
1.520

Absorption:
0.1

Size range:
0.020 to 2000.000 um

Obscuration:
3.45 %

Dispersant Name:

Dispersant RI:
1.000

Weighted Residual:
0.077 %

Result Emulation:
Off

Concentration:
0.0017 %Vol

Span :
4.235

Uniformity:
1.28

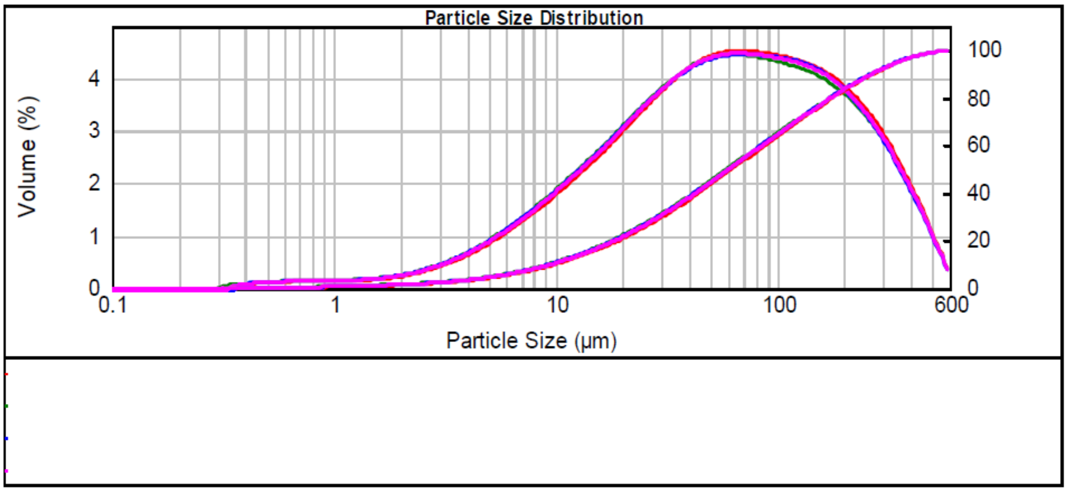
Result units:
Volume

Specific Surface Area:
0.348 m²/g

Surface Weighted Mean D[3,2]:
17.230 um

Vol. Weighted Mean D[4,3]:
102.578 um

d(0.1): 9.299 um **d(0.5): 60.137 um** **d(0.9): 263.980 um**



Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.03
0.417	0.11
0.479	0.20
0.550	0.31
0.631	0.44
0.724	0.56
0.832	0.70
0.955	0.84
1.096	0.98
1.259	1.12
1.445	1.28
1.660	1.45
1.905	1.64
2.188	1.87
2.512	2.16
2.884	2.50
3.311	2.92
3.802	3.43
4.000	3.64
5.012	4.79
5.754	5.68
6.000	5.97
7.586	7.91
8.000	8.42
10.000	10.85
12.000	13.21
13.183	14.56
15.136	16.74
17.378	19.13
20.000	21.80
22.909	24.61
25.000	26.54
32.000	32.47
36.000	35.53
39.811	38.25
45.000	41.65
56.000	47.93
63.000	51.36
65.000	52.27
70.000	54.44
75.000	56.45
80.000	58.33
90.000	61.74
100.000	64.77
104.713	66.09
120.226	70.00
125.000	71.09
138.038	73.85
150.000	76.12
158.489	77.61
181.970	81.24
208.930	84.69
239.883	87.92
275.423	90.87
316.228	93.50
363.078	95.74
416.869	97.55
478.630	98.90
549.541	99.71
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.37 and Figure AI.37. Particle size distribution: Formulation AT 4.36.

Particle Name:
Default

Accessory Name:
Scirocco 2000

Analysis model:
General purpose (fine)

Sensitivity:
Normal

Particle RI:
1.520

Absorption:
0.1

Size range:
0.020 to 2000.000 um

Obscuration:
3.19 %

Dispersant Name:

Dispersant RI:
1.000

Weighted Residual:
0.151 %

Result Emulation:
Off

Concentration:
0.0015 %Vol

Span :
4.026

Uniformity:
1.23

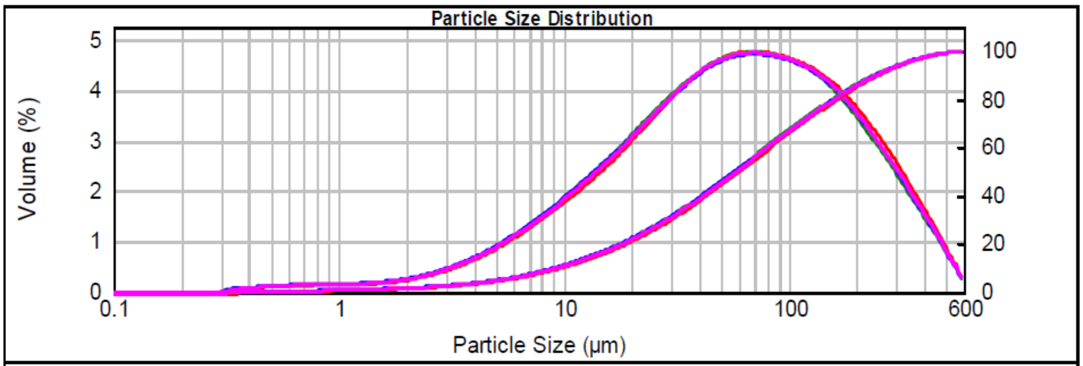
Result units:
Volume

Specific Surface Area:
0.36 m²/g

Surface Weighted Mean D[3,2]:
16.672 um

Vol. Weighted Mean D[4,3]:
96.265 um

d(0.1): 9.153 um **d(0.5): 57.932 um** **d(0.9): 242.385 um**

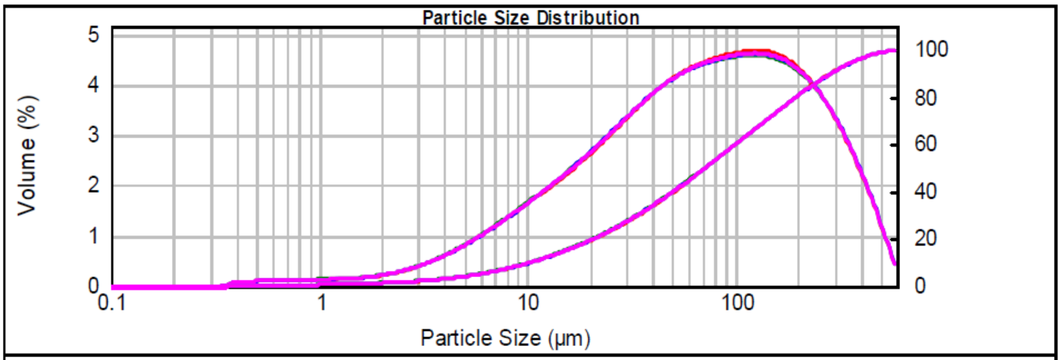


Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	1.73	20.000	22.02	125.000	73.42	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	1.97	22.909	24.85	138.038	76.24	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	2.27	25.000	26.81	150.000	78.54	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	2.62	32.000	32.86	158.489	80.02	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	3.05	36.000	36.01	181.970	83.57	2187.762	100.00
0.035	0.00	0.363	0.05	3.802	3.58	39.811	38.82	208.930	86.84	2511.886	100.00
0.040	0.00	0.417	0.13	4.000	3.79	45.000	42.37	239.883	89.79	2884.032	100.00
0.046	0.00	0.479	0.23	5.012	4.96	56.000	48.96	275.423	92.40	3311.311	100.00
0.052	0.00	0.550	0.34	5.754	5.84	63.000	52.59	316.228	94.66	3801.894	100.00
0.060	0.00	0.631	0.47	6.000	6.14	65.000	53.56	363.078	96.53	4365.158	100.00
0.069	0.00	0.724	0.60	7.586	8.08	70.000	55.85	416.869	98.02	5011.872	100.00
0.079	0.00	0.832	0.74	8.000	8.59	75.000	57.99	478.630	99.12	5754.399	100.00
0.091	0.00	0.955	0.88	10.000	11.02	80.000	59.99	549.541	99.77	6606.934	100.00
0.105	0.00	1.096	1.03	12.000	13.39	90.000	63.61	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	1.18	13.183	14.74	100.000	66.81	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	1.34	15.136	16.92	104.713	68.20	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	1.52	17.378	19.33	120.226	72.29	954.993	100.00		

Table AI.38 and Figure AI.38. Particle size distribution: Formulation AT 4.37.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 3.67 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.168 %	**Result Emulation:** Off
Concentration: 0.0020 %Vol	**Span :** 3.875	**Uniformity:** 1.18	**Result units:** Volume
Specific Surface Area: 0.313 m²/g	**Surface Weighted Mean D[3,2]:** 19.188 um	**Vol. Weighted Mean D[4,3]:** 113.832 um	

d(0.1): **10.162** **um** **d(0.5):** **71.297** **um** **d(0.9):** **286.455** **um**

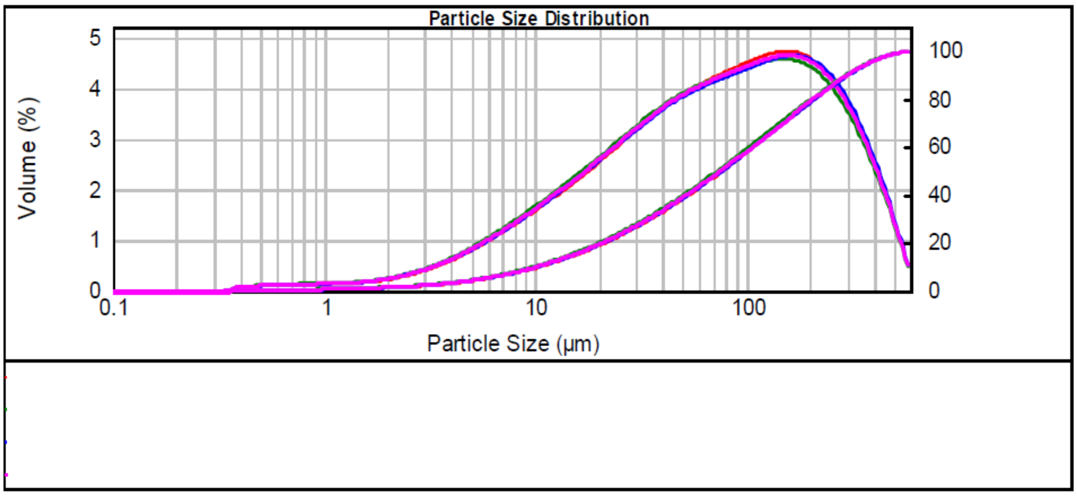


Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.08
0.479	0.16
0.550	0.26
0.631	0.37
0.724	0.48
0.832	0.60
0.955	0.72
1.096	0.84
1.259	0.97
1.445	1.11
1.660	1.26
1.905	1.44
2.188	1.65
2.512	1.90
2.884	2.22
3.311	2.60
3.802	3.07
4.000	3.26
5.012	4.32
5.754	5.13
6.000	5.40
7.586	7.17
8.000	7.63
10.000	9.82
12.000	11.94
13.183	13.14
15.136	15.06
17.378	17.16
20.000	19.50
22.909	21.95
25.000	23.64
32.000	28.88
36.000	31.63
39.811	34.09
45.000	37.22
56.000	43.13
63.000	46.44
65.000	47.33
70.000	49.47
75.000	51.47
80.000	53.37
90.000	56.86
100.000	60.01
104.713	61.40
120.226	65.57
125.000	66.75
138.038	69.75
150.000	72.26
158.489	73.91
181.970	77.98
208.930	81.91
239.883	85.64
275.423	89.08
316.228	92.18
363.078	94.85
416.869	97.03
478.630	98.67
549.541	99.65
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.39 and Figure AI.39. Particle size distribution: Formulation AT 4.38.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 3.62 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.102 %	**Result Emulation:** Off
Concentration: 0.0020 %Vol	**Span :** 3.848	**Uniformity:** 1.18	**Result units:** Volume
Specific Surface Area: 0.318 m²/g	**Surface Weighted Mean D[3,2]:** 18.870 um	**Vol. Weighted Mean D[4,3]:** 118.831 um	

d(0.1): **9.964** **um** **d(0.5):** **75.076** **um** **d(0.9):** **298.891** **um**

