

Melt Rheological Behavior of Intimately Mixed Short Sisal–Glass Hybrid Fiber-Reinforced Low-Density Polyethylene Composites. II. Chemical Modification

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ABSTRACT: The effect of chemical modification of both fiber and matrix on melt rheological behavior of intimately mixed short sisal–glass hybrid fiber-reinforced low-density polyethylene composites was studied with an Instron capillary rheometer. The variations of melt viscosity with different shear rate and shear stress values for different temperatures were studied. A temperature range of 130 to 150°C and shear rates of 16.4 to 5468 s⁻¹ were chosen for the analysis. Chemical modifications with stearic acid, maleic anhydride, silane, and peroxides were tested for their ability to improve the interaction between the matrix and fiber. The viscosity of the hybrid composites increases with every

chemical modification. In the case of peroxide-treated composites, the increase can be attributed to the peroxide-induced grafting of the polyethylene matrix to the fiber surface and to the crosslinking of the polyethylene matrix. These phenomena are both activated by temperature, whereas temperature causes a reverse effect for all other chemical modifications. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 443–450, 2003

Key words: modification; fibers; polyethylene (PE); composites; melt viscosity

INTRODUCTION

A strong interface between reinforcement and matrix is extremely important to develop polymer composites with improved physical and mechanical properties.^{1–3} The quality of the interface is controlled by the adhesion between fibers and matrices. The rational design of molding equipment requires knowledge of the flow behavior of the material to be molded at the processing conditions of temperature, pressure, and shear rate. Flow properties depend on fiber length, stiffness, and strength, volume fraction of fillers, and nature of fiber matrix adhesion. Chemical modification plays an important role in the enhancement in melt viscosity of fiber-filled polymeric composites. The enhancement is mainly attributed to the improvement in fiber matrix adhesion as a result of chemical modification. Recently, the effects of various chemical modifications on the melt flow behavior of natural fiber-filled polymer composites have been reported.^{4–7} The present study deals with the effect of chemical modifications, such as treatment with alkali, acetic anhydride, permanganate, maleic anhydride, dicumyl

peroxide, and benzoyl peroxide, on the flow behavior of sisal–glass–low-density polyethylene (LDPE) hybrid composites.

EXPERIMENTAL

Materials

Details of materials used (i.e., LDPE, sisal, and glass) are available in the Part I of this study.⁸

Silane A 174 [CH₂=C(CH₃)—COO(CH₂)₃Si(OCH₃)₃] was supplied by Union Carbide Company, Montreal, Canada. Dicumyl peroxide and benzoyl peroxide were obtained from BDH Chemicals, Poole, U.K. Other reagents, such as stearic acid, acetic acid, acetic anhydride sodium hydroxide, potassium permanganate, and maleic anhydride, were of reagent grade.

Fiber treatments

Sodium hydroxide treatment

The chopped sisal fibers were dipped in a solution of NaOH (5%) and the solution was stirred constantly for 0.5 h. Fibers were then taken out, repeatedly washed with distilled water, and then washed with slightly acidic water. Finally, the fiber samples were dried in an air oven at 50°C for 6 h.

Acetylation (using acetic anhydride)

Sisal fiber (~10 g) was kept soaked in glacial acetic acid for 1 h at room temperature, and then the acid

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was decanted. Next, the fiber was soaked for 10 min in acetic anhydride (50 mL) containing two drops of concentrated sulfuric acid. The fiber was separated with a Buckner funnel, washed with water, and then dried in an air oven at 50°C for 24 h.

Permanganate (KMnO₄) treatment

The alkali-treated sisal fibers were dipped in acetone solutions of KMnO₄ (0.06%) for 2 min. Fibers were then separated and dried in an air oven under the same conditions as already mentioned.

Stearic acid treatment

A solution of stearic acid in ethyl alcohol (4% by weight of the fiber) was added in a dropwise manner into the sisal fibers with continuous stirring. The fibers were then dried in an air oven at 95°C for 1 h.

