THE DYNAMIC-MECHANICAL BEHAVIOR OF EPOXY MATRIX COMPOSITES REINFORCED WITH RAMIE FIBERS

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Abstract

The exceptional tensile strength of ramie fiber has motivated investigations on its application as reinforcement in polymeric composites. In this study the temperature variation of the dynamic-mechanical parameters of epoxy matrix composites incorporated with up to 30% in volume of ramie fiber were investigated by DMA tests. The parameters were the storage modulus, loss modulus and tangent delta. The investigation was conducted in the temperature from 20 to 200°C in an equipment operating in its flexural mode at 1 Hz under nitrogen. The results showed that the incorporation of ramie fiber tends to increase the viscoelastic stiffness of the epoxy matrix. It was also observed sensible changes in the glass transition temperature and in the structure damping capacity when the fraction of fiber is increased in the composite. These results indicate that the molecular mobility of the epoxy resin is affected by interaction with ramie fibers in the composite.

Introduction

Natural fibers obtained from vegetables with a relatively large content of cellulose have been used since the beginning of humankind for making basic items such as baskets, rope and fabrics. Well known examples of these lignocellulosic fibers are the cotton, flax jute and hemp, especially used for cloth fabrication. A less known fiber of this kind is that extracted from the stem of the ramie plant (*Boehmeria Nivea*), illustrated in Fig 1.

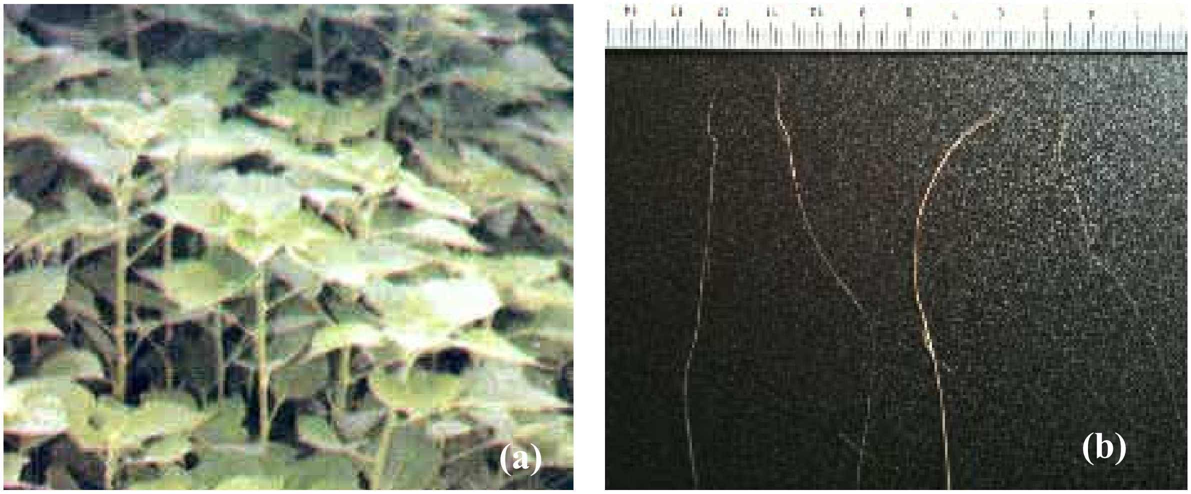

Figure 1. The ramie plant (a) and fibers (b) extracted from the stem.

In comparison with other natural fibers, ramie has an exceptional strength [1] but its textile application has continuously been replaced by synthetic fibers, mainly in clothes. An economical motivation to revive the culture of ramie could eventually occur by finding possible engineering applications such as composite reinforcement. In fact, in recent years there has been a growing interest in substituting natural fibers for synthetic ones like the glass fibers, as composites reinforcement [2-7].

