Morphology–property relationships in wood-fibre-based polyurethanes

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Many of the advances in material performance over the last decade can be attributed to developments in multicomponent polymer systems and, specifically, to multiphase materials such as incompatible polymer blends and fibre-reinforced composites. In these types of material, performance properties are often dominated by the interphase that defines the transition region from one pure phase to another. Although typically a minor component, the interphase effectively determines the mechanism and efficiency of stress transfer between the components that make up the material system. With the potential for chemical reaction across the interface, complications exist when viewing the material as an incompatible polymer blend or a reinforced polymer composite.

One example of this type of composite is polyurethanes incorporating a lignocellulosic fibre. This class of natural fibre is characterized by a hydroxy-rich surface that may react with the isocyanate group of the urethane formulation. A considerable volume of research has addressed the use of isocyanate resins as binders for traditional wood composites (e.g., particleboard, medium-density fibreboard and oriented strandboard) and has attributed the dramatic improvements in strength and moisture resistance to possible covalent binding [1–3]. Also, research has investigated the use of isolated wood polymers, such as lignin, as the polyol component in polyurethanes [4–6]. Considering the wood fibre as a reactive polyol-like component is a relatively recent development [7].

Wood-fibre polyurethanes that incorporate synthetic polyols are of interest because of the versatility that is afforded by urethane chemistry and the possibility of alternative market developments for wood composites. At the same time, research on this material may provide additional insight into the complexities of the fibre–polymer interfacial structure. In this report, preliminary results on the phase morphology of wood-fibre–urethane composites are presented. In addition, the effect of fibre and polyol characteristics on interfacial quality is discussed.

Two lignocellulosic fibres were investigated: firstly a hydropulped recycled paper fibre (mixed office waste) and secondly a virgin thermomechanical pulp fibre (southern pine). The composites were formulated using a difunctional (Multranol-3600) poly(propylene oxide)-based polyol, and a polyol-miscible isocyanate prepolymer (Blendur-5000) cross-linking agent (Miles Inc., Pittsburgh, PA). Composites of various fibre contents were prepared by first dispersing the required volume of polyisocyanate in the polyol and then spraying it on the oven-dried fibre. The hydroxyl number of the synthetic polyol was provided as 56, and a value of 190 was used for the wood fibres [7]. The component formulations were calculated using an isocyanate index of 1.25. The 6 in × 6 in fibre mat was manually formed and pressed for approximately 4 min at 175 °C in a Carver laboratory press. All panels were produced to a nominal thickness of 0.25 in and a target density of 45% fibre. The cured polyurethane composites were cooled under ambient conditions and stored over P_2O_5 in a vacuum desiccator until testing. Dynamic mechanical properties of the composites were measured from −75 to 200 °C at 5 °C intervals in three-point bending at a frequency of 6.28 cycles s^{-1} (Rheometrics, Inc.).

The dynamic mechanical spectra of composites prepared with different ratios of recycled fibre and synthetic diol (MOW-3600) are shown in Fig. 1. The strong tan δ peak centred at −40 °C for the pure synthetic polyurethane identifies the glass transition temperature, T_g, of this polymer. Replacement of only 25% of the synthetic polyol with recycled fibre increases this transition temperature to −26 °C and dramatically reduces the intensity of the tan δ peak from a maximum of 1.5 to 0.31. The trend towards a higher low-temperature T_g with reduced intensity continues with additional wood fibre in the composite formulation (see Table II later). Although this trend is expected with addition of a rigid segment into the polyurethane, the tan δ peak intensity is substantially lower than might be expected by a simple reduction in volume fraction of this pure phase.

