# Multiphase materials with lignin: 9. Effect of lignin content on interpenetrating polymer network properties

**Stephen S. Kelley*, Wolfgang G. Glasser and Thomas C. Ward**
*Department of Forest Products, Department of Chemistry, and Polymer Materials and Interfaces Laboratory, Virginia Tech, Blacksburg, VA 24061, USA*
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A series of lignin-based polyurethane/poly(methyl methacrylate) (LPU/PMMA) interpenetrating polymer networks (IPNs) were prepared by solvent casting in film form. While the LPU/PMMA ratio remained constant (1:1), the properties of the LPU were controlled by varying the composition of the hydroxypropyl lignin polyol via chain extension with propylene oxide. An increase in the lignin content of the polyol resulted in a decrease in the molecular weight between crosslinks ($M_c$) and change in the morphology of the LPU/PMMA composite. This effect resulted in the transition from a two-phase material to a single-phase material when the (true) lignin content of the composite rose above 25 wt%. As the lignin content increased, the strength properties of the composites increased. The dynamic mechanical, thermal and ultimate mechanical properties of the entire series of IPNs could be explained by dual phase continuity.

**(Keywords: lignin; interpenetrating networks; phase behaviour; multiphase materials)**

## INTRODUCTION

Controlled polymerization of two or more polymers in the presence of the other component(s) allows for the formation of interpenetrating polymer networks (IPNs)[1–7]. Typically one of the polymeric components is an elastomer, though both may be rigid materials. Under favourable circumstances the preparation of an IPN provides a synergistic interaction, which improves material properties[1–3].

A number of factors have been found to influence the properties of IPN composites. These include type and concentration of components, presence (or absence) of crosslinking, and homogeneity (i.e. morphology). The effects of composition and crosslinking have been investigated for lignin-based polyurethane/poly(methyl methacrylate) (LPU/PMMA) IPNs in a previous report[8]. Both the chemical nature of the components and the extent of crosslinking may influence the apparent homogeneity of the system. Typically, the most homogeneous IPNs provide the best mechanical properties.

The homogeneity of semi-1-IPNs and of (full) IPNs† may also be influenced by the molecular weight between crosslinks ($M_c$) of the first-formed component[1,9]. As $M_c$ of component 1 decreases, the mobility of the chains, usually an elastomer, decreases, and thus limits the amount of phase separation or the domain size. In one study[9], two transitions were observed when the polyurethane was lightly crosslinked and this was attributed to two-phase morphology. As crosslink density increased, a single tan $\delta$ was observed in the dynamic mechanical response, and this was interpreted as an indication of a homogeneous system. The tan $\delta$ peak half-width also increased as the crosslink increased. This was confirmed by transmission electron microscopy. The $M_c$ of the second-formed component was found not to have a substantial effect on IPN properties[10].

The extent of component mixing in IPNs can also be varied by changes in the composition of one of the two components[5,7,10]. Several studies have investigated the properties of three-component IPNs. By modifying the compositon of the rigid component, its solubility parameter was varied, and depending on the method of preparation, the miscibility of components, as measured by dynamic mechanical analysis, could be enhanced or reduced. One particular system[7] showed three broad peaks in the tan $\delta$ curve, each of which could be assigned to one of the three constituents present.

Secondary interactions may influence the miscibility of polymer blends[11–13]. They may also influence the miscibility of IPN components. Secondary interactions between the carbonyl groups of PMMA and the aromatic electrons of a second polymer component have been revealed previously[14,15]. This interaction was reflected in a change of glass transition temperature ($T_g$) of the components.

Lignin-based polyurethane (LPUs) have previously been used as IPN components[8]. Component properties were shown to vary in a consistent manner with composition, and with type of preparation. In the present study the effects of the LPU composition, and of elastomer $M_c$, were investigated. Specifically, the effects of lignin content on dynamic mechanical, thermal and mechanical properties of IPNs were investigated at constant LPU/PMMA composition.