Silane treatment

Treatment of sisal fiber Ten grams of oven-dried and alkali-treated sisal fiber was mixed with silane (5% by weight of fiber), carbon tetrachloride, and dicumyl peroxide (2.5% by weight of the fiber). The mixture was heated under reflux with continuous stirring using a magnetic stirrer for 2 h. The fiber was filtered and dried in an air oven for 2 h.

Treatment of glass fiber A solution of silane coupling agent was prepared in 0.1 M acetic acid (silane concentration, 0.5 weight %). The chopped glass fibers were dipped into this solution and then dried at 100°C for 20 min. The fibers were subsequently rinsed with a sufficient quantity of methanol to remove physisorbed silane from the glass surface. The fibers were then dried in an air oven at 50°C for 2 h.

Peroxide treatment

Benzoyl peroxide (BPO; 0.8% by weight of polymer) and dicumyl peroxide (DCP; 1% by weight of polymer) treatments were accomplished by a solution mixing technique with toluene as the solvent. Respective peroxides were added to a molten mass of the PE at the time of mixing with fibers.

Maleic anhydride-modified polyethylene (MAPE) treatment

Preparation of MAPE

MAPE was prepared by melt mixing LDPE (100 g) with maleic anhydride (5 g) and benzoyl peroxide (0.3 g). The melt mixing was carried out in a Brabender Plasticorder at 125°C and 60 rpm. MAPE (8% by

weight of LDPE) was added to the melt of LDPE during its solution mixing with fibers.

Preparation of composite samples

Intimately mixed sisal-glass LDPE blends were prepared by a solution mixing technique in which the fibers (both treated and untreated) were mixed with a slurry of LDPE in toluene with the help of a mechanical agitator at 125°. To avoid agglomeration of fibers during mixing, glass fibers were added first to the slurry followed by sisal fibers. The solvent from the resultant mix was then removed by evaporation under vacuum. The dry mix was then extruded through a ram-type hand extruder at 125 ± 3°C. The extrudates with a diameter of 4 mm were collected and cut into small pieces for the rheological study. The terms SRP, GRP, and SGRP used in this study correspond to sisal-reinforced polyethylene, glass-reinforced polyethylene, and intimately mixed glass-sisal-reinforced polyethylene composites, respectively. All composites analyzed in this study contained the same volume percentage (i.e., 20%) of fiber.

Infrared (IR) spectroscopy analysis

A Shimadzu IR-490 spectrophotometer was used to analyze the changes in the chemical structure of fibers with various types of treatments. Powdered fiber that was pelletized with potassium bromide was used for recording the IR spectra.

RESULTS AND DISCUSSION

Effect of chemical modifications

To improve the fiber-matrix interaction, sisal, glass, and LDPE were subjected to several chemical modifications. The effect of chemical modifications on the melt viscosity of SGRP as a function of shear rate with 50/50 compositions of sisal and glass fibers at a temperature of 130°C is shown in Figure 1. Studies on hybrid as well as nonhybrid composite materials have shown that the interfacial bonding between the reinforcing fiber and matrix has a significant effect on the properties of the hybrid composite. Good interfacial bonding can be achieved by modifying the fiber-matrix interface with various surface modifiers or coupling agents.⁹⁻¹³

As seen in Figure 1, the melt viscosity of SGRP composites increased as a result of chemical modification. These results indicate that the viscosity difference between untreated⁸ and treated SGRP composites is marginal, especially at high shear rate. The improved interface adhesion due to different coupling agents is explained as follows. In the case of maleic anhydride modification, the interfacial adhesion between fiber

