

Preparation and Characterization of Poly(vinyl chloride)/Virgin and Treated Sisal Fiber Composites

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ABSTRACT: Mechanical property changes, thermal stability, and water absorption capacity of poly(vinyl chloride) (PVC)/sisal fiber composites were assessed with respect to the effect of maleic anhydride chemical treatments of the sisal fiber, for five different sisal fiber contents, varying from 0 to 30% by weight in the composite. The composites prepared with the untreated sisal exhibited higher tensile modulus and hardness than the unloaded resin, while elongation and tensile strength were reduced. The deterioration in the mechanical properties of PVC blended with sisal fiber is attributed to the presence of moisture, interfacial defects at the fiber and polymer interface, and fiber dispersion in the PVC matrix. The amount of absorbed

water is a function of the amount of fiber in the composite (F0 = 0 phr, F5 = 0.77 phr, and F20 = 4.83 phr). The comparison of the results of characterization of F5, F20, and F30 formulations prepared with the untreated fibers and the treated ones showed a reduction in absorbed water after the chemical treatment of fiber with maleic anhydride (F0 = 0 phr, F5 = 0.28 phr, and F20 = 2.99 phr), thus improving the mechanical properties of composites prepared with the treated sisal. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3630–3636, 2007

Key words: PVC; sisal fiber; moisture; mechanical properties; thermal stability

INTRODUCTION

Natural fibers blended with synthetic polymers represent a new area that has interested many researchers for the last two decades from both the academic and the technological angles, particularly in North America,^{1–3} although wood–plastic composites (WPC) have been developed in United States since 1980s and represent a new class of intermediate materials between nonbiodegradable thermoplastics and completely biodegradable natural polymers.⁴

The advantages of natural fibers (wood flour, jute, sisal, etc.) include low density, low equipment abrasiveness, low cost, pleasing esthetics, improved acoustics, good biodegradability, and ready availability from natural and renewable sources. However, thermoplastics provide composites with good moisture and decay resistance.

The advantages forecast a high demand for these composites in the domains of building construction products and automotive applications.

Many systems of both polymer and natural fibers have been investigated and reviewed.^{5–12} The difficulty of such material applications resides in tempera-

ture limits in processing (thermal stability limitation of wood), the difficulty in having a homogeneous dispersion of the fiber in the polymeric matrix, and a weak interfacial adhesion.

To enhance the compatibility between sisal and polyethylene, Kalaprasad et al.⁵ worked on the pretreatment and modification of sisal fiber to improve the interfacial adhesion. Treatments with reagents such as alkali, acetic anhydride, stearic acid, permanganate (KMnO₄), silane, and maleic anhydride (MA) composites were tried in sisal/LDPE composites so as to improve the performance of mechanical properties. They found acetylation as the most efficient treatment according to cost/performance ratio analysis.

The influence of acetylation on mechanical, thermal, and thermodegradative behavior of sisal fiber-reinforced PP and PP/HDPE, and PP/HDPE-functionalized and nonfunctionalized EPR composites was studied by Ichazo et al.¹³ They found that the acetylation of the fiber improved adhesion of the fiber to the polyolefin matrix. This treatment also improves tensile strength, modulus, and thermal properties.

Arzondo et al.¹⁴ carried out detailed investigation on sisal fiber/polypropylene composites. Maleic anhydride-grafted polypropylene (MA-g-PP) was used as coupling agent to improve adhesion between the polar sisal fiber and the nonpolar polypropylene matrix. The SF/MA-g-PP pellets have a fiber content

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of 70% (w/w). The prepared composites have final fiber contents ranging about 3.5–24.5% (w/w). They reported that the PP tensile strength increased by 126% and the heat distortion temperature (HDT) by about 35 K. They also analyzed the samples by FTIR and SEM micrographic observation and, they found that the MA-g-PP was covalently bonded to SF through esterification.

Among these treatments, alkali treatment is the most economically viable. Some authors have employed this technique for sisal and jute fiber and changes occurring in the composite properties have been reported.

Gassan and Bledzki¹⁵ treated isometric jute yarns with 25% NaOH solution for 20 min and reported a 60% improvement in the treated jute/epoxy composite properties.

All these studies reveal that chemical modification plays a major role in improving the overall performance of the composites.

