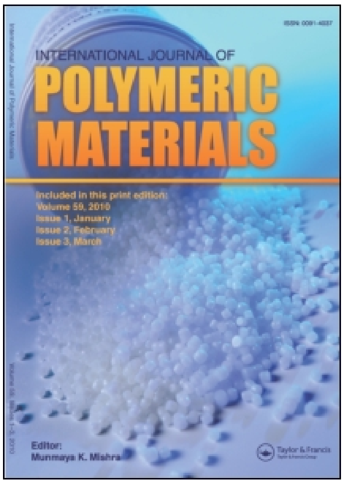

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Thermal, Thermomechanical, and Morphological Properties of *Spartium junceum* Fiber Reinforced Polypropylene Composites

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The composites investigated in this article were polypropylene reinforced with Spanish broom (Spartium junceum) *fibers. These fibers were modified with N[-3 Trimethoxysilyl propyl] ethylene diamine (Z6020) or stearic acid, which work as coupling agents between fibers and matrix. This work studied the thermal (differential scanning calorimetry) and thermomechanical (dynamic mechanical thermal) analysis. The surfaces of the composites were characterized by electron microscopy. It was found that silane-treated fiber composites show superior properties compared with the specimens made of pure polypropylene. Microscopic observations correlate with these results.*

Keywords: composites, dynamic mechanical thermal properties, natural fibers, surface treatment, thermal analysis

INTRODUCTION

Replacing glass fibers with various types of cellulose fibers is a very attractive way to produce green composites [1]. Polymeric matrix filled with vegetable reinforcements offer a high specific stiffness and

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strength, flexibility during processing with no harm to the equipment, low cost, low density, and ability to chemical modification [2–3]. Nevertheless, these promising fibers possess also some negative characteristics: they are highly hydrophilic and they can vary a lot in properties, which makes accurate predictions of the respective composite properties difficult.

The natural fibers have a complex structure consisting of cellulose, hemicellulose, pectin, lignin, and others, and thus they are not to be considered in the same, straightforward way as monofilament fibers [4–5].

The fibers and matrix must interact in the composite to produce an effective load-bearing system. This cooperation between the fibers and the matrix will not exist without an interface, which acts as a load transfer layer between them. Further, because each fiber forms an individual interface with the matrix, the interfacial area is very large. Interfacial bonding gives good wetting of the fibers by the matrix as well as the formation of a chemical bond between the fiber and the matrix [6].

The aim of this study is to investigate the thermal behavior and dynamic mechanical properties of polypropylene (PP)/broom fibers composites, by means of differential scanning calorimetry (DSC) and dynamic mechanical thermal (DMTA) instrumented testing. Effects of silane and stearic acid used as coupling agents are also considered. In order to explore the effect of treatment of the PP/broom fibers composites, morphological examination of fractured surfaces is performed by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The polymer matrix used in this study is polypropylene (PP) "B-UP 123" (Eton Mobil Chemical), having a density of 905 kg/m^3 and a melt flow index (MFI) of 8.7 g/10 min at 230°C. Polypropylene was selected as the matrix because it is of the major commodity plastics, which may be processed below the decomposition temperature of cellulosic fiber (about 220°C).

Broom fiber was prepared in the laboratory. The broom fiber *Spartium junceum* was obtained from local sources; the shruo can be cultivated in Algeria. The fiber was cleaned and chopped into the desired length ranging from 2 to 4 mm.

As pretreatment, the fibers were dewaxed in toluene–ethanol solution (2:1) for 24 h with stirring to remove the woving size (potato starch and waxes) flowed by washing the fibers in distilled water. After filtration, the fibers were dried at 105°C for 15 h.

Treatment with Silane and Stearic Acid

N [-3 Trimethoxysilyl propyl] ethylene diamine and stearic acid were separately dissolved in toluene. The broom fiber was immersed in the solution and kept there for 15 h with stirring at ambiant temperature. The broom fiber was filtered and then kept in oven at 105°C for 15 h. The quantity of silane or stearic acid used was calculated as 1.5 wt% of the broom fibers.

Processing

The composite materials were prepared by mixing the polymer matrix and the broom fibers at 180°C in a two roll mixer. Different PP/broom fiber composites were prepared; the broom fiber amounts employed were 10, 20, 30, 40, and 50 wt%.

Pressed sheets of the composites were obtained by compression molding at 190°C under a pressure of 250 kg/cm^2, followed by air cooling. Rectangular specimens were cut from the sheets to size ($20 \times 8 \times 1$ mm).

Thermal and Thermomechanical Analysis

A differential scanning calorimeter (DSC 2920 Modulated, TA instrument) was used. Samples (10–20 mg) were cut from a dumbell specimen and then placed in aluminium pans. The heating rate was 10°C per minute. A nitrogen flow (50 ml/min) was maintained throughout the test. Thermograms were calibrated by using indium at a heating rate at which samples were analyzed. The melting point, T_m, was determined from the maximum of the melting peak.

The dynamic mechanical properties of the composites were determined using a dynamic mechanical thermal analyzer (Polymer Laboratories DMTA MK III), at fixed frequencies of 0.1, 1, and 10 Hz and a heating rate of 1°C/min, from -50 to 170°C. The dynamic storage modulus (E′), loss modulus (E″) and loss factor (tan δ) of the specimen were measured as a function of temperature.

Microscopy Observations

Fractured surfaces of composite specimens were studied by using LEICA STEREOSCA 440 scanning electron microscope (SEM), to investigate the morphology and interface between the fiber and matrix in the composites.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

Thermal Characteristics of the PP Composites

Figure 1 shows the thermograms of PP/Broom Fiber composites; it was noticed that the melting temperature obtained is 168°C. The incorporation of untreated broom fiber in the polymeric matrix has no significant impact on this value nor on the shape of the melting peak. The decomposition temperature of the fiber is about 220°C, not very far from that of the matrix. These results are in agreement with those presented by Amash and Zugenmaier [7], Avérous et al. [8], and Le Digabel et al. [9].