In the particular case of the ramie fibers, only a limited amount of works [8-14] has been so far dedicated to investigation on its use as reinforcement phase of polymer composites. Among these works, one evaluated the dynamic-mechanical behavior of ramie fibers reinforced polyester matrix composites [12]. It was found that the viscoelastic stiffness of the matrix is increased with the amount of incorporated ramie fibers. To extend this investigation to another thermoset matrix, the present work investigated the temperature dependence of the dynamical-mechanical parameters of epoxy composites reinforced with ramie fibers.

Experimental Procedure

A lot of 5 kg of ramie fibers was commercially supplied by the Brazilian firm SISALSUL. The diameter and length were statistically characterized based, respectively, on profile projector and caliper measurement performed on 100 fibers randomly taken from the lot [13,14]. The fiber length varied from 40 to 400 mm with a mean value of 158 mm, as can be seen in the Fig 2. The fiber diameter varied from 0.003 to 0.20 mm with a mean value of 0,011mm, also shown in Fig 2. Before using, the ramie fibers were cleaned and dried at 60°C for 24 hours.

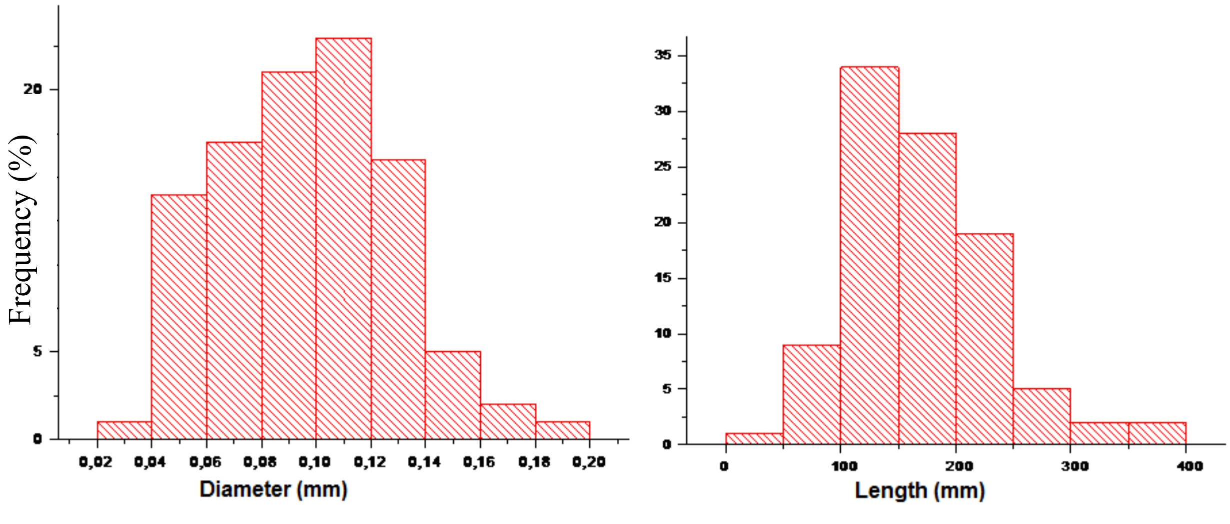

Figure 2. Statistical distribution of length and diameter of the lot of ramie fibers for this work.

Rectangular 50x13x5mm specimens were prepared for the dynamic-mechanical (DMA) tests. The preparation began by laying down continuous and aligned fibers, in separated volume fractions up to 30%, inside silicone molds. A still fluid epoxy resin type diglycidyl ether of the bisphenol-A (DGEBA), hardened with stoichiometric triethylene tetramine (TETA), was then placed onto the fibers. These composite specimens were cured at room temperature for 24 hours. Figure 3 illustrates the aspect of the DMA specimens used in the present work.

