

STRUCTURE AND PROPERTIES OF LONG GLASS FIBRE REINFORCED POLYAMIDE-66 MODIFIED WITH THERMOSET RESIN

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ABSTRACT

Structure and properties of LGF reinforced polyamide-66 (PA66) blended with a phenol formaldehyde resin (PFR) are discussed. The blending of PA66 with PFR resulted in a decreased water uptake of the composites, which is reflected in the mechanical behaviour. Tensile strength, modulus and toughness values of the LGF reinforced PA66-PFR blends are reported. It is assumed that the developed LGF composites could replace metals in automotive applications such as parts of the cooling system.

1. INTRODUCTION

Several attempts to modify aliphatic polyamides (PA) in order to further improve mechanical performance or to achieve new desirable properties have been published in literature during recent years. One of the best known modification methods is blending of PA with other thermoplastics or with rubbers [1-3]. By blending it is possible to achieve a broad range of properties, which has made this method a popular way of modification also in industrial scale. Usually the targets in blending of PA with other polymers are improvement of impact toughness in dry state and at low temperature, decrease of water absorption and improvement of dimensional stability. The properties of the blends depend on the component properties and on their interaction between each others, but also on mixing ratio and the final morphology of the blend [4]. For example, blending of polyamide with unpolar polymers like polyethylene or polypropylene leads to a rough blend morphology and poor mechanical properties, but finer morphology and better properties are achieved by adding small amount of graft copolymers of polyolefins as a compatibilising agent [5]. Blends of aliphatic polyamides *e.g.* with polyethylene [5,6], polypropylene [7,8] and various rubbers [9,10] have been demonstrated in literature. Additionally, blending of PA with thermosets has recently attained attention as a novel route to achieve new property combinations. From earlier reports it is known that phenol based thermosets have an ability to form strong physical (hydrogen) bonds with several thermoplastic resins, including polyamides [11-13]. The recent studies of our group demonstrated that strong hydrogen bonding exists between carboxylic group of PA66 and hydroxyl group of phenolic formaldehyde resin [14]. This was evidenced by the quantum mechanical calculations for the small molecular weight model compounds, as well as by the experimental analyses by Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

Often PA is reinforced with short glass fibres to further increase the stiffness, the strength and the toughness. By using long glass fibre (LGF) reinforcement with fibre length-to-diameter ratio up to 1000, mechanical requirements needed in high-load-bearing applications can be achieved. On the other hand, it is also commonly known that water affects on properties of polyamide (PA) due to the plastification effect and hydrolysis reaction, which leads to the decreased strength and the modulus. In this respect, water absorption is considered as a fundamental issue in the case of polyamide and in its composites. The present paper reports our findings considering the properties of LGF reinforced PA66-PFR blends. Water absorption of the blends, as well as the mechanical properties of the composites after different treatments are reported.

2. EXPERIMENTAL

LGF PA66 composite pellets (with 11 mm fibre length) based on the polyamide-PFR blends were manufactured by the production technology of FACT GmbH. The bone shaped specimens were then injection moulded using Arburg Allrounder 320 C 600-250 injection moulding machine with a maximum clamping force of 600 kN. The processing temperature was 240-300 °C and the mould temperature 60 °C.

Tensile test was carried out according to the standard ISO 527 using bone shaped specimens. Unnotched Charpy impact toughness analysis was performed according to the standard ISO 179. Dynamic mechanical thermal analysis (DMTA) spectra were taken on rectangular specimens (55 x 10 x 4 mm³; length x width x thickness) in tensile mode at 10 Hz using a Eplexor 25 N device of Gabo Qualimeter. Complex modulus (E^*) and its constituents (E' and E''), mechanical loss factor ($\tan\delta$) were measured at a heating rate of 1 °C/min. Scanning electron microscopy (SEM) was used to analyse the fracture surfaces after impact toughness test.

