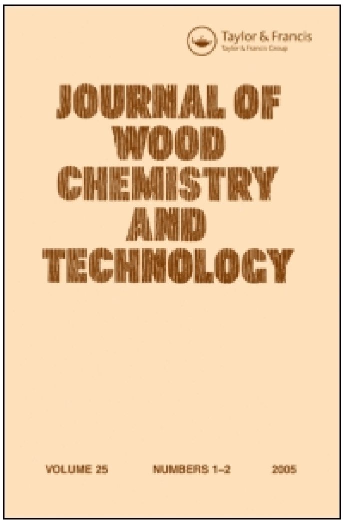

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# Multiphase Materials with Lignin. XIV. Star-Like Copolymers with Styrene

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# MULTIPHASE MATERIALS WITH LIGNIN. XIV.
# STAR-LIKE COPOLYMERS WITH STYRENE

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## ABSTRACT

Star-like copolymers of a lignin derivative, hydroxypropyl lignin (L), with polystyrene (PS) have been synthesized using the L-component as the soft segment and PS blocks of 10,200 molecular weight as the hard segment according to a procedure previously described. The usefulness of LPS star-like copolymers to assist in the dispersion of L-component in PS, and in the formation of multiphase polyblends, was demonstrated by scanning electron microscopy. Other structure-property effects were obscure by the inability to isolate a PS segment-free LPS preparation either because a part of the PS segment failed to gain appropriate functionality, or because it failed to become incorporated by covalent attachment to the L-component.

## INTRODUCTION

The blending of polymers is the most popular method for engineering new materials because this is based on the mixing of two or more polymeric components to obtain products with desirable characteristics. However, polymer compatibility usually produces interfacial tension and weak adhesion between the different polymer phases. Interfacial tension is responsible for poor dispersion of the minor component in the mixture and this contributes to gross phase separation[1]. The adhesion between polymers, and the dispersion of the minor component in a continuous matrix of the major component, can be improved by the addition of block or graft copolymers that represent a combination of the two polymers to be mixed. Such copolymers are generally called "compatibilizers", and their function is to penetrate into the phases by creating the capability of mixing their individual chain segments at the interphase[2]. There are numerous examples in the literature describing this phenomenon for man-made polymers[3-6]; however, this has not been explored extensively with natural biomaterials.

Earlier articles in this series have described the synthesis and properties of star-like copolymers of lignin (and its derivatives) with caprolactone and cellulose propionate[7,8]. Polystyrene and lignin are known to be immiscible; and so are polystyrene (PS) and hydroxypropyl lignin (L). It was therefore the objective of the present study to explore the potential utility of lignin-polystyrene copolymers to influence the phase morphology of polystyrene blends with lignin. Novel star-like copolymers of LPS were synthesize, characterized and their performance was evaluated with regard to a compatibilization effect on PS/L blends.

## RESULTS AND DISCUSSION

The synthesis of lignin (derivative)-polystyrene (LPS) star-like block copolymers paralleled those of similar copolymers of lignin with caprolactone and cellulose propionate[7,8]. The synthesis procedure is schematically illustrated in Figure 1. The resulting LPS copolymer was analyzed by gel permeation chromatography (GPC), H-NMR spectroscopy, and thermal analysis. Unfortunately, GPC revealed that the copolymer preparation remained non-uniform despite all efforts to produce a uniform copolymer. This non-uniformity revealed itself in the tenacious presence of a signal in the gel permeation chromatogram which represented starting PS segment. Although the contamination with PS segment was small (an estimated 10 to 20% based on the strength of the GPC signal), the presence of this impurity obscured all attempts at decisive thermal and mechanical analysis. The presence of this impurity must be