On the other hand, few studies have focused on poly(vinyl chloride) (PVC)/natural fibers composite. Gilson et al.¹⁶ studied the composites obtained on plasticized PVC with a liquid plasticizer (polyester) and a permanent solid plasticizer (ethylene/vinyl acetate/carbon monoxide copolymer) reinforced with sisal fibers. The influence of size and quantity of sisal fibers in the composites has been studied. For both matrices, the elastic modulus is increased as the sisal fibers are added, compared to unloading matrices.

The thermal degradation reactions of short sisal fiber-reinforced ENR/PVC composites were analyzed and studied by Zhang.¹⁷ They found that the thermal stability of the composite rose with an increasing amount of short sisal fiber and fell with an increasing ratio of PVC in the composite.

This study focuses precisely on the research and characterization of WPCs made of dioctyl phthalate (DOP)-plasticized PVC matrix, reinforced with sisal fibers. The objective of this study is to evaluate the tensile properties, water absorption, impact strength, and hardness of PVC/sisal composites with various fiber concentrations.

To enhance the compatibility between fibers and polymer, it is necessary to pretreat or modify the sisal, so that the interfacial adhesion can be increased. The comparative results of the properties of PVC/untreated sisal composites and those of PVC/sisal treated with MA are presented in this article.

EXPERIMENTAL

Materials

All of the PVC–sisal composite formulations used in this work were prepared based on PVC type 4000M produced by “Entreprise Nationale des Industrie Pét-

rochimiques (ENIP)” at Skikda in North Eastern Algeria. The polymer has the following physical characteristics: Kwert, 67; powder density, 0.56 g mL⁻¹; thermal stability, 60 min at 180°C. The additive used in the preparation of the various formulations was DOP as a plasticizer with a viscosity ranging from 80 to 85 MPa s, a molecular weight of 390 g mol⁻¹, a boiling temperature of 233°C, a thermal stabilizer system based on Ba-Cd-Zn and soya bean oil as a lubricant.

Sisal fibers from Mexico were used as the filler, having a density of 1.5 g cm⁻³, a length of around 125 μm, and a chemical composition of 65.8 phr of cellulose, 12.0 phr of hemicellulose, 10.0 phr of lignin, and 10 phr of water.

Chemical treatment of sisal fibers

Sisal fibers were esterified to improve their compatibility with the PVC matrix using a commercial maleic anhydride (MA) (LABOSI: France). The sisal fibers were dried at 80°C in a vacuum oven until a constant weight was reached. The purification of fibers was carried out by immersion in an acetone solution for 24 h to eliminate all contaminants and impurities followed by vacuum filtration.

The esterification reactions were carried out by immersing the sisal fibers in a solution of 340 mL of xylene containing 20 g of MA and benzoyl peroxide as catalyst and then heating at reflux temperature (140°C) for 4 h. The esterified fibers were separated from the solution and washed with distilled water to eliminate the unreacted materials. Finally, the fibers were dried at 70°C in a vacuum oven until a constant weight was achieved.⁴

The mass composition of the different formulations is reported in Table I.

Sample preparation

Blends based on PVC powder, the various additives, untreated and treated sisal fibers were placed in a high-speed twin steel-wall mixer and processed at a speed of 3000 rpm at 50°C, below the glass transition temperature of PVC. The different PVC formulations obtained were used to prepare the preblended films by the calendaring process at 180°C with a residence time of 8 min. The films thus obtained were placed in an aluminum mold and the mold which was placed

TABLE I
The Mass Composition of the Different Composites

Component	F0 (g)	F5 (g)	F20 (g)	F30 (g)
PVC resin	100.00	100.00	100.00	100.00
Plasticizer	30.00	30.00	30.00	30.00
Stabilizer	02.00	02.00	02.00	02.00
Lubricant	00.50	00.50	00.50	00.50
Sisal fibers	00.00	05.00	20.00	30.00