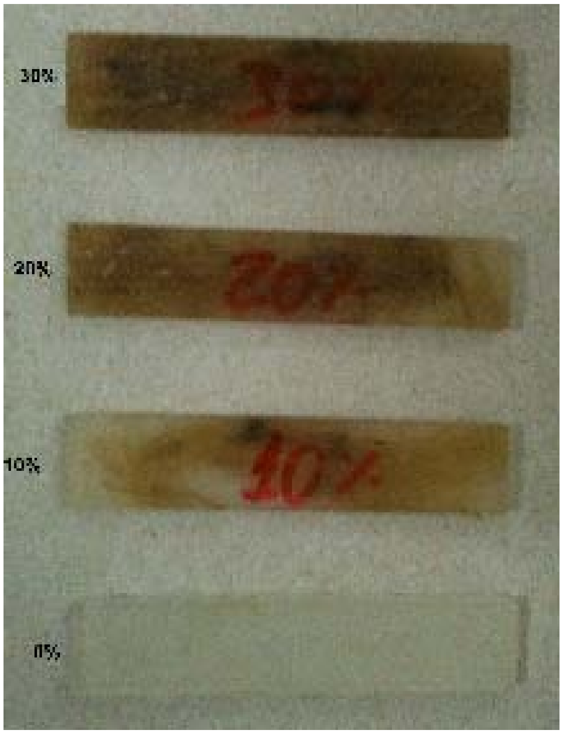

Figure 3. DMA specimens of DGEBA/TETA epoxy composites incorporated with different volume fractions of ramie fibers

Each composite specimen, including that for the pure DGEBA/TETA epoxy, was tested in a model Q 800 TA Instruments DMA equipment operating with its three points flexural mode at 1Hz of frequency, heating rate of 3^oC/min under nitrogen. Curves for the storage modulus (E'), loss modulus (E'') and tangent delta (tan δ) were simultaneously registered from 20 to 200^oC. After a first run, each specimen was reheated under the same condition to follow the effect of thermal treatment caused by the first continuous exposure until 200^oC.

Results and Discussion

Figures 4 and 5 present complete sets of DMA curves (E', E'' and tan δ) respectively for the pure epoxy and for 30% ramie fibers composites specimens both for a first, Fig. 4(a) and 5(a) as well as second, Fig. 4(b) and 5(b), heating. In these figures it should be noted that the first heating curves display multiple peaks in their DMA spectra. These multiple peaks are associated with macromolecular reactions characteristics of the epoxy polymerization curing process, which continue to occur with increasing temperature, usually above 100°C.

By contrast, the second heating under the same conditions, Figure 4 (b) and 5 (b), for samples already treated up to 200^oC in the first heating, no longer present multiple peaks. For this reason, only results corresponding to a second heating, i.e. completely cured samples, will be considered for discussion in the present work.

