

Natural Nanozeolite as Desiccant and Reinforcement Additive in Recycled Polymer Blends from Post-Consumer Flexible Packaging

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This study concerned with the upgrading of a mixed polyolefin material, obtained by the sorting and mechanical recycling of flexible packaging of small size (< 0.125 m²). It is mainly composed of polyethylene and a minor amount of polypropylene, with traces of polar contaminants. These latter are responsible for material's hygroscopicity, which negatively affects its processability and final performances.

In the present work, the recycle was melt compounded with different amounts of a nanometric natural zeolite by means of a single-screw extruder. The idea was to take advantage of the potential double function of this additive, as desiccant and reinforcement.

The neat recycle and its blends with the nanozeolite were extruded in the form of ribbons that were submitted to tensile mechanical tests. Significant increases of both stiffness and strain at break were observed for the systems Fil-s/nanozeolite compared to the neat recycle, due to an efficient drying and reinforcement action of the selected nanozeolite, despite the non-optimal dispersion of the nanofiller.

1. Introduction

The issue addressed in this study mainly concerns the hygroscopicity of mixed polyolefin recycles. A particular fraction of post-consumer plastic films waste, denoted as Fil-s, was investigated. It results from the mechanical recycling of flexible packaging with a size smaller than A3 (0.125 m²) and, even if it is essentially composed of polyethylene and polypropylene, the presence of polar contaminants allows moisture adsorption, negatively affecting its processability and macroscopic properties (Garofalo et al., 2018). In fact, at the high temperatures during polymer processing, water can become steam, giving rise to the formation of defects, such as streaks and surface bubbles, until the onset of severe deformations and breakages. Furthermore, water molecules can diffuse within the polymer structure, binding to macromolecules and causing the reduction of intermolecular bonds. This makes the material more flexible and causes a reduction in the elastic modulus, the hardness and the mechanical resistance. Moreover, the water in the melt polymer can accelerate degradation mechanisms (hydrolysis reactions), causing chains break with the formation of by-products, and, consequently, lowering the material molecular weight. As a consequence, before processing these materials, an "unconventional" drying step for polyolefin is required, which increases the manufacturing costs and makes these recycles not economically viable.

In this study we provided an innovative solution, alternative to drying, based on the use of zeolites as desiccant additives during the recycle processing. Even if the desiccant function of zeolites is well known in literature (Kajtár et al., 2017) (Kenyó, 2013), at the best of our knowledge, their use as moisture adsorbers during the extrusion of polymers has not yet been tested. Some peculiar characteristics of zeolites, such as the rapid water adsorption kinetic, even at low relative humidity, and their ability to retain it at high temperatures, make them potentially more suitable for this purpose than other physical (clays, active carbon, silica gel, etc.) or chemical (CaO, CaSO₄, etc.) desiccants. In fact, the processing of thermoplastic polymers takes place in a short time and at high temperatures.

In particular, for the present research a zeolite of nanometric dimensions was selected, since the outstanding performances of polymer nanocomposites have been extensively demonstrated in literature (Cinelli et al., 2017). Small amounts of a nanofiller (generally equal to 3-6%) allow obtaining a significant increase of both structural and functional properties (Garofalo et al., 2017) of the polymer matrix, without the undesirable effects due to the addition of micrometric inorganic additives (increase in density, embrittlement, reduction of processability). Recently, several authors (Zare et al., 2013) (Garofalo et al., 2019) have also reported on the potentialities of the nanoparticles as waste management strategy that offers the combination of improved properties, ease of processing and low cost.

In this study, the nanozeolite was added, in different weight amounts, during the processing of Fil-s by means of a single screw extruder to produce manufactures in the form of ribbons. The obtained samples were characterized by tensile mechanical tests and their performances were compared with the ones of neat Fil-s, not previously heat-dried. In order to evaluate the dispersion degree of the nanozeolite inside Fil-s, rheological and SEM analysis were also performed on the hybrid systems.

2. Experimental

2.1 Materials and production of the composites

The batch of plastic waste stream, 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 plastics obtained by the sorting and mechanical recycling of post-consumer packaging films of small size (< 0.125 m²). As extensively reported in our recent works (Garofalo et al., 2015), (Garofalo et al., 2018), (Garofalo et al., 2019), the physical-chemical characterization of this recycled material evidenced that it is essentially constituted of polyethylene (LLDPE and LDPE) and a minor fraction of polypropylene (from 5% to 15 % by weight), with traces of other polymers, such as polyesters and polyamides, and of low molecular weight contaminants. In this study, a Fil-s batch with a content of polypropylene of ca 8wt% was used.

