

Rheological, Thermal, and Mechanical Characterization of Fly Ash-Thermoplastic Composites With Different Coupling Agents

S.G. Pardo,¹ C. Bernal,² A. Ares,¹ M.J. Abad,¹ J. Cano¹

¹Grupo de Polímeros, Departamento de Física, E.U.P.-Ferrol, Universidad de A Coruña, Avda. 19 febrero, s/n, Ferrol 15405, Spain

²Grupo de Materiales Avanzados, INTECIN (UBA-CONICET), Depto. de Ing. Mecánica, Fac. de Ingeniería, Universidad de Buenos Aires, Av. Paseo Colón 850, Buenos Aires C1063ACV, Argentina

Composite materials were prepared by mixing fly ash obtained from biomass combustion as filler and isotactic polypropylene (PP) as matrix. Three silane-type coupling agents mainly differing in the size of their functional groups were used to improve the compatibility between both components. Uniaxial tensile tests showed that the incorporation of untreated ash into PP led to stiffer but also more brittle and weaker materials, as Young's modulus significantly increased and tensile strength and elongation at break decreased. Furthermore, an enhancement in storage and loss moduli as well as in composite viscosity was observed with the addition of fly ash. Hardness tests and thermal and fracture surface analyzes revealed tensile test results similar to those mentioned earlier. In summary, after analyzing the effects of the three silanes on mechanical, thermal, morphological, and rheological properties, the silane containing the vinyl functional group (XL10) was selected as the most appropriate for the PP/ash composites investigated. POLYM. COMPOS., 31:1722-1730, 2010. © 2010 Society of Plastics Engineers

INTRODUCTION

One of the main challenges of current industries is to obtain new plastics with better properties and processability at low cost. Hence, a common practice in industry is the use of inorganic fillers in plastic items.

Moreover, reusing industrial wastes is also a goal of research and development. Fly ash seems to be an attractive alternative for mineral fillers. It is cheaper and more environmentally friendly given it is obtained from industrial wastes. Both ashes and fly ashes are solid industrial

wastes produced from the combustion of carbon and other fossil fuels. Inorganic fly ashes are generally mainly composed of a significant amount of SiO₂ and lower contents of Al₂O₃, Fe₂O₃, Na₂O, MgO, K₂O, etc.

Polymer composites reinforced with different types of ash have already been the subject of several studies [1–14]. Normally, ash fillers with a particular chemical composition, reduced size and shape (towards nanoparticles) are selected; however, this approach generates residues and entails a multi-stage process.

Furthermore, when inorganic fillers are used poor interaction and/or interfacial adhesion between polymer and filler is generally observed. To improve interfacial adhesion, and therefore obtain better composite properties, different additives are frequently applied to the fillers or the matrix. Coupling agents added to the filler react with it, improving filler/matrix interaction. These coupling agents have reactive groups that are compatible with the chemical nature of the polymer and the filler [15, 16].

Silane-type coupling agents are frequently used [4]. They have two kinds of inorganic and organic reactive groups in the same molecule. Their typical structure is Y-Si(OR)₃, where OR is a hydrolyzable group such as methoxy, ethoxy or acetoxy, and Y is an organofunctional group such as amine, methacryloxy or epoxy.

During the treatment of the filler with silane, a chemical reaction between the filler functional groups (such as OH) and the alkoxy groups of silane is expected, creating a silane-functionalized surface. Treatment with silane also creates a protective layer which prevents filler particle agglomeration.

Filler inclusion in a plastic matrix causes changes in its processability. Similarly, the addition of coupling agents affects the flow properties of the polymer molecules. Generally, if the interactions between the filler particles and the polymer matrix increase, the viscosity of the system rises. However, when compatibilizers or cou-

Correspondence to: M.J. Abad; e-mail: labpolim@udc.es

DOI 10.1002/pc.20962

View this article online at wileyonlinelibrary.com.

© 2010 Society of Plastics Engineers

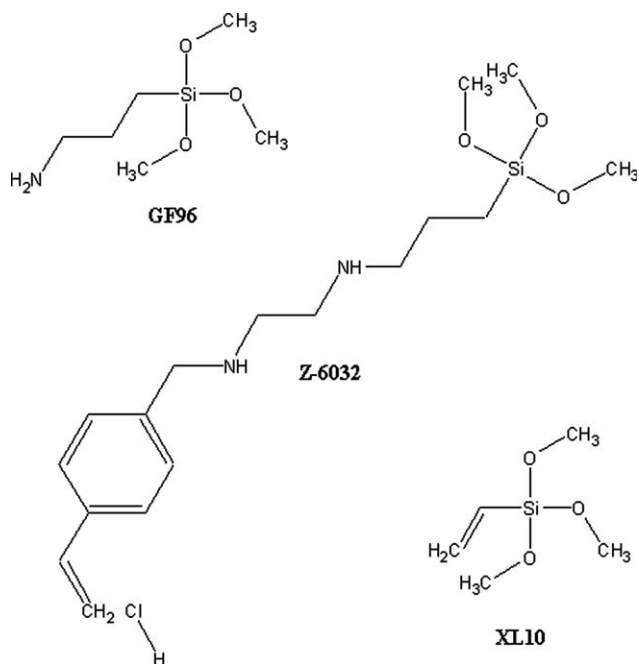


FIG. 1. Chemical structure of the different silanes used.

pling agents are incorporated into the composite formulation, the melt viscosity can be reduced due to the higher dispersion of the filler particles into the matrix. The effect of different coupling agents on composite rheology has already been studied for other materials [17–21]. These rheological studies (high shear) are extremely important to analyze composite processing by injection molding or extrusion.

In this work, the compatibilizing effect of three different types of silane coupling agents on PP/ash composites was evaluated. The main difference between them is the size of the functional groups, as specified in the Materials section.

Moreover, to characterize new PP/ash composites from the results of tensile and hardness tests and thermal and fracture surface analyzes, the role of the three different coupling agents in the viscosity of the composites was studied. Then, the rheological behavior of composites as a function of the coupling agent used was correlated with the morphology and other properties of the composites.

The originality of this work is based on the use of ashes from industrial wastes as reinforcement in thermoplastics. This study proves that it is possible to obtain composites with good properties and low cost, while recycling these industrial residues.

