Mechanical and Morphological Studies of Poly(propylene)-Filled Eggshell Composites

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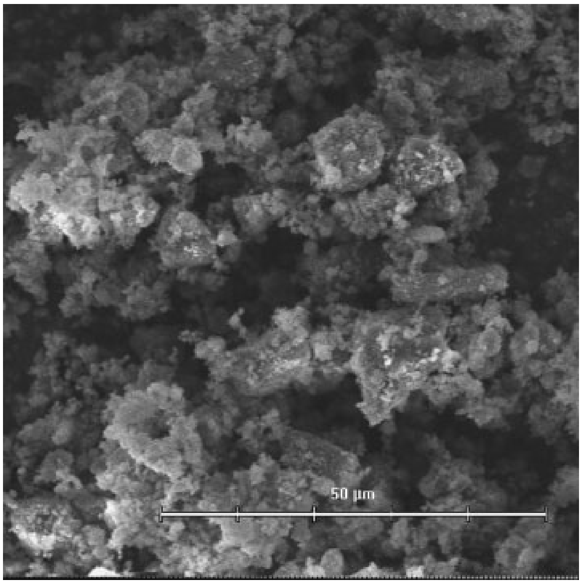
Poly(propylene) (PP) composites were prepared by using eggshell (ES) as filler and their mechanical properties were compared with those using talc (TA) and calcium carbonate (CC) of different grain sizes (X_{50}). A decrease in impact strength and deformation at break with increase in filler content was observed. The PP composite with ES ($X_{50} = 8.4$ μm) was stiffer than those with CC ($X_{50} = 0.7$ μm). The hybrid composite PP-ES-TA showed a similar stiffness as the PP-TA composites due to the similar morphology of TA ($X_{50} = 0.5$ μm) and ES, when TA was replaced up to 75 wt.-% by ES. SEM study revealed evidence of improved interfacial bonding between PP and ES in theirs composites.



Introduction

The use of fillers from various sources in poly(propylene) (PP) has been an accepted route to achieve enhancement in material properties and cost saving possibilities.[1,2] These fillers can be categorized as inorganic and organic. In terms of inorganic fillers, carbon black, silica, calcium carbonate (CC), and talc (TA) are used in PP composites.[3,4] Among such fillers, CC and TA are the most commonly used fillers in PP, which is the most widely used thermoplastic polymer in the plastic industry.[5–7] However, over the past two decades, organic fillers have become a strong competitor to inorganic fillers due to their low densities, very low cost, non-abrasiveness, high filling levels, recyclability, biodegradability, and renewable nature.[8] These organic fillers can be used in either powder or fiber form. In recent years, the use of fibers and powders derived from agricultural sources such as banana, kenaf, hemp, sisal, pineapple, wood flour, rice-husk, and jute has become a subject of interest in polymer composites, mainly due to the above-mentioned advantages.[9–14]

In recent years there has been substantial growth in the research, development, and application of biocomposites.

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A composite containing at least one constituent, e.g., matrix or reinforcement derived from readily renewable resources may be considered a biocomposite. Many efforts to manufacture new materials less dependent on petroleum supplies have been carried out in the polymer industry.

Eggshell (ES) is a biomaterial containing 95% by weight of CC and 5% by weight of organic materials. Waste ES is often turned into a low protein supplement for animal feed making it a marginally profitable venture with supply exceeding demand. In addition the ES is an abundant byproduct of poultry industry. These characteristics qualify ES as excellent candidates for bulk quantity, inexpensive, low-load bearing composite applications such as the automotive industry, trucks, homes, offices, and factories.

A patent on the process and use of ES as biofiller for different PP was registered by the Universidad de Chile. This patent discloses the use of the ES as reinforcing material in PP composites.[15]

The aim of this study was to investigate the mechanical properties of PP samples filled with ES as a biofiller compared with those composites obtained by using traditional inorganic fillers such as TA and CC. Furthermore, scanning electron microscopy (SEM) was used to examine the morphology of the composites and to justify the variation of the measured mechanical properties. The goal of this study is also to show the possibility of replacing the traditional inorganic fillers with ES as biofiller. Furthermore, using the ES from agricultural waste, not only reduce waste but also reduce the energy consumed for manufacturing materials with readily available and inexpensive new reinforcement for thermoplastic polymer composites.

