



Enhancement of mechanical properties of waste-sourced biocomposites through peroxide induced crosslinking



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ABSTRACT

The enhancement of mechanical performance of waste-sourced biocomposites through peroxide induced crosslinking was investigated in order to expand their range of applications. Biocomposites containing 25 to 35 wt% of residual Kraft-pulp cellulose fibers, 1.5 wt% of a selected maleic-anhydride-modified polyethylene coupling agent and a 60/40 (w/w) of recycled agricultural plastic/post-consumer plastic blend were compounded in an extrusion-compounding pilot-plant. Changes in the blend structure due to the presence of the organic peroxide used were studied by spectroscopy and thermal analysis. It was found that the addition of extremely low amounts of peroxide (0.025–0.050 wt%) results in remarkable improvements in stiffness, strength and toughness of biocomposites, without compromising processability. Thus, their tensile strength and energy at break increased up to 89.4% and 138%, respectively, with regard to uncrosslinked biocomposites. Scanning electron microscopy revealed an improvement of the fiber–matrix adhesion due to the treatment with the peroxide.

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1. Introduction

The low density, good specific mechanical properties or the high sound damping ability imparted by natural fibers to plastic-matrix composites, along with the multiple economic and environmental advantages of natural fibers over synthetic ones have been driving the research on natural fiber-reinforced composites (also known as biocomposites) during the last decades [1,2].

However, the mechanical properties of biocomposites are limited by the low compatibility between the hydrophobic polymers mostly used as matrices (polyolefins) and the hydrophilic fibers used as reinforcements, which hinders an adequate stress transfer from the matrix to the fibers. The use of coupling agents and several fiber treatments have been usually put forward to overcome this drawback [1–6]. Coupling agents provide remarkable property enhancements to biocomposites, but the contribution of natural fibers to the strength of these biocomposites is still far from their top reinforcing capability [7,8]. It is therefore necessary to find

other ways to improve the performance of composites made from cellulose and polyolefins, so as to expand their range of applications.

Peroxide induced crosslinking is a promising way to improve the interfacial adhesion and consequently the properties of these biocomposites. This technique, when applied at a relevant degree on neat virgin polyethylene (PE), has been reported to improve impact strength, environmental stress crack resistance, creep resistance and abrasion resistance, with a deleterious effect on stiffness [9]. However, noticeable enhancements of stiffness have also been found, even at low peroxide contents, through reactive extrusion of high density polyethylene (HDPE) in a twin-screw extruder [10]. Effects on tensile strength have not been clearly established and have been found dependent on the molecular weight of polyethylene [11]. For peroxide-initiated crosslinked low-density polyethylene (LDPE) tensile strength was found to increase and subsequently decrease at increasing degree of crosslinking [12]. Also, the processability of PE can be compromised when a high degree of crosslinking is achieved during reactive extrusion, since melt flow index shows a drastic decrease. Nevertheless, it has been stated that low peroxide contents used with neat PE still lead to

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property enhancements without compromising processability [13], while remarkable improvements in virgin-PE biocomposite properties have also been achieved when a moderate amount of peroxides was used [14,15]. Moreover, it is expected that the use of low amounts of peroxide leads to just slightly crosslinked materials, thereby preventing a severe drop in the biodegradability thereof. For these slightly crosslinked biocomposites, the property enhancements were assigned to the formation of covalent bonds between the reinforcement and the matrix, thus improving interfacial adhesion [14,15].

On another hand, crosslinking induced by peroxides may become complex when using polymeric blends, since each polymer can be affected in different ways. Thus, while polypropylene is degraded by peroxides, PE is crosslinked, although in PE-rich binary PE/PP blends tensile modulus and strength are improved by crosslinking [11]. Moreover, although the presence of impurities of other polymers in residual plastics may add further complexities to crosslinking, this technique has been satisfactorily used for compatibilizing plastic mixed wastes as well as for the modification of blends of different PEs [11].

Despite the promising results of the few studies devoted to peroxide induced crosslinking of natural fiber-reinforced composites, to our knowledge no studies have been dedicated to this topic when using residual polymeric blends as matrices and residual cellulose fibers as reinforcement.

Therefore, the present work is devoted to investigate the effects of peroxide induced crosslinking in a slight degree on the mechanical properties of biocomposites made from polymeric and industrial wastes. A blend of a recycled agricultural plastic (referred to as RAP and mainly consisting of LDPE) and post-consumer HDPE (referred to as rHDPE) was used as matrix, while residual cellulose fibers from the Kraft pulp industry were used as reinforcement. Based on previous research results with this kind of biocomposites [7], a maleic anhydride polyethylene copolymer (MAPE) was used for enhancing the matrix-reinforcement compatibility.

