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Processing and Properties of Polypropylene-Based Composites Containing Inertized Fly Ash from Municipal Solid Waste Incineration

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ABSTRACT: This article reports for the first time the results about the use of inertized fly ash from municipal solid waste incineration as a filler for polypropylene (PP). An innovative process based on the stabilization with colloidal silica has been used for fly ash inertization. Polymer–filler composites containing different filler amounts up to 30 wt % have then been formulated and prepared by means of melt compounding process. Structural, morphological, mechanical, and thermal characterization of their properties has been performed and discussed in detail. Remarkable enhancements of tensile (+ 93%) and flexural (+ 107%) elastic moduli if compared to pristine PP, together with enhancements of flexural resistance (+ 36%) and deflection temperature under load (+ 50%), have been observed when adding filler 30 wt % in suitable processing conditions. Moreover the filler has been shown to interact with polymer crystalline structure and positively influence the thermal-oxidative stability. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4157–4164, 2013

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INTRODUCTION

Disposal methods commonly include incineration, ludge-dewatering, wastewater treatment, waste-to-energy (WTE), and secure landfilling. WTE facilities have played an essential role in the region's integrated waste management.[1] They ensure that, if disposed in an environmentally safe manner, waste can generate valuable energy resources like steam and electricity. However, WTE technology produces large quantities of fly ash, with a potential health hazard because of the presence of toxic metals such as lead, cadmium, copper, and zinc as well as small amounts of dioxins and furans. Generally, fly ash from municipal solid waste incineration process (MSWI) is disposed in landfills.

A new method, based on the use of colloidal silica,[2] has recently shown its effectiveness in heavy metals entrapment for fly ash inertization. Moreover the obtained inertized product (COSMOS, acronym for COlloidal Silica Medium to Obtain Safe inert) showed interesting performances when used as a filler in building materials as a substitute for sand.[3]

Polypropylene (PP) is a well know thermoplastic polymer, a commodity produced in large quantities worldwide and it is used extensively in applications like packaging, automotive, household, and accessories.[4] The tailoring of PP properties is usually obtained by the addition of inorganic fillers. For example, the poor fracture behavior has been improved by means of the addition of rigid inorganic particles.[5] Other studies have been focused on the increase of PP stiffness and heat deflection temperature, shrinkage decrease, improvement of appearance and decrease of the final costs.[6] On the other hand talc, commonly used as a reinforcing filler for PP is leading to several environmental issues like abiotic depletion and pollution as it is a nonrenewable natural resource.[7]

Standard MSWI fly ash has already been tested as a filler in PP and the obtained composites have then been exposed to outdoor weathering in order to assess heavy metals release.[8] In other studies, MSWI fly ash inertized by means of vitrification process was successfully tested as reinforcement of plastics, thermoplastics, bituminous composites.[9] Fly ash from rice husk ash has been used too as reinforcing agent for PP, but a compatibilizer is required to obtain a suitable and effective dispersion of the filler.[10]

In this article the synthesis and extensive structural [X-ray diffraction (XRD), scanning electron microscopy], physical (mechanical testings) and thermal (thermo-gravimetric, calorimetric, and dynamic-mechanical analyses) characterization of innovative PP/COSMOS-based composites are reported. The aim of this study is the assessment of the effectiveness of COSMOS as a reinforcing filler for thermoplastic composites, hence not only decreasing the environmental impact of MSWI fly ash, but even producing, at reduced costs, valuable polymer-based composites characterized by peculiar features.

EXPERIMENTAL

Materials

Three different fly ashes were used in COSMOS manufacturing process: MSWI fly ash, flue gas desulfurization (FGD) fly ash, and coal fly ashes. The inertization was obtained by adding about 25 wt % of colloidal silica solution (Ludox SM-30, W.R. Grace, USA) to the mixture of MSWI fly ash, FGD residues fly ash and coal fly ash (65, 20, and 15 wt %, respectively).[11] Then the obtained inert was washed to remove the soluble salts. The solid recovered after filtration has been labeled COSMOS (COlloidal Silica Medium to Obtain Safe inert). The base-polymer chosen for this study was a standard injection molding grade PP homopolymer (PPH 7062, Total Petrochemicals, Feluy, Belgium) with a melt flow index of 12 g/10 min (230°C and 2.16 kg).

Composites Preparation

A co-rotating twin screw extruder (TSE, Dr. Collin Gmbh. Mod. ZK25) with a screw diameter of 25 mm and an *L*/*D* ratio of 27 has been used for PP/COSMOS composites production. The extruder was equipped with a classic main volumetric feed hopper for polymer granules and with a vacuum venting system in order to remove vapor and gases from the molten mixture. Polymer and filler were previously dried overnight at 90°C in a circulating oven and then predry-blended in a turbo-mixer. Composite blends containing, respectively, 5, 15, and 30 wt % of filler were prepared without using compatibilizers. During the extrusion a temperature profile ranging from 130°C (feeding zone) to 180°C (die) was used, working at a screw speed of 50 rpm (25% of maximum screws speed). The samples produced with these parameters were labeled M1.

