

E-COAT SUSTAINABLE LONG - FIBER THERMOPLASTIC COMPOSITES FOR STRUCTURAL AUTOMOTIVE APPLICATIONS

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Abstract

Polypropylene and glass fibre (PP/GF) based Long Fibre Reinforced thermoplastics (LFT) are nowadays established as state of the art materials for semi-structural applications in the automotive industry. However, PP/GF LFT materials are limited for producing automotive components for use in general assembly. The use of LFT based components for structural applications and their implementation directly into the body in white assembly is still a challenge for the automotive industry.

In order to develop LFT materials for such applications, a feasibility study to investigate the e-coating process sustainability of LFT materials was conducted. The current article addresses the developed LFT formulations and their basic mechanical properties. For this purpose polyamide / glass fibre (PA/GF) based LFT materials were thoroughly investigated. The change of mechanical performance of the LFT materials due to applied temperatures of the e-coating process was investigated by benchmarking of non-temperature-treated against tempered LFT specimens. In addition, the combined influence of temperatures and chemicals on the LFT properties was evaluated by running the LFT specimens through the actual painting line that included e-coating and subsequent painting and drying processes. Finally it was found that it is possible to manufacture LFT parts capable of withstanding the e-coating process without causing major changes in the performance of the LFT materials.

Introduction

LFT-D/ILC Processing Technology

Long fibre reinforced thermoplastics (LFT) have gained an increasing market share in the automotive sector during the last few years. The direct processes for LFT production (LFT-D) have also been established on the market. The LFT-D processes avoid semi-finished materials by manufacturing products directly from the raw materials such as glass fibres, thermoplastic resins and if necessary the modifiers. The LFT-D processes are well known to offer excellent cost-performance-ratio [1-4].

Recent processes such as LFT-D technology combined with the in-line compounding of the matrix polymer (LFT-D/ILC) by Dieffenbacher GmbH and other machine makers (e.g. Husky, Krauss Maffei etc.) allows the matrix polymer to be compounded with various additives. As shown in figure 1, first the various additives are compounded with the matrix polymer in the in-line (IL) compounding extruder. The modified matrix is then compounded with the glass fibres in the mixing extruder. By using LFT-D/ILC technology it is therefore possible to adjust the materials' composition to fulfil individual demands of the products [5-7].

Matrix Resins, additives, fillers etc.

Reinforcing fibers:

- Glass fibers
- Natural fibers (Hemp, Flax etc.)
- Carbon fibers
- Man-made polymer fibers, e.g. Rayon, Polyester etc.

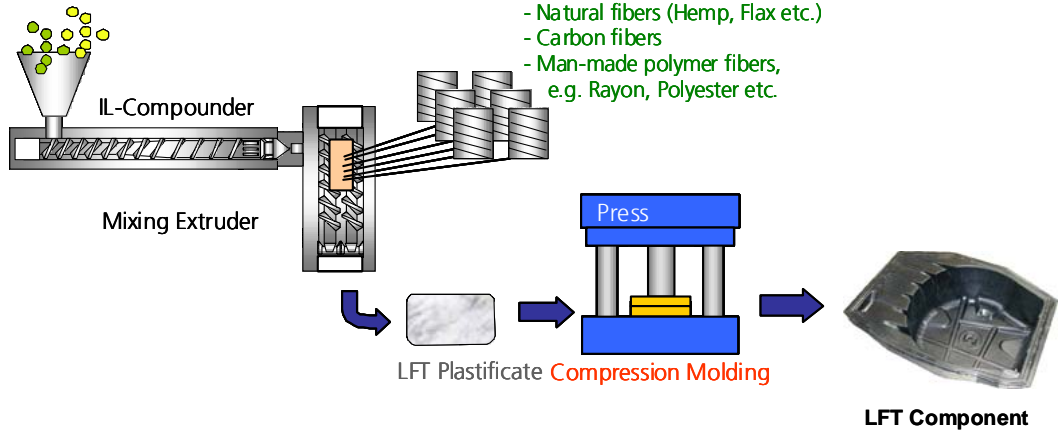


Figure 1: LFT-D/ILC Processing Technology

Today, most LFT end products are produced for the automobile industry. These moulded parts include body panels, sound shields, front-end assemblies, structural body parts, truck panels and housings as well as doors, tailgates and fender (wing) sections. Intensive development is also being carried out in other application areas in the electrical and building industries [6, 8].

