THE EFFECT OF THE FUNCTIONALIZING AGENT TYPE ON PROCESSABILITY, MECHANICAL AND THERMAL PROPERTIES OF POLYPROPYLENE-BASED COMPOSITES

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The aim of this study is to monitor the influence of the addition of glass fibers (GF_s) treated with polydimethylsiloxane (PDMS) and aminopropyltrimethoxysilane (APTMS) on processability and mechanical and thermal properties of polypropylene. The composites based on PP/GFs were processed on a twin screw extruder-granulator, using 20% glass fibers, relative to the polymer mixture (PP/PP-g-MA). Composite granules obtained by extrusion were used in order to determine flow indices and the values obtained demonstrate that the addition of 20% GF_s does not raise serious processability problems (viscosity of the mixture does not vary very widely). Thermal stability tests under load - HDT demonstrate that the best thermal stability is that of the composite reinforced with GF_s-PDMS. Mechanical tests also demonstrate that tensile strength, resistance to bending, modulus and elongation at break are superior for the composite reinforced with PP/GF_s-PDMS compared with the one reinforced with GF_s-APTMS. This can be attributed to the fact that there is a better compatibility between polydimethylsiloxane-treated fibers and the polypropylene matrix compared with those functionalized with aminopropyltrimethoxysilane. Moreover, glass fibers treated with polydimethylsiloxane are more stable to changes in temperature and pressure that the composite is subjected to during processing. TG-DSC results demonstrate a higher thermal stability of the composite with the addition of functionalized fibers.

Keywords: polypropylene, melt flow index, thermal behavior.

INTRODUCTION

Short glass fibers (GFs) are the most commonly used reinforcing agents in composites based on polypropylene (PP), mainly due to their physical and mechanical properties and the cost price (Biswas *et al.*, 2014; Aguilar *et al.*, 2014). Final properties of composite materials are strongly influenced by the strength and stability of the interphase that develops at the fiber/polymer matrix boundary and by mass ratio between components (Etcheverry and Barbosa, 2012). Adhesion between phases is also affected by aggressive environmental conditions, temperature, humidity as well as final tests that the material will be subjected to during the exploitation process (Ota *et al.*, 2005). Due to the non-polar nature of polypropylene (PP), interaction with inorganic disperse phase is low. Both chemical compounds (functionalization agents) applied to the fiber surface, and coupling agents may be used to improve compatibility. Functionalization agents improve adherence to interface through physical and chemical bonds that develop between components in the system (Zaretsky *et al.*, 2004). Moreover, functionalization agents protect glass fiber surface from aggressive environmental conditions such as humidity and reactive fluids (Sockalingam and Nilakantan, 2012).

Organosilanes are considered the most widely used functionalization agents that improve interfacial bonding of glass fibers reinforced composites. Organosilanes' ability to improve adherence depends on several factors such as the nature, type, silane layer thickness, and surface treatment method used for fibers (Broughton *et al.,* 2010; Rausch *et al.,* 2010).

Another commonly used method to improve the glass fiber/polymer interphase is the introduction of a low amount of a polymer modified with specific groups in the thermoplastic matrix (Lin *et al.,* 2015).

Polar groups may be introduced in the polypropylene chains by reactions with species that contain functional groups in their structure, such as ester, carboxylic or anhydride groups (Mäder *et al.,* 1996). This methodology is used in composites based on PP/GF_s, where small amounts of polypropylene-graft-maleic anhydride (PP-g-MA) is introduced into the mixture, in order to react with the amino group on the surface of the silanized glass fibers (Szentes *et al.,* 2012).

MATERIALS AND METODS

Materials

The materials used in this study were the following: polypropylene co-polimer TIPPLEN K 948; polypropylene-graft-maleic anhydride (PP-g-AM), average Mw~9.200 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 wt.%; poly (dimethylsiloxane) (PDMS), grade: analytical standard, vapor pressure: 153 mmHg (20^0C), density: 0.82 g/mL, molecular weight: 236.53 wt.%; (3-aminopropyl)trimethoxysilane (APTMS): assay: 97%, refractive index n20/D0: 1.424, density: 1.027 g/mL, molecular weight: 179.29 wt.%; borosilicatic fiber type E, length=4.5 mm, diameter=13 μm, alkaline oxide content>1.