EXPERIMENTAL

Materials

The fly ashes used were obtained from biomass combustion [kindly supplied by Industrias del Tablero S.A.

(INTASA)], when part of the waste generated during fiberboard manufacturing is burned to obtain electrical energy. Their chemical composition is about 55% SiO₂, 14% Al₂O₃, 6% Fe₂O₃, 6% K₂O, 6% CaO and lower contents of MgO, Na₂O, etc. The ashes were separated using a 400- μ m mesh sieve, obtaining a mean size distribution of 110 μ m in diameter. The thermoplastic matrix was an isotactic polypropylene (PP 044W3F) delivered by Repsol-YPF, with a melt flow index of 3.0 g/10 min (230°C, 2.16 kg) and a density of 0.902 g/cm³.

Fly ash/polypropylene composites with fly ash contents of 0 wt%, 30 wt%, and 60 wt% were prepared. The composite with 60 wt% ash was compatibilized with three coupling agents containing different reactive functional groups: amine (GF96), vinyl (XL10) and vinyl-benzylamine (Z-6032). The chemical structure of the compatibilizers is presented in Fig. 1. A 0.5 wt% coupling agent with respect to ash weight was incorporated into the filler. Previous tests showed that a greater amount of silane did not further improve the results. Coupling agents were prepared in an aqueous solution at the desired concentration. Then, treated ashes were dried in an oven at 105°C for 24 h. In the case of silane Z-6032, a hydrolysis in an acid medium was also performed.

Preparation of Composites

Different amounts of ash and polypropylene were mixed in an internal mixer (W 50 EHT from Brandender) at 200°C and 35 rpm. Temperature and torque data were obtained from the equipment and the system was considered to be well mixed when torque remained constant. Time of mixture was minimized to avoid thermal degradation of the polymer. Then, the composites were compression-molded into 2 mm plaques at 230°C, under a pressure of 10 bar for 10 min followed by 70 bar for 5 min. Finally, the plaques were rapidly cooled down by circulating water within the press plates under a pressure of 100 bar for 5 min.

Mechanical Characterization

Uniaxial tensile tests were performed in an Instron dynamometer 5566 at 5 mm/min in accordance with ASTM D-638-02 standard recommendations [22]. Stress-strain curves were obtained from these tests. Young's modulus, tensile strength and elongation at break were determined from these curves. A minimum of six specimens was tested for each system. The average values of the mechanical parameters and their standard deviations were calculated.

Shore D hardness values were also determined by using a Durotech MD-202 durometer in accordance with ISO 868 standard [23]. The measurements were carried out 15 s after the durometer tip had touched the sample.

All mechanical tests were performed at room temperature.

SEM Fractography

Some specimens were fractured at cryogenic temperature in liquid nitrogen. Then, their fracture surfaces and those of specimens broken in tensile tests were examined using a JEOL JSM-6400 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The samples were sputter-coated with a thin layer of gold before they were observed.

Density

The density measurements were performed by the gravimetric method according to ISO 845 standard [24] using an analytical balance. At least three measurements were made for each sample. Average values and their standard deviations were calculated.

Thermal Analysis

The thermal degradation behavior of fly ash and the composites was studied using a Perkin-Elmer TGA7 analyzer. The samples (around 5–10 mg) were heated from 50°C to 900°C at a heating rate of 10°C/min in argon atmosphere. Weight loss as a function of sample temperature was recorded.

The VICAT temperature of the composites was also measured with an HDT 3 VICAT instrument (Ceast SpA) according to ISO 306 [25] with a heating rate of 50°C/h and applying a force of 10 N on the samples. Three samples were tested for each composite. Average values and standard deviations were calculated.

Rheological Measurements

Composite viscoelastic characterization was performed using a controlled strain rheometer (ARES, TA Instruments) with parallel-plate geometry (25 mm diameter, 1 mm gap) at 200°C. Complex viscosity (η^*), storage modulus (G') and loss modulus (G'') were measured as a function of frequency (ω). The tests were performed in the linear viscoelastic region (LVE) (where the modulus is independent of strain). This linear viscoelastic region was determined by a strain sweep before testing the viscoelasticity of the composites under a frequency test. The frequency sweep measurements were set up in a frequency range of 1×10^{-2} to 6×10^1 rad/s.

When studying filled systems, frequently associated repeatability problems can appear due to the sensitivity of the materials' response to the state of agglomeration of the fillers. To minimize these problems, in this study the same protocol was followed for sample loading and testing. To select these conditions, sample recovery was studied. The highest recovery after specimen loading occurred during the first 10 min. Consequently, the samples were left to rest for 10 min before beginning the measurements.

RESULTS AND DISCUSSION

Mechanical Properties

Torque values obtained during the mixing of PP and fly ash are shown in Fig. 2. They indicate that the composites investigated can be successfully processed with similar parameters (temperature and rate of screw) to those for pure polyolefin. The incorporation of 30 wt% ash did not significantly alter the torque value of the system. When the material was mixed with 60 wt% ash the torque increased, although the maximum value was still within the limits of the system processability at 200°C. The incorporation of ashes treated with the different organosilanes slightly varied the torque values during the mixing of the materials. In Fig. 2, the torque curve for the 40PP/60ash composite with vinyl-benzylamine silane (Z-6032) is displayed as example. The other silanes presented similar behavior. However, these changes did not alter the processability of the samples.