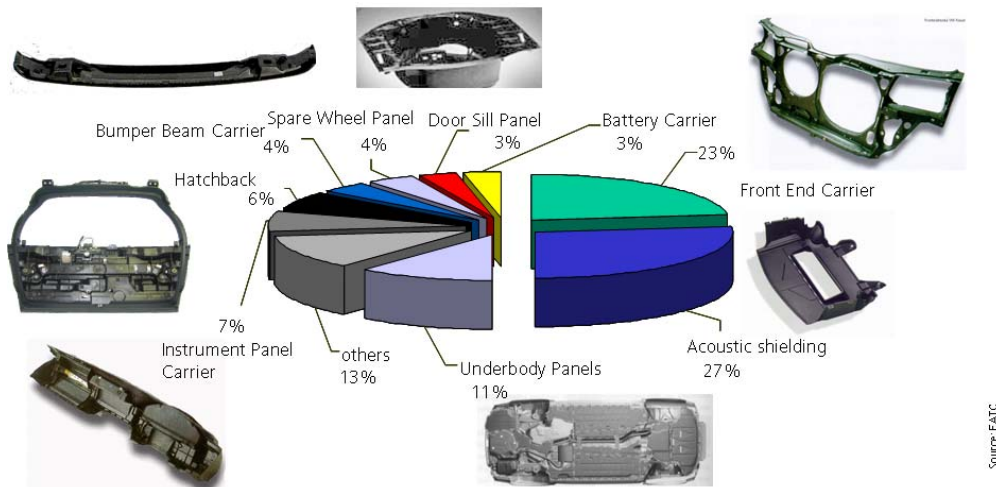


Figure 2: Automotive applications of long fibre reinforced PP

For most applications LFT-D/ILC Processing Technology currently utilises Polypropylene (PP) as the matrix material for the production of components for the automotive industry. It is worth mentioning that there are currently no LFT components in the automotive industry that are produced using engineering thermoplastic matrices such as Polyamides, Polyesters etc when compared to Polypropylene. Little evaluation has been carried out into the use of engineering thermoplastics for the production of LFT materials [9].

The low melting temperature of PP against the engineering thermoplastics does not allow the PP/GF based LFT components to be implemented directly into the body in white

assembly prior to the e-coating process. The body in white (BIW) assembly is sent through the e-coating process, painting process and the drying stages where it is exposed to high temperature and chemical treatments. The temperature can reach up to 215°C during such treatments, which means that the implementation of the PP based composites into the BIW is not feasible prior to such e-coating process.

E-coating process

The E-coating process, also known as the cathaphoretic painting process, is one of the most important steps during the serial painting of automobiles. During the e-coating process the surface of the body in white components is first of all cleaned so that it is grease free. Afterwards a corrosion protection layer is applied to the steel components of the body in white. This layer has an additional function as an adhesive substrate for paints applied during later stages. The surface preparation by the e-coating process is one of the most important and indispensable treatments, as the adhesion quality of the paints applied to the BIW in later stages strongly depends on it.

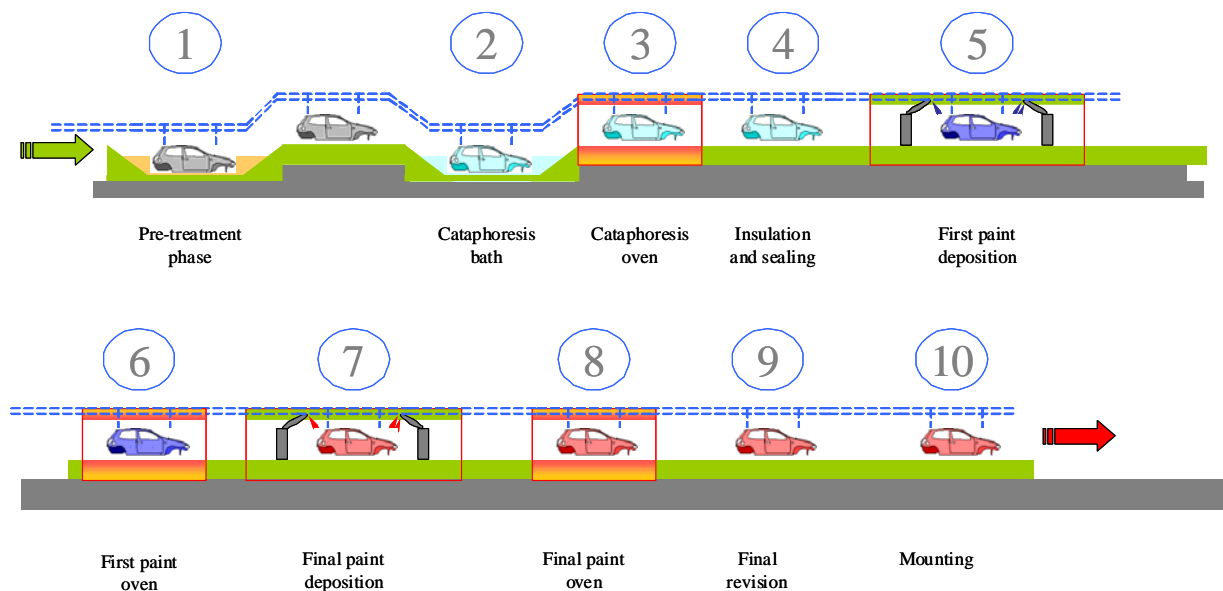


Figure 3: Paint line for e-coating process and its subsequent painting and drying stages [Reference: European Funded project *Super Light Car*]

Table I summarizes the most important process parameters such as applied temperatures and various treatments by acids, paints etc. to which the BIW is subjected. Considering that the components of the BIW have to sustain these high temperature conditions, the described activities were aimed to develop LFT materials based on engineering thermoplastics that would be capable of withstanding the e-coating process and subsequent painting and drying processes.

Note: In some cases, depending on the OEMs, the maximum temperature can be as high as 215°C.