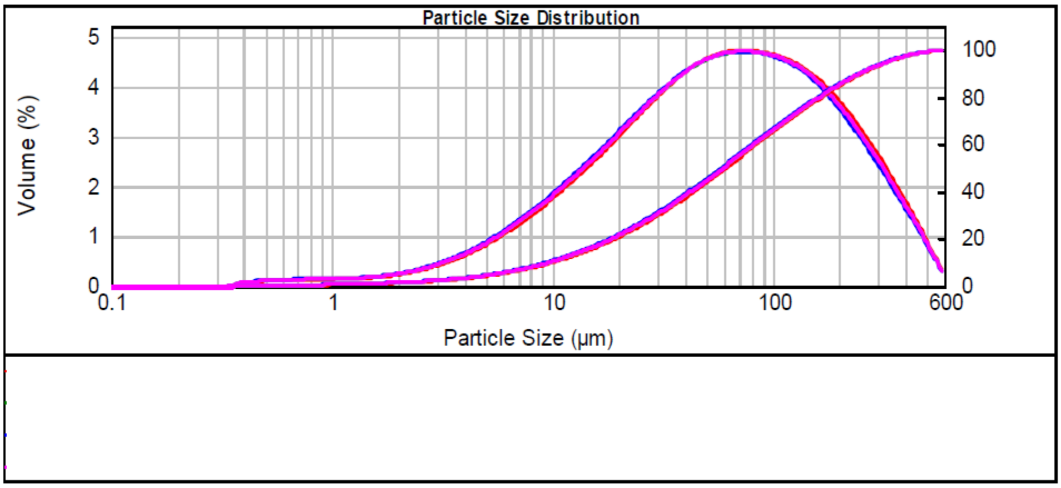


Size (µm)	Vol Under %
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.08
0.479	0.16
0.550	0.27
0.631	0.38
0.724	0.50
0.832	0.62
0.955	0.75
1.096	0.88
1.259	1.02
1.445	1.17
1.660	1.34
1.905	1.53
2.188	1.76
2.512	2.03
2.884	2.37
3.311	2.77
3.802	3.26
4.000	3.47
5.012	4.55
5.754	5.37
6.000	5.64
7.586	7.41
8.000	7.86
10.000	10.04
12.000	12.13
13.183	13.31
15.136	15.20
17.378	17.27
20.000	19.56
22.909	21.95
25.000	23.59
32.000	28.63
36.000	31.25
39.811	33.59
45.000	36.55
56.000	42.10
63.000	45.22
65.000	46.06
70.000	48.07
75.000	49.97
80.000	51.77
90.000	55.10
100.000	58.14
104.713	59.48
120.226	63.57
125.000	64.73
138.038	67.73
150.000	70.26
158.489	71.94
181.970	76.13
208.930	80.26
239.883	84.23
275.423	87.95
316.228	91.33
363.078	94.28
416.869	96.69
478.630	98.51
549.541	99.61
630.957	100.00
724.436	100.00
831.764	100.00
954.993	100.00
1096.478	100.00
1258.925	100.00
1445.440	100.00
1659.587	100.00
2187.762	100.00
2511.886	100.00
2884.032	100.00
3311.311	100.00
3801.894	100.00
4365.158	100.00
5011.872	100.00
5754.399	100.00
6606.934	100.00
7585.776	100.00
8709.636	100.00
10000.000	100.00

Table AI.40 and Figure AI.40. Particle size distribution: Formulation AT 4.39.

Particle Name: Default	**Accessory Name:** Scirocco 2000	**Analysis model:** General purpose (fine)	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 2.89 %
Dispersant Name:	**Dispersant RI:** 1.000	**Weighted Residual:** 0.121 %	**Result Emulation:** Off
Concentration: 0.0014 %Vol	**Span :** 4.013	**Uniformity:** 1.22	**Result units:** Volume
Specific Surface Area: 0.341 m²/g	**Surface Weighted Mean D[3,2]:** 17.573 um	**Vol. Weighted Mean D[4,3]:** 97.940 um	

d(0.1): **9.476** **um** **d(0.5):** **59.105** **um** **d(0.9):** **246.669** **um**



Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %	Size (μm)	Vol Under %
0.017	0.00	0.182	0.00	1.905	1.59	20.000	21.61	125.000	72.79	1096.478	100.00
0.020	0.00	0.209	0.00	2.188	1.83	22.909	24.45	138.038	75.65	1258.925	100.00
0.023	0.00	0.240	0.00	2.512	2.11	25.000	26.40	150.000	77.97	1445.440	100.00
0.026	0.00	0.275	0.00	2.884	2.45	32.000	32.43	158.489	79.47	1659.587	100.00
0.030	0.00	0.316	0.00	3.311	2.87	36.000	35.55	181.970	83.07	2187.762	100.00
0.035	0.00	0.363	0.00	3.802	3.37	39.811	38.33	208.930	86.40	2511.886	100.00
0.040	0.00	0.417	0.08	4.000	3.58	45.000	41.84	239.883	89.43	2884.032	100.00
0.046	0.00	0.479	0.17	5.012	4.70	56.000	48.36	275.423	92.11	3311.311	100.00
0.052	0.00	0.550	0.28	5.754	5.55	63.000	51.95	316.228	94.44	3801.894	100.00
0.060	0.00	0.631	0.40	6.000	5.84	65.000	52.92	363.078	96.39	4365.158	100.00
0.069	0.00	0.724	0.52	7.586	7.73	70.000	55.20	416.869	97.93	5011.872	100.00
0.079	0.00	0.832	0.65	8.000	8.23	75.000	57.33	478.630	99.08	5754.399	100.00
0.091	0.00	0.955	0.79	10.000	10.62	80.000	59.32	549.541	99.76	6606.934	100.00
0.105	0.00	1.096	0.92	12.000	12.97	90.000	62.94	630.957	100.00	7585.776	100.00
0.120	0.00	1.259	1.07	13.183	14.33	100.000	66.15	724.436	100.00	8709.636	100.00
0.138	0.00	1.445	1.22	15.136	16.51	104.713	67.54	831.764	100.00	10000.000	100.00
0.158	0.00	1.660	1.40	17.378	18.92	120.226	71.65	954.993	100.00		

ANNEX II

AT 3.1

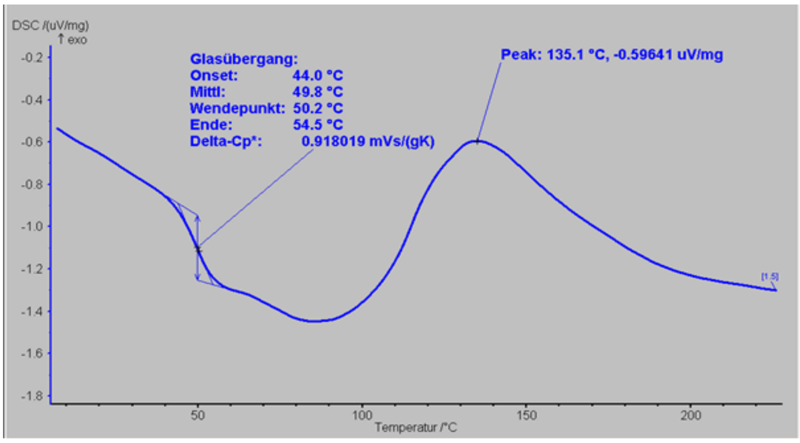


Figure AII.1.Differential Scanning Calorimetry (DSC, raw material). Formulation AT 3.1.

AT 3.2

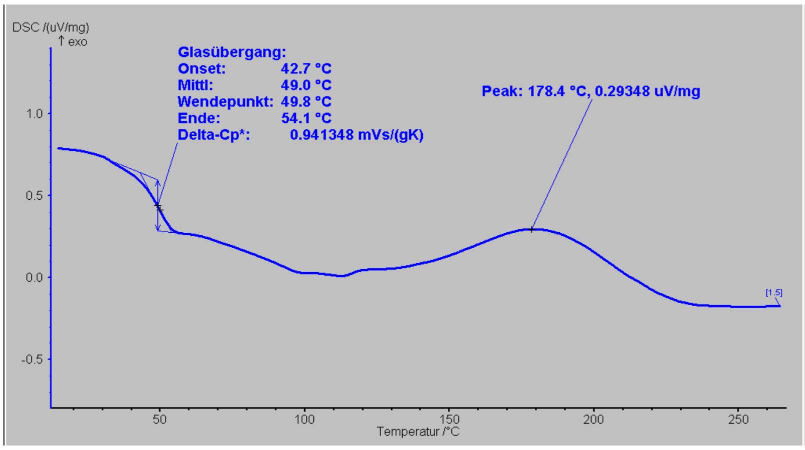


Figure AII.2. DSC (raw material). Formulation AT 3.2.

AT 3.3

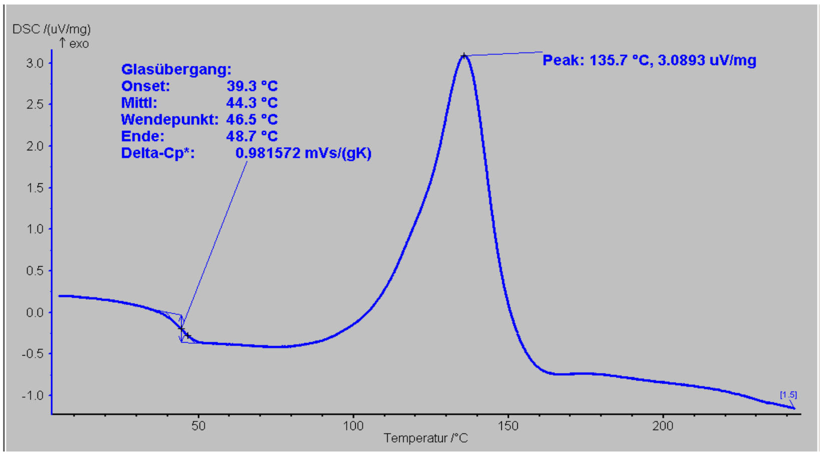


Figure AII.3. DSC (raw material). Formulation AT 3.3.

AT 3.4

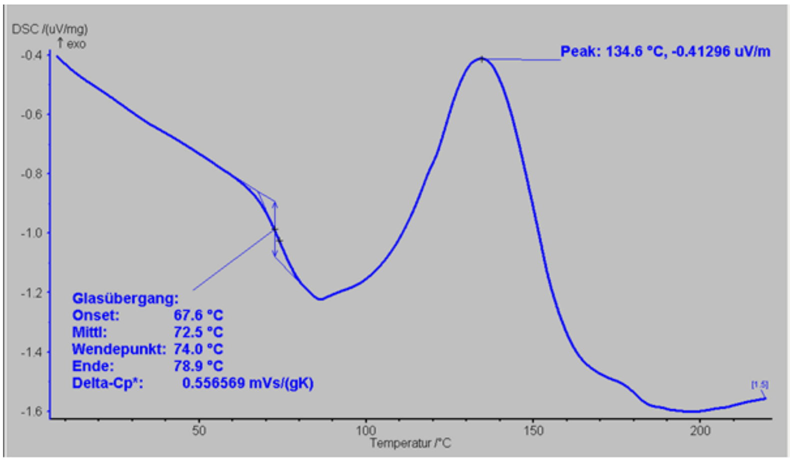


Figure AII.4. DSC (raw material). Formulation AT 3.4.

AT 3.2 120°C

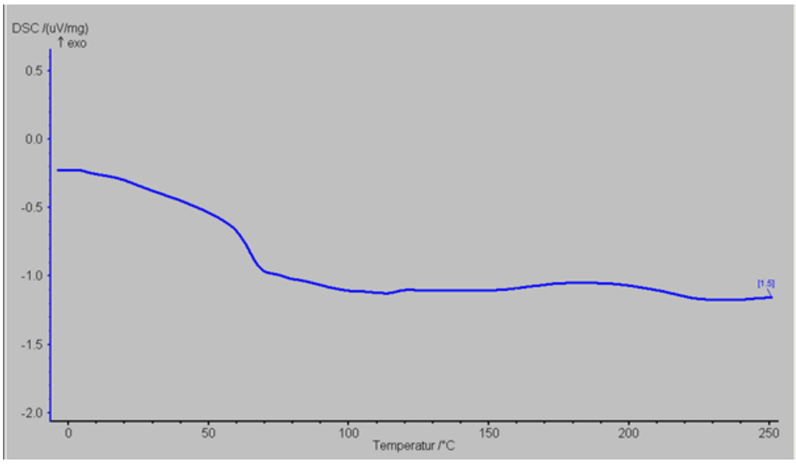


Figure AII.5. DSC (cured material at 120°C). Formulation AT 3.2.

