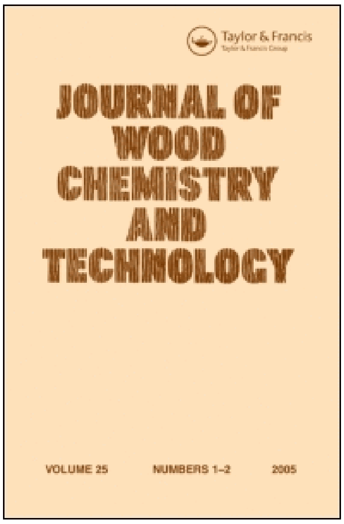

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MULTIPHASE MATERIALS WITH LIGNIN. III. POLYBLENDS WITH ETHYLENE-VINYL ACETATE COPOLYMERS

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ABSTRACT

Organosolv lignin (OSL) from red oak, and its corresponding hydroxypropyl lignin (HPL) derivative, were blended in the melt with polyethylene and with ethylene-vinyl acetate (EVA) copolymer, and injection molded. Lignin (derivative) content and vinyl acetate (VA) content both served as process variables. All mixtures produced immiscible blends, both by scanning electron microscopy and dynamic mechanical analysis. However, the compatibility of the two polymers increased with VA content. Both lignin products proved to be effective modulus builders, but HPL was more effective than OSL at VA contents above 20%. Modulus increased roughly in accordance with the rule of mixing. Inferior tensile strength properties were observed with the EVA copolymer if VA content was below 10%, and superior characteristics were noted in materials containing more than 25% VA and between 5 and 20% HPL.

INTRODUCTION

The mixing of two polymers in the melt, and the formation of this fluid mixture into solid materials by extrusion or injection molding and cooling, constitutes the simplest and lowest cost method for the development of new materials[1-4]. Polyblends in general combine the properties of the individual components to different degrees. Positive reinforcement of desirable properties is viewed as synergism whereas the strengthening of undesirable properties distracts from blending.

Lignin is an abundant and low-cost natural polymer[5] which has been shown to become thermoplastic following modification with propylene oxide[6,7]. Hydroxypropyl lignins (HPL) are low T_g, organic solvent soluble materials with uniform hydroxyl functionality[7,8]. Their usefulness in the production of thermosetting polyurethanes has been demonstrated[9,10]. Polyethylene (PE) is the most widely used industrial polymer, and it is of low cost, also. The combination of these two low-cost and abundant materials, lignin and PE, is motivated by the desire to explore material properties which neither individual component can achieve by itself. Polyblends of PE with HPL or lignin represent low-cost material combinations whose properties remain unexplored.

Since previous research has demonstrated that both polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) produce some degree of interaction when blended with HPL, the modification of PE by copolymerization with vinyl acetate (VA) offers opportunities for improving engineering properties via interaction with the carbonyl containing component of the copolymer. The solubility parameter (δ), serves as a convenient indicator for the strength of molecular attraction between molecules[12]. In order for two polymers to mix, their solubility parameters must match[12,13]. Thus, knowledge of the solubility parameters of two polymers allows one to predict whether a basis for mixing exists. The solubility parameter of pure (low density) PE is 8.0 (cal $cm^{-3})^{1/2}$,[12] that of HPL is 9.7[14], and that of pure organosolv lignin (OSL) is 11.2[15]. Since these values are quite dissimilar, compatibility would not be expected between the respective molecular species. Copolymerization with VA, whose solubility parameter is 9.0 (cal $cm^{-3})^{1/2}$, can be expected to raise the compatibility between HPL and the ethylene-vinyl acetate (EVA) copolymer. It was the objective of this study to explore the properties of injection molded polyblends of PE with OSL and HPL in relation to VA and lignin (derivative) contents.

