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Effect of surface treatments on the dynamic mechanical behavior of piassava fiber–polyester matrix composites

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Abstract The effect of several fiber surface treatments upon the dynamic mechanical behavior of piassava fiber-reinforced composites was evaluated. In the light of the experimental results obtained the critical volume fraction for the fibers to effectively perform as reinforcement was established. The results show that all treatments performed (mercerization, acetylation, and mercerization + acetylation) enhance the fiber/matrix adhesion, but some treatments also affect the fiber's integrity. At the elastic region the storage modulus of the composites fabricated with treated fibers was higher than that of the untreated fiber-reinforced composite. However, only the composite manufactured with 10 wt% mercerized fibers showed a statistically significant increase of the storage modulus. Above T_g the storage modulus was primarily governed by the volume fraction of fibers. Therefore, raw and treated fiber composites had essentially the same behavior.

Keywords Piassava fibers · Interface · Thermomechanical properties · Micro-mechanics

Introduction

Lignocellulosic fibers have several advantages to be used as reinforcement in polymer-matrix composites. One can cite, for example, their biodegrability and their neutrality in respect to CO_2 emission [1]. Besides, lignocellulosic fibers are available all around the world and their increasingly use can be a source of spreading welfare if the development of lignocellulosic-fiber-based composite industries supports local communities.

One of the greatest concerns regarding the use of lignocellulosic fibers, as reinforcement in polymer-matrix composites is the commonly poor interface developed between the hydrophilic fibers and the usually hydrophobic matrices. To overcome this issue, several chemical and/or physical surface treatments were developed in order to guarantee a better fiber–matrix adhesion [2, 3]. The evaluation of how effective a treatment is can be made by several methods, including scanning electron microscopy and mechanical tests. Dynamic mechanical analysis (DMA) methods are particularly useful and are being largely used to investigate fiber/matrix adhesion [4], as well as the structure and the visco-elastic behavior of polymers and polymer composites [5, 6].

Piassava (*Attalea funifera*) is a stiff fiber extracted from the leaves of a palm tree of natural occurrence at the Brazilian Atlantic rain forest. It has mechanical properties similar to that of coir fibers [7], and has a great potential to be used as reinforcement in resin-matrix composites, even when one envisages the use of leftover fibers. These residues are composed by long fibers, and do not compete with the traditional markets where piassava is used nowadays [8]. Therefore, in this work, the effect of several surface treatments on the fiber/matrix adhesion of piassava fiber–polyester matrix composites was evaluated by DMA.

Materials and experimental methods

Piassava fibers disregarded by a broom industry were used in this work. The lengths of these fibers do not met the

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industry requisites to manufacture brooms, but are long enough to be considered as long fibers when used to reinforce polymers [8]. The composites were fabricated using raw (as-received) fibers and surface-treated fibers. The surface treatments performed were mercerization (with 2, 5, 10, and 15 wt% solutions of NaOH); acetylation, and mercerization (15 wt% solution of NaOH) + acetylation. Details of these treatments are given in another work, and are not repeated here for the sake of shortness [9].

The composites were fabricated by the compression molding technique. The piassava fibers were laid down longitudinally aligned at the mold's cavity and then the resin matrix was poured into the mold. A commercial isophtalic polyester resin mixed with 0.6 wt% of cobalt octoate accelerator and with 1 wt% of methyl–ethyl–ketone catalyst was used as matrix. The cure of the composites was done at room temperature, 23 ± 3 °C, under a pressure of 0.7 MPa. Composites with 22 wt% of fibers were manufactured.

Specimens 15 mm long, 6 mm large, and 3.5 mm thick were machined from the composites. These specimens were machined with the fibers aligned along their lengths. The dynamic mechanical properties were measured using a Perkin-Elmer model DMA7 equipment. The three-point bending flexure fixture was used, and the tests were performed with the following experimental setup: frequency = 1 Hz; static force 550 mN; dynamic force = 500 mN; heating ratio = 3 °C/min; temperature range = 0–180 °C. Five specimens were tested per composite analyzed. The bare matrix was also tested using the same specimens' dimensions and experimental parameters.