Method

Composite materials based on polypropylene reinforced with glass fibres are obtained in two stages:

- In the first stage – 100g of glass fibers were added in 1 litre of solution containing ethyl alcohol, distilled water and a percentage of 0.5% of functionalizing agent (PDMS or APTMS), relative to the amount of glass fibers. The mixture was maintained under continuous stirring for 24 hours, followed by drying in a hot air oven at a temperature of 80°C and subsequently at 130°C to complete the silanization reaction and evaporation of alcohol.
- The second stage consists in developing the composite on a counter-rotating twin screw extruder granulator as follows: polypropylene powder is introduced in the extruder along with maleic anhydride grafted polypropylene, and glass fibers functionalized with PDMS or APTMS, according to the following 9 zones temperature profile of the extruder: 130-138-161-174-193-189-167- 156-146°C, with screw rotation speed of 100-300 rpm. From composite granules, specimens with the size of 100x10x4 mm were obtained in a laboratory electric press, with the following processing parameters: Temperature = 175°C; Pressure = approx. 150 kN; Preheating time = 15 min; pressing time = 15 min; Cooling time (at 300 kN pressing) = 12 min.

After conditioning at room temperature the specimens were subjected to mechanical and thermal determinations.

Tested formulas based on composites reinforced with glass fiber are presented in Table 1.

Table 1. Formulas of composites based on polypropylene reinforced with treated or untreated glass fibers

Raw materials / Symbol	MU	PP	P0	P01	P1	P2	P3
PP K948	%	100	97	90	77	77	77
PP-g-AM	%	-	3	-	3	3	3
PP/GF_S untreated	%			20	20	-	-
GF_S - PDMS	%	-	-	-	-	20	-
GF_S - APTES	%	-	-	-	-	-	20

Characterization

*C*ounter-rotating twin screw extruder granulator, TSE 35 type; Electrically heated press, TP 600 with the following characteristics: pump pressure max. 300 bar, pressing surface 400 x 400 mm, work temperature 150-300°C adjustable; HDT thermal stability under load was evaluated using Qualitest HDT1, according to SR EN ISO 75, using 2°C/min heating rate, 0.34 mm standard deflection at 1.8 MPa flexural stress, in siliconic oil environment; Tensile and flexural (3-point bending) tests were performed using INSTRON 5982 machine, equipped with 10 and 100 kN load cells, on a minimum of 6 specimen per test; Thermal behaviour (DSC-TG) of the samples was determined with the Netzsch 449C STA Jupiter device. Samples were introduced in a closed aluminium crucible and heated at 10 K min^{-1} from room temperature to 200°C, with dry air flow of 20 mL min^{-1}.

RESULTS AND DISCUSSION

Mechanical Tests

Table 2 shows the physical-mechanical values obtained for the control sample (PP) and those of composites based on polypropylene reinforced with 20% glass fibers treated with PDMS or APTMS and untreated.

The hardness of composites does not vary significantly, relative to the reference value (PP) of approximately 6°Sh D. Increasing mixture hardness within these (acceptable) limits does not raise serious technological problems during processing.

Flexural strength, Young's modulus and breaking load of the mixtures are significantly improved when using GF_s functionalized with PDMS (P2) and APTMS (P3), due to bonds that form at the interphase, compared with values obtained for the control sample (PP). This can be attributed to the interactions occurring between amino groups present on the surface of treated GF_s and anhydride groups of PP-g-AM. In composites reinforced with untreated GF_s (P01 and P1) values obtained from mechanical determinations are much lower. This is due to reinforcing phase crowding and pores generating in the material, due to evaporation of water molecules on the surface of glass fibers.

Elongation% is maximum in the case of mixture (P0) due to the addition of 3% PP-g-MA. It acts as a plasticizer and reduces the viscosity of the mixture. In the case of

mixture (P01), elongation value decreases to 1.95% due to the introduction of 20%, untreated glass fibers which leads to increased viscosity of the mixture. As shown in the case of composites containing both PP-g-AM and GF_s-PDMS or GF_s-APTMS (P2 and P3), elongation at break values increase due to a better adhesion between phases. Moreover, depending on the type of functionalizing agent applied to the surface of the fibers, elongation shows maximum values comparable to those of the mixture (P0). This allows the use of high amounts of reinforcing agents without affecting processability.

The density of the tested mixtures increases with the addition of glass fibers.

Table 2. Values of physical-mechanical determinations obtained for control samples and composite materials

Determinations/Symbol	PP	P0	P01	P1	P2	P3
Hardness °Sh D	66	65	69	70	72	70
Tear load, N	50.48	51.02	53	54.71	67.42	60.94
Resistance to bending, MPa	33.38	33.81	33.73	34.19	40.98	38.62
Young's modulus (GPa)	1.63	1.73	2.34	2.45	2.75	2.55
Elongation (%)	3	3.28	1.95	2.3	3.13	2.9
Density, g/cm^3	0.694	0.682	1.093	1.190	1.190	1.190

Melt Flow Index (MFI)

Tests for determining the melt index were carried out at a temperature of 180°C using a pressing force of 5 kg.

