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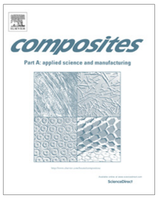

Wool fibres functionalised with a silane-based coupling agent for reinforced polypropylene composites

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ABSTRACT

Polypropylene (PP)-based composites containing 20 wt.% wool fibres were successfully prepared using a simple melt blending procedure. A blend of a commercial-grade PP and a maleinised PP was chosen as the matrix. To investigate the effects of modifying the fibre surface on the fibre/matrix adhesion, wool fibres were used as received, oxidised, or functionalised with a silane-based coupling agent, capable in principle of reacting with both the fibres and the polyolefinic matrix. The silanisation of the fibres and the consequent surface modifications were assessed using infrared spectroscopy and scanning electron microscopy. The resulting PP-based composites were thoroughly characterised in terms of their morphology, thermal stability and mechanical behaviour.

1. Introduction

Protein fibre by-products from the textile industry, waste wool from farms and butchery, and poultry feathers generate a large waste biomass stream that is not subject to adequate forms of valorisation. Nevertheless, using protein fibres to reinforce polymer-based composites for new commodities and/or value-added applications may exploit this untapped resource. Protein fibres are naturally hydrophilic, fire-resistant, biodegradable, biocompatible and renewable in addition to exhibiting mechanical or chemical processability [1–9].

In the last decade, the valorisation of short fibres from poultry feathers for reinforcing polyolefin- and polylactide-based composites has been investigated [5,10]. Multi-step pulverisation technologies have been developed to produce ultra-fine ground wool [11,12] as an additive for polypropylene (PP)-based films produced through extrusion and compression moulding. However, the mechanical properties of the obtained materials decline significantly as the wool powder content increases [2]. Another work revealed that wool fibrils can act as a matrix reinforcement increasing the material modulus and yield stress, even though the elongation at break resulted consistently decreased [13]. In a more recent study, silk/wool hybrid fibre PP composites [14] were produced by simple compression moulding and suggested as potential substitutes for the conventional glass/epoxy composites used as electrical insulating materials in printed circuit boards because these composites have characteristically low thermal conductivity.

Isotropic composites based on commercial PP containing up to 60 wt.% highly dispersed wool fibres were prepared using a simple melt blending process and a maleinised PP as a compatibiliser [4]. Although improvements in the thermal stability and elastic modulus were observed, and the presence of the compatibiliser was beneficial, the composites were weaker with respect to the polyolefinic matrix partially because the fibres are shortened during the melt blending process. Therefore, optimising the process conditions to reduce wool fibre fragmentation and improving the fibre/matrix adhesion are critical for producing materials with a better performance.

The hydrophilicity of the natural fibres adversely affects their adhesion to the hydrophobic PP matrix. For cellulosic fibres, several chemical methods for modifying their surfaces, such as graft polymerisation using monomers and macromonomers, and the use of suitable coupling agents were proposed in the literature [10,15–19]. Coupling agents, such as maleic anhydride copolymers,

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isocyanates and silanes, can bridge the interface between the fibrous reinforcement and the polymer matrix. Silanes have versatile multifunctional structures and have been successfully applied in polymer composites reinforced with inorganic fillers [20–26] and natural fibres [10,15,17–19,27]. Chemically modifying keratin-based fibres modifies their dye affinity, reduces felting, and improves their wettability in textile wet processing [28–31]. However, to the best of our knowledge, no articles have reported silanising wool fibres and using them to prepare polymer-based composites.

In this work, wool fibres were functionalised with a silane-based coupling agent that might react with both the fibres and the matrix during the mixing process to improve the fibre/matrix adhesion. A silane bearing only one reactive methoxy group was also tested to verify the effectiveness of the silanisation reaction onto the fibres.

PP-based composites containing 20 wt.% of silanised wool fibres were then prepared via melt blending: their morphology was investigated by SEM imaging while their thermal and mechanical behaviour was investigated using thermogravimetric analysis (TGA) and uniaxial tensile tests, respectively. The new materials were compared to composites containing pristine or oxidised wool fibres to evaluate the efficiency of the fibre treatment. The data from mechanical analysis were also compared with theoretical models and the mechanical characteristics of analogous composites containing PP and uncut aligned wool fibres.

2. Experimental

2.1. Materials

Polypropylene *Moplen® HP520H* (PP) with a 0.9 g/cm^3 density and 2 g/10 min melt flow index at 230 °C, 2.16 kg (ISO1133) was supplied in the pellet form by Lyondellbasell Industries S.r.l. (Ferrara, Italy). A polypropylene grafted with maleic anhydride, *Compoline® CO/PP C05* (C05) with 3 g/10 min melt flow index at 230 °C, 2.16 kg (ISO1133), was supplied by Auserpolimeri S.r.l. (Lucca, Italy), and used as a compatibiliser. Wool fibres (WF) in the form of slivers 18 μm in diameter were supplied by The Woolmark Co., Italy. Before mixing, the WF were cut into snippets approximately 2 cm long, washed in a Soxhlet extractor with acetone for 2 h and dried under vacuum at 105 °C for 4 h. [3-(methacryloyloxy)propyl]trimethoxysilane (MPTS) from Evonik Industries AG (Rheinfelden, Germany) and methoxy(dimethyl)octadecylsilane (MDOS) from Sigma–Aldrich S.r.l. (Milano, Italy) were used as received as coupling agents. Other chemicals were purchased from Sigma–Aldrich.