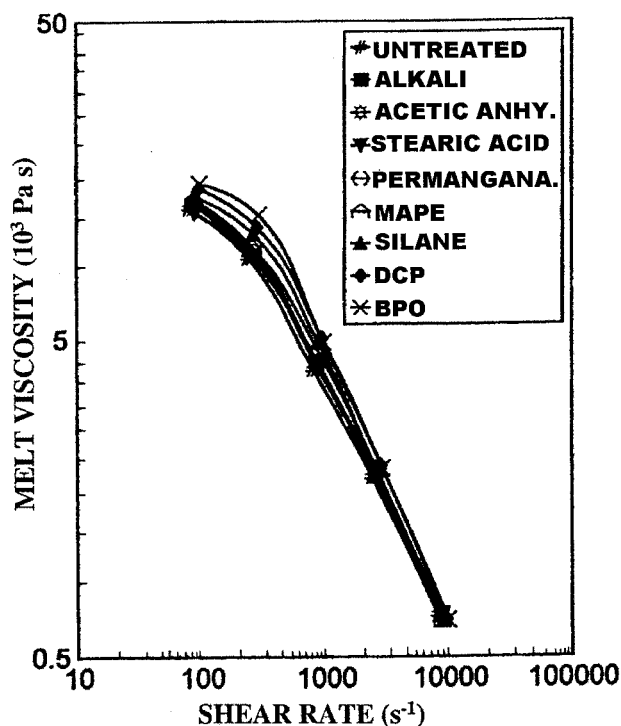


Figure 1 Variation of melt viscosity (η) with shear rate ($\dot{\gamma}$) of untreated and treated SGRP composites (50/50) at 130°C.

and LDPE can be explained on the basis of the schematic model shown in the Figure 2. MAPE is obtained by the grafting of maleic anhydride onto LDPE in the presence of benzoyl peroxide. The mechanism of the reaction is shown in Scheme 1. The resulting anhydride groups of MAPE provide links to cellulose by the formation of hydrogen bonds through their —OH groups. Similar hydrogen bonding may also occur with the —OH group present on the glass fiber surface. As a result of this bonding, a strong interaction is induced, especially at the sisal-LDPE interface. This strong interaction results in an increase in viscosity of MAPE-modified SGRP composites. The IR spectra of unmodified LDPE and MAPE are shown in Figures 3a and 3b, respectively. The spectra were recorded only after removing the unreacted maleic anhydride with acetone. A strong peak at 1640 cm^{-1} in the MAPE

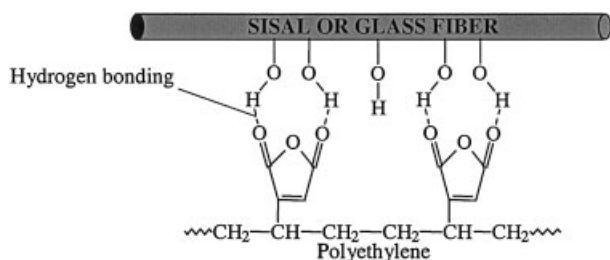
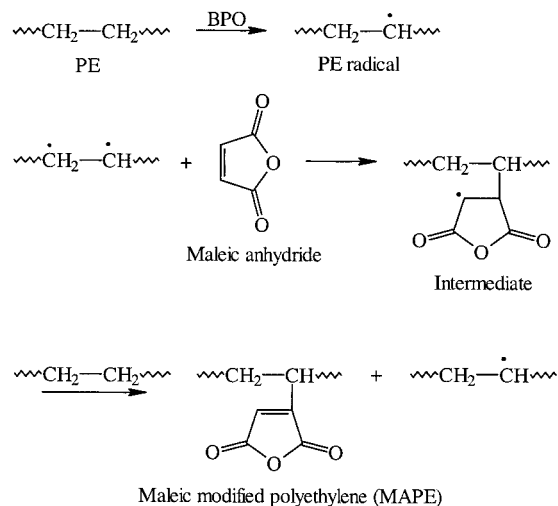


Figure 2 Hypothetical chemical structure of PE-maleic anhydride-sisal (cellulose) or PE-maleic anhydride-glass interface.



Scheme 1 Reaction mechanism of maleic anhydride modification of PE.

spectrum indicates the stretching frequency of the carbonyl groups of the anhydride part that are present in the polymer.

