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ABSTRACT: This study is devoted to the analysis of the properties of continuous bamboo fiber (BF)-reinforced polyamide 11 (PA 11) composites. The SEM observations highlighted continuity between BFs and the polymeric matrix showing a high density of hydrogen bonds. The comparative calorimetric study of the matrix and its composites showed that the crystallinity of PA 11 was not modified by the presence of bamboo fibers. The physical aging observed in PA 11 is no more observed in composites due to physical interactions between PA 11 and BFs. The mechanical properties were investigated by tensile strength and dynamic mechanical analysis. The introduction of BFs enhanced Young's modulus of the matrix by a factor of 10. The presence of BFs also improved the storage shear modulus G' over the whole temperature range. © 2019 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 47623.

INTRODUCTION

The substitution of synthetic reinforcing fibers by natural fibers is an attractive objective for tailoring of new composites in materials science. Among natural fibers, bamboo has an environmental advantage because of its rapid growth. Abundant literature is available on bamboo flour or short bamboo fibers for reinforcing polymeric matrices.[1,2] These studies were first focused on the ultimate mechanical properties. Interesting data were obtained with thermoset matrices like polyester[3] or epoxy.[4] Thermoplastic polymers were also used as matrix. For polyolefin, the use of coupling agents is required.[5,6] The approach was analogous even for polar polymers.[7,8] Composites with continuous bamboo fibers were also processed and specific attention was paid to their tensile strength and impact resistance.[9–12] Nevertheless, the interest in mechanical analysis in the linear region like dynamic mechanical analyses (DMAs) was emphasized.[13]

In this work, composites were prepared with continuous bamboo fiber-reinforced biobased polyamide 11 (PA 11). The thermal stability of bamboo fibers was controlled by thermogravimetric analyses in order to define the processing conditions and the fiber content of the composites. Then, differential scanning calorimetry of composites allows us to determine the influence of fibers on the physical structure of the polyamide matrix. The mechanical properties were measured by tensile tests in order to evaluate Young's modulus and by DMA to calculate the complex shear modulus.

EXPERIMENTAL

Materials

Continuous Natural Fibers. The *Dendrocalamus membranaceus* bamboo fibers (BFs) were supplied by the Vietnam Academy of Science and Technology (Vietnam). The fibers were about 20 cm long with a section of about 100 μm. The fibers were mercerized in an alkaline solution at 3% NaOH, at 70 °C for 2 h. Then, they were washed using water before drying at 70 °C for 24 h. As shown in Figure 1, a BF is a bundle of about 10 elementary fibers.

Before processing of the composites, the thermal stability of the BF was determined by thermogravimetric analysis using a TGA Q50 (TA Instruments, New Castle, DE, USA). A dynamic test was performed from room temperature to 1000 °C, at 20 °C min^{-1}, under a synthetic air flow. The increase in the weight and the derivative are reported in Figure 2. There is a weight loss
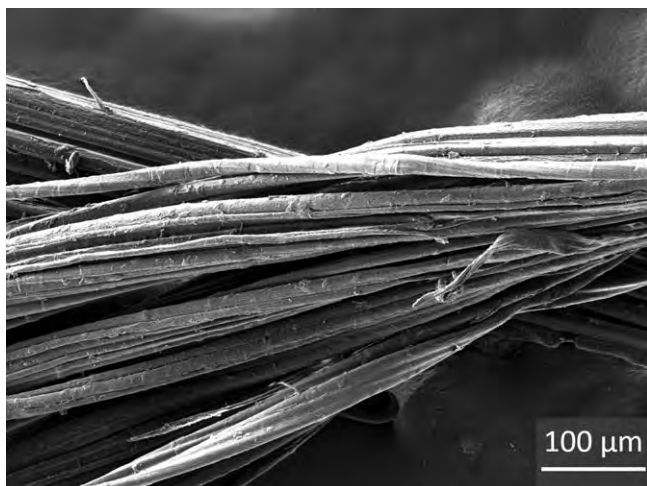
Figure 1. SEM observation of the bamboo fibers.

before 100 °C related to water desorption. The complex degradation occurs from 200 to 500 °C.[14,15] The residue is about 3%. The maximal processing temperature is set at 200 °C.

Moreover, an isothermal test was performed at 200 °C for 100 min under a synthetic air flow. Figure 3 shows the increase in weight of BF. Up to 15 min, there is mass loss of about 8%: it is associated with water desorption. There is no significant variation of weight (<1%), showing that the BFs are not damaged. In conclusion, 200 °C can be taken as the processing temperature.