Table 1 shows tensile property values for PP/ash composites with different ash contents and the composites with 60 wt% ash with different coupling agents along with their standard deviations in parentheses. Although neat polypropylene displayed ductile behavior exhibiting strain hardening with high elongation at break (59.5%), the incorporation of ash to PP led to more brittle and weaker materials, as both tensile strength and elongation at break significantly decreased. In contrast, material stiffness increased. This effect was more pronounced as ash content increased, as previously reported [26, 27]. The increase in stiffness observed in the composites was expected from the incorporation of a stiffer second phase [7]. In addition, the loss of strength could be attributed to the lack of interfacial adhesion between PP and ash. It has been reported [28] that poor tensile strength and low failure strain are caused by particle debonding from the matrix prior to yielding as a result of poor interfacial adhesion. The presence of big particles with a wide parti-

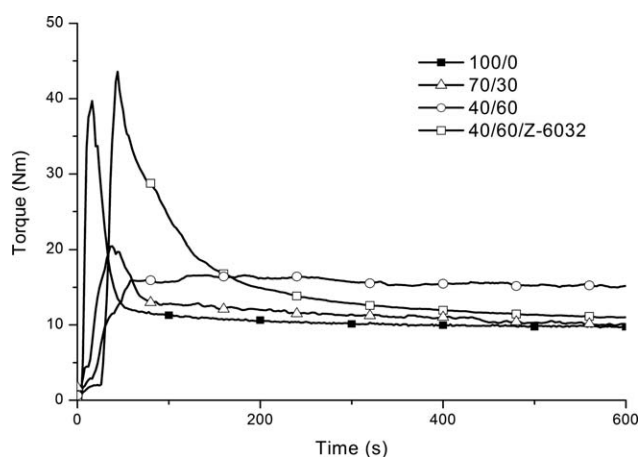


FIG. 2. Torque values obtained during the mixing of PP and fly ash.

TABLE 1. Mechanical properties for the different PP/ash composites (average values and standard deviations in parentheses).

PP/ash	Ash content wt%	Young's Modulus E (MPa)	Tensile strength σ_u (MPa)	Strain at break ϵ_b (%)	Tensile toughness (MPa)	Hardness (Shore D)
100/0	0	527 (11)	29.3 (1.4)	59.5 (1.4)	12.4 (0.8)	–
70/30	30	711 (85)	21.3 (0.9)	12.8 (7.9)	2.1 (1.6)	–
40/60	60	1317 (11)	17.8 (1.0)	3.2 (1.4)	0.3 (0.1)	73.6 (0.4)
40/60/Z-6032	60	1205 (61)	17.3 (1.1)	2.7 (0.6)	–	75.2 (0.8)
40/60/GF96	60	2136 (131)	20.6 (0.6)	1.6 (0.2)	–	77.5 (0.7)
40/60/XL10	60	2517 (76)	24.7 (3.4)	1.5 (0.4)	–	78.1 (1.0)

cle size distribution, as will be shown later, also contributed to the embrittlement effect observed.

In addition, loss of ductility frequently leads to a decrease in material toughness [4, 29]. This effect was also observed in the composites studied in this work, using the results of tensile toughness (Table 1) obtained from the area under the tensile stress-strain curves.

Furthermore, Table 1 shows that the coupling agents containing amine (GF96) and vinyl (XL10) functional groups gave higher stiffness and strength values compared to those obtained without compatibilizer [30]. In contrast, the system with the coupling agent having the vinyl-benzylamine group (Z-6032) presents a more ductile composite and even yield before fracture (see Fig. 3). However, no significant changes in Young's modulus, tensile strength and strain at break values were observed in comparison to the uncompatibilized composite [31, 32].

Note that interfacial adhesion is not expected to have a significant influence on material stiffness as determined at low strains where the interface is still intact [33]. In addition, vinyl and amino reactive groups (XL10 and GF96) seem to have shorter and more rigid couplings with the polyolefin than the vinyl-benzylamine group (Z-6032) whose molecular structure produced more flexible bonds with the polypropylene chains. Therefore, the results obtained for Young's modulus seem to be more related to the presence of the stiffer second phase and to the stiffness of the couplings rather than to interfacial adhesion.

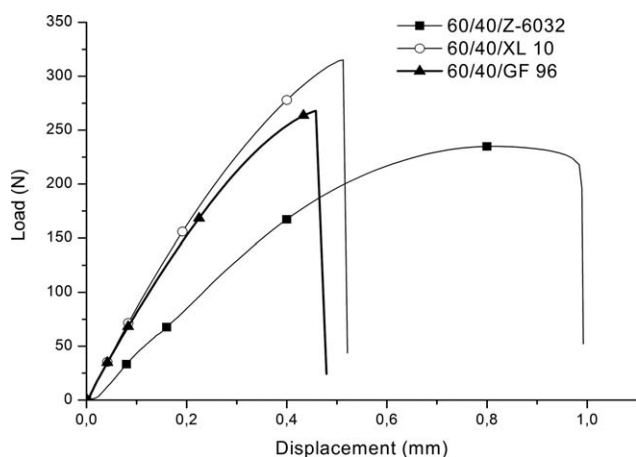


FIG. 3. Load-displacement curves obtained for the different composites (60% ash).

The aforementioned results are in accordance with the results of density measurements (see last column of Table 2). A rise in density was found with the increase in ash content in the formulations, as expected. However, by comparing the different 40/60 PP/ash composites, it can be observed that silane treatment produced changes in material density. The composites processed with treated ashes exhibited lower density than those with the untreated. Then, composite density also depended on the type of silane used: as material stiffness increased, its density decreased. These results can be explained in terms of free volume, which is inversely proportional to density. The use of coupling agents produced a surface modification of the ash particles, which increased the free volume of the materials with respect to the composites with untreated ash. Using the coupling agents with shorter reactive groups (the amino and vinyl coupling agents), the increase in free volume was lower than when the Z-6032 silane with a voluminous reactive group was used.

In the case of strength, however, the degree of filler-matrix interaction promoted by the coupling agents played an essential role. The composites with coupling agents containing amine (GF96) and vinyl (XL10) functional groups were stronger than the uncompatibilized system or the system with the vinyl-benzylamine group (Z-6032). This suggests a better interaction between ash and PP in the former systems, which will be confirmed later from fracture surface analyzes.

Hardness values for the different composites investigated are also shown in Table 1. The increase in the interaction between the filler and the matrix as a result of the incorporation of the silane coupling agents containing amine and vinyl functional groups was also reflected by the improved hardness exhibited by these composites.

Fracture Surface Analysis

Fracture surfaces observed by SEM are presented in Fig. 4 for the specimens fractured at cryogenic temperature. Figure 4a and b shows that in the composites with untreated ash or with ash treated with the coupling agent containing the vinyl-benzylamine group (Z-6032), ash particles are clearly visible and clean of the matrix material, suggesting a poor filler-matrix interaction. Then, in the composites with coupling agents containing the amine (GF96) and vinyl (XL10) functional groups (Fig.