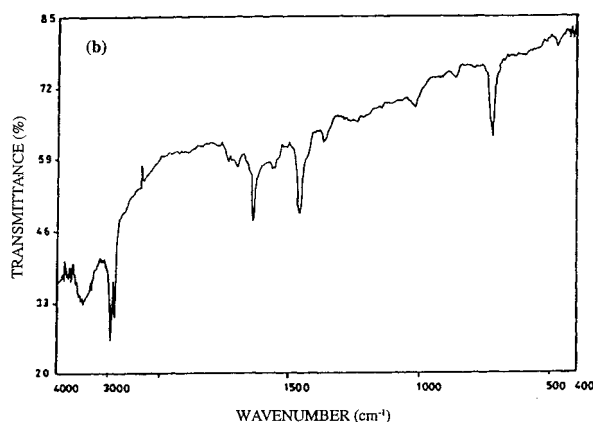
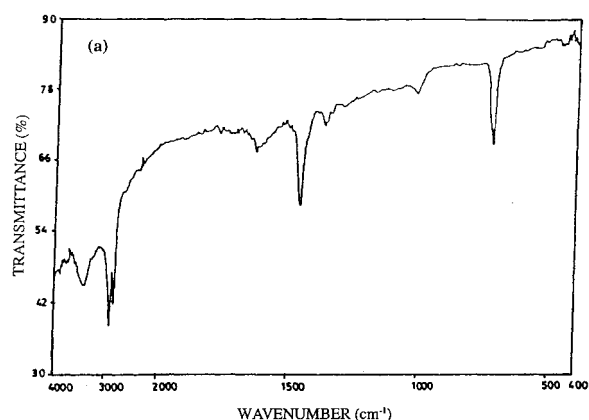
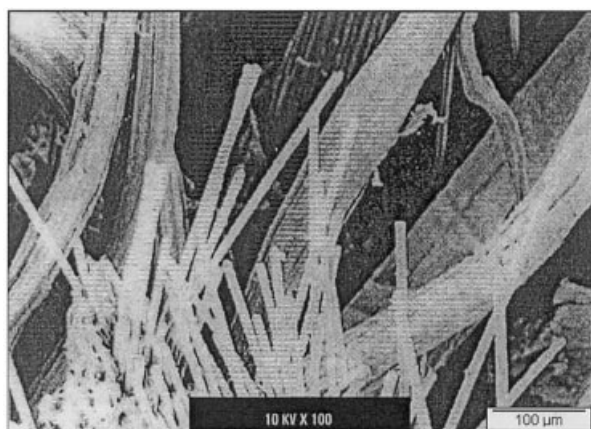
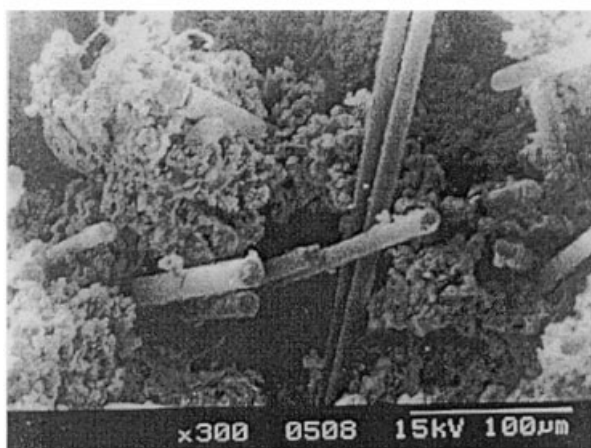


Figure 3

Figure 3 Infrared spectra of (a) unmodified PE and (b) MAPE.



(a)

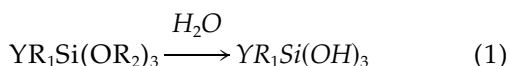


(b)

Figure 4 Scanning electron micrographs of tensile fracture surfaces of (a) untreated SGRP composite and (b) maleic anhydride-modified SGRP (50/50, sisal-glass) composite.

