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THERMAL AND MECHANICAL CHARACTERISTICS OF POLYURETHANE/CURAUA FIBER COMPOSITES

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Polyurethane composites reinforced with curaua fiber at 5, 10 and 20% mass/mass proportions were prepared by using the conventional melt-mixing method. The influence of curaua fibers on the thermal behavior and polymer cohesiveness in polyurethane matrix was evaluated by dynamic mechanical thermal analysis (DMTA) and by differential scanning calorimetry (DSC). This specific interaction between the fibers and the hard segment domain was influenced by the behavior of the storage modulus *E*' and the loss modulus *E*" curves. The polyurethane PU80 is much stiffer and resistant than the other composites at low temperatures up to 70°C. All samples were thermoplastic and presented a rubbery plateau over a wide temperature range above the glass transition temperature and a thermoplastic flow around 170°C.

Keywords: *curaua fibers, DSC, dynamical mechanical analysis, polyurethane*

Introduction

The mechanical characteristics of a fiber-reinforced composite depend not only on the properties of the fiber and the polymer matrix but also on the degree to which an applied load is transmitted to the fibers by the matrix phase. The extent of the load transmittance is controlled by the magnitude of the interfacial bond between the fiber and the matrix phases. In addition to the geometry, the distribution and the orientation effects of the fiber, the interfacial bond responds for the major fiber-matrix strength, which it sustains the composite cohesiveness [1, 2].

The knowledge and the understanding of the dependence of the composites mechanical behavior on the relative amounts the properties and the interplay of the constituents' phases will make it possible to design materials having properties combinations that are better than those found in polymeric materials, specifically biodegradable elastomeric materials with high stiffness and tear resistance [2, 3].

Thermoplastic polyurethanes have a wide range of technological applications due to the commercial availability of diisocyanates and alkanediols of diversified chemical structures. In addition, along with the wide range of physical properties attainable by relative composition variation it allows the syntheses of elastomeric to flexible plastic urethane materials [4, 5].

It is well established that polyurethanes present a microphase-separated structure comprising soft and hard segments. The soft segments are usually oligomers with long methylene, oxy-methylene or other aliphatic sequences, while the hard segments are urethane sequences brought together by reaction of short alkanediol with diisocyanate. The high polar nature of the urethane linkages is responsible for the thermodynamic micro-heterogeneous phase separation and often in combination with the crystallization of either or both segments leads to the formation of hard and soft domains, which in turn regulates its physical and mechanical behavior [5, 6].

The conventional method which have so far been applied to increase polyurethane' modulus of elasticity bring about certain disadvantages. The increase of modulus through formation of crystalline domain leads to a trade-off in elongation and impact strength and usually products with greater brittleness are obtained. The incorporation of fibers as reinforcement in multiblock segmented polyurethane elastomer can improve the modulus and at the same time it maintains the impact of resistance [6].

The fiber-reinforced composites are among the most important materials characterized by high specific strength and/or specific modulus (strength and stiffness on a mass basis). Fiber-reinforced composites with exceptionally high specific strengths and modulus have been prepared by using low-density fiber materials. Curaua fiber, *Ananas erectifolius* is a hydrophilous species from the Brazilian Amazon region. The curaua fruit is similar to the pineapple however the farmers' interest is in its fibers. The curaua fruit leaves are hard, erect and have flat surfaces. It contains 70.7% of cellulose and 11.1% of lignin [2, 7, 8].

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The dynamic mechanical thermal analysis of polymeric materials has been applied in the technological development of materials with higher mechanical stability, thermal and sound isolation. Furthermore, in combination with the damping energy determination associated to molecular motions displayed by a polymer in solid-state it can be applied to the study of morphology in multiphase systems [9].

Although most of published literature [10–14] interprets the tanδ height and its temperature spread in a dynamic-mechanical analysis as the damping capacity, this interpretation has received some criticism and the application of the integration of the area under the linear loss modulus as a function of temperature curves has been suggested as a quantitative measurement of the damping capacity of the material by several authors [15–18], supported by the fact that the loss modulus E'' is directly proportional to the heat dissipated per cycle of dynamic deformation.

Representative probable chemical structure of the polyurethane and the cellulose curaua fiber studied here are displayed in Fig. 1.