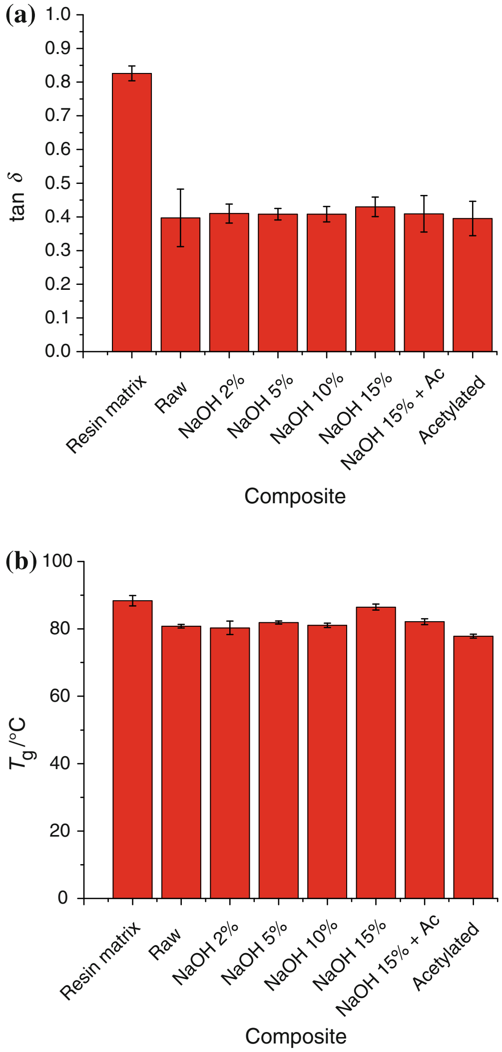

Fig. 1 Polyester matrix and its fiber-reinforced composites. **a** tan δ peak intensity and **b** T_g

Experimental results and discussion

Figure 1 shows the experimental values obtained for tan δ and T_g. The incorporation of the fibers caused a marked decrease of tan δ. A similar behavior was obtained for other lignocellulosic fiber-reinforced composites [6, 10–14], as well as for untreated piassava–polyester composites [15]. This behavior can be associated to macromolecular chain mobility restrictions at the neighborhood of the fibers [16], but can also be partially attributed to the lesser polymer content at the composite in respect to the neat matrix. In fact, as described by Nair et al. [11], the damping behavior of a composite at the glass-transition region has several contributions, namely: (i) mechanical relaxation of the matrix and of the fibers; (ii) the fiber/matrix interface; and (iii) the length and fraction of the fiber.

In respect to the fiber/matrix interface, Pothan et al. [14] associated the height of the tan δ peak to the amount of the absorbed energy, and the shorter the tan δ peak is the lesser energy is dissipated. Therefore, since weak interfaces are a source for crack initiation and deviation, weak interfaces will contribute to higher energy dissipation than strong interfaces. Thus, a material with a weak fiber/matrix interface will have a higher tan δ peak than a material with a strong fiber/matrix interface [4, 14, 17, 18]. Aziz and Ansell [17] found a decrease of the tan δ peak when treated kenaf fibers were used to reinforce a polyester matrix. The same behavior was found for a hemp fiber–polymer composite when the fibers were treated with a 6% NaOH solution [18]. For the treatments used in this work, however, the tan δ peak values are statistically equal, within a 5% of significance using the Fisher test [least square difference (LSD)], when treated and untreated fiber composites are compared. Figure 2 illustrates the tan δ curves, clearly showing the reduction of the tan δ peak height with fiber incorporation, but only small differences between treated and untreated composites.

