INFLUENCE OF COUPLING AGENTS ON THE POLYMERIC MATERIAL / DISPERSE MATERIAL INTERFACE

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This paper presents the method of obtaining and the characterization of polypropylene-based composites reinforced with glass fibers and treated with coupling agents based on polydimethylsiloxane (PDMS), in the presence of a coupling agent such as polypropylene grafted with maleic anhydride (PP-g-MA), processed using a twin screw extruder granulator. The influence of coupling agents plays an important role in adhesion to the interface and in determining the properties of the composite. A major disadvantage of polypropylene matrix is given by the lack of functional groups, while the introduction of treated glass fibers results in composites similar to those obtained in the presence of conventional reinforcing agents (talcum, calcium carbonate, etc.). In this regard, adding 3% PP-g-MA in the polypropylene matrix under the influence of temperature and shear forces developed within the processing machine (extruder) results in opening the maleic ring, and the resulting carboxylic groups react with functional groups present on the surface of reinforcing materials, improving dispersion and interfacial adhesion. The materials used, both glass fibers and the resulting composite, were characterized physico-chemically, morphologically by SEM, and structurally by XRD, FTIR, etc. The results demonstrate good compatibility between phases in the presence of a coupling agent and of treated glass fibers compared with samples obtained in the absence thereof.

Keywords: composite, coupling agent, glass fibres

INTRODUCTION

An important class of engineering materials is produced by compounding of short glass fibers and thermoplastics. These composites offer excellent mechanical properties, economy and are easily produced into different shapes by injection molding, compression molding, or extrusion (Karsli and Aytac, 2011).

In last few decades, intensive research efforts have been devoted, especially, to achieve a better understanding of the interphase between reinforcement and matrix since the mechanical properties of composite materials highly depend on the interphase properties (Fonseca *et al.*, 2014). The key factors to manufacture high mechanical performance lie on the equilibrium between the fibre content and their aspect ratio (length/diameter), and the adhesion level between the constituents (interphase) (Zhuang *et al.*, 2010). Interphases between reinforcement and matrix are formed by the inter-diffusion of sizing and matrix (Kano-Ibarretxe *et al.*, 2012), resulting in different compositions and properties compared to the bulk matrix.

Polypropylene is a commodity thermoplastic belonging to the polyolefin group of polymers, which are widely used due to their low cost and excellent chemical resistance. However an, inherent property of the polyolefin group is that they are nonpolar which means that they have a low chemical affinity with other materials,

therefore much of the interface strength is provided by mechanical interlocking and compressive residual stresses created during cooling (Yan *et al.*, 2013).

Many studies have been conducted on physical and chemical methods to improve the adhesion between the fiber and matrix through a modification of the fiber and/ or the polymer matrix (Feller and Grohens, 2004). A coupling agent is just like a molecular bridge in the interface of inorganic filler and organic polymer matrix. Because of the hydrophilic nature, the fiber does not wet or interact with hydrophobic polymer due to the difference in surface energies. It is necessary to treat the fiber with a coupling agent in order to improve the compatibility between filler and matrix. A widely used coupling agent is organic silanes, which formula can be simply written as $RSiX_3$, where R is a non-hydrolyzable organic group which can be combined with polymers, and X is a hydrolyzable group, for instance, an alkoxy group such as —OC2H5, —OCH3 etc (Liu *et al.*, 2008).

The polydimethylsiloxane coupling agent, with Si-O-Si backbone shows excellent heat and UV radiation stability, low-temperature flexibility, good hydrophobicity, and excellent moisture resistance (Bogoeva-Gaceva and Grozdanov, 2006).

According with the literature (Noranizan *et al.*, 2012), an efficient method to enhance the adhesion between different types of fibres and polypropylene matrices, and therefore improve the final overall mechanical characteristics of the composite, is the addition of polypropylene grafted maleic anhydride (PP-g-MA) to the system (Etcheverry and Barbosa, 2012; Biswas *et al.*, 2014).

MATERIALS AND METODS

Materials

The materials used in this study were the following: polypropylene homopolimer TIPPLEN H 949A, manufactured by Tiszai Vegyi Kombinat RT (TVK), HUNGARY; polypropylene-graft-maleic anhydride (PP-g-AM), average Mw~9.200 by GPC, average Mn~3,900 by GPC, maleic anhydride 8-10 Wt.%, manufactured by Sigma Aldrich USA; poly (dimethylsiloxane), grade: analytical standard, vapor pressure: 5 mmHg (20^0C), mol wt - average M_w ~95,000, average M_n ~50,000, manufactured by Sigma Aldrich USA, borosilicatic fiber type E, length=4.5 mm, diameter=13 µm, alkaline oxide content>1, manufactured by Polydis, RO.