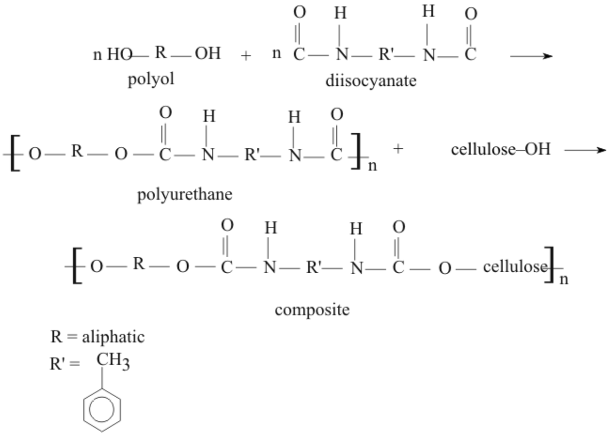

Fig. 1 Probable reaction between the isocyanate groups of the polyurethane and cellulosic curaua fiber

Experimental

Materials

The commercial polyurethane was produced by the reaction of an isocyanate (MDI – methylene diphenyl 4,4'-diisocyanate) and a poly(ester ether)polyol. This commercial polyurethane pellets were supplied by Cofade, Sociedade Fabricadora de Elastômeros, Bahia, Brazil.

The curaua fiber was supplied by FCA – Universidade Estadual Paulista. The fiber was dried in air at 100°C for 24 h and then it was mechanically milled in a knife mill with the length of fiber in the range of 6 to 20 mm.

Methods

Composites preparation

The composites of polyurethane pellets and curaua fiber with 5, 10 and 20% (*m*/*m*) were prepared by the melt-mixing method in a Haake Rheomix 600 rheometer at 100°C, 60 rpm for 15 min.

Curing of the samples

The samples were cured in a Carver C press at 130°C and 10000 lb in^{-2} during 15 min, as according to the ASTM D1708-93.

Characterization by DMTA

A Rheometrics Scientific DMTA V was used to perform tension tests. Each sample was cut to a small rectangular film within the following range of dimensions: length of 23 to 26 mm, width of 2 to 3 mm and thickness of 0.4 to 0.6 mm. A strain limit of 0.1% and a frequency of 1 Hz were applied in the temperature range from –80 to 200°C at a heating rate of 2°C min^{-1}.

Characterization by DSC

Mettler-Toledo Star System model DSC 822 in the temperature range of –40 to 200°C in flowing N_2 atmosphere.

Results and discussion

The DMTA results of curing samples are shown in Tables 1–2 and Figs 2–4. The DMTA tanδ spectrum of the original polyurethane (PU100) showed one main relaxation peak attributed to the flexible polyol segment rotation around –17.1°C and is related to the glass transition. Compared to the original thermoplastic polyurethane, the tanδ transition temperature of the composites increased with the addition of the dispersed fiber indicating a stronger interaction of fiber with the hard domain of the polyurethane. Indeed, consequential increase in the segregation of the flexible segment domain, which similar results have been reported previously in polyurethane's interpenetrating networks [19, 20]. The interfacial interaction between the curaua fibers and the hard segment of the polyurethane is believed to occur through hydrogen bonds among hydroxyl groups of cellulose glucose units and carboxyl groups of polyurethane.

The interaction between the fibers and the hard segment domain was also observed by the behavior of the storage modulus E' and the loss modulus E'' curves. The polyurethane PU 80 is much stiffer and resistant than the other composites in the whole range

Table 1 Damping and transition temperature of composites and polyurethane

Composite	Temp. at tanδ peak/°C	tanδ at peak	Damping (*E*" temp)/GPa K
PU100 (1)	–17.1	0.48	4.2
PU95 (2)	–18.2	0.38	3.5
PU90 (3)	–17.9	0.35	3.0
PU80 (4)	–17.6	0.28	4.7

Table 2 Storage modulus of composites and polyurethane at different temperatures

	E'/GPa at –60°C	*E*'/GPa at –18°C	*E*'/MPa at 20°C
PU 100	2.08	0.2	23.6
PU 95	1.85	0.2	36.5
PU 90	1.44	0.2	36.8
PU 80	2.34	0.4	80.7

