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Green composites of organic materials and recycled post-consumer polyethylene

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Abstract: Addition of organic fillers to post-consumer recycled plastics can give rise to several advantages. First of all, the cost of these fillers is usually very low, the organic fillers are biodegradable contributing to an improved environmental impact and, last but not least, some mechanical and thermomechanical properties can be enhanced. Organic fillers are not widely used in the plastic industry although their use is increasing. Bad dispersion into the polymer matrix at high-level content and poor adhesion with the matrix are the more important obstacles to this approach. In this work various organic fillers have been used with a post-consumer plastic material originating from films for greenhouses. The properties of these green composites have been compared with those of materials filled with a conventional inorganic filler. The organic fillers cause slightly worse processability, due to an increase of viscosity, an enhancement of the rigidity and of the thermomechanical resistance similar to that measured for the inorganic filler, while a reduction of the impact strength is observed.

Keywords: green composites; post-consumer films; organic fillers; mechanical properties; rheological properties

INTRODUCTION

Although the first and more important fillers studied and utilized for polymer-based composites are inorganic, a new series of fillers has recently been investigated: the organic ones. Low cost, environmental issues, lower hazard for the health of the operators, low specific weight in comparison to mineral filler, etc, are the main advantages of using these organic materials.^{1–6}

The possible use of natural-organic fillers with plastics to give ‘green composites’ has been considered by several researchers. In particular, great interest exists in the use of organic fillers with recycled polymers, because of the increasing widespread concern about ecology and environment, and also because of the industrial need for lower costs. Furthermore, thermoplastic materials reinforced with natural fibres present mechanical properties similar to the ones with common inorganic fillers (eg talc and calcium carbonate) added but with lower density, less harm to health, low abrasiveness, good acoustic and thermal-insulating properties and, of course, partial replacement of a non-biodegradable polymer with a biodegradable filler.^{7–9}

Selke and Childress¹⁰ investigated the effect of addition of wood fibres to high-density polyethylene

(HDPE) coming from food packaging, while Simpson and Selke¹¹ and Oksman¹² studied the effect of addition of the same wood fibres to a polypropylene matrix, PP, originating from ketchup bottles.

Yam *et al.*¹³ showed that incorporation of aspen wood fibres into HDPE from milk bottles, leads to a significant increase of tensile and flexural modulus and to a better resistance to creep. However tensile strength and impact strength are lower than those of unfilled HDPE.

The problem of dispersion of the fibres of natural fillers within the polymeric matrix has been investigated by Park and Balatinez¹⁴ and Li *et al.*¹⁵ using recycled thermoplastic polymers in two different processing equipments: a batch mixer and a single-screw extruder. Better results have been achieved with the extruder, perhaps because of better homogenization of the material components.

On the whole, natural organic materials are environmentally friendly fillers and, combined with recycled plastics, allow one to obtain low-cost materials with properties good enough for applications like interior car parts, plastic lumber, window and door frames, gardening items, paddocks, road signs, casing, packaging and, in general, for any application which does not require very high strength.^{16–19}

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In this work, the effects of the addition of various organic fillers on the mechanical and rheological properties of a recycled post-consumer plastic material coming from films for greenhouses have been investigated. The organic fillers come from natural sources (sawdust, ground olive stones, sago) and have been compared with calcium carbonate filler.

The addition of the investigated organic fillers to the post-consumer plastic matrix causes an enhancement of elastic modulus (and therefore of stiffness) and of thermomechanical resistance, while a reduction of tensile strength and elongation at break is observed. A slight increase of the viscosity does not worsen the processability of the polymer matrix. Although in some cases the inorganic filler gives rise to the best enhancement of the overall performance of the plastic matrix, organic fillers may be considered as valid substitutes. In particular, materials filled with very cheap fillers such as sawdust and olive stones show appreciable properties.

EXPERIMENTAL

The post-consumer films for greenhouses, RPE, were collected in the province of Ragusa (Sicilia, Italy, where the most important covered cultivation production is located). The recycled polymer contains low-density polyethylene (LDPE) (65–75 %), linear low density polyethylene (LLDPE) (10–15 %) and poly(ethylene-co-vinylacetate) (EVA) (10–12 %). Small amounts of inert fillers and UV stabilizers (about 2500 ppm) are also present.²⁰

Three organic fillers were used to prepare the filled polymers: sago starch (SS), olive stones (OS) and sawdust (SD).

