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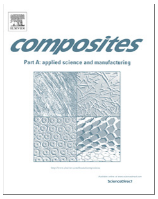

Expanded graphite nanoplatelets as coupling agents in glass fiber reinforced polypropylene composites

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ABSTRACT

The interfacial adhesion between E-glass fibers and various types of nanomodified polypropylene (PP) matrices have been investigated on single-fiber model composites. In particular, an evaluation of the fiber–matrix interfacial shear strength was performed by the fragmentation tests on model composites prepared by using PP matrices containing various amounts (up to 7 wt%) of expanded graphite nanoplatelets (xGnP).

The presence of xGnP in the polymer matrix resulted in a remarkable increase of the interfacial shear strength values (up to a factor of about 6 for a 7 wt% content of xGnP) if compared to neat PP. Moreover, wettability measurements in various liquids evidenced that the work of adhesion of the polymer matrix with respect to glass fiber, was improved by the presence of xGnP.

1. Introduction

It has been widely recognized that the fiber/matrix interfacial shear strength is one of the key factors determining the mechanical properties of fiber reinforced composite materials, in particular the fracture resistance parameters [1]. Concurrently, the interphase region often exhibits properties markedly deviating from those of the surrounding bulk matrix [1].

Polypropylene (PP) is one of the most widely used thermoplastic matrices for the production of glass fiber (GF) reinforced composites with excellent performance/cost ratio [2]. Due to the non-polar nature of the matrix, interfacial adhesion is a critical issue for PP/GF composites [3]. In fact, some of the available literature data for uncoupled PP/GF composites, indicate that an interfacial shear strength (ISS) values in the range 1–6 MPa can be considered [4–11]. In a recent study by Yang and Thomason [12], reporting a careful experimental research involving both fiber pull-out and microbond tests, a value in the range 3–4 MPa was provided.

According to the scientific literature, two main strategies have been adopted to improve the fiber/matrix adhesion in PP/glass composites: (i) the development of specific fiber sizings/coatings [4,5,7,8,10,11,13] and/or (ii) the incorporation of coupling agents into the PP matrix [7,8]. Both strategies showed a good capability to improve the fiber/matrix adhesion level.

For example, Thomason and Schoolenberg [10] observed that the use of silane coupling agents have only a slight effect on the improvement of PP/GF interfacial shear strength. Moreover, they experimentally observed that full commercial coating formulation applied to glass fibers is very important for the interface strength: variations of one order of magnitude in PP/GF adhesion were observed depending on the nature of the glass fiber coating. Etcheverry et al. [4,14] evidenced that a chemical anchoring of the PP matrix polymer on glass fibers by direct metallocenic polymerization, may lead to an increase of the ISS with respect to the untreated fibers by a factor of 2.1 [4]. On the other hand, Mäder and Freitag [7] proved that the bond strength in a PP/GF system can be significantly increased by modifications of the PP matrix, such as the addition of polypropylene grafted with acrylic acid or irradiation with electron beams.

Recent investigations demonstrated that nanoparticles homogeneously dispersed in a polymer matrix [15–17] or localized at the interfacial region [18–20] may also promote the fiber/matrix interfacial adhesion in several types of fiber reinforced composites.

In a recent work of our group, it was shown how the addition of both non-functionalized and dimethyldichlorosilane-functionalized silica nanoparticles led to a remarkable (up to a factor of about 5) increase of the interfacial strength in the PP/GF system [21]. The observed effect was explained by considering that the presence of silica nanoparticles cause an increase of the work of adhesion of polypropylene with respect to glass, as proven by wettability tests with various liquids. Concurrently, with the incorporation of nanoparticles an enhancement of the mechanical properties of

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the polymer matrix can be obtained [17] or specific functionalities can be attained [22].

There has been a recent increasing interest in thermoplastic matrices modified with expanded graphite nanoplatelets (xGnP) [23,24]. Most of the research was focused on the preparation method and on the thermo-mechanical characterization, but no investigations can be found regarding the effect of the matrix modification on the interfacial properties in fiber-reinforced structural composites.

Therefore, the aim of this study is to investigate the possibility to improve the adhesion between E-glass fibers and PP by dispersing xGnP in the polymer matrix.

2. Experimental section

2.1. Materials and samples preparation

The PP matrix used in this work was an isotactic homo-polypropylene matrix (code PPH-B-10-FB) produced by Polychim Industrie (Loon-Plage, France) and kindly provided by Lati Industria Termoplastici (Varese, Italy). FUSABOND® P M-613-05 maleic anhydride modified polypropylene (PPgMA) was supplied by DuPont™ de Nemours (Geneva, Switzerland).

Exfoliated graphite nanoplateletes xGnP®-M-5 have been supplied by XG Sciences Inc. (East Lansing, USA). Details on the exfoliation process as well as on the morphology of xGnP can be found elsewhere [25].

E-glass fibers (GFs), designed as RO99 P319, were supplied by Saint-GobainVetrotex (Vado Ligure, Italy) and used as-received. These GFs are indicated as treated with a proprietary silane based coupling agent specifically designed for polypropylene matrices.

Unfilled matrix was denoted as PP, while nanocomposites were designated indicating the matrix, the compatibilizer (if any) with its content, the filler and its amount. For instance, a sample filled with 5 wt% of PPgMA and 5 wt% of xGnP was indicated as PP-PPgMA-5-xGnP-5.