TABLE 2. Thermal properties for the PP/ash composites (standard deviations in parentheses).

PP/ash/silane composition	Ash content wt%	TGA first onset temperature (°C)	Loss mass at 600°C (%)	DTG (°C)	VICAT (°C)	Density (g/cm ³)
100/0	0	378	0	417	146.1 (0.9)	0.902
70/30	30	373	26.0	407	149.3 (0.9)	1.098
40/60	60	395	55.7	445	154.9 (0.3)	1.421
40/60/Z-6032	60	393	53.2	448	153.7 (0.0)	1.262
40/60/GF96	60	407	54.7	457	153.5 (0.8)	1.295
40/60/XL10	60	415	51.9	474	153.1 (0.1)	1.401

4c and d), ash particles are encapsulated by the PP matrix and they are less visible, evidencing the improved interaction between both components promoted by these coupling agents. In addition, given the filler used was normal ash, which is not well separated [5], uneven particle sizes, many coarse particles and irregularly-shaped impurities were observed in the micrographs.

Figure 5a–c shows the SEM micrographs of fracture surfaces of the specimens broken in tensile tests and Fig. 6a–c presents closer views of the same samples. These Figures show that the composite with the Z-6032 coupling agent (Figs. 5a and 6a) exhibited ductile tearing of the PP

matrix widely spread throughout the material. In contrast, composites with GF96 and XL10 coupling agents (Figs. 5b,c and 6b,c) showed more restricted and localized matrix yielding. Therefore, SEM observations confirmed the more ductile behavior exhibited by the composite with the Z-6032 coupling agent in tensile tests. It has been reported [34, 35] that poor interfacial adhesion between ductile polymers and more rigid fillers promotes debonding of the particles from the matrix, which subsequently causes ductile tearing around these particles. The incorporation of Z-6032 coupling agent might promote the deformation mechanism mentioned earlier, probably due to a

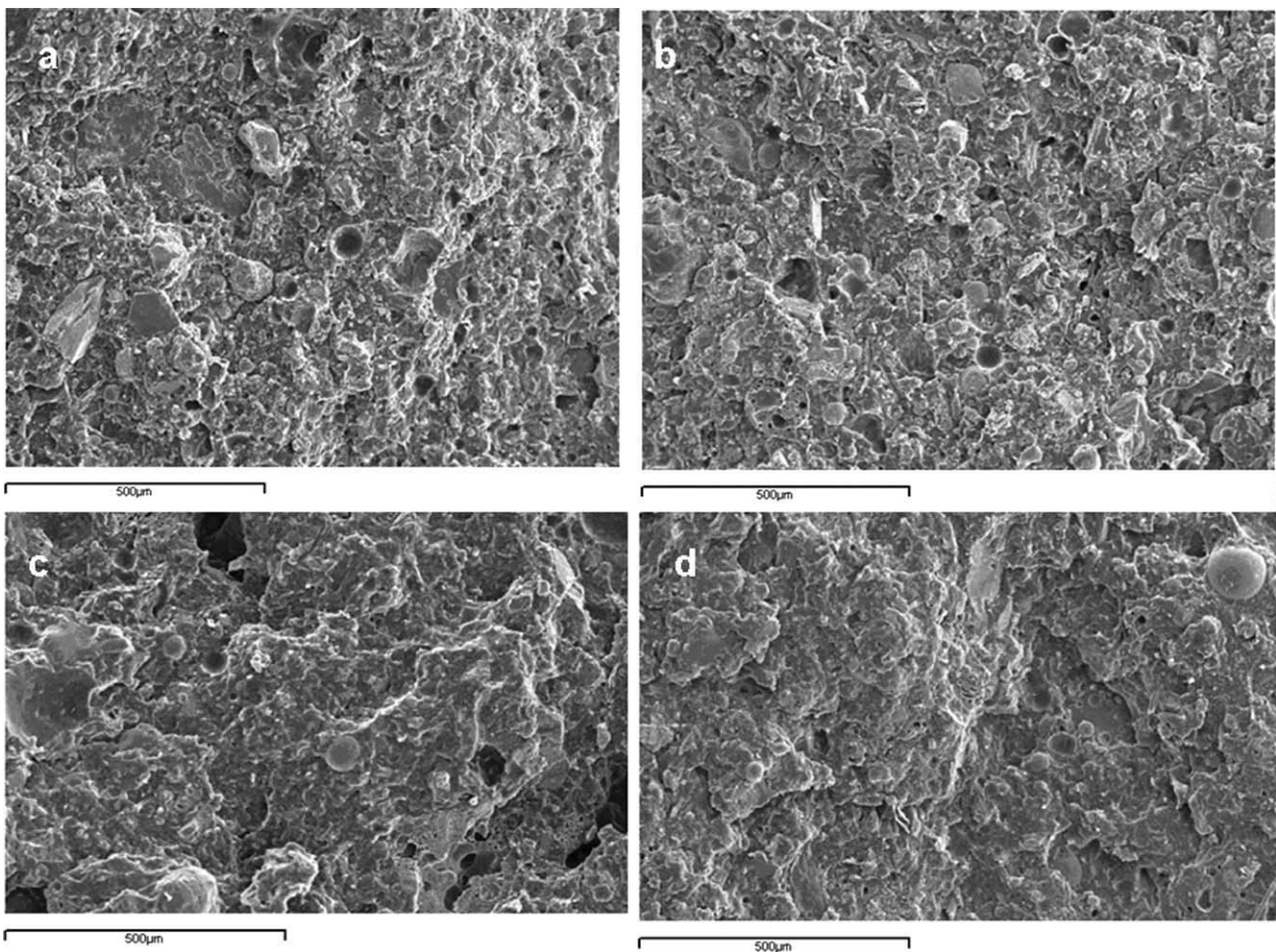


FIG. 4. SEM micrographs of the fracture surfaces of the specimens fractured at cryogenic temperature (ash content: 60 wt%). (a) Composite with untreated ash. (b) Composite with Z-6032 coupling agent. (c) Composite with GF96 coupling agent. (d) Composite with XL10 coupling agent.