Polymeric Matrix. PA 11 is a biobased thermoplastic synthesized by Arkema (France) under the trade name Rilsan BESVO A. Its water uptake at room temperature is 1%. Due to its melting temperature of around 190 °C,[16] it is well suited for constituting the matrix of continuous bamboo fiber composites. It was provided as pellets for the processing of composites.

Processing of Composites. First, the PA 11 pellets were pressed at 220 °C in order to obtain a film that was cut into rectangular sheets of 100 × 10 mm. Then, the fibers were disposed as a unidirectional layer between two films of polyamide (Figure 4). The bamboo fiber/polyamide weight ratio was m_{BF}/m_{PA} = 3/2. All composites have the same composition. The composite was pressed at 198 °C for 15 min. Finally, the samples were naturally cooled (about 20 °C min^{-1}).

For the polymeric reference samples, several films were overlaid to be as thick as the composites, and then were pressed at 198 °C. All the samples were stored at room temperature for 24 h before any analyses. The water uptake is then 5%.

Methods

Scanning Electron Microscopy. The interface between the matrix and the fibers was observed by scanning electron microscopy (SEM). The samples were cryo-fractured by breaking the composites frozen in liquid nitrogen. The samples were coated using platinum. Their morphology was observed using a JSM 6700F (JEOL, Japan), equipped with a field emission gun electron, at a voltage of 5 kV. This is equipped with a secondary electron detector.

Differential Scanning Calorimetry. The physical structure was analyzed using a Diamond DSC (Perkin Elmer) at a range of 30 to –220 °C at 10 °C min^{-1} under a helium atmosphere. The samples (around 12 mg) were placed in closed aluminium pans. After the first scan, the samples were immediately cooled at the same rate, and the second scan is recorded always at the same heating rate.

Tensile Test. The tensile tests were performed using a Criterion Model 43 (MTS). Rectangular samples were analyzed at a tensile
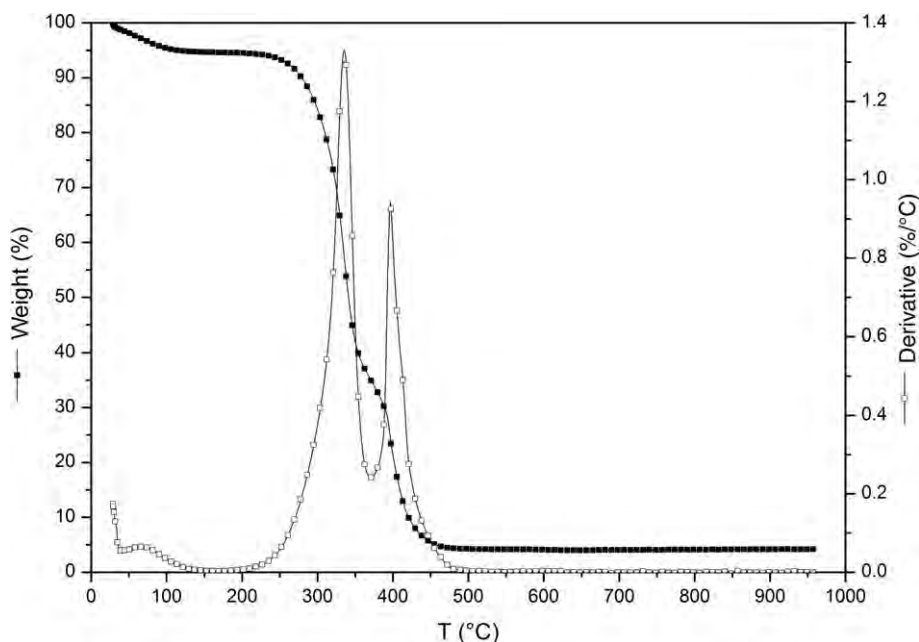