AT 3.2 130°C

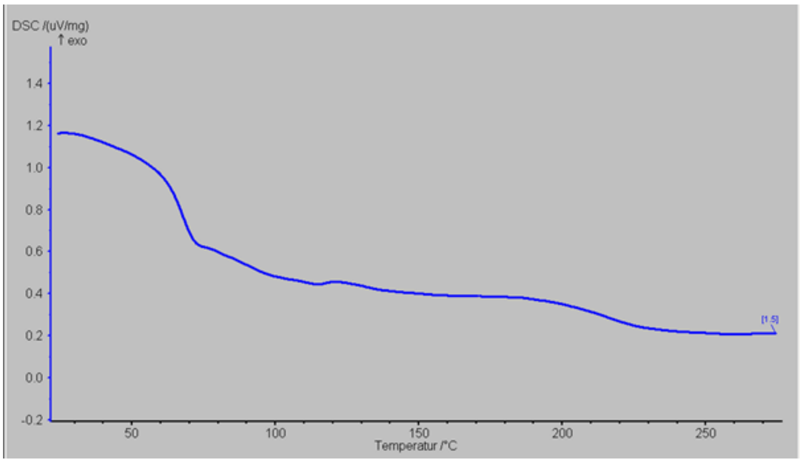


Figure AII.6. DSC (cured material at 130°C). Formulation AT 3.2.

AT 3.2 140°C

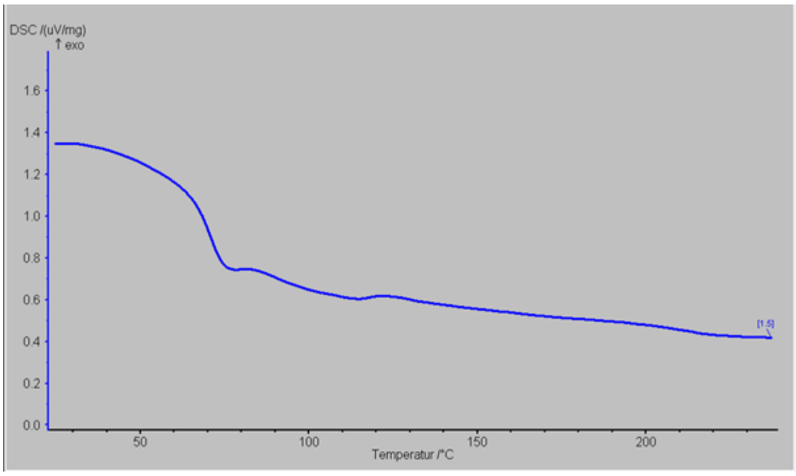


Figure AII.7. DSC (cured material at 140°C). Formulation AT 3.2.

AT 3.3 120°C

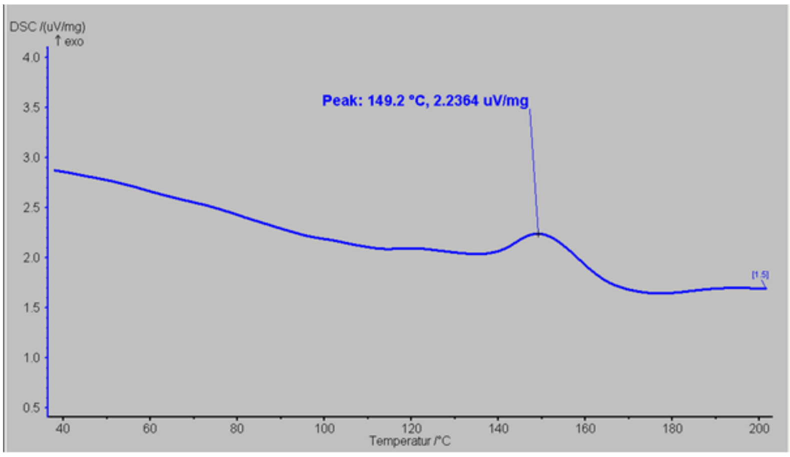


Figure AII.8. DSC (cured material at 120°C). Formulation AT 3.3.

AT 3.3 130°C

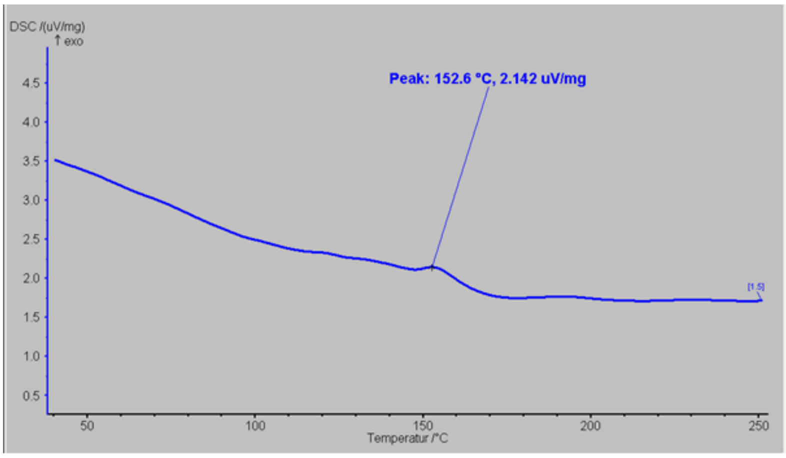


Figure AII.9. DSC (cured material at 130°C). Formulation AT 3.3.

AT 3.3. 140°C

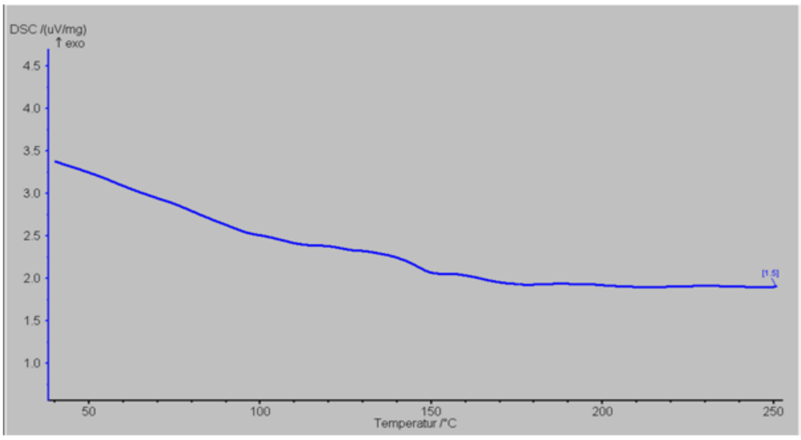


Figure AII.10. DSC (cured material at 140°C). Formulation AT 3.3.

AT 3.4 120°C

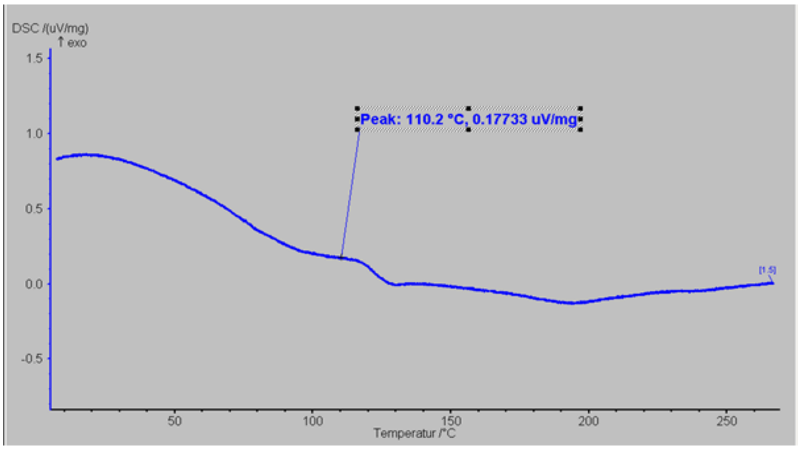


Figure AII.11. DSC (cured material at 120°C). Formulation AT 3.4.

AT 3.4 130°C

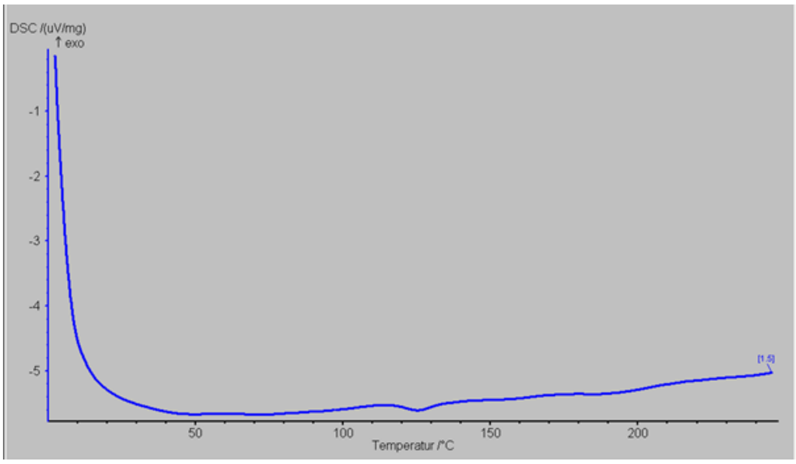


Figure AII.12. DSC (cured material at 130°C). Formulation AT 3.4.

AT 3.4 140°C

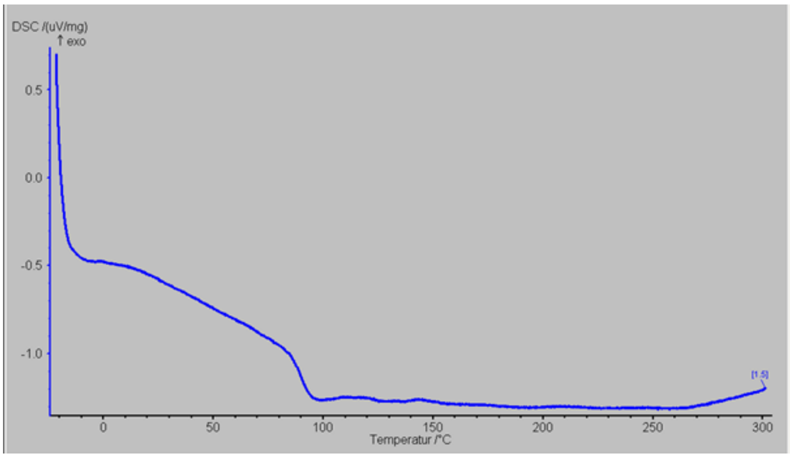


Figure AII.13. DSC (cured material at 140°C). Formulation AT 3.4.

AT 4.10

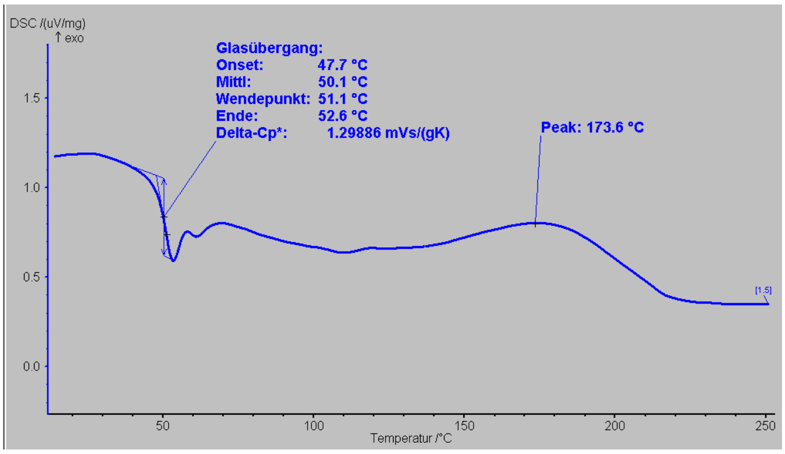


Figure AII.14. DSC (raw material). Formulation AT 4.10.