EXPERIMENTAL

Materials

Low density polyethylene (PE) (catalog # 042, lot # 8) and ethylene-vinyl acetate (EVA) copolymers with vinyl acetate (VA) contents of 9, 18, 25, 28, 33, and 40% were obtained from Scientific Polymer Products, Inc. Organosolv lignin (OSL) was isolated from red oak wood chips by pulping with 70% aqueous methanol and 1% (on wood weight) sulfuric acid in a standard fashion[16]. Hydroxypropyl lignin (HPL) was produced from the OSL in a normal propoxylation reaction[6]. Resulting molecular weight characteristics were 900 and 3,000 for $\overline{M}_n$ and $\overline{M}_w$, respectively, for OSL; and 940 and 4,000, respectively for HPL[17,18].

Methods

Injection molding was performed in a Mini-Max Molder by Custom Scientific Instruments of New Jersey, and both dumbbells for tensile testing and dog bones for dynamic mechanical thermal analysis were prepared in this manner[19].

Dynamic mechanical thermal analysis (DMTA) was performed on equipment by Polymer Laboratories, Ltd., Shropshire, England, interfaced with an HP 9816 computer, using single-cantilever beam geometry, and a frequency of 10 Hz.

Tensile testing was performed on a standard Instron testing machine using a crosshead speed of 1 mm/min. Tests were replicated five times, and data were averaged.

Scanning electron microscopy (SEM) was performed using specimens that were broken in liquid nitrogen, on an Advanced Metals Research (AMR) instrument following coating with gold-palladium. Photographs were taken at 500 and 5000 times magnification.

RESULTS AND DISCUSSION¹⁾

When mixtures of polymers are melted and extruded or injection molded, the specimens will not reach their thermodynamic equilibrium due to the freezing of molecular motion in the glassy or viscoelastic state. Blend morphology will then be the result of the rate of cooling, and the specimen's microstructure will differ from that resulting from solvent

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¹⁾See Experimental section for glossary of terms.

casting. However, keeping cooling rate a constant dictated by instrumental configurations and environmental conditions, meaningful data can be generated from non-equilibrated polyblends by using a sufficient number of replications. This represents a relatively simple system through which the effects of VA and lignin (derivative) content can be evaluated in a relatively superficial fashion.

All properties of the EVA copolymer were found to vary with VA content. Glass transition temperature (T_g) decreased from -5°C to -15°C as VA content rose from 0 to 18%, and it remained at this level at higher VA contents. These changes must be considered when differences in polyblend properties are being related to lignin (derivative) content.

Dynamic mechanical thermal analysis is a convenient technique for determining thermal, mechanical, and morphological parameters in polymer blends[20]. Phase separation is indicated by the separation of individual tan δ (damping) peaks in the DMTA thermogram (Figure 1). Storage modulus (log E') declines from the glassy to the rubbery (or flow) region in relation to contributions by the individual components. The temperature range of greatest material usefulness usually lies between the T_g values of the individual polymer components[4]. The thermogram of the 40% HPL/EVA(18)²⁾ sample (Figure 1) illustrates how HPL

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²⁾Polyblend composition is designated by the weight fraction of the minor component first, and the major component next. The number in parenthesis gives the VA content of the EVA copolymer.