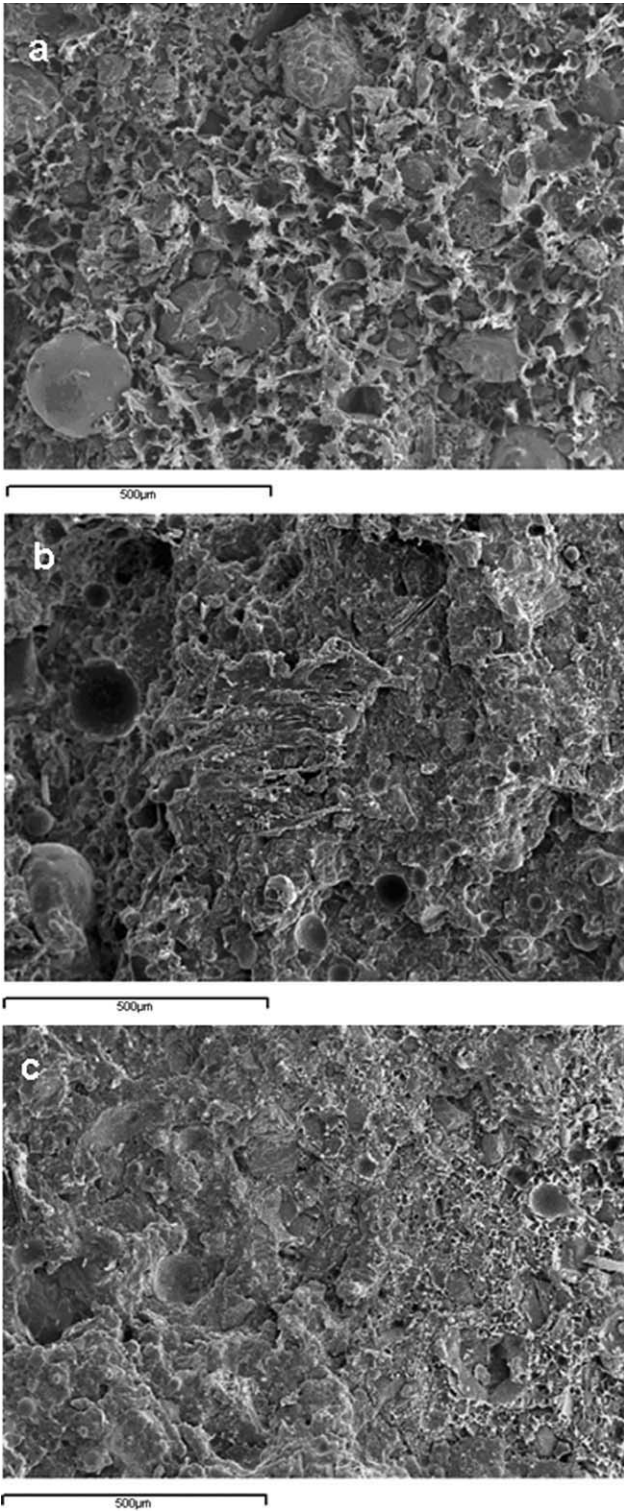


FIG. 5. SEM micrographs of the fracture surfaces of the specimens broken in tensile tests (ash content: 60 wt%). (a) Composite with Z-6032 coupling agent. (b) Composite with GF96 coupling agent. (c) Composite with XL10 coupling agent.

slight improvement in filler particle dispersion in the matrix with respect to the composite with untreated ash. Composites with GF96 and XL10 coupling agents, how-

ever, presented rigid particles that were more tightly adhered to the matrix, hindering debonding at the particle/matrix interface. Hence, microvoid formation, which plays an important role in initiating the toughening mech-

