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Wool keratin-polypropylene composites: Properties and thermal degradation

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ABSTRACT

Wool fibres were submitted to green hydrolysis with superheated water in a microwave reactor, in view of potential valorisation of keratin-based wastes. The keratin hydrolysates containing free amino acids, peptides and low molecular weight proteins, were exploited as a biofiller in preparing polypropylene matrix composites. Maleic anhydride grafted polypropylene was used as a compatibilizer to promote dispersion of keratin. The thermal and mechanical properties were investigated in dependence of keratin and compatibilizer loadings, and related to morphological characteristics. The presence of keratin preserved the molecular weight of the polymer matrix during the processing and gave good overall mechanical properties to the compatibilized composites. The keratin hydrolysates strongly interfered on the crystallization behaviour and thermo-oxidative degradation of the polypropylene. The increase of polypropylene crystallization rate and the enhancement of thermal stability were observed as a function of the keratin amount in the compatibilized composites.

1. Introduction

The development of new commodities from biomass derived materials is of significantly high interest to convert agricultural and industrial wastes into value added items. Over the last years, many efforts have been focused on the valorisation of the keratin-based waste stream, made of low quality wools from stock-farming, fibre byproducts from the wool textile industry and hairs, feathers, horns and nails from butchery. Keratin, one of the most abundant non-food protein, is a renewable, cheap feedstock, estimated worldwide several million tonnes per year, which is mostly disposed in landfills since burning for fuel is inefficient and polluting, due to its high sulphur content [1,2]. Keratin is naturally hydrophilic, non-burning, biodegradable, biocompatible, and can be exploited in different ways via chemical processing.

Keratins have been extracted by cleavage of the disulphide cystine bonds via reduction or oxidation treatments and regenerated into various forms for biotechnological application, such as films [3–8], sponges [9,10], fibres [11–13], alone or blended with other natural or synthetic polymers. The hydrolysis of wool and feathers keratin to oligopeptides or amino-acids was also proposed as an alternative route to provide building blocks for the synthesis of novel polymers. Hydrolysis can be carried out in different process conditions, with different chemical agents. Boiling in alkali media represents a common way to carry out a strong hydrolysis of keratin by cleavage of peptide bonds, primary amide bonds and cystine disulfide bonds. However, partial hydrolysis under controlled process conditions, with the aim of tailoring the peptide length, is drawing the attention of many researchers [14,15]. Green processes such as steam explosion and treatment with superheated water have also been taken into account [2,16,17].

In the recent years, studies have been proposed to valorize keratin wastes, either through surface grafting of synthetic polymers or by blending, to prepare innovative polymer composites. Low- and high-density polyethylene composites with improved mechanical properties were prepared using keratin feather fibre by Barone et al. [18,19]. The physico-mechanical properties of the composites resulted strongly influenced by the nature of the polymer matrix and by the thermal and mechanical mixing conditions. Keratin biofibres from poultry feathers showed promising results as reinforcement for a polymethylmethacrylate composite matrix [20,21]. Their hydrophobic nature allowed a regular distribution within and adherence to polymers. The Young's modulus and the storage modulus at room temperature increased in the composites and, at high temperature, the reinforcement provided higher stability. Composites made of feather fibre, polypropylene and maleic anhydride modified polypropylene were prepared by Bullions et al. [22]. The composites showed improvement in mechanical properties suggesting that maleic anhydride can react with certain amino acid groups within keratin protein. Jin et al.

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Table 1
Composition by weight of the investigated materials.

Sample	iPP/PPg/KER	Sample code
iPP	100/0/0	PP
iPP/KER	90/0/10	PK
iPP/PPg	95/5/0	PgP
iPP/PPg/KER	90.25/4.75/5	PgPK5
iPP/PPg/KER	85.5/4.5/10	PgPK10
iPP/PPg/KER	76/4/20	PgPK20

modified feather fibre through graft polymerization with methyl acrylate and prepared films by compression moulding grafted feathers with glycerol as a plasticizer [23].

In this work, wool keratin wastes were subjected to microwave-assisted green hydrolysis with superheated water and keratin-based microsized particles were produced. The keratin particles were blended with polypropylene matrices with the aim of manufacturing composite materials with novel properties.

2. Experimental

2.1. Materials

Keratin hydrolysates were prepared by treating 40 g sheep wool (The Woolmark Co., Italy) in 150 ml superheated water, for 30 min at 180 °C, using a 400 ml ceramic autoclave placed in a microwave oven Milestone Ethos 1600. At the end of the process, the autoclave was cooled and the resulting product, consisting of yellowish-brown slurry, was filtered with a 120 mesh stainless steel sieve. The liquid phase was further filtered by a 0.65 μm pore size, tangential flow filter Millipore Pellicon XL and then freeze-dried. The yield of the freeze-dried powder (KER) consisting of water-soluble proteins, oligo-peptides and free amino acids corresponded to 31% of the initial wool sample weight.