For PP/COSMOS 30 wt % formulation a sample has been produced even working at 100 rpm (50% of maximum screws speed) in order to increase specific mixing energy and hence to evaluate the effects of processing conditions on composite structure and properties. This sample was labeled M2.

The pellets obtained were then dried and used to produce mechanical testing specimens according to UNI ISO 527 and UNI ISO 178 standards. In a perspective of industrialization the obtained composites can in fact be used directly for the net shape forming process, without the need of dilution with neat polymer even for the compound containing 30wt % of filler.

A temperature profile ranging from 180°C to 200°C was used for injection molding press (CanBio 55V, Negri Bossi, Italy), with a mold temperature of 20°C and injection pressure of 3 MPa (postpressure 7 MPa for 30 s). No particular effects were evidenced about the influence of using various levels of fillers in the injection moulding setup.

The real amount of filler in polymer/ash composites has been evaluated by calcination at 900°C in air (see characterization paragraph for details about experimental procedure). Experimental results are reported in Table I and have been calculated considering the total weight loss after the same thermal treatment for composites and pure components (21.1 wt % for COSMOS and 100.0 wt % for PP).

Characterization

Structural and microstructural characterization was performed by a Bruker 'D8 Advance' diffractometer operating with Cu tube (40 kV and 40 mA) and by RIGAKU D-MAX Rapid Diffractometer (Cu tube) equipped with an Image Plate detector that allowed to collect 2D diffraction images.

Surface morphology was studied by a LEO EVO 40XVP scanning electron microscope (SEM) equipped with a Link Analytical probe for energy dispersive X-ray spectroscopy.

Tensile properties were measured with a Galdabini model SUN2500 universal machine imposing a uniaxial deformation speed of 1 mm min^{-1} for the evaluation of elastic modulus and 50 mm min^{-1} for yield stress and elongation at break, according with UNI ISO 527. Regarding flexural properties measurements, a crosshead speed of 2 mm min^{-1} has been used with a supports span of 64 mm according to UNI ISO 178. A minimum of five test specimens have been tested for each sample after having been conditioned in air at 23°C for at least 48 hours after molding. Impact tests have been performed with a pendulum Ceast model 9010 equipped with a 1 J hammer and operating with notched specimens according to ISO 180. A minimum of 10 specimens have been tested for each sample evaluating the average value and the experimental standard deviation.

Table I. Thermal Properties for PP/COSMOS Composites

	Cosmos content (wt %)				
	0	5-M1	15-M1	30-M1	30-M2
Measured filler content[a](wt %)	0	4.6 ± 0.1	16.6 ± 0.5	29.6 ± 0.8	28.6 ± 0.7
Crystallization temperature, T_c (°C)	119.9 ± 1.7	118.5 ± 1.8	120.5 ± 1.8	127.2 ± 1.9	125.2 ± 1.8
Melting temperature, T_m (°C)	166.1 ± 1.0	166.8 ± 1.0	166.7 ± 1.0	165.5 ± 1.0	165.3 ± 1.0
DTUL (°C)	49.9 ± 2.9	53.2 ± 2.1	55.6 ± 3.3	65.6 ± 3.9	68.1 ± 3.4
Temperature at 50wt % weight loss (°C)	378.5 ± 1.5	385.5 ± 1.5	395.6 ± 1.5	403.8 ± 1.5	409.8 ± 1.5

[a] Measured as TGA residue at 900°C (air) and calculated considering pure PP and pure COSMOS residues at the same temperature

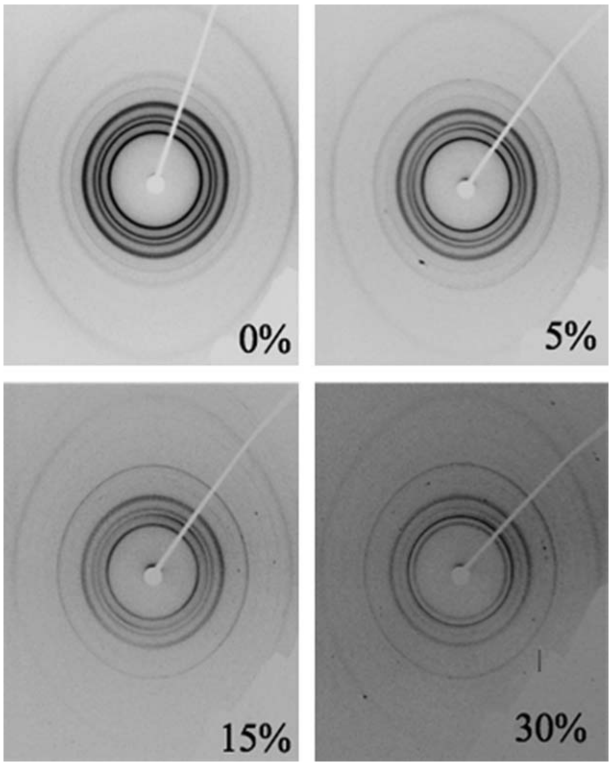

Figure 1. 2D diffraction images collected for M1 series samples varying COSMOS content.

