Silica nanoparticles as coupling agents for polypropylene/glass composites

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ABSTRACT

An evaluation of the fibre/matrix interfacial shear strength was performed by the single-fibre fragmentation tests on polypropylene–glass fibre microcomposites filled with various types and amounts of silica nanoparticles. In particular, both non-functionalized and dimethyldichlorosilane-functionalized silica nanoparticles were added up to a weight content of 7%. Moreover, the effect of various amounts of maleic anhydride modified polypropylene (PPgMA) on the fibre/matrix adhesion was also investigated, including some selected formulations containing both PPgMA and silica nanoparticles.

Interfacial shear strength was found to remarkably increase (up to a factor of about 5 for a 7 wt% content of surface treated nanoparticles) with respect to the case of neat polypropylene matrix. The observed effect was explained by considering that silica nanoparticles increase the work of adhesion of polypropylene with respect to glass, as proven by contact angle measurements in different liquids.

In addition, silica nanoparticles promoted a remarkable enhancement of both elastic modulus and creep stability of the selected polypropylene matrix.

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1. Introduction

It has been widely recognized that the fibre/matrix interfacial shear strength controls several mechanical properties of composite materials, in particular the off-axis parameters [1]. At the same time, the interphase region often manifests properties markedly deviating from those of the surrounding bulk matrix [2].

Among thermoplastic resins, polypropylene (PP) is one of the most widely used matrices for the production of glass fibre (GF) reinforced composites [3]. Due to the non-polar nature of the matrix, interfacial adhesion is a critical issue for PP/GF composites [4]. Several authors evaluated the fibre/matrix interfacial shear strength (ISS) for PP/GF microcomposites by microdebonding [5–10] or fragmentation [11–16] tests. From the analysis of the extended literature data, it emerges that for uncoupled PP/GF composites an average ISS value of 4.0 ± 1.4 MPa can be estimated. This value has been also recently confirmed by Yang and Thomason [17] on the basis of a careful experimental work involving both fibre pull-out and microbond methods.

Over the years, two main strategies have been proposed to improve the fibre/matrix adhesion in PP/glass composites: (i) the development of specific fibre sizings/coatings [5,7–10,16,18,19] and/or (ii) the addition of coupling agents to the PP matrix [7,8]. Both strategies lead to interesting results in terms of improvement of the fibre/matrix adhesion level. For example,

Thomason and Schoolenberg [9] observed that the use of silane coupling agents have little effect on the level of PP/GF interfacial shear strength. At the same time, they experimentally observed that full commercial coating formulation applied to glass fibres 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 fibre coating. As reported by Etcheverry et al. [12,16] a chemical anchoring of the matrix polymer on glass fibres was also attempted by direct metallocenic polymerization of PP onto the GF surface. Depending on the hydroxy-α-olefin concentration, the surface treatment induced an increase of the ISS with respect of the untreated fibres by a factor ranging from 1.7 up to 2.1 [16].

On the other hand, Mäder and Freitag [7] evidenced how the bond strength in the PP/GF system can be remarkably enhanced by modifications of the PP matrix, such as the addition of polypropylene grafted with acrylic acid or irradiation with electron beams.

More recently, some indications emerged on the fact that nanoparticles homogeneously dispersed in a polymer matrix [20–22] or localized at the interfacial region [23–25] could play a beneficial role on the fibre/matrix interfacial adhesion in several types of structural composites. Moreover, with the addition of nanoparticles a simultaneous enhancement of the mechanical properties of the polymer matrix can be reached [20] or specific functionalities can be added [26].

The purpose of this study is to investigate the possibility to improve the interfacial adhesion between E-glass fibres and polypropylene by dispersing various types and amounts of silica nanoparticles in the polymer matrix.

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2. Experimental section

2.1. Materials and samples preparation

The matrix of the microcomposites used in this work was an isotactic homopolymer polypropylene (MFI at 190 °C and 2.16 kg = 6.9 g/10', density = 0.904 g cm^{-3}) produced by Polychim Industrie S.A.S. (LOON-PLAGE, France) and provided by Lati Industria Termoplastici S.p.A (Varese, Italy) with the commercial code PPH-B-10-FB. FUSABOND® P M-613-05 maleic anhydride modified polypropylene (PPgMA) (MFI at 190 °C and 2.16 kg = 106.8 g/10', density = 0.903 g cm^{-3}, maleic anhydride content = 0.35–0.70 wt%), was supplied by DuPont™ de Nemours (Geneva, Switzerland).

Both untreated and surface treated fumed silica nanoparticles were supplied by Evonik Industries AG (Hanau, Germany). Untreated nanoparticles (Aerosil® A380) had an average primary particle size of 7 nm and a specific surface area of 321 ± 3 m^2/g, as determined by BET analysis [27]. Dimethyldichlorosilane functionalized silica nanoparticles (Aerosil® R974) were characterized by an average primary particle size of 12 nm and a BET specific surface area of 124 ± 1 m^2/g. Silica nanoparticles were dried for 24 h at 100 °C before to be used for nanocomposite production. E-glass fibres designed as RO99 P319, were supplied by Saint-GobainVetrotex (Chambèry Cedex, France) and were used as-received. These GF are indicated as treated with a silane based coupling agent specifically designed for polypropylene matrices.