Effect of Different Treatments

The comparison between the thermograms obtained from virgin PP and the composites filled with 30 wt% of broom fiber untreated and treated with silane and stearic acid at 1.5 wt%, is presented in Figure 2. It was observed that the treatment had no significant effect on the melting temperature.

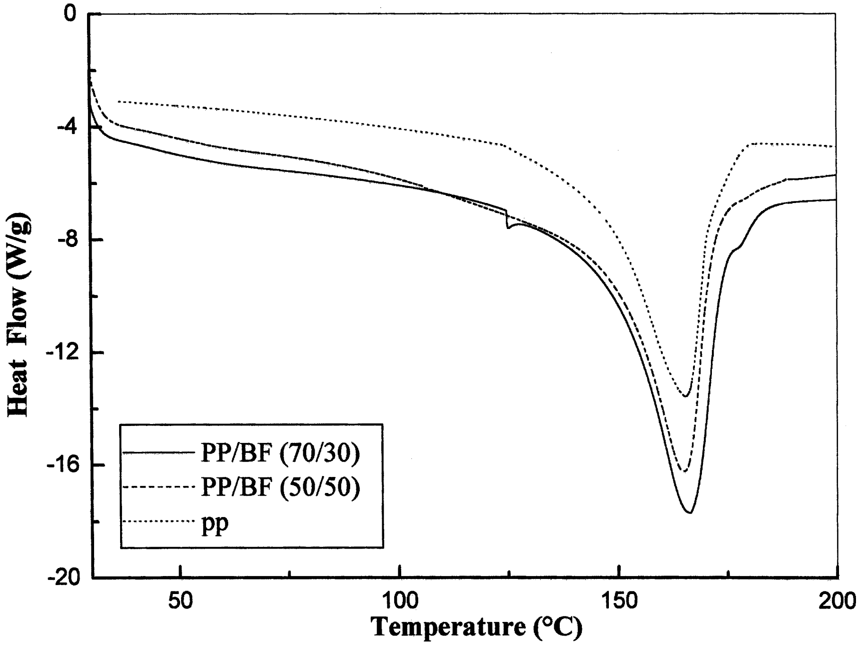

FIGURE 1 DSC thermograms of different PP samples filled with untreated broom fiber.

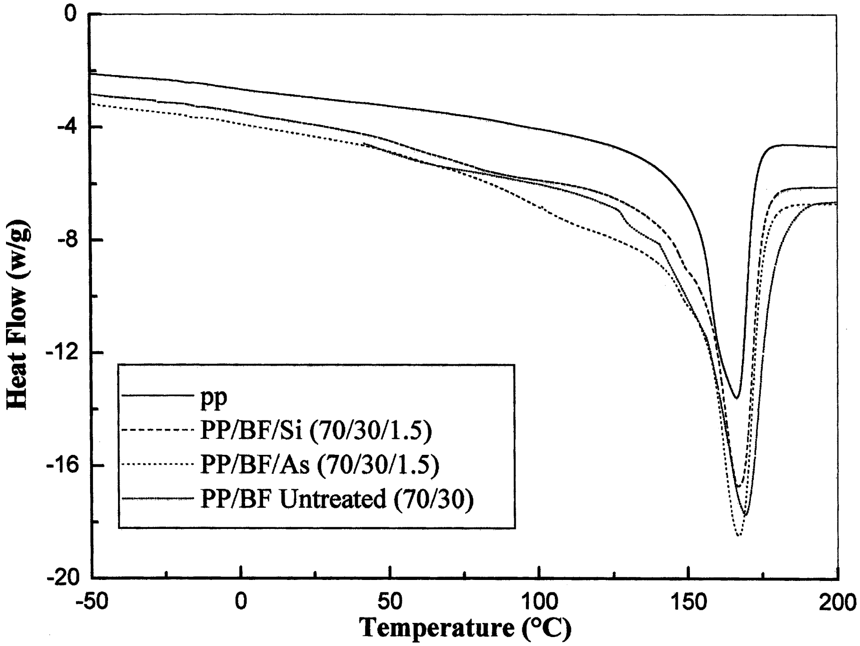

FIGURE 2 DSC thermograms of PP and composites at 30 wt% broom fiber with different treatments.

Effect of Different Scans

A comparison of Tm at different scans corresponding to first and second scan of broom fiber/PP composites containing 30 wt% and 50 wt%, respectively, is represented in Table 1. It is clear that the Tm for the first scan is greater than that of the second one.

Effect of Moisture

Samples from different composites were submerged in distilled water at a temperature of 85°C for 48 h. The thermograms of the

TABLE 1 Values of Melting Temperature of PP/Broom Fiber Composite, Effect of Different Scans

Specimens	Tm (°C) first scan	Tm (°C) second scan
70/30 untreated	169	165
50/50 untreated	168	165

composites with 30 wt% of silane-treated fiber resented in Figure 3 and those treated with stearic acid given in Figure 4, show three peaks at 0°C, 100°C, and 168°C. The peak at 0°C correspond to the freezing of water, that at 100°C to the water vaporization and that at 168°C corresponds to the melting temperature of the composite.

Thermograms obtained during the second scan show only one peak, which corresponds to the melting temperature. In general, the properties of these materials are affected by moisture, which change the structure and properties of the fibers, matrix and the interface between them. Once the moisture penetrates inside the composite materials, the fibers tend to swell. The matrix structure can also be affected by water absorption such as chain reorientation and shrinkage. Water absorption and its resulting effects contribute to the loss of compatibilization between fibers and matrix, which results in debonding and weakening of the interface adhesion [1].