3. RESULTS & DISCUSSION

In a previous work it was shown that PA66 is able to form strong hydrogen bonds between PFR resins [14]. This physical connection between the blend components is based on the carboxylic group of the amide moieties of PA66 and on the hydroxyl groups of PFR. It was shown that the strength of such hydrogen bonds may exceed that of the amide-amide or amide-water hydrogen bonds, indicating that PFR could protect PA66 against water absorption. Furthermore, this hydrogen bond connection leads to a molecular level miscibility in blends. However, it is known that the morphology of thermoplastic-PFR blends can be controlled by the addition of cross-linking agent, leading to the phase separation [15]. In the present work, the PFR part was cross-linked with hexamethylene tetramine, which was noticed to lead to a partial phase separation. This was evidenced by the particle formation as shown in a micrograph of Fig. 1, and also by the two T_g values as determined by DSC.

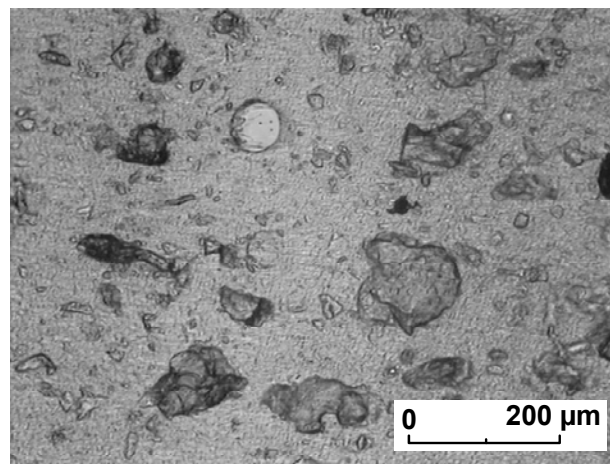


Fig. 1. Optical micrograph of PA66-PFR blend (10 wt-% of PFR) showing the phase separation.

It can be expected that water absorption of PA66 is decreased upon blending with PFR (even after cross-linking of PFR), since the hydrogen bonding strength between amide functionalities and hydroxyl groups of phenol is relatively strong. Fig. 2 shows the water uptake of matrix against exposure time in the PA66 composites with and without PFR (75 % relative humidity at 23 °C). Large difference in absorption rate can be noticed, so that at equilibrium state mass gain of *ca.* 4.7 wt-% is observed for PA66 and *ca.* 3.3 wt-% for the blend sample. This result demonstrates the protective effect of thermoset resins against water, when blended with PA66.

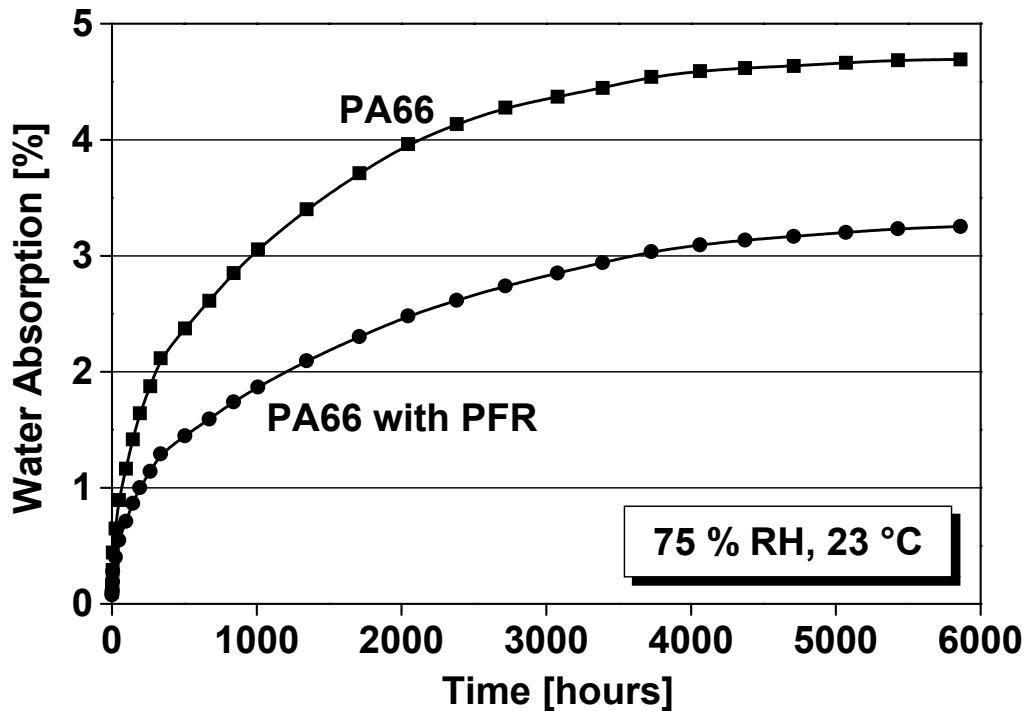


Fig. 2. Water absorption of PA66 and PA66-PFR blend as a function of time.