The use of the peroxide was aimed at promoting crosslinking both within the matrix (improving polymer/polymer compatibility and enhancing matrix performance) and between the matrix and the reinforcement, thus enhancing interfacial adhesion and improving the mechanical properties of biocomposites. In a first step, the effect of the organic peroxide on the neat matrix was studied at a laboratory scale in order to verify the occurrence of crosslinking and to confirm the preservation of the photostabilizers present in the recycled agricultural plastic, which confer additional value to its biocomposites [7,16]. Subsequently, the neat matrix blend was compounded with low amounts of peroxide at a pilot-plant scale by reactive extrusion in a twin-screw extruder, to determine which of them lead to a greater improvement in the properties of the blend without compromising its processability. For this purpose, rheological and tensile tests, as well as thermal analyses were conducted. Finally, slightly crosslinked biocomposites were produced, following the same pilot-plant scale process, to assess the effect of both reinforcement and peroxide contents on their main tensile and flexural properties.

The results obtained revealed that the use of little amounts of the organic peroxide with the neat polymeric blend leads to its crosslinking in a slight degree and substantially improves its mechanical properties with no deleterious effect on its processability. When the peroxide is added to the biocomposites, it leads to simultaneous remarkable enhancements of stiffness, strength and toughness, with regard to the uncrosslinked ones, without compromising their processability, thus widening their industrial applications and contributing to industrial and post-consumer waste minimization.

2. Materials and methods

2.1. Materials and reagents

A blend of two residual plastics was used as matrix for the biocomposites. The recycled agricultural plastic (RAP), obtained from agricultural plastic film wastes, mainly consisted of LDPE and was supplied by BEFESA Plásticos (Spain), in pellet form, as ALFATEN 200™. The residual post-consumer plastic flakes were obtained from bottles and other containers recovered from municipal solid wastes after separation, milling and washing stages. They were supplied by TERSA (Spain) and mainly consisted of HDPE with polypropylene impurities (ca. 7.5 wt%). The flakes were previously pelletized in order to obtain a homogeneous material (rHDPE) and to facilitate its dosing during melt compounding. For all experiments, a 60/40 (weight ratio) was held between both plastics in the composite matrix and 0.3 wt% of the thermal stabilizer Irganox B900 (Ciba, Spain) was also used. Residual cellulose fibers (RCF) used as reinforcement were supplied by ENCE-Navia (Spain). They mainly consisted of unbleached *Eucalyptus globulus* cellulose. Further details regarding the features of RAP, RCF and Irganox B900 can be found in a previous work [7].

The coupling agent (MAPE) was Licocene PE MA 4351 GR, a commercially available maleic anhydride-modified polyethylene copolymer supplied by Clariant Ibérica (Spain). It has an acid number of 43, a density at 23 °C of 990 kg/m³ and a viscosity at 140 °C of 300 mPa s, approx.

The crosslinking agent, supplied by AKZO NOBEL (Spain), was TRIGONOX™ 145-45B-PD (referred to as TRIGONOX), containing a 45 wt% of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3 on calcium carbonate and silica carrier.

2.2. Preparation of slightly crosslinked blends and biocomposites

Little amounts of slightly crosslinked polymer blends (SCPB), with 0.050 and 0.100 wt% of TRIGONOX, were prepared by reactive extrusion in a microextruder (Rondol, UK) at 70 rpm with a residence time of ca. 3 min. The barrel temperature profile from hopper to die was 125–150–160–160–165 °C. The polymer blend without peroxide was also prepared as reference. This process was then followed by a pelletizing stage. Sheet specimens for the spectroscopic characterization were obtained as films by compression molding in a hot-plate press (IQAP LAP, Spain) at 180 °C, using a pressure of 200 kg/m² for 5 min.

Pilot-plant scale batches of SCPB with 0.025, 0.050, 0.100, 0.150 and 0.250 wt% of TRIGONOX were prepared by reactive extrusion in a Berstorff ZE25 co-rotating intermeshing twin-screw extruder (Germany) at 150 rpm. Total throughput was 4 kg/h. Barrel temperature profile from hopper to die was 155–152–149–146–143–140–137–140 °C. The polymer blend without peroxide was also prepared as reference.

Slightly crosslinked biocomposites (SCbC) with 25, 30 and 35 wt% of RCF and 0.025 and 0.050 wt% of TRIGONOX peroxide were prepared in the same way as SCPB, except for the barrel temperature profile, which slightly changed in this case. It was 155–152–149–146–143–140–143–155 °C, from hopper to die. A 1.5 wt% of the MAPE coupling agent was used for both composites and reference materials. Reference materials without reinforcement and 0.025 and 0.050 wt% of TRIGONOX were also prepared.

In the compounding process, the raw plastics, as well as the organic peroxide, the thermal stabilizer and the coupling agent were fed by continuous dosing at the head of the extruder, whereas the RCF were fed through a side feeding port. This process was then followed by a pelletizing stage. Pellets obtained were injection molded to obtain ISO 3167 test specimens in a 450 kN

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