## EXPERIMENTAL

### *Materials*

The sources and methods of preparation of the IPN components were described previously[8]. The hydroxy-

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*Current address: Eastman Chemicals Division, Box 1972, Kingsport, TN 37662, USA

† For IPN nomenclature, see refs. 1 and 8

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propyl lignin polyols varied in molar substitution with propylene oxide, and they have been discussed previously also[16]. The current study employed an IPN preparation method in which both components (LPU and PMMA) were crosslinked. The compositions of the various IPNs are listed in *Table 1*.

### *Methods*

The dynamic mechanical, thermal and ultimate mechanical properties of the IPNs were determined using standard techniques described elsewhere[16].

## RESULTS AND DISCUSSION

### *Dynamic mechanical and thermal properties*

Differences in the hydroxypropyl ether chain length of chain-extended hydroxypropyl lignin (CEHPL) have previously been shown to influence dramatically the material properties of the polyol as well as the network polymer produced by crosslinking with diisocyanates[16]. CEHPL may be pictured as a star-like macromer consisting of an aromatic centre with radiating polyoxypropylene arms. The arms contain a terminal hydroxyl group, which can react with suitable diisocyanates, such as hexamethylene diisocyanate (HDI), to form lignin-based polyurethanes (LPU). The average number of propylene oxide units in a radiating arm is expressed as molar substitution (*MS*). Variations in *MS* have been shown to affect significantly the properties of the resulting LPU[16]. Increasing *MS* has resulted in networks with reduced $T_g$, reduced modulus and increased average molecular weight between crosslinks ($M_c$)[16]. An increase in *MS* corresponds to a reduction in lignin content and aromaticity. Differences in *MS* of the CEHPLs incorporated into IPN composites are expected to affect material properties by producing variations in the network structure of the first-formed component of the IPN[16].

*Effects of LPU composition.* A series of simultaneous IPNs consisting of 50% LPU and 50% crosslinked PMMA were prepared according to procedures reported elsewhere[8]. True lignin contents ranged between 13 and 28%. (IPN preparations were designated referring to the true lignin content in the LPU, *Table 1*.) Dynamic mechanical analysis responses for several representative composite materials (*Figure 1*) show two tan δ peaks, which merge into a single transition in relation to *MS* of the CEHPL component. The two peaks, which are separated from each other by 130°C for IPN-13, merge into a single broad peak centred at 76°C for IPN-28. The merger for the two peaks indicates the formation of single-phase material. The storage modulus (log *E*′) curve (*Figure 1*) also reflects the changes seen in the tan δ behaviour. As *MS* decreases and lignin content increases, the log *E*′ response progresses from two separate declines with heating, to a gradual broad decrease, and eventually to a single sharp drop. This significant variation in thermal transition behaviour is exhibited by both d.s.c. and d.m.t.a. analysis (*Table 2*). Both the tan δ peak temperatures and the $T_g$ values merged as the lignin content of the IPNs increased (or the *MS* of the CEHPL decreased). This trend (*Figure 2*) is consistent with increases in the $T_g$ of LPU films from chain-extended hydroxypropyl lignins prepared previously in several PMMA-free polyurethane materials[16]. The rigid aromatic group provides for more stiffness in the polymer, increasing the material's $T_g$. However, the observed increase in $T_g$ may also be a consequence of secondary interactions between the LPU and PMMA.

**Table 1** Composition of LPU/PMMA composites prepared using chain-extended hydroxypropyl lignins

| Composite type | Code[a] | *MS* of CEHPL[b] | True lignin content[c] (%) |
|---|---|---|---|
| Simultaneous | IPN-13 | 6.3 | 13 |
| (full) | IPN-15 | 5.3 | 15 |
| IPN: | IPN-17 | 4.5 | 17 |
| both | IPN-19 | 4.0 | 19 |
| components | IPN-21 | 2.5 | 21 |
| crosslinked | IPN-25 | 2.1 | 25 |
| simultaneously | IPN-28 | 1.7 | 28 |

