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Novel soy oil based polyurethane composites: Fabrication and dynamic mechanical properties evaluation

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Recent years have seen a growing interest in the development of bio-based products that can reduce the widespread dependence on fossil fuels. Indeed, the inevitable depletion of petroleum reserves with the attending high cost have prompted researchers to develop polymers from cheap and renewable resources.

Polyurethanes (PURs) are usually made from petroleum based polyols and isocyanates and have widespread applications in automotive parts, coatings, sealants, adhesives and other infrastructure uses [1, 2]. Today, polyurethanes are finding a growing interest for applications as composites due to the increasing demand for lightweight, durable and cost effective compounds for sectors such as the automotive market [3]. Owing to the versatility of polyurethane chemistry, a broad range of properties and applications are possible for reinforced composites, such as seat frames, sun shades, door panels, package trays and truck box panels. Adhesion between the polyurethane matrix and the fiber surface is also an important factor in the improvement of mechanical performances [4–6].

Polyurethanes based on renewable resources can be prepared by reacting a polyol made from a plant oil and an isocyanate. Indeed, castor oil, a hydroxyl rich triglyceride and other plant oils have been used for making polyol functional compounds [7–10]. Among the possible renewable resources useful to make a polyol, soybean oil is of particular interest because of its abundance (ca. 70 millions metric tons/year in USA) and low price (ca. 0.1 US $/kg).

In this study, we investigated the dynamical mechanical properties of polyurethane composites made from soybean phosphate ester polyol (SOPEP). This polyol (ATOFINA Chemicals, Inc. Blooming Prairie, MN) is made by acid hydrolysis of epoxidized soybean oil. Polyurethane thermosets can be prepared from SOPEP and polymeric methylene diphenyl isocyanate (pMDI). Reinforcement of such polyurethane with fibers, natural or synthetic, should improve mechanical properties if good fiber-matrix adhesion is achieved. We compare the mechanical properties of composites made from this SOPEP based polyurethane matrix with a lignocellulosic fiber, i.e., hemp, as well as with E-glass fiber as reinforcements.

The composites were prepared by first mixing SOPEP and the pMDI. The hydroxyl number of the polyol was 139 mg KOH/g and the isocyanate index used was 130. The mixture was stirred for 2 min and then impregnated into both sides of a fiber mat (140 × 178 mm), which was previously dried overnight at 80 °C in a vacuum oven. The pure hemp non woven mat was received from Flaxcraft Inc., Cresskill, NJ and the chopped E-glass fiber nonwoven mat from Kemlite Inc. Joliet, IL. The prepregged mats were maintained under vacuum at room temperature to remove trapped gas (ca. 5 min) and then compression molded for 10 min at 110 °C in a Carver® laboratory press to a thickness of 2.5 mm. After postcuring at 130 °C for 2 h in an air oven, neat SOPEP based polyurethane resin and its composites containing 20 wt% of fiber were obtained.

Densities of the neat polyurethane and its composites with hemp and E-glass fibers were determined by the classical equation, i.e., the ratio of mass to volume. With incorporation of hemp fiber, the average density slightly increases from 1130 ± 10 (neat resin) to 1150 ± 10 kg/m^3 but the error bars overlap. In the case of reinforcement with E-glass, the average density is clearly higher, i.e., 1240 ± 50 kg/m^3, due to the higher density of glass compared to hemp (Table I).

Dynamic mechanical analysis (DMA) of these soybean based polyurethanes was performed with a DMA

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TABLE I Comparative properties and cost of E-glass and hemp fibers

Fiber type	Density (kg/m^3)	E-modulus (GPa)	Cost (US $/kg)
E-glass	2600	73	0.4
Hemp	1500	70	0.13

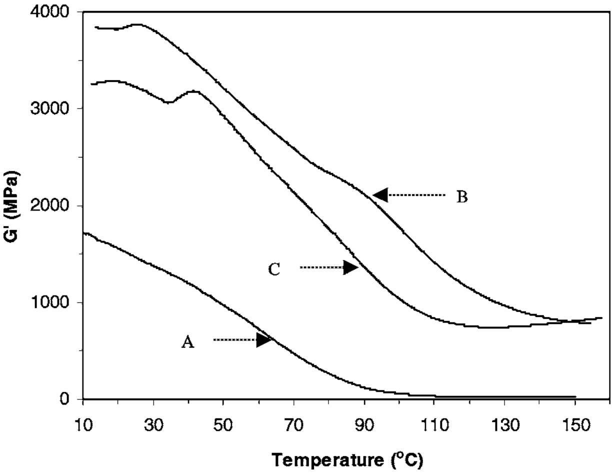

Figure 1 Temperature dependence of the storage modulus (G') of SOPEP based polyurethane composites: (A) neat polyurethane, (B) hemp reinforced (20 wt%) and (C) glass reinforced (20 wt%).