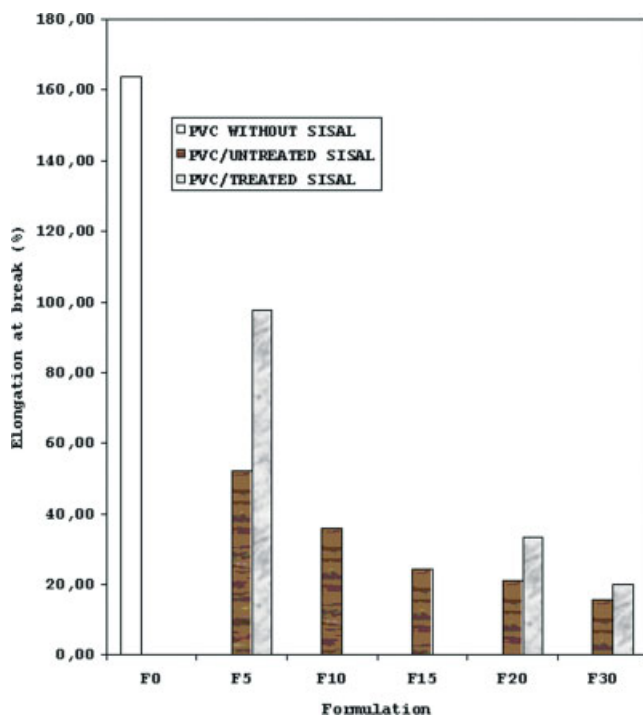


Figure 1 Effect of sisal fiber content before and after treatment on the elongation at break of PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

between two steel platens. A Fontume Holand Hydraulic oil-heated press with a nominal maximum pressure level up to 250 kN was used for the compression-molding. The press platens were maintained at 170°C for 3 min. The 2-mm thick plates obtained were then removed to be used in various characterizations.

Mechanical properties

Five samples of each test were used to determine tensile and impact properties. The tensile test was performed on a ADAMEL LHOMARGY tensile testing apparatus at a cross-head speed of 20 mm min⁻¹, following test procedure CEI 60811-1-1. The size of the specimen was 75 × 13 × 4 mm³.

Charpy impact tests, following ISO178, were performed on CÉAST TORIWO (6546/000) Impact tester. The size of the specimens used for the impact test was 8 × 1 × 0.2 cm³.

The hardness test was carried out on a Durometer Shore D following standard NF ISO T 51-123 with specimen dimensions of 10 × 10 × 0.2 cm³. Hardness is the average of five measurements taken on each sample.

Both the sample preparation and the characterization were carried out in the laboratory of CABEL ("cablerie Electrique") d'Alger located in the capital Algiers (Algeria).

Water absorption

Water absorption measurements were performed according to ASTM standard method D 570-99 (ASTM 1999). For each composite, five 3 × 12 × 50 mm³ samples were cut from the plates of the compression-molded sheets.

The samples were subjected to heat treatment in an oven at 50°C for about 24 h, then immediately weighed (W_0). To measure water absorption in the composite, all the samples were then immersed in distilled water at ambient temperature for 24 h, then taken out and weighed again (W_f). The percent weight gain (PWG) was calculated as:

$$PWG = [(W_f - W_0)/W_0] \times 100\%$$

RESULTS AND DISCUSSION

Mechanical properties

Tensile properties

The effect of the amount of sisal fibers on the mechanical properties of the PVC/untreated sisal composites was examined by varying the sisal loadings. Figures 1 and 2 represent respectively, the histograms of elongation and strain at break of the various PVC/sisal composite samples containing different sisal fiber amounts. Generally, increasing the sisal fiber content resulted in a very similar trend of decrease in elongation and strain at break.

In terms of tensile properties, the decrease of elongation and strength at break was probably caused by a

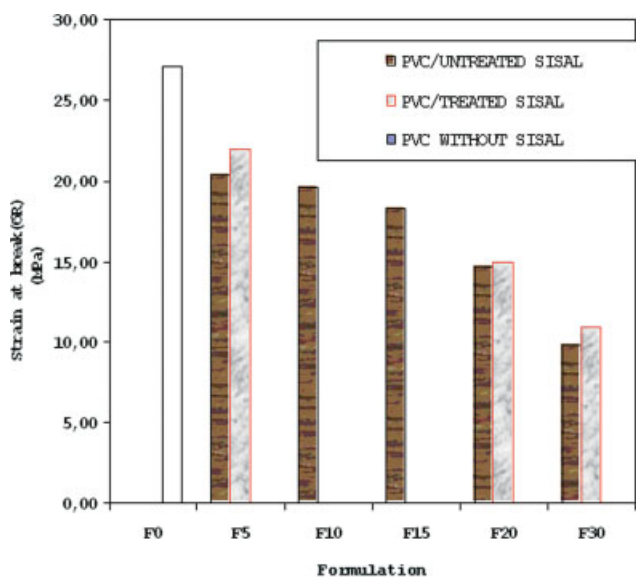


Figure 2 Effect of sisal fiber content before and after treatment on the strain at break of PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