Table I: The E-coating process and subsequent painting and drying process conditions

Operation	Process parameters
1. Pre-treatment phase	Washing cycle at 60°C for few minutes Phosphating (anticorrosive treatment) with lightly acid solutions
2 & 3. Cataphoretic deposition phase	2. Cathodic electrodeposition in paint bath tank - tension 300 volts, 30°C, 3 minutes 3. Furnace up to 185°C (sometimes 200°C), 20-30 minutes
5 & 6 First paint deposition phase	5. First paint deposition 6. Paint drying furnace up to 160°C, 20-30 minutes
7 & 8 Final paint deposition phase	7. Final paint deposition phase and furnace up to 150°C 8. Paint drying furnace up to 150°C, 20-30 minutes

As the maximum temperature during such treatments can reach 215°C, theoretically commercially available polyamides such as polyamide 66 (PA 66) or polyamide 6 (PA 66), and polyesters such as polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) were considered to be the most promising thermoplastic materials for use in such applications. The melting temperatures of PA6 and PBT thermoplastics are very close to the maximum temperatures (215°C) that can occur during such treatments. However, the melting temperatures of PA66 and PET are comparatively higher. Due to significantly high melting temperatures of PA66 and PET, these both materials theoretically show high potential for the development of LFT materials which can sustain the temperature conditions of the e-coating process and subsequent painting and drying processes.

Table II: Melting temperature comparison for polyamides and polyesters

Thermoplastic matrix	Melting temperature
Polyamides	
PA6	220°C
PA66	260°C
Polyesters	
PBT	220°C
PET	260

Materials

During this feasibility study into the development of LFT material formulations capable of withstanding the e-coating process conditions, the main focus was on the evaluation of polyamide based LFT materials. As mentioned above, PA66 shows high potential for such developments; consequently it was chosen as one of the engineering thermoplastic matrix materials for these investigations. At the same time PA6 based LFTs were also investigated to benchmark them against the performance of the PA66 based LFT materials. Johns Manville glass fibres (JM858) were chosen as reinforcing glass fibres for polyamide resins during the processing of LFT materials. The chosen matrix materials (PA6 & PA66) and reinforcing glass fibres were processed using LFT-D/ILC Processing Technology to produce LFT materials for material characterisation.

Material characterization

In order to characterise the polyamide / glass fibre (PA/GF) LFT materials, plaques 400 x 400 x 4 mm³ in size were produced. Rheology was given a special consideration in order to investigate the effect of glass fibre orientation on the LFT mechanical properties. The LFT samples were compression moulded as shown in figure 4 by placing the LFT plastificate from the extruder along one of the sides of the plaque mould followed by compression moulding.

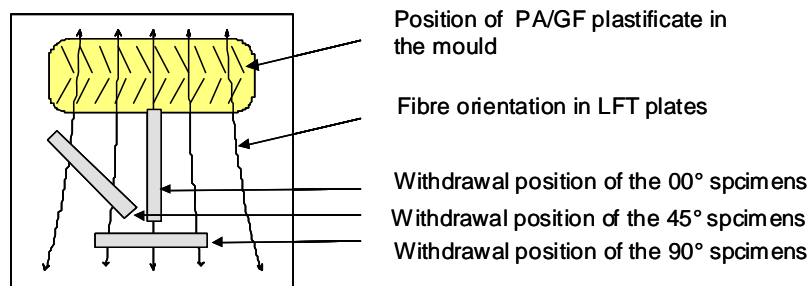


Figure 4: Schematic of material flow in the mould and sample positions for testing

The flow of material during the compression phase in the mould establishes the final flow orientation as shown in figure 4. In order to evaluate the influence of fibre orientation on the mechanical properties of the LFT composites, samples were cut at 00° (in flow direction) and 90° (perpendicular to flow direction) relative to the flow direction. Testing of the materials by this approach allowed minimum and high level of mechanical properties to be studied. It is important to mention that samples were cut from the produced plates by the water jet cutting method. Samples produced by this method have rough edges compared to injection moulded samples. For this reason the measured values of the mechanical properties of the water-jet-cut LFT samples can be lowered.

In order to investigate and achieve the e-coating process sustainability of the LFT materials, purely mechanical characterisation of the LFT materials after their processing was not sufficient. This development was particularly focussed on evaluating the possibility of producing automotive components based on LFT materials that can be implemented directly into the body in white assembly prior to the e-coating process. It was therefore essential to evaluate the effect of temperature conditions and also the effect of various surface treatments with acids and paints etc. (i.e. chemical treatments) on the performance of the LFT materials.

With this in view, a step by step approach was used to evaluate the effect of these various parameters on the performance of LFT materials as follows –

1. Basic LFT material properties

Focus on characterisation of the basic LFT materials exposed to neither heat nor chemical treatments

2. Effect of temperature on matrix materials

Considering that the temperature can reach up to 215°C during such treatments, glass fibres are not expected to undergo any material changes due to heat treatments. The investigation was consequently focused on the influence of temperature on the performance of the matrix materials

3. Effect of temperature conditions on LFT materials (only temperature effects)

Focus on investigation of the LFT material properties on exposure to the temperature conditions of the e-coating process and subsequent painting and drying processes. This allowed the effect of temperature on the LFT materials to be investigated (independent of other factors), and the material will not be exposed to the actual e-coating process (i.e. the LFT materials will not be exposed to any chemical surface treatments)