The filler content and thermal stability of the produced composites has been measured using a thermo-gravimetric analyzer (TGA, TA Instruments model Q600) and operating from ambient temperature to 900°C at an heating rate of 20°C min^{-1} and an air flow rate of 70 cm^3 min^{-1}.

Dynamic mechanical analysis (TA Instruments model Q800) measurements were carried out in order to analyze the deflection temperature under load (DTUL). Temperature ramp measurements were done in three-points bending geometry (span 15 mm) mode with a load of 3.23 N as calculated from ASTM D648 considering sample dimensions. A temperature ramp of 1°C min^{-1} has been used and the temperature value corresponding to a relative displacement of 0.121% has been considered. The average value and standard deviation have been calculated considering the whole specimens tested for each sample.

Crystallization/melting properties were also investigated by means of standard differential scanning calorimeter (DSC, TA Instruments model Q200). Specimens were cyclically heated and cooled from 0°C to 220°C, using ramps of 10°C min^{-1}.

RESULTS AND DISCUSSION

2D XRD patterns for pristine PP and PP/COSMOS composites (M1 series), collected in transmission mode, are shown in Figure 1: the Debye rings appear continuous, excluding preferred orientation effects. Conventional XRD patterns of COSMOS, pristine PP and PP/COSMOS composites (M1 series samples) are shown in Figure 2 (2D XRD and conventional XRD patterns of M2 sample are not reported because they are very similar to corresponding M1 one).

Pristine PP shows four peaks at angular values of about 14°, 17°, 18°, and 22°, which correspond to α monoclinic form PP crystals.[12] In PP/COSMOS blends, the peak at about 29.4° increases with COSMOS content. This peak can be attributed to the filler as it corresponds to the main peak of calcite (a component of COSMOS).

XRD patterns (Figure 2) of all M1 samples show that the intensities of PP peaks are reduced in presence of filler. Absorption of X-ray radiation by COSMOS particles cannot justify this strong decrease.[13] Figure 1 indicates that this change is not related to preferred orientation effect, hence suggesting a structural reorganization of the PP crystalline phase because of filler. Moreover, the decrease of PP peaks intensity suggests that COSMOS may reduce polymer crystallinity. Indeed, it was already reported that the crystalline phase/orientation of the polymer chains can be appreciably affected by the incorporation of fillers.[6]

The structure of PP/COSMOS composites has been studied also by means of DSC and experimental results have been reported in Table I. Samples collected from injection molded specimens have been considered in order to compare the results with the ones obtained by XRD characterization. In particular, a nucleating effect has been evidenced during cooling step from the melt (Table I). For pristine PP the measured crystallization temperature (T_c) is of about 112°C; when increasing COSMOS content, a shift of this value towards higher temperatures can be evidenced. A remarkable increase in T_c may be noted even with the addition of 15 wt % of filler, whereas the highest value of T_c (about 127°C) can be reached only for COSMOS 30 wt %.

The crystallinity of PP and PP/COSMOS blends were evaluated even by XRD, comparing the integrated area of crystalline and amorphous peaks,[15] a basic approach that can be applied as the polymer is randomly oriented (see Figure 1). The change of crystallinity was calculated also by DSC by measuring the specific melting enthalpies of the blends rescaled considering real COSMOS content experimentally measured by TGA. Percent

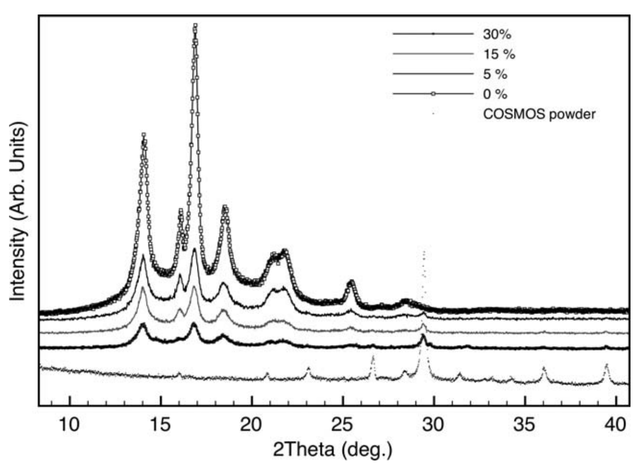

Figure 2. XRD patterns collected for M1 series samples and COSMOS pristine powder.