Interestingly, in the 25% recycled fibre composite a broad shoulder is apparent at 0 °C, which suggests that a new relaxation process may be coupled to the pure urethane transition. As the fibre content of the composite is increased further, two additional relaxation processes become more clearly defined. A broad relaxation centred at about 50 °C in the 75% wood-fibre composite becomes obscured at low fibre contents. Finally, a high-temperature transition that begins between 150 and 200 °C becomes more

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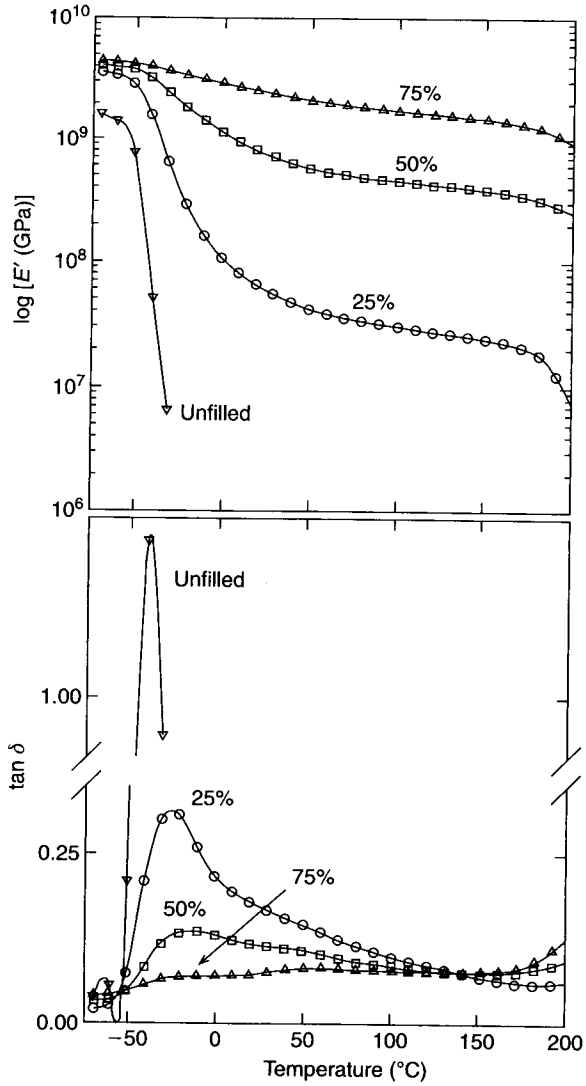

Figure 1 The influence of fibre content on the dynamic mechanical spectrum of recycled-fibre-based composites. The percentages represent the weight fractions of fibres in the formulation.

pronounced as the fibre content is increased. This relaxation process can be attributed to the onset of the T_g for the dry fibre's amorphous polymers; hemicelluloses and lignin [8].

The storage modulus, E', provides a measure of material stiffness and dramatically illustrates the contribution of the lignocellulosic fibre to the composite properties (Fig. 1). For the polyurethane formulated without fibre, the storage modulus catastrophically drops from approximately 1.5 GPa at −75 °C to less than 1.0 MPa above T_g, exhibiting no rubbery plateau region. With 25% fibre in the formulation, the low-temperature or glassy modulus is increased substantially over that of the purely synthetic polymer. At T_g, a decline of several decades is observed until a plateau is reached near 5.0 MPa. As the fibre content is increased, the glassy modulus of the composite increases only slightly; however, a continual increase in the plateau modulus is exhibited. This behaviour is reminiscent of a multiphase copolymer where the plateau modulus increases with increasing volume fraction of a hard component.

Table I compares the behaviour of the low-temperature tan δ peak for composites prepared with the synthetic diol, and either recycled (MOW) or virgin (TMP) fibres. For both fibre sources, the glass transition shifts to higher temperatures and is dramatically reduced in intensity with the addition of wood fibre. At all levels of fibre replacement, the intensity of the tan δ peak in the virgin fibre composites is greater than that found for the recycled composites. In addition, a significantly higher glass transition temperature is found for the virgin fibre composite systems, the difference reaching a maximum of 10 °C at 75% fibre-to-polyol ratio.