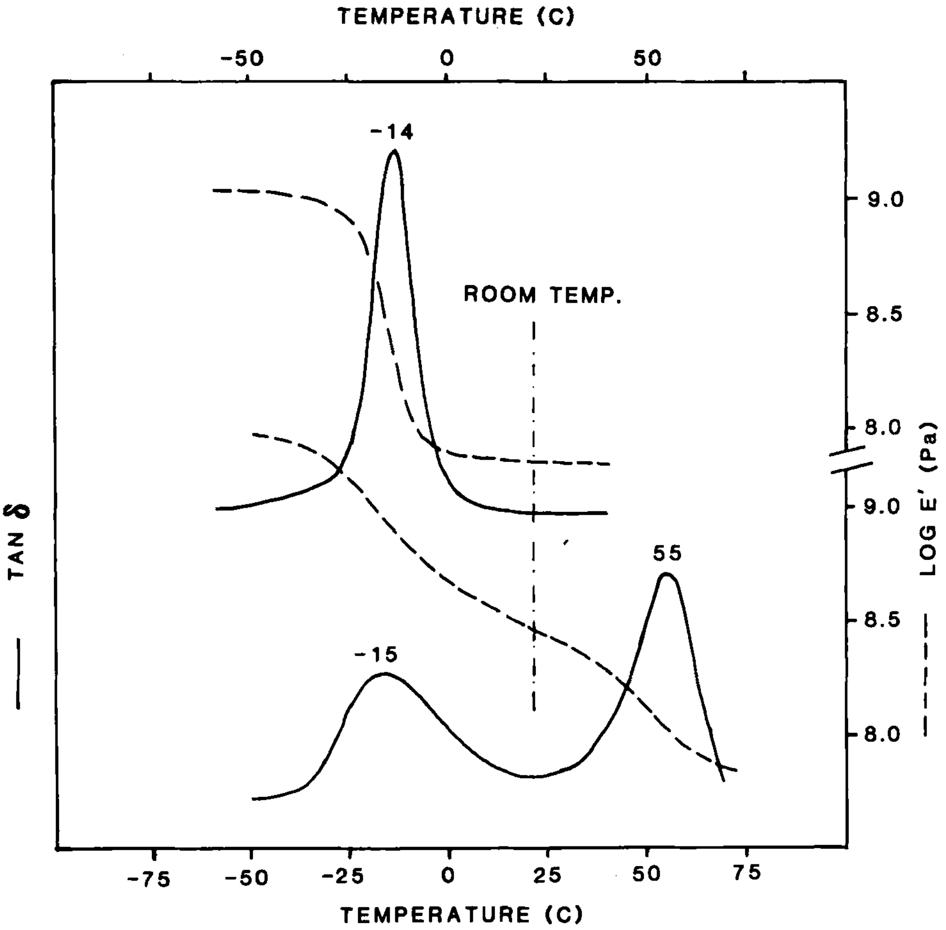

Figure 1. DMTA thermograms, tan δ and log E' curves, of EVA(40) (A) and 40% HPL/EVA(18). (The room temperature intersect with the log E' curve indicates the expected modulus at room temperature.) (See footnote 2 for blend designation.)

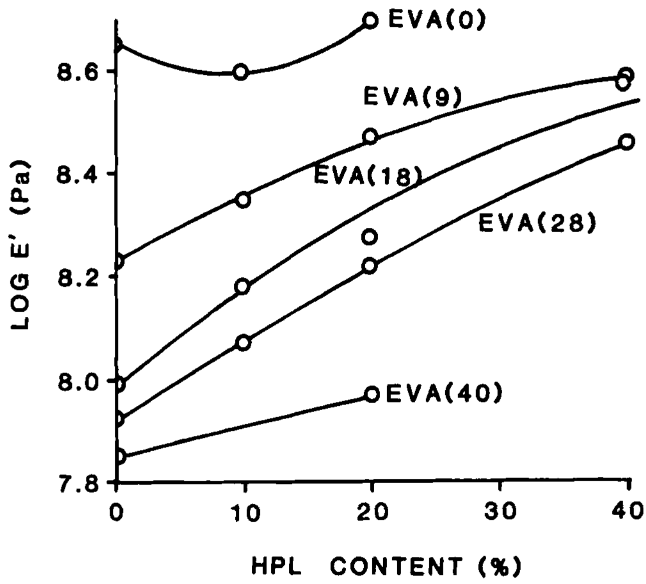

Figure 2. Relationship between log E' and HPL content for EVA of different composition. (Numbers in parenthesis refer to VA content.)

content raises log E' at room temperature. The relationship between HPL content and storage modulus for various EVA copolymers (Figure 2) illustrates that the increase in modulus differs with copolymer composition. However, plotting Young's modulus vs. HPL content (Figure 3) reveals that moduli closely follow values predicted by the rule of mixing[21].