Binary nanocomposites containing 1, 3, 5 and 7 wt% of both untreated and surface treated silica nanoparticles 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 hot press (temperature = 190 °C, pressure = 0.76 MPa, time = 10 min), in order to get plane square sheets with a thickness of around 0.7 mm. Under the same processing conditions, ternary nanocomposites were also prepared by adding PPgMA as a compatibilizer in three different amounts (1, 3 and 5 wt%) to the systems containing 1, 3 and 5 wt% of silica. Thin (70–80 μm) matrix films required 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).

Unfilled matrix was denoted as PP, while nanocomposites were designated indicating the matrix, the compatibilizer (if any) with its content, the kind of filler and its amount. For instance, a sample filled with 5 wt% of PPgMA and 5 wt% of Aerosil® A380 was indicated as PP-PPgMA-5-A380-5.

2.2. Experimental techniques

2.2.1. Fibre strength and elastic modulus evaluation

Tensile tests on single GFs were carried out according to ASTM C 1557-03 standard. Single fibres of three different gauge lengths (5, 15 and 30 mm) were fixed on paper tab frames and tested with an Instron (Norwood, USA) model 4502 tensile machine equipped with a 2.5 N load cell, at a strain rate of 0.2 min^{-1}. Prior testing, fibre diameter was measured on three locations on each specimens by an optical microscope (Leitz Ortholux II POL-BK) through a video-camera (PIKE F032C).

2.2.2. Single fibre fragmentation tests (SFFTs)

Microcomposite were prepared according to a procedure well assessed for thermoplastic matrices [16,28,29]. About 10 fibres were aligned between two thin polymer films, sandwiched between two Mylar® foils and two aluminium plates. This assembly was placed in a vacuum oven at a temperature of 165 °C under a pressure of 10 kPa for 20 min and then cooled in air. The specimens were obtained by cutting strips (0.18 × 5 × 25 mm^3) containing one single fibre longitudinally aligned in the centre line.

Fragmentation tests were performed at room temperature by a tensile tester (Minimat, by Polymer Laboratories, Loughborough, UK) located under a polarized optical stereo-microscope (Wild M3Z by Leica). At least five specimens for each sample were tested at a strain rate of 0.05 mm^{-1} up to a strain of 10%, necessary to assure the saturation of the fragmentation process. The mean fibre length, L_s, was evaluated by an image analysis software (Image J). The fibre critical length, L_c, was taken as $4/3L_s$ [2]. Interfacial shear strength (ISS) values were derived according to the simplified micromechanical models proposed by Kelly–Tyson [30] and by Cox [31].

According to the Kelly–Tyson approach an average value of ISS is the result of the static equilibrium between the tensile force acting on a fibre and the shear force transferred through the fibre–matrix interface:

$$\text{ISS} = \frac{\sigma_{fb(Lc)}d}{2L_c} \tag{1}$$

where d is the fibre diameter and $\sigma_{fb(Lc)}$ is the tensile strength of a fibre with a critical length L_c, which was computed on the basis of Eq. (2).

$$\sigma_{fb(Lc)} = \sigma_0 \left(\frac{L}{L_0}\right)^{-1/m} \Gamma\left(1 + \frac{1}{m}\right) \tag{2}$$

where Γ is the Gamma function, while σ_0 and m are the scale and shape parameters of the Weibull distribution, respectively, which were estimated from strength data determined at one single gauge length by fitting the distribution of failure probability.

On the other hand, the traditional shear-lag model assumes a number of hypotheses, such as: perfectly elastic and isotropic matrix and fibre properties, proportionality between interfacial shear force and the difference between the displacement in the matrix and the displacement that would exist if the fibre were absent, perfect bonding between matrix and fibre, same lateral stiffness of fibre and matrix, no residual stresses furthermore, the stress is taken as uniform through a radial section of fibre, and the stress is entirely transferred from matrix to fibre by shear at the interface. The axial stress σ_f in the fibre can thus be writtens as:

$$\sigma_f = E_f \varepsilon_f \left(1 - \frac{\cosh(\beta z)}{\cosh(\beta t)}\right) \tag{3}$$

where ε_f is the far-field applied strain, E_f is the elastic modulus of the fibre, z is the axial coordinate, t is the fibre half-length, while β shear-lag parameter is defined as:

$$\beta = \left[\frac{H}{\pi R_f^2 E_f}\right]^{1/2} \tag{4}$$

with

$$H = \frac{\pi E_m}{(1 + v_m)\ln(R_m/R_f)} \tag{5}$$

where E_m and v_m are the matrix elastic modulus and Poisson's ratio, while R_m and R_f are the matrix and fibre radii, respectively. The interfacial shear stress profile $\tau(z)$ can be calculated as:

$$\tau = \frac{E_f R_f \varepsilon_f \beta}{2} \left(\frac{\sinh(\beta z)}{\sinh(\beta t)}\right) \tag{6}$$

2.2.3. Surfaces energetics and roughness

The wettability of some selected matrix compositions and the glass fibre was measured by contact angle measurements with