Experimental Part

Materials

A commercial sample of PP, from Petroquim S. A. Chile, having a density of 0.9 $g \cdot cm^3$ and melt flow index of 14 g per 10 min at 230 °C, 2.16 kg was used. ES was obtained from a Chilean poultry industry. Commercial TA samples with different grain sizes were designated as: TA1 purchased from Rocco Industry, TA2 and TA3 from Imifabi LLC Industry were used. Commercial CC samples with different grain sizes were designated as CC1 from Trucco Industry, CC2 and CC3 from Reverte Industry were used.

Irganox 1010/Irgafos 168 with a 2:1 ratio from CIBA was used as antioxidant.

Filler Characterization

A Mastersizer from Malvern Instruments was used for the particles size characterization of ES, TA, and CC fillers. The particle sizes of the fillers were examined on the water dispersion of these particles using a refractive Malvern particle device Mastersizer model MSX1. The particle size was obtained from the value X_i (with $i = 10, 50, 90$), which means the i vol.-% of particles smaller than X_i, where the X_i with $i = 50$ was assigned as the mean particle size value (X_{50}).

Brunnauer-Emmett-Teller (BET) specific surface area of the fillers was determined from nitrogen adsorption isotherms using a Micrometrics ASAP 2010 apparatus. All fillers were degassed in vacuum at 200 °C previous to the adsorption measurements.

The morphology of the filler surface and of the fractured surfaces of the composites after electrospraying with gold was analyzed by using a Tesla model BS343 scanning electron microscope.

Preparation and Characterization of the Composites

PP, ES biofiller, and mineral fillers such as TA and CC, when appropriate, were mixed with 0.2% w/w of antioxidant in a nitrogen atmosphere by using a Brabender Plasticorder internal mixer model PLE 331 at 190 °C for15 min and 75 rpm. After melt blending, the composite was pelletized and then pressed at 190 °C and 50 bar for 1 min to prepare the samples for tensile mechanical testing.

The tensile measurements were carried out with five samples for each composite (1.5 mm thick, 12 mm wide, and 120 mm long according to the ASTM standard method D638) at 23 °C and a relative humidity of 32%, using a dynamometer model HP D500. Cross-head speed was $50 \text{ mm} \cdot \text{min}^{-1}$. Tensile strength "$\sigma$", tensile modulus "$E$", and elongation at break "ε" were obtained from the stress–strain curve of the prepared composites. The E value was determined according to the ASTM standard method D638, that is, modulus was calculated by extending the initial linear portion of the load extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain. The elastic modulus value was calculated by using the average initial cross-sectional area of the test specimens.

The Charpy impact test was performed at −20 °C according to the ASTM standard method D256-93a by using a Capitol model D55 impact test machine. The impact strength ($J \cdot m^{-1}$) of neat PP and different PP composites was obtained as the mean value of measuring six specimens of 2 mm thick, 12 mm wide, and 130 mm long.

Results and Discussion

Characterization of the Fillers

Physical properties of the commercial fillers and the different sieved ES biofillers obtained from the as received ES were determined by measuring the particles size and specific surface area and the results are presented in Table 1. The morphology of these fillers was studied by using SEM and the micrographs obtained are shown in Figure 1.

The ES was donated by a local poultry industry. The ES was transformed to a biofiller after washing with distilled water, dried at 90 °C for 8 h, grounded, and sieved to standard mesh 125 (ES125), 250 (ES250), and 400 (ES400).

Table 1. Physical properties of calcium carbonates (CC), talcs (TAs), and eggshells (ES) biofillers.