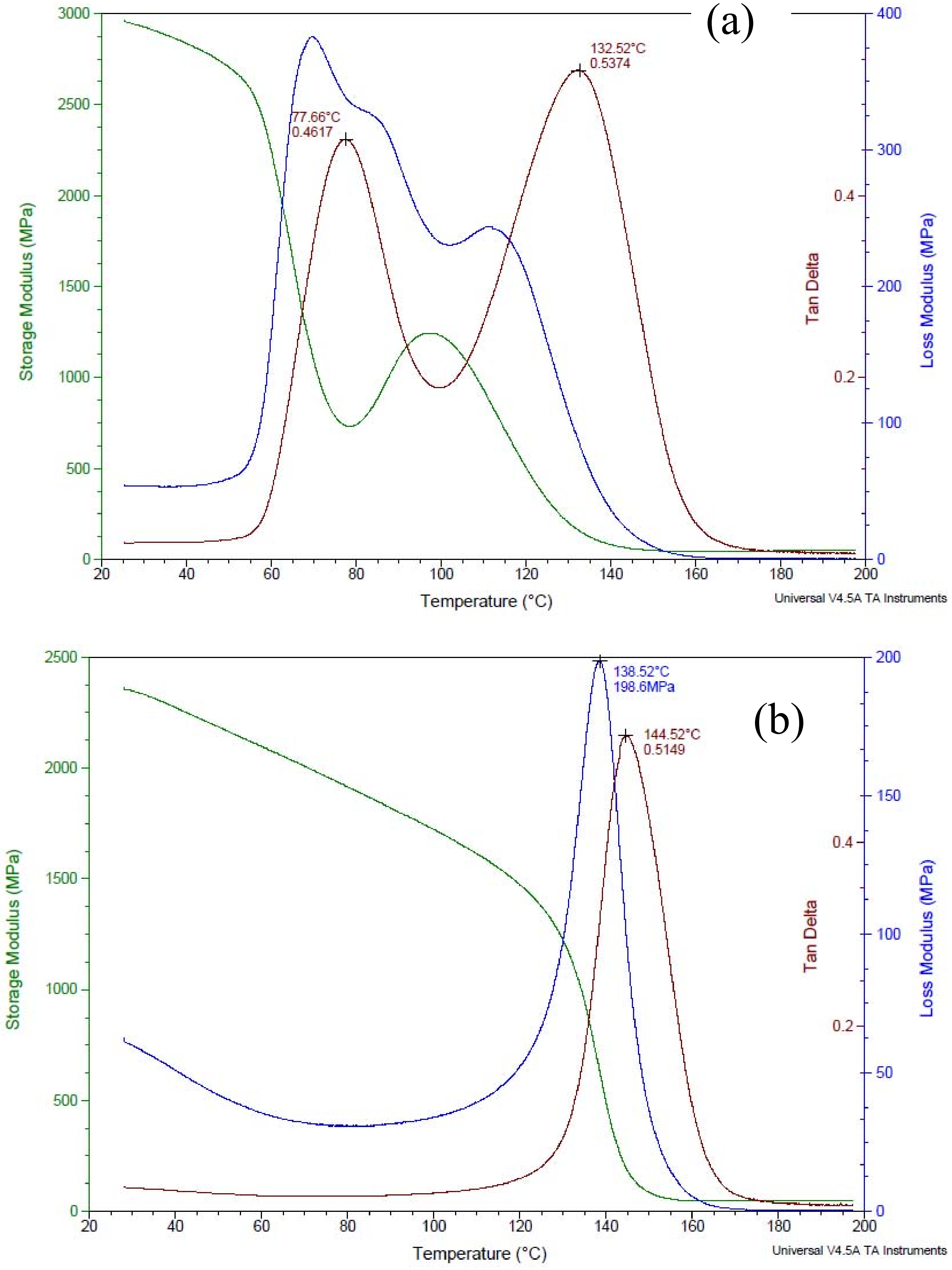

Figure 4. DMA E’, E’’ and tan δ curves for samples of pure epoxy (0% ramie fibers) (a) first test and (b) second test .