Composites based on polypropylene reinforced with glass fibres are obtained in two phases:

- In the first stage – 100g of glass fibers were added in 1litre of solution of PDMS 0.5%, and allowed to react at room temperature for 8h. The fibers dried in advance at 80°C and thereafter are subjected to a heat treatment at 130°C for 20 min.

- The second stage consists in developing the composite on a counter-rotating twin screw extruder granulator: polypropylene powder is introduced in the extruder with the glass fibres untreated and treated with coupling agents poly (dimethylsiloxane) and polypropylene grafted with maleic anhydride at the temperature profile of 155°-160°-165°-170°-175°-180°C, residence time of 80s and rotation of 100 rpm. The composite is then granulated and dried in the pelletizer and subsequently subjected to physical-mechanical, structural and morphologic tests. We developed 7 variants of polymeric composites based on polypropylene reinforced with glass fibres untreated in an amount of 10, 20 and 30% and polypropylene/3%PP-g-AM reinforced with glass fibres treated with PDMS in an amount of 10, 20 and 30%.

The specimens for mechanical tests were prepared by electrically heated press (TP 600 Fontijne Grotnes, Nederland) at a temperature of 165°C, preheat = 10 min, pressing=15 min, cooling=12 min and pressure of 150kN.

Influence of PP-g-MAH compatibilizer on the morphology, structural and mechanical properties of short glass fiber reinforced polypropylene composites was examined.

Characterization: counter-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, two work spaces, work temperature 150-300°C ADJUSTABLE, manufactured by Fontijne Grotnes, Nederland; FTIR microscopy by using a Thermo iN10 MX FTIR microscope operated in reflection mode; X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature, Cu-Kα radiation from a Cu X-ray tube (ran at 15mA and 30 kV) was used; SEM images were recorded on a HITACHI S2600N electron microscope coupled with an EDS detector, on samples covered with a very thin silver layer.

RESULTS AND DISCUSSION

In Table 1 are presented the results of physical and mechanical determinations: hardness and tensile strength of polypropylene, PP / 3%PP-g-MA, of the polypropylene based composites reinforced with glass fiber percentage between 10-30% in the absence of the coupling agent and PP / 3% PP-g-MA / PDMS treated glass fibers in a percentage of 10-30% based composite.

- Hardness Values - varies considerable from 73°SH D for reference sample - PP (isotactic polypropylene) to 49°Sh D for PP / 3% PP-g-MA composite. The addition of relatively low amount of compatibilizer (PP-g-MA) influences the hardness by decreasing the degree of crystallinity and hence the viscosity of the polymer. For composites with 10, 20 and 30% treated and untreated fibers, an increase in hardness is observed with increasing amount of reinforcing agent.

- Tensile strength - for the reference mixture (PP) values are 6.21 N/mm^2 compared with the value of 5.6 N/mm^2 in the case of mixtures PP / 3% PP-g-MA which demonstrates that adding compatibilizer decreases tensile strength of the composite. 10-20% of untreated fiber composite shows improved value 25-28 N/mm^2 to 6.21 N/mm^2 reference value and 5.6 N/mm^2 obtained in the absence of polymer composite fiberglass. For composite with 10 and 20% treated fibers and in the presence of compatibilizing agent, the interactions (Van der Waals) that develops at the interface matrix polymer / compatibilizer / coupling agent on the surface of glass fibers induce an appreciable increase in tensile strength values 30-34.6 N/mm^2. This can be attributed to the fact that it deposits a significant amount of coupling agent, during treatment, on the surface of glass fibers. The composites with 30% treated fiber and PP-g-MA present, improves the tensile strength values to 22N/mm^2 of the composition with the same percentage of fibers, but untreated 11N/mm^2. These values demonstrate that the 30% levels of the untreated fiber composite lower the tensile strengths than those with 10% and 20% treated because: increase the melt viscosity and generate gaps in the material which are points for microcracks spreading in to large cracks.

Table 1. Tensile strength and hardness of PP, PP/3%PP-g-AM and developed composites

Symbol	Hardness ^{0}ShD	Tensile strength N/mm^2
PP	73	6.21
PP/3%PP-g-AM	49	5.6
PP/FG 10%	65	25
PP/FG 20%	68	28
PP/FG 30%	70	11
PP/3%PP-g-AM/ 10%FS treated with PDMS	63	30
PP/3%PP-g-AM/ 20%FS treated with PDMS	66	34.6
PP/3%PP-g-AM/ 30%FS treated with PDMS	67	22

Silanization was established on the basis of the comparative FTIR commercial glass fiber and treated the PDMS (Figure 1). It may easily see that the spectrum of the material change considerably due to silanization of fiber surface (CH_2 stretching bands intensifies the 2800-2900cm^{-1}) and the growth of physical bonded water (1740 and 3500cm^{-1}). Physical water appears because, after treatment applied, heat treated glass fibers PDMS at 130°C, they were washed with water to remove unreacted silane.