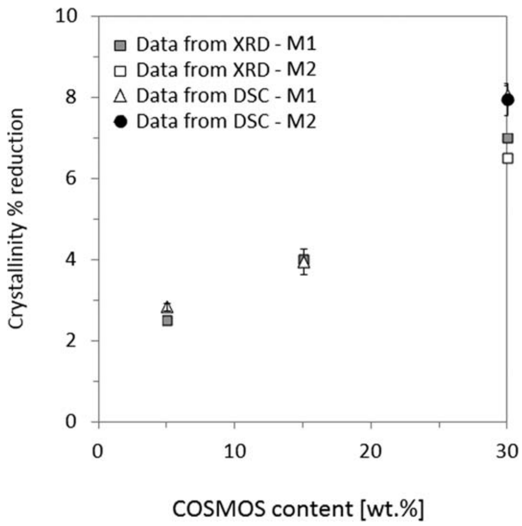

Figure 3. Percent of crystallinity reduction for the PP in PP/COSMOS composites calculated with respect to pristine PP, as a function of filler amount. M1 and M2 (only for PP/COSMOS 30 wt % sample) indicate the different processing conditions.

amounts of crystallinity reduction evaluated by means of XRD and DSC are shown in Figure 3. Considering experimental errors, the trends are in good agreement indicating a slightly but progressive reduction of PP crystalline phase (hence the increasing of the amorphous PP phase) when increasing COSMOS content.

A further thermal property has been considered, that is the deflection temperature under load (DTUL), corresponding to the temperature at which a certain specific displacement is reached for a specimen solicited with a constant load in a three-point bending geometry. The data show a constant linear increase for DTUL as a function of COSMOS content (Table I) as a further evidence of the reinforcing effect of COSMOS filler at macro scale. A remarkable increase of about + 36% with respect to pristine PP value can be observed regarding PP/COSMOS 30 wt % samples.

In Figure 4 a comparison between TGA curves (air) obtained for pure polymer and composites has been reported. The addition of filler brings to a remarkable improvement of thermal-oxidative stability with an increase of about 30°C for the temperature of 50% weight loss for PP/COSMOS 30 wt % if compared to pristine PP (see also Table I). This is in accordance with the previous results reported by other authors,[14,15] even if a convincing theory regarding the specific mechanism of fly ashes improving PP thermal stability has not been purposed yet as for the case of polycarbonate/fly ash-based composites.[16]

Mechanical properties investigation can give further elements in order to assess COSMOS effect on composites macro scale properties. Hence tensile and flexural properties have been analyzed together with the impact behavior. In Figure 5parameters deriving from tensile tests and normalized with respect to the corresponding values of pure PP have been plotted. A remarkable, linear increase of tensile modulus (1.1 GPa for the pristine PP) can be observed when increasing COSMOS content, because of the reinforcing effect given by filler particles. On the other hand, an exponential decrease in elongation at break occurs, with a reduction of about 80% with respect to pure PP (111% is the pristine PP value) already at the low filler contents (5 wt %). A ductile–brittle failure transition occurs and above 5 wt % of COSMOS the tensile behavior of the composites changes dramatically, with the disappearing of necking formation at yielding point, typical of ductile pristine PP. This phenomenon affects even the value of maximum tensile strength, measured at yield point for pure PP (ductile behavior, with a value of 29.8 MPa) but corresponding to strength at break for COSMOS 15 and 30 wt % M1 composites (fragile behavior). On the other hand the strength at break for M2 composite appears quite similar to the one measured for pure PP (17.4 MPa), revealing that, despite a reduction of the elongation break, an increase of the mixing energy during composite

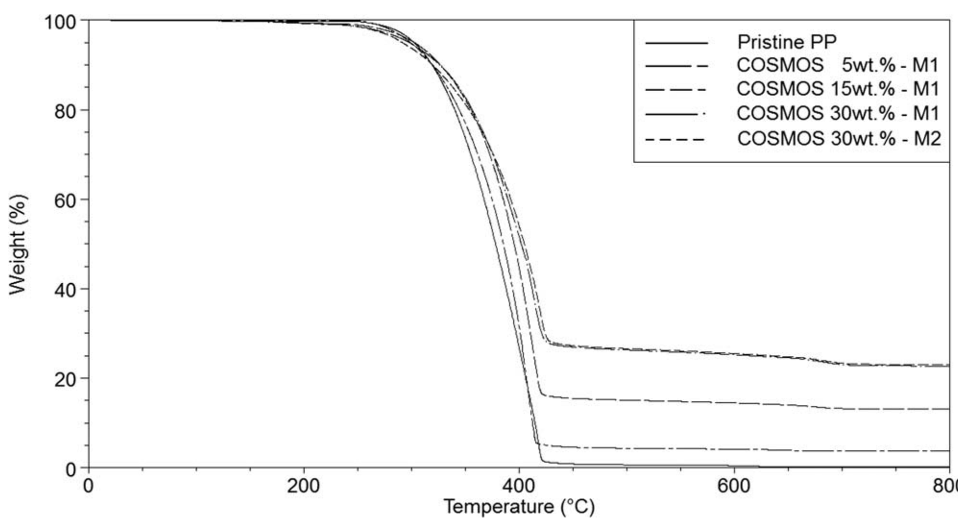

Figure 4. Comparison between TGA analyses for pristine PP and PP/COSMOS composites (air, 20°C min^{-1}). M1 and M2 (only for PP/COSMOS 30 wt %) sample indicate the different processing conditions.