[a] The number following the 'IPN' designates the lignin content of the IPN

[b] Molar substitution (*MS*) is the average number of propylene oxide units attached to each other as a propyl ether chain. This number is distinct from the degree of substitution (*DS*), which expresses the average number of propylene oxide units attached to the average lignin repeat unit, determined by $^1$H n.m.r. as reported previously[8]

[c] True lignin content is the weight fraction of unmodified (parent) lignin incorporated into the composite as the hydroxypropyl derivative. The weight fraction of LPU was 50 wt% for all the IPNs

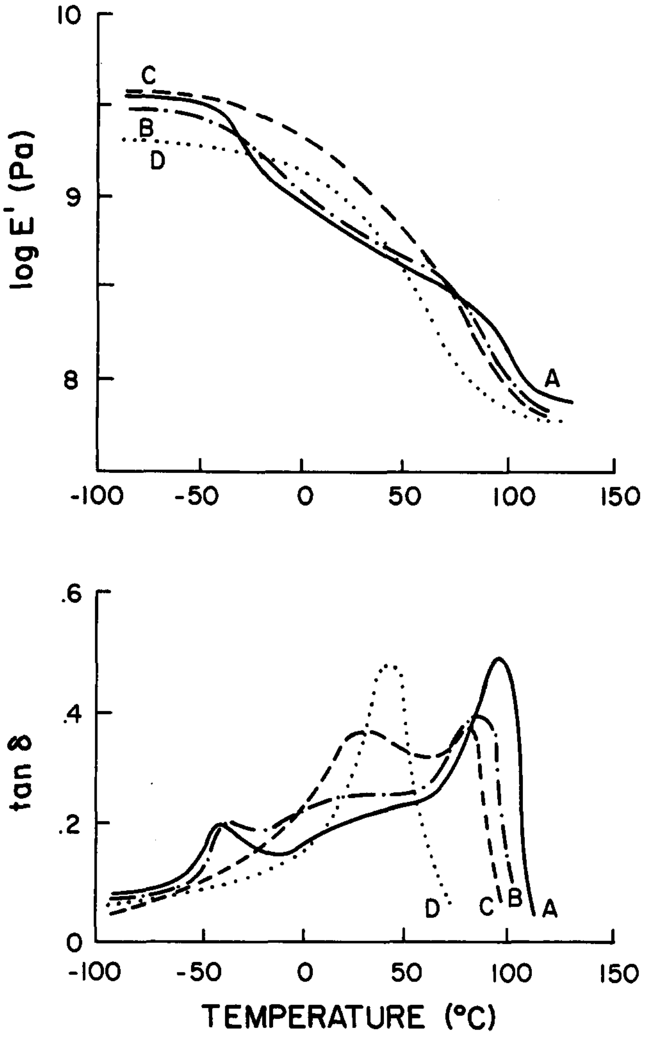

**Figure 1** Effect of lignin content (and *MS* of CEHPL) on dynamic mechanical properties of LPU/PMMA IPNs: A, IPN-13; B, IPN-17; C, IPN-2; D, IPN-28

**Table 2** Effect of lignin content on thermal properties of IPNs prepared with different CEHPLs

| Composite type | D.m.t.a: tan $\delta$ peak temp. (°C) |  | D.s.c.: $T_g$ (°C) |  |
|---|---|---|---|---|
|  | LPU | PMMA | LPU | PMMA |
| IPN-13 | −22 | 108 | −29 | 106 |
| IPN-15 | −20 | 102 | −26 | 92 |
| IPN-17 | −15 | 98 | −20 | 89 |
| IPN-19 | 15 | 83 | 8 | 78 |
| IPN-21 | 42 | 72 | 35 | 65 |
| IPN-25 | 48[a] |  | 44 |  |
| IPN-28 | 76 |  | 70 |  |