2980 TA Instruments. The samples were tested in a three-point bending mode at fixed frequency (1 Hz) with a heating rate of 4 °C/min. A typical plot of the temperature dependence of the storage modulus (G') of the SOPEP based polyurethane and its composites are shown in Fig. 1. The value of G' was almost constant at low temperature (glassy state) before dropping in the region between 20 and 90 °C. As the temperature further increased, G' levels off in the rubbery state. The presence of a region where the storage modulus remains relatively constant indicates that a stable crosslinked network exists. The patterns of the curves of temperature dependence for the composite specimens are similar in nature to the neat polyurethane. However, over the temperature range studied, G' is substantially increased in the composite due to fiber loading and stress transfer at the matrix-fiber interface, therefore increasing the stiffness of the overall material.

A comparison of the average G' values measured at 30 °C is shown in Fig. 2 together with the specific G' (G'/specific gravity). At this temperature, G' increased from an average of 1200 MPa (SOPEP based polyurethane) to 2900 MPa in the 20 wt% hemp reinforced polyurethane and 2800 MPa when 20 wt% of E-glass is added. These values represent respective improvements of 142 and 133% compared to the neat SOPEP based polyurethane. It bears mentioning that the error bars overlap thus indicating that the specific G' may be the same in both composites.

The glass transition temperatures (T_g) were determined from the peak of the tan delta (ratio of loss modulus, G'', to storage modulus, G') curves. Only one T_g (95.6 ± 1.3 °C) was observed for the polyurethane suggesting a single phase system. Upon fiber loading, the T_g of this biobased polyurethane shifted to higher values and was determined to be 110.6 ± 1 °C for the hemp-reinforced composite while no increase was noticed when E-glass was used as reinforcement (95.6 ± 0.2 °C). The increase in T_g for the hemp polyurethane composites suggests a restricted mobility of polymer chains in the network. This may be the result of the increased number of hydroxyl groups available on the hemp fiber. Those groups react with isocyanate and result in immobilization of polyurethane molecules on fibers. The intensity of tan delta decreases in composites due to the net volume reduction of the polyurethane resin but also as a result of the lower chain mobility (Fig. 3).

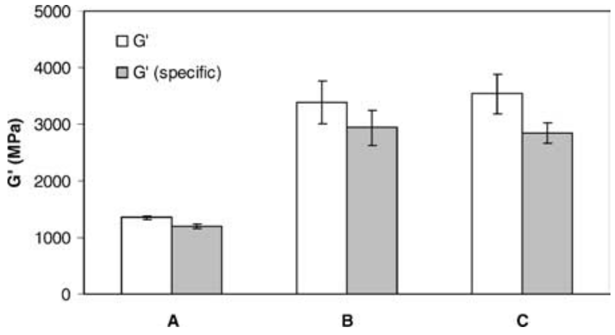

Figure 2 Comparison of the storage modulus and the specific storage modulus (calculated using the specific gravity) of SOPEP based polyurethanes composites: (A) neat polyurethane, (B) hemp reinforced (20 wt%) and (C) glass reinforced (20 wt%).

Good dispersion, efficient wetting and good adhesion at the fiber-matrix interface are requirements for composites with improved mechanical properties [11]. Environmental scanning electron microscopy (ESEM) was used to study the morphology of the polyurethane composites in order to correlate it to the observations made. ESEM micrographs of impact fracture (at room temperature) surfaces of neat biobased polyurethanes and its composites with hemp and E-glass fibers are shown in Fig. 4. ESEM shows that in both cases good dispersion and wetting are achieved. However, the nature of the fiber-matrix adhesion has changed. Fig. 4A is a micrograph of hemp fibers coated with

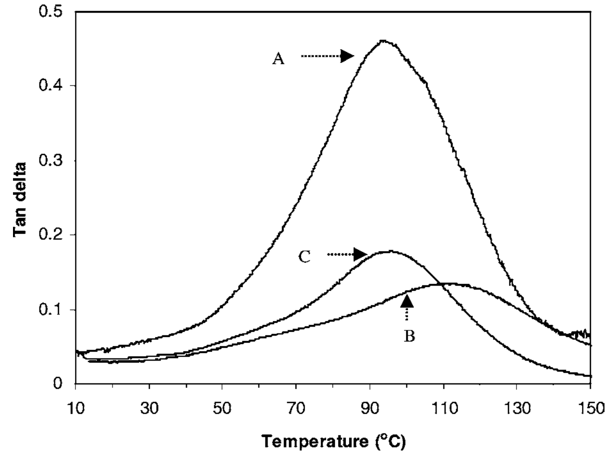

Figure 3 Glass transition temperature (T_g) of SOPEP based polyurethanes composites: (A) neat polyurethane, (B) hemp reinforced (20 wt%) and (C) glass reinforced (20 wt%).

the polyurethane matrix showing very good fiber matrix adhesion. Whereas in the case of glass reinforcement, comparatively clean fiber pulled out was observed (Fig. 4B).

