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DYNAMIC-MECHANICAL BEHAVIOR OF MALVA FIBER REINFORCED EPOXY MATRIX COMPOSITES[1]

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Abstract
Dynamic-mechanical (DMA) tests have not yet been conducted in malva aligned fiber reinforcing polymeric composites. In this work, the temperature dependence of the DMA parameters in epoxy matrix composites reinforced with up to 30% in volume of continuous and aligned malva fibers was investigated. These parameters were the storage and the loss modulus as well as the tangent delta. The investigation was conducted in the temperature interval from -10 to 180^{o}C using a Perking-Elmer DMA equipment operating in flexural mode. The results showed that the incorporation of malva fibers tends to increase the viscoelastic stiffness of the epoxy matrix. Sensible modifications in the glass transition temperature and the damping capacity of the structure were found with the amount of fiber in the composite. The molecular mobility of the epoxy matrix is affected by its interaction with the malva fibers.
Keywords: Malva fiber; Epoxy composite; Glass transition temperature.

COMPORTAMENTO DINÂMICO-MECÂNICO DE COMPÓSITOS EPOXÍDICOS REFORÇADOS COM FIBRAS DE MALVA

Resumo
Ensaios Dinâmico-mecânico (DMA) ainda não foram realizados em compósitos poliméricos usando como reforço as fibra de malva. Neste trabalho, foi investigada a dependência da temperatura e dos parâmetros de DMA, em matrizes epoxídicas reforçadas com até 30% em volume de fibras contínuas e alinhadas de malva. Estes parâmetros foram o módulo de armazenamento, o módulo de perda, assim como a tangente delta. O estudo do DMA, foi realizado no intervalo de temperatura de -10 a 180^{o}C utilizando um equipamento perking-Elmer operando no modo de flexão. Os resultados mostraram que a incorporação de fibras de malva, tende a aumentar a rigidez viscoelástica da matriz de epóxi. Sensíveis modificações foram encontrados na temperatura de transição vítrea, e na capacidade de amortecimento da estrutura com o aumento da quantidade de fibras incorporadas no compósito. A mobilidade molecular da matriz de epóxi é afetada por sua interação com as fibras de malva.
Palavras-chave: Fibra de Malva; Compósito de epóxi; Temperatura de transição vítrea.

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1 INTRODUCTION

Natural fibers with high amount of cellulose, also known as lignocellulosic fibers, have been used from primeval times of our civilization. In the last century, synthetic fibers such as nylon, carbon, aramid and glass fibers gained interest owing to superior strength and precise dimensional control. Natural fibers were then replaced by synthetics in many fields such as textiles, sports goods and appliances. In the past decades, however, environmental issues drawn, once again, the attention to lignocellulosic fibers as possible substitute for intensive energy-consuming and long term polluting synthetics, specially the glass fiber.[1] In particular, research works have disclosed the potential advantages associated with the use of lignocellulosic fibers as the reinforcing phase in polymer composites.[2,3] Among the advantages it is worth mentioning the renewability, recyclability, biodegradability and the fact that natural fibers are neutral with respect to CO_2 emissions responsible for global warming. Moreover, as compared to synthetics, lignocellulosic fibers present lower density and cost as well as reduced wear caused to the processing equipment.[4] On the other hand, in terms of composite reinforcement, hydrophilic lignocellulosic fibers present drawbacks such as weak adhesion to hydrophobic polymeric matrices in addition to dimensional limitations and non-uniform properties.[5]

Among the lignocellulosic fibers with significant strength to be considered as composite reinforcement, that extracted from the malva plant has not yet either been investigated or industrially applied. Table 1 presents basic characteristics and properties of the malva stem fibers.

Table 1. Properties of the malva fiber

Density (g/cm³)	Diameter (µm)	Cellulose (%)	Hemi cellulose (%)	Lignin (%)	MicroFibril Angle (degree)	Tensile strength (MPa)	Elastic Modulus (GPa)
1.04	30 - 450	60 - 65	6 - 8	5 – 10	12 - 11	300-800	1.5 - 5

The objective of this work was to investigate the temperature variation of the dynamic-mechanical parameters, by DMA test, of epoxy composites incorporated with up to 30% in volume fraction of continuous and aligned malva fibers.