Filler	Nomenclature	Particle size			BET area
		µm			$m^2 \cdot g^{-1}$
		X_{10}	X_{50}	X_{90}	
CC	CC 1	2.7	17.1	42.6	2.2
	CC 2	0.4	2.0	10.2	3.2
	CC 3	0.3	0.7	1.7	9.1
TA	TA 1	3.0	10.7	29.5	4.6
	TA 2	0.7	2.4	6.5	6.3
	TA3	0.4	0.5	2.8	11.9
ES	ES125	63.0	90.0	125.0	2.9
	ES250	45.0	50.0	63.0	2.7
	ES400	1.7	8.4	27.5	18.0

The physical and morphological properties of ES125, ES250, and ES400 biofillers are summarized in Table 1 and in Figure 1. The morphology of a TA sample (TA2) and of a CC sample (CC2) filler are shown and compared with that of ES400 biofiller in Figure 1.

X_{10}, X_{50}, and X_{90} values were determined for all the fillers used in this work. These values represent the percentage of the volume that is smaller than the size indicated or the weight percent if the density for all the particles is the same. Therefore, X_{50} is the mean particle size representing one type of mean particle size only. The X_{10} and X_{90} are the reference values related to the aspect of the distribution curve of the filler. In general, for fillers with smaller X_{50} value a higher specific surface area was found. In the case of CC2 and TA2 the twice higher specific surface area of TA2 could be related with smaller difference between X_{50} and X_{10} or X_{90} value for TA2 compared with CC2 where the difference between its X_{50} values with X_{10} or X_{90} values is large. The narrower particles size distribution determined for TA2 compared with that determined for CC2 could explain the values of 6.3 $m^2 \cdot g^{-1}$ for specific surface area of TA2 compared with that of 3.2 $m^2 \cdot g^{-1}$ for CC2. Higher aspect ratio (surface/volume) could be estimated for TA2 from the morphological study of TA2 and CC2 fillers, as shown in Figure 1. This finding could explain the higher value of specific surface area of TA2 compared to that of CC2.

The highest value obtained for the specific surface area (18 $m^2 \cdot g^{-1}$) for the ES400 biofiller could be explained by considering the similar morphology observed for this filler in comparison with that of TA2 which is principally of laminar shape. Moreover, the presence of the porous organic membrane, a natural component of the ES, could contribute to the higher value of the specific surface area found for ES400 biofiller.

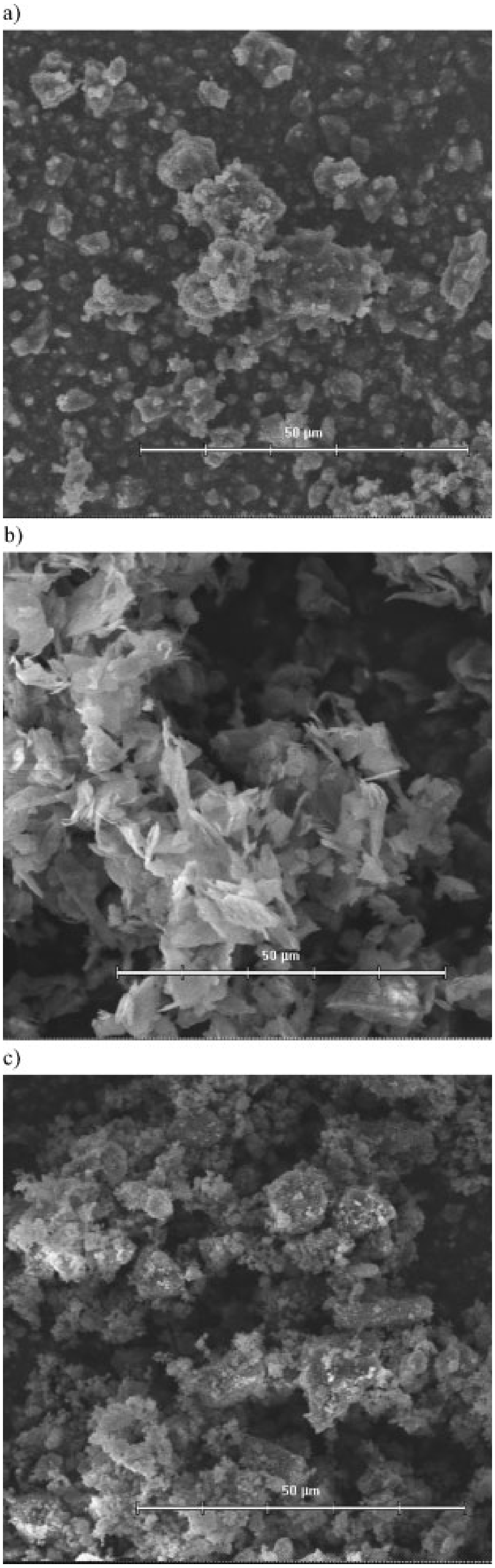

Figure 1. Scanning electron micrographs of (a) CC2, (b) TA2, and (c) ES400 (Bar = 50 µm; 1700×).