Sawdust was obtained by milling wood in a blade mill through two different mesh grids, giving two fractions: SD_f ranging from 0 to 0.25 mm and, SD_c, in the range 0.25–1 mm.

Sago starch is extracted from the trunk of a number of palms, principally the *Metroxylon Sagus*, and used as whitish granules. The filler has an average particle size of 20 μm and a decomposition temperature of about 230 °C.²¹

Olive stones are produced from the residues of olive oil production. After extracting the olive oil, there is a residue of pulp and stone mixed with water. Water is evaporated and the solid residue is extracted with hexane to recover the remaining oil. After drying, the solid residue is separated into pulp and stone. The stone residue has been ground to about 315 μm average particle size. The chemical composition is about 8 % lignin, 26 % hemicelluloses and 66 % cellulose.

For comparison, some tests were also carried out using a cheap inorganic filler, namely calcium carbonate (Omya 2T-UM, Dav ≈ 10 μm), coated with stearic acid for better adhesion.

The RPE composites were prepared with two compositions, namely 30 % and 60 % (by weight) of filler by using a co-rotating intermeshing twin-screw

extruder (OMC, Italy, diameter = 19 mm and length/diameter = 35) was running at 200 rev min⁻¹ and with a thermal profile of 120–130–140–150–160–170–180 °C.

The specimens of the RPE composites were prepared by injection moulding using a Sandretto machine (Italy). In this study the processing parameters for all blends were set using conditions typical for LDPE: melt temperature; 190 °C; nozzle temperature; 190 °C; mould temperature; 30 °C; screw speed; 300 rev min⁻¹.

The tensile properties were measured with an Instron universal testing machine model 4443 on the injection-moulded specimens (about 2 mm thick and 20 mm in width). The crosshead speed was 5 mm min⁻¹ and the initial length was 30 mm.

The impact strength has been evaluated on notched samples in Izod mode using a CEAST (Italy) apparatus model 6545.

Heat deflection temperature (HDT) values were determined following ASTM D 2990-77 (flexural load 1.8 MPa, rate of increase of the temperature 120 °C h⁻¹) using an automatic CEAST apparatus.

Rheological properties were measured using a capillary viscometer Rheoscope (CEAST) at 180 °C with a capillary having diameter = 1 mm and length/diameter = 40.

For all the mechanical tests at least seven specimens were tested. The experimental data were quite reproducible (±8 %) for the composites with 30 % of fillers, and better for the pure recycled polymer, while the reproducibility was less good (±10–12 %) for the more filled samples, maybe because of poorer filler dispersion within the matrix.

RESULTS AND DISCUSSION

The presence of inorganic fillers in a polymer blend usually worsens the processability of the matrix because of the rise of the viscosity. In Fig 1 the flow curve of the matrix and of the composites with 60 % of all the investigated fillers are reported. As expected, the flow curves of all the composites are well above that of the unfilled polymer and the flow curves of all the composites are relatively near each other. However, among the fillers, fine sawdust particles causes the largest increase of viscosity, while the sago-starch-filled RPE is the composite with the lowest viscosity. This behaviour and the effect of the filler content is evident in Fig 2 where the values of the viscosity at a shear rate of 300 s⁻¹ are plotted as a function of the filler content. The viscosity increases with the filler content, but this growth becomes more significant at high values of the filler load.

As noted above, the viscosity increases with the amount of filler present; however, this difference reduces with increasing shear rate. Indeed, the molten polymer presents more pronounced non-Newtonian behaviour viscosity with the increasing. In particular, at high shear rates, typical of the injection-moulding

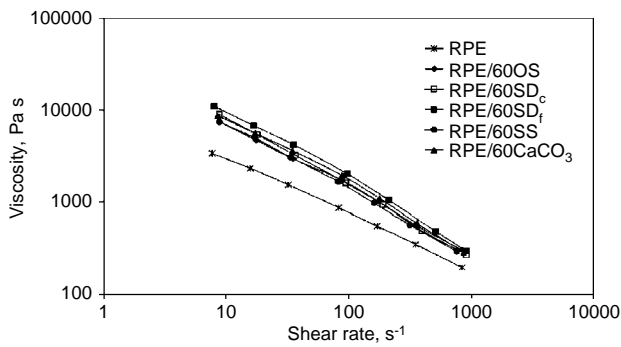


Figure 1. Flow curves of the unfilled polymer and of the composites with 60 % of filler.