2. EXPERIMENTAL PROCEDURE

For this study, the malva fiber (*Urena lobata, L*) extracted for the stem of the plant was used. The malva is a Liberian fiber occurring between the layer of the exchange involving the spinal central woody stem and the outer bark. It is grown in the Northern Brazil and is classified as a lignocellulosic fiber, together with the jute, kenaf, rosella, etc. Since the malva fiber is one of the less studied, DMA tests should disclose relevant results in terms of dynamic-mechanical properties and glass transition characteristics[6-9] as a function of temperature. Figure 1 illustrates the plant, as well as the appearance of malva fibers drying after the degumming process.

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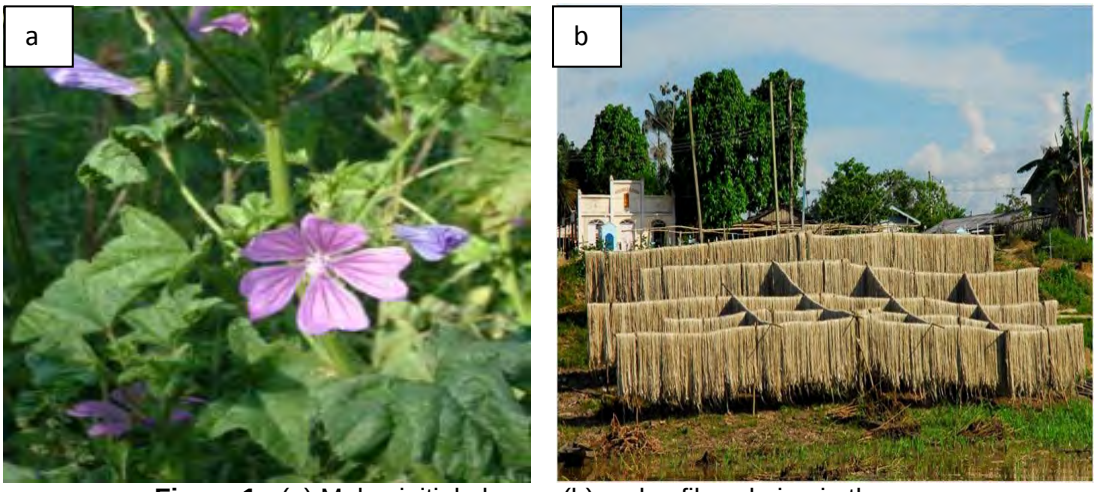

Figure 1 - (a) Malva initial phase; (b) malva fiber drying in the sun.

The equivalent diameter of the as-extracted malva fibers was measured with profile projector at 7 points along the length and then the fibers were turn 90 degrees and measured again. This procedure was conducted to ensure the correct mean diameter due to the cylindrical characteristic of the lignocellulosic fibers. The average equivalent diameter was found to be 0.02 mm, which is similar to those obtained for other natural fibers.[10,11]

Rectangular specimens, with 50x13x5 mm, were fabricated for the dynamic-mechanical, DMA, tests. Initially, the malva fibers were lay down inside silicone molds with different volume fraction and a still fluid epoxy resin, already mixed with proper percentage of fibers with diglycidyl ether of bisphenol A (DGEBA) with triethylene tetramina (TETA) as hardener, was then poured onto the molds to make composites with up to 30% in volume of malva fibers. These composite specimens were cured for 24 hours at room temperature. The aspect of the DMA specimens is shown in Figure 2.

Each specimen was tested in a Perkin-Elmer DMA equipment operating in a three points flexural mode at 1Hz of frequency and heating rate of 3°C/min under nitrogen. The storage modulus, E', loss modulus, E", and tangent delta, tan δ, curves were simultaneously registered from -10 to 180°C.