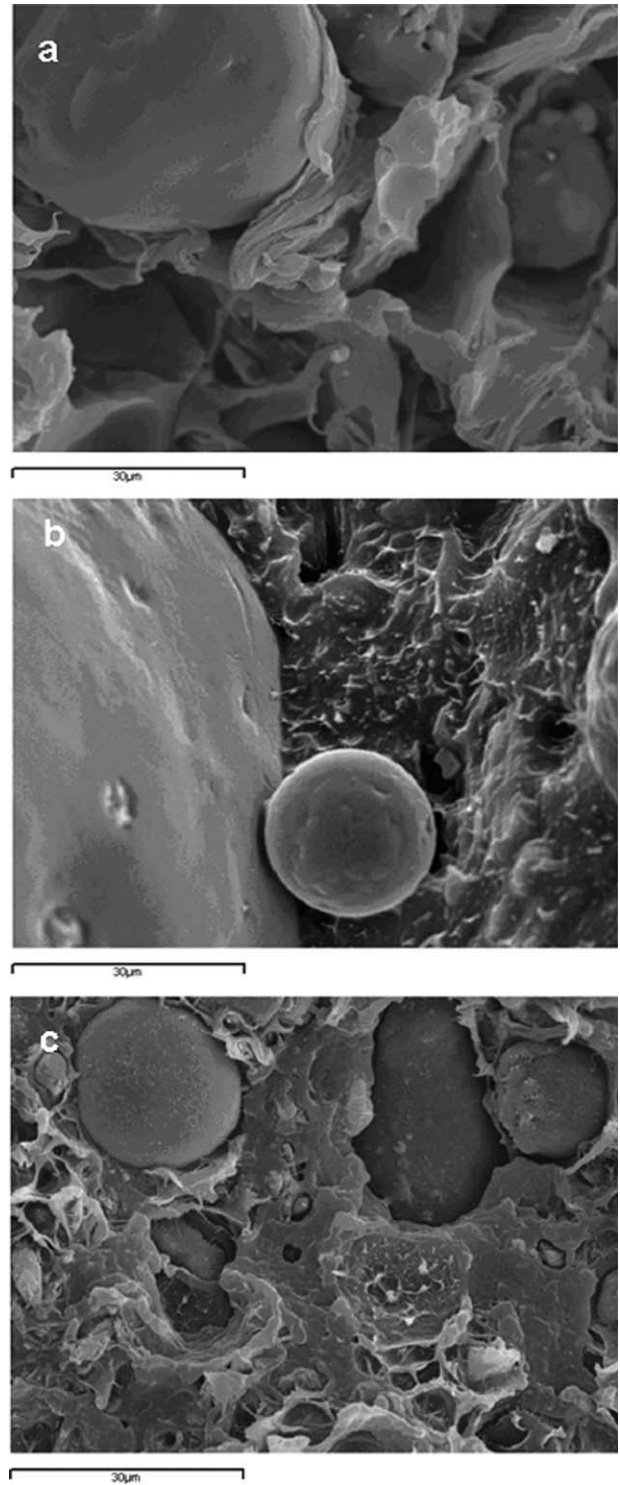


FIG. 6. Closer views of the SEM micrographs of the fracture surfaces of the specimens broken in tensile tests (ash content: 60 wt%). (a) Composite with Z-6032 coupling agent. (b) Composite with GF96 coupling agent. (c) Composite with XL10 coupling agent.

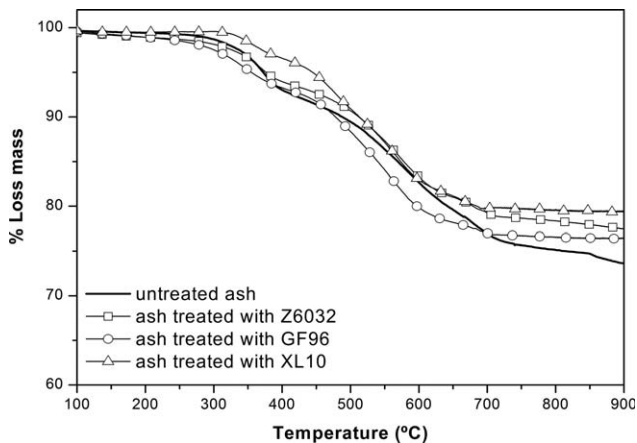


FIG. 7. TGA curves. Percent mass loss versus temperature. Untreated ash and ash treated with the different silane coupling agents assayed.

anism in particle-filled semicrystalline polymers, was more difficult [35].

Thermal Analysis

The weight loss curve of fly ash (Fig. 7) reveals its thermal stability at the processing temperature used, however, its degradation starts at 300°C. The curve displays two steps (one between 50–450°C and the other between 450–700°C), which correspond to the loss of water and the degradation of the organic components (cellulose and lignin) present in the fly ash due to the incomplete combustion of the biomass, respectively. The organic components calculated as percent mass loss measured at 800°C was 25% ash mass. For treated ash (see Fig. 7), this quantity was lower (around 20%). However, the ash treatment with silanes slightly affected its thermal stability.

Table 2 shows the thermal data with their standard deviations in parentheses for the different PP/ash composites. The thermal degradation tests showed that the presence of ash improved the thermal stability of PP. This improvement was greater in the composites containing treated ash. Samples treated with vinyl and amino silanes showed a higher onset temperature, which was also strongly dependent on filler-matrix adhesion. Again, the stronger bonds obtained with the vinyl and amino silanes led to higher thermal stability than the composites treated with the vinyl-benzylamine silane.

The aforementioned results are in accordance with the VICAT test results (Table 2): as the filler content increased, the VICAT temperature also became higher. However, no significant differences were found among the composites with different silanes and the composite with untreated ash.

Rheological Analysis

First, the effect of fly ash addition on the rheology of the composites was studied. In Fig. 8 the effect of filler

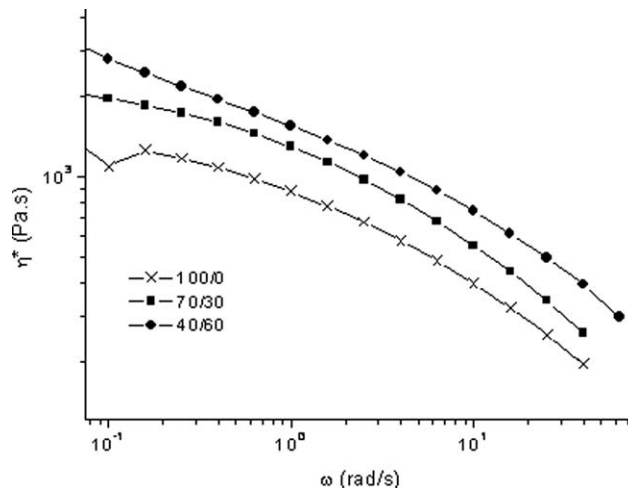


FIG. 8. Dynamic viscosity as a function of frequency for PP/ash composites.

addition on complex viscosity as a function of frequency is observed. An increase in viscosity is shown with increasing filler concentration. The presence of fly ash particles perturbs normal polymer flow and hinders the mobility of chain segments; therefore, the viscosity of the filled polymer increases with the amount of filler.

All composites show shear thinning behavior as previously observed in other filler melts [36, 37]. This behavior can be attributed to a greater degree of polymer-filler interaction, which requires higher shear stress and longer relaxation times for the composites to flow.

The same trend was observed for dynamic moduli when filler content was increased. In Fig. 9, an increase in storage modulus (G') and loss modulus (G'') is observed with increasing levels of fly ash. This behavior can be explained by the fact that filler particles restrict deformation in the same manner as that observed for viscosity.

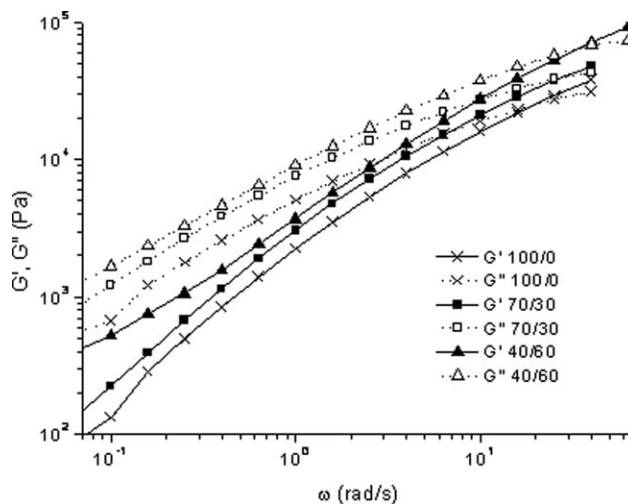


FIG. 9. Dynamic moduli as a function of frequency for PP/ash composites.