It is difficult to attribute the observed urethane phase T_g behaviour to a specific factor from these limited data. Generally, an increase in T_g can be explained either by an increase in the degree of cross-linking or by copolymerization with a high-T_g segment. Either of these explanations can be invoked in this case since it is conceivable that low-molecular-weight lignin fragments or sugars could be solubilized and effectively serve as a multifunctional polyol component. Alternatively, because the lignocellulosic fibres are inherently hygroscopic, it is reasonable to assume that a higher fibre content necessarily leads to the increased presence of moisture and the formation of polyurea segments that could elevate the synthetic phase T_g. It is likely, however, that the observed increased in T_g results from restricted chain mobility and the development of a fibre–synthetic interphase. The hydroxy-rich surface of the fibre may create a high-chain-density interphase (as evidenced by the high-temperature shoulder) that elevates the transition temperature of the pure urethane component.

Considering the influence of fibre type on the storage modulus, E', at low (glassy) and high (rubbery) temperatures provides additional insight into the phase morphology that is established in the composite. As seen in Table II, the glassy modulus of the recycled fibre composite increases from 1.62 GPa with no fibre to 4.45 GPa for the 75%

TABLE I Variation in the synthetic urethane component's tan δ peak temperature and peak maximum with fibre type and fibre content

Fibre content (wt %)	MOW/3600		TMP/3600	
	T_{peak} (°C)	tan δ maximum	T_{peak} (°C)	tan δ maximum
0	−40.1	1.5248	−40.1	1.5248
25	−26.3	0.3135	−28.4	0.3860
50	−16.2	0.1353	−5.8	0.1558
75	−10.7	0.0684	−0.8	0.0882

TABLE II Summary of the glassy (−70 °C) and high-temperature (100 °C) storage modulus, log E', for the polyurethanes filled with different weight fractions of virgin TMP and recycled MOW fibre

Fibre content (wt %)	log [E' (GPa)], −70 °C		log [E' (GPa)], 100 °C	
	MOW/3600	TMP/3600	MOW/3600	TMP/3600
0	1.620	1.620	—	—
25	3.545	1.678	0.0299	<0.0001
50	4.080	3.102	0.4347	0.2319
75	4.451	2.984	1.6506	1.0591
100		4.020		3.000

fibre formulation. The high-temperature storage modulus increases dramatically as the fibre content increases from 25% to 75%. This high-temperature behaviour is, again, reminiscent of a cross-linked multicomponent polymer system and further supports the concept of covalent bonding across the fibre–matrix phase boundary.

The inferior stiffness properties of the composites produced with thermomechanical pulp runs counter to expectations. Recycled fibres are routinely characterized as heavily damaged from the process of fibre regeneration. This damage typically leads to diminished stiffness properties, on the order of a decade reduction when compared with virgin fibres [9]. As such, the composites with TMP fibre should exhibit greater stiffness in both the glassy and the rubbery regions. The fibre regeneration process, however, tends to tear the fibre wall, thereby increasing the area of exposed fibre wall and enhancing the availability of reactive hydroxy functionality. Comparatively, the virgin TMP fibre provides a relatively clean fibre surface with significantly different functionality (i.e., the lignin-rich surface provides more phenolic hydroxyl groups). The difference in surface chemical composition and surface topology that distinguishes these two fibre types apparently leads to substantial differences in the extent of covalent bonding that is established across the interface. If proven, this fact could lend credence to studying these materials from a multicomponent polymer standpoint rather than as a short-fibre-reinforced composite.

These observations indicate that wood-fibre–urethane composites produced with long-chain diols exhibit dynamic mechanical properties characteristic of multicomponent polymers. The introduction of natural polymer fibres inherently introduces an immiscible phase which is evidenced by the development of a high-temperature rubbery plateau. In addition, the increasing low-temperature T_g cannot be completely explained from this limited work. This behaviour can develop from partial miscibility of the two components, substantial interphase development that restricts the synthetic polymer mobility, or formation of polyurea components from water reactions. The systematic changes in mechanical behaviour shown by this hybrid composite suggest that a high degree of engineering is feasible.

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