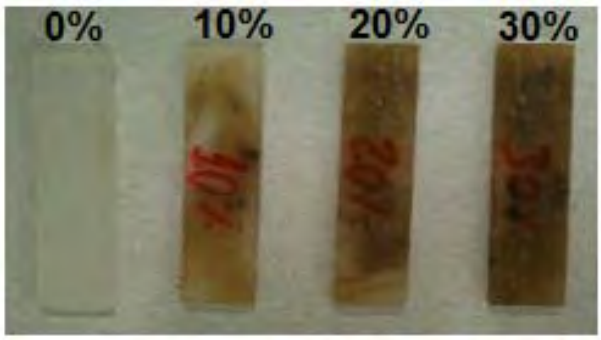

Figure 2. DMA specimens of epoxy matrix composites incorporated with different volume fraction of malva fiber.

3. RESULTS AND DISCUSSION

Figure 3 shows the DMA curves for the first run of a neat DGEBA/TETA epoxy (0% malva fiber) specimen. These curves served as comparative reference for the corresponding DMA curves after the second run under the same conditions of a

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3°C/min heating rate up to 180°C. Figure 5 presents DMA curves for the same neat epoxy specimen (0% malva fiber) after a second run. A comparison between the two set of DMA curves, first run in Figure 3 and second run in Figure 4, indicates similar temperatures associated with the peaks in the loss modulus, E" and tan δ. These peaks are usually attributed to the lower and upper limits of the glass transition temperature, T_g.[12,13]

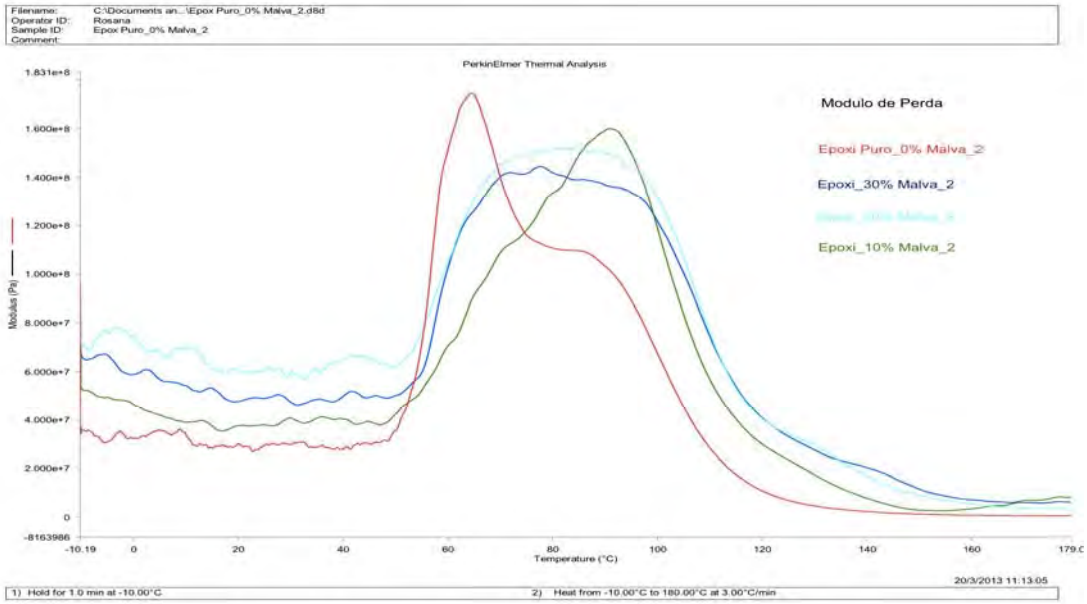

Figure 3 - DMA curves for the first run of neat DGEBA/TETA epoxy.

