PLASMA MODIFICATION OF SISAL AND HIGH-DENSITY POLYETHYLENE COMPOSITES: EFFECT ON MECHANICAL PROPERTIES

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Abstract

Sisal fibers and finely powdered high-density polyethylene were surface functionalized using dichlorosilane (DS) under R-F plasma conditions to improve interfacial adhesion between the two dissimilar substrates. The functionalized polyethylene (70%) and sisal (30%) were compounded on four different ways using thermokinetic mixer and injected molded into composites specimens for test. Some improvements in mechanical properties of the composites due to the plasma treatments were achieved. Scanning Electronic Microscopy (SEM) data indicated that some compatibilization of the two plasma modified phases had taken place as compared to non-plasma treated composite.

Key words: Sisal, polyethylene, surface functionalization, cold plasma, composite.

Introduction

There is an increasing demand for natural polymer/thermoplastic-bmmed composites for applications in a variety of industries, from packing and automotive to aviation and construction. The development of advanced composites from predominantly renewable fibrous natural materials will meet the requirements of nature technologies by the generation of environmentally safe products such as biodegradable material. However, composites from these dissimilar materials exhibit poor interfacial adhesion which significantly affects the mechanical properties of the resulting end-products (1-3).

High performance light-weight thermoplastics like polyethylene and polypropylene are nonpolar and chemically inert; these properties have resulted in conventional research efforts to functionalize the polymers to make them compatible with their natural counterparts. These approaches are often costly and environmentally unfriendly (1).

Cold-plasma technique is a very promising approach for the surface-functionalization of polymeric materials. It has been demonstrated that efficient surface-modification reactions can be carried out even on inert substrate surfaces, such as polyethylene and polypropylene (4-12). However, natural fibers- and polyolefins-based materials require the presence of thermoplastics in the molten state during composite preparations. This, obviously will assure a very good contact between the fiber surface and the matrix, and will allow the development of the desired chemical and physical interactions in the interface zone. Accordingly, cold-plasma enhanced functionalization reactions will only be adequate for the modification of the polyolefin components if the surface area of the substrate is very large relative to its volume (e.g. extremely fine powder). In this case, even in the molten state of the thermoplastic a considerable amount of the functionalized macromolecules will remain on the surface, which is crucial for the development of interaction between the fibers and the matrix.
Materials and Methods

High density polyethylene (PE) powder, type IE-59 U3, having a melt-index of 5.0 g/10 min (ASTM-1238) and density of 0.959 g/cm³ (ASTM-D792) and the sisal (S) fibers were supplied by Politeno and Incomar-Brazilian Industry Company. Dichlorosilane (DS) were purchased from Aldrich and Gelest Co.

All plasma treatments were carried out in an originally designed rotating, 13.56 MHz-RF-plasma installation capable of uniform surface-treating of powdery and fiber-type substrates.

In composite preparation the fibers were run through a Ball & Jewell granulator (Sterling, Inc., Milwaukee, WI) provided with a 9.5mm screen to reduce the fibers to approximately 6-7mm length. The fibers and PE (30% sisal and 70% PE by weight) were compounded in a one-liter thermokinetic mixer (K-Mixer, Synergistics Ltd., Canada), a high intensity kinetic mixer, where the only source of heat is generated through the kinetic energy of rotating blades.

The mixture was done at 5700 rpm. which resulted in a tip speed of about 37.2 m/s. The compound mass was then automatically discharged at 190°C. A total weight of 150g was used - for each composition. The total residence time of the blending averaged about 55 seconds. The discharged mass was then cooled by pressing in a cold press and then granulated and dried at 105°C by overnight.

The granules were injection molded into ASTM standard specimens using a Frohring mini-jector molding machine, model SP50, at 140°C. Samples were placed in a controlled humidity room for three days prior to testing to assure complete thermal stability of the test samples.

The evaluation of mechanical properties was performed under test conditions according to the following ASTM standards: tensile testing (ASTM D638), flexural testing (ASTM D790) and impact testing (ASTM D256).

Plasma modification of surface morphologies of PE substrates and composites have been carried out using Scanning Electron Microscopy (SEM). Images were produced using a LEO 982 Field Emission, Digital Scanning Microscope.

Results and Discussion

Figure 1 shows the tensile strength of the PE/sisal (70%/30% based composites prepared from UN-modified sisal/PE - UN/UN, DS-plasma-treated PE/ DS-plasma treated sisal - T/T, DS-plasma-treated PE/sisal - T/UN and DS-plasma-treated sisal/PE - UN/T, plasma-treated 100% PE and untreated 100% PE. It can be observed that the tensile strength properties of composites prepared from T/T and T/UN PE/sisal record the highest tensile strength values, while composites resulting from UN/T PE/sisal exhibit tensile strength values comparable to those resulting from UN/UN PE/sisal. This might be explained by polar nature of the sisal fibers (DS-plasma exposure of sisal will result in the formation of -0-Si-OH functionalities on the natural polymeric substrate surfaces whose reactivity is comparable to the reactivity of inherent -C-OH functionalities) and also by the development of possible DS-plasma-induced destruction and cross-linking reaction mechanisms on sisal fiber surfaces, which obviously will result in the partial loss of C-OH functionalities (13).