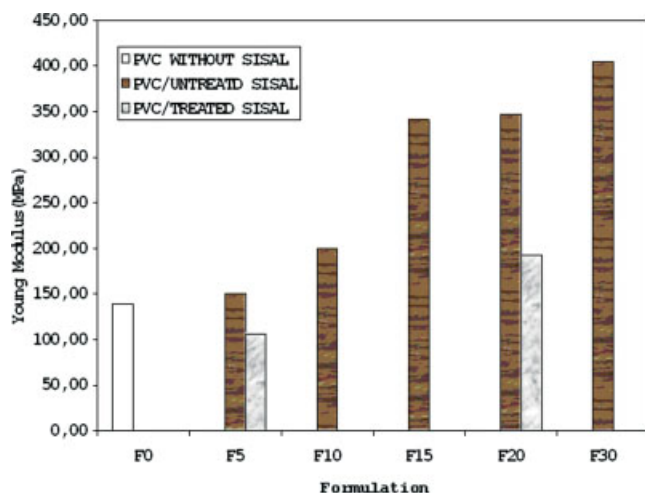


Figure 3 Effect of sisal fiber content before and after treatment on the Young's modulus of PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

number of factors, including moisture pick-up, poor dispersion of fibers in the matrix, and an increase of interfacial defects in debonding between polymer and fibers. Results found were in perfect correlation with those found by Sombatsompop et al. with the samples of PVC/sawdust composites.⁹ The tensile properties of highly viscous thermoplastics, rubber materials, or plasticized PVC depend on several factors, such as dispersion of fiber, increase in stress concentration at fiber ends, and amount of air imprisoned in the composite during mixing.¹⁸

In the case of polystyrene, Murray and Hull^{19,20} observed that microvoids occurred within the crazes at the fiber ends and coalesced to generate planar cavities and cracking within the crazes. The chance for some amount of opened cleavage-type fracture during the pull out process of fibers was also reported.²⁰ The broken ends of the fibers formed during the tensile deformation may induce crazes and cracks in the matrix and may lead to a decrease in the tensile strength.⁸

For the Young's modulus of the composites reinforced with sisal fiber, we can see in Figure 3, the increased values with raised amount of sisal fiber. It can be seen that the Young's modulus at 30 phr of untreated sisal loading presents an increment of ~ 249%. This is due to the solid particle of sisal fiber reinforcement leading to greater stiffness in polymer composites and because the fiber usually retains most of its lignin.

Impact properties

For the results of the impact strength of the composites represented in Figure 4, we can note that the addition of sisal fiber had no effect on impact strength

properties at concentrations below 20% (samples are resistant and nonbrittle).

The formulations created with weak or moderate levels of sisal fiber are unbreakable; their impact strength exceeds that produced by the Charpy machine. In this case, the plasticization effect that gives the material flexibility and elasticity is greater than the rigidity of the fiber.

Above 20% sisal fiber, the samples become breakable, with the rigidity of the fibers becoming greater than the flexibility of the plasticization. The impact strength properties were affected, samples become breakable and we recorded low values of 0.9 and 0.36 J for the composites F20 and F30, respectively. The decrease in impact strength was probably due to the dilution effect. As the sisal fiber content increased, the ductile portion (PVC matrix) was automatically reduced, thus decreasing the composite toughness.

Hardness and the esthetic aspect of the PVC/sisal composite samples

Hardness of the composite samples is shown in Figure 5. The graph shows clearly the increase in hardness as we increase the quantity of fibers. This conclusion is valid for the two types of composites prepared with treated and untreated sisal.