The mechanisms responsible for adhesion between the fibers and the polyurethane matrix is not clearly determined. The enhancement of stiffness and T_g in hemp reinforced polyurethane is attributed to good fiber dispersion, efficient wetting and good fiber-matrix adhesion. Adhesion through chemical bonding can be favored since covalent bonds may be formed by reaction of free hydroxyl groups on the surface of the fiber with the isocyanate, as suggested in the literature [12]. In the case of E-glass reinforced polyurethane, the interaction between the fiber and matrix appears to be different as observed in the ESEM photomicrographs. A study carried out in our laboratory on the nature of interfacial interactions between polyurethane and glass showed that the contribution of chemical bonding, covalent or ionic, is not important. Formation of an interphase region in which hydrogen bonding plays a key role is more likely to occur in glass reinforced polyurethanes [13, 14].

These results reveal that polyurethane composites reinforced with 20 wt% of either hemp or glass fibers that have improved mechanical properties (due to good fiber distribution and efficient wetting) can be obtained with these soybean-based polyols despite the differences in surface chemical composition and topology of these two fibers. It is worthy to notice that the natural lignocellulosic fiber used, i.e., hemp, proved to be a better reinforcement at the same weight percentage than E-glass when one considers the higher T_g (by 15 °C) and the lower density of the composites but also the price of this fiber (one third that of glass).