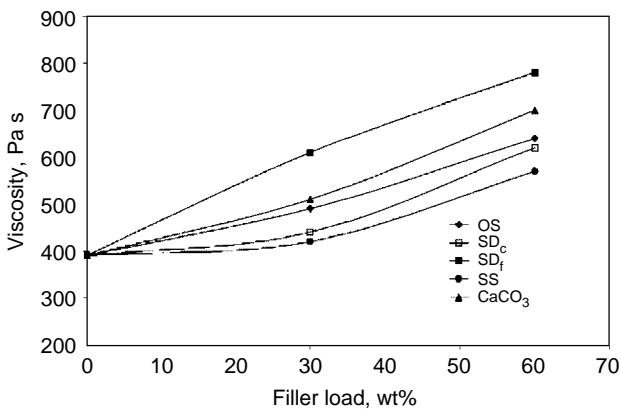


Figure 2. Viscosity at 300 s^{-1} as a function of the filler content.

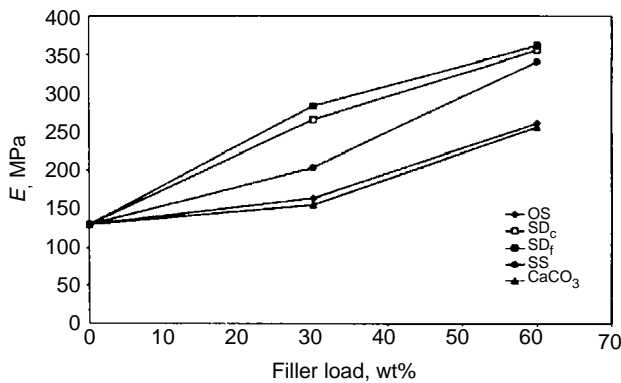


Figure 3. Elastic modulus as a function of the filler content.

processes, the viscosity of the unfilled polymer and of the filled systems approach each other. For this reason the injection-moulding conditions have been kept constant for all the materials investigated.

The values of the tensile properties (elastic modulus, E , tensile strength, TS , and elongation at break, EB) are plotted in the Figs 3–5 as functions of the filler content for all the samples.

All the filled systems show some degree of stiffening, which increases with the filler content, and, as a consequence, the material becomes more and more fragile: the presence of the organic filler causes an increase in elastic modulus, whereas a decrease in tensile strength and elongation at break is observed.

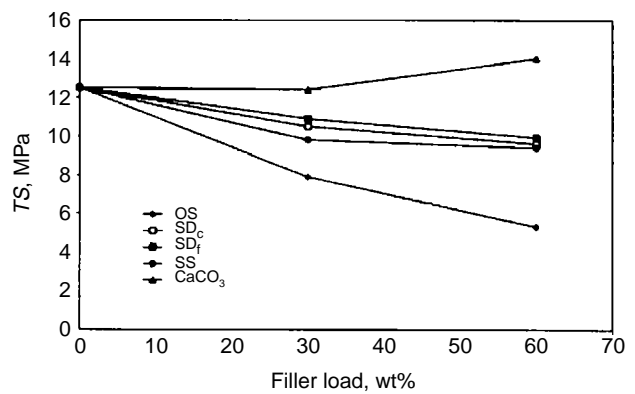


Figure 4. Tensile strength as a function of the filler content.

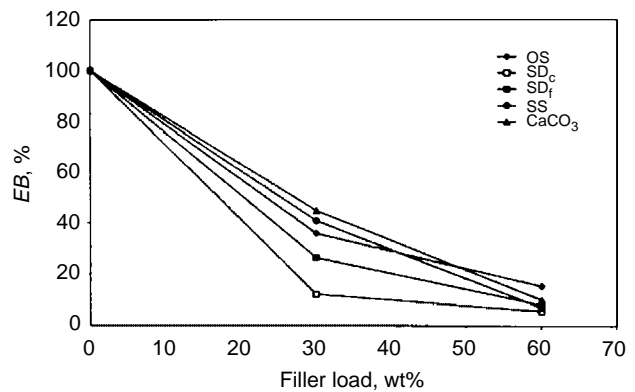


Figure 5. Elongation at break as a function of the filler content.