The tensile properties of LGF reinforced PA66-PFR composites were analysed at dry state, but also after exposure in humid climate of 75 % humidity for 9000 hours. The gained values were normalised to 20 vol-% fibre content to distinguish the effect of PFR addition on properties. Fig. 3 shows the tensile modulus of the studied blends as a function of PFR concentration in matrix. At dry state, the modulus was almost unaffected by the addition of PFR. Therefore, the phase separated PFR did not result in increase of the stiffness, which was somewhat unexpected. After conditioning in humid climate, the stiffness of the all formulations decreased considerably. However, the modulus of blends including PFR was somewhat higher, presumably due to the lower amount of absorbed water.

Normalised tensile strength values of PA66-PFR blends are shown in Fig. 4 as a function of PFR content. As shown, the dry state strength of the composites decreases by *ca.* 25 MPa upon PFR addition. However, at moist state there is no difference between the samples with and without PFR. Decrease in strength values at dry state is most probably related to a phase separation process taking place in blends, resulting in PFR particle formation. Also in previous studies it has been observed that particulate inclusions (like mineral fillers) in polyamide cause the loss of the strength [16].

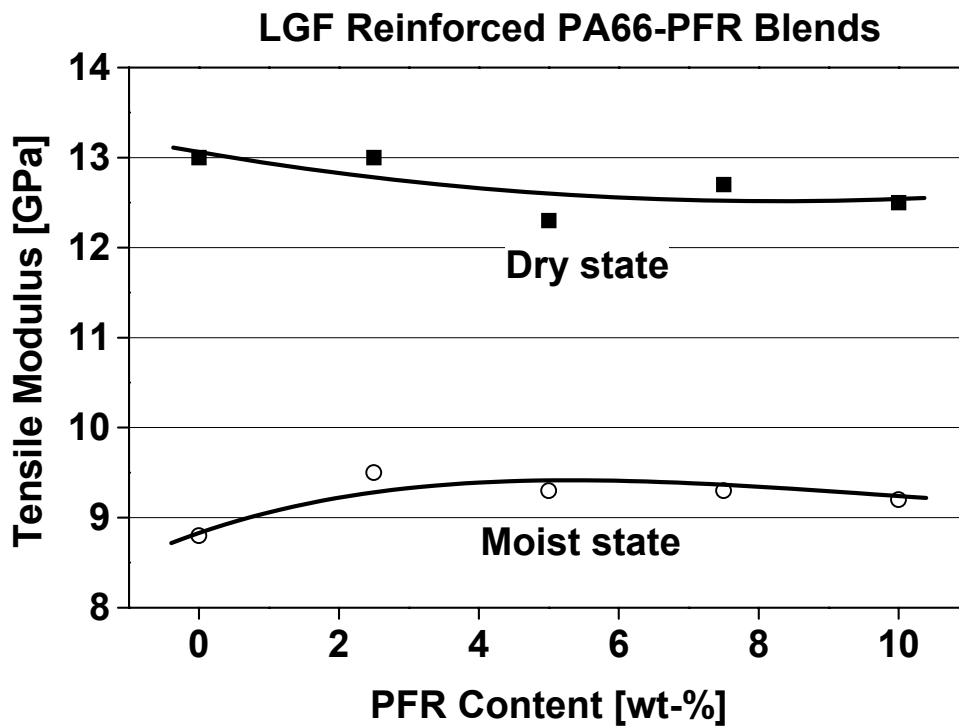


Fig. 3. Normalised tensile modulus of LGF reinforced PA66-PFR blends including 20 vol-% of fibres in average: in dry state and after 9000 hours storing at 75 % RH (RT).