4.17

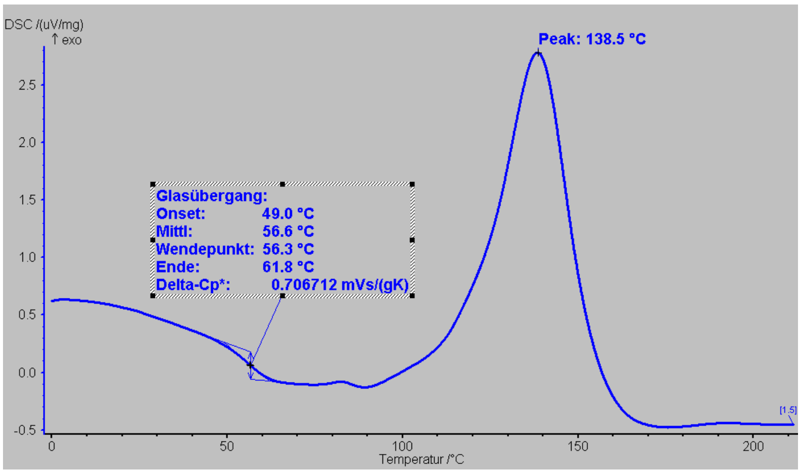


Figure AII.15. DSC (raw material). Formulation AT 4.17.

AT 4.18

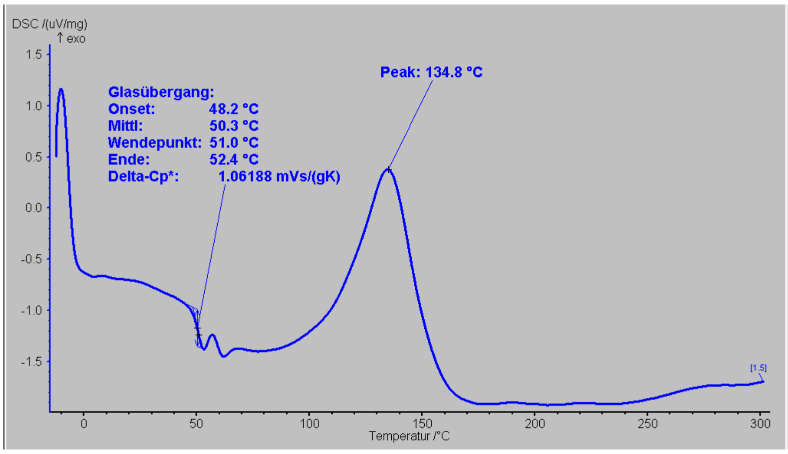


Figure AII.16. DSC (raw material). Formulation AT 4.18.

AT 4.26

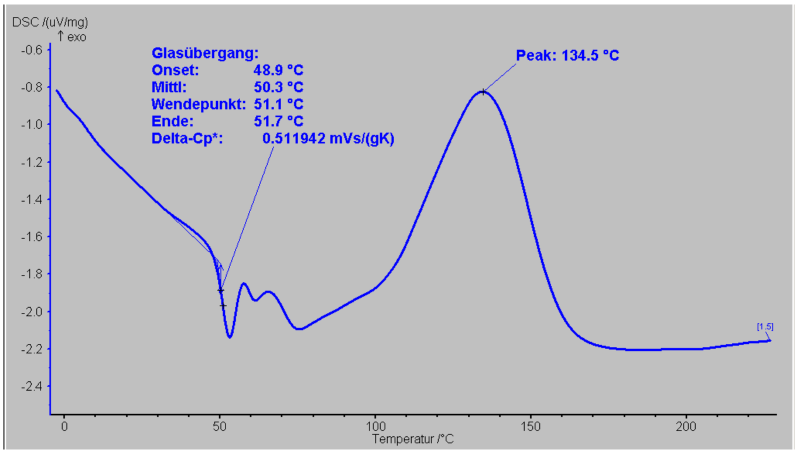


Figure AII.17. DSC (raw material). Formulation AT 4.26.

AT 4.10 130°C

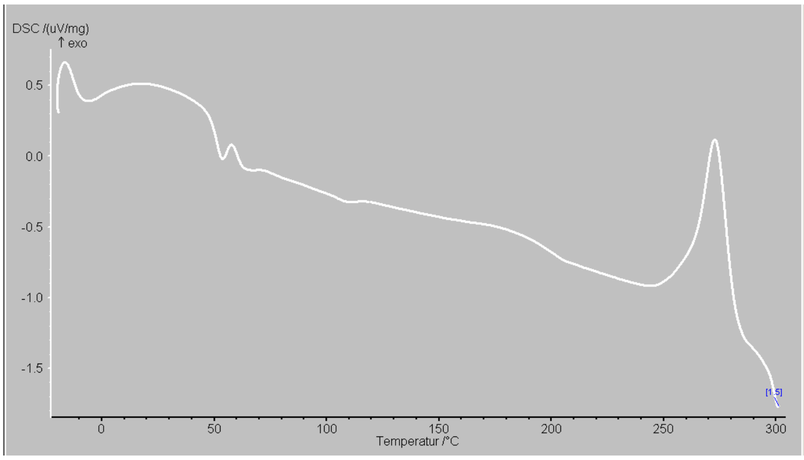


Figure AII.18. DSC (cured material at 130°C). Formulation AT 4.10.

AT 4.10 140°C

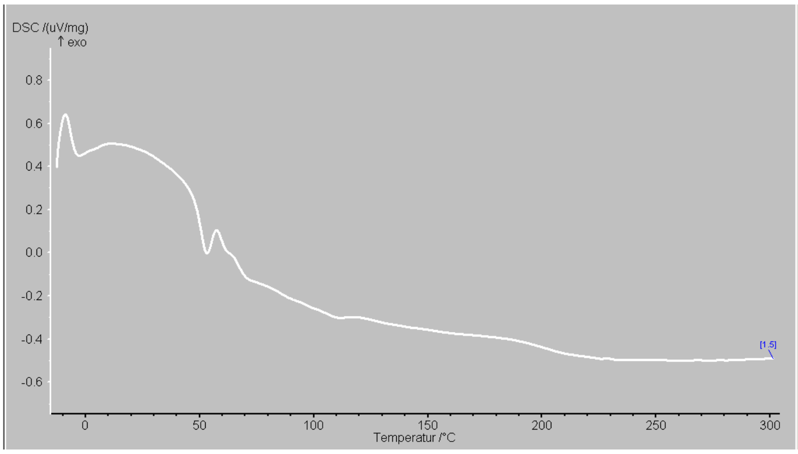


Figure AII.19. DSC (cured material at 140°C). Formulation AT 4.10.

AT 4.17 130°C

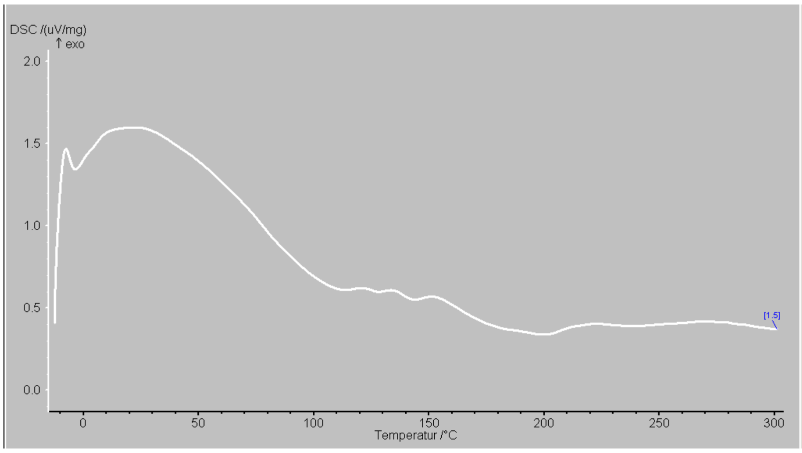


Figure AII.19. DSC (cured material at 130°C). Formulation AT 4.17.

AT 4.17 140°C

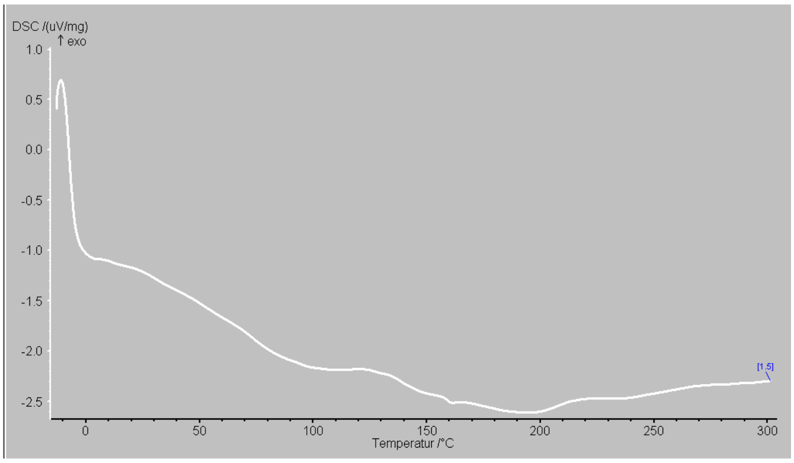


Figure AII.20. DSC (cured material at 140°C). Formulation AT 4.17.

AT 4.18 130°C

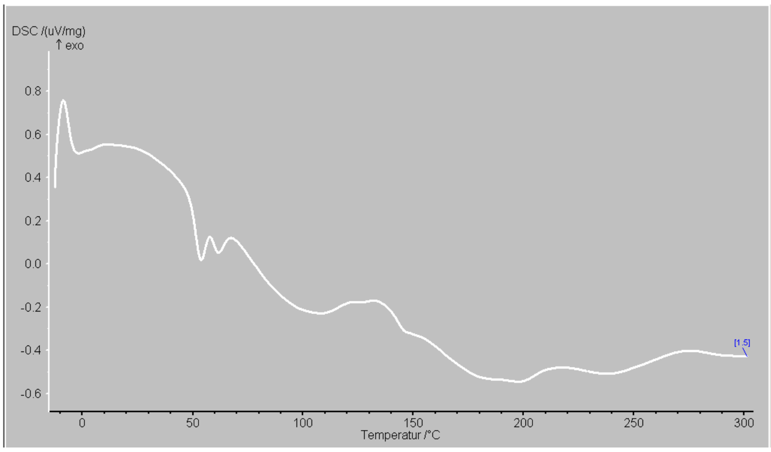


Figure AII.21. DSC (cured material at 130°C). Formulation AT 4.18.

AT 4.18 140°C

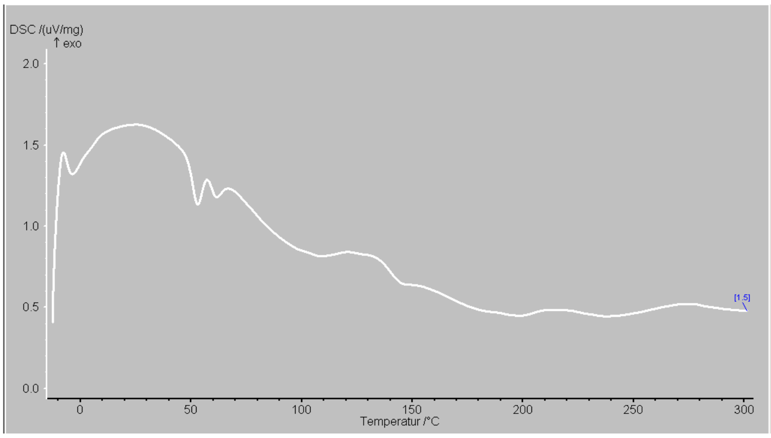


Figure AII.22. DSC (cured material at 140°C). Formulation AT 4.18.

AT 4.26. 130°C

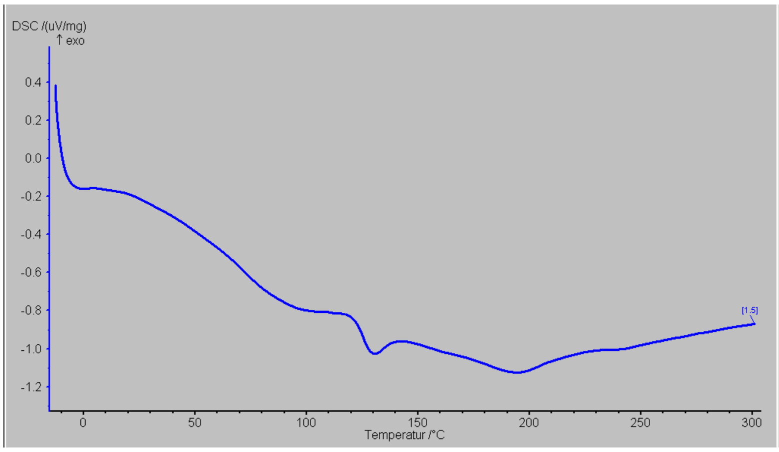


Figure AII.22. DSC (cured material at 130°C). Formulation AT 4.26.