The Figure 6 shows the photo of the different PVC/sisal composite samples. We can clearly see that the samples are esthetic in pleasing, light, and can easily

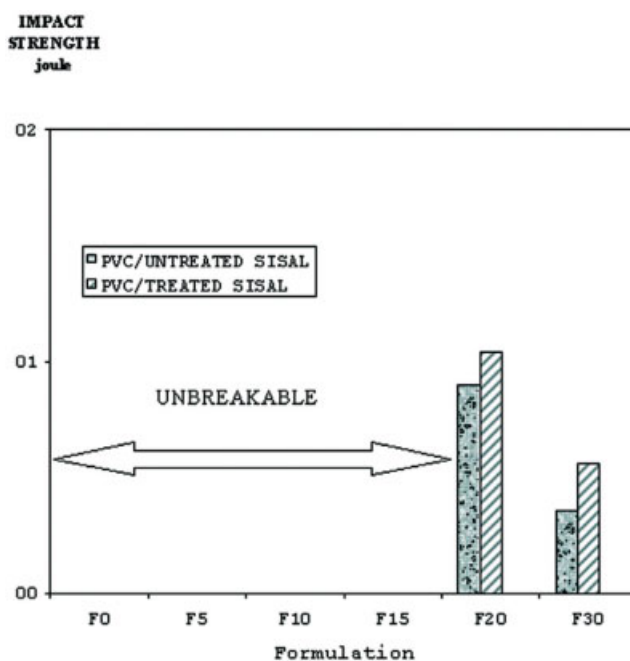


Figure 4 Effect of sisal fiber content before and after treatment on the impact strength of PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

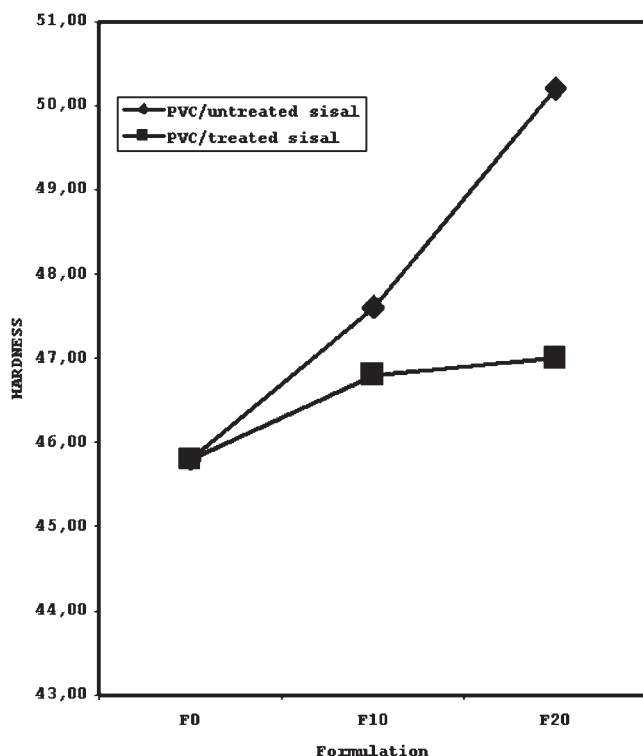


Figure 5 Effect of sisal fiber content before and after treatment on the hardness of PVC/sisal composites.

be used in decoration object manufacture instead of imitating natural wood.

Water absorption

In this section, results of water absorption testing for virgin PVC and different PVC/sisal composite samples are described.

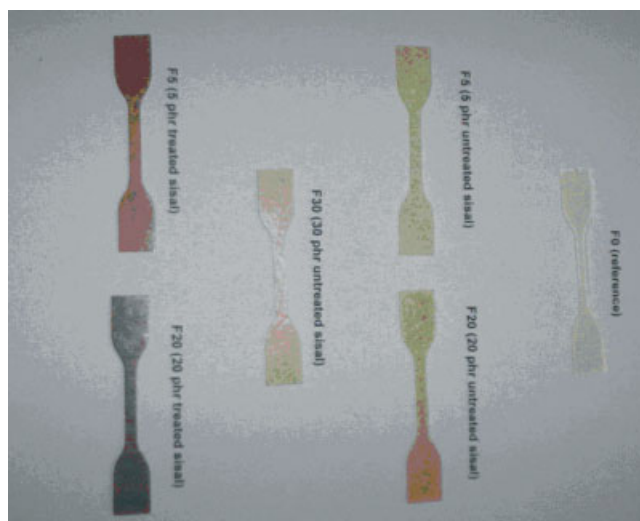


Figure 6 Photo of different PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To minimize the errors of experiments on such uneven surfaces, the presence of macrovoids on the surface, nondistribution of fibers in the composites samples, and balance error, we have used five specimens for each formulation.