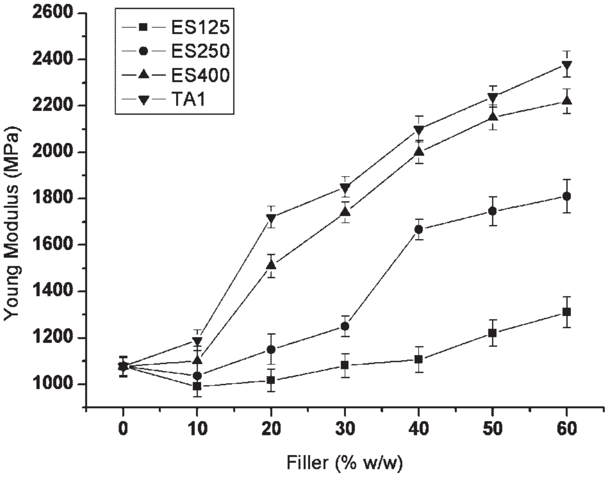

Figure 2. Young's modulus of PP-ES composites with ES of different grain sizes compared with PP-TA1 composites.

Tensile Properties of PP-Filled Composites

Effect of ES Grain Size on the Mechanical Properties of PP ES-Filled Composites

The effect of ES grain size on the mechanical properties of PP composites was studied in order to determine the optimum ES biofiller grain size that produced a composite with best mechanical properties. Three different ES biofiller, namely ES125, ES250, and ES400 were used as filler for preparing the PP composites and their mechanical properties were evaluated. The ES-biofiller content of the composites varied from 20 to 60% by weight. As shown in Figure 2, a higher stiffness was found for the PP composites containing ES400 as biofiller than those prepared by using ES125 and ES250. A smaller grain size of the filler could produce a maximal interface contact because of larger specific surface area. When the filler particles are small and homogeneously distributed in the polymer matrix, originate a more rigid structure. Other mechanical properties such as the maximal strength σ and deformation at break ε had typical values as for a rigid material, that is, lower σ and ε values than the net polymer matrix (Table 2).

Furthermore, a comparison of the mechanical behavior among PP-filled composites was made using filler of similar X_{50} grain sizes (Figure 3). This comparison included CC (CC1), TA (TA1), and ES400. The objective was to determine the influence of the filler content from 20 wt.-% up to 60 wt.-% on the mechanical performance of these PP-filled composites. The PP-ES400 composite showed a higher E value than that found for PP-CC1 composite for all filler content and similar principal inorganic component which is the CC. Moreover, the E value for PP-ES400 composite was lower than the E value for PP-TA1 composite. Besides, it was found that a comparative enhancement of stiffness between the PP-TA1 and PP-ES400 composites exist when the filler content increased from 20 wt.-% up to 60 wt.-% (Figure 3). These similar E values of the composites PP-ES400 and PP-TA1 could be related with the similar aspect ratio of these fillers as revealed from the SEM micrographs of the ES400 biofiller and TA filler such as TA2 (Figure 1). Furthermore, the better dispersion and distribution of the ES400 and TA2 fillers in the polymeric matrix, as seen from Figure 7, compared with the CC2 filler could be correlated with the corresponding CC1- and TA1-filled composites. This evidence could explain the existence of different E values between these PP composites and remarkable lower E value of all CC1 filled composites.

In general, the increase in E could be due to both the incorporation of a rigid phase in PP matrix as well as the movement restriction and rigidity of the filler, where the ES400 biofiller and TA1 filler gave a better continuity of the matrix than the CC1 filler. This is most probably due to the laminar shape as well as specific surface area and

Table 2. Mechanical properties of PP filled composites.