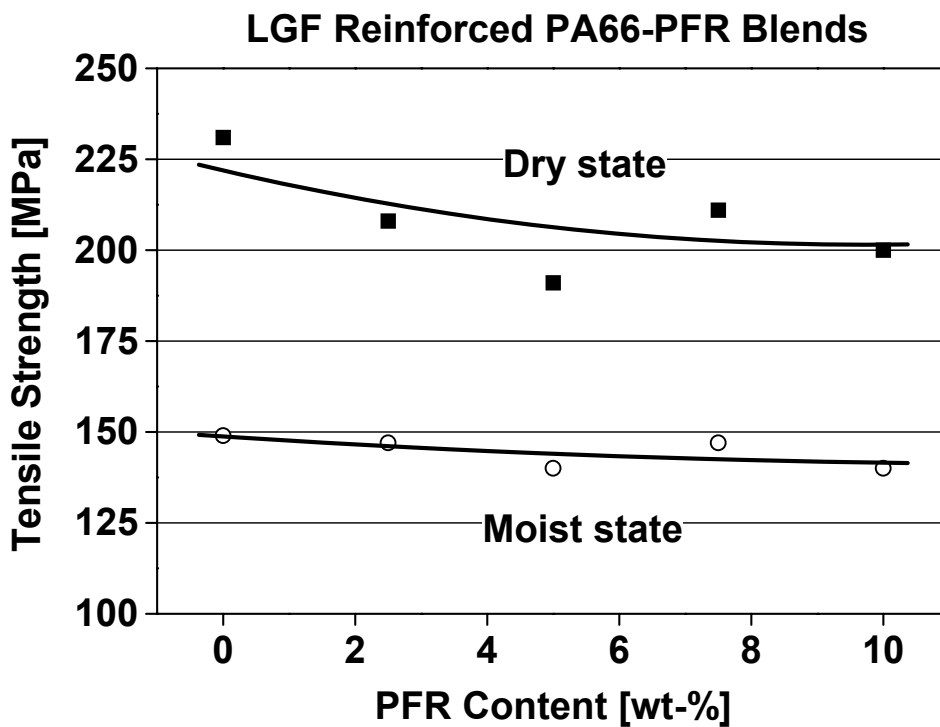


Fig. 4. Normalised tensile strength values of LGF reinforced PA66-PFR blends including 20 vol-% of fibres in average: in dry state and after 9000 hours storing at 75 % RH (RT).

It is widely reported that water molecules enhance the impact toughness of polyamide due to the plasticization effect, which “softens” the polymer and improves its capability to absorb energy during the impact loading. In this work the effect of water uptake on Charpy impact toughness of PA66-PFR blends was analysed by using both unreinforced and reinforced samples, in order to distinguish the influence of PFR from fibre related factors. The water treatment was in this case carried out by immersing the specimens in water for 200 hours at 50 °C. Results of the impact toughness tests are collected in Table 1. As it can be seen, the toughness of the unreinforced blends including HMTA is considerably lower compared to the corresponding samples without cross-linking agent. This can be explained by the phase separation process of the cross-linked samples, since the formed PFR particles may work as crack initiation points in PA66 during the impact loading. Upon water treatment of the samples without HMTA, the toughness of the blend with 5 wt-% of PFR increases considerably but that of the sample with 10 wt-% of PFR even decreases. This can be explained by the fact that in the sample including 5 wt-% of PFR there are more available amide groups that are not connected with phenolic groups (and therefore they can be bonded with water), compared to higher PFR concentration. On the other hand, increase of toughness after water treatment is observed also in the case of 5 wt-% samples as PFR is cross-linked with HMTA. In this case there are less oligomeric PFR molecules available that can hydrogen bond to amide groups in molecular level compared to samples without HMTA, due to the reason that part of the PFR is partly in phase separated, particulate form.

As PA66-PFR blends are reinforced with 30 vol-% of LGF, toughness is at much higher level compared to unreinforced samples. Secondly, in this case there are only small differences between the different formulations. However, it can be seen that, similarly as in the case of unreinforced samples, the cross-linking of the PFR components with HMTA results in decreased toughness. After immersion of the reinforced PA66-PFR samples in water for 200 hours at 50 °C, the toughness values increase but not as dramatically as in the case of unreinforced blends. The explanation for this behaviour is the fact that the long glass fibres dominate in the fracture process of reinforced samples rather than the matrix.