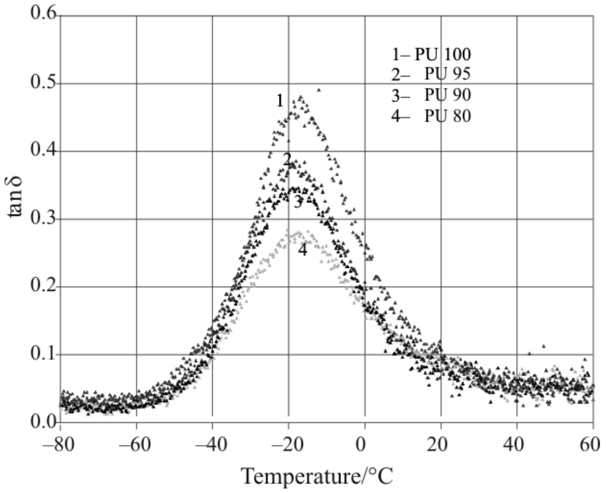

Fig. 2 Tanδ *vs.* temperature for PU commercial and PU composites with curaua

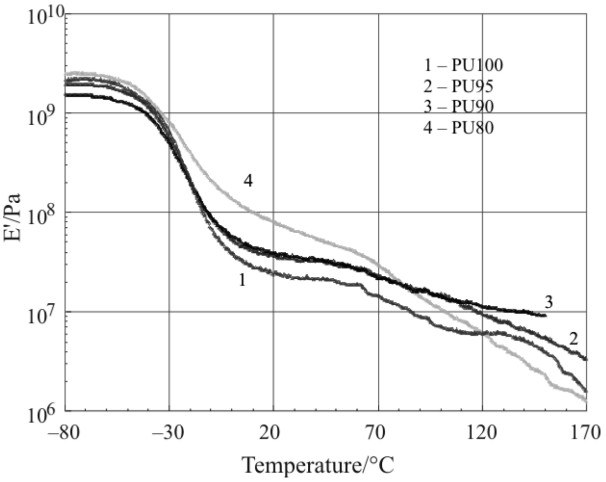

Fig. 3 Storage modulus *E*', for PU commercial and PU composites with curaua

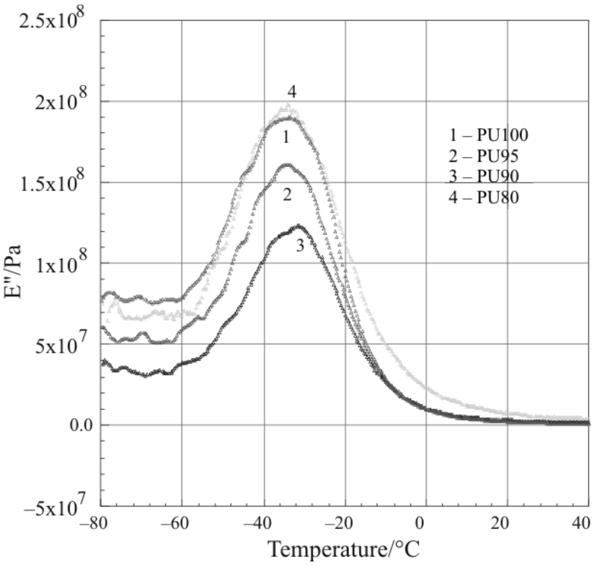

Fig. 4 Loss modulus *E*", for PU commercial and PU composites with curaua

of temperature, as expected. All samples were thermoplastic and presented a rubbery plateau over a wide temperature range above glass transition and the thermoplastic flow was observed around 170°C.

Damping is the most sensitive indicator of all kinds of molecular motions displayed by a polymer in solid-state [9]. The loss modulus *E*" is directly proportional to the heat dissipated per cycle. The area under the linear loss modulus *vs.* temperature curves is a quantitative measurement of the damping behavior [18], which can be correlated to many transitions, relaxation processes, structural heterogeneities, the morphology of multiphase and the crosslinked systems. The linear loss modulus areas of the flexible phase of polyurethane were determined (Table 1 and Fig. 4) and a correlation was established between the linear loss modulus areas and the curaua fiber content of each composite, resulting in the plot shown in Fig. 5. The solid line represents the calculated values of damping correspondent to the amount of polyurethane in each sample and it is displayed to show the deviations presented by the composites with curaua.

A linear decrease in the damping, which is the area under the linear *E*" *vs.* temperature, was first observed until 10% of fiber content. Then, a significant increase was observed for the PU 80 even if a reduction of the relative concentration of polyurethane took place and the observed damping was much higher than the original polyurethane. The increase of the damping in the polyurethane PU 80 was attributed to an increase in the interphase volume of the flexible segment, which is formed by the hard segments bonded to the fibers and also to the heat dissipation due to the molecular motion into the fiber surface.

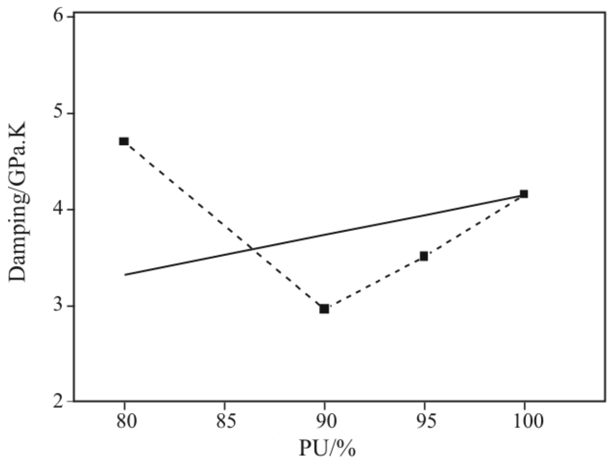

Fig. 5 PU concentration (%) *vs.* damping (GPa K)

The storage modulus of the polyurethane/curaua composites presented a complex behavior with temperature although a reinforcement effect was observed in all samples in the rubbery plateau from 0 to 70°C. The mechanical behavior of these composites is ruled by the morphology of the matrix formed by the polyurethane as previously observed in other polyurethane systems by DMTA and the scanning electron microscopy [21–25]. As a matter of fact polyurethane is a multiphase polymer that can be described as comprised by a flexible amorphous major component composed by polyol segment in which crystallites and hard segments (urethane segments) are imbedded. The distribution and size domain of each phase might be disturbed by the presence of the curaua fibers through hydrogen bonds and by the induced chain orientation effect.