AT 4.26. 140°C

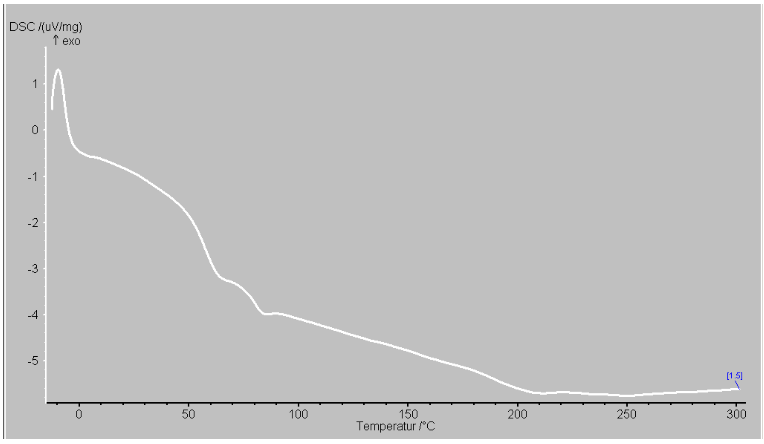


Figure AII.22. DSC (cured material at 140°C). Formulation AT 4.26.

ANNEX III

AT 3.1

Table AII.1. Surface energy for each solvent. Formulation AT 3.1.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	110,8	Water (Ström)	72.80	21.80	51.00
1	101,2	Glycerol (Ström)	63.40	37.00	26.40
2	88,1	Ethylene glycol (Ström)	47.70	30.90	16.80
3	30,1	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.2. Surface energy results. Formulation AT 3.1.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 23.77 [mN/m] Polar Part = 0.00 [mN/m] Total Surface Energy = 23.77 [mN/m]

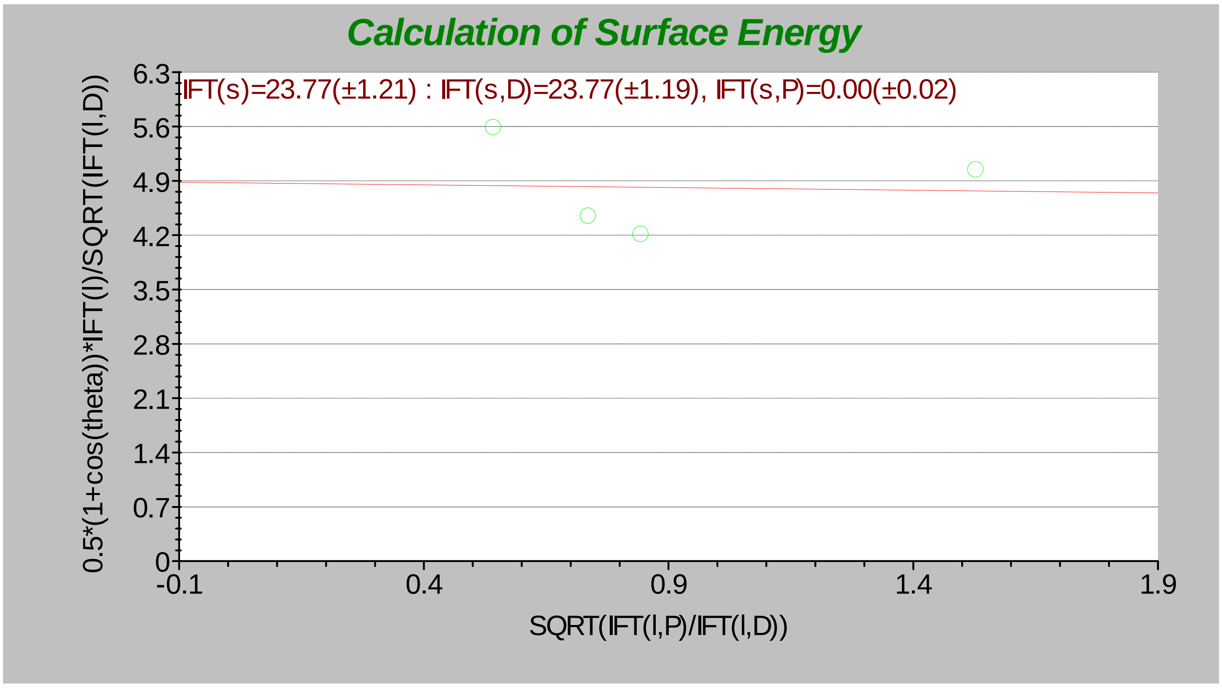


Figure AIII.1. Calculation of surface energy. Formulation AT 3.1.

AT 3.2

Table AII.3. Surface energy for each solvent. Formulation AT 3.2.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	94,1	Water (Ström)	72.80	21.80	51.00
1	86,2	Glycerol (Ström)	63.40	37.00	26.40
2	73,2	Ethylene glycol (Ström)	47.70	30.90	16.80
3	26,6	1-Octanol (Schultz)	27.60	21.30	6.30
4	16,7	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.4. Surface energy results. Formulation AT 3.2.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 22.26 [mN/m] Polar Part = 2.13 [mN/m] Total Surface Energy = 24.39 [mN/m]

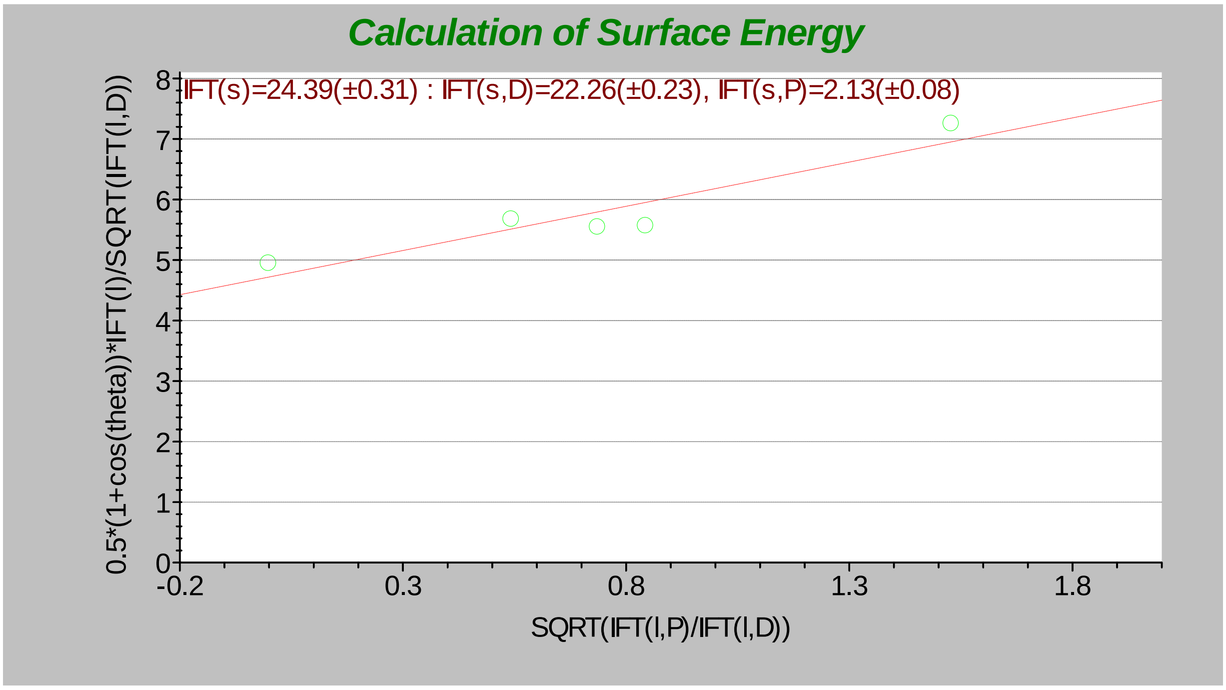


Figure AIII.2. Calculation of surface energy. Formulation AT 3.2.

AT 3.3

Table AII.5. Surface energy for each solvent. Formulation AT 3.3.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	93,8	Water (Ström)	72.80	21.80	51.00
1	91,6	Glycerol (Ström)	63.40	37.00	26.40
2	76,4	Ethylene glycol (Ström)	47.70	30.90	16.80
3	20,6	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.6. Surface energy results. Formulation AT 3.3.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 16.94 [mN/m] Polar Part = 3.63 [mN/m] Total Surface Energy = 20.57 [mN/m]

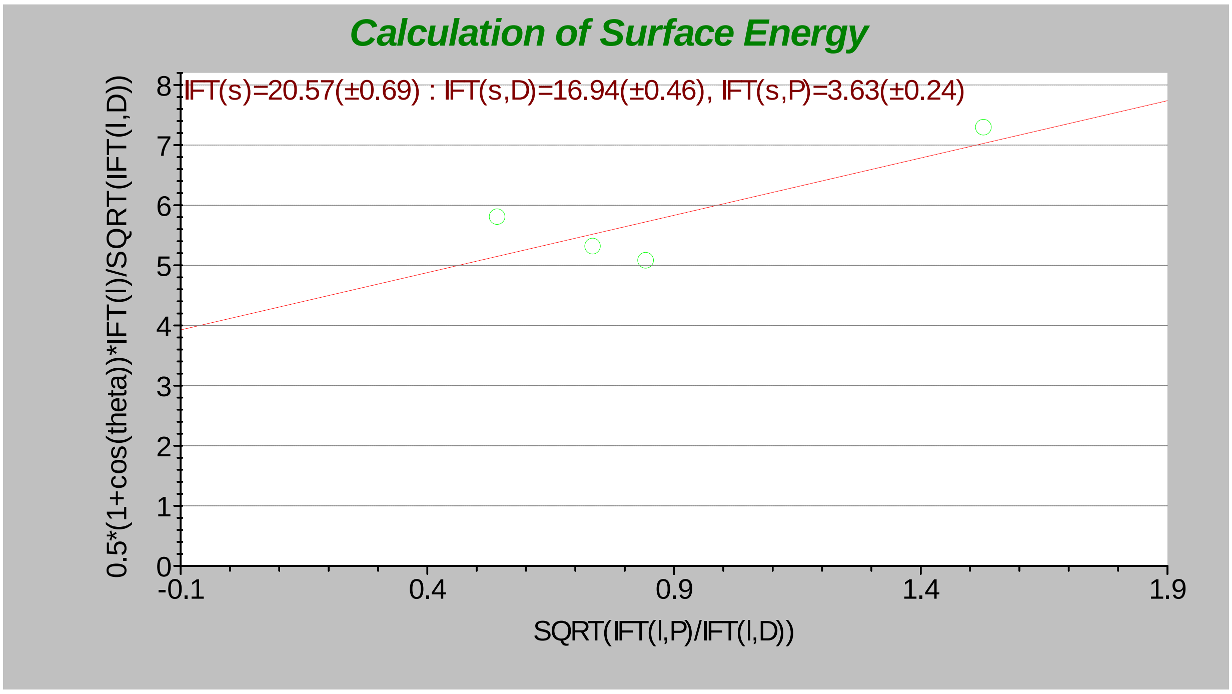


Figure AIII.3. Calculation of surface energy. Formulation AT 3.3.