4. Effect of the e-coating process on LFT materials (temperature and chemical effects)

Focus on investigation of LFT material properties on exposure to actual e-coating process and subsequent painting and drying processes. This allowed investigation of the combined effect of chemical treatments and temperature on the LFT materials

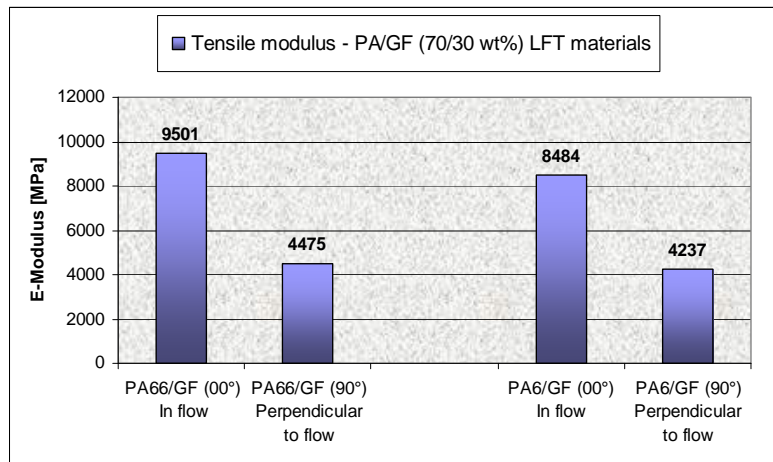
This testing program allowed the influence of the most important parameters - mainly temperature effects and a combination of chemical treatments and temperature effects - on the LFT materials to be investigated. Initially LFT materials based on polyamides (PA6 & PA66) with 20, 30 and 40wt% glass fibres were processed to produce plaques for material characterisation. As is well known, polyamides are hygroscopic in nature and their mechanical properties are significantly affected by the presence of moisture. It should also be noted that the moisture absorption is higher for PA6 than PA66. For this reason, all the LFT materials were carefully dried in a vacuum oven at 80°C for 12 hrs. After drying the samples were cooled to room temperature and then tested. The LFT materials containing PA6 with 30wt% glass fibres and PA66 with 30wt% glass fibres were chosen for evaluations at a later stage with a focus on investigating the LFT materials' performance due to heat treatment and a combination of chemical and heat treatments. The investigation results for these material combinations are discussed in the section below.

Note: The tensile testing was conducted according to ISO 527 and the charpy impact strength (notched edgewise) was conducted according to ISO 179.

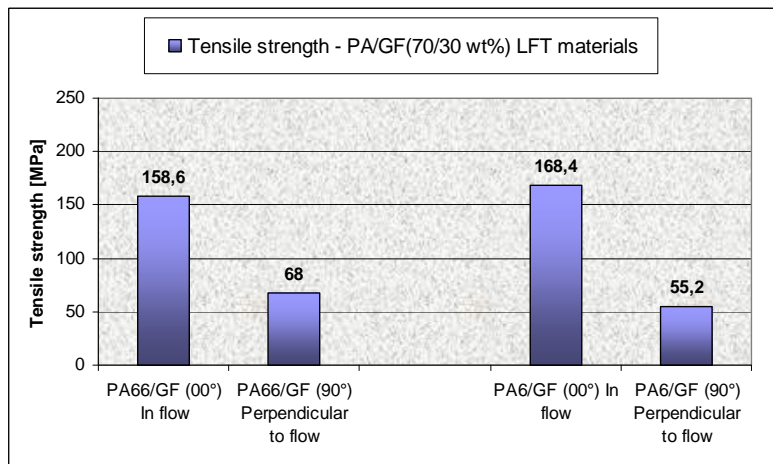
Results and discussions

Basic LFT material properties

Figures 5 (a) and 5 (b) show respectively tensile modulus and tensile strength, and figure 6 shows charpy notched edgewise impact strength for compression molded PA6/GF and PA66/GF LFT materials.



(a)



(b)

Figure 5: Tensile properties for PA66/GF and PA6/GF LFT materials – (a) Tensile modulus (b) Tensile strength

In both figures 5 and 6 it can be seen that the glass fiber orientation obtained in the end component after processing has a significant influence on the properties of the LFT materials. The material properties in the flow direction (00°) are significantly higher than the material properties in the direction perpendicular to flow (90°). Also, the modulus of PA66/GF LFT materials was found to be higher than the modulus of PA6/GF LFT materials, whereas the tensile strength was found to be approximately the same for both the material systems. The higher value of the modulus for PA66/GF LFT materials against PA6/GF LFT materials can be partially explained by the fact that the modulus of PA66 is higher than PA6 [see figure 8].