The tensile fracture surfaces of untreated and MAPE-treated hybrid composites, shown in Figures 4a and 4b, respectively, indicate the presence of a strong fiber-matrix interaction. Comparison of Figures 4a (untreated) and 4b (MAPE-modified SGRP) indicates that PE traces stick to the surface of sisal and glass fibers and, therefore, there is a strong adhesion between MAPE and the sisal and glass fibers.

The increase in viscosity of silane-treated hybrid composites is due to the enhanced interaction of sisal and glass fibers with the LDPE matrix. The general formula for silane coupling agents is $YR_1Si(OR_2)_3$, where Y is the polymerizable vinyl group of silane and OR_2 is a hydrolyzable group. During silane treatment, the OR_2 group of the silane may hydrolyze to some extent to form silanols:



The resulting $-OH$ groups of silanol or $-OR_2$ groups of unhydrolyzed silane interact with cellulose through their $-OH$ groups by the formation of hydrogen bonds. The DCP, which is used as the initiator in this treatment, facilitates the polymerization of the vinyl groups of silane. This hydrophobic polymer chain of polymerized silane (connecting individual silane molecules that are supposed to attach to cellulose fiber) can adhere to PE because of van der Waals-type adhesive forces. As a result, a strong interaction is induced at the fiber-matrix interface and, therefore, the friction between the polymer and sisal fiber is increased.¹⁴ To some extent, this strong interaction contributes to the increase in viscosity of silane-treated SGRP composites. A hypothetical model of the silane-treated interface between sisal fiber and PE is shown in Figure 5.

IR spectra of untreated and silane-treated sisal fiber are shown in Figures 6a and 6b, respectively. The intensity of the $-OH$ peak is reduced after silane treatment, which indicates a reaction between the cellulosic $-OH$ groups and silane. The peak at 1720 cm^{-1} in the spectrum of silane-treated sisal indicates the carbonyl stretching frequency of the ester group in silane. The spectrum of silane-treated sisal has a peak at 820 cm^{-1} , which confirms the presence of a $Si-O$ bond. The broad peak at 3400 cm^{-1} represents $O-H$ stretching vibrations of the $Si-OH$ group and the cellulosic $-OH$ group.

The molecular water already present in the glass fiber surface hydrolyzes silane to silanols. These silanols form hydrogen bonds with the $-OH$ groups formed on the glass fiber surface. Water is removed when the treated glass fiber surface is dried, and a reversible reaction may occur between the silanol and the fiber surface. The result of this expected condensation reaction is the formation of a polysiloxane layer on the glass fiber surface. The other end of the silane is physisorbed onto PE by van der Waals-type of interactions. Such interactions increase the viscosity of silane-treated hybrid composites. The mechanism of this reaction is depicted in Figure 7.

The fracture surface of silane-treated SGRP is shown in Figure 8. Both sisal and glass fiber pullout is less at

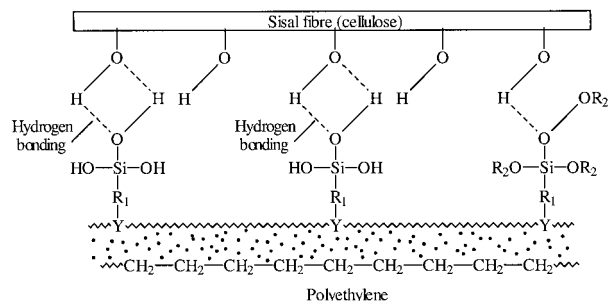


Figure 5 Hypothetical chemical structure of sisal(cellulose)-silane-PE interface.