AT 3.4

Table AII.5. Surface energy for each solvent. Formulation AT 3.3.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	73,0	Water (Ström)	72.80	21.80	51.00
1	73,4	Glycerol (Ström)	63.40	37.00	26.40
2	56,5	Ethylene glycol (Ström)	47.70	30.90	16.80
3	-	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.6. Surface energy results. Formulation AT 3.3.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 9.70 [mN/m] Polar Part = 20.48 [mN/m] Total Surface Energy = 30.18 [mN/m]

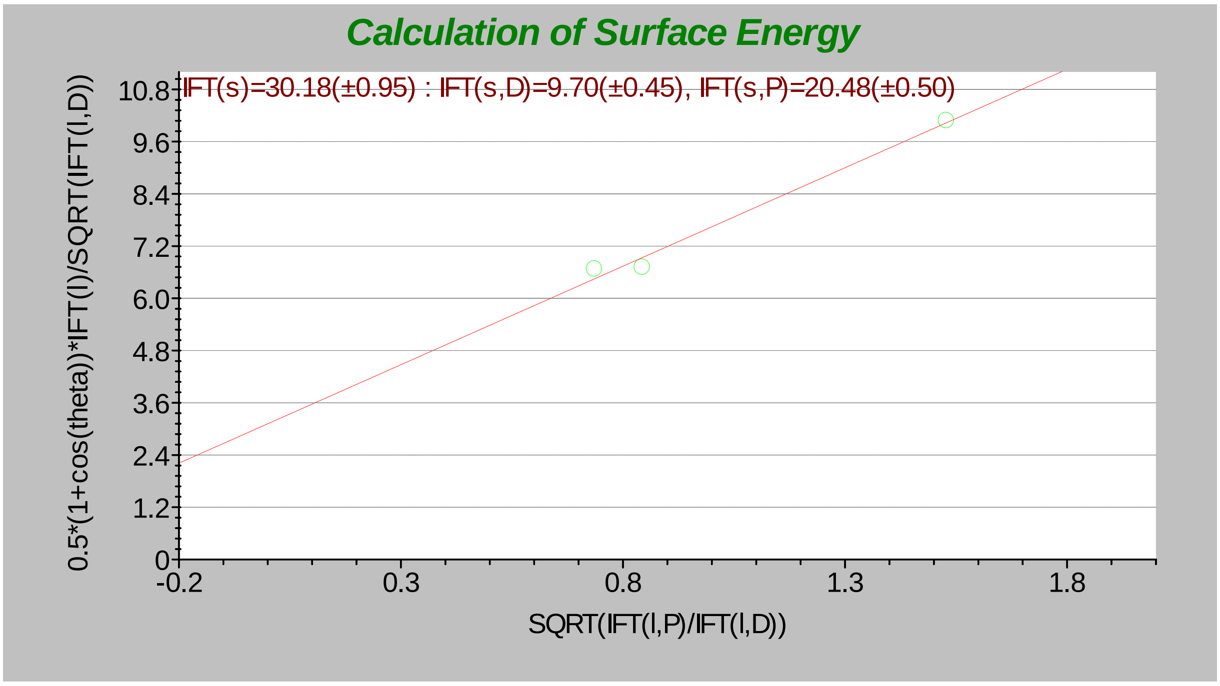


Figure AIII.4. Calculation of surface energy. Formulation AT 3.4.

AT 3.5

Table AII.9. Surface energy for each solvent. Formulation AT 3.5.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	73,4	Water (Ström)	72.80	21.80	51.00
1	72,3	Glycerol (Ström)	63.40	37.00	26.40
2	50,3	Ethylene glycol (Ström)	47.70	30.90	16.80
3	14,4	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.10. Surface energy results. Formulation AT 3.5.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 13.39 [mN/m] Polar Part = 17.07 [mN/m] Total Surface Energy = 30.46 [mN/m]

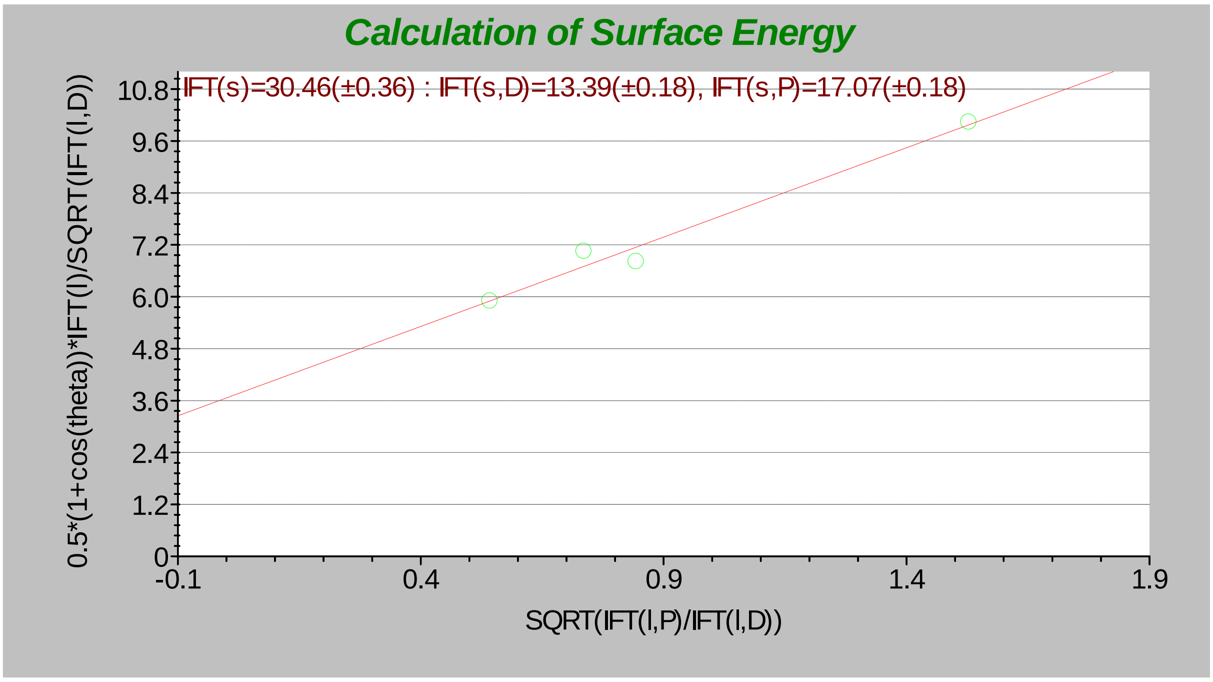


Figure AIII.5. Calculation of surface energy. Formulation AT 3.5.

AT 4.10

Table AII.11. Surface energy for each solvent. Formulation AT 4.10.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	105,3	Water (Ström)	72.80	21.80	51.00
1	97,6	Glycerol (Ström)	63.40	37.00	26.40
2	85,3	Ethylene glycol (Ström)	47.70	30.90	16.80
3	42,1	1-Octanol (Schultz)	27.60	21.30	6.30
4	33,6	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.12. Surface energy results. Formulation AT 4.10.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 20.10 [mN/m] Polar Part = 0.40 [mN/m] Total Surface Energy = 20.50 [mN/m]

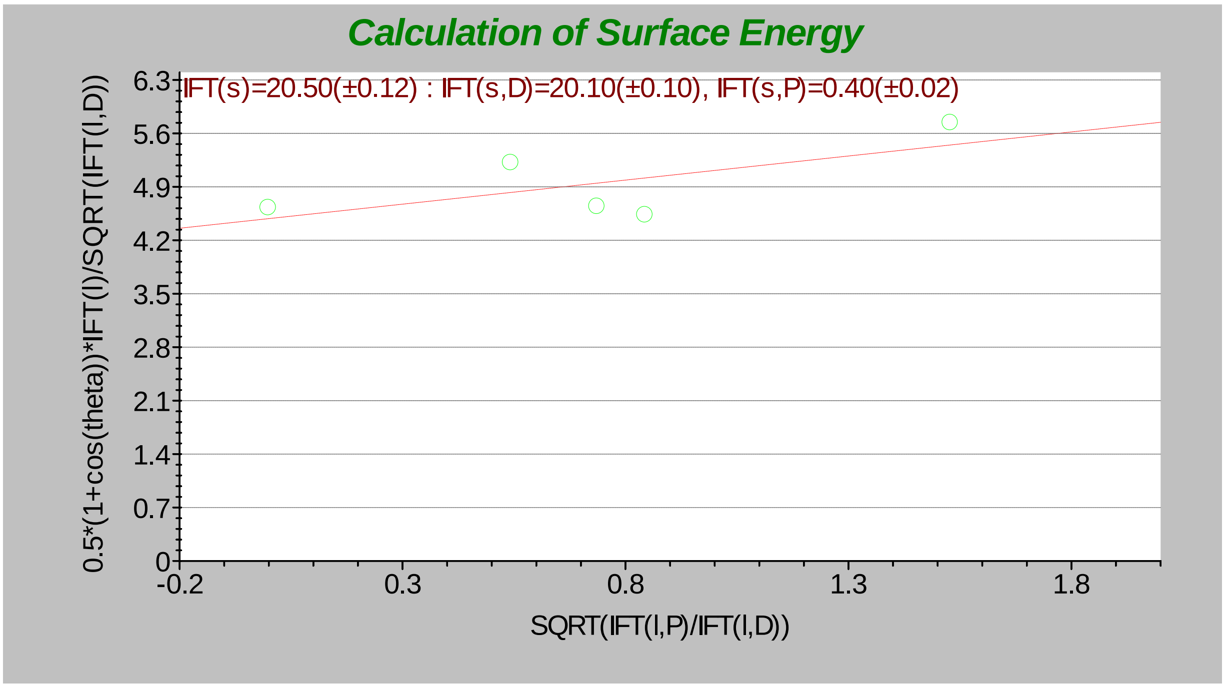


Figure AIII.6. Calculation of surface energy. Formulation AT 4.10.

AT 4.17

Table AII.13. Surface energy for each solvent. Formulation AT 4.17.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	96,0	Water (Ström)	72.80	21.80	51.00
1	90,0	Glycerol (Ström)	63.40	37.00	26.40
2	74,7	Ethylene glycol (Ström)	47.70	30.90	16.80
3	19,2	1-Octanol (Schultz)	27.60	21.30	6.30
4	-	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.14. Surface energy results. Formulation AT 4.17.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 20.18 [mN/m] Polar Part = 2.23 [mN/m] Total Surface Energy = 22.41 [mN/m]

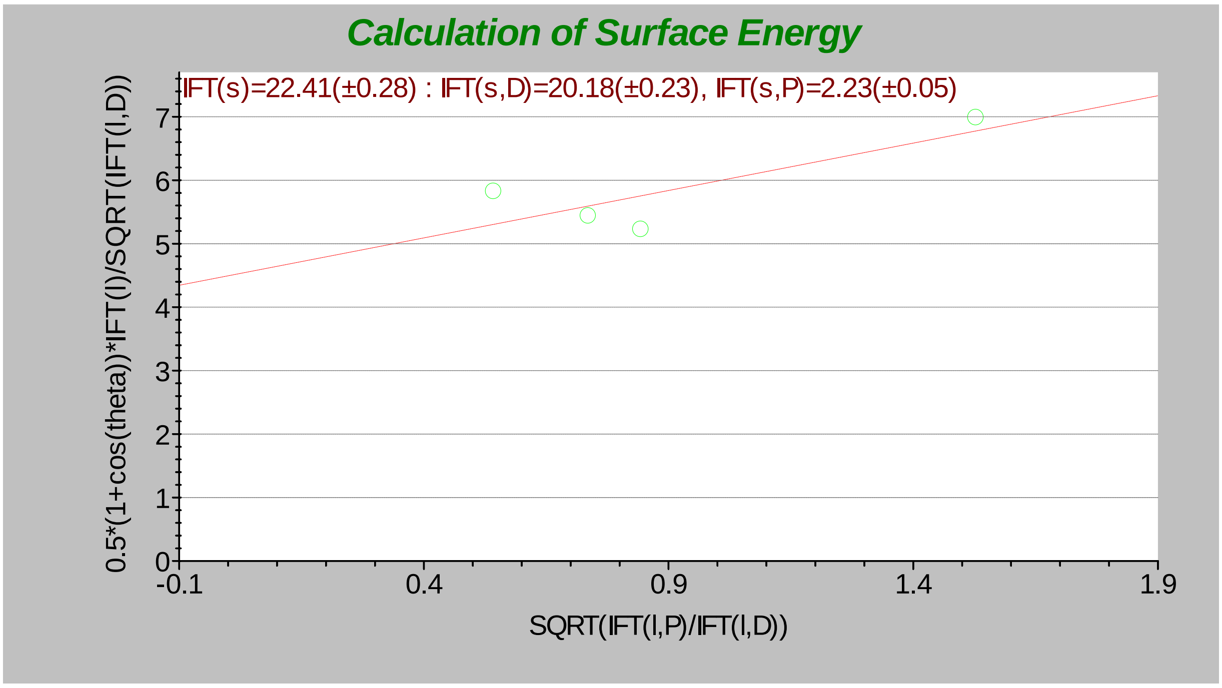


Figure AIII.7. Calculation of surface energy. Formulation AT 4.17.