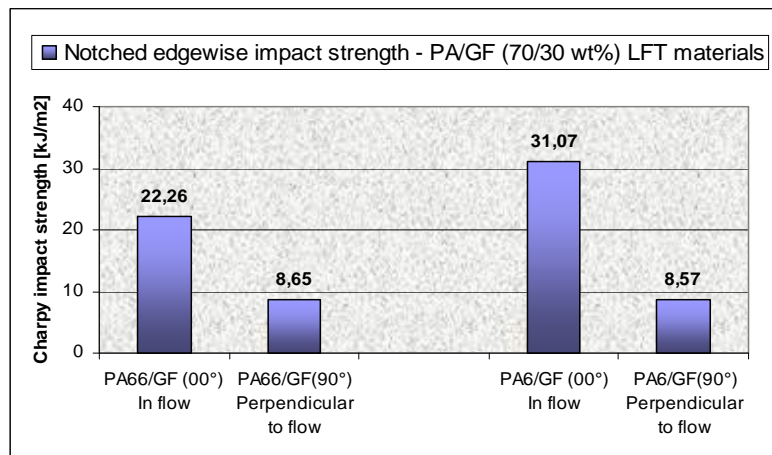


Figure 6: Charpy impact strength for PA66/GF and PA6/GF LFT materials – notched samples tested edgewise

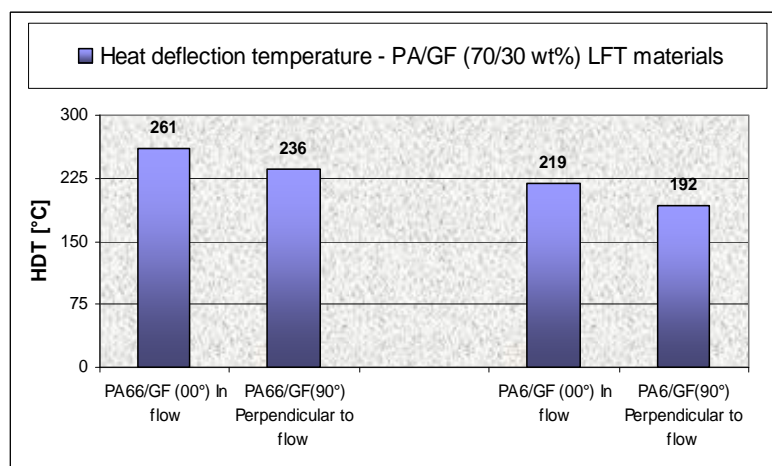


Figure 7: Heat deflection temperatures for PA66/GF and PA6/GF LFT materials

Similarly, figure 7 shows the influence of the matrix resin and fiber orientation on the heat deflection temperature for PA66/GF and PA6/GF LFT materials. The PA66/GF LFT materials were observed to exhibit significantly higher heat deflection temperature values as compared to PA6/GF LFT materials. It should also be noted that for PA66/GF LFT materials, for both fiber orientation directions, i.e. in flow direction and perpendicular to flow direction, the heat deflection temperature values were higher than the maximum temperature of 215°C that can arise during the e-coating process and subsequent drying and painting processes. On the other hand, PA6/LFT materials can withstand such processes if the temperature remains below 190°C.

Effect of temperature conditions on the LFT matrix materials

With regard to temperature conditions applied during the e-coating process and subsequent painting and drying processes, as mentioned earlier a maximum temperature of 215°C may arise.

In principle if LFT materials are subjected to such temperature conditions then it is important to understand the changes that can occur in the matrix materials. As glass fibres have a melting temperature considerably higher than 215°C, glass fibres are not expected to undergo any changes due to heat treatments. In order to investigate the effect of temperature conditions on the LFT matrix materials, the selected PA6 and PA66 matrix materials were injection moulded without glass fibre reinforcements. The injection moulded specimens were then exposed to the temperature profile of the e-coating process and subsequent painting and drying processes (as mentioned in table I). Figure 8 (a) and 8 (b) and figure 9 show the effect of temperature on the properties of PA66 and PA6 injection moulded specimens. As shown, the tensile modulus, tensile strength and impact strength of PA66 was unaffected by heat treatment. On the other hand the tensile modulus of PA6 was found to increase significantly whereas tensile strength and impact strength were found to decrease due to heat treatment. In order to understand the change of properties of PA6 where the properties of PA66 remained unchanged, differential scanning calorimetry (DSC) analysis was conducted for PA66 and PA6 injection molded specimens before and after heat treatment.

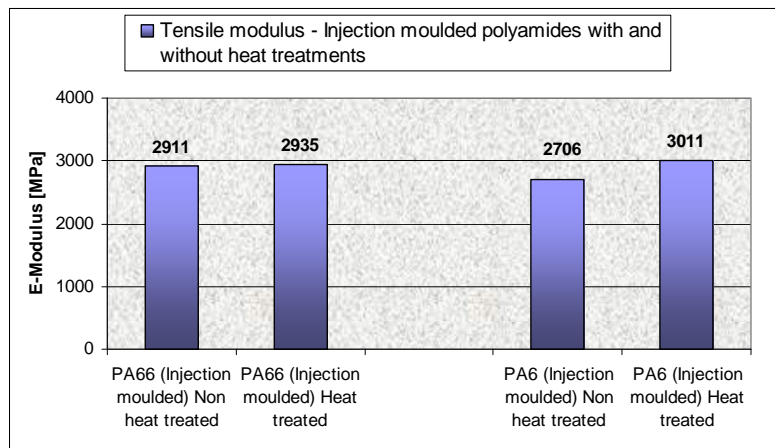


Figure 8 (a)