Regarding the desiccant, a natural zeolite (TMAZ-7) was provided by Europa Chemica (Slavonia – Osijek). In particular, it is a nanometer zeolite with particle size ranging from 5-30 nm, pore size of 4-7 Å and Si/Al ratio of about 5. Moreover, its chemical composition is reported in Table 1.

Table 1: Chemical composition of the nanozeolite TMAZ-7

SiO ₂ [%]	Al ₂ O ₃ [%]	Fe ₂ O ₃ [%]	CaO [%]	MgO [%]	Na ₂ O [%]	K ₂ O [%]	TiO ₂ [%]	MnO [%]
66.15	12.33	1.32	5.35	0.62	1.42	2.77	0.16	0.04

The neat Fil-s and its blends with the nanozeolite (at 3 and 5wt%) were extruded using a Brabender Do-Corder 330 (GmbH, Germany) single-screw extruder (Dscrew=20 mm and L/D=20), equipped with a flat die (20 mm x 1 mm). A screw speed of 20 rpm and a temperature profile of 165-170-160°C from hopper to die were imposed.

2.2 Characterization techniques

Moisture adsorption isotherms for Fil-s and the nanozeolite were determined using an environmental chamber Challenge ACS CH250 (Angelantoni, Italy), which provided constant temperature and humidity control.

The initial moisture content of the recyclate pellets, which resulted equal to 250 ± 15 ppm, was measured (on a dry-weight basis) after drying the samples in a hot-air oven at 70 ± 5°C until constant weight was obtained. In order to remove the adsorbed water vapor or other volatiles, the nanozeolite was dehydrated at 300°C for 16 h before use (Gabruś et al., 2015). Then, the moisture adsorption isotherms were determined by exposing 10 g of the dehydrated zeolite and Fil-s inside the climatic chamber at 25 ± 1°C and relative humidity RH= 50%, in order to simulate standard environmental climatic conditions. The weight increase of the samples (expressed as percentage of the adsorbed water) was reported as a function of time.

Rheological experiments in oscillatory mode were conducted with a Rheometric Scientific rotational rheometer, ARES, under a nitrogen atmosphere. Rheological measurements were performed at 190°C in an angular frequency range from 0.1 to 100 rad/s, using 25 mm diameter parallel plates. The deformation of 1% of strain amplitude was proven to ensure linear viscoelasticity during the dynamic tests.

The external surfaces and the sections (obtained by cryo-fracturing the specimens in liquid nitrogen normally to the extrusion direction) of Fil-s ribbons were observed with a Zeiss Axioskop microscope (Carl Zeiss Vision, Germany). Scanning electron microscopy (SEM) analysis was conducted using a Zeiss EVO MA10 microscope with a secondary electron detector (Carl Zeiss SMT AG, München-Hallbergmoos, Germany),

operating at 14 kV. The images were taken on specimens cryo-fractured in liquid nitrogen and sputter-coated with a 200–440 Å thick gold layer by means of a Leica EMSCD005 metallization device.

Mechanical tests were carried out, according to ASTM standard D882, by a CMT4000 Series dynamometer (MTS, Shenzhen China). The ribbons were tested with a grip distance of 50 mm and a crosshead speed of 5 mm/min to measure the Young's modulus and 500 mm/min to determine the stress and elongation at break.

3. Results and discussion

Figure 1 shows the moisture adsorption isotherms of Fil-s pellets and nanozeolite powder, determined by gravimetric procedure at 25°C and relative humidity RH=50%.

