

Study of the morphology and mechanical properties of polypropylene composites with silica or rice-husk

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Abstract: The mechanical, morphological behavior and water absorption characteristics of polypropylene (PP) and silica, or PP and rice-husk, composites have been studied. The silica used in this study as filler was a commercial type produced from soluble glass or rice husks. The compatibilizing effect of PP grafted with monomethyl itaconate (PP-*g*-MMI) and/or with vinyltriethoxysilane (PP-*g*-VTES) as polar monomers on the mechanical properties and water absorption was also investigated. In general, a high loading of the studied fillers in the polymer matrix increases the stiffness and the water absorption capacity. This effect is more noticeable in the tensile modulus of the PP/silica composite with PP-*g*-VTES as compatibilizer. However, the increase of the rice-husk charge as a natural filler in the PP matrix decreases the stiffness, and in the presence of PP-*g*-MMI as compatibilizer in PP/rice-husk, the tensile modulus and water absorption of the composite were improved. The better adhesion and phase continuity in the PP/silica and PP/rice-husk composites with different compatibilizers was confirmed by the morphological study.

Keywords: polypropylene; polypropylene composites; silica, rice-husk; compatibilizer

INTRODUCTION

Polypropylene (PP) is the thermoplastic polymer that has undergone the greatest increase in consumption over the last decade. Its applications can be extended if its mechanical and thermal properties are improved. To achieve this it is necessary to develop PP-based composites reinforced with organic and/or inorganic materials. Incorporating particles and/or fibers (organic and inorganic) as reinforcement together with PP grafted with polar monomers as compatibilizers are ways to achieve this objective. The PP/glass fiber composite with PP grafted with organosilane as binding agent,¹ PP reinforced with sisal fibers,² curauá fibers,³ rice-husk (RH),⁴ sawdust with PP grafted with maleic anhydride (MAPP) as compatibilizer,⁵ and PP reinforced with talc⁶ composites have already been studied. Improvement of the mechanical properties of blends of PP/ethylene-propylene-diene copolymer (EPDM) by adding a filler, namely a silica obtained from a natural product such as rice-husk, has also been reported.⁷ The addition of this silica to a PP-based/natural rubber composite and by using 3-aminopropyl-triethoxysilane and poly(propylene-co-ethylene) (PP-co-PE) copolymer,

commonly called ethylene-propylene copolymer or EPR, grafted with acrylic acid as compatibilizer was found to have different effects on the vulcanization kinetics of the elastomer.^{8,9} In general, the use of natural fibers as reinforcing filler reduces the cost of the composites and increases the stiffness and tensile strength of a thermoplastic material such as PP.²

The addition of different types of silica and rice-husk to PP-co-PE were studied in order to evaluate the water absorption and mechanical properties of the resulting composites. Compatibilizers, mainly functionalized polyolefins, were incorporated to lower the interfacial tension between the PP-co-PE matrix and the different fillers. In addition, the fracture surface was studied by scanning electron microscopy (SEM) to elucidate the interfacial region between the PP-co-PE matrix and the fillers.

EXPERIMENTAL Materials

Heterophasic PP copolymer, poly(propylene-co-ethylene) containing 9.5 wt% ethylene; with a melt flow index (MFI) of 6.2 was supplied by Petroquim-Chile

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Table 1. Silica properties

Silica origin	Type	Surface area (m ² g ⁻¹)	Pore diameter (Å)	Particle size d(50) (µm)
Commercial	EP10X	289 ^a	261	111
	EP17G	285	250	37
	EP41	324	281	116 ^a
	ES70	259	235	35 ^a
Obtained from soluble glass	VSSi	364	96	19
Obtained from rice-husk	RHSi	223	52	184

^a Taken from technical data sheet

with product number PCC0610. The compatibilizer, polypropylene grafted with 1 % monomethyl itaconate (PP-*g*-MMI), was synthesized at the Universidad de Chile.¹⁰ Polypropylene grafted with 1.1 % vinyltriethoxysilane (PP-*g*-VTES) was provided by Professor RS Mauler, Institute of Chemistry, UFRGS, Porto Alegre, Brazil.¹¹ Commercial silicas (EP41, ES70, EP10X and EP17G) were obtained from Crossfield Group, Warrington. Synthetic silica (VSSi) was obtained starting from soluble glass¹² and natural silica (RHSi) was obtained from calcination of previously acid-washed rice-husk (700 °C for 3 h),¹³ particle size d(50) = 184 µm. Rice-husk (RH) was washed with water, dried at 90 °C for 3 h and sieved to mesh 10–14 to have 10 m² g⁻¹ and d(50) = 370 µm. Irganox 1010/Irgafos 168 (50/50) antioxidant was from CIBA. The silica and the rice-husk were characterized by their particle size, surface area and pore diameter (Table 1).