[a] Single transition

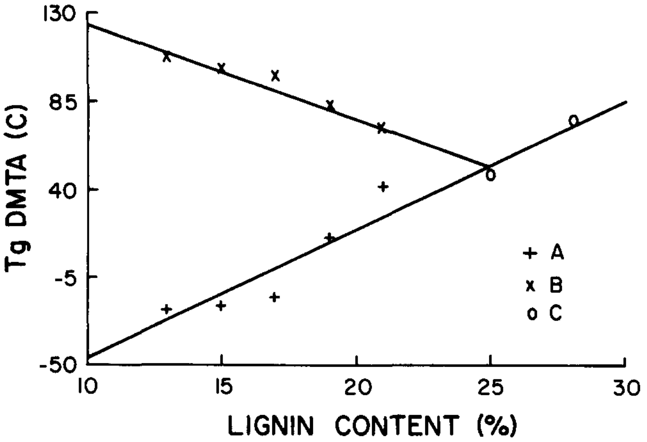

**Figure 2** Relationship between lignin content and $T_g$ (by d.m.t.a.) for LPU/PMMA composites prepared with several chain-extended hydroxypropyl lignins. (The $T_g$ of LPU and PMMA components are indicated by the data points A and B, respectively; and single $T_g$ is represented by C)

Secondary interactions between aromatic polymers and PMMA have been attributed to electronic effects between the aromatic $\pi$ electrons and the n–$\pi$ electrons in the ester pendant group of PMMA[14]. Both the increased lignin content and the potential interaction with PMMA might be responsible for the raising of the $T_g$ of LPU in the LPU/PMMA composite. To separate these effects, changes in the $T_g$ of PMMA need to be examined. These changes, if any, should be due solely to secondary interactions since the network structure of the PMMA should not change with lignin composition. In the absence of interactions the PMMA tan $\delta$ peak temperature should not deviate from its initial value (116°C). However, experimental data reveal that the tan $\delta$ peak temperature for the PMMA component steadily declines (*Figure 2*). The steadiness of this decline can be attributed to gradually increasing interaction between the PMMA and the LPU component in relation to lignin content. The increase in the (single) $T_g$ of IPN-28 compared to that of IPN-25 is probably due to an increase in the $T_g$ of the LPU component.

The results reveal that the extent of interaction between the (low-$T_g$) LPU and the (high-$T_g$) PMMA component increases as the aromatic content of the LPU increases. This results in a reduction in $T_g$ of the PMMA component. While a similar change in the $T_g$ of PMMA has been observed in other two-phase systems with an aromatic component[14,15], this had not been unequivocally attributed to interaction. One might speculate that interactions are promoted by limitations on LPU mobility in relation to declining $M_c$, which in turn could limit the mobility of the reacting PMMA chain ends. However, since the polymerization of the PMMA was carried out at temperatures above the $T_g$ of LPU, mobility restraints appear unlikely.

Thus, the convergence of $T_g$ in the LPU/PMMA composites in response to lignin content can be attributed to a combination of two effects. First, the LPU $T_g$ increases due to an increase in lignin content; and secondly, the $T_g$ of the LPU increased while that of the PMMA decreases, due to specific interactions between the two components.

*Effect of $M_c$*. The morphology of the composites may also be affected by variations in $M_c$ of the LPU constituent[9,17]. The effect of $M_c$ may be observed by comparing the IPNs with similar lignin contents but with differing $M_c$. The lignin polyol used to prepare IPN-28 has $MS = 1.8$, a lignin content of 28%, and a relatively low $M_c$ (ref. 16). In a separate work[8] the lignin polyol used to prepare IPN(0.75)* has $MS = 4.5$, a lignin content of 23% and a relatively high $M_c$ (ref. 16). A comparison of the $T_g$ values shows that IPN-28 has a single intermediate $T_g$, while IPN(0.75) has two separate, though not completely resolved, $T_g$ values. Since the $M_c$ of the LPU in IPN-28 was lower than that in IPN(0.75), one might suspect that $M_c$ affects the extent of interaction. A low $M_c$ potentially increases the extent of interaction by limiting phase separation between IPN components. Thus it appears that aromaticity and $M_c$ both influence the morphology of the LPU/PMMA composites.