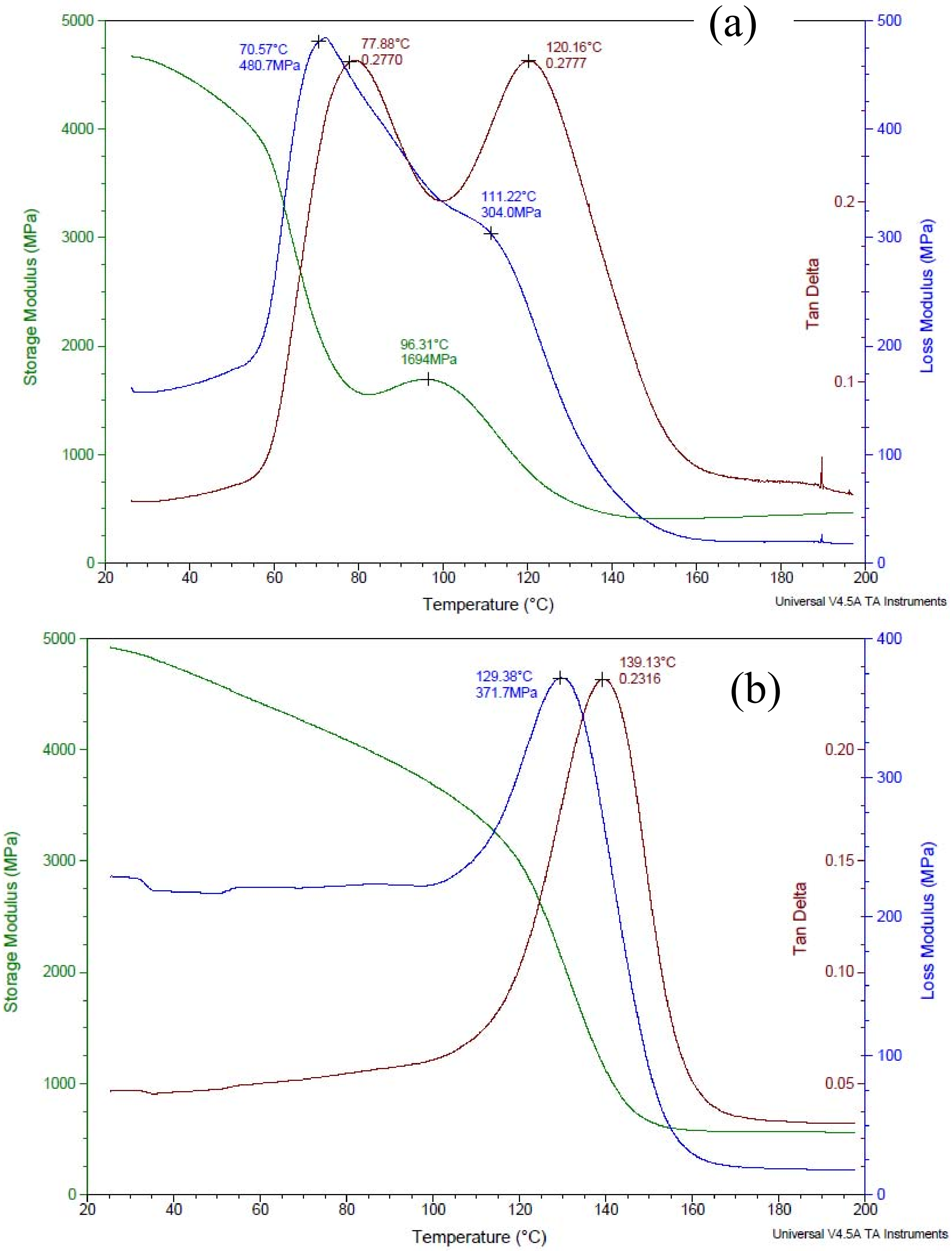

Figure 5. DMA E', E'' and tan δ curves for samples of epoxy with 30% ramie fibers: (c) first test and (d) second test

Figure 6 compares the variation of the storage modulus, E', for the different composites investigated, as a function of the temperature. The curves in this figure revealed that the incorporation of ramie fiber sensibly increase the value of E'. In fact at 25°C, E' for pure epoxy is around 2.3 GPa and for 30% fiber composite is around 4.9 GPa. This means that the ramie fibers increase the epoxy matrix capacity to support mechanical constraints with recoverable viscoelastic deformation. In particular the composite stiffness is substantially increased with ramie fiber incorporation.