Figure 2. TGA and DTGA: variation of the weight of BF and its derivative versus temperature.
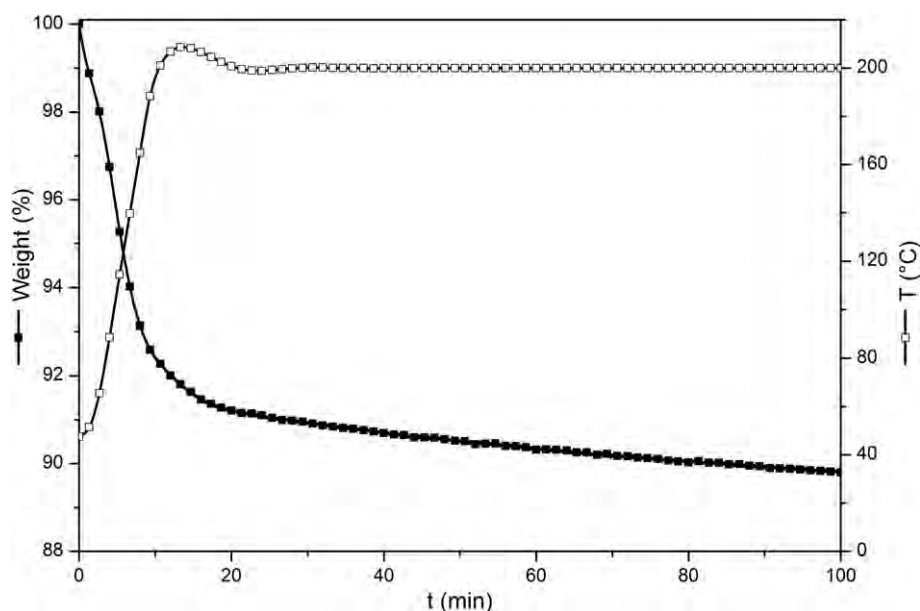
Figure 3. TGA: variation of the weight of BF and that of temperature versus time.
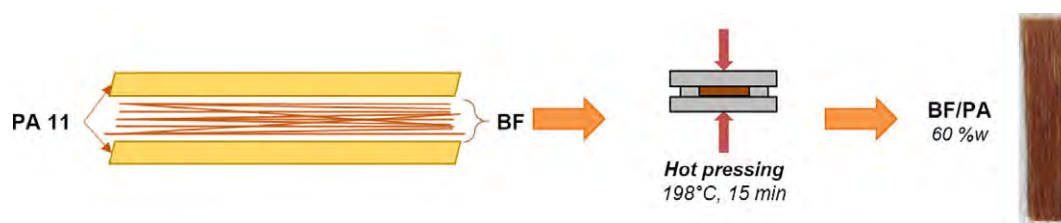

Figure 4. Schema of the processing of bamboo fiber/polyamide 11 composites. [Color figure can be viewed at wileyonlinelibrary.com]

speed of 1 mm s^{-1}. The tests were performed on six samples of each matrix, of the bamboo fibers, and of each composite.

Dynamic Mechanical Analysis. The mechanical behavior was determined by DMA using an Advanced Rheometric Expansion System setup (Rheometric Scientific). Rectangular samples were used for the trials. The measurements were performed at a temperature ranging from −130 to 150 °C and a heating rate of 3 °C min^{-1}, under a nitrogen flow, at an angular frequency of 1 rad s^{-1} with a dynamic strain of 0.1%. After the first scan, the samples were immediately cooled at the same rate and the second scan is always recorded at the same heating rate. The tests were performed using six samples.

The complex shear modulus G^* is defined using eq. (1)

$$G^*(\omega, T) = G'(\omega, T) + iG''(\omega, T) \qquad (1)$$

where G' is the storage modulus and G'' is the loss modulus.

RESULTS AND DISCUSSION

Morphology Analysis

Figure 5 shows the morphology of the interfaces in the BF/PA 11 composite observed by SEM. There is a continuity of matter between the matrix and the reinforcement. This observation highlights a good compatibility between the natural fibers and the polar matrix. This continuity is analogous with the

one observed on the composite when the filler is treated with a coupling agent.[17–19] A previous study on polyamide matrix composites filled with bamboo flour showed that this kind of treatment is not necessary with the PA 11 composite due to the formation of hydrogen bonds between the polymer and the fibers.[20]
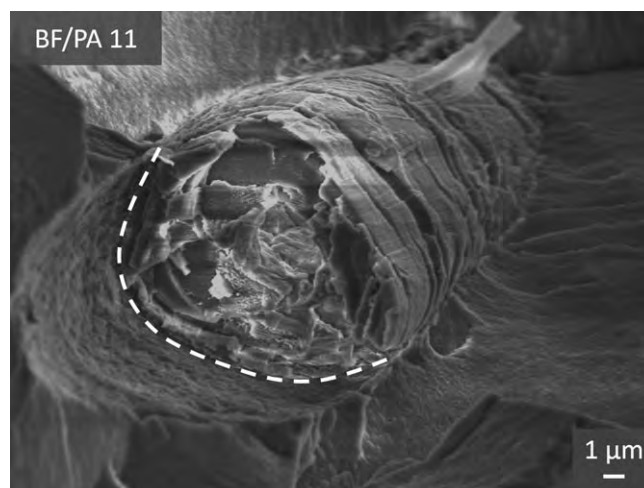