Figure 2 shows the tensile modulus of all PE/sisal-based composites UN/UN, T/T, T/UN and UN/T indicate a significant property improvement versus 100 % PE. The highest tensile, modulus values (> 400%) have also been recorded for the samples resulting from T/T and TNN PWsisal. However, it should be noted that even the composites UN/UN PE/sisal record a significant increase of the tensile modulus in comparison to untreated and plasma-treated 100% PE. The influence of coupling on the tensile modulus is not yet fully understood. It has been demonstrated that some fiber systems, for instance, will show a decrease in tensile modulus, even with a coupled system (14).
Figures 3 and 4 show that all composites involving plasma-treated substrates have higher flexural strength and modulus values in comparison to specimens resulting from UN/UN PE/sisal, plasma-treated 100% PE, and 100% PE. The highest flexural modulus values are associated with T/T and UN/T PE/sisal in comparison to the composites UN/UN PE/sisal. It is noteworthy that all composites which involve DS-plasma-exposed substrates have flexural strength and modulus values lower in comparison to the values resulting from composites UN/UN PE/sisal (Figure 4). It also can be noted that the composite UN/T PE/sisal have the closest flexural strength and flexural modulus values to the composites UN/UN PE/sisal. This clearly indicate that during the composite preparation, most of the plasma-functionalized surface layers of PE have been incorporated (buried) into the bulk of the PE matrix, avoiding on this way the development of molecular interaction between the functionalized PE molecules and sisal fibers.

This is a very significant finding because it indicates that special mixing techniques should be developed for composite preparations, which involve lignicellulosic fibers and surface-functionalized thermoplastic substrates. It also should be concluded that higher the
thermoplastic component specific surface area (surface/volume ratio) better are the chances to generate more intense molecular interaction between the substrates.

Figure 5 exhibits the notched and un-notched, Izod impact properties of PE/sisal composites. It can be observed that plasma-treatment of sisal reduces in both notched and un-notched cases the impact toughness of the composites. The highest impact toughness values are associates with the composites T/UN and UN/UN PE/sisal. This data also substantiate the earlier conclusion that plasma-exposure of sisal fibers might induce significant surface-decomposition and surface-crosslinking reaction mechanisms which obviously will limit the molecular interaction on the PE/sisal interfaces.

![Graph showing impact properties of PE/sisal composites](image)

**Fig. 5.** Notched and un-noched, Izod impact properties of PE/sisal (70/30%) composites.

The following compatibilization mechanism can be suggested for the PE/sisal interfaces:

![Chemical structures showing compatibilization mechanisms](image)

Figures 6 and 7 exhibit SEM images of composites UN/UN and T/T PE/sisal, respectively. In composite UN/UN PE/sisal can be observed that the sisal fibers pulled out from the PE, as a result of mechanical failure, have smooth surface topographies and that the fibers
have been dislocated from the PE matrix. This indicates that the interaction on interface level between the two components were minimal during the composite preparation process. Composite T/T PE/sisal indicate that the sisal fibers have been coated with PE, and even after the mechanical failure of the test-specimens the presence of PE layers are clearly apparent on the fiber surfaces. It also can be observed that fibrous matrix-connections are present between the sisal and PE substrate surfaces.

It can be concluded, that only the surface functionalization of PE granules plays a crucial role in the development of significant interactions between the sisal and PE surfaces. This might be explained by the inert nature of PE and the sensitivity of cellulose-type structures to DS-plasma environments.

Figs. 6 and 7. SEM images of UN/UN and T/T based composites.

Conclusions

DS-RF-plasma conditions are proper for the surface functionalization of PE substrate. Sisal fibers exposed to DS-plasma result in the formation of C-O-SiH,Cl, groups on the fiber surfaces. These reaction mechanisms are accompanied by decomposition processes of the cellulosic structure of the surface layers of the plasma-exposed fibers. This degradation mechanism is also reflected in the poor mechanical properties of plasma-modified PE- and plasma-modified sisal-based composites. Accordingly, it is suggested that for composite preparations only the thermoplastic substrate should be plasma-functionalized.

The modest mechanical properties achieved even in the cases of composites T/UN PE/sisal clearly suggest that the conventional mixing and composite-preparation techniques are not adequate for thermoplastic substrates which were only functionalized on their surfaces.

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