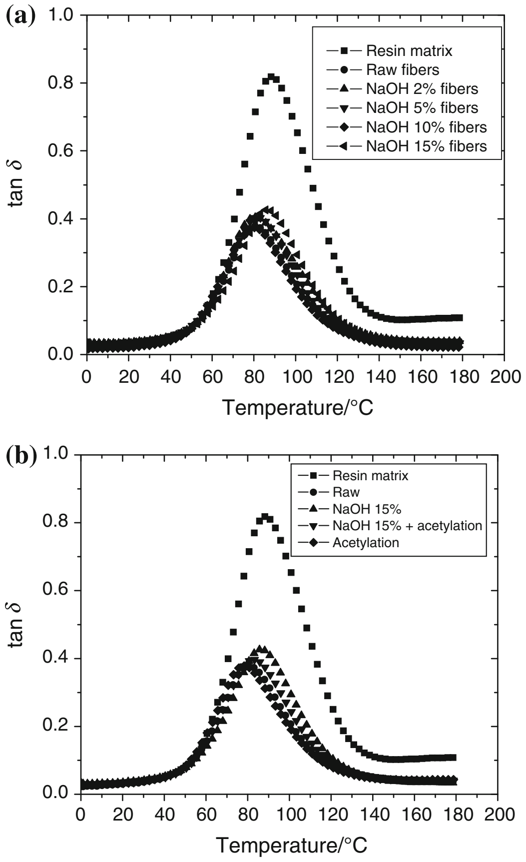

Fig. 2 Tan δ curves for the neat resin matrix and its piassava composites. **a** Comparison between the raw- and mercerized-fiber composites and **b** idem for the acetylated fibers

In respect to T_g one can see from Fig. 1 that fiber incorporation caused a statistically significant reduction of the values. This was, indeed, an unexpected result, since fiber incorporation into a polymeric matrix usually increases T_g values [19]. However, other authors also reported T_g reduction, attributing it to the presence of residual solvent at the composite [11] or to the incorporation of a volume fraction below a certain reinforcing threshold [14]. For banana fiber/polyester composites, for example, only the incorporation of 40% of fiber caused an increase of the T_g value [14]. These same authors point out, however, that incorporation of lignocellulosic fibers brings a much more strong reduction on the tan δ peak than changes on T_g values. The results obtained here do indicate that the fraction of fibers used was below the necessary threshold.

In order to verify if the fraction of fibers used was low, the critical volume fraction was estimated from the micromechanical analysis of composites [20]. Namely,

$$V_{\mathrm{crit}} = \frac{\sigma_{\mathrm{m}} - \sigma'_{\mathrm{m}}}{\sigma_{\mathrm{f}} - \sigma'_{\mathrm{m}}}, \qquad (1)$$

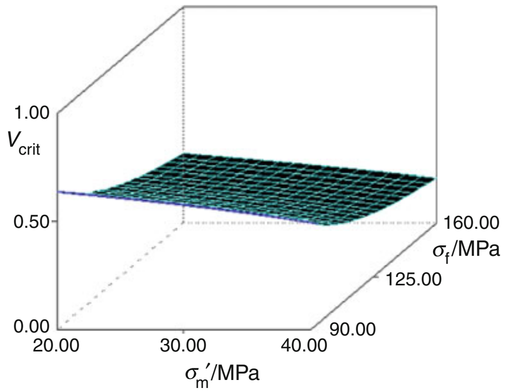

Fig. 3 Variation of V_{crit} with the tensile strength of the fiber (σ_{f}) and the stress at the matrix at the failure strain of the fibers (σ'_{m})

where σ_{m} is the tensile strength of the matrix, σ'_{m} is the stress at the matrix at the failure strain of the fibers, and σ_{f} is the tensile strength of the reinforcing fiber.

Figure 3 plots the variation of V_{crit} against σ'_{m} and σ_{f} for a model piassava–polyester composite. The bounds used at the model were $20 < \sigma'_{\mathrm{m}} < 40$ MPa (values extrapolated from the tensile stress–strain curve of the matrix and from the average tensile failure strain of the fibers) and $90 \leq \sigma_{\mathrm{f}} \leq 160$ MPa [21].

One can see that V_{crit} is high, and even using at the model the fibers with the higher value of strength (i.e., 160 MPa), V_{crit} has a value above 20%. On the average, one can expect that V_{crit} should fall between 30 and 40%. Therefore, the volume fraction used in this work was, indeed, below an average threshold. This evaluation also explains the difference found between the results presented in this work and those found for untreated piassava–polyester composites, where an increase of T_g was noticed [15], since those composites have a higher volume fraction of fibers, viz. 40%.

The discussion made above, freely compared volume and mass fractions, but one can be aware that this can be made only when the composite is made up from materials with similar densities, as is the case here. A discussion about this issue can be found elsewhere [22].