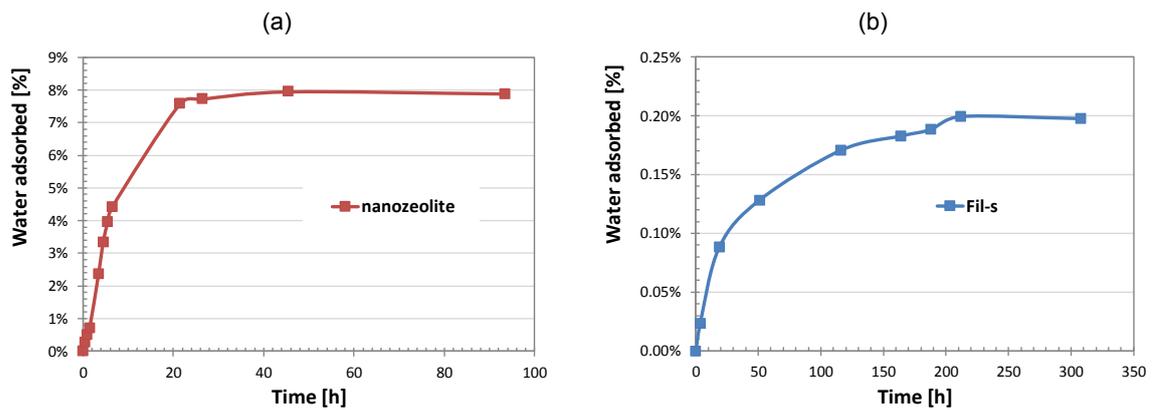


Figure 1: Moisture adsorption isotherms at $T=25^{\circ}\text{C}$ and $\text{RH}=50\%$ for (a) Fil-s and (b) the nanozeolite

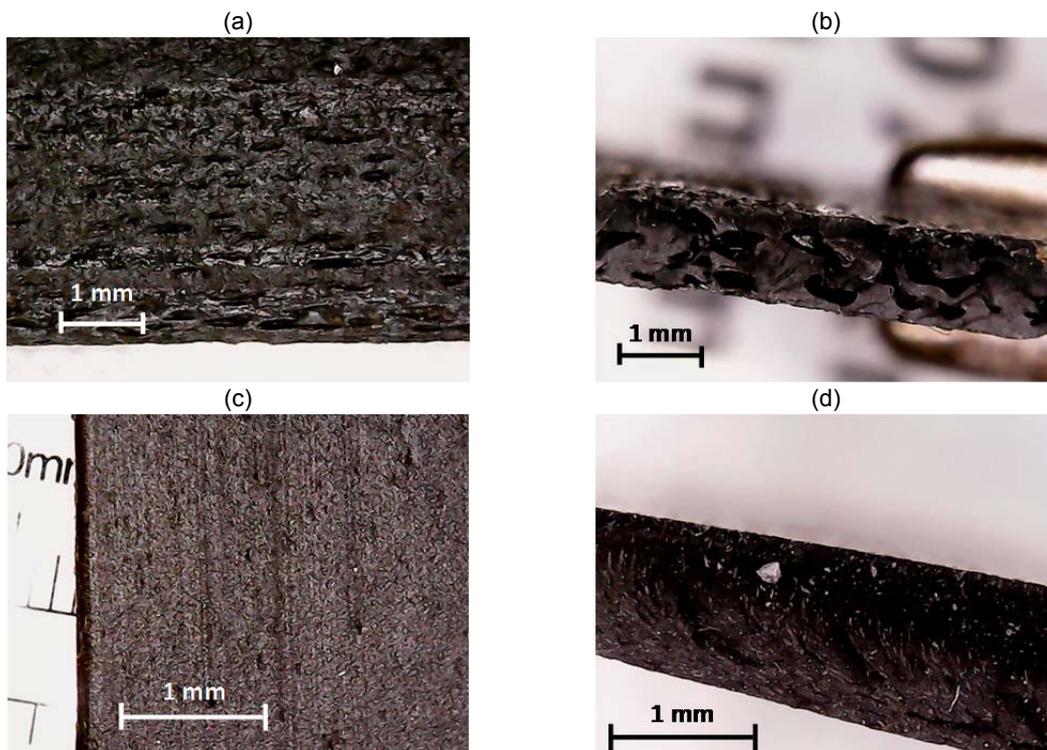


Figure 2: Images of the neat Fil-s (a, b) and Fil-s+5% nanozeolite system (c, d), performed with an optical microscopy on the surface and the cross section of the samples, respectively.

As it can be observed from the graphs, the moisture adsorption curves show a typical Fickian behavior, increasing with the time until equilibrium conditions were reached. The main differences, in terms of moisture adsorption behavior for the recycleate respect to the nanozeolite, concern the adsorption rates and their

adsorption capacities. In particular, the selected nanozeolite shows a very fast water adsorption rate, reaching an equilibrium moisture content, equal to 8% by weight, after only 24 hours from the start of conditioning in the climatic chamber. In the case of Fil-s, a significant lower moisture content at equilibrium (about 0.2%) was achieved after a time (ca. 200 hours) of one magnitude order higher than the one assessed for the nanozeolite. Based on the measured moisture adsorption capacities for Fil-s and the nanozeolite, the weight percentages of the nanofiller to add inside Fil-s during its extrusion were properly established at 3 and 5%. The aim was of mixing the recyclate with amounts of nanozeolite enough to ideally capture all the water molecules contained inside Fil-s.