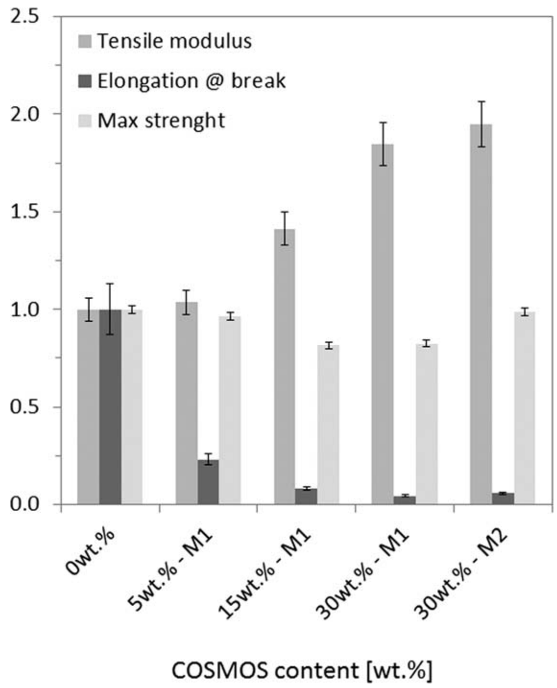

Figure 5. Tensile properties normalized with respect to pristine PP values. M1 and M2 (only for PP/COSMOS 30 wt %) sample indicate the different processing conditions.

production can results in a more effective filler dispersion (see also morphological characterization).

Flexural properties have been reported in Figure 6 (data are normalized with respect to pure PP). Flexural modulus behavior (pristine PP value is 815 MPa) follows with good agreement the

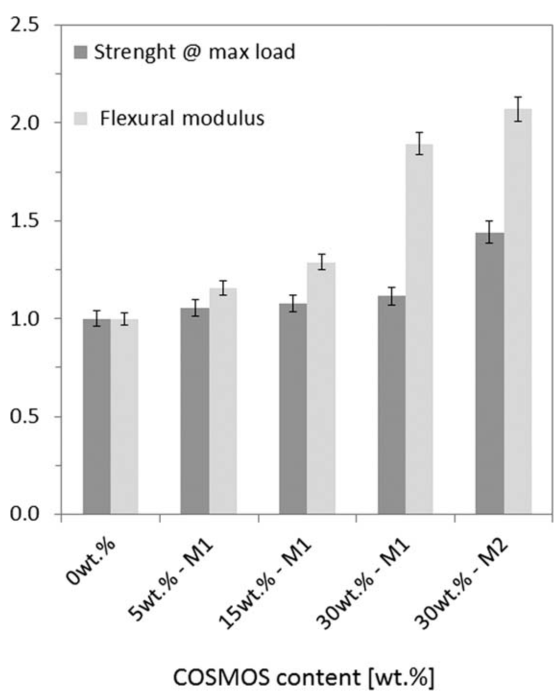

Figure 6. Flexural properties normalized with respect to pristine PP values. M1 and M2 (only for PP/COSMOS 30 wt %) sample indicate the different processing conditions.

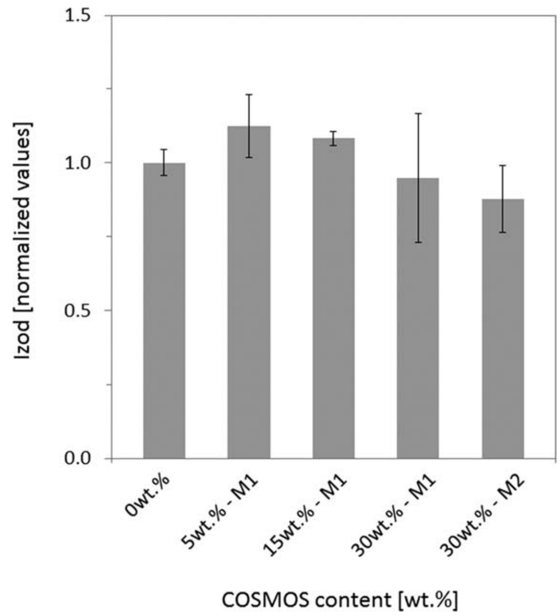

Figure 7. IZOD impact values (normalized with respect to pure PP) trend as a function of COSMOS content. M1 and M2 (only for PP/COSMOS 30 wt %) sample indicate the different processing conditions.

trend of tensile one, linearly increasing as a function of COSMOS addition, while the maximum strength (pristine PP value is 27 MPa) is characterized by a slighter increase as a function of COSMOS content (M1 series samples). For this test specimens length together with three-point bending support span allowed a maximum deformation of 6%, reached by all the composites without showing differences in brittleness with respect to COSMOS content.