The variation of the storage modulus, E', is shown in Fig. 4. Table 1 lists the storage modulus at several different temperatures: 30, 160 °C, and at the temperatures where the loss modulus is maximum (E''_{max}) and where tan δ is maximum (at the tan δ peak). These two last temperatures were chosen because they are representative of the glass-transition temperature of the composite [23].

At 30 °C, and in respect to the composites with mercerized fibers (Fig. 4a), the statistical analysis of the results using the Fisher test (LSD) at a significance level of 5% showed that only the composites manufactured with the

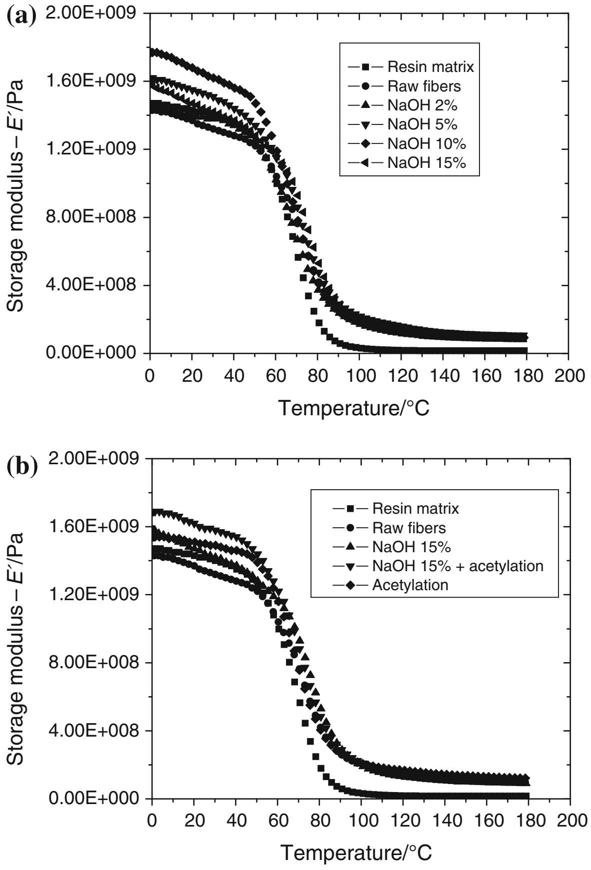

Fig. 4 Variation of the storage modulus. **a** Comparison between the raw and mercerized fiber composites and **b** idem for the acetylated fibers

10 wt% NaOH solution presented an increase of the storage modulus in relation to the value of the composites manufactured with untreated fibers. For the composite fabricated with fibers treated with the 15 wt% NaOH solution one could, in fact, observe a tendency of E' to decrease.

The increase of E' has been associated to the development of better fiber/matrix interfaces [4, 11, 17–19]. This result agrees with the topographic features observed at piassava fiber surface when mercerized. For the fibers treated with 10 wt% solution, the outer parenchymatic layer of the fibers is almost entirely removed, exposing an array of protrusions, and increasing fiber roughness and the contact area with the polymeric matrix [9]. Besides, the compactness of the fibers is also reduced, facilitating penetration of the liquid thermosetting matrix inside fiber fibrils. The small decrease observed when the fiber was treated with the 15 wt% NaOH solution can be attributed to an "over treatment" that degrades the fiber tensile strength. In fact, fibers treated with the 15 wt% solution showed the smaller Weibull modulus among the mercerized fibers, what can be associated to a heterogeneous distribution of strengths due to damages introduced by the treatment [21].

Acetylation also increased E' in relation to the value obtained when untreated fibers were used, Fig. 4b, indicating that the fiber/matrix interface was suitably modified. However, these treatments (acetylation and mercerization + acetylation) have caused strong modifications at the fiber surface, and a detrimental effect on the fiber tensile strength occurred, as identified by a sharp reduction of the Weibull modulus [21]. Therefore, it appears that the acetylation treatments performed have to be best tailored in respect to the duration of the treatment, to increase the fiber/matrix interface adhesion without affecting the fiber strength.

The same overall trend described above for the storage modulus at 30 °C, was observed when the storage modulus is analyzed at the temperature were E'' is maximum, Table 1. As this temperature is slight below the glass-transition temperature, and therefore in the elastic domain of the composites, one can say that for the elastic region, all performed treatments increased the fiber/matrix adhesion, since E' increased in respect to the value presented by the composite with untreated fibers.