Then, the undried recyclate was mechanically mixed with the different contents of the nanofiller and extruded by means a single screw extruder. For comparison purposes, the undried Fil-s was also extruded as such. By a visual inspection of the obtained specimens (Figures 2), the effectiveness of the selected nanozeolite as a desiccant can be easily deduced.

In fact, while the composite Fil-s/nanozeolite resulted in homogeneous products without naked-eye detectable defects, the neat Fil-s sample showed several macroscopic voids and streaks on both the surface and in bulk, due to the water evaporation at the high extrusion temperatures.

The obtained manufactures were also characterized by means of tensile tests and their main mechanical properties are compared in Table 2.

Table 2: Tensile mechanical properties (E , Young's modulus; ε_y , ε_b strain at yield and at break; σ_y , σ_b , stress at yield and at break) for Fil-s and Fil-s/nanozeolite composites

Sample			E [MPa]	ε_y [%]	σ_y [MPa]	ε_b [%]	σ_b [MPa]
Fil-s			230 ± 15	16.3 ± 1.2	7.4 ± 0.1	41 ± 9	7.1 ± 0.1
Fil-s + nanozeolite	3%		330 ± 20	19.7 ± 0.7	11.4 ± 0.4	170 ± 115	9.6 ± 0.5
Fil-s + nanozeolite	5%		370 ± 10	18.5 ± 0.6	11.8 ± 0.2	150 ± 110	10.0 ± 0.7

The nanozeolite addition determines significant increments in the Young's modulus compared to the neat Fil-s. In particular, stiffness increases of 40%, for the composite with 3wt% of the nanofiller, and of about 60%, with the higher zeolite content, can be observed.

As regards the ductility of the composites, the presence of the nanozeolite determines a significant increase (about 260%) in the average value of the deformation at break respect to the neat Fil-s, but a non-homogeneous behaviour is recorded, as clearly highlighted by the high value of the standard deviation reported in Table 2. In particular, 20 specimens for each composite system were tested with the dynamometer and about 60% of them showed values of the strain at break in the range 220 ± 90 , while the remaining 40% of the specimens showed ε_b values comparable to the ones of the undried Fil-s.

These results highlight that nanozeolite works very well as reinforcement and it also shows great potentialities as a drying agent during the recyclate processing. However, this latter function is strongly affected by the dispersion degree of this additive inside the recycled matrix.

In this regards, dynamic rheological analysis and morphological characterization were performed on the neat Fil-s and Fil-s/nanozeolite composites, in order to obtain information about the dispersion/distribution of the nanofiller inside the recycled material. In Figure 3 the plots of the complex viscosity (η^*) for Fil-s and its composite at 5% of nanozeolite are compared. The addition of the nanofiller does not cause any significant changes in the values of η^* respect to the neat Fil-s, suggesting a poor dispersion degree of the nanozeolite, as also confirmed by SEM images of the composite (Figure 3b).

The micrograph of Fil-s shows a dispersion of polypropylene droplets (lower phase) in the PE matrix (continuous phase). In particular, the poor interfacial adhesion between these polymeric fractions can be clearly deduced by the images, as it has already been observed in literature for similar polyolefin blends (Bertin and Robin, 2002). Moreover, in the micrograph of the composite material, zeolite aggregates of the order of several microns (highlighted inside red circles) are also clearly visible.