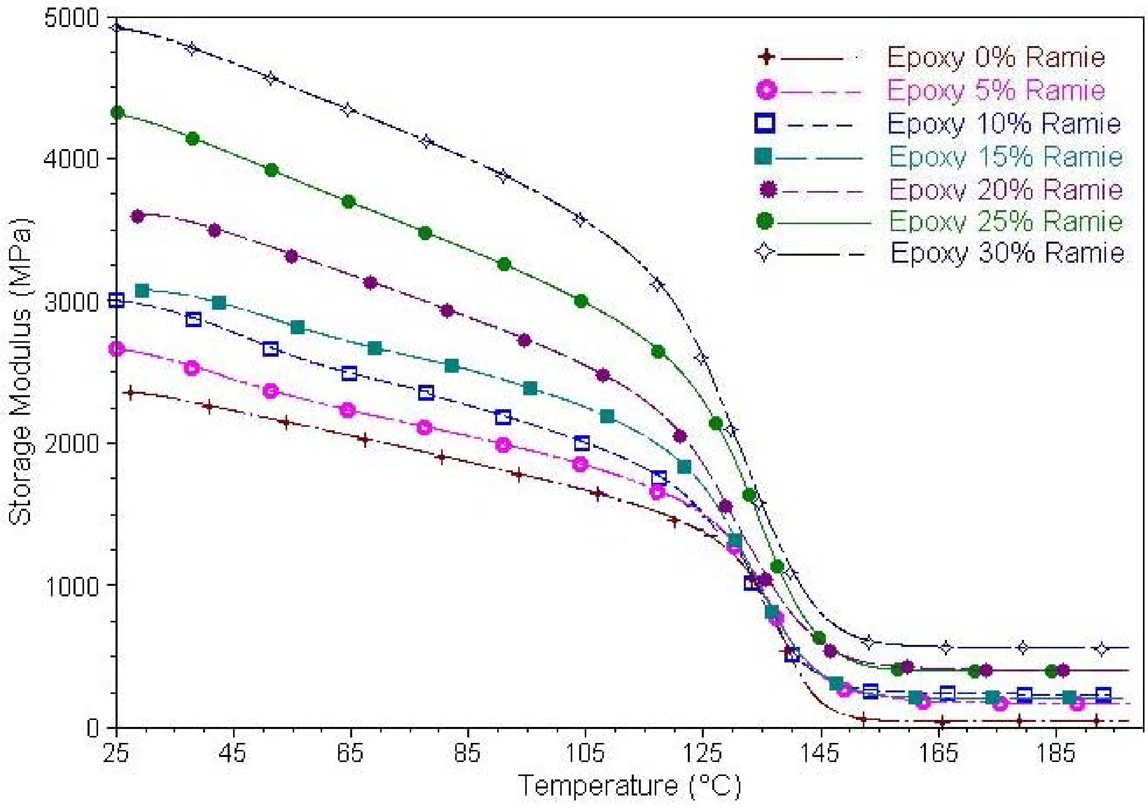

Figure 6. Variation of the storage modulus with the temperature for the pure epoxy and the composites reinforced with different volume fractions of ramie fibers.

Additionally, the incorporation of ramie fibers decreases the temperature at which the composites begin to suffer an abrupt decrease in E'. For the pure epoxy this occurs around 130°C while for the 30% fibers composites at 120°C. Since the onset of this abrupt decrease is related to the initial process of matrix softening by amorphous transition, the ramie fibers is apparently helping amorphization to occur at slightly lower temperatures. In other words, the ramie fibers facilitate the composite thermal softening.

It is suggested that the lignocellulosic fiber, having hydroxylic, carboxylic and phenolic groups, provides ample scope for an anchorage of epoxy resin segments since some of these groups could be present at the fiber surface. The cellulosic, hemicellulosic and lignin constituents in the natural fiber, which by itself is a natural composite, become integral parts of the amine cured epoxy network. As a consequence, the overall modification of the fiber/epoxy interface and of the interfacial region at the matrix is such that the fiber reinforced epoxy network composite, with 30% of volume fraction, shows nearly comparable values for loss modulus and glass transition temperature. This also reveals a reinforcing role of the ramie fibers in the form relatively values for the storage modulus.

For polyester matrix composites reinforced with ramie fibers, the inverse behavior occurs [11]. The reason for these distinct DMA results is still not clear. However, the possibility of different interfacial strengths in ramie fibers interaction with polyester [11] or epoxy (present work) could provide an explanation. The degree of fibers adhesion affects the mobility of the epoxy molecular chains and hence its temperature transition to an amorphous structure.

Figure 7 compares the variation of the loss modulus, E'', for the different composites investigated, as a function of the temperature. All E'' curves in this figure show peaks with distinct amplitude and temperatures positions. These can be associated with the α peak of structural relaxation. According to Mohanty et al [14], this relaxation is attributed to the chain mobility of the polymeric matrix.