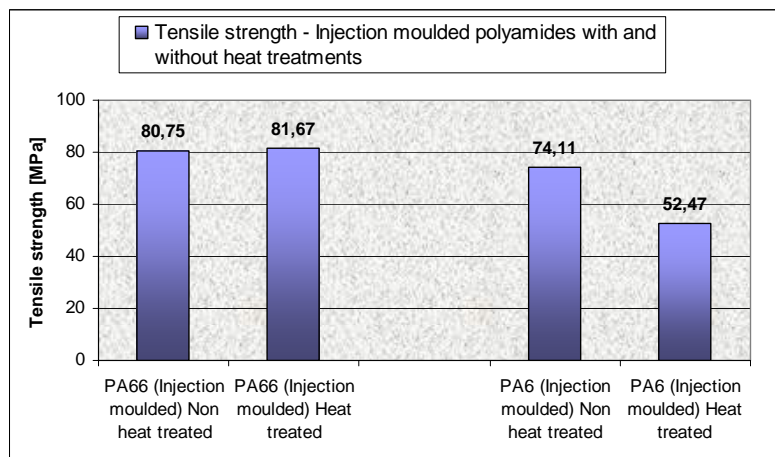


Figure 8 (b)

Figure 8: Tensile properties of non-heat-treated and heat treated PA66 and PA6
(a) Tensile modulus (b) Tensile strength

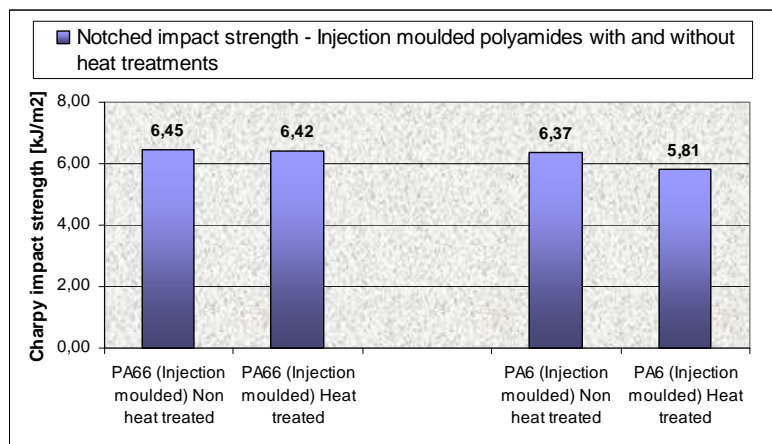


Figure 9: Notched Charpy impact strength of non-heat-treated and heat treated PA66 and PA6

From the results summarized in table III the degree of crystallinity of PA66 resins was found to be unaffected by heat treatment. However, PA6 specimens were found to exhibit additional post crystallization effects due to heat treatment. Similar findings for post crystallization behavior of PA6 due to temperature effects have been reported previously [10]. This effect is the most probable reason for the observed increase in tensile modulus and decrease in tensile strength and impact strength for PA6 after heat treatment.

Table III: DSC analysis for PA66 and PA6 before and after heat treatment

Matrix polymer	Before heat treatment		After heat treatment	
	Heat of melting (J/g)	Degree of crystallinity (%)	Heat of melting (J/g)	Degree of crystallinity (%)
PA66	64.06	34%	62.54	33%
PA6	68.14	36%	72.64	39%

Effect of temperature conditions on LFT materials

The main goal of these investigations was to evaluate the performance of LFT materials after application of the temperature profile and also to evaluate the effect of chemical surface treatments carried out during the e-coating process and subsequent drying and painting processes. In order to understand these effects in detail, in the first step only the effect of temperature on LFT material properties was investigated. As mentioned in table I, various temperatures are applied to the body in white during such treatments. The PA66/GF and PA6/GF LFT samples were exposed to a similar temperature profile in an oven and tested.

Figures 10 (a) and 10 (b) and figure 11 show the effect of temperature on the PA66/GF and PA6/GF LFT material properties in comparison to the non-heat-treated LFT materials. As shown, the mechanical properties of these LFT materials did not change significantly as a result of exposure to the temperature profile used during the e-coating process and subsequent drying and painting processes.

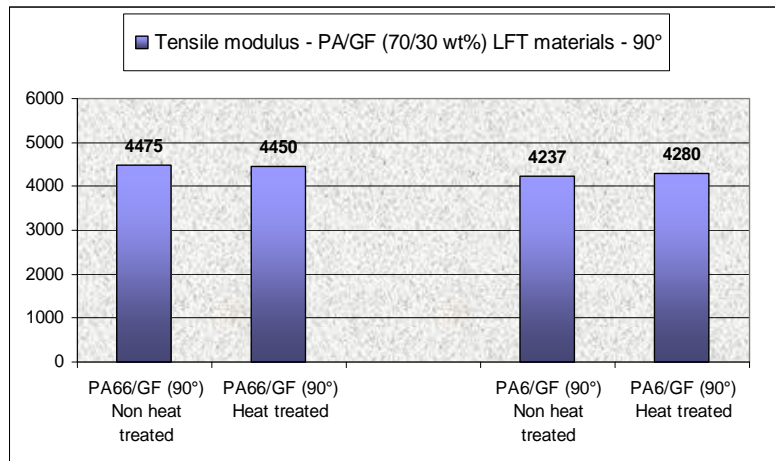


Figure 10 (a)