From the DSC studies, we notice that in the second scan there is no peak of water evaporation in the thermogram which means that the water was only absorbed at the surface of the fiber.

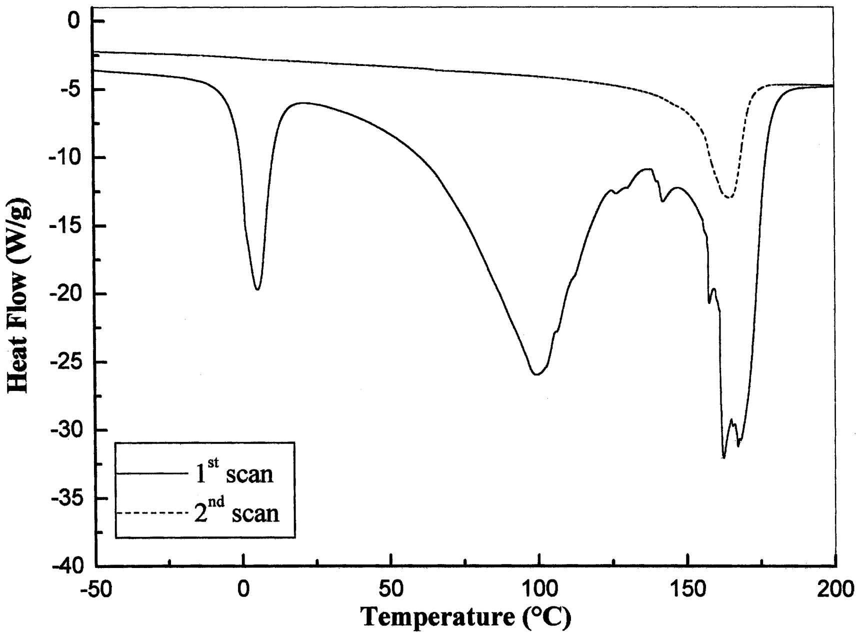

FIGURE 3 DSC thermograms of PP filled with 30 wt% of broom fiber treated with 1.5 wt% of silane, effect of water at T = 85°C.

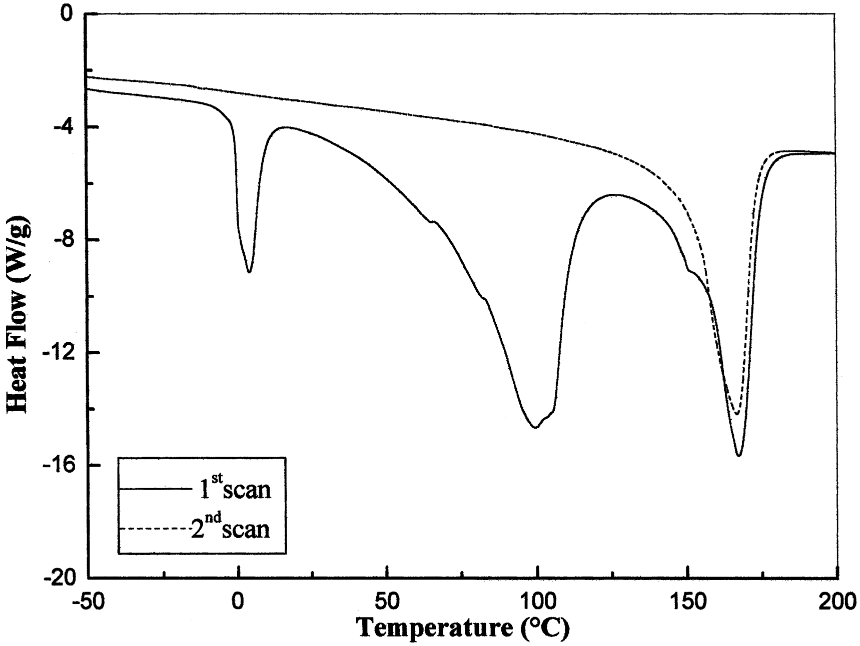

FIGURE 4 DSC thermograms of PP filled with 30 wt% of broom fiber treated with 1.5 wt% of stearic acid, effect of water at T = 85°C.

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis of PP

The dynamic mechanical properties such as storage modulus (E′), loss modulus (E″) and the loss factor (tan δ) of pure polypropylene and polypropylene/broom fiber composites were evaluated in a temperature range between −50 to 170°C.

Figure 5 shows the curves of E′ as a function of temperature for pure PP at different frequencies. Notice that E′ decreases with temperature due to an increased segmental mobility. In semicrystalline materials like PP, during transition, only the amorphous part undergoes segmental motion, whereas the crystalline region remains solid until its melting temperature. Dynamic modulus increased with increasing frequency due to the reduced segmental mobility.