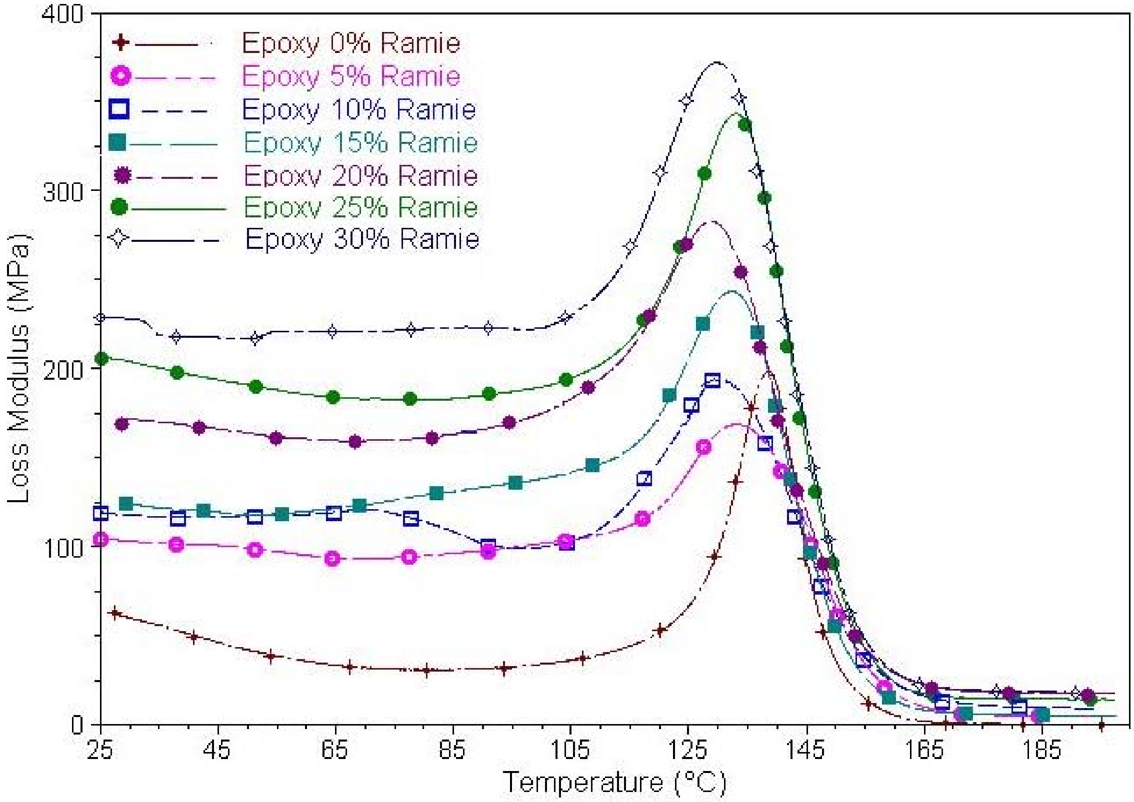

Figure 7. Variation of the loss modulus with the temperature for the pure epoxy and the composites reinforced with different volume fraction of ramie fibers.

It should be noticed in Fig. 7 that the all composite peaks are displaced to lower temperatures in comparation to the pure epoxi peaks. This is possibly due to an increase in the flexibility of the epoxy chains caused by the incorporation of ramie fibers. Once again, a low interfacial strength could permit the chains to move without much restriction at the contact with the ramie fibers. On the contrary, the peaks of E'' for the polyester composites [11] are displaced to higher temperatures indicating a reduction in the chain flexibility.

Figure 8 compares the temperature dependence of tan δ for the different composites investigated. In this figure one should notice the characteristic peaks associated with the upper temperature limit of the glass transition temperature, Tg. In fact, tan δ also indicates the composite damping capacity [14], which has a maximum value at the amorphous transition.