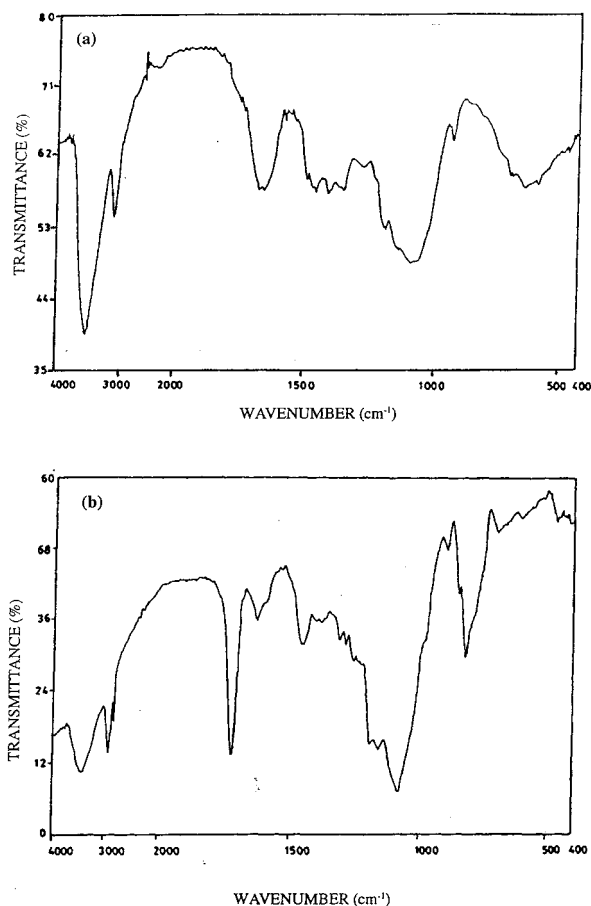


Figure 6 IR spectra of (a) untreated and (b) silane-treated sisal fiber.

the fracture surface, which confirms the presence of strong adhesion between the sisal and glass fibers and the PE matrix. The micrograph in Figure 8 also reveals that silane treatment is more or less equally effective in improving the adhesion of both fibers to the PE matrix.

The peroxide-treated composites also show higher viscosity than untreated composites because of the grafting of PE onto sisal fibers in the presence of peroxides. Grafting takes place through the free radical combination of PE and fibers. The expected mechanism of the peroxide-induced grafting is shown in eqs. 2–6:

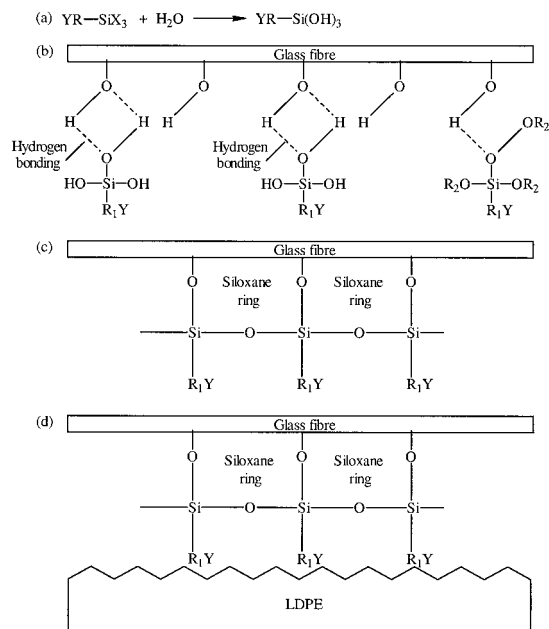
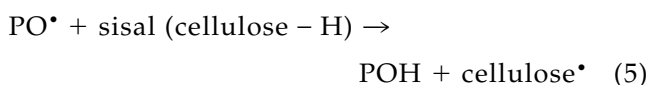
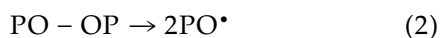
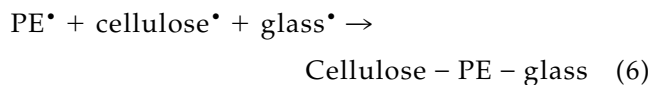


Figure 7 The reaction mechanism of silane treatment of glass fiber: (a) hydrolysis of silane; (b) hydrogen bonding between hydrolyzed silane and hydroxyl group on the glass surface; (c) formation of polysiloxane ring on the surface of glass fiber; (d) hypothetical chemical structure of glass-silane-PE interface.