PP/COSMOS 30 wt % sample (M2 series) shows an additional improvement of flexural elastic modulus, with respect to the corresponding M1 ones. A remarkable result is the value obtained for maximum strength regarding M2 sample, that results + 36% higher than the one of pure PP. Other researchers observed an improvement of flexural strength in PP as a function of fly ash (coal fly ash) addition with a maximum improvement of about + 20% at 30 wt % filler content.[17,18]

Impact properties revealed an interesting behavior for COSMOS-based composites, as evidenced in Figure 7, where normalized specific impact energies are reported (IZOD method). It is generally know that the incorporation of mineral fillers in polymers does not improve (but often decreases) the impact strength of polymer matrices.[19] Surprisingly, even considering the brittle transition previously described, the impact properties for all composites did not show significant decrease with respect to pure PP property.

An aspect shall be considered, that is the crystalline phase structure. Friedrich[20] and Ouederni et al.[21] found, in fact, that an increase in crystallinity or spherulites size could decrease toughness. For the case we consider, XRD and DSC analyses showed that the crystalline phase amount decreases when increasing COSMOS content hence, IZOD results can partially arise even from variations regarding crystalline structure.

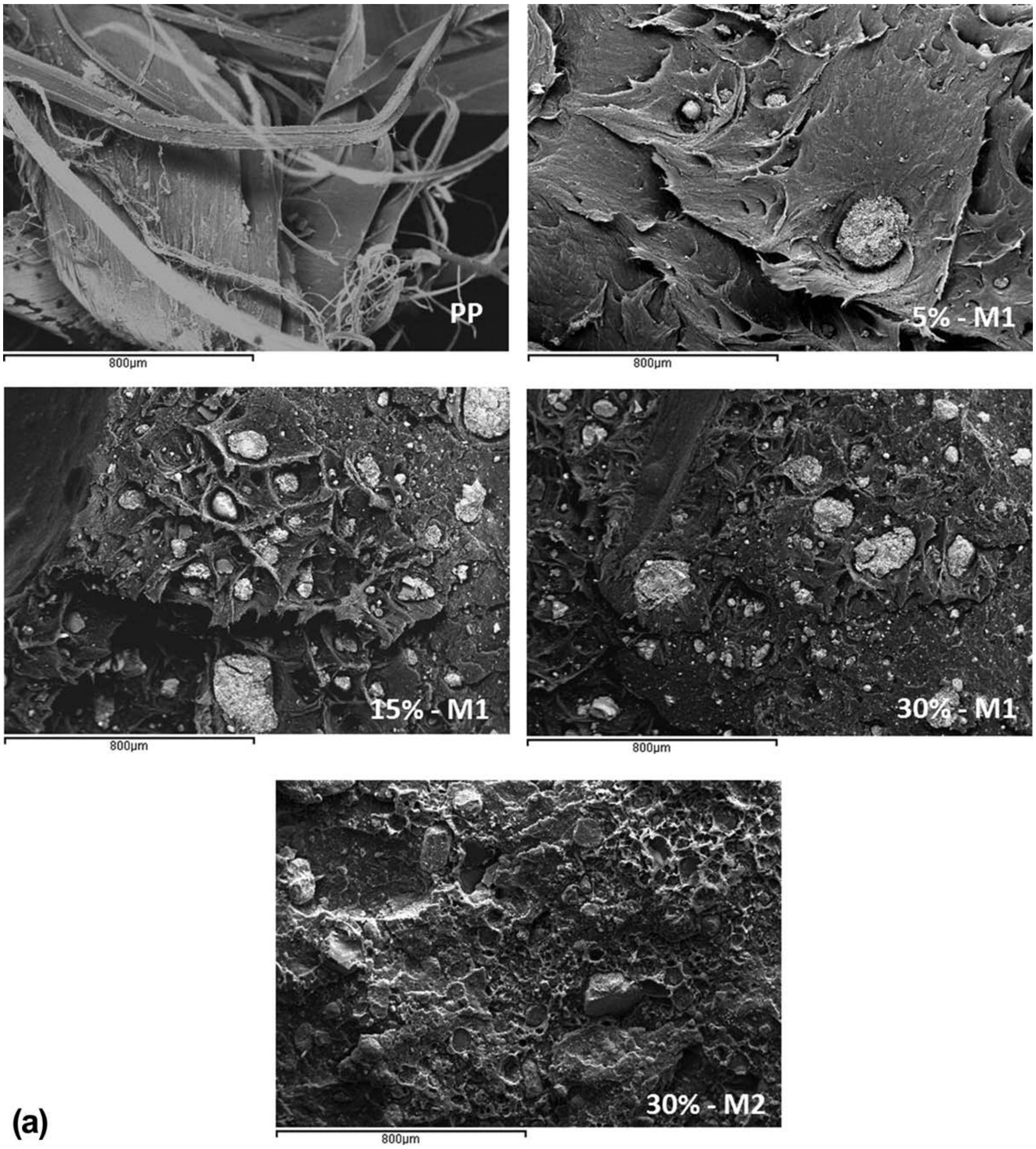

Figure 8. SEM images at different magnifications of all the PP/COSMOS samples.