SEM analysis was performed by Professor JL Arias, of the Bioceramics Laboratory, Facultad de Ciencias Veterinarias, Universidad de Chile, using a Tesla electron microscope, model BS 343A.

Preparation of the composites

The PP-*co*-PE, silica and compatibilizer, when appropriate, were mixed with 0.2 % w/w of antioxidant in a nitrogen atmosphere using a model PLE331 Brabender Plasticorder internal mixer at 190 °C for 5 min and 75 rev min⁻¹. After blending, the composite was pelletized and then pressed to prepare the samples for the mechanical and water absorption tests.

The mechanical tests were carried out with five samples for each composite (1.5 mm thick, 12 mm wide and 120 mm long, ASTM standard method D638) at 23 °C and a relative humidity of 32 %, using a dynamometer model HP D500. The cross-head speed was 50 mm min⁻¹. Tensile strength σ , tensile modulus and elongation at break (ϵ) were measured.

In order to determine the water absorption, five samples of each composite (3.0 mm thick, 12 mm wide and 50 mm long, ASTM standard method D570) were immersed in distilled water at 23 °C for one week. The samples were weighed before and after treatment, and

the percent weight gain (PWG) was calculated by

$$\text{PWG} = (W_f - W_o)/W_o \times 100 \%$$

where W_o is the initial weight of the sample and W_f its final weight.

RESULTS AND DISCUSSION

Mechanical properties

PP-*co*-PE-silica and PP-*co*-PE-RH composites without compatibilizer

The results of the tensile tests of these composites are shown in Table 2. The tensile modulus generally increased as the silica content of the composites increased, owing to the well-known reinforcing effect of silica particles as filler. In addition, and according to the SEM analysis of these composites, it can be seen in Fig 1 that the silica particles are dispersed with certain degree of homogeneity in the PP-*co*-PE phase according to the particle size and distribution. The increase in tensile modulus of PP-*co*-PE-silica composites is more evident when the silica content increases and when the size as well as the distribution of the silica particles is smaller and narrower, respectively. This is valid in the case of the commercial silicas, EP10X and ES70, in agreement with their characterization (Table 1). The reinforcing effect of silica in the PP-*co*-PE-silica composites will depend on particle size in achieving a microstructure with a high degree of dispersion and/or discontinuity in the different phases of the composite.

PP-*co*-PE-silica composites containing compatibilizer

The improvement of the mechanical properties of the composites depends mainly on the existence of interactions between the polymer matrix and the reinforcing material. In this context a maximum interaction should be achieved between the reinforcement and polymer. For this effect the presence of a coupling agent or compatibilizer would complete that mission. The chemical

Table 2. Mechanical properties of PP-*co*-PE and PP-*co*-PE-silica composites without compatibilizer

Silica type (% by weight)	Tensile modulus ^a (MPa)	σ^a (MPa)	ϵ^a (%)
(0)	890 (19)	24 (2)	74 (3)
EP10X (10)	979 (21)	24 (1)	16 (2)
EP10X (30)	1074 (17)	25 (2)	5 (1)
EP41 (10)	982 (26)	24 (2)	19 (3)
EP41 (30)	1112 (34)	26 (3)	4 (1)
EP17G (10)	1019 (48)	25 (5)	20 (4)
EP17G (30)	1069 (32)	26 (4)	6 (1)
ES70 (10)	1047 (79)	26 (3)	6 (2)
ES70 (30)	1150 (60)	28 (2)	7 (1)
VSSI (10)	1007 (48)	25 (3)	22 (3)
VSSI (30)	1059 (36)	26 (2)	9 (1)
RHSi (10)	955 (26)	24 (1)	26 (3)
RHSi (30)	1060 (66)	25 (2)	6 (1)

^a Standard deviations are given in parentheses.