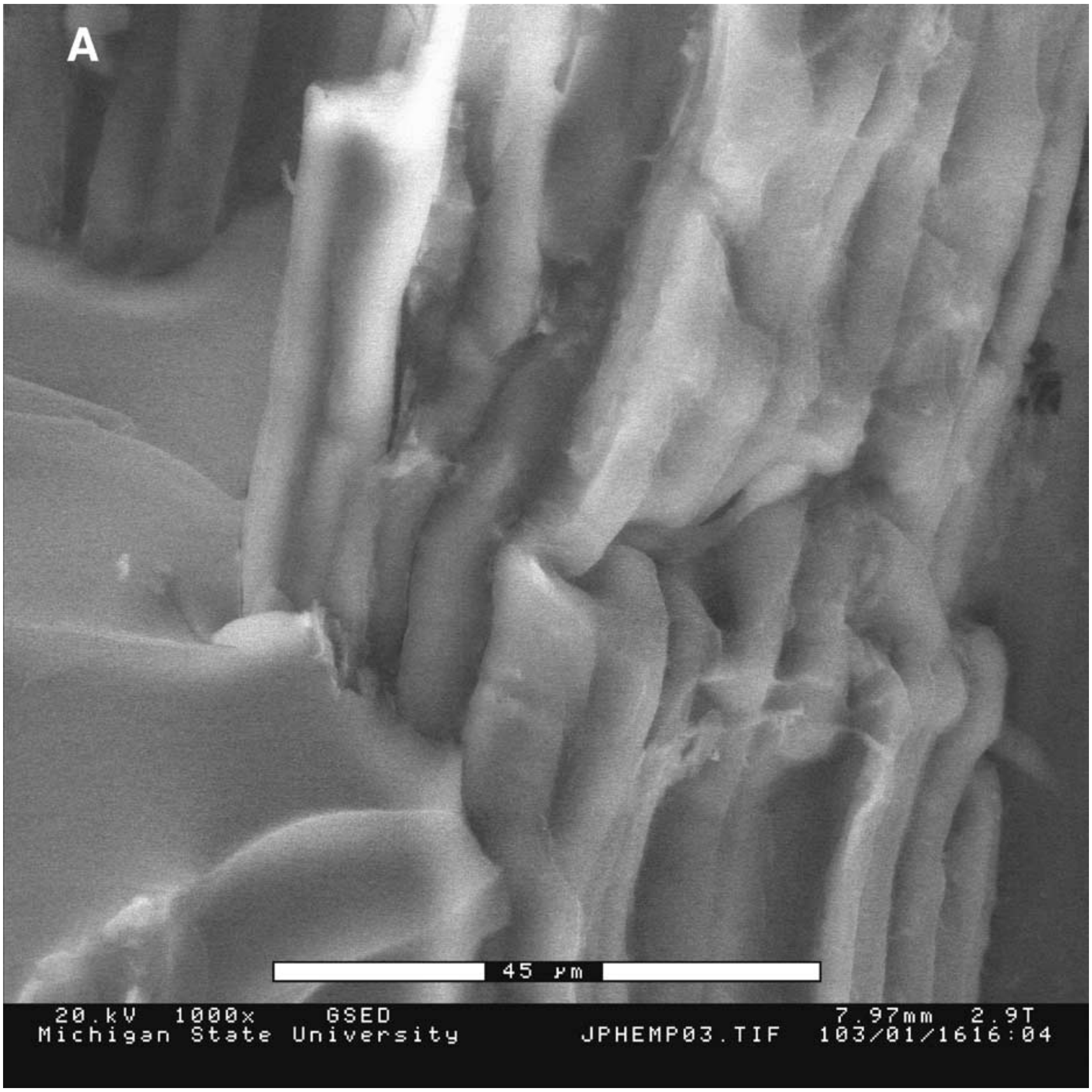

Figure 4 ESEM micrographs of SOPEP based polyurethanes composites (1000×, scale bar 45 μm): (A) hemp reinforced (20 wt%) and (B) glass reinforced (20 wt%). (*Continued*)

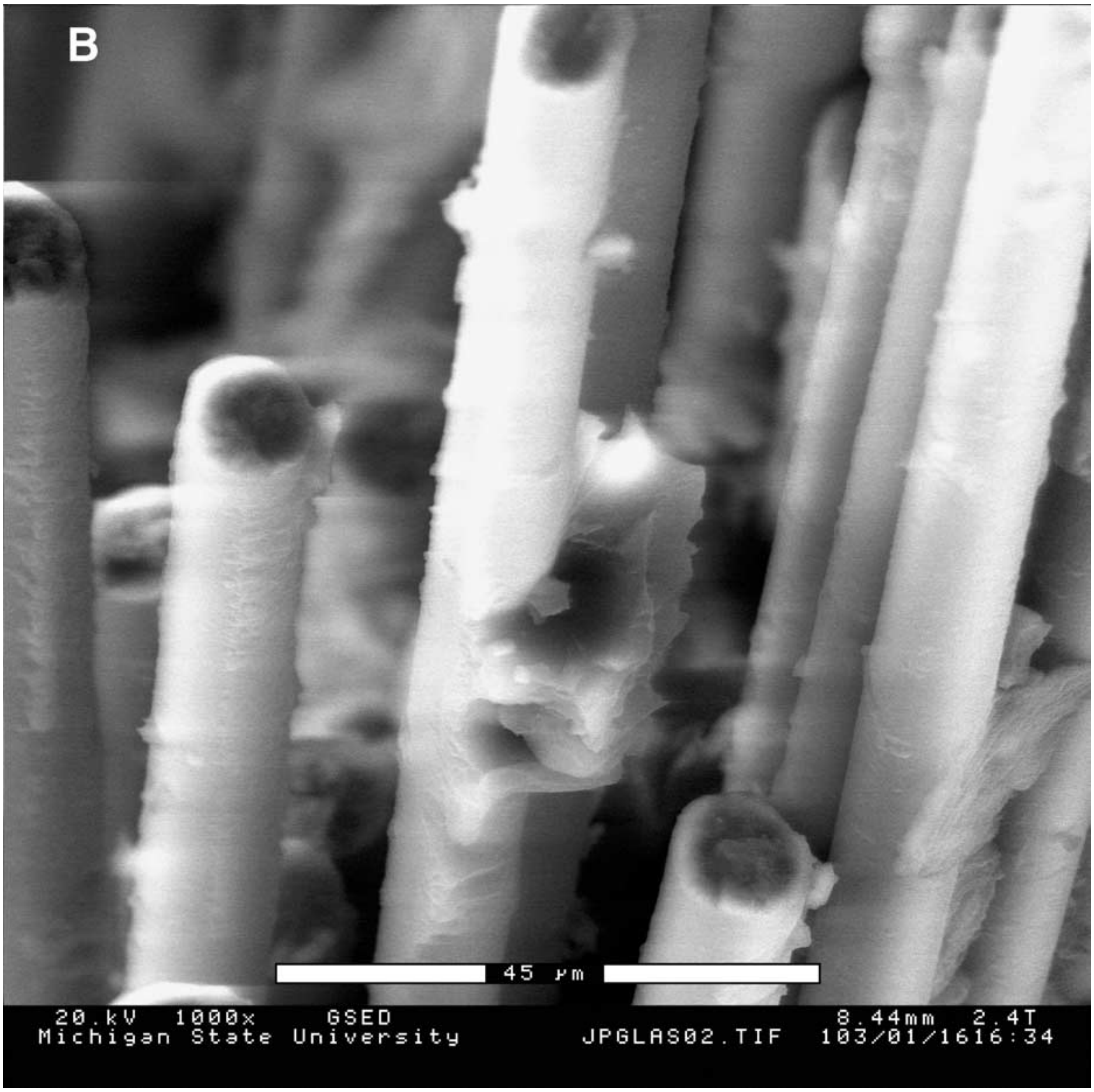

Figure 4 (*Continued*).

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