AT 4.18

Table AII.15. Surface energy for each solvent. Formulation AT 4.18.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	108,9	Water (Ström)	72.80	21.80	51.00
1	97,2	Glycerol (Ström)	63.40	37.00	26.40
2	85,4	Ethylene glycol (Ström)	47.70	30.90	16.80
3	43,7	1-Octanol (Schultz)	27.60	21.30	6.30
4	33,4	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.16. Surface energy results. Formulation AT 4.18.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 21.19 [mN/m] Polar Part = 0.11 [mN/m] Total Surface Energy = 21.30 [mN/m]

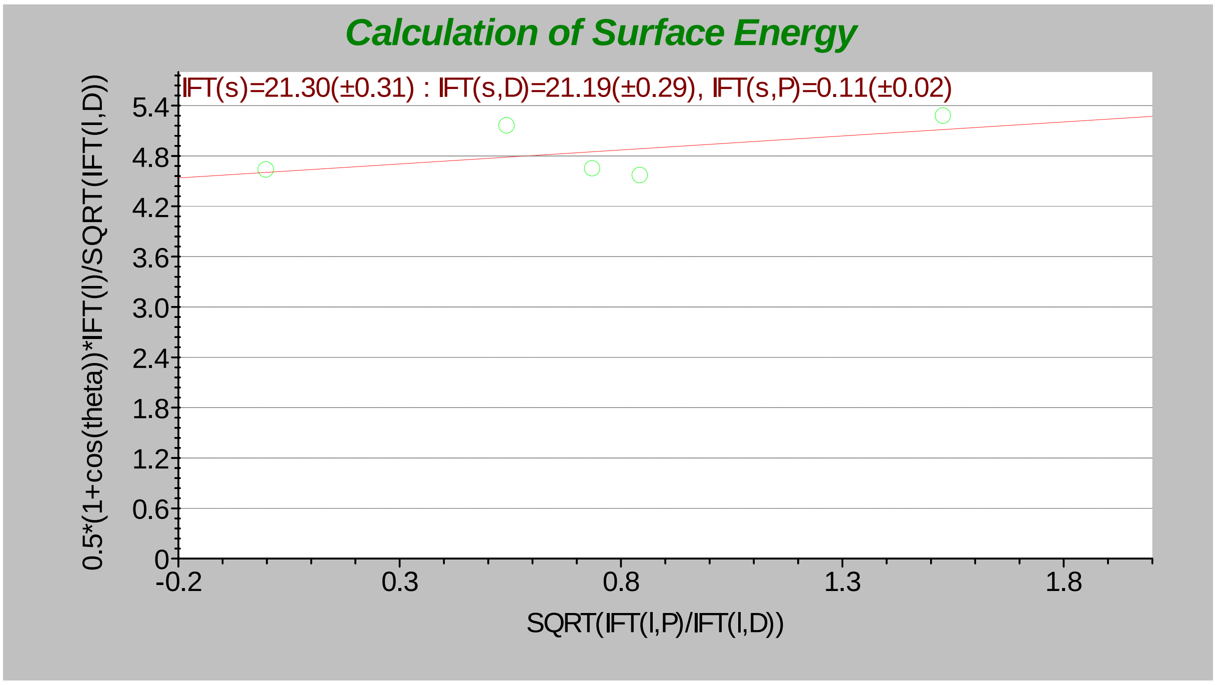


Figure AIII.8. Calculation of surface energy. Formulation AT 4.18.

AT 4.26

Table AII.17. Surface energy for each solvent. Formulation AT 4.26.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	104,2	Water (Ström)	72.80	21.80	51.00
1	98,5	Glycerol (Ström)	63.40	37.00	26.40
2	86,0	Ethylene glycol (Ström)	47.70	30.90	16.80
3	35,1	1-Octanol (Schultz)	27.60	21.30	6.30
4	25,5	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.18. Surface energy results. Formulation AT 4.26**.**

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 21.19 [mN/m] Polar Part = 0.34 [mN/m] Total Surface Energy = 21.53 [mN/m]

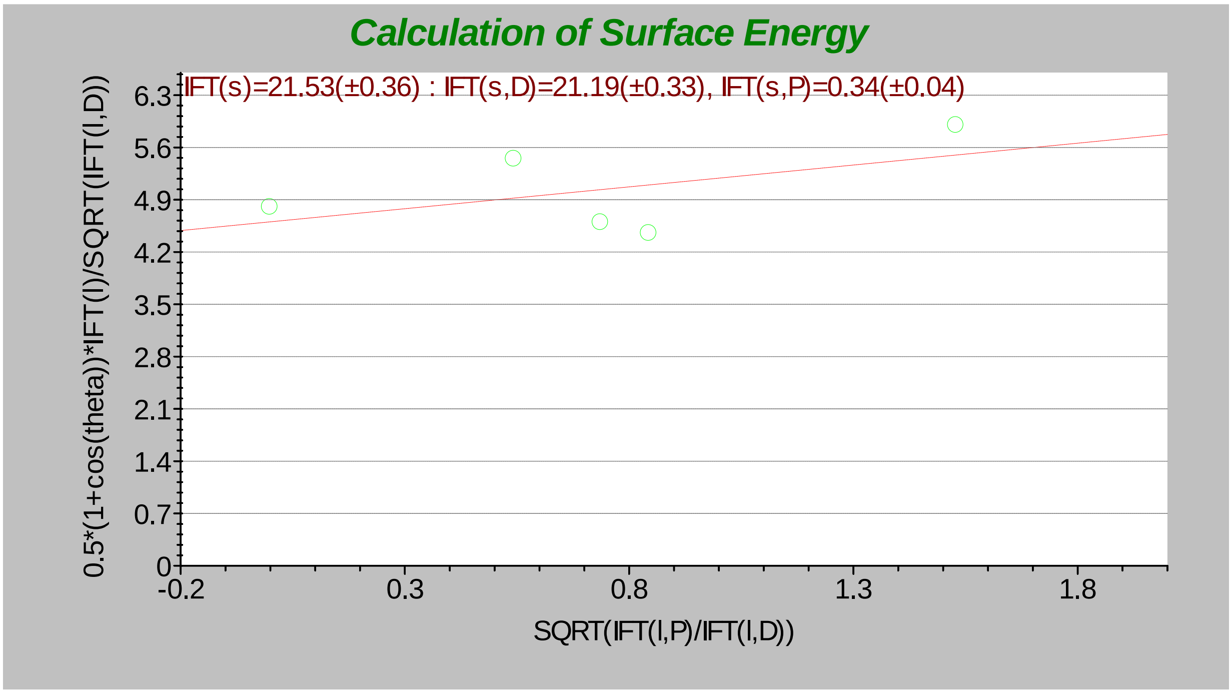


Figure AIII.9. Calculation of surface energy. Formulation AT 4.26.

AT 4.33

Table AII.19. Surface energy for each solvent. Formulation AT 4.33.

No.	Theta [°]	Liquid Name	IFT [mN/m]	DispersePt	PolarPt
0	85,9	Water (Ström)	72.80	21.80	51.00
1	81,7	Glycerol (Ström)	63.40	37.00	26.40
2	64,5	Ethylene glycol (Ström)	47.70	30.90	16.80
3	14,8	1-Octanol (Schultz)	27.60	21.30	6.30
4	10,5	n-Dodecane (Ström)	25.40	25.40	0.00

Table AII.20. Surface energy results. Formulation AT 4.33.

Calculation Results [Method: Owens-Wendt]:
Disperse Part = 22.02 [mN/m] Polar Part = 4.63 [mN/m] Total Surface Energy = 26.65 [mN/m]

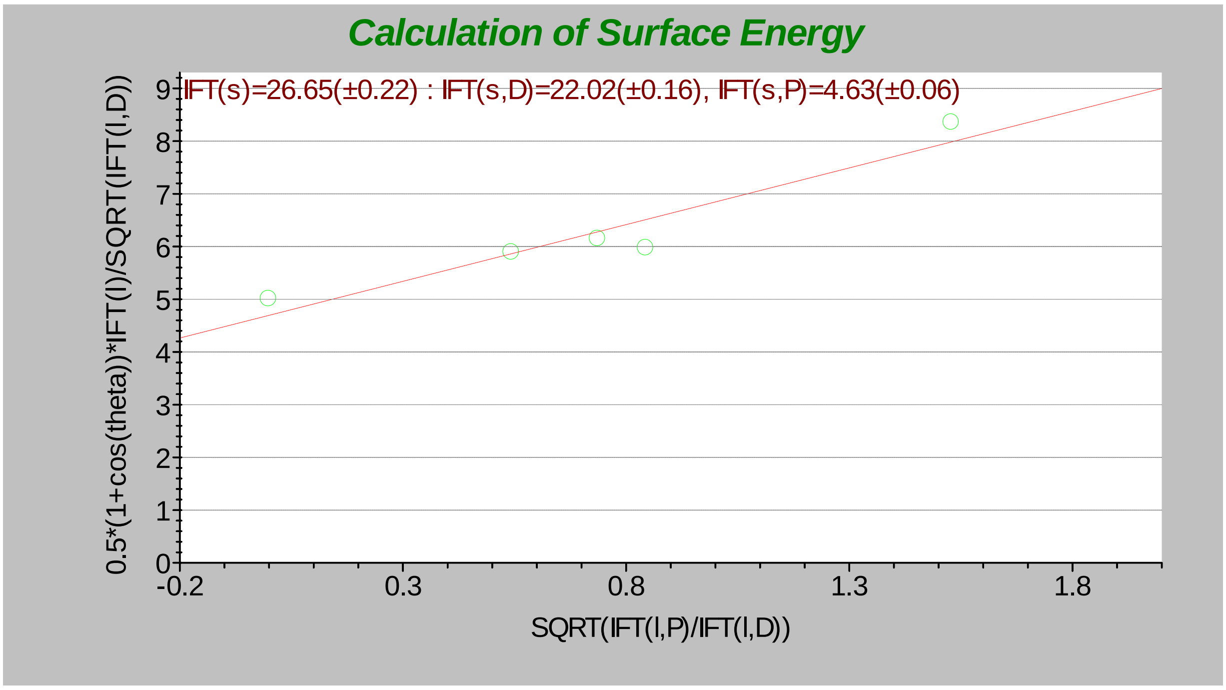


Figure AIII.10. Calculation of surface energy. Formulation AT 4.33.

ANNEX IV

Table AIV.1. Values of viscosity.

Base	Elongation (cm)
AT 3.2	2
AT 4.10	2,1
AT 3.3	1,5
AT 4. 17	1,9
AT 4.18	1,8
AT 3.4	1,5
AT 4.26	1,4
AT 3.5	22
AT 4.33	24,2

Table AIV.2. Values of chemical stability.

Base	$T_{\text{Chemical stability}}$ (°C)
AT 3.2	134
AT 4.10	129
AT 3.3	102
AT 4.17	99
AT 4.18	102
AT 3.4	105
AT 4.26	100
AT 3.5	165
AT 4.33	160

Table AIV.3. Values of Erichsen test.

	Resistance (mm)								
T (°C)	80	90	100	110	120	130	140	150	160
AT 3.2	1,2	1,2	1,2	1,3	1,7	1,9	2,1	1,9	1,9
AT 4.10	0,4	0,5	0,5	0,5	0,5	0,9	3,2	3,9	3,9
AT 3.3	0,6	0,6	0,7	5,5	6,3	6,3	6,3	6,3	6,8
AT 4.17	0,1	0,1	2,4	4,1	4,6	4,7	5,6	6,1	6,3
AT 4.18	1,3	1,5	1,9	3,1	4,5	4,4	5,4	5,4	6,1
AT 3.4	1,3	1,5	1,4	1,6	3,2	4,7	6,9	7	7
AT 4.26	0,6	0,6	1,6	6,3	6,4	7,1	7,4	7,4	7,4
AT 3.5	0,2	0,2	0,2	0,3	2,4	6,8	6,9	7	7,5
AT 4.33	0,2	0,2	0,2	0,2	2	2,5	2,6	2,6	3,3

ANNEX V

Table AV.1. Formulation AT 3.1.

AT3.1 - 2K - Epoxy Adhesion Test Base

Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	634,26	443,98
886	Hardenner H886	228,68	160,07
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**		
312	Resin epoxy H312 (self crosslink)	634,26	443,98
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		771,32	539,93

After extrusion			**needs to be recaltulated!**
886	Hardenner H886	228,68	160,07

Table AV.2. Formulation AT 4.1.

AT4.1			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	619,56	433,69
886	Acceletaror H886	223,38	156,36
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3076	Internal Releaser 1	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	619,56	433,69
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3076	Internal Releaser 1	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		776,62	543,64

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	223,38	156,36

Table AV.3. Formulation AT 4.2.