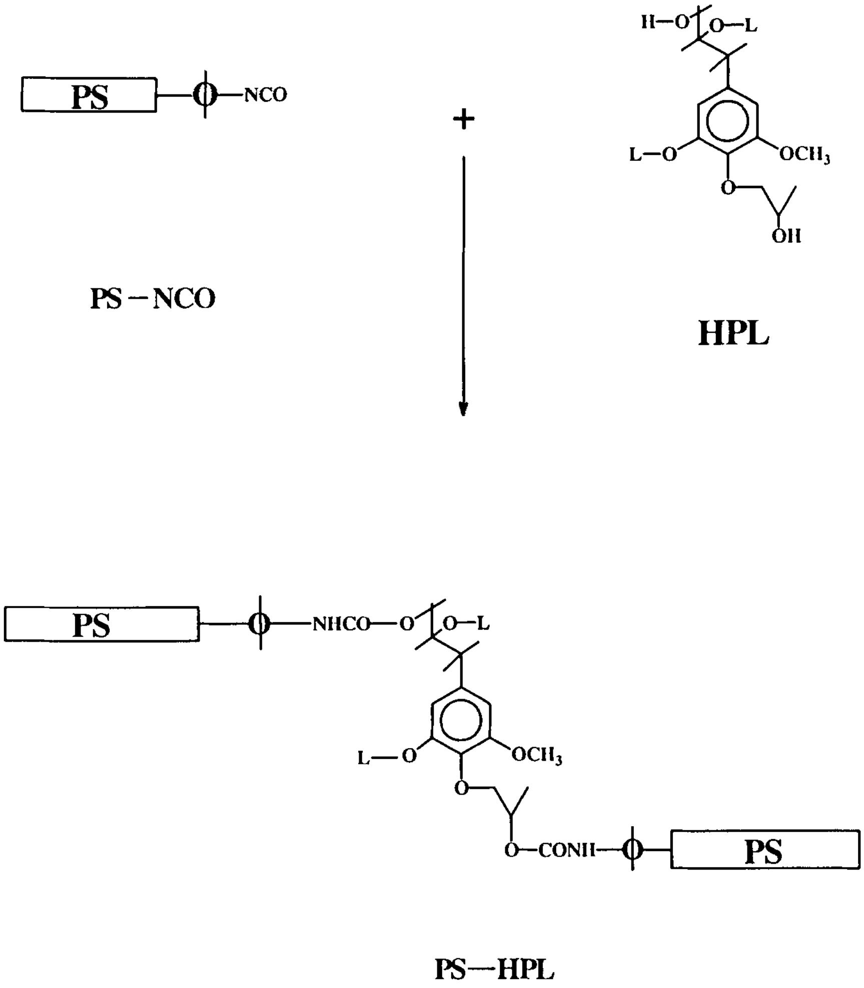

FIGURE 1 Schematic synthesis route for the preparation of star-like lignin-polystyrene copolymers via grafting of NCO-capped polystyrene segments (PS-NCO) onto hydroxypropyl lignin (L).

attributed to failure to convert all PS segment into copolymer either by failure to properly functionalize all PS segment, or by failure to achieve complete incorporation of NCO-functional segment into copolymer. (A multitude of circumstantial evidence suggests that the commercial mono-hydroxy terminated segment preparation represents a mixture of unfunctional and mono-hydroxy functional PS).

Thermal and mechanical analysis are both too sensitive to the presence of low molecular weight polymer components to be interpreted with certitude in light of the presence of a recognized impurity. However, thermal analysis (not shown) revealed that the copolymer had a dual glass transition temperature, one representing the L-component and a second representing the PS component; and the addition of LPS to L/PS blends failed to contribute to a significant shift in $T_g$-values in relation to copolymer presence. This suggests failure to contribute to *thermal* compatibilization by LPS-copolymer.

Likewise, mechanical analysis (not shown) failed to provide unequivocal evidence for distinct structure property effects of the presence of LPS in the L/PS blend system. Such effects have been described with similar block copolymers[9].

However, scanning electron microscopy (SEM) did reveal significantly improved compatibility of PS with L following the addition of LPS (Figure 2). The three series of blends illustrated in Figure 2 represent blends with 5, 10, and 20% L-content (left column to right column); and with 0, 5, and 10% LPS-component (top row to bottom row). The fractographic analysis reveals "cheesy" type of blend materials with cavities of about 5 to 7 $\mu$m which are formed when the rubbery L-particles are pulled away from the fractured PS surface. This separation of surfaces creates the clean and smooth holes seen at the fracture surfaces. The addition of 5 and 10% LPS produces improved adhesion as indicated by the reduced number of cavities. This implies that more L-particles are "anchored" to the PS matrix. By adding LPS copolymer, cavities of smaller and more uniform size are obtained, especially in the 10% L blend series (about 1 to 3 $\mu$m). The effect diminishes when the L content rises to