2.2. Modification of wool fibres

Oxidation. Oxidised wool fibres (WFO) were prepared by using hydrogen peroxide. WF were soaked in a pre-heated (60 °C) aqueous solution containing 0.54 wt.% of hydrogen peroxide, 0.1 g/L of nonylphenol and 2 g/L of sodium pyrophosphate; the mixture was maintained for 2 h at the same temperature. Finally, the fibres were washed with distilled water and dried at 60 °C for 24 h.

Silanisation. Silane-treated wool fibres were prepared from WF or WFO. The silane (typically 10 wt.% relative to the fibres) was dissolved in methanol–water–acetic acid (75/8/17 v/v/v) at 25 °C with continuous stirring for 10 min. The fibres were moistened with the silane-containing mixture and dried at 60 °C for 24 h. The silanisation reaction was completed after raising the temperature to 120 °C for 2 h. Afterward, the wool fibres were treated with acetone via Soxhlet and dried to remove unreacted silane.

The effective acetone solubility of the two silanes and the product obtained after self-polymerising the MPTS for 2 h at 120 °C was previously verified.

For the WFO silanised with MPTS, various silane/fibre ratios (3, 6, 10 wt.%) were tested.

2.3. Preparation of the composites

Based on the results obtained by the authors in a previous paper [4], a PP/C05 95/5 wt/wt blend (PPC05) was used as a matrix and a reference. The PPC05 blend was obtained under the same experimental conditions used to prepare the composites. Composites containing 20 wt.% wool fibres (WF, WFO or WFO treated with 10 wt.% MPTS) were prepared via melt blending with a W50 EHT Plasti Corder® (Brabender) internal mixer. PP and C05 pellets (95/5 wt/wt) were introduced in the mixer chamber at 170 °C and mixed (60 rpm rotor speed) for approximately 1 min; the fibres were then quickly added and mixing was completed in 10 min (total).

After mixing, all the samples were moulded using a P 200E semi-automatic laboratory press (Collin GmbH) at 180 °C (5 min at 0.5 MPa and 5 min at 18 MPa) to obtain 0.32 mm thick sheets suitable for characterisation.

Samples with a single fibre were used to measure the critical length (L_c) of the wool fibres into the PPC05 matrix (see below) and were prepared by compression moulding (5 min at 0.5 MPa and 5 min at 18 MPa) a slightly stretched uncut fibre (>8 cm long) between two 0.05 mm thick PPC05 sheets at 180 °C.

Composites containing uncut oriented wool fibres (unidirectional composites) were also prepared by placing combed and slightly stretched WF between two 0.3 mm thick PPC05 sheets and moulding them at 180 °C (5 min at 0.1 MPa and 5 min at 3 MPa). Unidirectional composites with 14.3, 15.7 and 16.6 wt.% wool contents were prepared using WF, WFO and WFO modified with 10 wt.% MPTS (WFO_{10MPTS}), respectively.

2.4. Characterisation

The Fourier transform infrared (FTIR) analyses of MPTS, MDOS and treated wool fibres were performed using a Bruker IFS 28 FTIR spectrophotometer in transmission mode. The liquid silanes were characterised by spreading a drop on a KBr window; for wool fibres, the KBr method was used.

Thermogravimetric analysis (TGA) was carried out with a TGA7 (Perkin Elmer) instrument on samples of approximately 7 mg. The decomposition temperatures at 5 and 50 wt.% mass loss (T_5 and T_{50}, respectively) of the composites were measured while heating at 20 °C/min under O_2 (35–880 °C) at 40 mL/min. TGA analyses of the pristine and treated wool fibres were also performed under the same conditions as the composites. The grafted silane content (wt.%) was obtained using the value of the residue at 880 °C, that corresponds to the amount of SiO_2 formed upon silane combustion:

$$\text{Grafted silane(wt.\%)} = \frac{SiO_2(\text{wt.\%})}{FW_{SiO_2}} \cdot FW_{\text{Grafted silane}} \qquad (1)$$

where SiO_2 (wt.%) is the residue at 880 °C, FW_{SiO2} and $FW_{\text{Grafted silane}}$ are the formula weights of SiO_2 and the grafted silane moiety, respectively.

For each composite sample, the length and diameter of at least 150 wool fibres were measured using a Polyvar Pol (Reichert) optical microscope equipped with a CCD camera. Because the fibres were tangled, their concentration in the composites was reduced via dilution with neat PP; i.e. each composite sheet was pressed between two PP films to obtain very thin films with few fibre overlaps.