The enhancement observed in the modulus values is significantly higher at low frequencies than at high frequencies (the typical frequency of conventional manufacturing techniques such as extrusion and injection molding). For both, storage and loss moduli, the slope of the modulus curves diminishes with increasing amounts of filler [38, 39].

Second, the effect of coupling agents on the rheological behavior was studied. Figure 10 shows the effect of the three coupling agents on the flow behavior at 200°C for the 40 PP/60 fly ash composites. A reduction in viscosity was observed when the ash was treated with 0.5% amine silane (GF 96). This decrease in viscosity was from 5524 Pa s (for the composite with untreated ash) to 2002 Pa s (with treated ash) at a frequency of 10^{-2} rad/s. When the XL10 and Z6032 coupling agents were used, an enhancement in the composite melt viscosity was observed.

The flow behavior in all composites, irrespectively of the presence of coupling agent, could be characterized as shear thinning; complex viscosity decreases with frequency, indicating pseudoplastic behavior. The strong shear thinning behavior that appears in composites without coupling agent due to the inadequate dispersion of the filler was weakened by surface treatment of the filler with amine silane (GF 96). Figure 10 suggests that dispersion of the filler particles in the polypropylene melt was improved to some extent by the use of this kind of coupling agent.

The rise in viscosity values of composite with vinyl silane (XL 10) suggests a more restrained matrix due to a better filler-matrix interaction in the presence of this coupling agent. With this silane, a three-dimensional network structure was formed in the material and the flow of PP molecules became more restricted. The molecular alignment in the flow direction under shear is less probable, resulting in higher viscosity values. The previously reported mechanical properties and morphology results

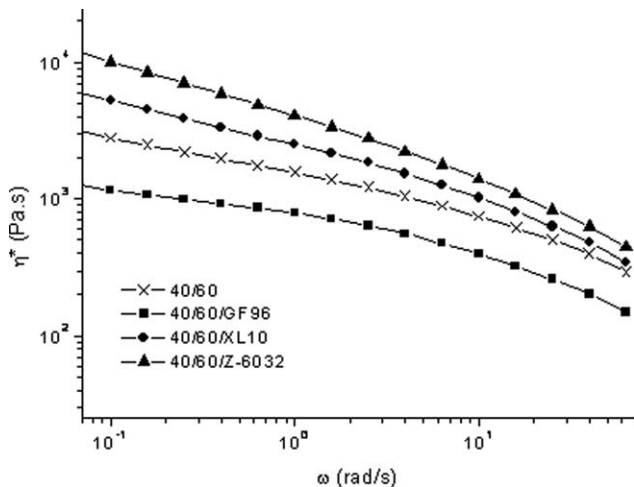


FIG. 10. Dynamic viscosity as a function of frequency for 40/60 PP/fly ash composite with three silanes.

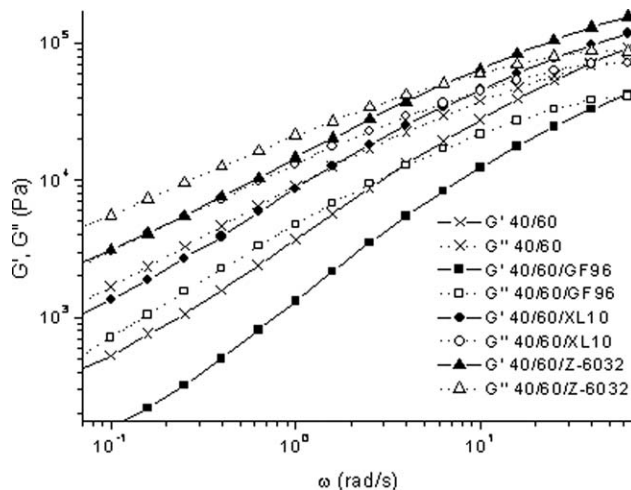


FIG. 11. Dynamic moduli as a function of frequency for 40/60 PP/fly ash composite with three silanes.

also suggested better filler-matrix interaction in the presence of this kind of silane.

The viscosity increase of Z6032 silane can be due to a restriction to flow due to the benzylamine group. This explanation is in agreement with the data obtained for mechanical properties and the SEM micrographs where bad adhesion between filler and polypropylene is observed when the ash is treated with the Z6032 coupling agent. In this case, viscosity enhancement is more related to an impediment to molecular flow due to the bulky size of its functional group rather than to a compatibilizing effect.

The same behavior is observed in the storage modulus (G') versus frequency curves (Fig. 11) for composite 40 PP/60 fly ash untreated and treated with the three silanes. The modulus values of composites can be sorted as Z6032 > XL10 > untreated fly ash > GF 96 following the same tendency as that observed in the viscosity data.

CONCLUSIONS

The incorporation of ash into PP led to stiffer but also more brittle and weaker materials.

When coupling agents containing amine and vinyl functional groups were added to the composite formulation, materials with improved stiffness and strength were obtained. The results found for Young's modulus seem to be related to the presence of the stiffer second phase and to the stiffness of the couplings. In the case of strength, however, the improvement was attributed to the higher degree of filler-matrix interaction promoted by these coupling agents. This was also confirmed from fracture surface analysis.

In contrast, when the coupling agent had a vinyl-benzylamine group, no significant differences between the corresponding composite and the composite with untreated ash were observed. However, this material exhibited the most ductile behavior, even displaying yield

before fracture. This behavior could be attributed to a change in particle dispersion in the matrix which would have been yielded induced from debonding of better dispersed ash particles.

The thermal properties revealed that PP/ash composites have a higher thermal stability than PP. With the treated ashes, these properties improved as the degree of filler-matrix interaction increased.