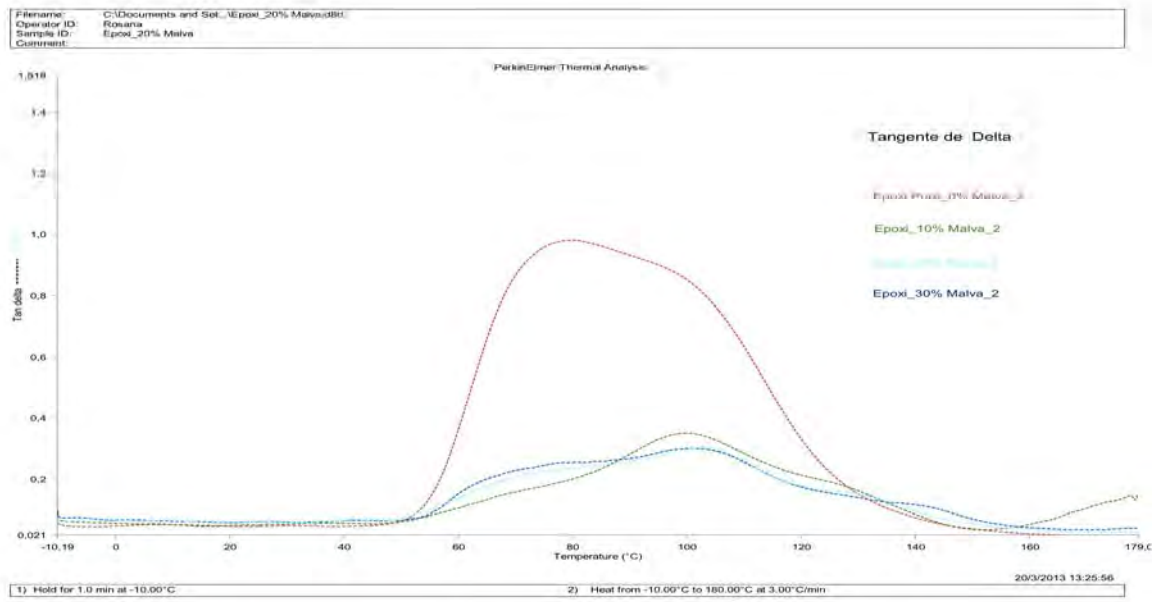

Figure 4 - DMA curves for the second run of neat DGEBA/TETA epoxy.

Another relevant aspect in comparing the curves of Figure 3 and 4 is the sensible increasing occurring in the storage modulus, E', after the second run. The value of E' is related to the viscoelastic stiffness of the material. It can be seen that the re-heating promoted by the second run not only increased the lower T_g but also the level of E'. The reason for this behavior can be explained by the epoxy curing process. As the temperature is increased in the first run, Figure 4, the TETA

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hardener continues to react with the epoxy chains, which promotes further reticulations that retard the amorphous transformation and increase the matrix stiffness.

Figure 5 shows the curves of E', E'' and tan δ for a 30% vol of long and aligned malva fibers incorporated in epoxy matrix. Similar results were found for epoxy composites with 10 and 20 % vol of continuous and aligned malva fibers. Due to space limitation, only the second run DMA results for 30% composite, Figure 5, are now discussed. The analysis of the curves in this figure starts with the comparison of the storage modulus, E', with the neat epoxy curves, as a function of the temperature. This analysis revealed that the incorporation of malva fibers significantly increases the value of E'. In fact at 54.76^{o}C, E' for pure epoxy is around 5.7 GPa and for 30% fiber composite it goes up to 7.3 GPa and the transition temperature to 48.04^{o}C. The relative difference is even higher at 200^{o}C. This means that the malva fibers increase the epoxy matrix capacity to support mechanical constraints with recoverable viscoelastic deformation.(8)

Additionally, the incorporation of malva fibers increases the temperature at which the composites end the abrupt decrease in E'. For the pure epoxy this occurs around 60^{o}C while for the 30% fibers composites at 85^{o}C. Since both the onset and end of this abrupt decrease are related to the process of matrix softening by amorphous transition, the malva fibers is apparently promoting amorphization to occur at slightly lower temperatures. In other words, the fibers turn more difficult the composite thermal softening.(7-11,14)

The second point of interest compares the variation of the loss modulus, E'', for the neat epoxy with the 30% volume fraction of malva fiber composite. The E'' curves in both Figures 4 and 5 show peaks with distinct amplitude and temperatures positions. These can be associated with the DMA α peak of structural relaxation, and attributed to the chain mobility of the polymeric matrix.