Moreover it must be considered that, even using a low energy hammer, the impact properties of pure PP are particularly low because of its brittleness (see impact energies values). Hence, probably, this test cannot effectively discretize composites impact behavior from the one of the matrix polymer.

The filler dispersion of in the polymer matrix can have a significant effect on the mechanical properties of the composites. Then, to justify the change in mechanical properties of PP/COSMOS blends, SEM images were collected for all samples. The SEM images of all PP/COSMOS blends, collected in secondary electron mode on the fractured surfaces, are reported in Figure 8. It can be noted that ductility is reduced in filled samples as evidenced by the smaller deformation patterns if compared to pure PP behavior. Moreover images show that the dispersion of COSMOS filler at the microscopic level is quite ineffective for M1 series samples. The surfaces show the presence of microsized agglomerates that seem to coincide with the cracks paths. Moreover, with the increase of COSMOS content, the number of particles on the scanned surface increased in average dimension indicating a reduced effectiveness of mixing process reducing the size of original filler agglomerates. Regarding polymer–filler interface, void formation phenomena can be observed at PP–COSMOS interface.

Basically, regarding M1 series samples, the poor dispersion of filler results in a distribution of filler undispersed aggregates (mainly at higher loadings), which cause a reduction in the

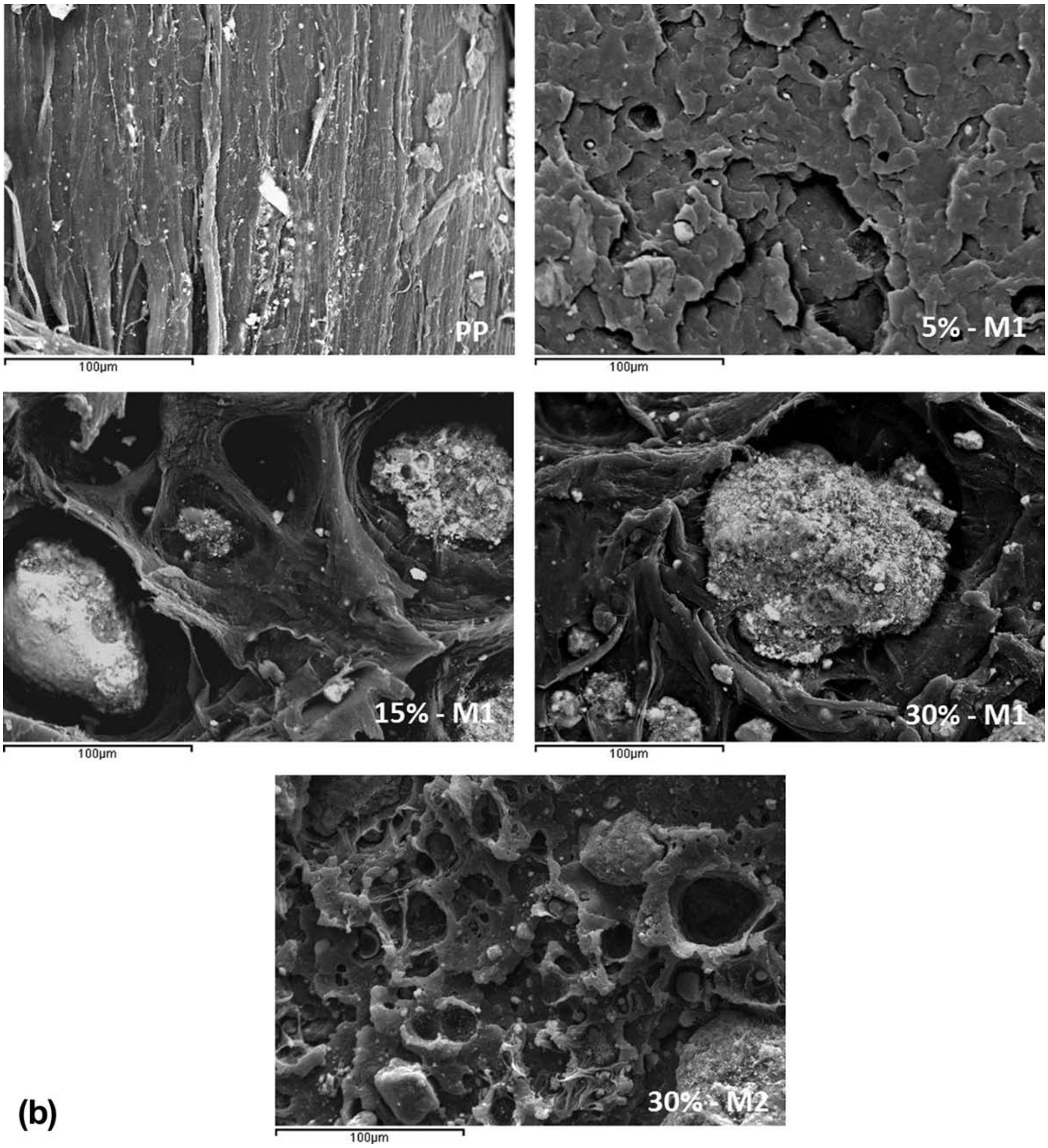

Figure 8. (Continued)

effectiveness to transfer applied load during deformation. On the contrary, M2 sample shows a remarkably different behavior (see Figure 8), with the filler that is homogeneously dispersed in the polymer. The increase of the flexural strength for this composite, with respect to pure PP matrix, indicates that, despite the decrease regarding M2 sample ductility, a good interaction can be obtained between filler and matrix when suitable processing conditions are adopted (higher specific mechanical energy).