Figure 6 shows the variations of tan δ as a function of temperature. Two relaxations are observed over the temperature range studied; a lower temperature relaxation between −20 and 20°C, which is attributed to the glass transition of the amorphous phase. Another one

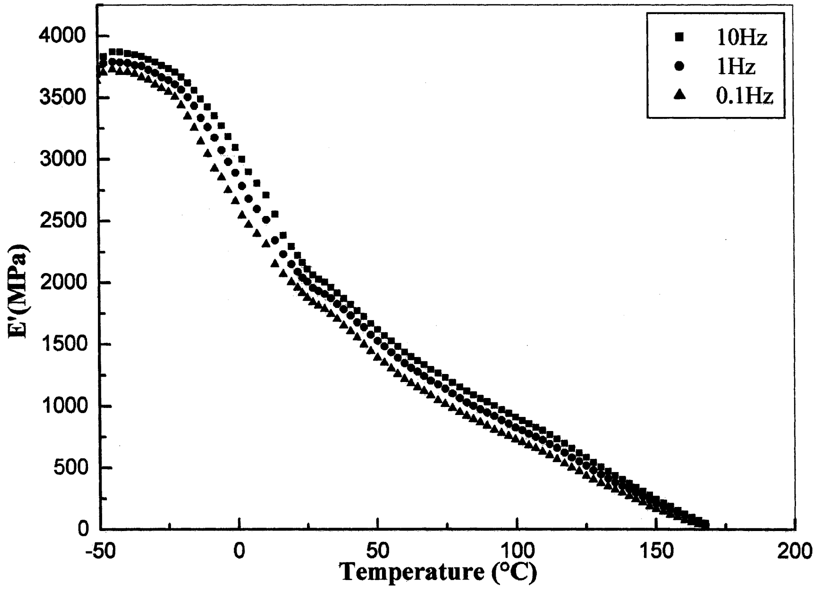

FIGURE 5 Course of storage modulus E′ as a function of temperature for pure PP at different frequencies.

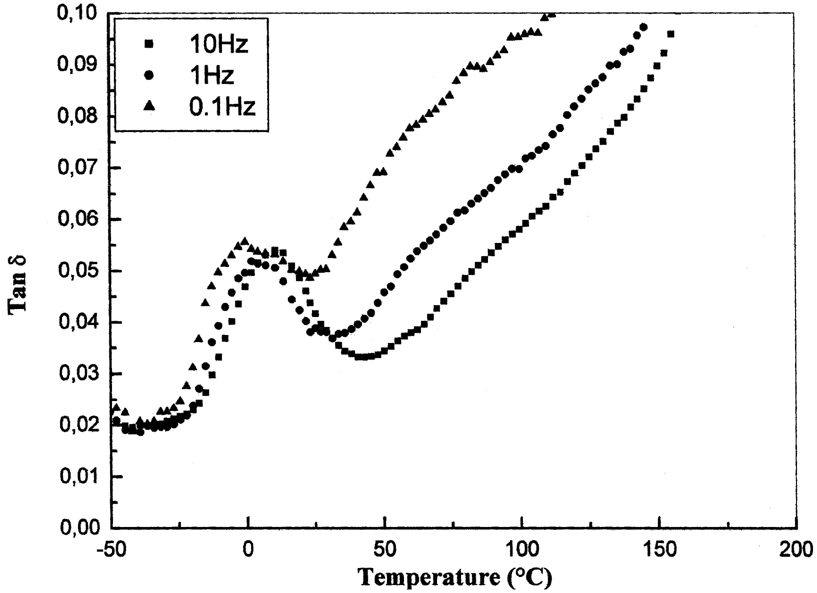

FIGURE 6 Course of loss factor tan δ as a function of temperature for pure PP at different frequencies.

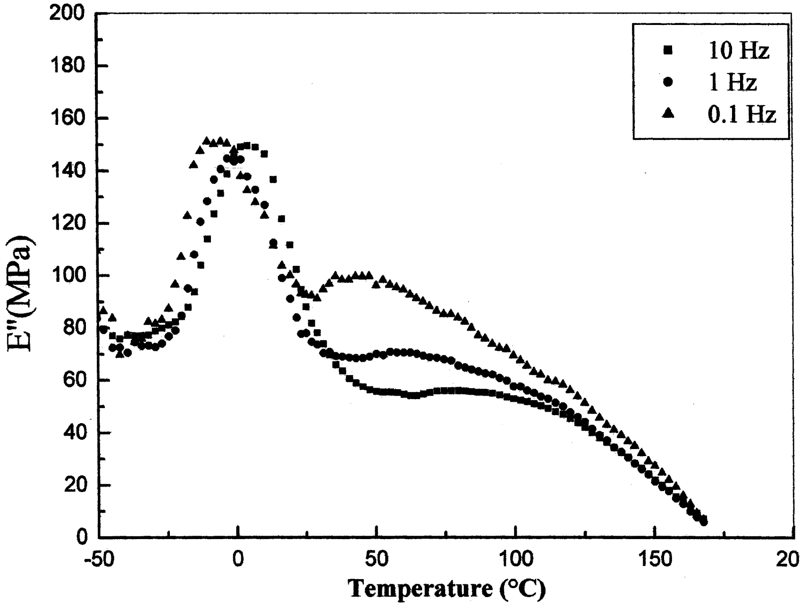

FIGURE 7 Course of loss modulus E″ as a function of temperature for pure PP at different frequencies.

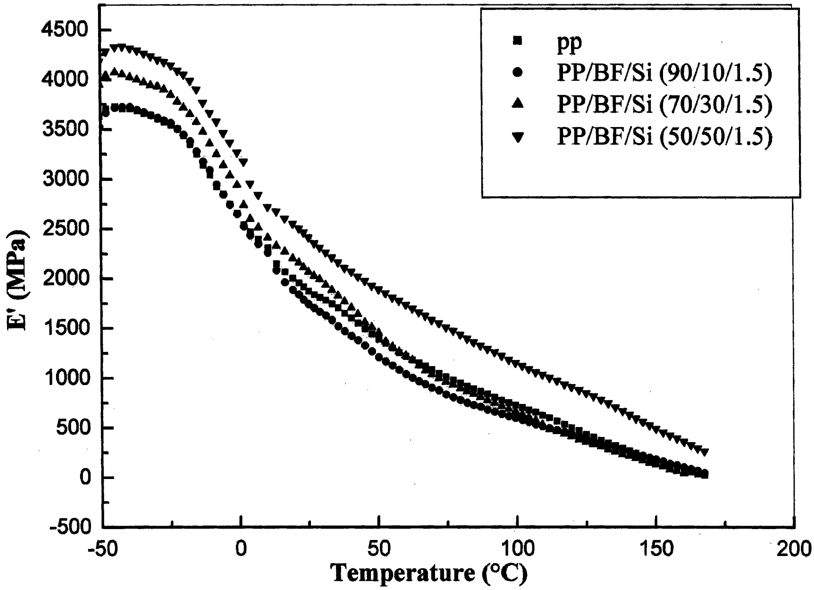

FIGURE 8 Course of storage modulus E′ as a function of temperature for pure PP and PP/broom fiber composites treated with 1.5 wt% of silane at 0.1 Hz.