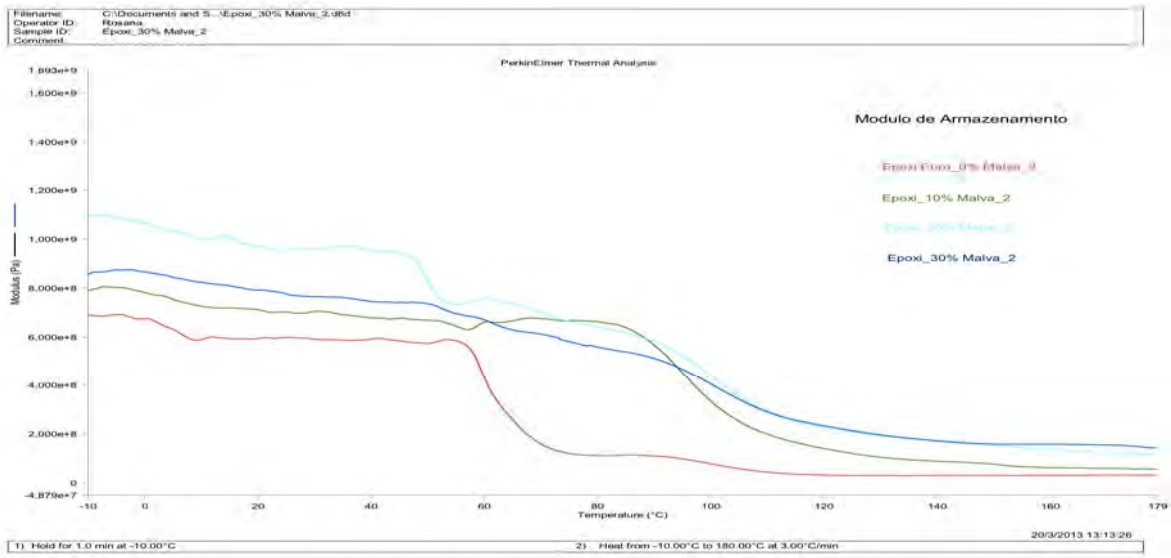

Figure 5 - DMA curves for the second run of epoxy composites incorporated with 30 % vol of malva fibers.

It should be noticed that the E'' for the 30% composite peaks are displaced to significantly higher temperatures in comparison to the pure epoxy peaks. This is possibly due to a restrain in the flexibility of the epoxy chains caused by the

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incorporation of malva fibers. Once again, this may be associated with a reduction in the chain flexibility.

The third point of analysis corresponds to the temperature dependence of tan δ for the composites investigated. By comparing both Fig. 4 and 5, it should be noticed tan δ peaks, associated with the upper temperature limit of the glass transition temperature, T_g, are markedly displaced to higher temperatures with 30% of malva fibers incorporation.

It can also be seen in Figure 4 and 5 that the composites present lower amplitude tan δ peaks as compared to the pure epoxy. This suggests, as also found with E'',, that the malva fibers reduces the mobility of the epoxy chains. Consequently, the transition to amorphous structure could be impaired by the fibers incorporation.

As a final remark, the interfacial strength could play a major role in the DMA behavior. It is suggested that malva fibers present a reasonable adherence to the matrix, which restrains the epoxy macromolecular mobility and then increases the glass transition temperature.

4. CONCLUSIONS

Epoxy composites present an increase in viscoelastic stiffness, measured by the DMA storage modulus, E', with the volume fraction of continuous and aligned malva fibers.

The onset of epoxy matrix softening in E' as well as the α peaks in the E'' and the upper T_g peaks in tan δ are slightly displaced toward higher temperature with incorporation of malva fibers.

It is suggested that these displacements are associated with a small reduction in the flexibility of the epoxy chains that not compromise of material performance. This could be a consequence of a reasonable interfacial resistance, which restrains the epoxy macromolecular mobility at the contact with the malva fibers.

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