Latin American Applied Research 42:83-87 (2012)

MODIFICATION OF RICE HUSK TO IMPROVE THE INTERFACE IN ISOTACTIC POLYPROPYLENE COMPOSITES

E. GUILBERT-GARCÍA[†], R. SALGADO-DELGADO[†], N.A. RANGEL-VÁZQUEZ[‡],
E. GARCÍA-HERNÁNDEZ[†], E. RUBIO-ROSAS[‡†] and R. SALGADO-RODRÍGUEZ[‡‡]

† División de Estudios de Posgrado e Investigación del Instituto Tecnológico de Zacatepec. Calzada Tecnológico No. 27, Col. Centro, C.P. 62780, A.P. 45, Zacatepec, Morelos, México. renesalgado@hotmail.com

‡ Departamento de Metalmecánica. Instituto Tecnológico de Querétaro. Ave. Tecnológico Esq. Mariano Escobedo S/N Col. Centro, CP 89440, Querétaro, Querétaro, México. norma_rangel79@yahoo.com.mx

** Centro Universitario de Vinculación de la BUAP, Calle 29 Oriente No. 601-1, Col. Ladrillera de Benítez Puebla, Puebla, México*

§ Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, A.P. 1166, 22000 Tijuana, BC, México

***Abstract*— The effect of surface treatment on the properties of rice husk/polypropylene composites was investigated. Rice husk with particle sizes of 20, 30, 40 and 60 mesh was modified by alkaline treatment and coupling of silanes with and without previous alkaline treatment. The rice husk was characterized by FTIR, TGA, SEM and a qualitative hydrophilicity test by using a water-toluene system. The TGA results and the qualitative hydrophilicity test indicated that silanized rice husk decreased their hydrophilic character and increased their thermal stability. SEM images showed a regular geometry in the 60 mesh husk which consisted of short fibers. Test specimens were obtained according to ASTM D-1708 standard, by molding injection process using a ratio of 30 % rice husk/70 % polypropylene (PP) based on weight. A quantitative improvement in tensile strength was observed in composites filled with alkali treated rice husk and silanized rice husk in comparison with composites filled with untreated rice husk.**

***Keywords*— Composites; alkali treatment; silane; mechanical properties; rice husk.**

I. INTRODUCTION

For the last two decades, natural fibers have been used as fillers and reinforcement in low-melting-point thermoplastics. These organic filler fibers have been shown to represent low-cost renewable reinforcements that enhance material properties such as stiffness and strength (Rodríguez *et al.,* 2003). Yet another attraction of using these materials is the fact that it would allow various agro-wastes to be appropriately (Han-Seung *et al.,* 2004).

In terms of organic fillers, rice husk obtained from milling process of rice, Oryza sativa, one of the major food crops in the world, can be used as organic filler because of its availability. Disposal of rice husk is a particularly serious problem, which requires special attention due to the large quantities. It is estimated that rice husk of approximately 20% is obtained from the total rice by the milling process. Rice husk roughly contains 35% cellulose, 35% hemicellulose, 20% lignin and 10% ash (94% silica), by dry weight basis (Prachayawarakorn and Yaembunying, 2005). On the other hand, PP is one of the universal polymers and has many advantages such as easy processibility, corrosion resistance, mechanical rigidity, low density, and low cost (Toro *et al.,* 2005*;* Jang and Lee, 2001). The main problem in the broad use of these fibers in thermoplastics has been the poor compatibility between the fibers and the matrix, and the inherent high moisture sorption, which brings about dimensional changes in the lignocellulosic based fibers. The efficiency of a fiber reinforced composite depends on the fiber-matrix interface and the ability to transfer stress from the matrix to the fiber. This stress transfer efficiency plays a dominant role in determining the mechanical properties of the composite and also in the material's ability to withstand environmentally severe conditions. Additionally, it is important to maintain good stiffness to impact strength balance in order to expand the applicability of these natural fiber-reinforced composites (Karnani *et al.,* 1997).

II. METHODS

A. Materials

The thermoplastic polymer, Isotactic Polypropylene (PP), was supplied by Aldrich Chemical Company Inc. In the form of homopolymer pellets with a density of 0.9 g/cm^3, MFI of 4 g/10 min, Tm of 160-165^{o}C, Mn = 97,000, Mw = 340,000. Silane coupling agents used in this study were Trichlorovinylsilane (TCVS) 97% supplied by Aldrich and Dichlorodimethylsilane (DCDMS) 99% supplied by Dow Corning, rice husk was supplied by rice company San José, Jojutla, Mor., Morelos variety A70 (20, 30, 40 and 60 mesh), Sodium hydroxide 97.6% and anhydrous ethanol 99.9%, were supplied by J.T. Baker.