The relationship between storage modulus and VA content for pure copolymer, and for 20% blends with HPL or OSL (Figure 4) illustrates the modulus building characteristic of lignin. The different behavior observed for the OSL and HPL blends can be

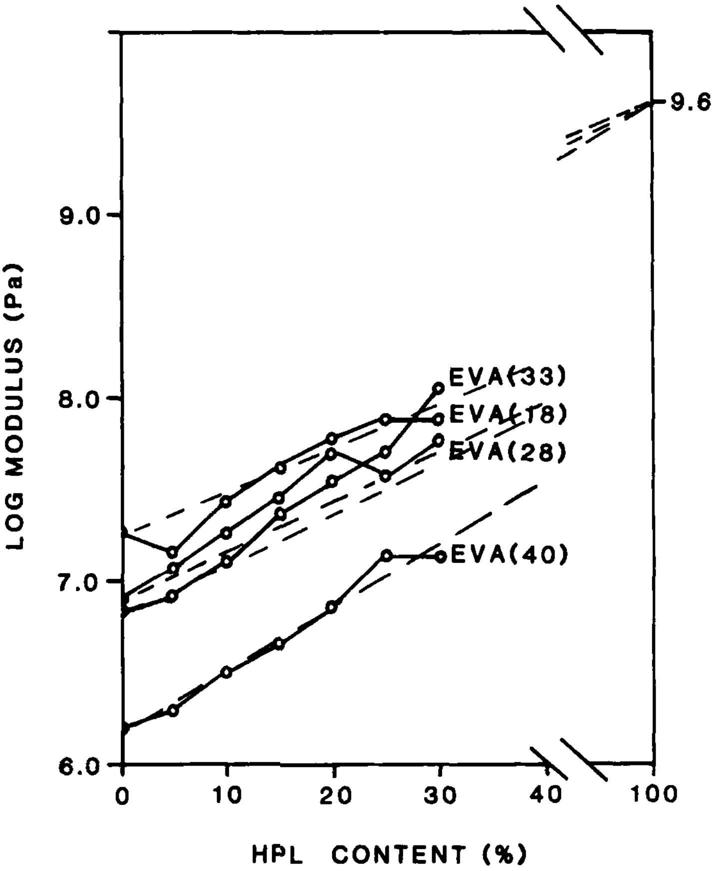

Figure 3. Rule of mixing applied to the relationship between MOE and HPL content of HPL/EVA blends. (Numbers in parenthesis refer to VA content.)

explained by the ability of HPL to build modulus more effectively than OSL as VA content rises above 10%. In order to evaluate whether this phenomenon can be explained with differences in solubility parameters and compatibilities, Tg behavior and scanning electron micrographs of freeze fracture surfaces were examined.

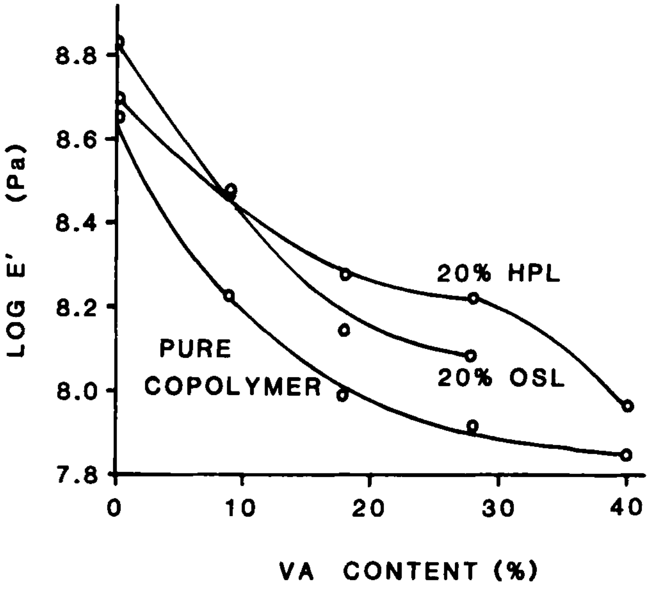

Figure 4. Relationship between log E' and VA content for pure copolymer (A), 20% OSL content (B), and 20% HPL content (C).