Table 1. Charpy impact toughness of unreinforced PA66-PFR and the blends including 30 vol-% of LGF at dry state and after water immersion for 200 hours at 50 °C. Formulations are given as PA66/PFR (wt-%).

<i>Formulation</i>	<i>Cross-linking with HTMA</i>	<i>LGF reinforcement</i>	<i>Charpy at dry state [kJ/m²]</i>	<i>Charpy at moist state [kJ/m²]</i>
PA66	No	No	n.b.	n.b.
95/5	No	No	40 ± 11	78 ± 20
90/10	No	No	38 ± 6	30 ± 11
95/5	Yes	No	21 ± 3	33 ± 13
90/10	Yes	No	12 ± 4	16 ± 1
PA66	No	Yes	84 ± 10	105 ± 6
95/5	No	Yes	88 ± 9	111 ± 6
90/10	No	Yes	78 ± 4	101 ± 10
95/5	Yes	Yes	79 ± 8	103 ± 6
90/10	Yes	Yes	77 ± 6	97 ± 3

Information about the thermal behaviour of the blends can be obtained by dynamic mechanical thermal analysis, DMTA. Fig. 5 shows the DMTA spectra of unreinforced PA66 and its blend with 5 wt-% of PFR. At room temperature the complex modulus $|E^*|$ is somewhat higher in the case of PA66-PFR blend compared to neat PA66, which can be explained by the hydrogen bonding network taking place upon blending. However, as temperature is increased, the differences between the samples become minor so that the curves coincide at temperature of about 110 °C. This phenomenon shows that the hydrogen bonding density decreases upon heating.

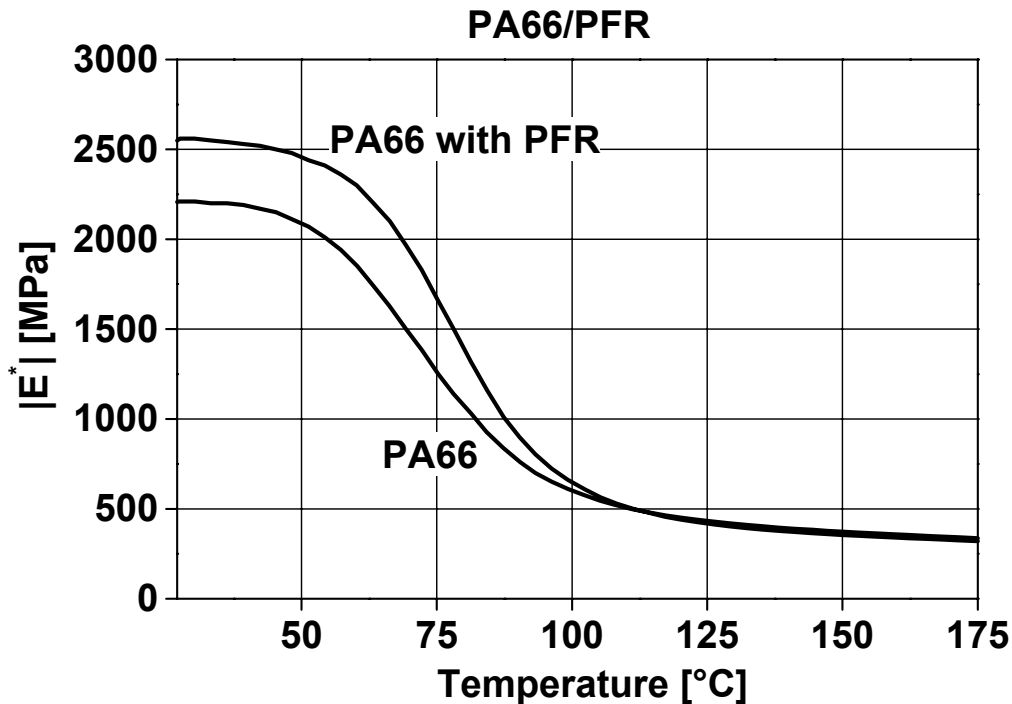


Fig. 5. DMTA spectra of unreinforced PA66 and a PA66-PFR blend.