### *Mechanical properties*

The ultimate properties of the IPNs were examined. Previous studies reflected a substantial improvement in mechanical properties with increased IPN homogeneity[18]. The use of different CEHPLs in the preparation of LPU/PMMA materials produced homogeneous (by d.m.t.a.) systems with Young's modulus (*MOE*), ultimate strength and ultimate strain properties varying in relation to lignin content (*Figure 3*). The mechanical properties are strongly correlated with the lignin content. Surprisingly the mechanical properties of IPN-25 and IPN-28, which both show a single $T_g$ in contrast to all other samples, reflect a trend consistent with two-phase (i.e. less homogeneous) IPNs. This may be rationalized with dual phase continuity of the LPU/PMMA IPNs in accordance with earlier conclusions[8].

With the observation of a single $T_g$ for IPN-25 and IPN-28, the materials can be considered homogeneous. The display of two $T_g$ values in all other composites indicates the presence of discrete LPU or PMMA domains, and this should significantly affect the mechanical properties of these materials. The continuity and consistency of change, however, contradict this expectation, and support dual phase continuity throughout the composite.

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* This composite was prepared in an analogous manner and was a simultaneous IPN comprising a CEHPL crosslinked with HDI, and a crosslinked PMMA, in 75:25 weight fraction, respectively[8]

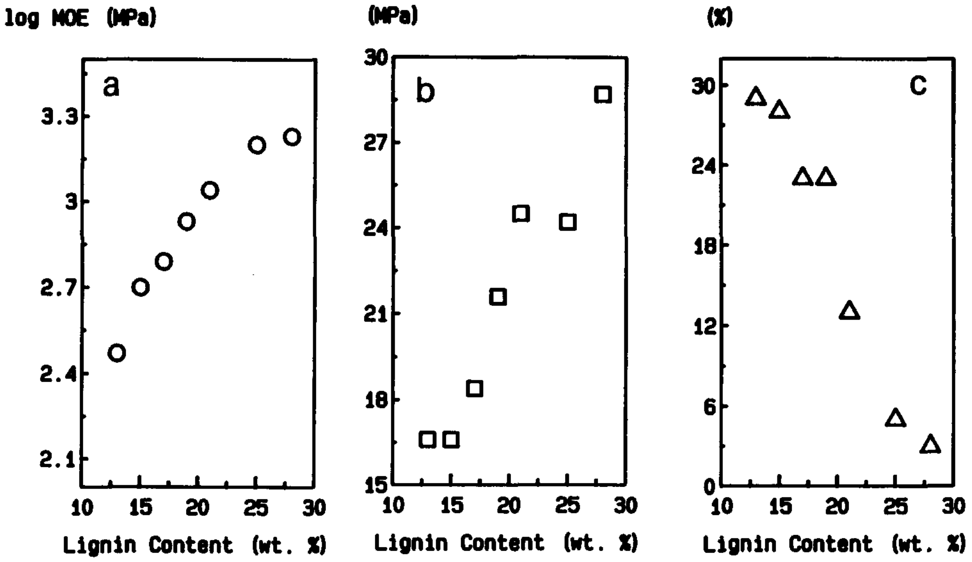

**Figure 3** Effect of lignin content on various mechanical properties of LPU/PMMA composites: Young's modulus (a); ultimate strength (b); and ultimate strain (c)

## CONCLUSIONS

Preparation of LPU/PMMA simultaneous IPNs from chain-extended HPL derivatives produces materials with different lignin contents. The dynamic mechanical and thermal properties were related to lignin content. The two $T_g$ values representing the components of the composite were seen to merge as lignin content increased. A single broad transition was indicated at lignin content >25%. This is explained with specific interactions between the components, and with restrictions on phase separation by the highly crosslinked LPU.

The mechanical properties of the IPNs also depended on lignin content. *MOE* and ultimate strength increased, and ultimate strain decreased, as lignin content rose. The mechanical properties varied consistently with lignin content and did not seem to depend on the presence of two or one thermal transitions. This observation supports the arguments made in an earlier work for dual phase continuity.

## ACKNOWLEDGEMENTS

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