AT4.2			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	597,51	239,00
886	Acceletaror H886	215,43	86,17
867	Leveling Agent 867	15,00	6,00
11…3581	Wax 11…3581	10,00	4,00
11…3434	Internal Releaser 2	50,00	20,00
10519	Antipin hole 519	7,50	3,00
10689	Wax 689	2,50	1,00
769	Wax 769	2,06	0,82
00100030	Pigment 30	100	40,00
		1000,00	400,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	597,51	239,00
867	Leveling Agent 867	15,00	6,00
11…3581	Wax 11…3581	10,00	4,00
11…3434	Internal Releaser 2	50,00	20,00
10519	Antipin hole 519	7,50	3,00
10689	Wax 689	2,50	1,00
769	Wax 769	2,06	0,82
00100030	Pigment 30	100,00	40,00
		784,57	700,00

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	215,43	86,17

Table AV.4. Formulation AT 4.3.

AT4.3			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	615,89	431,12
886	Acceletaror H886	222,05	155,44
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3011	Internal Releaser 3	5,00	3,50
11…3013	Internal Releaser 4	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	615,89	431,12
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3011	Internal Releaser 3	5,00	3,50
11…3013	Internal Releaser 4	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		777,95	544,56

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	222,05	155,44

Table AV.5. Formulation AT 4.4.

AT4.4			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	619,56	433,69
886	Acceletaror H886	223,38	156,36
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3013	Internal Releaser 4	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	Description	Quantity	
312	Resin epoxy H312 (self crosslink)	619,56	433,69
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3013	Internal Releaser 4	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		776,62	543,64

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	223,38	156,36

Table AV.6. Formulation AT 4.5.

AT4.5			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	625,07	437,55
886	Acceletaror H886	225,36	157,76
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3210	Internal Releaser 5	12,50	8,75
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	625,07	437,55
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3210	Internal Releaser 5	12,50	8,75
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		774,63	542,24

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	225,36	157,76

Table AV.7. Formulation AT 4.6.

AT4.6			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	619,56	433,69
886	Acceletaror H886	223,38	156,36
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
11…3489	Internal Releaser 6	20,00	14,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	619,560	433,69
867	Leveling Agent 867	15,000	10,50
11…3581	Wax 11…3581	10,000	7,00
11…3489	Internal Releaser 6	20,000	14,00
10519	Antipin hole 519	7,500	5,25
10689	Wax 689	2,500	1,75
769	Wax 769	2,060	1,44
00100030	Pigment 30	100,000	70,00
		776,620	543,64

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	223,38	156,36

Table AV.8. Formulation AT 4.7.

AT4.7			
Compound	**Description**	**Quantity**	**Quantity**
312	Resin epoxy H312 (self crosslink)	612,21	428,55
886	Acceletaror H886	220,73	154,51
867	Leveling Agent 867	15,00	10,50
11…3581	Wax 11…3581	10,00	7,00
	Internal Releaser 7	30,00	21,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100	70,00
		1000,00	700,00

Compound	**Description**	**Quantity**	
312	Resin epoxy H312 (self crosslink)	612,210	428,55
867	Leveling Agent 867	15,000	10,50
11…3581	Wax 11…3581	10,000	7,00
11…4444	Internal Releaser 7	30,000	21,00
10519	Antipin hole 519	7,500	5,25
10689	Wax 689	2,500	1,75
769	Wax 769	2,060	1,44
00100030	Pigment 30	100,000	70,00
		779,270	545,49

After extrusion			**needs to be recaltulated!**
886	Acceletaror H886	220,73	154,51

Table AV.9. Formulation AT 3.2.

AT3.2 - Polyester (Dovista) Adhesion Test Base			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	805,03	563,52
910	Hardenner 910	68,44	47,91
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
00100030	Pigment 30	100	70,00
		1000,00	700,00

Table AV.10. Formulation AT 4.9.

AT4.9			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	786,60	550,62
910	Hardenner 910	66,87	46,81
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3076	Internal Releaser 1	20,00	14,00
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.11. Formulation AT 4.10.

AT4.10			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	758,95	531,26
910	Hardenner 910	64,52	45,17
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3434	Internal Releaser 2	50,00	35,00
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.12. Formulation AT 4.11.

AT4.11			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	781,99	547,39
910	Hardenner 910	66,48	46,54
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3011	Internal Releaser 3	5,00	3,50
11…3013	Internal Releaser 4	20,00	14,00
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.13. Formulation AT 4.12.

AT4.12			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	786,60	550,62
910	Hardenner 910	66,87	46,81
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3013	Internal Releaser 4	20,00	14,00
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.14. Formulation AT 4.13.

AT4.13			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	793,51	555,46
910	Hardenner 910	67,46	47,22
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3210	Internal Releaser 5	12,50	8,75
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.15. Formulation AT 4.14.

AT4.14			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	786,60	550,62
910	Hardenner 910	66,87	46,81
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…3489	Internal Releaser 6	20,00	14,00
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.16. Formulation AT 4.15.

AT4.15			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	802,26	561,58
910	Hardenner 910	68,21	47,74
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
11…4444	Internal Releaser 7	3,00	2,10
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.17. Formulation AT 4.16.

AT4.16			
Compound	**Description**	**Quantity**	**Quantity**
30006055	Polyester resin H 6055	801,34	560,94
910	Hardenner 910	68,13	47,69
10447	Accelerator 447	6,01	4,21
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	4,30	3,01
0	Internal Releaser 8	4,00	2,80
10905	Wax 905	1,32	0,92
10480	Wax 480	4,90	3,43
100030	Pigment 30	100,00	70,00
		1000,00	700

Table AV.18. Formulation AT 3.3.

AT3.3 -SC Epoxy Type 1, Adhesion Test Base			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	830,56	581,39
1058	Accelerator 1058	37,38	26,16
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.19. Formulation AT 4.17.

AT4.17			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11...3076	Internal Releaser 1	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.20. Formulation AT 4.18.

AT4.18			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	782,72	547,90
1058	Accelerator 1058	35,22	24,66
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11...3434	Internal Releaser 2	50,00	35,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.21. Formulation AT 4.19.

AT4.19			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	806,64	564,65
1058	Accelerator 1058	36,30	25,41
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3011	Internal Releaser 3	5,00	3,50
11...3013	Internal Releaser 4	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.22. Formulation AT 4.20.

AT4.20			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11...3013	Internal Releaser 4	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.23. Formulation AT 4.21.

AT4.21			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	818,60	573,02
1058	Accelerator 1058	36,84	25,79
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3210	Internal Releaser 5	12,50	8,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.24. Formulation AT 4.22.

AT4.22			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3489	Internal Releaser 6	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.25. Formulation AT 4.23.

AT4.23			
Compound	**Description**	**Quantity**	**Quantity**
11…3426	Epoxy resin D 671 (self crosslink)	827,69	579,39
1058	Accelerator 1058	37,25	26,07
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…4444	Internal Releaser 7	3,00	2,10
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.26. Formulation AT 3.4.

AT3.4 -SC Epoxy Type 4, Adhesion Test Base			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	830,56	581,39
1058	Accelerator 1058	37,38	26,16
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1000,00	700,00

Table AV.27. Formulation AT 4.25.

AT4.25			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3076	Internal Releaser 1	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.28. Formulation AT 4.26.

AT4.26			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	782,72	547,90
1058	Accelerator 1058	35,22	24,66
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3434	Internal Releaser 2	50,00	35,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.29. Formulation AT 4.27.

AT4.27			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	806,64	564,65
1058	Accelerator 1058	36,30	25,41
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3011	Internal Releaser 3	5,00	3,50
11…3013	Internal Releaser 4	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.30. Formulation AT 4.28.

AT4.28			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3013	Internal Releaser 4	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.31. Formulation AT 4.29.

AT4.29			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	818,60	573,02
1058	Accelerator 1058	36,84	25,79
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…3210	Internal Releaser 5	12,50	8,75
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.32. Formulation AT 4.30.

AT4.30			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	811,43	568,00
1058	Accelerator 1058	36,51	25,56
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Internal Releaser 6	7,50	5,25
10689	Wax 689	2,50	1,75
11…3489	Internal Releaser 6	20,00	14,00
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.33. Formulation AT 4.31.

AT4.31			
Compound	**Description**	**Quantity**	**Quantity**
H417	Epoxy resin D 664 (self crosslink)	827,69	579,39
1058	Accelerator 1058	37,25	26,07
867	Leveling Agent 867	10,00	7,00
11…3581	Wax 11…3581	10,00	7,00
10519	Antipin hole 519	7,50	5,25
10689	Wax 689	2,50	1,75
11…4444	Internal Releaser 7	3,00	2,10
769	Wax 769	2,06	1,44
00100030	Pigment 30	100,00	70,00
		1.000,00	700,00

Table AV.34. Formulation AT 3.5.

AT 3.5Acrylic. Type 5, Adhesion Test Base			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	790,18	553,12
11271	Hardenner DDA	169,81	118,87
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.35. Formulation AT 4.33.

AT 4.33			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	773,75	541,62
11271	Hardenner DDA	166,28	116,39
11…3076	Internal Releaser 1	20	14,00
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.36. Formulation AT 4.34.

AT 4.34			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	749	524,29
11271	Hardenner DDA	160,96	112,67
11…3434	Internal Releaser 2	50	35,00
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.37. Formulation AT 4.35.

AT 4.35			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	769,6	538,71
11271	Hardenner DDA	165,39	115,77
11…3011	Internal Releaser 3	5	3,50
11…3013	Internal Releaser 4	20	14,00
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.38. Formulation AT 4.36.

AT 4.36			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	773,75	541,62
11271	Hardenner DDA	166,28	116,39
11…3013	Internal Releaser 4	20	14,00
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.39. Formulation AT 4.37.

AT 4.37			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	779,86	545,90
11271	Hardenner DDA	167,59	117,31
11…3210	Internal Releaser 5	12,5	8,75
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.40. Formulation AT 4.38.

AT 4.38			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	773,75	541,62
11271	Hardenner DDA	166,28	116,39
11…3489	Internal Releaser 6	20	14,00
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

Table AV.41. Formulation AT 4.39.

AT 4.39			
Compound	**Description**	**Quantity**	**Quantity**
215	Resin acrylic 7610	787,71	551,39
11271	Hardenner DDA	169,28	118,49
11…4444	Internal Releaser 7	3	2,10
10867	Wax 867	9	6,30
10408	Gloss Enhancer 542 DG	10	7,00
10427	UV absorber 622 SF	5	3,50
10192	UV absorber 405	10	7,00
10123	antioxidant 126	3	2,10
10204	antioxidant 1076	3	2,10
10548	optical brighteners 548	0,02	0,014
		1000,0	700

ANNEX VI

Table AVI.1. Extrusion Parameters (Releaser formulations).

Powder	T extrusion (°C)	Rpm
AT4.1	50/90/100/100/100	300
AT4.2	50/90/100/100/100	300
AT4.3	50/90/100/100/100	300
AT4.4	50/90/100/100/100	300
AT4.5	50/90/100/100/100	300
AT4.6	50/90/100/100/100	300
AT4.7	50/90/100/100/100	300
AT4.9	50/80/90/90/90	300
AT4.10	50/80/90/90/90	300
AT4.11	50/80/90/90/90	300
AT4.12	50/80/90/90/90	300
AT4.13	50/80/90/90/90	300
AT4.14	50/80/90/90/90	300
AT4.15	50/80/90/90/90	300
AT4.17	50/80/90/90/90	300
AT4.18	50/80/90/90/90	300
AT4.19	50/80/90/90/90	300
AT4.20	50/80/90/90/90	300
AT4.21	50/80/90/90/90	300
AT4.22	50/80/90/90/90	300
AT4.23	50/80/90/90/90	300
AT4.25	50/90/115/115/105	300
AT4.26	50/90/115/115/105	300
AT4.27	50/90/115/115/105	300
AT4.28	50/90/115/115/105	300
AT4.29	50/90/115/115/105	300
AT4.30	50/90/115/115/105	300
AT4.31	50/90/115/115/105	300
AT 4.33	60/80/100/100/100	600
AT 4.34	60/80/100/100/100	600
AT 4.35	60/80/100/100/100	600
AT 4.36	60/80/100/100/100	600
AT 4.37	60/80/100/100/100	600
AT 4.38	60/80/100/100/100	600
AT 4.39	60/80/100/100/100	600

Table AVI.2. Extrusion Parameters (Mother formulations).

Powder	**T extrusion (°C)**	**Rpm**
AT3.1	50/90/100/100/100	300
AT3.2	50/80/90/90/90	300
AT3.3	50/80/90/90/90	300
AT3.4	50/90/115/115/105	400
AT 3.5	60/80/100/100/100	600