appears near 75°C and is due to the α transition related to the formation of crystallites. These results are in agreement with those presented by Joseph et al. [10].

The variations of loss modulus (E″) with temperature presented in Figure 7 also show the same behavior as that described for tan δ.

Effects of Chemical Treatments

Figure 8 depicts the dynamic mechanical spectra E′ as a function of temperature for neat PP and the composites filled with 10, 30, and 50 wt% of fibers treated with silane. The comparison of neat PP and PP/broom fiber composites shows that the addition of fibers results in an increase of the composite stiffness and a loss in bending modulus. The incorporation of treated fibers induces reinforcement effect, due to the fact that silane coupling agent modifies the interface fibre–matrix with the formation of chemical bridge bonds between the two components. That's why an increase is noticed in modulus values when the treated fibers with silane are used, indicating better interfacial bonding between polymer and the fiber [11].

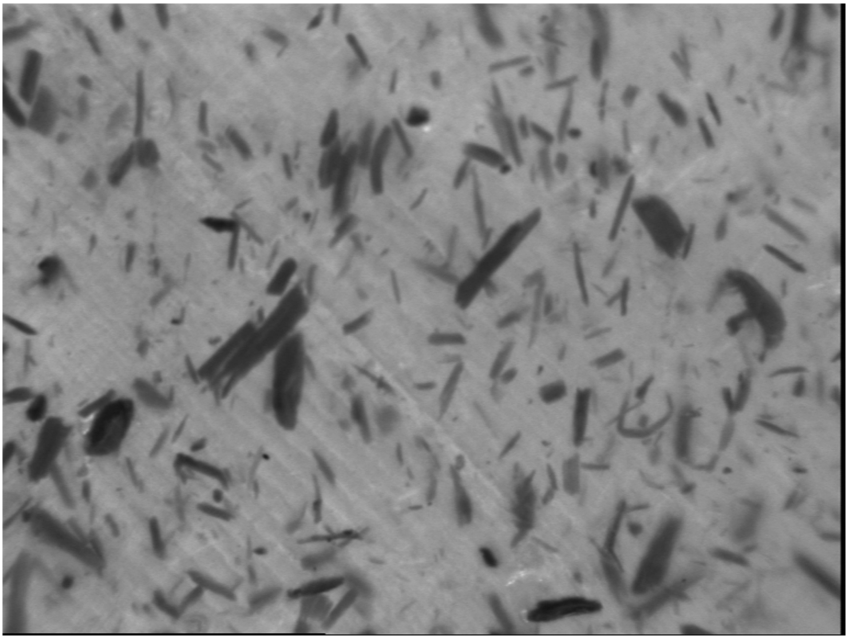

FIGURE 9 Image of dispersion of PP/broom fiber/silane (90/10/1.5).

Many studies showed that silane coupling agent displays a good affinity toward cellulosic substrates. It is known that the methoxy groups (–OCH_3) in the silane can be hydrolyzed to produce silanol (–Si $(OH)_3$), during the fiber pretreatment process [12–13].

These silanol groups can either develop covalent siloxane bond, or form hydrogen bonds with –OH groups of cellulosic fiber. The amino groups have relatively high miscibility with polyethylene (PE) and PP. Thus, during the compounding of modified cellulosic fiber and PP there will be a possible reaction of these functional groups with any polarizable groups and bonds present in PP [13]. Figure 9 is an optical image of the dispersion of PP/broom fiber/silane (90/10/1.5). The micrograph points out the better dispersion of the broom fiber in the PP matrix when it is treated with silane.

Figure 10 shows the variation of (tan δ) as a function of temperature for neat PP and for silane treated composites. Two relaxations can be observed: (β) and (α). The dominant (β) peak represents the transition of the amorphous portions in PP, and the temperature of the

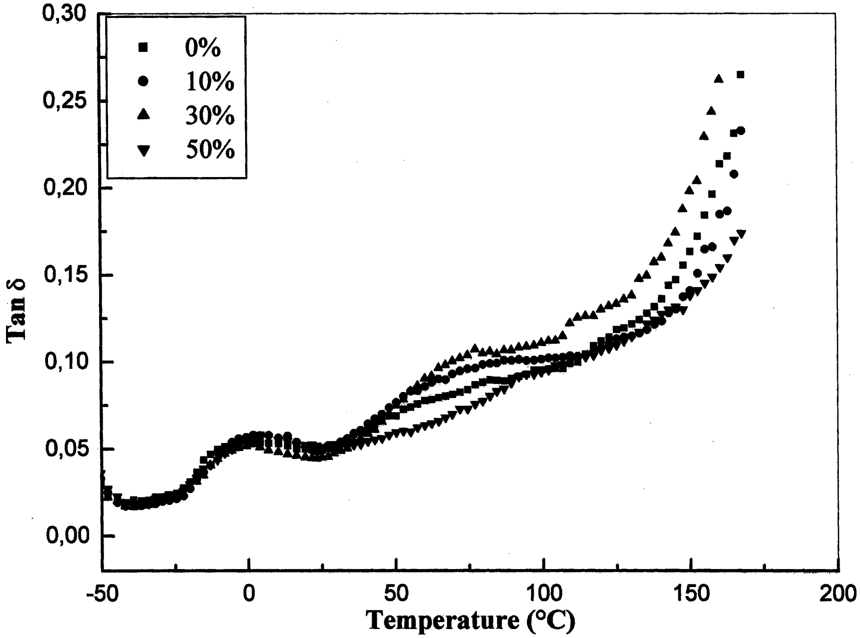

FIGURE 10 Course of loss factor tan δ as a function of temperature for PP and PP/broom fiber composites treated with 1.5 wt% of silane at 0.1 Hz.