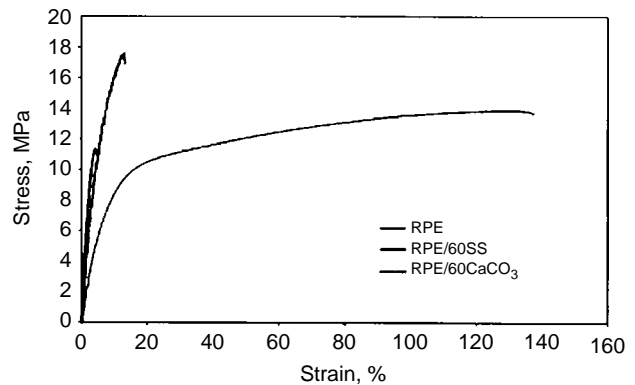


Figure 6. Stress–strain curves for some materials.

The picture is quite different for the composite with the inorganic filler: in this case there is an increase of the tensile strength.

In Fig 6 typical stress–strain curves for three samples are reported. The three curves clearly show that the initial slope is higher and that the decrease of the tensile strength for the organic filled samples is to be attributed to the brittleness of the filled samples; thus the premature rupture of the sample causes a lower value of the stress at break. In contrast, the sample filled with CaCO_3 shows a similar slope but a slightly larger elongation at break and a consequent higher stress at break.

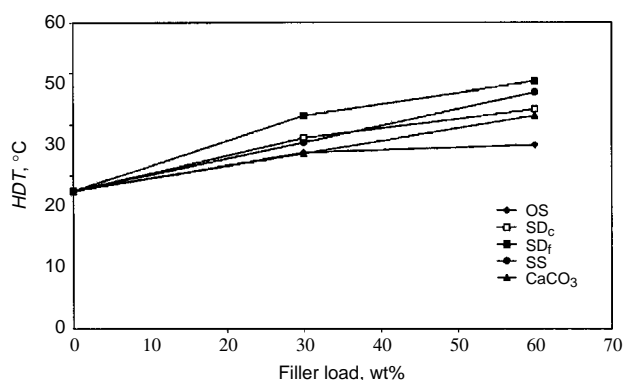


Figure 7. HDT as a function of the filler content.

The best performance among all the fillers is shown by the sawdust. The finer granulometry does not seem to impart better properties with respect to the material filled than the same filler having larger particle size. In particular, with 60 % of this filler the modulus is twofold the initial value, while the reduction of the breaking characteristics is the higher one.

The impact strength values are reported in Table 1, where it is seen that impact strength worsens for all the samples, probably because of poor adhesion with the non-polar matrix. Again, the inorganic filler shows the best results while olive stones presents the best performance among the organic fillers and sago starch the poorest results.

Heat deflection temperature values are plotted in Fig 7. It is easy to observe a significant increase in HDT with increasing the filler content (even though the enhancement obtained passing from 30 % to 60 % wt% percent is less than one could expect). The best results are achieved with sago and with the finer sawdust. The HDT value is mainly dependent on the initial value of the elastic modulus, being the same matrix for all the samples. The HDT values obtained are in line with the values of the elastic modulus reported above.

CONCLUSIONS

The addition of organic fillers to the post-consumer plastic matrices causes an enhancement of elastic modulus (and therefore of stiffness) and of the thermomechanical resistance, while a reduction of tensile strength and elongation at break is observed.

These effects become more marked with increasing filler content. Although in some cases the inorganic fillers give rise to as best enhancement of the overall performances of the plastic matrix, organic fillers may be considered as valid substitutes. In particular, materials filled with very cheap fillers such as sawdust and olive stones show appreciable properties.

All the filled systems show a higher viscosity than the virgin matrix, but this behaviour does not significantly worsen the processability of the composites.

Table 1. Impact strength ($J m^{-1}$) for the materials

Filler load (wt%)	Olive stones	SD _c sawdust	SD _f sawdust	Sago starch	CaCO ₃
0	nb	nb	nb	nb	nb
30	nb	185	99	nb	nb
60	90	70	69	58	180

nb = no break.

Ground olive stones, sago and sawdust are therefore interesting alternatives to inorganic fillers to produce materials that are both low-cost and more environment-friendly than pure polymers, especially in the field of recycled polymers.

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