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Reactive compatibilization and melt compounding with nanosilicates of post-consumer flexible plastic packagings

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ABSTRACT

Flexible plastic packagings are rapidly gaining market share since they offer significant functional benefits. However, they also pose a challenge from a recycling perspective. In fact, due to the presence of different polymeric fractions and to contamination by organic substances and out-of-target materials, such as paper and metals, the mechanical properties of the recycled material are relatively poor.

Addition of nanoparticles to plastic waste can offer the combinations of improved properties and processing, and reduce operational cost. Moreover, in recent studies it was demonstrated that they can also act as blend compatibilizers.

The aim of this study is the upgrading of Fil-s (acronym for film-small), a fraction of mixed plastic waste stream obtained by the separation and mechanical recycling of post-consumer packaging films of small size. Physical, chemical and rheological characterization evidenced that Fil-s stream is mainly composed of polyethylene and a smaller fraction of polypropylene. With the purpose to improve the performances of Fil-s, lamellar and acicular organoclays were melt compounded with the recycled material in a twin-screw extruder. Moreover, in order to enhance the compatibility between the polyolefin components and the nanofiller dispersion in the mixed polymer matrix, the functionalization of Fil-s with maleic anhydride (MAH) was realized by reactive extrusion.

Morphological, thermal, rheological and mechanical properties of the functionalized materials and the nanocomposite systems were extensively discussed. The positive effect of the MAH-grafting on the compatibilization between the two polyolefin components of Fil-s was pointed out and an interesting improvement in ductility of Fil-s was obtained. The further addition of the nanoclays also significantly increased the stiffness of the systems.

1. Introduction

Plastic represents an integral and important part of the global economy, since it combines unrivalled functional properties with competitive cost. While delivering many benefits, plastic economy has important environmental drawbacks that are becoming more apparent day by day.

As evidenced by the World Economic Forum in 2017 [1], only 14% of plastic packaging, that currently represents the largest application of the produced plastics, is globally collected for recycling, while 72% is not recovered at all, generating significant degradation of natural systems.

However, this collected-for-recycling rate varies tremendously by format and material type. In particular, certain material/format combinations — mainly rigid packaging, such as PET and HDPE bottles, and post-commercial films — are already recycled at relatively high volumes. The reason for these differences in recycling rates is the extent to which the format and packaging design enable high-purity after-use streams at competitive prices and in significant volumes, a key driver for recycling economics.

At this regards, flexible packaging items, that generally consist of blends of different plastics or combines layers of different materials (several plastic types, thin metal foils or coatings and/or layers of paper), pose a challenge from a recycling perspective. In particular, the presence of different polymeric materials can remarkably increase the difficulty of recycling operations. In fact, different melting points could induce degradation of some components of the mixtures, and even very low amounts of

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contaminants may have negative synergistic effects on thermo-mechanical degradation of the recycled material during processing. Moreover, recycled mixed polymeric blends usually show low compatibility between the different polymeric components, which leads to polymeric dispersion microstructures with limited interfacial adhesion and thus poor mechanical properties [3]. Besides, flexible packaging tends to be more problematic during the collection and sorting stages, due to the low weight-to-volume ratio of films and plastic bags.

On the other hand, the potential benefits of flexible packaging recycling, in terms of resource efficiency, diversion from landfill and emission savings, are very high considering that these packaging types are rapidly gaining market share from other sectors, such as traditional rigid packaging [2]. In fact, the switch to flexible packaging benefits: (1) manufacturers by reducing weight and costs in warehousing and shipping and reducing energy during production; (2) retailers by reducing weight/size, increasing shelf-life and improving graphics to attract customer attention; and (3) customers by offering convenient features that weren't available in cans and bottles, as well as improved taste in food.

Improvements in the procedures for separating commingled waste streams may lead to more effective mechanical recycling, but this procedure alone is never fully effective, in particular for flexible packaging. Another possibility for the mechanical recycling of mixed waste streams could be the upgrading of polymeric blends through the inclusion of suitable additives, which could stabilize the system and improve the interfacial adhesion and dispersion of the mixture components (compatibilization) [4].

It is worth to point out that compatibilization of mixed plastic waste is a more difficult task, because the degree of degradation of individual polymers may have a broad distribution, due to differences in lifetime history of the articles which form the source of the waste.

Many commercial compatibilizers base their function on physical or chemical effects [5,6]. Non-reactive compatibilizers are usually graft or block copolymers, in which the blocks must be chemically similar or even identical to the blend components to be compatibilized. As a consequence, traditional block and graft copolymers are specific, relatively expensive to engineer, and very difficult to produce for polymeric mixtures with more than two components.