E' values obtained at 160 °C and at the temperature where tan δ is maximum showed a different behavior in respect to that obtained below T_g. As shown in Table 1, the storage modulus of the composites at these two temperatures is far higher than that of the bare resin. Besides, E' did not vary with any of the treatments, when one compares the

Table 1 Values of the storage modulus, E'/MPa, at different temperatures

Material	30 °C	160 °C	$E''_{\max}$	Tan δ peak
Polyester	1,398 ± 240	16 ± 1	674 ± 77	69 ± 6
Raw piassava	1,320 ± 43	104 ± 21	767 ± 57	412 ± 110
Piassava NaOH 2%	1,380 ± 106	85 ± 12	707 ± 57	374 ± 61
Piassava NaOH 5%	1,507 ± 96	113 ± 11	869 ± 61	439 ± 37
Piassava NaOH 10%	1,621 ± 145	99 ± 3	909 ± 106	393 ± 54
Piassava NaOH 15%	1,419 ± 139	96 ± 9	789 ± 103	358 ± 55
Piassava acetylated	1,378 ± 116	118 ± 28	816 ± 54	445 ± 64
Piassava NaOH 15% + acetylation	1,506 ± 143	98 ± 12	859 ± 59	404 ± 101

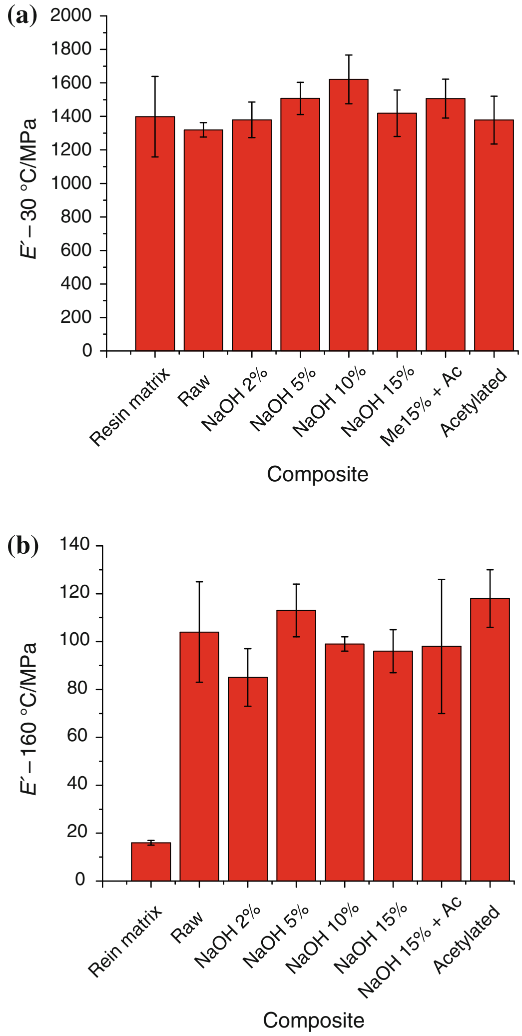

Fig. 5 Variation of E' below T_g (**a**) and above T_g (**b**)

composite with untreated fibers with the composites with treated fibers. Since at these temperatures the matrix is already at its viscous region, the overall behavior of the composites is being governed by the still elastic fibers, and E' is dependent on the volume fraction of fibers rather than on any fiber/matrix adhesion.

The strong difference of behavior between E' below and above T_g, for all composites, is highlighted at the bar plot in Fig. 5.

The values of the loss modulus, E'', are shown at Table 2. The behavior of E'' as a function of the treatments performed is shown in Fig. 6. The loss modulus represents the viscous component of the composites, and therefore is very sensible to molecular movements [14]. The statistical analysis of the results shows that there is a statistically significant difference for the composites treated with 5 and 10 wt% NaOH solution, and also for the acetylated and 15 wt% NaOH + acetylation treated fibers in respect to the value of the neat resin.