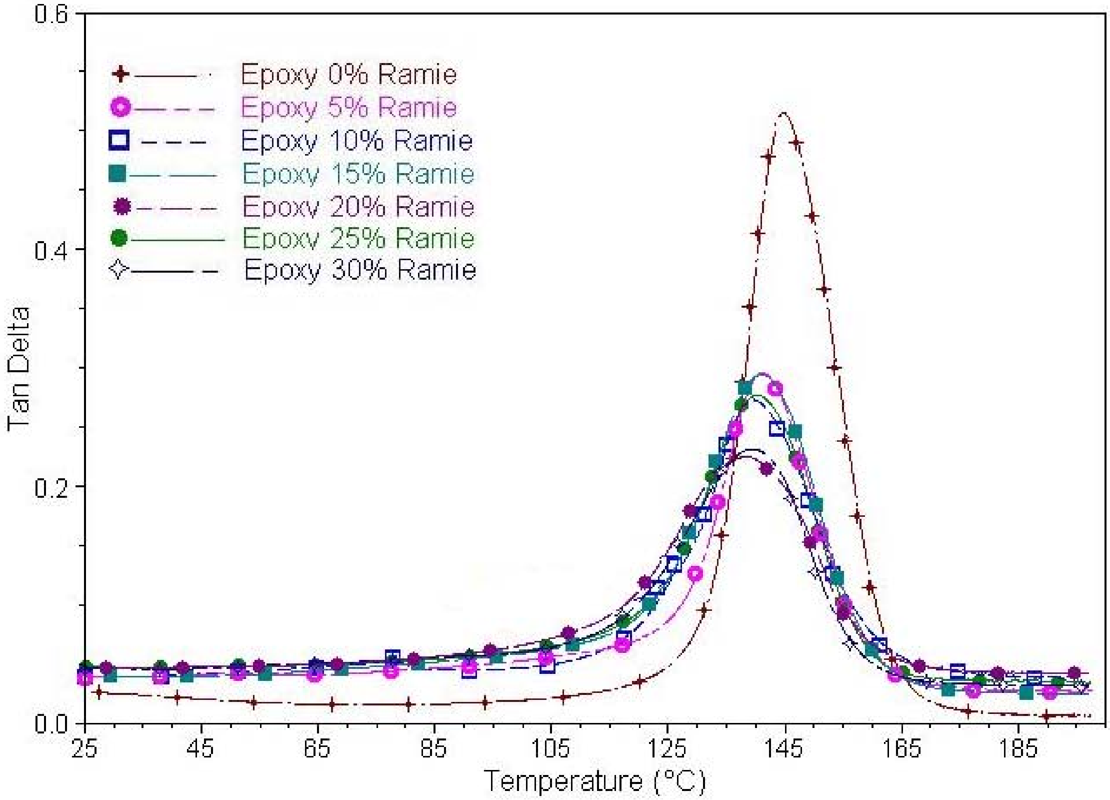

Figure 8. Temperature dependence of tan δ for the pure epoxy, and the composites reinforced with different volume fraction of ramie fibers.

In Fig. 8 it can also be seen that the composites present lower amplitude peaks as compared to the pure epoxy as the volume fraction of ramie fibers increases. Moreover, these peaks are displaced toward lower temperatures. This suggests, as also found with E'' in Fig 7, that the incorporation of ramie fibers increases the mobility of the epoxy chains. As a consequence, the transition from glassy to rubbery state could occur at lower temperature. An inverse situation was found for the polyester composites [11], in which the composite tan δ peaks are displaced toward higher temperatures indicating a reduction in the epoxy chain mobility.

Once again, the interfacial strength could play a major role in the explanation of this contradictory behavior. It is suggested that ramie fibers have a superior adherence to the polyester matrix but a weak adhesion to the epoxy matrix.

Conclusions

- DGEBA/TETA epoxy composites present an increase in viscoelastic stiffness, measured by the DMA storage modulus, E', with the volume fraction of continuous and aligned ramie fibers.
- The onset of epoxy matrix abrupt softening in E' as well as the α peaks in the E'' and the upper Tg peaks in tan δ are slightly displaced toward lower temperature with incorporation of ramie fibers.
- It is suggested that these displacements associated with an increase in the flexibility of the epoxy chains, could be a consequence of low interfacial strength permitting these chains to move without much restriction at the contact with the ramie fibers.

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