Adhesion between glass fibres and polyamide matrix was analysed by scanning electron microscopy for tensile fracture surfaces (Fig. 6). To see the effect of water, chemicals and temperature on adhesion, the samples were immersed in water-glycol 1:1 mixture for 250 hours at 130 °C, after which they were fractured by using a standard tensile test. It can be seen that in the case of LGF PA66 the fibres are poorly connected to the matrix and the fibre surfaces are not any more covered with polyamide, after hydrolysis and aging treatment (Fig. 6a). This indicates that the immersion in water-glycol mixture has disrupted the adhesion between the fibres and the matrix. The failure mode of the matrix is changed to more ductile, as indicated by the matrix deformation patterns. Also in PA66-PFR blends the fibre-matrix adhesion is poorer than in the case of untreated composites, but in this case the fibres are still connected to the matrix (Fig. 6b). Additionally, there is still some matrix which is covering the fibre surfaces. This suggests that the used of PA66-thermoset resins as a matrix in LGF composites could lead to a better stability of the material. However, the phenomenon needs some further investigations for explicit conclusions.

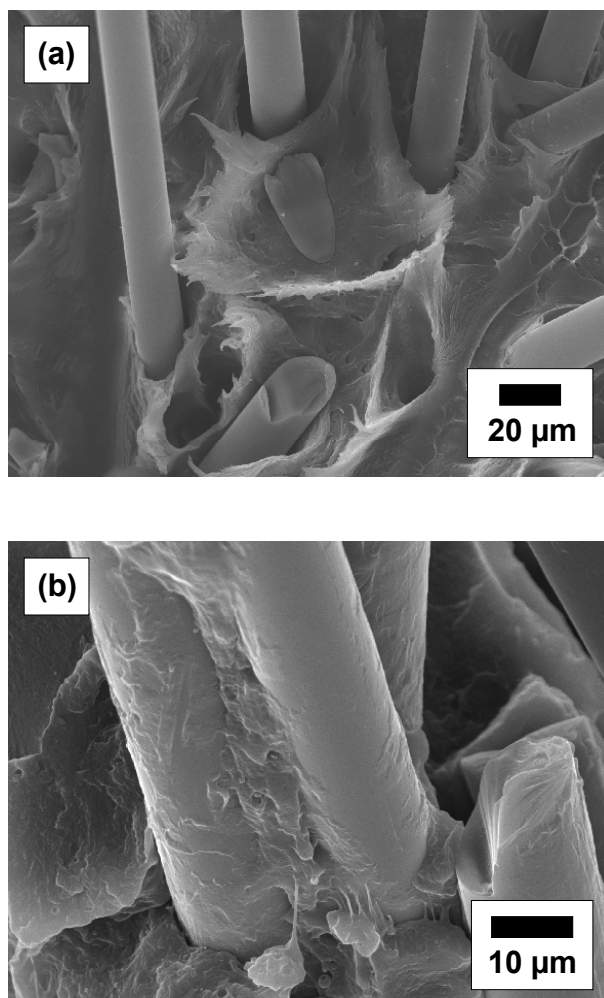


Fig. 6. SEM fractographs after Charpy impact toughness test for aged samples (250 hours immersion in water-glycol mixture at 130 °C): a) LGF reinforced PA66 and b) LGF reinforced PA66-PFR blend with 5 wt-% of PFR part.

4. CONCLUSIONS

As PA66-PFR blends were used as a matrix in LGF reinforced composite materials, water absorption was decreased by 30 % compared to LGF PA66. The decrease in water uptake was also reflected in mechanical properties like tensile modulus, which was higher in the case of blend samples compared to LGF PA66 after treatment in humid conditions. Impact toughness of LGF reinforced PA66 remained more or less unaffected upon blending with PFR. DMTA analyses showed that the hydrogen bonding density between PA66 and PFR is decreased at elevated temperature. Furthermore, SEM micrographs showed that the fibre-matrix adhesion in LGF PA66 composites was essentially lost after aging in water-glycol mixture, whereas in the case of LGF reinforced PA66-PFR blends there is still some interfacial adhesion left. Therefore, it seems that PFR can protect the interface between long glass fibres and the polyamide matrix, resulting in better overall stability of the composite. Applications of the developed composite materials are found in parts of the automobile cooling systems, where the materials are subjected to high temperatures and chemicals. However, before the materials can be applied in such parts, further optimisation of the material system must be carried out (proper selection of the components, optimised mixing ratio *etc.*)

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