% Filler	E				σ				ε			
	MPa				MPa				%			
	ES125	ES250	ES400	TA1	ES125	ES250	ES400	TA1	ES125	ES250	ES400	TA1
0	1 077 ± 40	1 077 ± 45	1 077 ± 39	1 077 ± 45	31 ± 2	31 ± 2	31 ± 2	31 ± 2	260 ± 15	260 ± 15	260 ± 15	260 ± 15
10	990 ± 45	1 037 ± 56	1 100 ± 63	1 190 ± 44	32 ± 3	29 ± 5	31 ± 5	30 ± 3	39 ± 14	40 ± 13	37 ± 9	10 ± 3
20	1 016 ± 49	1 150 ± 65	1 510 ± 50	1 720 ± 47	31 ± 2	26 ± 1	31 ± 2	29 ± 2	38 ± 2	37 ± 11	35 ± 7	6 ± 2
30	1 080 ± 52	1 250 ± 45	1 740 ± 45	1 850 ± 45	31 ± 3	23 ± 3	31 ± 3	28 ± 3	12 ± 2	11 ± 3	10 ± 3	3 ± 1
40	1 106 ± 55	1 667 ± 45	2 000 ± 49	2 100 ± 56	32 ± 3	29 ± 4	27 ± 3	25 ± 2	7 ± 2	5 ± 2	6 ± 2	2 ± 1
50	1 220 ± 56	1 745 ± 62	2 150 ± 54	2 240 ± 45	31 ± 2	27 ± 3	15 ± 5	20 ± 3	4 ± 2	3 ± 2	3 ± 1	2 ± 1
60	1 310 ± 66	1 810 ± 72	2 220 ± 53	2 810 ± 57	30 ± 2	28 ± 2	13 ± 3	22 ± 1	3 ± 2	2 ± 1	3 ± 1	2 ± 1

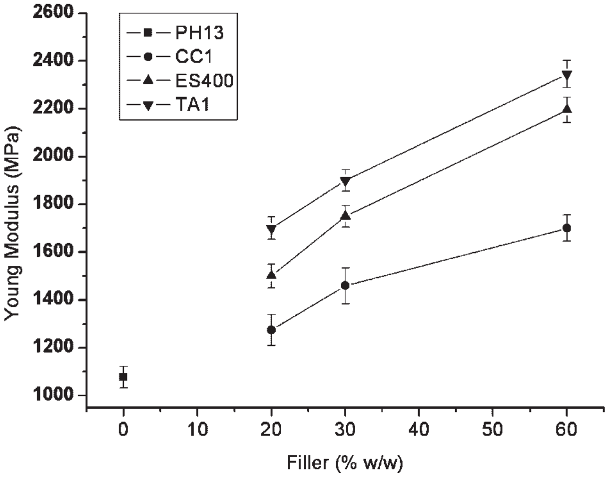

Figure 3. Young's modulus of PP composites filled with either, CC1, TA1, or ES400.

X_{50} grain size of the TA and ES biofiller particles allowing less free space in the polymer-filler interface.

Effect of the Nature and Grain Size of Fillers on the Tensile Properties of PP-Filled Composites

The variation of the Young's modulus for PP composites containing 40 wt.-% of filler was determined as function of the type and X_{50} of CCs and TA fillers compared with the ES400 biofiller in Figure 4. This property was increased by decreasing X_{50} of CCs and TAs for all filled composites as would be expected when a rigid filler is incorporated in the polymeric matrix. The reinforcing effect of mineral filler in the PP-filled composites will depend on its amount and grain size to achieve a microstructure with a high degree of dispersion and the presence of voids between the phases of the composite. The modulus of the TA composites was significantly higher than the modulus of ES400 and CC-filled composites. This may be due to the laminar morphology and higher surface area of TA particles compared with other fillers. As the specific surface area is increased, filler-matrix adhesion is improved resulting in decrease in mobility of the macromolecules. Irrespective of the filler type, incorporation of the filler resulted in an abrupt drop in elongation at break compared to the elongation at break of PP (Table 2). A similar behavior has been reported by Qiu et al.[16] It is also reported that the Young's modulus increases while elongation at break decreases with increasing filler loading.[17] A similar trend can be seen here for these composites studied in this work. As far as elongation at break is concerned, ES400 can be regarded as comparable to TA filler for PP composites (Table 2).