B. Alkali treatment

The rice husk was soaked in a 0.5N NaOH solution at room temperature maintaining a ratio of (500mL alkali solution /50g rice husk) rice husk was kept immersed in the alkali solution for 2 h. The fibers were then washed several times with fresh water to remove any NaOH sticking to the fiber surface, neutralized with dilute hydrochloric acid and finally washed again with distilled water. Final pH maintained was 7. The fibers were then dried at 70°C for 24 h.

C. Silane treatment

The chlorosilanes (DCDMS or TCVS) were added to anhydrous ethanol to yield a 2% solution. The chlorosilane-ethanol solution was stirred for 30 min at room temperature. Then rice husk was immersed and stirred in the chlorosilane-ethanol solution for 30 min in a proportion of 9g/50mL and finally filtered and cured for 9 min at 180 °C (Plueddemann, 1982). The different treatments of rice husk with 20-mesh are presented in Table 1.

D. Preparation of tensile strength specimens

Rice husk (RH) was dried at 70°C for 24h before being melt mixed with PP pellets using the internal mixer attachment of an injection molding machine model I.MM. Test specimens were prepared in a proportion of (0.3g Rice Husk/0.7g PP), the melt mixing temperature and speed were 190°C and 30 rpm, respectively. The composites were blended for 7 min inside the internal mixer and then taken out and palletized for injection molding according to ASTM D-1708 standard.

E. Characterization of rice husk

The FTIR spectra of various samples in KBr pellets were obtained using a Perkin Elmer-FTIR instrument with a resolution of 4 cm^{-1}. The average of 16 scans was used to obtain each spectrum. Scanning electron microscopy (SEM) was performed for sample microstructural analysis on an electron microscope Joel JSV 5800 LV model. The voltage of acceleration was of 15 Kw.

Table 1 Treatments of rice husk

TREATMENT	DENOTED NAMES (example for 20 mesh size)	DESCRIPTION
Untreatment	20Nat	20-mesh rice husk, wasted with distilled water
Alkaline	20Al	20-mesh rice husk, treatment with 0.5N NaOH at room temperature
Silanization with DCDMS	20-DCDMS	Untreatment 20-mesh rice husk, silanized with dicholodimethylsilane
	20Al-DCDMS	Alkali treatment 20-mesh rice husk, silanized with dicholodimethylsilane
Silanization with TCVS	20-TCVS	Untreatment 20-mesh rice husk, silanized with tricholovinylsinale
	20Al-TCVS	Alkali treatment 20-mesh rice husk, silanized with tricholovinylsilane

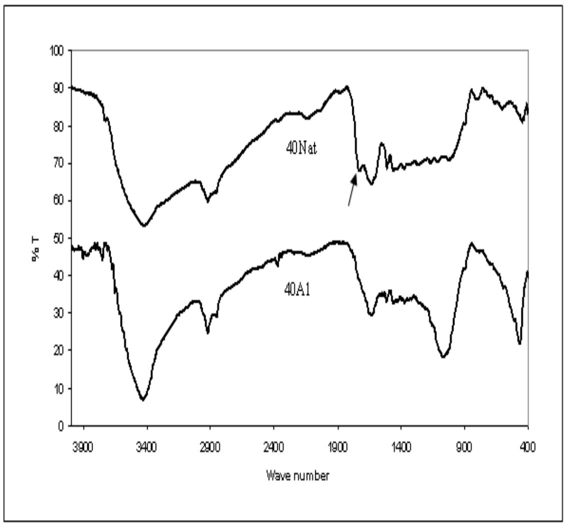

Fig. 1: FTIR comparative analysis between untreated and alkali treated rice husk.

Thermogravimetric analysis (TGA) was carried out in a SDT (Simultaneous DSC-TGA) Q600 instrument at a heating rate of 10ºC min^{-1} in nitrogen atmosphere. The test samples were heated in an oven at 70°C for 24 h and then conditioned at 25°C and 80% relative humidity for more than one day. The rice husk hydrophilicity was analyzed by hydrophilicity test by using a water-toluene system.