The graph in Figure 7 illustrates the amount of water absorption in different samples of the PVC/fiber composites. We can clearly see an increase in the water absorption rate with the increase in fiber quantity. This result can be explained by the fact that the sisal fiber has a hollow central region, the lumen, which gives access to water penetration by capillary action.

Thermal stability

Figure 8 shows the evolution of the thermal stability of the PVC/sisal composites according to the quantity of sisal fiber. The shapes of the two curves, that of the PVC/untreated sisal composites and that of the PVC/MA-treated sisal are completely different. Indeed, the untreated one records a linear increase in thermal stability with the increase in the quantity of sisal. On the other hand, an abrupt reduction in thermal stability is recorded with the increase in the quantity of chemi-

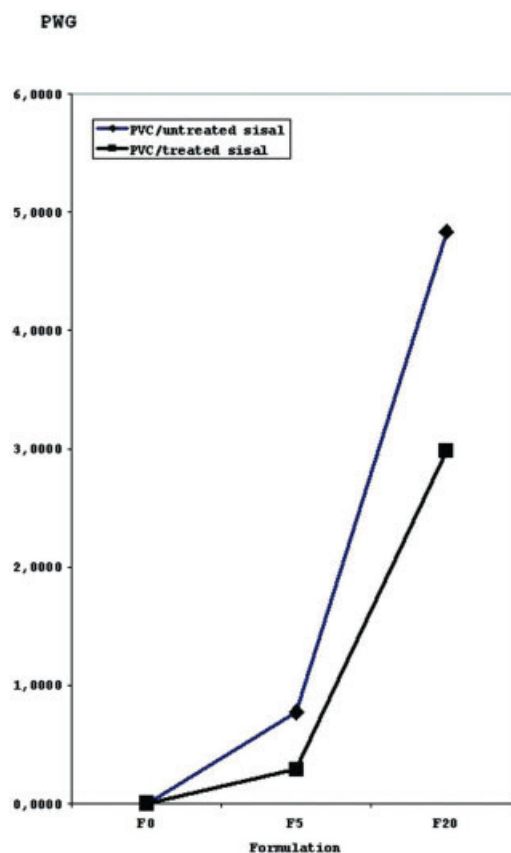


Figure 7 Effect of sisal fiber content before and after treatment on the amount of water absorption in PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal stability of PVC/sisal fibers composites

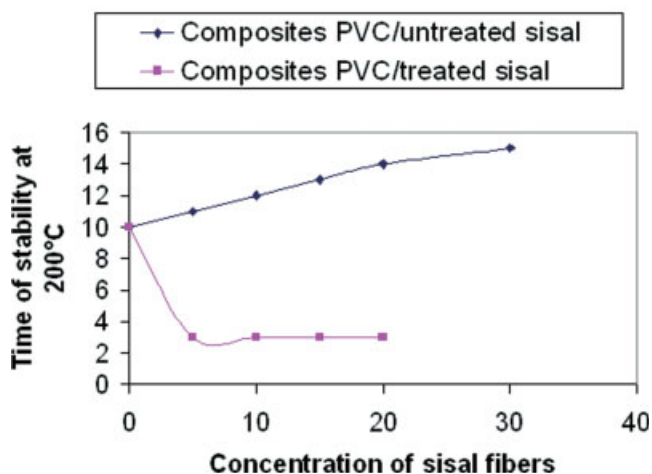


Figure 8 Effect of sisal fiber content before and after treatment on the thermal stability of PVC/sisal composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cally treated sisal. The thermal behavior of the PVC/untreated sisal composite was already confirmed by the results found by Zhang.¹⁷

The improved thermal stability of the PVC/untreated sisal composites with the augmentation of the concentration of sisal fibers can be explained by the poor dispersion of the fibers within the matrix. This poor dispersion causes the development of aggregations that form a protective surface layer preventing the material from liberating and diffusing HCl. Consequently, stability improves.

On the other hand, we attribute the diminution of thermal stability with the augmentation of the level of chemically treated sisal fibers to a greater dispersion of the fibers within the polymer matrix. This good dispersion permits better heat conduction by these fibers within the matrix, which in turn favors the formation and early liberation of HCl. This leads to the formation of double bounds. The latter translates into a reduction in thermal stability.

Effect of MA chemical treatment on sisal fibers

Concerning the effect of the MA chemical treatment of sisal fibers on elongation, strain at break, and Young's modulus, generally, the properties of the mixture depend mainly on the polymer/fiber interface. Indeed, bad interfacial adhesion favors incompatibility and consequently, the decrease in elongation and strain at break.