The MFI results of the six samples are shown in Figure 1 and indicate that with the addition of treated or untreated glass fibers, the MFI value decreases. This can be attributed to the presence of fibers in the melt and their partial alignment, which affect the viscoelastic dynamic of the melt and thus decrease the mobility of molecular chains. However, the flow properties of blends that contain glass fibers are improved significantly by the introduction of coupling agents such as PP-g-MA, and depending on the type of organosilane applied to the surface of the fibers. The best yield, relative to the control sample (PP) is that of mixture (P0), because the PP-g-MA reduces the degree of crystallinity (molecular weight) of polypropylene. In the case of the mixture (P2, and P3, respectively) containing PDMS or APTMS treated glass fiber and PP-g-MA, the flow properties are far superior (71-69.6 g/10min) compared to the mixtures (P01 and P1). This demonstrates that by the appropriate treatment of the glass fibers surface and by introducing PP-g-AM, the viscosity of the mixture is significantly reduced and can be processed easily by injection with high amounts of reinforcing agent without raising serious processability problems and excessive wear of equipment.

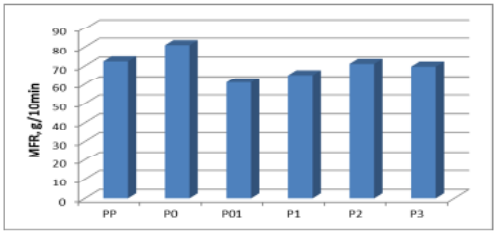

Figure 1. Values of flow index obtained on control samples and PP/ GF_s treated and untreated composite samples

Thermal Stability under Mechanical Loading - HDT

Softening or deflection temperature determinations (HDT) of blends based on polypropylene reinforced with treated and untreated glass fibers were performed in compliance with SR EN ISO 75, and the resulting values are presented in table 3.

The analysis shows that the thermal stability of the blends reinforced with untreated glass fibers (P01), GF_s-PDMS (P2) or GF_s-APTMS (P3) improve the thermal stability of the composites compared with the control sample (PP) by about 60°C. This can be attributed to the fact that by adding glass fibers thermal stability improves and flammability of the products reduces. However, the best thermal stability is that of P2 blend, due to the presence of Si-O-Si group in the PDMS main chain, which gives an excellent temperature stability.

Table 3. Values of HDT deflection temperature obtained on control samples and PP/GF_s composite samples

Symbol	Temp [°C]
PP (K 948) (175 °C)	64,9
P0 (175 °C)	71,1
P01 (175 °C)	80
P1 (170 °C)	95,3
P2 (170 °C)	125,5
P3 (170 °C)	109,6

Complex Thermal Analyses

The thermal analyses of the four samples reveal important differences from both thermal behavior and mass changes in the range of 30 to 900°C. From the point of view of the thermal behavior we can observe that the melting point of the four samples is in the 170 and 180°C.

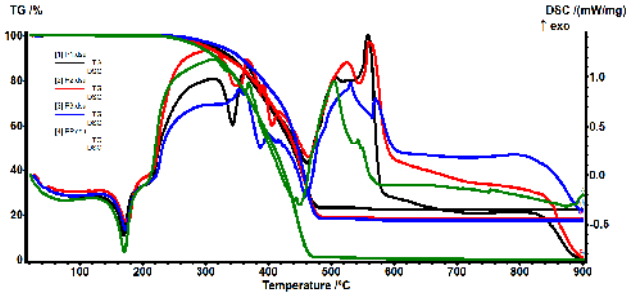

Figure 2. DSC-TG curves recorded on control samples and PP/PP-g-AM/GFs composite samples

The use of the functionalized glass fibers lead to an increasing stability of the samples, the melting point increasing while, the use of bare glass fibers lead to a decrease of the stability proved by the decreasing of the melting point. The very good compatibility between PP and GF_s-PDMS can be highlighted by the splitting of this peak into two peaks (centered at 172.0 and 178.0°C). All the three composite samples are completely burned at ~600^0C, the last strong burning effect being centered at 558.4;

560.2 and 570.3°C while the bare PP exhibit this effect at 550°C. The mass loss was analyzed and based on these data it can conclude that P2 and P3 lost 4.19 and respectively 4.90% comparing to P1 which means that the degree of functionalization of GF_s was ~22% in both cases.

CONCLUSIONS

The results obtained from mechanical determinations show that the addition of small amounts of coupling agent (PP-g-MA) and surface treatment of fibers with organo-silanes, especially PDMS, considerably improve adherence to interphase through amino and anhydride groups. The flow properties of blends are strongly influenced by the type of treatment applied to the surface of the fibers and the presence of a coupling agent because they influence the viscosity of the mixture, in a positive sense. Thermal stability, HDT, shows significantly higher values compared with the control sample (PP), in composites containing glass fibers, especially in the case of blends containing PDMS modified glass fibers.

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