The T_g of the individual components was found to remain constant in the HPL/EVA polyblends regardless of composition. It was, however, seen to rise slightly, by 2 to 6°C, with the blends involving OSL. This may be attributed to an antiplasticization effect observed earlier with HPL[22]. Scanning electron microscopy (Figure 5) was inconclusive. No substantial differences between samples were found in relation to VA or lignin (derivative) content.

Ultimate properties tested on dumbbell-shaped specimens (not ASTM standard)[23] reveal consistent trends in relation to VA

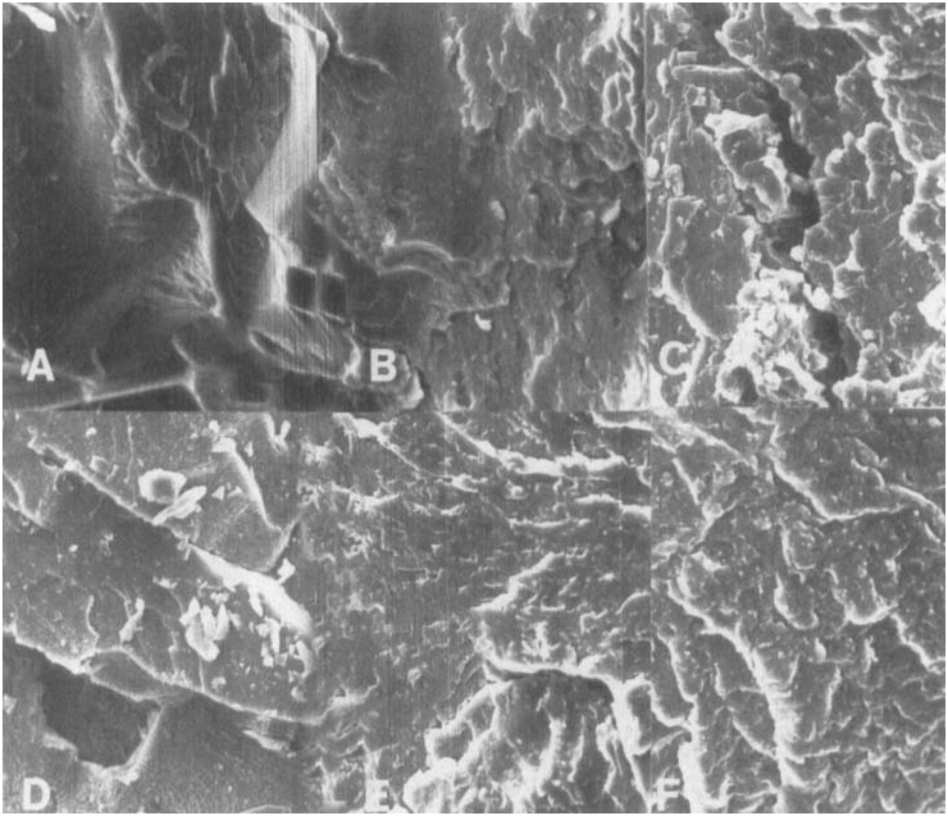

Figure 5. Scanning electron micrographs of 0% HPL/EVA(18) (A); 10% HPL/EVA(18) (B); 40% HPL/EVA(18) (C); 20% HPL/EVA(0) (D), 20% HPL/EVA(9) (E); and 20% OSL/EVA(40) (F). (See footnote 2 for blend designation.)