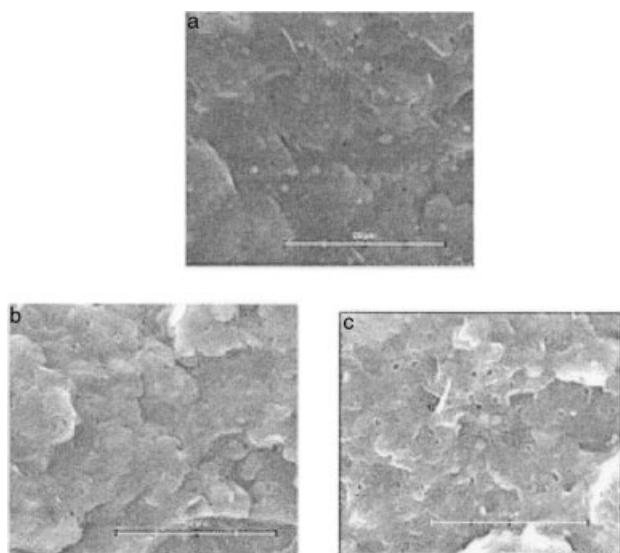


Figure 1. SEM micrographs of the fracture surface of PP-co-PE/EP10X silica composite with and without compatibilizers: (a) PP-co-PE/EP10X silica (90/10); (b) PP-co-PE/PP-g-VIES/EP10X silica (85/5/10) and (c) PP-co-PE/PP-g-MMI/RH/EP10X silica (85/5/10).

nature of the PP-g-VTES compatibilizer and the similarity between the functional groups of silane-grafted PP-co-PE and the superficial silanol groups of the silica improve the dispersion and/or incorporation by means of higher interactions between the silica and the polymer matrix. This would produce a better anchored structure with higher energy requirements to achieve the stress-transfer efficiency of the composite. In this way the tensile modulus of the PP-co-PE-EP10X silica-PP-g-VTES composite is higher than the same composite without the use of PP-g-VTES as compatibilizer (Table 3).

A higher tensile modulus was obtained for the PP-co-PE-EP10X silica composites when PP-g-VTES was used as compatibilizer compared with the same composite with PP-g-MMI as compatibilizer. The factors that strongly influence the higher tensile modulus of PP composites containing PP-g-VTES as compatibilizer would be the similar chemical structure and the degree of association of the silanol groups of the silica with PP-g-VTES compared with PP-g-MMI, as well as the different degrees of grafted polar groups in the polymer matrix of both compatibilizers (Table 3).

Furthermore the effect of the use of compatibilizers on the tensile strength, σ , of PP-co-PE composites with EP10X silica particles was not observed, probably

Table 3. Mechanical properties of PP-co-PE/silica (EP10X)/compatibilizer (85/10/5) composites

Compatibilizer	Tensile modulus (MPa)	σ (MPa)	ϵ (%)
	890	24	74
PP-g-MMI	905	23	16
PP-g-VTES	1021	25	14

because of the poor interface adhesion between the silica and PP-co-PE matrix (Table 3). Among the composites of different compatibilizer types, the PP-g-VTES promoted the compatibility between the PP matrix and the silica, and consequently values of tensile modulus and σ were higher. This can be seen in the SEM of these composites, which will be discussed shortly (Fig 1 and Table 3).

PP-co-PE-RH and PP-co-PE-RH-PP-g-MMI composites

The addition of RH to the PP matrix did not cause an increase in the tensile modulus of the composite compared with those composites containing 10, 30 and 50 % by weight of silica particles. This fact may be associated with the different interaction taking place between the RH with a fibrous aspect and the silica particles with the PP-co-PE matrix (Table 4). Furthermore, the fact that tensile modulus was affected primarily by the RH content shows a lack of continuity, and the interfacial area due to the formation of voids as can be seen from SEM micrographs (Fig 1).

The effect of PP-g-MMI as compatibilizer in the PP-co-PE-RH composite showed an increase of the tensile modulus due to the higher degree of interaction of RH with PP-co-PE, probably through hydrogen-bonding. The addition of 5 % by weight of PP-g-MMI to PP-co-PE-RH composites led to a tensile modulus increase. Further increase of the modulus was found as the amount of RH in the PP-co-PE matrix increased from 30 to 50 % by weight. This points to the chemical affinity of the main components of RH (glucosidic residues and lignin) with the carboxyl groups of MMI when PP-g-MMI was used as compatibilizer instead of PP-g-VTES (Table 4).

The filler morphology and the different chemical or physical affinity between the filler and the PP-co-PE may be the main factor in achieving a composite structure with homogeneous phases. In the case of the silica particles, it was seen that size and size distribution were decisive in obtaining a more rigid structure. When RH fibers are used, factors such as morphology and the chemical nature of the fiber surface should be considered in order to consolidate a homogeneous and rigid structure of high tenacity.