F. Characterization of composites

The hydrophilicity of composites was analyzed by contact angle measurements; the tensile properties were evaluated in accordance with ASTM D-1708 standard and the failure mode was determined by SEM examination.

III. RESULTS AND DISCUSSION

A. FTIR analysis of rice husk

The FTIR analysis was used to confirm the chemical modification of rice husk. The removal of lignin by alkaline treatment was corroborated with a decrease in the peak at 1720-1740 cm^{-1}, this absorption was ascribed to C=O groups what are included in lignin, oils and waxes which are present in the rice husk (40Nat versus 40Al in Fig. 1). This absorption does not appear in the 40Al spectrum. On the other hand, the silane coupling in rice husk was verified with the broadening of the peak between 1000 and 1300 cm^{-1}, this absorption was ascribed to the vibrations of Si-O-Si and C-O-Si bonds, (Figs. 2 and 3) (Colthup *et al.*, 1990).

B. Thermogravimetric analysis (TGA) of rice husk

The TGA results of rice husk are showed in Fig. 4 and values are summarized in Table 2. As shown in the table 2, the hydrophilicity of alkali treated husk increased in comparison with untreated rice husk. This is due to the fact that the alkali treatment increases the exposed hydroxyl groups at the fiber by removing lignin, lipids and waxes. On the other hand, the hydrophobicity and thermal stability of silanized husks increased due to the properties of terminal groups of coupled silanes, which are according to data reported for other natural fibers where these treatments were used (García-Hernández *et al.,* 2004).

C. SEM analysis of rice husk

SEM observations in Fig. 5 showed a partial removal of rice husk surface as a result of alkali treatment resulting in a rough rice husk surface. The partial removal of rice husk surface increases the surface area in the alkali treated rice husk, which is according to the literature (Salgado-Delgado *et al,* 2002). 20-mesh rice husk showed an irregular shape and flaky nature.

Table. 2 TGA of untreated, alkali treated and silanized 40-mesh rice husk.

TREATMENT	HUMIDITY (%)	RESIDUE (%)	DESCOMPOSITION TEMPERATURE (°C)
40Nat	2.834	37.610	356
40-DCDMS	1.780	38.550	360
40-TCVS	2.076	39.024	360
40Al	3.088	32.022	334
40Al-DCDMS	2.461	23.439	355
40Al-TCVS	2.407	26.533	356

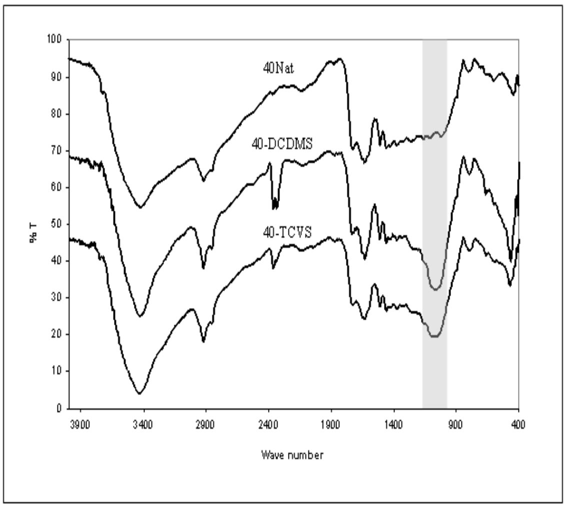

Fig. 2: FTIR comparative analysis between untreated and silanized rice husk.