Other reactions possible during the processing of the composites are (i) an increase of molecular weight and (ii) crosslinking of PE matrix by the combination of PE radicals:

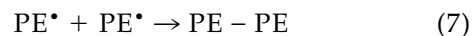


Figure 8 Scanning electron micrographs of tensile fracture surfaces of silane-treated SGRP (50/50, sisal-glass) composite.



Figure 9 Scanning electron micrographs of tensile fracture surfaces of DCP-treated SGRP (50/50, sisal-glass) composite.

All of these reactions result in an increase in viscosity.

The scanning electron micrographs of the tensile failure surfaces of DCP- and BPO-treated hybrid composites are shown in Figures 9 and 10, respectively. The micrographs clearly show that there is better adhesion between fiber and matrix in the cases of treated composites.

The treatments with alkali, acetic anhydride, stearic acid, permanganate, etc. were applied only in the case of sisal fiber. The increase in viscosity of NaOH-treated composite is attributed to the increased mechanical interlocking between sisal fibers and PE matrix. Alkali treatment makes the sisal fiber surface rougher by removing the waxy material present on the fiber surface. The rough surface produced on the sisal fiber leads to better mechanical anchoring with the PE matrix.

In the case of acetylated composites, the enhancement in viscosity is due to the better compatibility between the less hydrophilic acetylated sisal fiber and

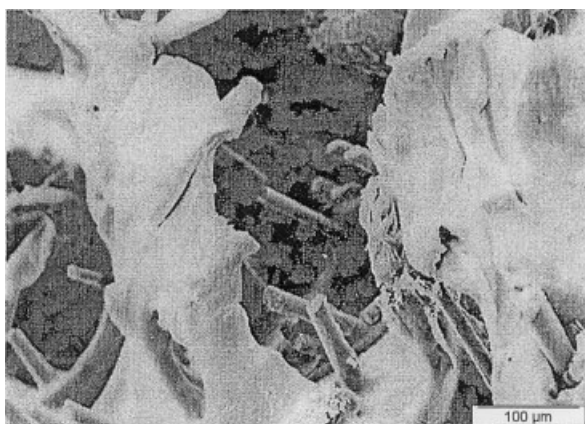


Figure 10 Scanning electron micrographs of tensile fracture surface of BPO-treated SGRP (50/50, sisal-glass) composite.

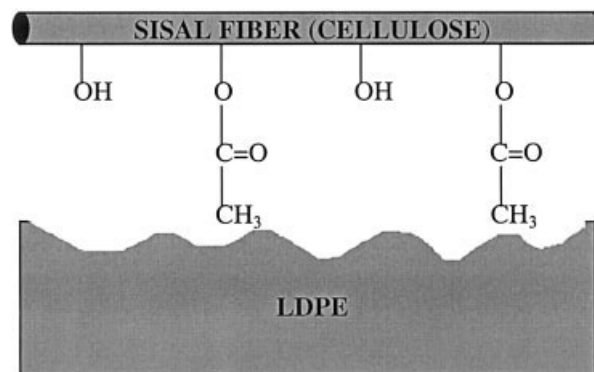
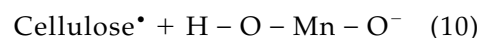
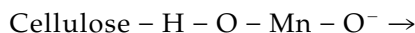
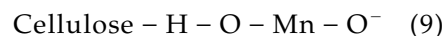


Figure 11 Hypothetical chemical structure of acetylated sisal in the sisal-PE interface of SGRP composites.

hydrophobic PE matrix. A hypothetical model of the interface between analytical sisal fiber and PE matrix is shown in Figure 11.

The increase in viscosity of the hybrid composite after stearic acid treatment is marginal compared with that of other treatments. Even though stearic acid reduces the hydrophilicity of sisal fiber, it plasticizes the entire system. This plasticization effect of stearic acid may be the reason for the reduction in viscosity.