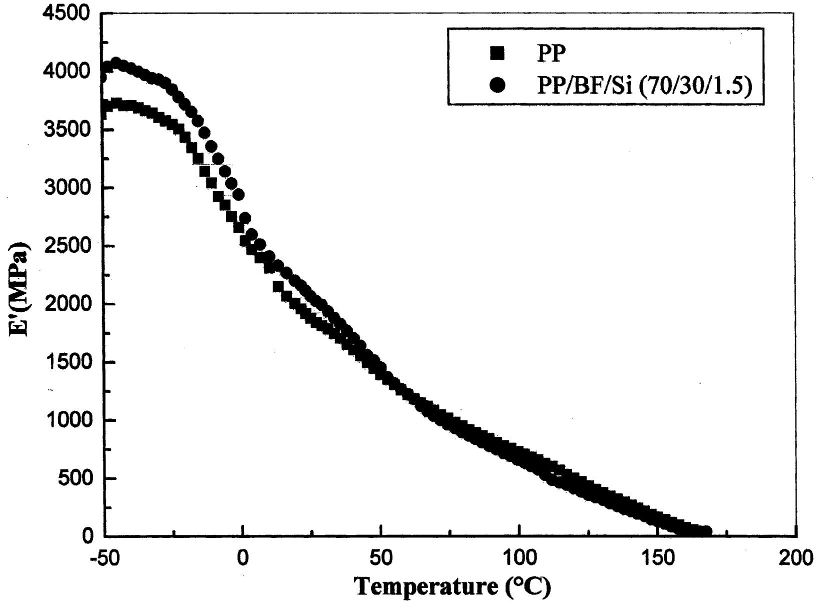

FIGURE 11 Effects of silane on the storage modulus E″ of PP and composites with 30 wt% broom fiber at 0.1 Hz.

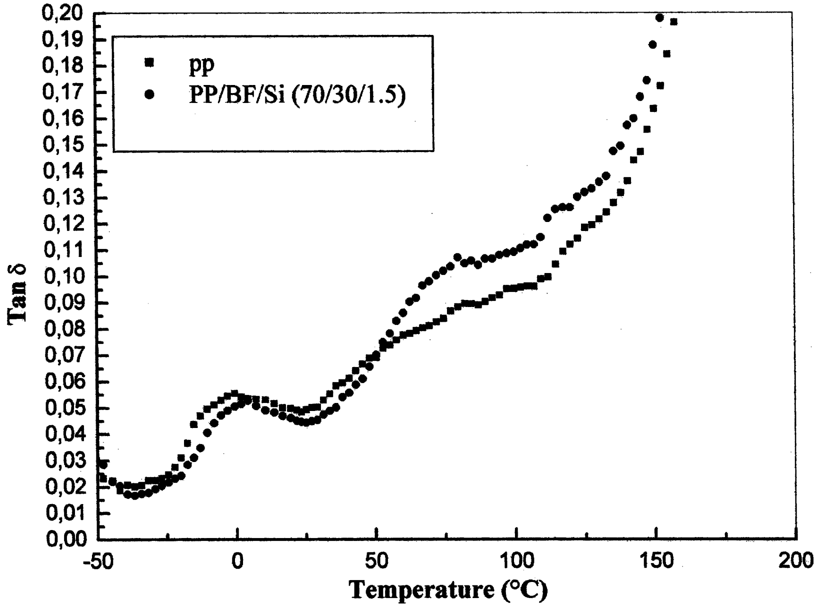

FIGURE 12 Effects of silane on the loss factor tan δ of PP and composites with 30 wt% broom fiber at 0.1 Hz.

loss peak maximum is assigned to the glass transition temperature (T_g) at 8°C. This transition corresponds to a significant decrease of the E′ modulus.

The reinforcement effect observed from the dynamic mechanical properties of the composites investigated is attributed to the strength and the efficiency of the interfacial adhesion and interaction between the broom fibers treated with the silane and the PP matrix. In general, the thermodynamic theory is most widely used to explain the adhesion mechanism. It describes the achievement of intimate contact and the development of physical forces at the interface. In addition to physical interactions, the resulting strong covalent bonds as well as hydrogen bonds considerably enhance the interfacial adhesion, stress transfer and improve the dispersion of filler and the compatibility between the hydrophilic cellulosic fiber and hydrophobic polypropylene matrix [14].