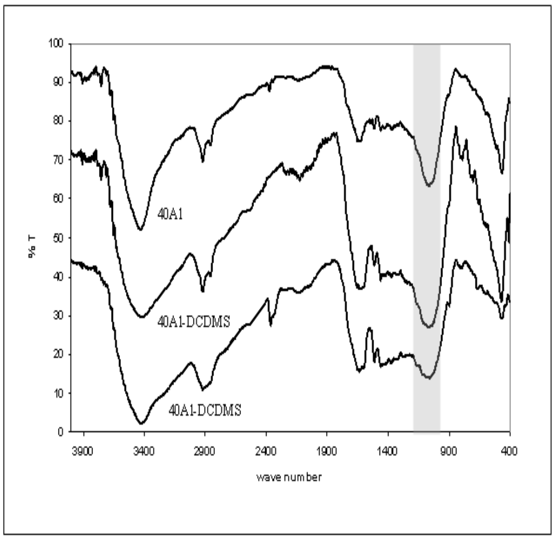

Fig. 3: FTIR comparative analysis between alkali treated and silanized rice husk

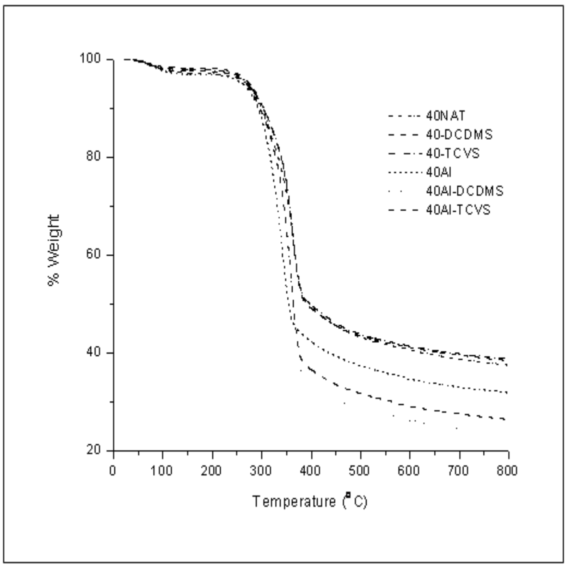

Fig. 4: Thermogravimetric analysis curves of treated rice husk.

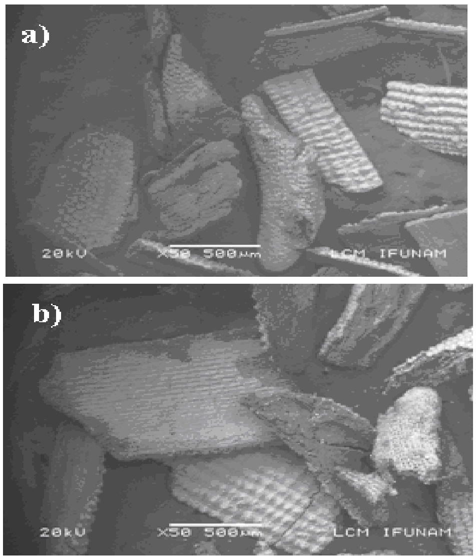

Fig. 5: SEM micrographs of: a) natural rice husk and b) alkali treated rice husk.

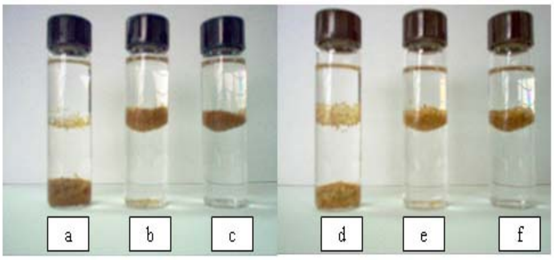

Fig. 6: Water affinity test in water-toluene system: a) 20Nat, b) 20-DCDMS, c) 20-TCVS, d) 20Al, e) 20Al-DCDMS and f) 20Al-TCVS.

D. Hydrophilicity test by using a water-toluene system

The hydrophilicity test results by using a water-toluene system of samples 20Nat, 20-DCDMS, 20-TCVS, 20Al, 20Al-DCDMS and 20Al-TCVS are shown in Fig. 6. As can be seen, the hydrophobicity of silanized husk samples increased since they stayed in the toluene phase, which is consistent with the results obtained by TGA.