Figure 5. SEM observations of the interface in the BF/PA 11 composite. The dashed lines are guidelines for the interfaces.
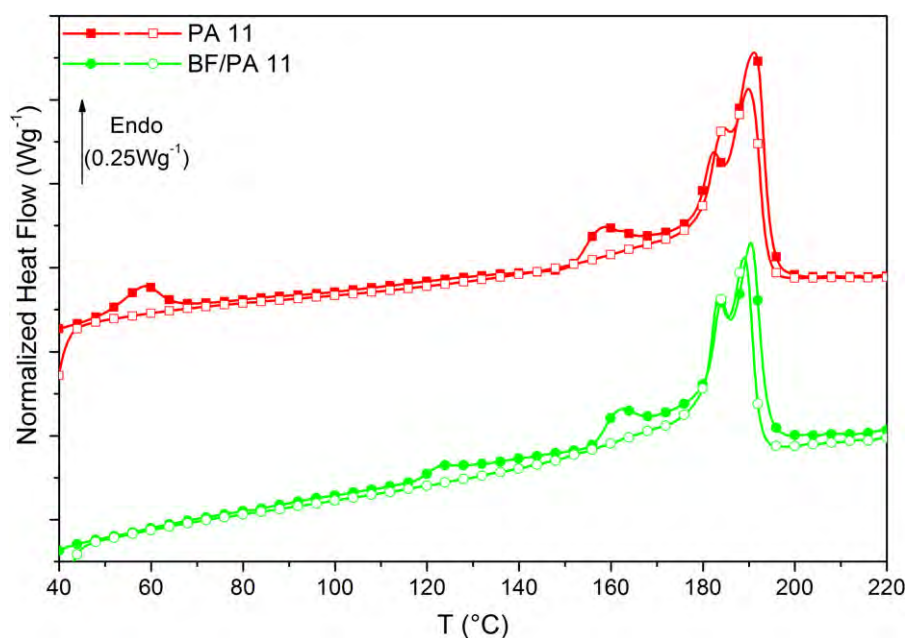
Figure 6. DSC curves of bulk PA 11 and BF/PA 11 composites. The first scan is represented by filled symbols, and the second scan is represented by open symbols. [Color figure can be viewed at wileyonlinelibrary.com]

Table I. Thermal Parameters of the PA 11 Matrix and the BF/PA 11 Composite

Sample	Scan	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})	Polymer content (% wt)
PA 11	First	38 (1)	183/189 (1)	64.6 (0.6)	100
	Second	–	184/188 (1)	53.8 (0.5)	
BF/PA 11	First	–	183/190 (2)	63 (4)	63 (4)
	Second	–	182/189 (1)	50 (3)	

Thermal Transitions

The calorimetric responses of the PA 11 matrix and the BF/PA 11 composite are shown in Figure 6. The thermal parameters of each sample are reported in Table I.

In the first scan shown in Figure 6, the glass transition temperature of PA 11 is at 38 °C, and a peak is superimposed on the heat capacity step. A peak observed at 160 °C is associated with a thermal treatment due to the previous tests performed using the samples. Finally, two melting peaks are observed at 183 and 189 °C, with a total ΔH_m of about 64.6 J g^{-1}. These two peaks are indicative of crystallites of different sizes.[21,22] In the second scan, the endothermic event at the glass transition vanishes: this behavior confirms that the initial event was due to physical aging. The melting temperatures are not modified. ΔH_m decreases due to the absence of the peak at 160 °C.

In the case of the BF/PA 11 composite, the glass transition is not visible; moreover, bamboo fibers prevent the physical aging of the matrix. The peak at 160 °C is still observed with the two melting peaks at 182 and 190 °C. The melting enthalpy (63 J g^{-1}) is close to the one of the matrix. In the second scan, the composite's behavior is analogous to the one of bulk PA 11.

This study shows that the presence of bamboo fibers does not significantly modify the thermal behavior of the crystalline phase of PA 11 in PA 11/BF composites. The shape and magnitude of the melting peak of PA 11 are unmodified.[20] Physical interactions in the amorphous phase of PA 11/BF composites inhibit the physical aging observed in the amorphous phase of bulk PA 11.