In Table 2 the storage modulus data in function of the temperature are summarized. In the glassy solid-state at –60°C only PU 80 has shown a reinforcement effect. Probably, the introduction of 5 to 10% of curaua fiber increased the entropy in the mixture and consequently it caused a reduction of composite matrix cohesion through loss in total hydrogen bonding and decreases of the size of the hard segments domains. At 20% level of reinforcement a compensation of matrix chain looseness was observed and an increase in the storage modulus is observed in the temperature range below the hard segments softening. However, in the range from 70 to 120°C hard segment domains are continuously reduced until significant viscous flow came into play at even higher temperatures.

Compared to other composites and to the neat PU in spite of its higher stiffness in the whole temperature range from –100 to 70°C PU 80 started to show thermoplastic flow at a lower temperature and this behavior confirm our explanation about the interplay of morphology and polyurethane cohesiveness disturbance by curaua fibers. At –18°C the mechanical properties of these composites are dominated by chain motions and composites PU 90 and PU 95 showed together the same storage modulus observed for neat polyurethane while PU 80 was much rigid.

The influence of curaua fibers on the thermal behavior and polymer cohesiveness in polyurethane matrix was also observed by DSC for samples before curing. Figure 6 shows a comparison of the first and the second run of DSC curves for PU 80 composite. The first curve showed a large endothermic event at about 80°C suggesting gel formation assisted melting of crystallites during the heating of the curaua fiber. Three temperatures of glass transition (T_g) could be observed: the first at –30°C, the second at 153.2°C, and the third at 176.1°C, since the material exhibits flexible (polyurethane) and rigid segments (polyurethane and curaua fiber). Overall, in DSC the sample is first heated to erase the previous thermal history, however, the second run of curve did not show clearly on the events but it suggested changes of the base- line.

Figure 7a–c, exhibits the morphology by optical micrograph of PU commercial and composites with curaua fiber (5, 10 and 20% *m*/*m*). Due to the length of the fillers be different, a heterogeneous and aleatoric distribution of the fiber in the polymeric matrix could be observed.

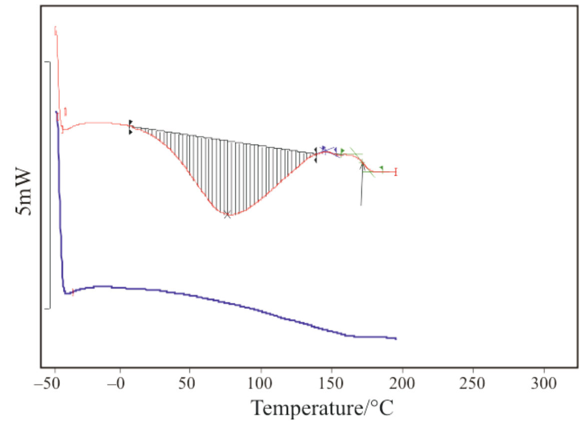

Fig. 6 First and second runs of DSC curves for PU 80 composite before curing

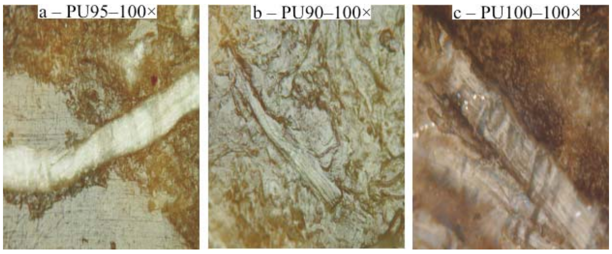

Fig. 7 Optical micrograph of a – PU commercial composites with curaua fiber a – 5, b – 10 and c – 20% *m*/*m*

Conclusions

Polyurethane composites were degraded in two stages and showed three glass transition temperatures since the material exhibits flexible and rigid segments. The PU 80 composite showed higher storage modulus and loss modulus than the PU commercial, which suggested that the PU 80 has the better interface fiber/polymeric matrix. The influence of curaua fibers on the thermal behavior and polymer cohesiveness in polyurethane matrix was also observed by DSC analysis.

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