Other relevant aspect related to the similar morphology between TA filler and ES400 biofiller was an advantage when the ES400 filler was replaced up to 75% with TA as filler in PP hybrid composite, which is a composite containing mixture of ES400 and TA. The hybrid composite PP-ES400-TA2 and PP-ES400-TA3 showed a similar *E* value compared with the PP-TA2 and/or PP-TA3 composites with the same total filler content (40 wt.-%). The PP/ES400/TA2 and PP/ES400/TA3 hybrid composites containing 20% by weight of either ES400 biofiller, TA2 or TA3 filler and the PP/ES400/TA3 with 30% by weight of ES400 biofiller and 10% by weight of TA3 have comparable Young's modulus to the composite without ES400 biofiller, that is, similar stiffness as PP/TA composite (Figure 5). Although these results confirm the above mentioned effect of the laminar morphology, X_{50} and specific surface area of these fillers on the mechanical properties of the composites, the organic

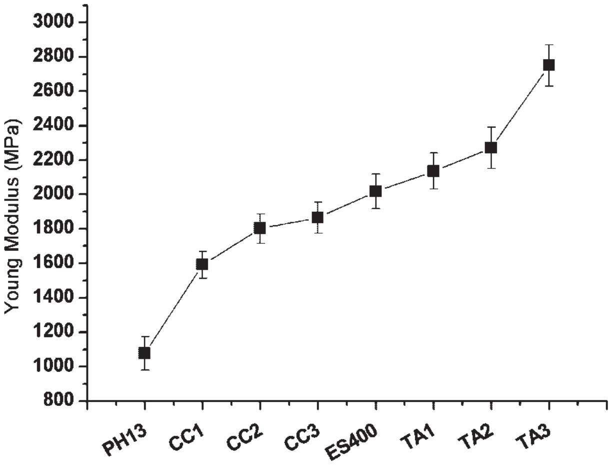

Figure 4. Young's modulus of PP-filled composites with 40% by weight of fillers with different grain sizes.

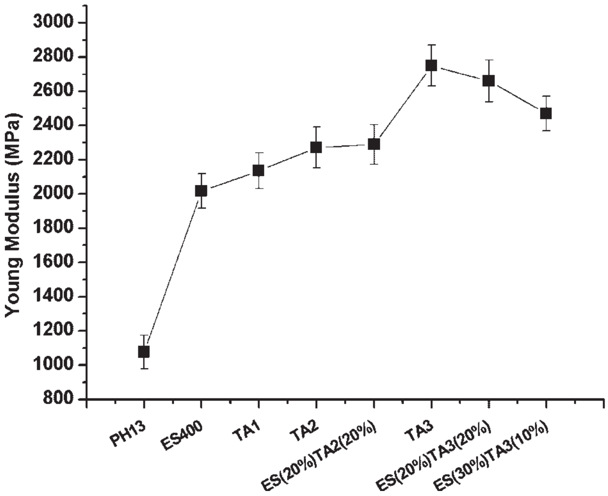

Figure 5. Young's modulus of PP and PP-filled composites with 40% by weight of different fillers compared with hybrid composites PP-ES400-TA2 and PP-ES400-TA3.

membrane contained in the ES biofiller could contribute to a better filler-matrix adhesion through a more efficient interaction with polymer matrix in spite of larger grain size of the ES400 biofiller than both TA fillers used in these hybrid composites.

Impact Strength of PP-Filled Composites

There is a gradual decrease in impact strength with increase in filler content for both ES400 biofiller and mineral fillers composites (Figure 6). When a crack is generated due to an impact, it propagates towards a poor interfacial region. Therefore, as the filler content increases, impact strength tends to decrease gradually. On the other hand, if the adhesion between the filler and the matrix is very strong, fillers restrict the mobility of the matrix. In turn, this also results in reduction in impact strength. It is well known that the stiffest composites exhibit the lowest impact properties as the high stress is transferred from the polymer matrix to the filler particles.