Mechanical Properties

Tensile Modulus. Young's moduli of the matrix, the bamboo fibers, and the composites are reported in Table II. For PA 11, Young's modulus is 1.2 GPa. The BFs exhibit a Young's modulus of 24.2 GPa. Due to the natural origin of the fibers, the literature shows Young's modulus ranging from 3 to 45 GPa.[23–28]

Table II. Young's Moduli of the PA 11 Matrix, the BF Bamboo Fiber, and the BF/PA 11 Composite

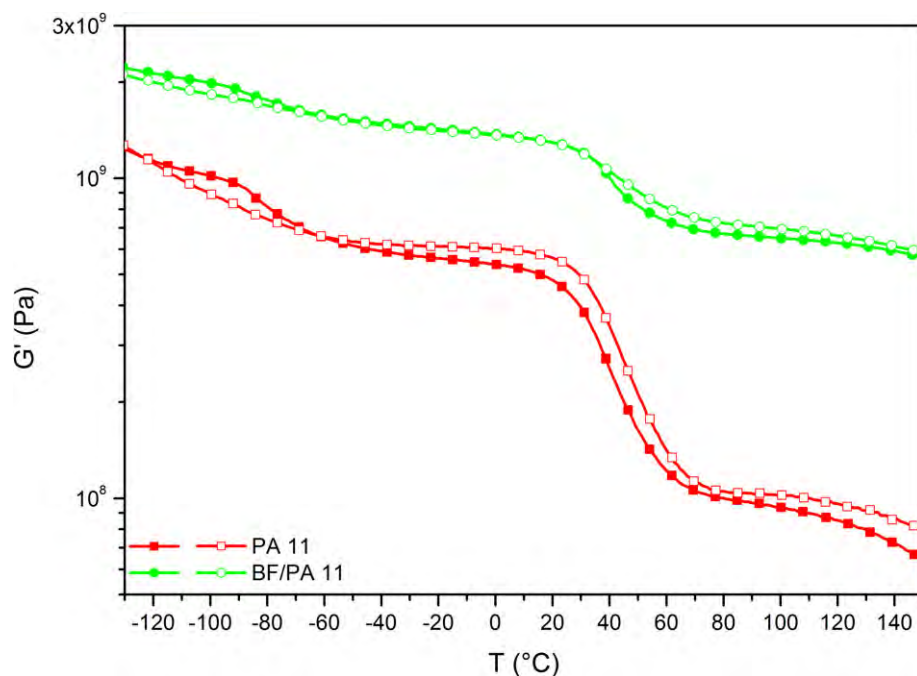| Sample	Young's modulus (GPa)
PA 11	1.2 (0.2)
BF	24.2 (0.5)
BF/PA 11	11.9 (0.4)

Figure 7. Conservative shear moduli G' versus temperature for the PA 11 matrix and the BF/PA 11 composite. The first scan is represented by filled symbols, and the second scan is represented by open symbols. [Color figure can be viewed at wileyonlinelibrary.com]

The modulus measured here is within the range of published data. The measured Young's modulus is 11.9 GPa for the BF/PA 11 composite. This value is consistent with the one predicted by the calculation: 14.5 GPa for the BF/PA 11 composite. The reinforcement effect due to natural fibers is significant.

Dynamic Shear Modulus. Figures 7 and 8 show the temperature variation of the storage modulus G' and the loss modulus G'' for

the polymeric matrix and the composite, respectively. The mechanical parameters for the two consecutive temperature scans are reported in Table III.