Chemical treatment with MA improves the interfacial adhesion by reducing the hydrophilic fiber and thus facilitates compatibility with the hydrophobic PVC.

The increase of strain at break is a sign of the improvement of the compatibility and the interfacial adhesion.

We can note that the chemical treatment of the sisal fiber with MA has improved impact strength properties by 16% for the F20 sample, which can be explained by the improvement of the compatibility between the treated sisal fiber and the PVC matrix.

As for the effect the MA-treated sisal on hardness, we can remark that the treatment reduced the hardness of samples, i.e., the hardness of F20/SNT = 50 and F20/ST = 47.

As for the PVC formulations with the treated sisal, they show an inferior water absorption amount compared to the untreated samples.

The reduction in water absorption with the chemical treatment is due to the fact that the treated fibers were subjected to a reaction of esterification, thus reducing the concentration of hydroxyls ($-OH$). As a result, the material became less hydrophilic.

CONCLUSIONS

The incorporation of untreated sisal fibers has affected the mechanical properties of the composites. The hydrophilic and polar characters of the fibers are the main causes of the incompatibility of PVC with sisal fibers.

In fact, this study has shown that the amount of water absorption increases remarkably as the sisal concentration in the composite is increased.

The solution implemented has been the chemical modification of the sisal fibers by MA treatment. This treatment permitted an improvement in the compatibility of the PVC/sisal composite mixtures, which translated into improvements in various functional properties:

- decrease in water absorption amount;
- better tensile properties;
- better impact properties;
- better hardness.

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References

1. Sombatsompop, N.; Chaochanchaikul, K. *Polym Int* 2004, 53, 1210.
2. Sombatsompop, N.; Chaochanchaikul, K.; Phromchirasuk, C.; Thongsang S. *Polym Int* 2003, 52, 1847.
3. Rodrigues, C. A.; Medina, J. A.; Reinecke, H. *J Appl Polym Sci* 2003, 90, 3466.
4. Acha, B. A.; Aranguren, M. I.; Marcovich, N. E.; Reboredo, M. M. *Polym Eng Sci* 2003, 43, 999.

5. Kalaprasad, G.; Francis, B.; Thomas, S.; Kumar, C. R.; Pavithran, C.; Groeninckx, G.; Thomas, S. *Polym Int* 2004, 53, 1624.
6. Ray, D.; Sarkar, B. K.; Rana, A. K. *J Appl Polym Sci* 2002, 85, 2588.
7. Fung, K. L.; Li, R. K. Y.; Tjong, S. C. *J Appl Polym Sci* 2002, 85, 169.
8. Nair, K. C. M.; Diwan, S. M.; Thomas, S. *J Appl Polym Sci* 1996, 60, 1483.
9. Singh, B.; Gupta, M.; Verma, A. *Polym Compos* 1996, 17, 910.
10. Cyrus, V. P.; Kenny, J. M.; Vazquez, A. *Polym Eng Sci* 2001, 41, 1521.
11. Mohanty, S.; Verma, S. K.; Nayak, S. K.; Tripathy, S. S. *J Appl Polym Sci* 2004, 94, 1336.
12. Oksman, K.; Wallstrom, L.; Berglund, L. A.; filho, R. D. T. *J Appl Polym Sci* 2002, 84, 2358.
13. Ichazo, M. N.; Albano, C.; Gonzalez, J. *Polym Int* 2000, 49, 1409.
14. Arzondo, L. M.; Pérez, C. J.; Carella, J. M. *Polym Eng Sci* 2005, 45, 613.
15. Gassan, J.; Bledzki, A. *J Appl Polym Sci* 1999, 71, 623.
16. Gilson, S. M.; Iozzi, M. A.; Martins, M. A.; Mattoso, L. H. C.; Ferreira, F. C. *Polimeros* 2004, 14, 326.
17. Zhang, B.-L. *J Rubber Res* 2001, 4, 2.
18. Qi, W.; Kadi, A. A.; Kaliaguine, S. *Polym Compos* 1992, 13, 414.
19. Murray, J.; Hull, D. *Polymer* 1969, 10, 451.
20. Hull, D. In *Polymeric Materials*; Baer, E., Ed.; ASM: Ohio, 1975; p 487.