Furthermore, a slight enhancement of the impact strength with increasing X_{50} of the filler was observed for the same content of filler in PP composites with different fillers but with the same sub-micrometric grain size range. This fact is also observed when the TA filler is used for preparing the PP composites namely TA1 and TA2. In general, a worsening of the impact strength was observed for all filler systems compared with the net polymer matrix. The lowering of the impact strength is more pronounced with increasing the filler content. Although crack-initiation sites or voids might not be abundant, they can hardly be detected from SEM micrographs (Figure 7). Crack propagation is very quick because of the lack of the ability of the composite to absorb the impact energy

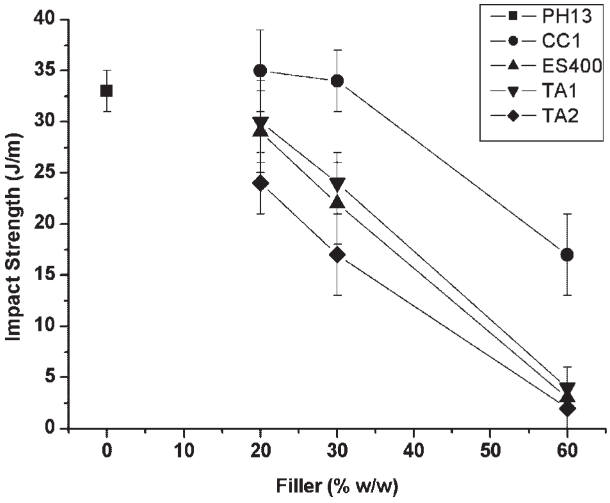

Figure 6. Impact strength of PP and PP-filled composites.