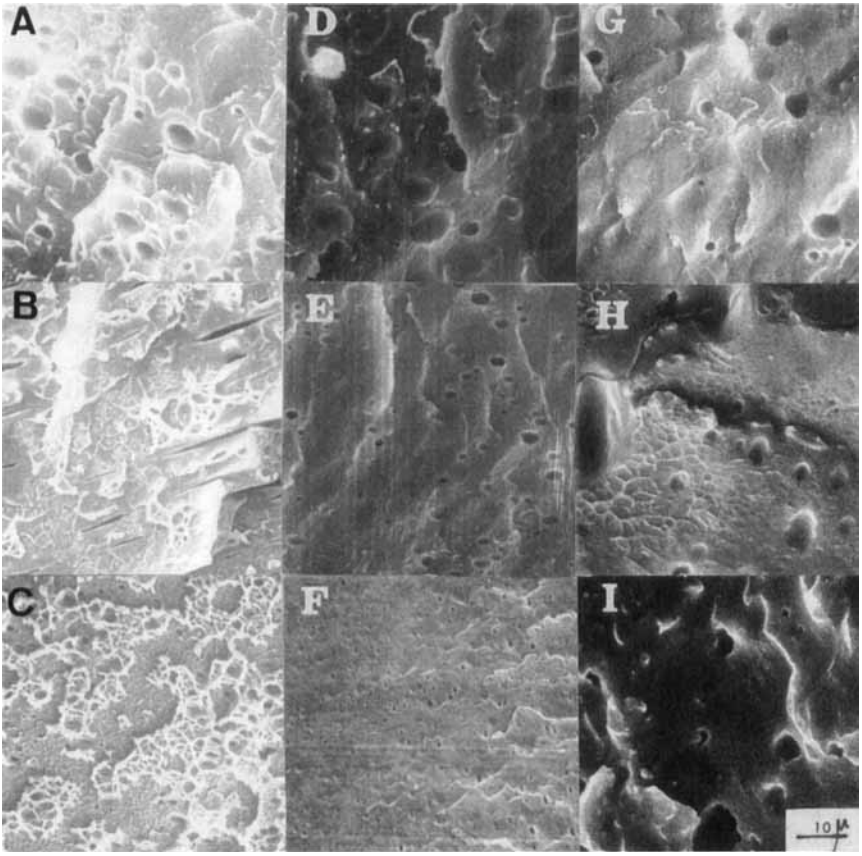

FIGURE 2 Scanning electron micrographs of L/PS/LPS blends (A) L/PS, 5/95% by weight; (B) L/PS/LPS, 5/90/5 wt.% copolymer; (C) L/PS/LPS, 5/85/10 wt.% copolymer; (D) L/PS, 10/90% by weight; (E) L/PS/LPS, 10/85/5 wt.% copolymer; (F) L/PS/LPS, 10/80/10 wt.% copolymer; (G) L/PS , 20/80% by weight; (H) L/PS/LPS, 20/75/5 wt.% copolymer, and (I) L/PS/LPS, 20/70/10 wt.% copolymer.

20% in the blend. The increased LPS copolymer content, which produces a finer dispersion with particles often less than 1 $\mu$m in diameter, supports the conclusion that LPS assists in the improved dispersion of L component in PS. This is an expected copolymer effect and can not be explained with the presence of low molecular weight PS segments.

## CONCLUSIONS

The addition of a lignin (derivative) - polystyrene star-like copolymer to a lignin (derivative)/polystyrene blend dramatically improves the blend morphology. The incorporation of LPS star-like copolymer produces an enhanced compatibility between the L and PS phases, and this is best observed in blends containing 10% L-component. This is expected behavior paralleling that of man-made materials.

## EXPERIMENTAL

### Materials

Lignin (Derivative) Component (L): The lignin component consisted of a chain extended hydroxypropyl lignin prepared in accordance with earlier work[10-13]. This isolated and partially purified derivative had a glass transition temperature below ambient; and it had an $M_n$ of 2,600 and an $M_w/M_n$ ratio of 15.

PS Segments: Mono-hydroxy terminated polystyrene segments with $M_n$ of 10,200 and $M_w/M_n$ of 1.1 were obtained from Scientific Polymer Products, Inc., and used without further purification.

It is suspected that this preparation consisted of a mixture of mono-functional and unfunctional PS segments. This had a $T_g$ of 90°C. PS polymer with $M_n$ of 250,000 was also obtained from Scientific Polymer Products, Inc.; it's $T_g$ was 100°C.

### Methods

Copolymer Synthesis: The synthesis of a star-like copolymer between (hydroxypropyl) lignin (L) and polystyrene segments (PS) paralleled the synthesis of analogous copolymers described elsewhere[7,8]. Briefly, the mono-hydroxy terminated PS segment was reacted with excess toluene diisocyanate (TDI) to prepare an NCO-functional segment. This was subsequently reacted with lignin derivative in homogeneous phase solution. The LPS copolymer had an $M_n$ 25,000, and $M_w/M_n$ ratio of 4.2; a Mark-Houwink-Sakurada exponential factor (a) of 0.2; and a glass transition temperature of 66°C.

Blend Preparation: The blends were prepared by solvent (THF) casting blend components in accordance with practice described previously[14,15]. Solvent cast films were kept in a vacuum desiccator for at least one week prior to examination.

Scanning Electron Microscopy (SEM): SEM was carried out on a Phillips EM-420 STEM operated in SEM mode. In order to obtain micrographs of fractured surfaces, the films were first immersed in liquid nitrogen and then fractured and analyzed at their fractured surfaces.

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