Table 4. Effect of PP-g-MMI as compatibilizer on the mechanical properties of PP-co-PE-RH composites

PP-co-PE-RH- compatibilizer (% by weight)	Tensile modulus (MPa)	σ (MPa)	ϵ (%)
100-0-0	890	24	74
90-10-0	829	22	6
70-30-0	774	18	3
50-50-0	715	16	3
85-10-5	965	25	5
65-30-5	1105	27	4
45-50-5	1181	28	3

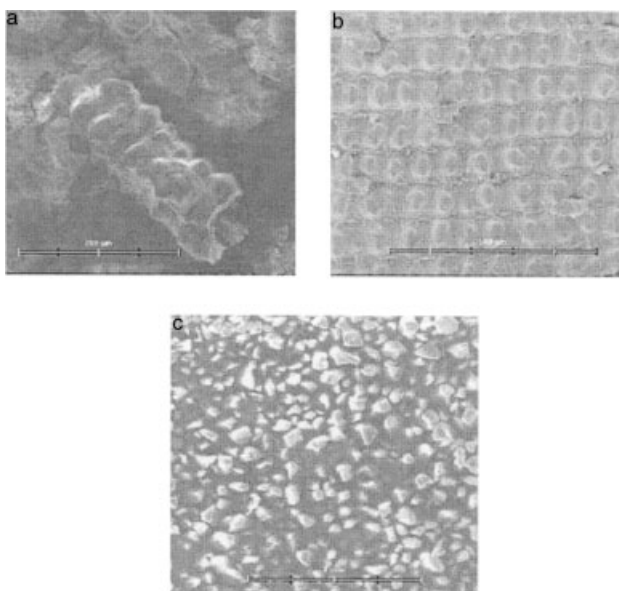


Figure 2. SEM micrographs of (a) RH, (b) silica obtained from RH and (c) a commercial silica (EP10X).

This can be appreciated from SEM micrographs of RH silica obtained from the RH and a commercial silica (EP10X) (Fig 2). This has already been reported in the literature for composites reinforced using materials with a fibrous aspect.^{14,15}

The values of tensile strength, σ , for the composite without compatibilizer are similar, probably because of the poor interfacial adhesion between the RH surface and the PP-*co*-PE matrix, resulting in poor stress transfer across the interface (Tables 3 and 4). In the composites with compatibilizer, optimization of the adhesion between the components of the mixture was achieved by using PP-*g*-MMI as compatibilizer, which has functional groups which are the same as those of the organic fraction of RH. However, this compatibilizer caused a better continuity between the PP-*co*-PE phase and RH in the composite. This compatibilizing effect can be seen in the SEM analysis (Fig 1 and Table 4).

Morphology

The morphology of the composites was evaluated by SEM studies. The fracture surfaces of the tensile test specimens showed good correlation with the mechanical properties of the composites. By means of these tests it could be seen that the interfacial region and the adhesion between the different phases of the composite, silica/RH/functionalized PP-*co*-PE (PP-*g*-VTES or PP-*g*-MMI), was improved.

Fig 1 shows the difference between the interphase of the PP-*co*-PE matrix and the EP10X silica with and without PP-*g*-VTES, and there is better adhesion and phase continuity in the presence of this compatibilizer. This contrasts with the composite where PP-*g*-MMI was used as compatibilizer. The PP-*g*-VTES allows a better distribution of the small particles of EP10X silica in the PP matrix, therefore producing fewer hollows or less phase discontinuity. This effectiveness

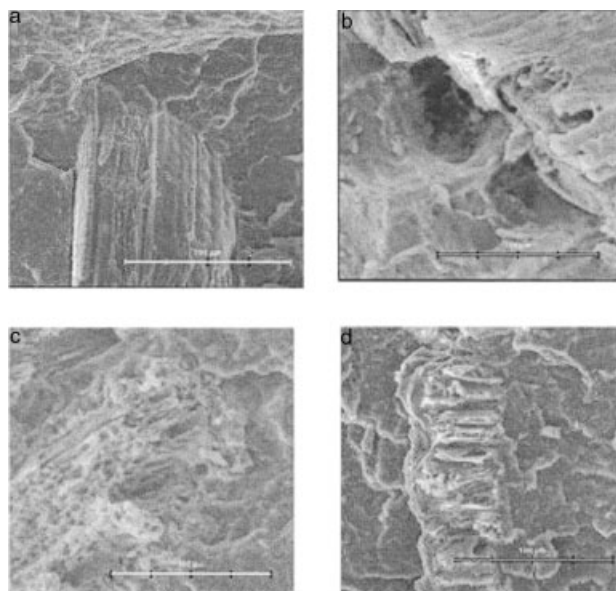


Figure 3. SEM micrographs of the fracture surface of PP-*co*-PE/RH composites with and without compatibilizer: (a) PP-*co*-PE/RH (90/10); (b) PP-*co*-PE/RH (70/30); (c) PP-*co*-PE/PP-*g*-MMI/RH (45/5/50) and (d) PP-*co*-PE/PP-*g*-MMI/RH (85/5/10).