Table 2 Values of the loss modulus, E'', and the temperature at which it occurs

Material	E''/MPa	Temperature/°C
Polyester	230 ± 24.4	69.0 ± 1.8
Raw piassava	215 ± 16.9	70.7 ± 2.0
Piassava NaOH 2%	212 ± 14.7	69.3 ± 2.0
Piassava NaOH 5%	262 ± 11.8	70.4 ± 1.3
Piassava NaOH 10%	246 ± 19.1	68.1 ± 2.7
Piassava NaOH 15%	237 ± 28.2	74.2 ± 2.1
Piassava acetylated	245 ± 21.0	68.3 ± 0.5
Piassava NaOH 15% + acetylation	246 ± 8.6	70.2 ± 2.1

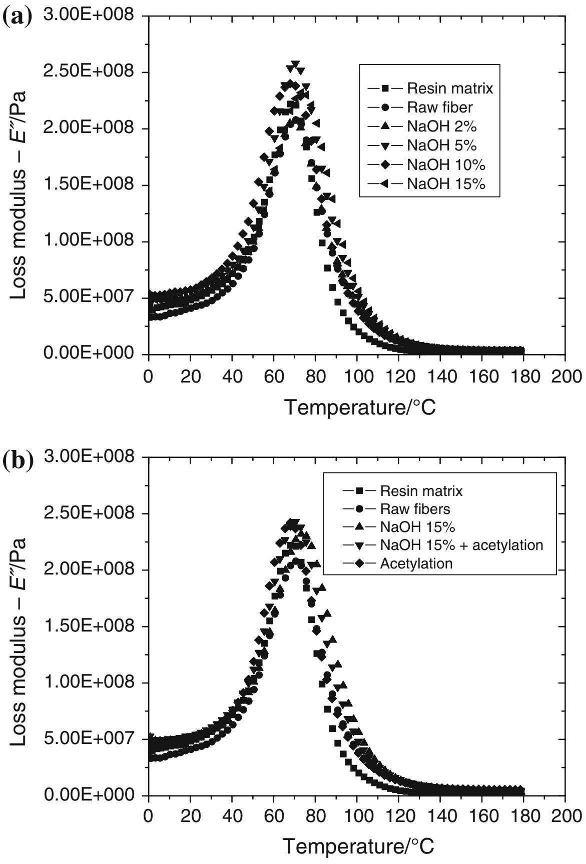

Fig. 6 Variation of E'' as a function of the fiber surface treatments. **a** Mercerized fibers and **b** acetylated fibers

The increase of the loss modulus peak was also observed for other lignocellulosic fiber-reinforced composites and was associated to a better fiber/matrix interfacial interaction [12]. However, this appears to be an open question, since the decrease of the loss modulus was also attributed to an increase of the fiber/matrix adhesion [18]. And, for thermoplastic matrix composites, variation of the loss modulus values was dependent on the relaxation peak under analysis. For jute/polyethylene composites E'' decreased at the γ relaxation peak and increased at the α

peak, with this behavior being associated to an increase of the fiber/matrix adhesion [4].

From the analysis of the results obtained for tan δ and for the storage modulus it can be inferred that, for the piassava/polyester composite here analyzed, the increase of the loss modulus is associated to an increase of the fiber/matrix adhesion.

Conclusions

The incorporation of piassava fibers produces a strong decrease of the tan δ peak height. This behavior was attributed to the presence of the fibers themselves, to macromolecular chain mobility restrictions at the neighborhood of the fibers and to the development of better fiber/matrix adhesion when treated fibers are used.

The decrease of the glass-transition temperature with the incorporation of fibers was associated to the use of a volume fraction below a threshold value defined by the critical volume fraction. This critical volume fraction was estimated to fall between 30 and 40% for piassava fibers and polyester matrix.

The effect of the treatments could be better evaluated by the variation caused on the storage modulus. At temperatures below T_g, at the elastic domain, the results show that the treatments increase the fiber/matrix adhesion. The effect caused by each particular treatment was, however, different, since some of the treatments also caused damage to the fiber surface, and thus a decrease of their tensile strength. Mercerization using a 10 wt% solution of NaOH produced the best results among the treatments analyzed here.

Above the glass-transition temperature the storage modulus value was primarily dependent on the volume fraction of fibers, and not on the surface treatments performed.

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