Square sheets (thickness of around 0.7 mm) of PP-xGnP, PP-PPgMA and PP-PPgMA-xGnP were prepared by melt mixing in a Thermo Haake internal mixer (temperature = 190 °C, rotor speed = 50 rpm, time = 10 min) followed by compression moulding in a Carver laboratory press (temperature = 190 °C, pressure = 0.76 MPa, time = 10 min). Thin (70–80 μm) matrix films used for the preparation of the microcomposites for the fragmentation test were obtained by a further hot pressing stage (temperature = 200 °C, pressure = 3.4 MPa, time = 10 min).

2.2. Testing methods

2.2.1. Filler characterization

Density measurements were carried out by an helium pycnometer (Micromeritics® Accupyc 1330, Norcross USA), at a temperature of 23 °C, using a testing chamber of 3.5 cm^3. Surface area and porosity measurements were performed utilizing an ASAP® 2010 Accelerated Surface Area and Porosimetry machine (Norcross, USA) referring to the nitrogen gas physisorption process, setting a saturation pressure of 738.57 mmHg and a bath temperature of 77.35 K.

The morphology of expanded graphite platelets was observed at various magnifications by using a Zeiss Supra 40 (Berlin, Germany) field emission scanning electron microscope (FESEM), at an acceleration voltage of 5 kV.

2.2.2. Single fiber fragmentation tests

Microcomposite samples were prepared by the following procedure. About 10 fibers were aligned between two films of the selected PP system, sandwiched between two Mylar® sheets (thickness of 0.5 mm) and two aluminum plates. The mold was placed in a vacuum oven at a temperature of 165 °C and at a pressure of about 10 kPa for about 20 min and then it was let to cool in air. The specimens were obtained by cutting strips containing one single fiber longitudinally aligned in the centerline. The microcomposites dimensions were roughly 0.18 mm in thickness, 5 mm in width and 25 mm in length. Single fiber fragmentation tests (SFFT) tests were performed at room temperature by using a custom-made apparatus represented by a small tensile tester (Minimat, by Polymer Laboratories) placed under a polarized optical stereomicroscope (Wild M3Z by Leica). Tests were performed at a strain rate of 0.05 mm^{-1}. At least five specimens were tested for each sample. All samples were loaded up to a strain of 10% in order to reach the saturation of the fragmentation process. The mean fiber length at saturation, L_s, was measured by means of an image analyzer system ImageJ v.1.46a on optical pictures taken under polarized light. According to Ohsawa et al. [26], the fiber critical length, L_c, was considered equal to 4/3 L_s.

2.2.3. Surfaces energetics and roughness

The wettability of the matrix samples and the glass fiber was measured by contact angle measurements with two different liquids: water as a polar liquid (milli-Q grade, surface tension $\gamma_1 = 72.8$ mN m^{-1}, polar component of surface tension $\gamma_1{}^p = 50.7$ mN m^{-1}, dispersive component of surface tension $\gamma_1{}^d = 22.1$ mN m^{-1}, polarity $X_1{}^p = \gamma_1{}^p/\gamma_1 = 0.7$), and ethylene glycol as a non-polar liquid (surface tension $\gamma_2 = 48.0$ mN m^{-1}, polar component of surface tension $\gamma_2{}^p = 19.0$ mN m^{-1}, dispersive component of surface tension $\gamma_2{}^d = 29.0$ mN m^{-1}, polarity $X_2{}^p = \gamma_2{}^p/\gamma_2 = 0.4$) [27].

The total surface tension (γ^{tot}) can be factorized by considering two additive terms: the dispersive surface tension (γ^d) and the polar surface tension (γ^p):

$$\gamma^{tot} = \gamma^d + \gamma^p \tag{1}$$

The estimation of the surface tension components of matrices with various compositions was done through the geometric mean [27] on the basis of vibration induced equilibrium contact angles (VIECA) [28] measured in both test liquids by a modified Wilhelmy technique. Surface tension components of glass fiber were estimated referring to the advancing contact angles measured by Wilhelmy technique and applying the geometric mean. Knowing the surface tension components of the adherends, the work of adhesion was evaluated using the harmonic mean (W_a^h) equation, applicable to predict interactions between low-energy materials [27]:

$$W_a^h = 4\left(\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}\right) \tag{2}$$

and the geometric mean (W_a^g) equation, more suitable to describe interactions between low-energy and high-energy materials:

$$W_a^g = 2\left(\sqrt{\gamma_1^d\gamma_2^d} + \sqrt{\gamma_1^p\gamma_2^p}\right) \tag{3}$$

where the superscripts d and p refer to the dispersive and polar components, respectively, while subscripts 1 and 2 refer to the two solids in contact (polymer and glass fiber), respectively.

The roughness of the samples was determined by a Wave System rugosimeter (Hommelwerke Waveline GmbH, Villingen-Schwenningen, Germany) scanning a 15 mm line at a speed of 0.50 mm min^{-1}. At least three measurements were performed per each sample on the same specimens previously adopted for the estimation of the contact angle. The ANOVA analysis was carried out on the means of R_a and R_{max} at a significance level of 5%.