in the interfacial adhesion of the phases can be attributed to the different chemical structure and degree of functionality of the compatibilizer, where the number of functional groups affects the degree of interaction between the phases of the composite. Consequently, the active form of the compatibilizer and its interaction with PP-*co*-PE matrix are the main factors in improving adhesion between silica or RH and the PP-*co*-PE matrix. This same effect is seen in the PP-*co*-PE–RH composite containing PP-*g*-MMI as compatibilizer (Fig 3). The RH fibers, as shown Fig 3, together with their chemical nature, would provide a more effective interaction, probably through hydrogen-bonding between PP-*co*-PE and RH, where good adhesion of the fibers with PP-*co*-PE was observed.

Water Absorption

The water absorption capacity of PP-*co*-PE/silica and PP-*co*-PE/RH/PP-*g*-MMI composites was evaluated by ASTM standard method D570. Table 5 shows that the water absorption capacity of the PP-*co*-PE/silica composite increases as the amount of silica increases. This increase may be associated with the silica particles that impart a hydrophilic character to the PP, at the same time promoting the formation of micropores in the PP-*co*-PE–silica interface, and therefore the PP-*co*-PE/silica composite would absorb more water than PP-*co*-PE.

However, for the PP-*co*-PE/RH composites the increase in water absorption with RH content is less than that found for the PP-*co*-PE composite with EP10X silica (Table 6). This difference can be attributed to the nature, morphology and specific surface area of silica and RH, respectively, as well as to the microstructure of the composite.

Table 5. Water absorption capacity of PP-co-PE/silica composites

Compound					
PP-co-PE (%)	EP10X (%)	EP17G (%)	VSSi (%)	RHSi (%)	Water absorption (%)
100	—	—	—	—	0.1
90	10	—	—	—	0.6
70	30	—	—	—	4.8
90	—	10	—	—	0.8
70	—	30	—	—	5.1
90	—	—	10	—	0.7
70	—	—	30	—	3.3
90	—	—	—	10	0.2
70	—	—	—	30	1.2

Table 6. Water absorption capacity of PP-co-PE/RH composites

Compound			
PP-co-PE (%)	PP-g-MMI (%)	RH (%)	Water absorption (%)
100	—	—	0.1
90	—	10	0.8
85	5	10	0.5
70	—	30	3.0
65	5	30	1.9
50	—	50	4.5
45	5	50	3.8

This is because the composite with RH had better adhesion between the phases. In addition, the effect of PP-g-MMI as compatibilizer in PP-co-PE/RH composites decreases water absorption due to the inhibition of the hydrophilic groups by association between the polar groups of the compatibilizer and the RH. The high efficiency as coupling agent is seen in the decreased water absorption when PP-g-MMI is present in the PP-co-PE/RH composite. A similar effect has been found in systems with other compatibilizers with the help of a coupling agent such as neopentyl(dialyl)oxytri(dioctyl)pyrophosphate titanate (LICA 38) and an ethylene copolymer with maleic anhydride.¹⁶

CONCLUSIONS

The use of silica as filler in PP-co-PE, either as particles or fibers, increases the stiffness and decreases deformation at breakage of PP-co-PE composites as the content of the filler increases.

The size and distribution of the silica particles were decisive factors in achieving better adhesion of the polymer matrix to the silica in PP-co-PE/silica composites with or without using PP-g-VTES as compatibilizer. The effect of using a compatibilizer is reflected in the modification of the mechanical properties as well as in better interfacial adhesion among the composite components as seen from SEM analyses.

Rice-husk fibers caused good interfacial adhesion of PP-co-PE composites containing PP-g-MMI as compatibilizer.

Water absorption by the PP/silica and PP/RH composites, with and without PP-g-MMI, showed, in general, a change that can be related to the nature and physical characteristics of the filler added to the composite.

New thermoplastic materials based on polypropylene reinforced with agricultural wastes such as rice-husk have been prepared. These composites have similar mechanical properties to those available commercially. It can be concluded that, among the filler materials studied in this work, rice-husk are an alternative filler for PP-co-PE composites. Moreover, the use of rice-husk as filler could lead to the preparation of PP-co-PE composites having possible industrial applications.

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