Recently, several groups have shown that organoclays can effectively reduce the domain size of polymer blends in several systems [7–13]. In fact, when the nanoparticles are well dispersed in the polymer matrix, they become very effective nucleating agents for in-situ graft formation. If more than one polymer is present, then adsorption of all the chains to the clay surface will occur. Since these fillers have a large surface area, they can deliver a large amount of grafts to the interface. These grafts can act the same function as block copolymers, effectively decreasing the interfacial tension and reducing the domain size. The relative simplicity of this method, and the fact that it is applicable to a wide variety of blends, makes it an attractive alternative to current technologies in processing recycled polymer wastes for which the composition can vary in an unpredictable manner and cost is a primary factor. Furthermore, addition of nanoparticles to recycled polymers can offer the combinations of improved properties, low-weight, ease of processing, and low cost which is not easily and concurrently found in other manufactured goods [14–28].

Apart from adding prefabricated modified polymers or other additives (such as nanofillers), compatibilization can be achieved by the addition of low-molecular-weight reactive compounds that could promote copolymer formation or (co-)cross-linking [5,6]. These are usually peroxides and monomers. Free radical reactions can lead to compatibilizing copolymers through recombination of the radicals on the polymer chains. These reactions can be more effective in the presence of a monomer as this lowers the reactivity of the macro-radical resulting in less degradation or cross-linking of the macromolecules. The low molecular weight compounds used in reactive extrusion are usually added at relatively low concentrations. For that reason they offer considerable economic advantages versus polymeric compatibilizers that are more expensive and usually only effective at higher concentrations.

The aim of this study is the effective recycling of Fil-s (acronym for film-small), a fraction of mixed plastic waste stream obtained by the sorting of post-consumer packaging films of small size (less than A3). To this purpose two organoclays (Dellite 67G and Sepiolite PM15), with different morphology (lamellar and acicular), were melt compounded with the recycled material in a twin-screw extruder, in order to mainly improve the mechanical properties of Fil-s, also taking advantage of the function of nanofillers as potential blend compatibilizers. To further enhance the compatibility between the polyolefin components of the post-consumer material and concurrently improve the nanofiller dispersion in the mixed polymer matrix, the recycled material was functionalized with maleic anhydride (MAH) by reactive extrusion. The reactive grafting/compatibilization of Fil-s was opportunely tuned through the optimization of two fundamental parameters, such as the content of maleic anhydride and the extrusion speed during the process, this latter being strictly correlated to the micro-mixing conditions inside the extruder.

The MAH-grafted Fil-s was successively compounded with the selected nanoparticles and the effect of both the grafting reaction and the nanofiller addition were evaluated through the extensive analysis of the thermal, morphological and mechanical properties of the obtained systems.

2. Experimental

2.1. Materials

The batch of waste analyzed in this work was provided by COREPLA (the Italian National Consortium for the Collection and Recycling of Plastic Packaging). It is denoted as Fil-s and represents a fraction of mixed plastic waste stream obtained by the sorting of post-consumer packaging films of small size ($\leq$A3 format, that is 29.7 × 42 cm).

Two organomodified nanoclays, Dellite 67G (named D67G), supplied by Laviosa Chimica Mineraria in Italy, and Sepiolite PM15 (named PM15), supplied by Tolsa Group in Spain, were used as nanofillers. Their main characteristics are reported in Table 1.

For the Fil-s functionalization dicumyl peroxide (DCP, analysis grade 98%), as the initiator (supplied by Sigma Aldrich), and the maleic anhydride (MAH, analysis grade $\geq$99%), as the grafting agent (supplied by Sigma Aldrich), were selected. All the other chemicals, also purchased from Sigma Aldrich, were reagent-grade products and were used without further purification.

2.2. Melt compounding and grafting procedure

The compounding of Fil-s and nanoclays was conducted using a twin-screw extruder (Dr. Collin GmbH – model ZK 25-48D, Germany) with co-rotating intermeshing screws (D_{screw} = 25 mm, L/D = 42). Prior to processing, the materials (both the polymer and the nanoclays) were dried in a vacuum oven at 70 °C for 18 h, to avoid bubble formation and polymer degradation during processing. A screw speed of 100 rpm and temperatures of 190 °C, along the barrel, and 160 °C, at the die, were used. Extruded materials were cooled into a water bath and pelletized. The hybrids were produced at 5 wt % of silicate content by making use of a volumetric