Composite materials based on glass fiber reinforced PP show the same range as that of PP not reinforced (Figure 2). The bandwith, Si-O-Si, characteristic for glass fibers can not be viewed due to the embbeding of fibers in the polymer matrix (Figure 3).

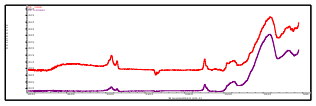


Figure 1. IR spectra of the treated and untreated glass fibers

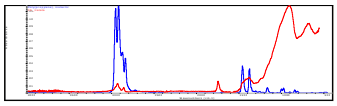


Figure 2. Standard IR spectra of PP and GF-treated PDMS

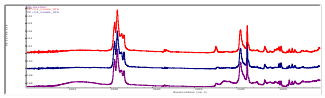


Figure 3. IR spectra of PP/3%PP-g-AM, PP/3%PP-g-AM/10 and 30%GF treated with PDMS

X Ray Diffraction (XRD)

Polypropylene has a high degree of crystallinity as evidenced by X-ray diffraction (Figure 4.). Using databases allowed identification of the bands characteristic of isotactic propylene and PP-g-MA used in a proportion of 3% compared to PP.

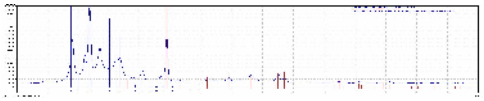


Figure 4. X-ray diffraction of the polypropylene plasticized with 3% PP-g-AM

If in the mass of plasticized polypropylene are embedded glass fibers, which may be identified, as the band intensity of 29.5 (Figure 5) is to note the large difference in intensity of this band where the analysis is performed on the surface or section resulting from mechanical tests. Much lower intensity for surface analysis is explained taking into account the embedding glass fibers in polymer matrix and thus shielding the signal, strong.

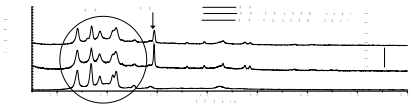
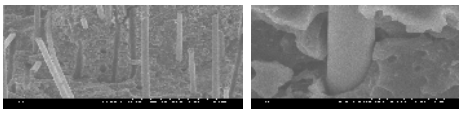


Figure 5. X-ray diffraction of the samples of PP, PP-treated GF 30%, registered in sectional respectively surface

Electron Microscopy

By scanning electron microscopy was possible to evaluate the efficiency of the dispersion of the treated and untreated glass fiber in the thermoplastic matrix and the capacity of wetting the surface fiber for thermoplastic matrix as a way to evaluate the efficiency of coupling agent.

Electron microscopy images recorded on samples PP / GF10% untreated (a) and PP/ 3%PP-g-AM / 10% GF treated with PDMS (b) were obtained in the section break and are presented in (Figure 6).



a) b)

Figure 6. Characteristic SEM images recorded on samples PP-FS10% untreated (a) respectively PP/3%PP-g-AM/GF treated with PDMS 10% (b)

Scanning electron microscopy (SEM) confirms micro morphological improvement of the connection strength: the compatibilizing agent PP-g-MA, PDMS-treated glass fibers and polymer matrix composites compared with using the untreated fiber. The compatibility of the thermodynamic characteristics of such compatibilized polymer matrix and the fibers treated with PDMS were found to be optimal because of strong adhesion between the fibers and the polymers matrix. This is evidenced also by SEM images (Figure 6b) of the fracture surfaces of obtained hybrid composites, seeing a significant deposition of coupling agent on the fiber surface. In addition, the film coating on the surface of the fibers (-Si-O-Si of polydimethylesilane) silane groups ionic and / or covalent can they bind very strongly to the existing functional groups on the surface of polypropylene -COO- groups, resulting from opening maleic cycle at high temperatures produced during extrusion.

Also presents some gaps in its structure, however the composite is more homogeneous, where the glass fibers are better attached to the polypropylene matrix, indicating that the PP-g-AM has acted positively on the interfacial adhesion of the polymeric matrix with reinforcement, which can be also indicated by the results of tensile strength the composites.

The images confirm the results obtained in mechanical tests where the compatibilized samples showed an increase of strength in relation to the non-compatibilized compositions.

CONCLUSIONS

Physical-mechanical and morphologic test results show good interfacial adhesion between polypropylene and glass fibers, due to both the surface coupling agent represented by PP-g-AM and to the treatment applied to glass fibers with poly (dimethylsiloxane) through reduction of thermal expansion coefficients which are completely different. SEM images show good compatibility between the polymer phase and disperse material and a good dispersion of glass fibers in the polypropylene mass. PP-g-AM has a double role, acting both as coupling agent and as plasticizer reducing the viscosity of the mixture. XRD provides information related to the existing crystalline phases, being able to identify peaks characteristic to polypropylene, glass fibers and a low amount of amorphous phase. Modifying the polymer matrix and the reinforcing agent improves adhesion, resistance to temperature and humidity.

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