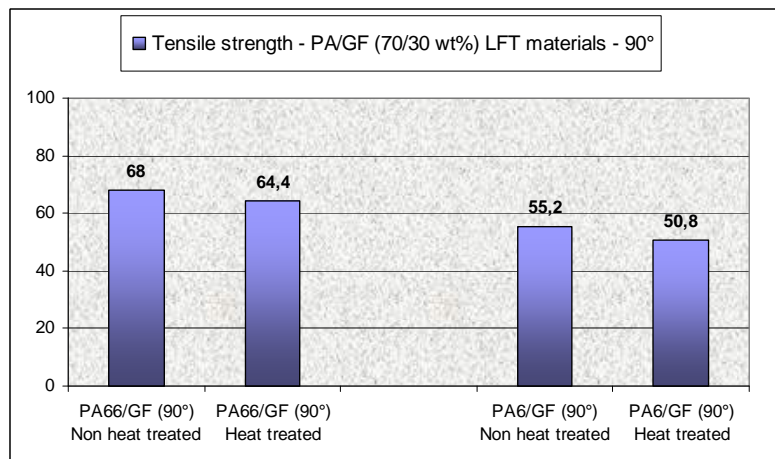


Figure 10 (b)

Figure 10: Tensile properties for PA66/GF and PA6/GF LFT materials before and after heat treatment (a) Tensile modulus (b) Tensile strength; LFT samples taken from perpendicular to flow direction (90°)

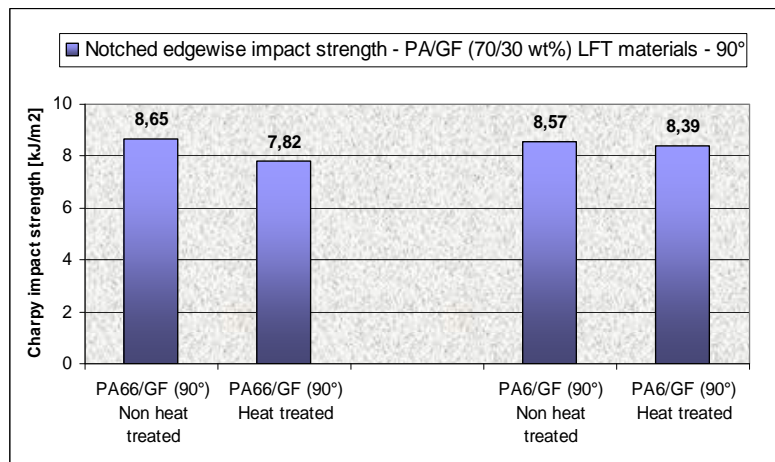


Figure 11: Charpy impact strength for PA66/GF and PA6/GF LFT materials with and without heat treatment

Only slight changes in the material properties were observed; for example the tensile modulus, tensile strength and impact strength of PA66/GF LFT materials were reduced slightly after heat treatment. For PA6/GF LFT materials the tensile modulus was found to increase slightly, tensile strength remained unchanged and impact strength decreased slightly after heat treatment.

Effect of the actual e-coating process on LFT materials

All the previous investigations showed that the neither the investigated LFT materials nor the matrices in the LFT materials display any significant change of material properties after heat treatment applied during the e-coating process. As a result, in the next step of the investigation, PA66/GF LFT and PA6/GF LFT plaques were run through the actual painting line as shown in figure 3, that included the e-coating process and subsequent painting and drying stages. The samples were then prepared for testing and conditioned as mentioned in the material characterization section.

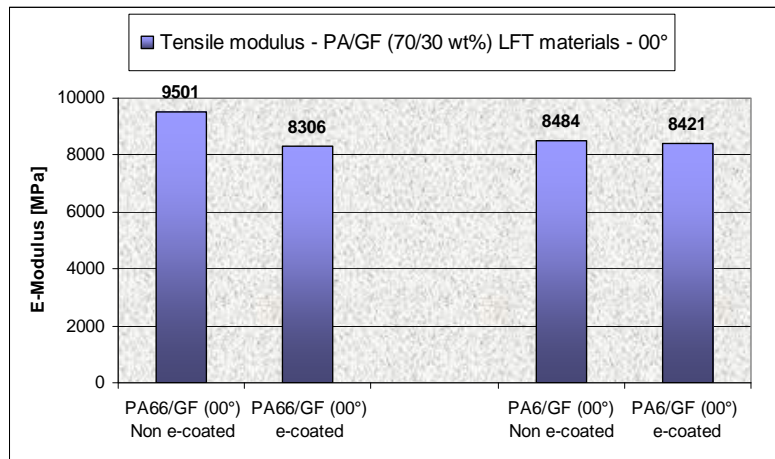


Figure 12 (a)