The enhancement in viscosity of the permanganate-treated composite is explained in terms of permanganate-induced grafting of PE onto sisal fibers. The highly reactive MnO_4^- ion is responsible for initiating the graft reaction. The mechanism of the reaction is as follows:



Effect of temperature

The effect of temperature on the hybrid composites (50/50) containing treated fiber was analyzed. Like untreated composites,⁸ the melt viscosity of treated composites decreases with increase in temperature, except in the case of BPO- and DCP-treated composites (the viscosities of the latter increase with increasing temperature). The increase in viscosity of the peroxide-treated hybrid composites, especially at 140°C, is mainly due to the peroxide-induced crosslinking of PE chains in the melt. However, at 150°C, a slight gradation in viscosity is observed for DCP- and BPO-

treated composites. This result may be due to the lower degree of crosslinking reactions at high temperature in presence of peroxide.

Extrudate characteristics

An ordinary photograph of the extrudate from untreated and treated SGRP hybrid composites (50/50) at a single shear rate are depicted in Figure 12. This photograph confirms that the extrudate diameter is more uniform in treated composites than in untreated composites. This uniformity is due to the better compatibility of fibers and matrix in treated composites.

Flow behavior index (n')

The flow behavior indexes of treated SGRP composites (50/50) are shown in Table I. The n' values for all

TABLE I
Flow Behavior Index of Treated SGRP (50/50) Composites

System	Flow behavior index (n')		
	130°C	140°C	150°C
Untreated	0.357	0.346	0.331
Alkali	0.311	0.291	0.282
Acetic anhydride	0.314	0.304	0.298
Stearic acid	0.294	0.294	0.281
Permanganate	0.299	0.295	0.285
MAPE	0.297	0.295	0.282
Silane	0.293	0.290	0.271
DCP	0.253	0.266	0.272
BPO	0.244	0.249	0.249

the treated composites are <1 , which is characteristic of the pseudoplastic nature of the composites. The degree of pseudoplasticity of all the composites increases with temperature. However, contrary to all other composites, BPO- and DCP-treated composites exhibit a slight increase in n' values with temperature. Also, the pseudoplasticity of all the treated composites is higher than that of untreated composites. The enhancement in pseudoplasticity is associated with the better orientation of the treated fiber with the LDPE molecules.

CONCLUSIONS

The melt rheological behavior of intimately mixed short sisal-glass hybrid fiber-reinforced LDPE composites was studied as a function of chemical modifications, shear stress, shear rate, and temperature. Chemical modifications increased the viscosity of the hybrid composites because of the increased fiber-matrix interaction. The melt flow studies, conducted in the temperature range 130–150°C, indicated that the viscosity of the composite melt decreased with increase of temperature. However, DCP- and BPO-treated composites showed an opposite trend because of the peroxide-induced grafting of the LDPE matrix to the fiber surface and because of the crosslinking of the LDPE matrix itself at high temperature.

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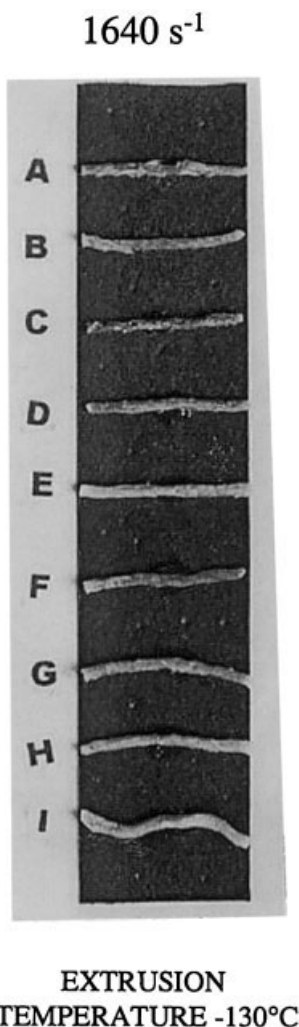


Figure 12 Ordinary photograph of the SGRP (50/50 sisal-glass) extrudate at a single shear rate (1640 s^{-1}): (A) untreated, and treated with (B)alkali, (C) acetic anhydride, (D) stearic acid, (E) permanganate, (F) maleic anhydride, (G) silane, (H) DCP, and (I) BPO.

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