The matrix polymer used in preparing the composites was isotactic polypropylene usually employed for fibre preparation, iPP (HP552R, Lyondell Basell, Italy) with a melt flow index (MFI) of 25 g/10 min (230 °C, 2.16 kg). Maleic anhydride grafted polypropylene, PPg (Compoline H60, Auserpolimeri, Italy) with MFI of 44 g/10 min (230 °C, 2.16 kg) and a maleic anhydride content of 0.5 wt.%, was used as a compatibilizer.

Table 2
Amino acid composition of keratin freeze-dried powder compared with the original wool sample.

Amino acid	Wool (mol%)	KER (mol%)
Cysteic acid	0.1	0.2
Aspartic acid	7.0	7.2
Serine	10.7	9.9
Glutamic acid	12.8	15.5
Glycine	8.0	10.9
Histidine	0.9	1.1
Arginine	6.9	7.4
Threonine	5.8	5.1
Alanine	5.2	7.0
Proline	6.4	7.2
Lanthionine	0	0.9
1/2 Cystine	11.3	0.7
Tyrosine	3.3	3.4
Valine	5.8	6.6
Methionine	0.4	0.6
Lysine	3.4	2.8
Isoleucine	3.1	3.6
Leucine	6.8	7.6
Phenylalanine	2.1	2.3

2.2. Composites preparation

Composites of iPP, PPg and KER were prepared by melt-mixing the components at 190 °C for 10 min at 60 rpm in a Brabender electronic plasticorder AEV 153 mixer with KER content equal to 5, 10 and 20% by weight. Before compounding the KER powder was heated at 110 °C for 2 h. A weight ratio of 95:5 between the isotactic polypropylene and the maleic grafted polypropylene was kept constant for all iPP/PPg/KER composites formulation. On processing dry nitrogen was continuously purged into the mixing chamber. Pure iPP and a blend of iPP/PPg 95/5 processed under identical conditions were prepared as reference materials. The compositions of the investigated samples are summarized in Table 1.

The samples were moulded in a heated press at 180 °C for 3 min without any applied pressure. After this period, a pressure of 50 bar was applied for 2 min, then the press plates were quickly cooled to room temperature by cold water. Films with a thickness of 100–120 μm were produced.

2.3. Methods

2.3.1. Keratin hydrolysates analysis

The protein amount was determined using the Bradford protein assay method (BioRad), in order to detect peptides with molecular weight higher than 3 kDa, i.e. proteins [24]. The protein content was obtained as the mean value of three determinations.

To determine the amino acids composition the freeze-dried powder and the original wool were hydrolysed with HCl 6 N at 110 °C for 24 h. Free amino acids residues were derivatized with 6-aminoquinolyl-N-hydroxysuccimildyl carbamate and eluted on a reversed-phase column. A Waters Alliance high-performance liquid chromatograph was used, and the eluate was detected at 254 nm. The quantitative amino acid composition was determined by calibration with the Amino Acid Standard H (Pierce), cysteic acid and lanthionine (TCI Europe) as external standards.

The molecular weight distribution of the proteins was determined by sodium dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE), according to the Laemmli's method [25]. The adopted experimental procedures were described in detail in a previous paper [26].

2.3.2. Composites analysis

The molecular characterization was carried out by size exclusion chromatography (SEC) using a Waters GPCV2000 system equipped with three PLGel Olexis columns and a differential refractometer detector in *o*-dichlorobenzene at 145 °C. The universal calibration was obtained from eighteen polystyrene standards, with the molar mass ranging from 162 to 3.28×10^6 g/mol.

Morphology of sample films was investigated by polarized optical microscopy (POM) by using a Nikon Eclipse TE 2000-U microscope equipped with a Linkam LTS420 stage system.

The isothermal crystallization kinetics was investigated by differential scanning calorimetry (DSC) using a Perkin–Elmer Pyris 1 system equipped with a liquid subambient device and calibrated with indium standard. The sample (ca. 3 mg) was heated up to 195 °C and held at this temperature for 3 min to cancel previous thermal history. Then, in the isothermal crystallization analysis, the sample was cooled at a nominal rate of 500 °C/min to the selected crystallization temperature of 127 °C. The heat flow evolved during the isothermal crystallization was recorded as a function of time.

Tensile dog-bone-shaped specimens were tested at room temperature using a Zwick Roell ProLine Z010 mechanical tester at a constant crosshead speed of 3 mm/min. Mechanical properties were evaluated from the strain–stress curves. For each material, at least five samples were tested.