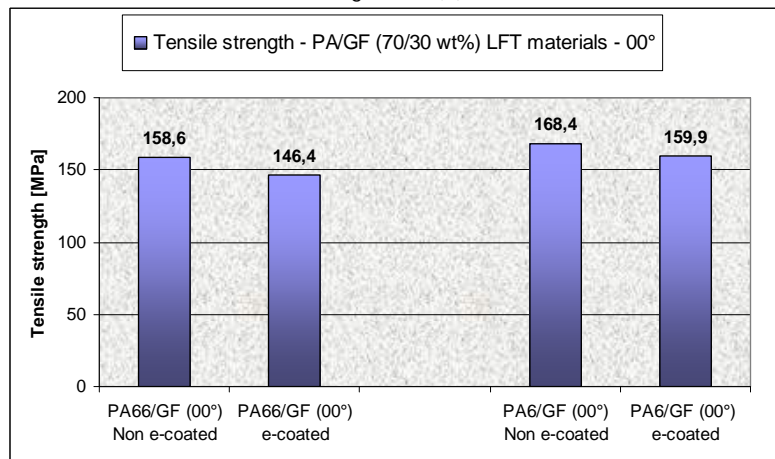


Figure 12 (b)

Figure 12: Tensile properties of non e-coated and e-coated PA66/GF and PA6/GF LFT materials
(a) Tensile modulus (b) Tensile strength

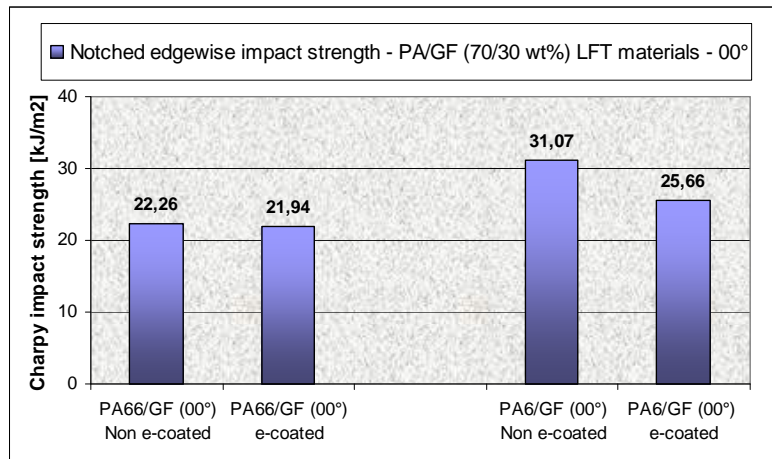


Figure 13: Notched charpy impact strength of non e-coated and e-coated PA66/GF and PA6/GF LFT materials

As shown in figure 12 (a) and 12 (b) and figure 13, the tensile and impact properties of PA66/GF and PA6/GF LFT materials were not significantly affected by the e-coating process. The results shown in figures 10 to 13 confirmed that the heat treatments and chemical treatments carried out during the e-coating process and subsequent painting and drying processes do not affect the performance of the LFT materials.

Summary

The feasibility study was conducted to evaluate the e-coating process sustainability of the LFT materials. The LFT material formulations for these investigations were based on PA6 and PA66 as matrix resins and 30 wt% reinforcing glass fibers. The most important conclusions of this feasibility study are as follows –

- The mechanical properties and heat deflection temperature for PA66/GF and PA6/GF LFT materials were found to depend significantly on the glass fiber orientation obtained in the final LFT components. However, irrespective of glass fiber orientation, PA66/GF LFT materials always exhibited heat deflection temperatures higher than the peak temperature of 215°C that may arise during the e-coating process and subsequent drying and painting processes.
- The investigated matrix materials and LFT materials did not undergo any significant change of properties during heat treatments.
- The investigated PA66/GF and PA6/GF LFT materials were run through an actual e-coating line where the materials were exposed to various surface and temperature treatments. The properties of the composites were not affected significantly by e-coating and subsequent painting and drying processes.

From these investigations it can be concluded that PA66/GF (70/30wt%) LFT materials show high potential for producing components that can be implemented directly into the body in white. LFT components produced using PA66 can sustain the heat treatments and chemical treatments applied to the body in white during e-coating and subsequent drying and painting processes.

It is important to mention that PA66/GF LFT materials have low moisture absorption compared to PA6/GF LFT materials, which is an added advantage for PA66/GF LFT materials for structural applications in the BIW.

The lower heat deflection temperature of PA6/GF LFT materials compared with PA66/GF LFT materials decreases their potential for such applications. However optimization of the glass fiber orientation, and limiting the peak temperature during such processes to 180°C-185°C can lead to a suitable solution.

The described feasibility study leads to the conclusion that PA/GF-based LFT materials might be suitable for structural application in the BIW. In order to evaluate such applications further it is important to conduct investigations to characterize the behaviour of the PA/GF LFT materials during the actual e-coating process. In the next step the use of Dynamic Mechanical Analysis (DMA) and Dynamic Impact Testing is recommended to characterize the materials further. This will help to understand the loss of stiffness of the LFT materials at the high temperatures arising during the e-coating process and subsequent painting and drying processes.

Nomenclature

LFT	-	Long fiber reinforced thermoplastics
LFT-D	-	Direct processing technology for long fiber reinforced thermoplastics
LFT-D/ILC	-	Direct processing technology for long fiber reinforced thermoplastics with in-line compounding facility
PP	-	Polypropylene
GF	-	Glass fibers
PA	-	Polyamide
PA6	-	Polyamide 6
PA66	-	Polyamide 66
PBT	-	Polybutylene terephthalate
PET	-	Polyethylene terephthalate
BIW	-	Body in white
DSC	-	Differential scanning calorimetry
DMA	-	Dynamic Mechanical Analysis

Acknowledgements

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