Figures 11 and 12 depict the dynamic mechanical spectra of E′ and tan δ as a function of temperature for neat PP and the composites

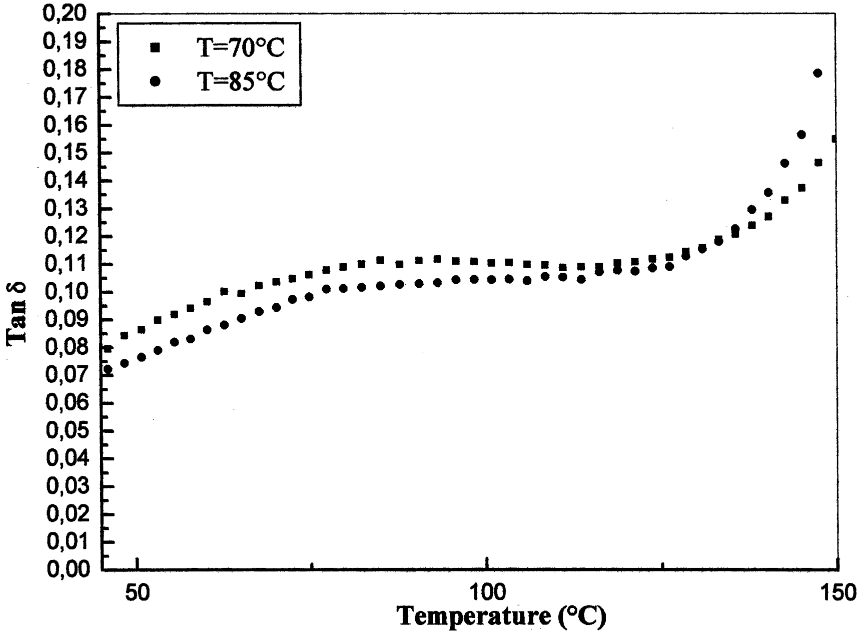

FIGURE 13 Effect of water absorption on the loss factor tan δ as a function of temperature for a composite filled with 30 wt% of broom fiber treated with 1.5 wt% of stearic acid at 0.1 Hz.

PP/30 wt% broom fiber treated with silane. The addition of broom fibers treated with silane in PP results in an increase of the storage modulus. This confirms the reinforcing effect of the silane treatment.

From the tan δ curves of virgin PP and the composite, two relaxations can be observed at 8°C (β transition) and at 75°C (α transition). The β peak represents the transition of the amorphous portions in PP, and the temperature of the loss peak maximum is assigned to the glass temperature.

Effects of Moisture and Temperature

Figures 13, 14, and 15 show the variation of tan δ as a function of temperature for composites filled with 30 wt% of broom fiber untreated and treated with both silane and stearic acid. The samples were previously submerged in distilled water at temperatures of 70 and 85°C. It was noticed that there are only small differences between the results. Water is only present at the surface and water absorption is not greatly affected by temperature.

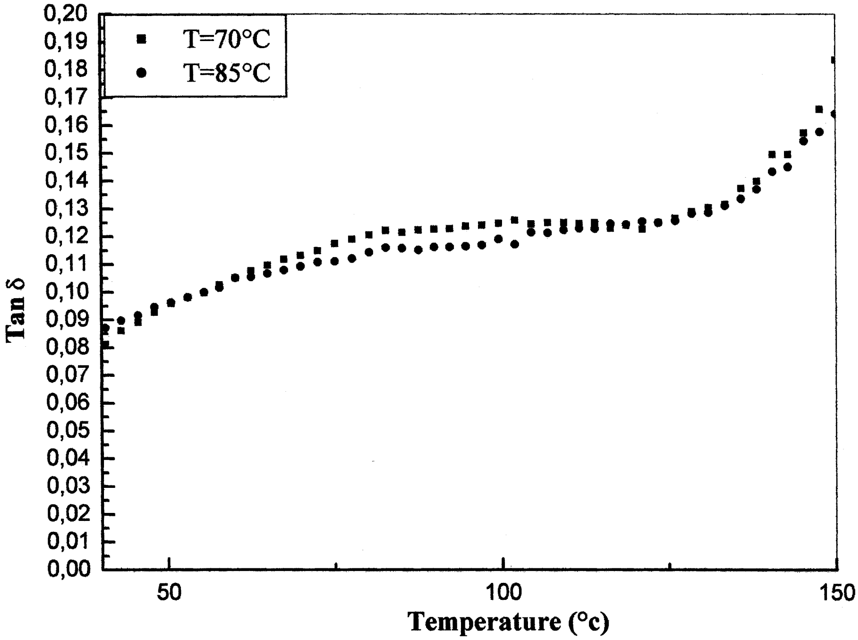

FIGURE 14 Effect of water absorption on the loss factor tan δ as a function of temperature for a composite filled with 30 wt% of broom fiber treated with 1.5 wt% of silane at 0.1 Hz.

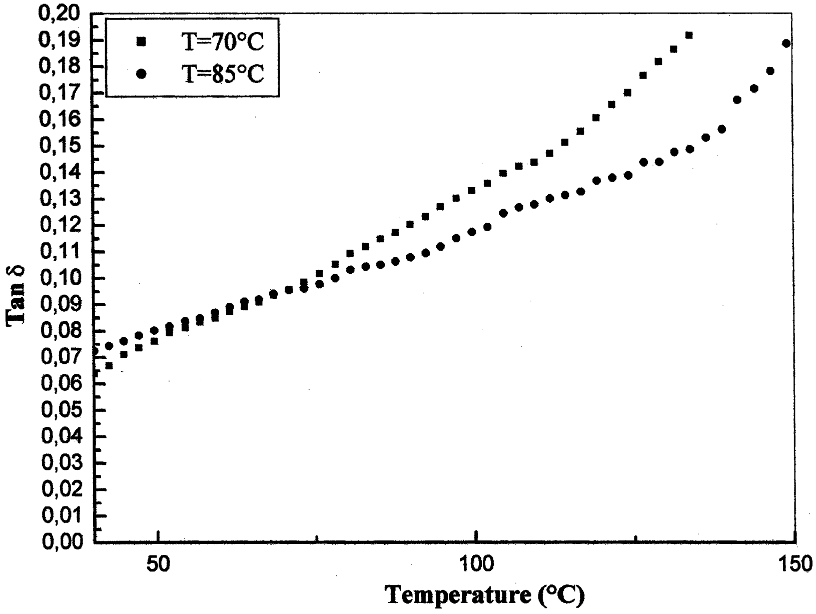

FIGURE 15 Effect of water absorption on the loss factor tan δ as a function of temperature for a composite filled with 30 wt% of untreated broom fiber at 0.1 Hz.