The effects of the filler and the addition of the three different coupling agents on the rheology of PP/fly ash composites were also investigated. All the blends showed a decrease in complex viscosity with increase in frequency, displaying pseudoplastic behavior. The viscosity and storage and loss moduli of the composites rose with the increase in filler content. Ash treatment with the different coupling agents causes diverse effects depending on the kind of coupling agent used. For the XL10 silane, the increase in composite viscosity has been attributed to a greater interaction between PP and fly ash and to better dispersion of the filler. For the GF 96 silane, a decrease in viscosity is observed due to better dispersion of the filler into the polypropylene matrix. And for the Z6032 coupling agent, the higher viscosity values obtained are attributed to the restrictions to flow caused by the benzylamine groups.

In summary, considering the properties studied, the effectiveness of the coupling agents in giving the best properties together with good processability of the composites can be sorted as follows: XL10 > GF96 > Z6032.

REFERENCES

1. S. Bose and P.A. Mahanwar, *J. Miner. Mater. Character. Eng.*, **3**, 65 (2004).
2. P.M. Stefani, V. Cyras, A. Tejeira Barchi, and A. Vazquez, *J. Appl. Polym. Sci.*, **99**, 2957 (2006).
3. P.M. Stefani, D. Garcia, J. Lopez, and A. Jiménez, *J. Therm. Anal. Cal.*, **81**, 315 (2005).
4. D.S. Chaudhary, M.C. Jollands, and F. Cser, *Adv. Polym. Tech.*, **23**, 147 (2004).
5. M. Wang, Z. Shen, C. Cai, S. Ma, and Y. Xing, *J. Appl. Polym. Sci.*, **92**, 126 (2004).
6. S. Siriwardena, H. Ismail, and U.S. Ishiaku, *Polym. Test.*, **20**, 105 (2001).
7. S. Siriwardena, H. Ismail, and U.S. Ishiaku, *J. Reinforce. Plast. Compos.*, **22**, 1645 (2003).
8. H. Ismail, H.B. Hong, C.Y. Ping, and H.P.S. Abdul Khalil, *J. Reinforce. Plast. Compos.*, **21**, 1685 (2002).
9. R.A. Kruger, M. Hovy, and D. Wardle, The Use of Fly Ash. Fillers in Rubber, in *International Ash Utilization Symposium, Paper 72* Lexington, Kentucky (USA) (1999).
10. J.Y. Hwang, Beneficial Use of Fly Ash, National Energy Technology Department. U.S. Department Energy. Available at: <http://www.netl.doe.gov/>.
11. N. Chand and S.R. Vashishtha, *Clay. Res.*, **19**, 49 (2000).
12. N. Chand and N. Khare, *Indian J. Eng. Mater. Sci.*, **6**, 342 (1999).
13. N. Chand and N. Khare, *Met. Mater. Process.*, **12**, 319 (2000).
14. N. Chand and A. Pandey, *Met. Mater. Process.*, **12**, 91 (2000).
15. J. Pionteck, V.B. Sadhu, L. Jakisch, P. Pötschke, L. Häubler, and A. Janke, *Polymer*, **46**, 6563 (2005).
16. S. Thongsang and N. Sombatsompop, *Polym. Compos.*, **27**, 30 (2006).
17. F. Suhara and S.K.N. Kutty, *Polym. Plast. Technol. Eng.*, **37**, 57 (1998).
18. M. Takahashi, J. Hayashi, and S. Suzuki, *J. Mater. Sci.*, **27**, 5297 (1992).
19. P. Agrawal, S.L. Oliveira, E.M. Araújo, and T.J.A. Melo, *J. Mater. Sci.*, **42**, 5007 (2007).
20. S. Joseph, A.R.R. Menon, J. Aju, and S. Thomas, *J. Mater. Sci.*, **42**, 2054 (2007).
21. S. Filipe, M. Joao, A. Duarte, C.R. Leal, and M.T. Cidade, *J. Appl. Polym. Sci.*, **98**, 694 (2005).
22. Standard Test Method of Tensile Properties of Plastics. ASTM D 638-03. Philadelphia, PA (USA) (2003).
23. ISO 868. Plastics and Ebonite—Determination of Indentation Hardness by Means of a Durometer (Shore Hardness), Geneva (2003).
24. ISO 845. Cellular Plastics and Rubbers—Determination of Apparent (Bulk) Density, Geneva (2006).
25. ISO 306. Thermoplastic Materials—Determination of Vicat Softening Temperature (VST), Geneva (2004).
26. M. Beltrán and C. Mijangos, *Polym. Eng. Sci.*, **40**, 1534 (2000).
27. F. Martí-Ferrer, F. Vilaplana, A. Ribes-Greus, A. Benedito-Borrás, and C. Sanz-Box, *J. Appl. Polym. Sci.*, **99**, 1823 (2006).
28. S.-C. Wong and Y.-W. Mai, *Polymer*, **40**, 1553 (1999).
29. D.S. Chaudhary and M.C. Jollands, *Polym. Compos.*, **13**, 627 (2005).
30. M. Pagnussat, M. Montoya, M.J. Abad, L. Barral, and C. Bernal, Deformation and fracture behavior of PP/ash composites under different loading conditions, in *3rd International Conference on Science and Technology of Composite Materials*, COMAT, Buenos Aires, Argentina, (2005).
31. D.S. Chaudhary and M.C. Jollands, *J. Mater. Sci.*, **40**, 4347 (2005).
32. W.C.J. Zuideduin, C. Westzaan, J. Huétink, and R.J. Gaymans, *Polymer*, **44**, 261 (2003).
33. B. Lauke, W. Beckert, and K. Schneider, *Appl. Compos. Mater.*, **1**, 267 (1994).
34. G.M. Kim and G.H. Michler, *Polymer*, **39**, 5689 (1998).
35. G.M. Kim and G.H. Michler, *Polymer*, **39**, 5699 (1998).
36. K. Lozano, J. Bonilla-Ríos, and E.V. Barrera, *J. Appl. Polym. Sci.*, **80**, 1162 (2001).
37. N.E. Marcovich, M.M. Reboredo, J. Kenny, and M.I. Aranguren, *Rheol. Acta.*, **43**, 293 (2004).
38. P. Pötschke, T.D. Fornes, and D.R. Paul, *Polymer*, **43**, 3247 (2002).
39. P.R. Hornsby, *J. Mater. Sci.*, **29**, 5293 (1994).