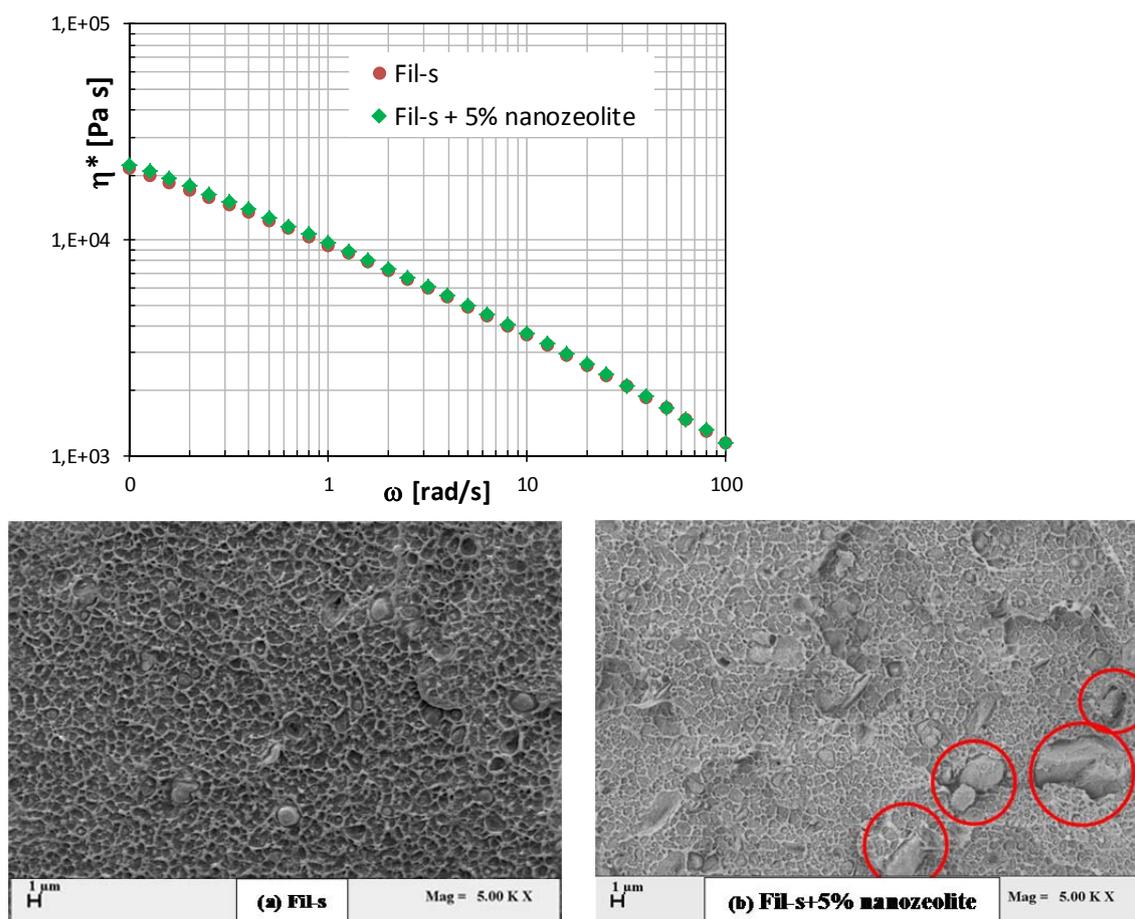


Figure 3: Complex viscosity plots as a function of frequency for the neat Fil-s and Fil-s+5%nanozeolite composite, with the corresponding SEM images.

Starting from these encouraging results, the future work will be focused on the enhancement of the nanofiller dispersion inside the recycled material, through the optimization of both the affinity between the matrix and the filler and the compounding processing conditions.

In particular, a proper chemical modification of the nanozeolite (mainly hydrophilic) and/or the recycle (predominantly hydrophobic) should be carried out, in order to match the polarity characteristics of the nanocomposites' components, so to positively affect the dispersion/distribution of the nanozeolite inside the recycled matrix. On the other hand, the preliminary preparation of masterbatches Fil-s/nanozeolite by means of a twin screw extruder may allow to concurrently improve the mixing degree of these composites and to provide the plastics converters with an easy-to-use desiccant. This latter strategy was already assessed in our previous work (accepted for publication in Journal of Cleaner Production), where Fil-s was compounded with micrometric zeolites. The produced masterbatches proved to have higher handiness and longer shelf-life, preserving the same effectiveness than the neat zeolites in possible industrial application as desiccants during the processing of recycled plastics.

4. Conclusions

The aim of this work was to solve the hygroscopicity issue of Fil-s, a mixed polyolefin recycle obtained from post-consumer flexible films, through the compounding of the recycled material with different amounts (3 and 5 wt%) of a nanometric natural zeolite, in order to take advantages of the potential double function of this additive as desiccant and reinforcement.

The addition of the nanozeolite during extrusion of Fil-s allowed obtaining specimens that were more regular and uniform in shape. Consequently, the absence of macroscopic superficial and volume defects in the composite systems strongly affected their final mechanical properties that resulted significantly better

compared to the neat Fil-s. However, these performances' enhancements were limited by the poor dispersion of the nanozeolite inside the recycle.

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