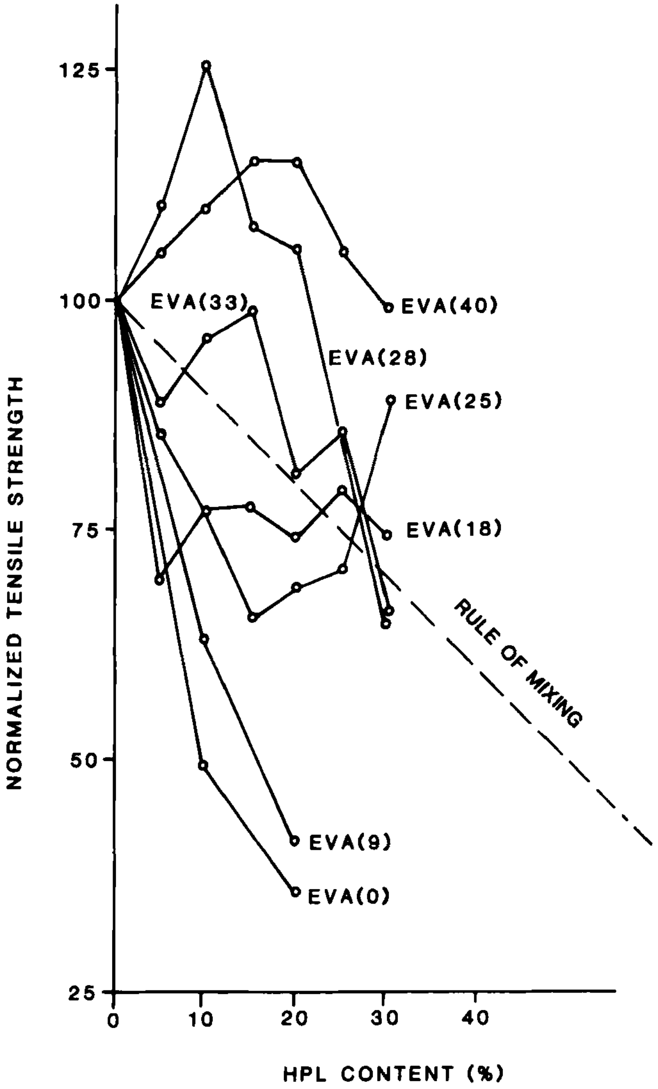

Figure 6. Rule of mixing applied to the relationships between normalized tensile strength and HPL content of EVA blends.
(See footnote 3 for normalization method; numbers in parenthesis refer to VA content.)

content. Normalized tensile strength³⁾ properties (Figure 6) in relation to theoretical (rule of mixing) behavior reveals negative deviation (i.e., reinforcement of undesirable properties) of blends with low VA content, and positive deviation (i.e., synergistic reinforcement of desirable features) of blends with high VA content, especially with the EVA(28-40) copolymers. A maximum gain of 26% tensile strength is seen for the 10% HPL/EVA(28) polyblend. This suggests that polymer pairs with satisfactory "mechanical compatibility"⁴ have HPL contents of between 5 and 25%, and VA contents of >25%. The contribution to tensile strength by small amounts of lignin derivative encourages further research into this subject matter.

CONCLUSIONS

1. All polyblends between EVA copolymer and lignin (derivative) were found to produce immiscible systems; however, the VA component enhances the mechanical compatibility between the two polymers.

2. The material's modulus rises in relation to lignin (derivative) content, and it closely follows the rule of mixing.

3. HPL is more sensitive to VA content than is OSL, and it builds modulus more effectively than OSL at higher VA contents (i.e., over 20%).

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3) Normalization was achieved by defining the strength of the unblended polymer sample as 100 and expressing strength gains/losses in relation to this value.

4. Tensile strength deviates from the rule of mixing, and a negative deviation is observed for low VA contents, whereas a strongly synergistic effect is noted for VA contents in excess of 25%, and with between 5 and 20% HPL.

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