Figure 9 shows 2D XRD patterns PP and the M1 PP/COSMOS blends, collected in transmission mode, on the broken area of tensile specimens (XRD patterns of M2 sample is not reported because it appears very similar to corresponding M1 one). 2D Microstructure of PP changes drastically with respect to what reported in Figure 1: the Debye rings now appear discontinuous, showing preferential orientation effect caused by the applied force. Thus, the higher elongation capacity before breaking showed by PP sample is reflected in the higher orientation of the polymer chains with respect to other samples. Indeed, for PP, the Debye rings intensity result concentrated, as a consequence of the strong orientation because of the applied load.

CONCLUSIONS

PP-based composites have been obtained for the first time by using up to 30 wt % of an innovative environmentally

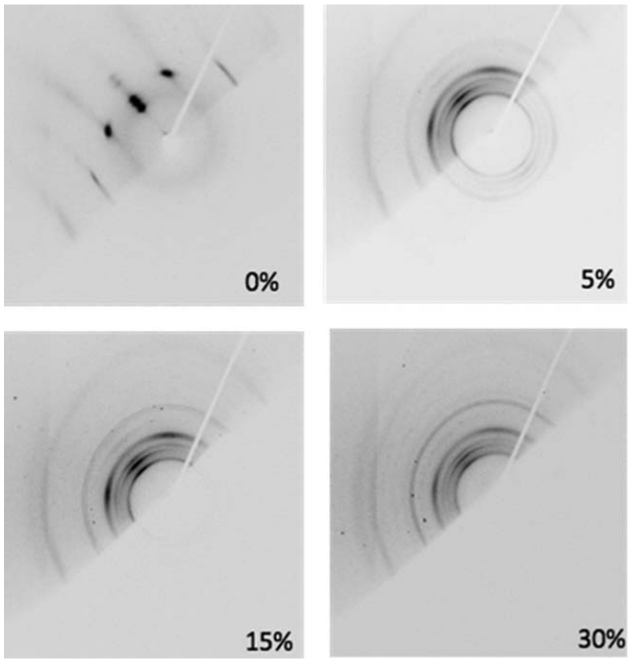

Figure 9. 2D diffraction images collected on all M1 samples on the failure area (tensile tests).

sustainable filler (COSMOS) obtained from the inertization of MSWI fly ash with colloidal silica.

Physical and morphological characterization of the composites evidenced, that when suitable melt compounding conditions are adopted, the addition of COSMOS results in improved mechanical properties with respect to pure PP, with remarkable enhancements of tensile and flexural moduli, flexural strength, and heat deflection temperature under load. It has been evidenced, in particular, as the optimization of processing conditions, mainly in terms of mixing speed during compounding, can have a remarkable effect on filler dispersion. On the other hand, the presence of microsized residue agglomerates because of uneffective mixing, together with ductile–brittle transition phenomena, leads to a sharp reduction of tensile elongation as well, without significative effects on impact behavior.

Conventional and 2D XRD measurements and DSC analysis indicated in fact that the structure and crystallinity of the polymer chains are affected by the incorporation of COSMOS filler, which even acts as nucleating agent for polymer matrix. A positive effect of COSMOS on polymer thermal stability has been assessed as well by means of TGA analyses, with an increase of about 30°C for the temperature of 50% weight at COSMOS 30 wt %.

Hence, considering the reported results the recycling and inertization of MSWI fly ash and its reuse as reinforcing filler for thermoplastics represents a promising opportunity to recover valuable raw-materials, to preserve natural resources avoiding the exploitation of traditional natural fillers (talc) together with manufacturing costs savings.

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