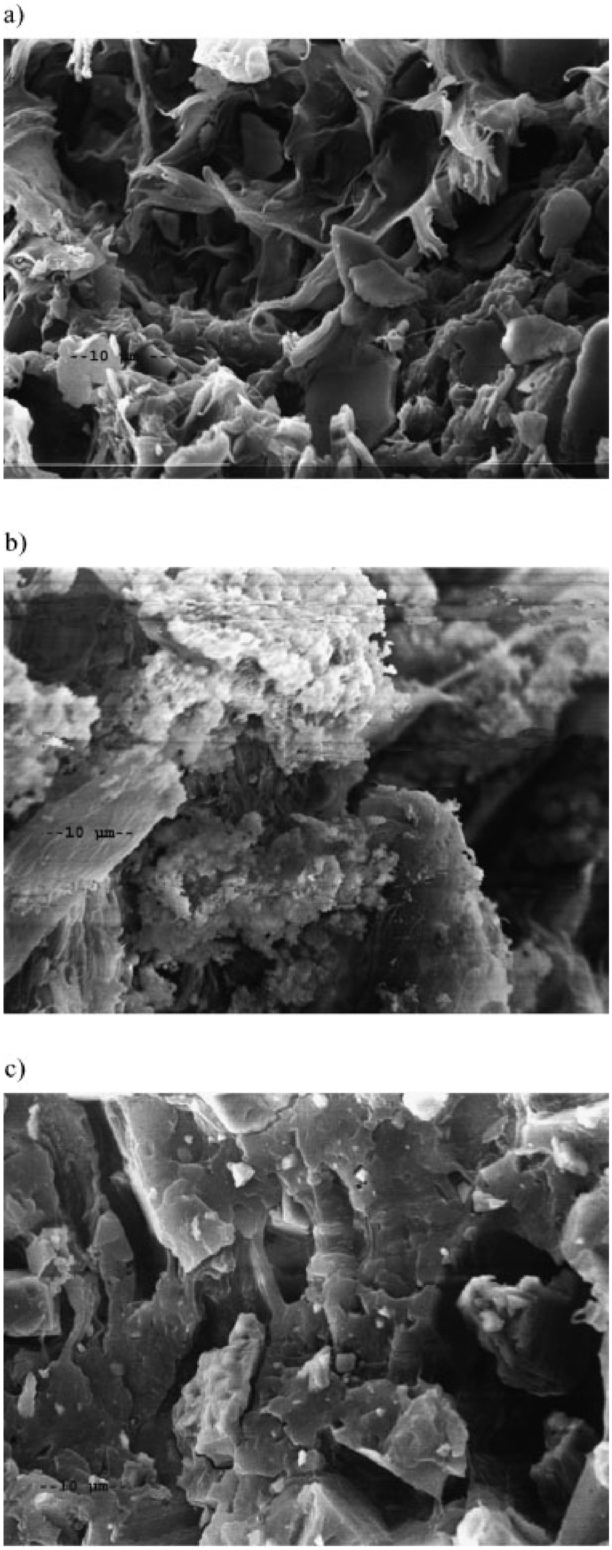

Figure 7. Scanning electron micrographs of PP composites containing 30% by weight of: (a) TA2, (b) ES400, (c) CC2 (Bar = 10 µm; 1 000×).

through plastic deformation. Furthermore, the adhesion of the PP matrix to the fillers used in this work depends on the morphology which determines the degree of embedding of these filler in the PP matrix. Moreover, neat PP possesses high impact properties, therefore, at higher filler loading, the amount of the PP matrix available becomes scarce and this leads to a decrease in the toughness and impact strength of the composite. The impact strength of PP/ES-400 composite was similar to the PP/TA1 composites prepared by using 20 wt.-% up to 60 wt.-% of filler. Finally, the results obtained in this study are in line with literature data for similar reinforced PP composites.[18,19] It can be concluded that ES400 offers a similar effect as TAs for improving the impact resistance of PP composites.

Morphology

The morphology of different fillers and that of the composites was evaluated by SEM. The fracture surface of the tensile test specimens of different composites filled either with TA2 and CC2 filler and ES400 biofiller are shown in Figure 7. The morphology of different fillers used in this study is shown in Figure 1. The laminar morphology of TA2 filler is seen clearly in Figure 1(b). As can be seen in Figure 1(b) and Figure 1(c), a similar morphology as that of TA2 is observed for the ES-400 biofiller. As can be seen in Figure 1, the morphology of CC2 filler is quite different from the other fillers.

The different morphology of the composites containing TA2, CC2, or ES400 can be seen from Figure 7. It is seen from this figure that the TA2 particles tend to orient more with the surface of the PP matrix. A similar behavior is observed for the ES-400 biofiller, where the filler is more deeply embedded in PP matrix than CC2 filler. These observations of the SEM analysis could be the result of a good interaction between the filler and polymer matrix. This could confirm the better mechanical properties of the PP-ES400 and PP-TA2 composites compared with the PP-CC2 composites. It can be appreciated from SEM analysis that good dispersion and less large voids are present in the case of composites filled with either TA2 or ES400. This is most probably due to the higher surface/volume ratio for TA2 and ES400 as fillers than that of CC2. Furthermore, as can be seen from Figure 7, a better interfacial interaction and adhesion between TA2 and/or ES400 and PP is observed as compared with CC2 and the polymeric matrix.

Conclusion

ES400 biofiller showed a better reinforcing property in PP composites than traditional commercial mineral fillers such as CC and TA. The nature, specific surface area, grain size, and morphology of the filler were found to be the relevant factor to improve the stiffness of the PP composites studied. The PP-ES400 composite showed a higher tensile modulus than the PP composites filled with CC of sub-micrometric particle size. The impact strength of the composites was reduced for all the fillers, especially when the filler content increase up to 60% by weight.

The similar morphology of ES400 and TA fillers was the most relevant factor for obtaining hybrid composites such as PP-ES400-TA2 or TA3 showing similar modulus as the PP-TA2 or PP-TA3 filled composites.

The best overall mechanical performance was provided by TA as filler. However, some problems in terms of the production and processing cost for TA should be considered. The use of ES as natural biofillers could be a good alternative. The SEM studies confirm the better mechanical behavior observed in relation to the interfacial interaction of ES400 biofiller with PP matrix in this composite. In particular, the ES400 tested in this study may be regarded as an appropriate substitute for the most frequently used commercial TA and CC fillers.

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