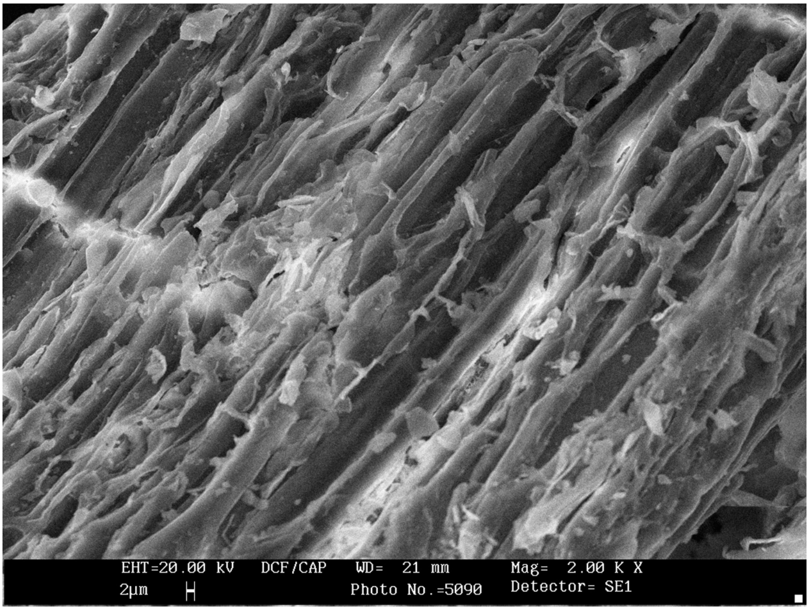

FIGURE 16 SEM observation of untreated broom fiber.

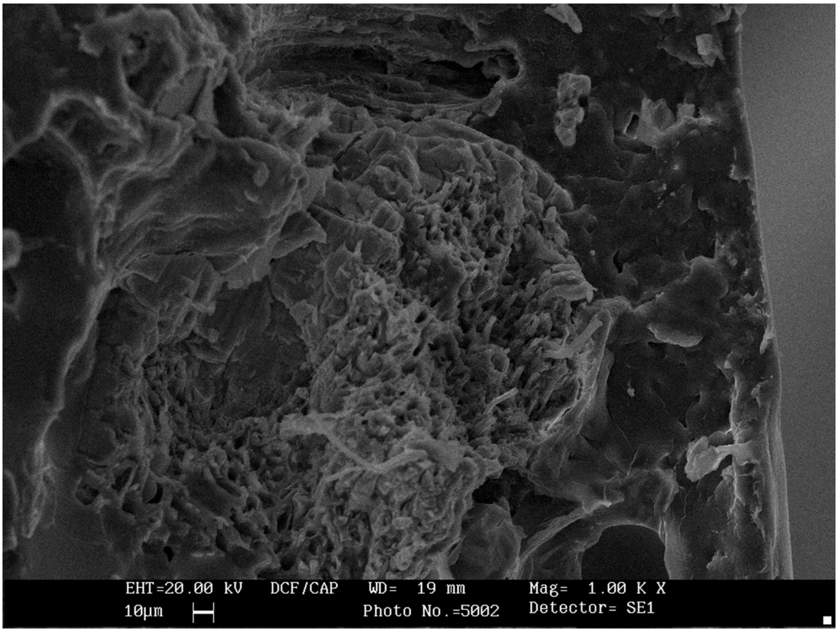

FIGURE 17 SEM observation of PP/broom fiber/silane (70/30/1.5).

SEM Observations

The SEM micrograph of broom fiber is shown in Figure 16. The fiber presents a three-dimensional structure with many distortions; and there is enough roughness that enhances the interpenetration with matrix. Broom fiber is multiple elementary fibers arranged in bundles. The elementary fibers are bound together by lignin; ultimate fibers are regular in shape, with a smooth surface and covered with compact granulation, and show irregularities and defects [15–16].

Figure 17 represents the micrograph of PP/broom fiber/silane (70/30/1.5) composite. It shows a better adhesion between the two phases and the formation of an interface. This observation well supports the thermomechanical results.

CONCLUSIONS

Composites based on the *Spartium junceum* fibers and polypropylene matrix with different fibers content and chemical treatments have been prepared. The thermal analysis (DSC) of pure polypropylene and polypropylene/broom fiber composites have been evaluated.

The incorporation of untreated broom fiber in polymeric matrix has no significant impact on the melting temperature value neither on the shape of the melting peak. It was concluded also that the treatment has no significant effect on the melting temperature.

The dynamic mechanical properties of pure PP show that storage modulus E′ decreases with temperature due to the increased segmental mobility. The loss factor tan δ values present two relaxations over the temperature range studied; a lower temperature relaxation appears between −20 and 20°C and is attributed to the glass transition of the PP amorphous phase. Another one is situated near 75°C and is due to the α transition related to the formation of crystallites.

The incorporation of treated fibers reveals a reinforcing effect. This fact is induced by silane coupling agent, which modifies the interface fiber–matrix by the creation of chemical bridge bonds between the two components.

The modification of the interface of the fiber by the treatment is also confirmed by SEM micrographs, which show a better adhesion between the two phases and the formation of an interface.

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