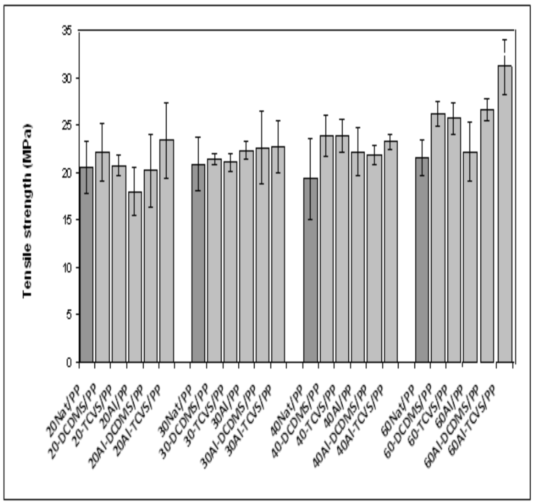

Fig. 7: Tensile strength for Rice Husk/PP

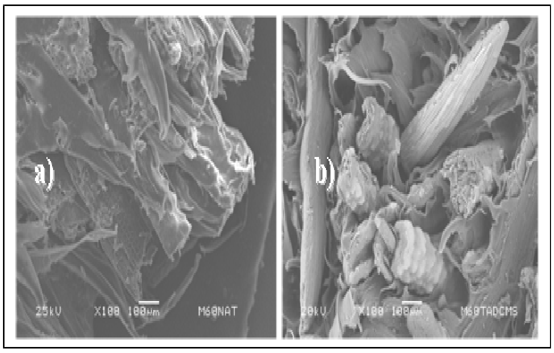

Fig. 8: SEM micrographs of the tensile fracture: a) 60Nat/PP and b) 60Al-DCDMS/PP.

E. Tensile test

The tensile strengths of the composites made of rice husk/PP are shown in Fig. 7 as a function of the mesh size and the surface modification of rice husk. It is clear that in most cases an improvement is observed.

The silane coupling agents had a positive effect on the tensile properties, because they strengthened the interfacial bonding between the filler and the matrix polymer. The tensile strength increased when alkali treated rice husk were used, the best result being observed with the alkali treated 60-mesh rice husk (60Al-TCVS/PP), the alkali treatment improved the tensile strengths by increasing of mechanical adhesion due to a higher ruggedness, on the other hand, the 60-mesh rice husk, so, this size samples caused higher interfacial shear strength of fiber-reinforced composites due to the lateral surface area of the fiber. For the 60Al-TCVS/PP composite the tensile strength increased to 31.23 MPa as compared to 21.57 MPa for the 60 Al/PP composite.

F. Fracture studies by SEM

Figure 8 shows the SEM micrographs of tensile fractured surface of the composites evaluated by tensile strength test. The 60Nat/PP sample was formulated with untreated 60-mesh husk whereas the 60Al-DCDMS/PP sample was prepared with alkali treated and silanized with DCDMS 60-mesh rice husk. It can be seen that in the composite reinforced with untreated husk (Fig. 8a) there are cavities with husk, which indicates that the failure mode occurred by pull-out, this is due to the low wettability of rice husk by melted PP. A tearing of the rice husk is observed in Fig. 8b which means a better interaction between husk and PP matrix.

Figure 9 shows the SEM micrographs of tensile fractured surface of the tensile specimens prepared with 60-mesh husk silanized with DCDMS (60-DCDMS/PP) at 1000x (Fig. 9a) and 500x (Figure 9b) magnification. As can be seen from Fig. 9a, the PP filaments are mechanically anchored in the fractured section of the rice husk. A small separation between the rice husk surface and the polymer matrix can be observed in Fig. 9b. 60-mesh rice husk showed cylindrical shape.

G. Contact Angle measurements

The contact angle measurements were made at 22°C in all cases, to apply reproducible uniform volume drops of deionised water, calibrated micropipette was used and the volume of the water drop used here was 2μl. Figure 10 shows the average values of contact angle as a function of time for water. All samples, including the unfilled PP showed contact angle decrements as time progressed, this is mainly due to evaporation. As can be seen, the material reinforced with alkali treated husk

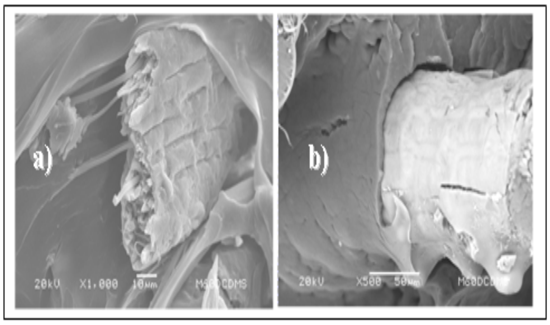

Fig. 9: SEM micrographs of the tensile fracture: a) 60-DCDMS/PP (1000x) and b) 60-CDMS/PP (500x)