In Figure 7, two relaxations are visible for PA 11: at about −80 °C, a step associated with the mobility of the amide groups, called the β mode, and about 35 °C, the viscoelastic step associated with the anelastic manifestation of the glass transition called the α mode. These relaxations are typical of polyamides.[29–32] The
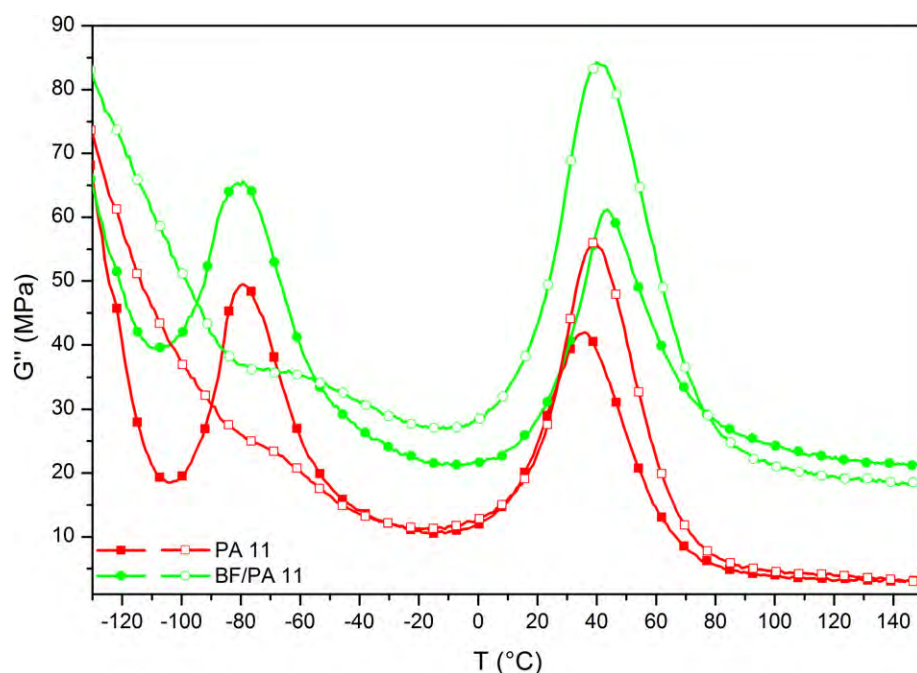

Figure 8. DMA of loss shear moduli G'' of the PA 11 matrix and the BF/PA 11 composite. The first scan is represented by filled symbols, and the second scan is represented by open symbols. [Color figure can be viewed at wileyonlinelibrary.com]

Table III. Storage Moduli, Loss Moduli, and Relaxation Temperatures of the PA 11 Matrix and the BF/PA 11 Composite

Sample	Scan	G'_g (0 °C) (GPa)	G'_r (100 °C) (MPa)	T_β (°C)	T_α (°C)
PA 11	First	0.57 (0.03)	102 (8)	−78 (2)	37 (1)
	Second	0.60 (0.02)	98 (5)	−65 (1)	39 (1)
BF/PA 11	First	1.4 (0.3)	530 (40)	−80 (2)	42 (1)
	Second	1.5 (0.3)	740 (60)	−64 (1)	40 (1)

temperature of the α relaxation is consistent with DSC results. In the second scan, the α relaxation is slightly shifted to a higher temperature. The main result exhibited by this comparative study is that the introduction of BF in PA 11 increases the modulus in the whole temperature range. The strain transfer is improved owing to hydrogen bonding.

In Figure 8, the loss modulus G'' is reported for each sample. For the PA 11 composite, the β relaxation is shifted from −78 to −65 °C. It highlights the double components of the β relaxation: the β_1 component related to the mobility of amide–amide interactions, and the β_2 component related to free amide groups. In the first scan, the β_2 component is mainly observed due to the presence of water molecules. In the second scan, the samples have been dried so that the β_2 component disappears. Then, the β_1 component can be observed. The same behavior is observed for the composites. For the BF/PA 11 composite, the β relaxation occurs at a temperature similar to that for the neat PA 11.

The α relaxation happens at a higher temperature (42 °C) in composites: this may be explained by the interactions with BFs that stiffen the matrix. In the second scan, the α relaxation is observed at 40 °C. The decrease is attributed to the relaxation of internal stresses induced upon processing.

CONCLUSIONS

In this study, continuous bamboo fiber-reinforced PA 11 composites have been processed and analyzed. The SEM observations showed a good compatibility between the natural fibers and the polar matrix without porosity due to hydrogen bonding.

DSC analyses highlight that the bamboo fibers do not modify the physical structure of the PA 11 composite. The mechanical properties were improved due to the presence of the BFs. Young's modulus of the polymers was 1.2 GPa for the PA 11 composite; it was increased to 11.9 GPa for the BF/PA 11 composite. The shear behavior was investigated by DMA. The temperatures of the relaxations were practically unmodified by the presence of bamboo fibers. The presence of the BFs into the PA 11 composite leads to enhancement of the conservative shear modulus over the whole temperature range. In other words, the charge transfer operates even in shear. These data show that it is unnecessary to introduce coupling agents. Such biobased composites that comply REACH environmental regulations allow weight saving. Considering their engineering performances, they appear as attractive materials for unloaded structures.

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