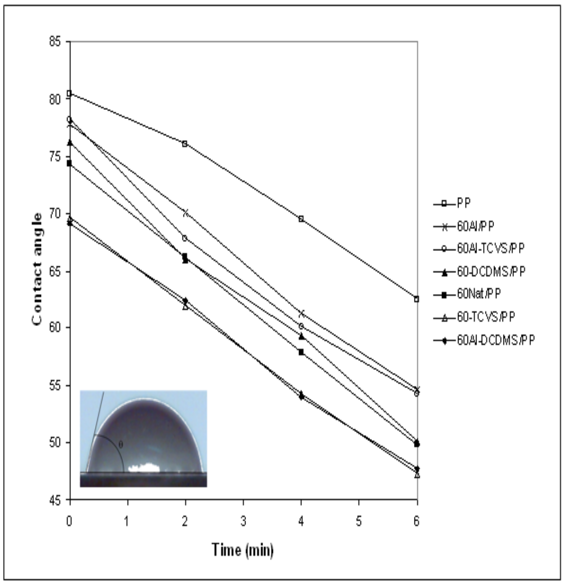

Fig. 10: Average values of contact angle as a function of time

showed a behavior more hydrophobic, which is according to the tensile test. This indicates that the rice husk was wetted by the PP matrix, which inhibited the interaction between rice husk and water.

IV. CONCLUSIONS

There were improvements in the tensile strength in the materials formulated with modified rice husk with re gard to those that did not undergo treatment. With regard to the results of the tensile strength test for the untreated husk, the best result was for the 60-mesh husk, this can be mainly due to the fact that this rice husk showed a regular shape (as short fibers). In contrast to the 20, 30 and 40 mesh husks that were larger in size and presented very irregular shape, as it was observed by SEM images. A decrease in the hydrophilicity of silanized samples was observed by the TGA. The same was observed in the affinity experiment using a water-toluene system. In accordance with the results obtained from contact angle measurements, the composites reinforced with 60Al husk presented higher hydrophobicities. Although the alkaline treatment can increase the number of exposed OH groups at the fiber surface and therefore increasing the hydrophilicity. This did not happen with the 60Al fiber since the fiber size reduction increases the surface area allowing that the fiber was wetted by the PP matrix. This resulted in better interaction between the fiber and the matrix, which is in accordance with the results obtained by the tensile strength test.

ACKNOWLEDGMENTS

The authors thank Dr. Víctor Manuel Castaño Meneses and Dr. Rodrigo Velásquez Castillo of Center for Applied Physics and Advanced Technology - UNAM Querétaro for their support in the evaluation of composites.

We are grateful to CoSNET-DGEST for a grant for master's degree and financial support of the authorized project by DGEST UR.ZAP2-06.

REFERENCES

Colthup, N.B., L.H. Daly and S.E. Wilberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press Inc., U.S.A. (1990).

García-Hernández, E., A. Licea-Claverie, A. Zizumbo, A. Alvarez-Castillo and P.J. Herrera-Franco, "Improvement of the Interfacial Compatibility Between Sugar Cane Bagasse Fibers and Polystyrene for Composites," *Polymer Composite*, **25,** 134-145 (2004).

Han-Seung, Y., K. Hyun-Joong, S. Jungil, P. Hee-Jun, L. Bum-Jae and H. Taek-Sung, "Rice-husk flour filled polypropylene composites; mechanical and morphological study," *Composite Structure,* **63**, 305-312 (2004).

Jang, J. and E. Lee, "Improvement of the Flame Retardancy of Papersludge/Polypropylene Composite," *Polymer Testing*, **20,** 7-13 (2001).

Karnani, R., M. Krishnan and R. Narayan, "Biofiber Reinforced Polypropylene Composites, Polymer Engineering and Science," *Polymer Engineering & Science*, **37**, 476-483 (1997)

Plueddemann, E.P., *Silane Coupling Agents*, Plenum Press, New York (1982).

Prachayawarakorn, J. and N. Yaembunying, "Effect of recycling on properties of rice husk-filled-polypropylene," *Journal of Science Technology*, **27**, 343-352 (2005).

Rodriguez, C.A., J.A. Medina and H. Reinecke, "Reinforced with Cellulose Based Fibers," *Journal of Applied Polymer Science,* **90,** 3466-3472 (2003).

Salgado-Delgado, S. Vasquez, E. Garcia, R. Lopez-Castanares, A. Alvarez-Castillo, V.M. Castaño and E. Martinez, "Numerical analysis of the mechanical properties of rice husk-polyester composites," *Advanced Composite Let*, **11,** 167-170 (2002).

Toro, P., R. Quijada, O. Murillo and M. Yazdani-Pedram, "Study of the morphology and mechanical properties of polypropylene composites with silica or rice-husk," *Polymer International*, **54**, 730-734 (2005).

Received: September 12, 2009.
Accepted: April 29, 2011.
Recommended by Subject Editor Ana Lea Cukierman.