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# Miscible Blends of Kraft Lignin Derivatives with Low-$T_g$ Polymers

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ABSTRACT: Alkylated and acylated kraft lignins are predominantly composed of well-defined supramacromolecular complexes assembled from thousands of individual components. The integrity of these very high molecular weight species can be compromised as kraft lignin derivatives (which alone are quite brittle) are plasticized when blended with miscible low-$T_g$ polymers. The complexes tend to be dismantled when the intermolecular interactions between the lignin components and low-$T_g$ polymer molecules are strong; this engenders a counterproductive increase in the proportion of polymeric plasticizer required to reach the plasticization threshold. X-ray powder diffraction analyses of the kraft lignin-based materials reveal two broad distributions of separation distances between the aromatic moieties; these are attributable to relative orientations of rings that are more or less edge-on and cofacially offset. Plasticization broadens the former significantly but has less impact on the latter. A similar effect is observed as the kraft lignin components themselves are reduced in molecular weight to the point where their mere presence enhances the plastic deformation that can be withstood before tensile fracture.

## Introduction

The first detailed report about the feasibility of producing polymeric materials with very high lignin contents appeared in 1997.[1] These thermoplastics were based on kraft lignins, the byproducts of converting wood chips to cellulosic fibers through the kraft process.[2] A little later, it was found that polymeric materials composed exclusively of ethylated and methylated kraft lignin derivatives can be very similar to polystyrene in their tensile behavior.[3] Then it was discovered that such alkylated kraft lignin preparations may be plasticized by blending with miscible aliphatic polyesters possessing low glass transition temperatures ($T_g$).[4] These simple formulations were expected to create the foundation of a new platform for producing useful thermoplastics from readily available lignin derivatives.[5] The mechanical behavior of lignin-based plastics rests on well-defined supramacromolecular complexes assembled from thousands of individual components.[6,7] Thus, predictability in the outcome of modulating the composition of such materials will require perspectives that are quite different from those appropriate to most polymer blends. These insights are the primary focus of the present work.

Lignins are prominent end products of phenylpropanoid metabolism in all vascular plants, where they are integrated into macromolecular cell wall matrices during their biosynthesis.[8] Indeed, lignins constitute the second most abundant group of biopolymers. As such, they deserve consideration as important raw materials in any scheme through which renewable feedstocks are generated by refining biomass to produce commodity chemicals and polymers.[9] In this context, consistent findings have repeatedly come to hand about the utility of formulations created by incorporating lignin derivatives covalently into other polymeric materials exhibiting good mechanical properties before being modified.[10] Such an approach has been typically confounded by a 25−40% (w/w) incorporation limit for the lignin derivatives being employed:[11] higher levels have usually produced materials that were brittle and weak.[12]

Similar findings pertain to heterogeneous blends of lignin derivatives with other polymeric materials. For example, an over 10-fold reduction in the tensile strength of cellulose acetate butyrate has been observed as a result of blending at 50% (w/w) levels with an organosolv lignin acetate, butyrate, or hexanoate.[13] In contrast, homogeneous blends of hardwood kraft lignin with poly(ethylene oxide) suffer a 1.6-fold decrease in tensile strength when the kraft lignin content has been reduced from 95% to 50% (w/w)—although the resulting materials remain fairly brittle with elongations to break increasing from 0.3% to 3.5%.[14] On the other hand, kraft lignin can act as a filler in polypropylene quite effectively: 60% (w/w) incorporation levels have been found to bring about a mere 1.4-fold reduction in tensile strength when 4% maleic anhydride-modified polypropylene had been introduced as a compatibilizer.[15]

However, if simple lignin derivatives are to find use as polymeric materials in their own right, then ethylated and methylated kraft lignins represent the most promising starting point identified so far.[3] Such materials are brittle, but they are readily plasticized in homogeneous blends with 30−35% (w/w) aliphatic main-chain polyesters possessing methylene/carboxylate group ratios ($CH_2$/COO's) of 2.0−4.0.[4] The corresponding elongations to break typically reach 50−75% when the kraft lignin content itself has fallen to 50%. Comparable windows of miscibility have been encountered in blends of aliphatic polyesters with certain other polymers. Thus, unbranched aliphatic polyesters are completely miscible with poly(bisphenol A carbonate),[16] poly(bisphenol A glycerolate),[17] and poly(tetramethylbisphenol A carbonate)[18] when the $CH_2$/COO's of the former vary from 2 to 5, 3 to 5, and 5 to 10 or more, respectively.

It is well recognized that, for polymers with moderate-to-high degrees of polymerization, the entropy of mixing decreases rapidly toward zero, and as a result the enthalpy of mixing has to be negative if a blend is to be miscible.[19] Indeed, the observed limits to the miscibility windows in the aliphatic polyester blends with the polycarbonates and polyglycerolate[16−18] were consistent with the signs (although not so much with the magnitudes) of the corresponding binary interaction energy

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densities calculated on the basis of a modified Guggenheim quasi-chemical group contribution model.[20] In a comparable manner, but using the Painter–Coleman association model,[21] a novolak-type phenolic resin was predicted to be miscible with aliphatic polyesters possessing $CH_2/COO$'s below 7; this was confirmed experimentally for polyester-$CH_2/COO$ values between 3 and 6.[22]

Even poly(vinyl chloride) was found to be completely miscible at all accessible temperatures with aliphatic polyesters possessing $CH_2/COO$'s between 4 and 10.[23] However, an exception to the usual pattern of behavior has been encountered in binary blends of aliphatic main-chain polyesters: miscibility only prevails when the $CH_2/COO$'s of the blend components differ by not more than 0.5 in the range 3.0–5.0.[24] Here the relatively small endothermic contribution to mixing that obtains in all binary aliphatic polyester blends has to be overcome by the entropic contribution to the overall free energy of the process.

The past work on aliphatic polyester blends with polymers other than lignin derivatives has dealt principally with phase behavior, while the mechanical properties of the ensuing materials have seldom received more than scant attention.[16–24] In contrast, the current stage of development for lignin-based thermoplastics merits quite different priorities. Although polymeric materials composed entirely of simple lignin derivatives (such as alkylated kraft lignins) may exhibit reasonable tensile strengths, they are invariably brittle.[3] Thus, the onset of plasticization at ambient temperatures is an important event in any series of lignin derivative blends with miscible low-$T_g$ polymers.

The plasticization threshold is inscribed in the corresponding $T_g$–composition curve which, for blends of aliphatic polyesters with alkylated kraft lignins, is concave.[4] It must be emphasized that this concavity is not a result of phase separation at the molecular level. Rather, it arises from the fact that the majority of the individual kraft lignin components are incorporated in their thousands into huge well-defined supramacromolecular complexes extending to very high ($\sim 10^8$) molecular weights.[6,25] These huge associated complexes have a considerable impact on the mechanical properties of kraft lignin-based thermoplastics.[1,4] They tend to become more dismantled when the intermolecular interactions between the individual kraft lignin components and the plasticizing polymer are stronger. Accordingly, the $T_g$–composition curve is less concave,[25] and more low-$T_g$ polymer is required to reach the plasticization threshold at ambient temperatures.[4] Consequently, plasticizer efficacy manifests itself in a poise between two opposing effects: the plasticizing polymer must be able to interact productively with the associated kraft lignin complexes, but it should not compromise their integrity significantly.

The present work is dedicated to establishing how the action of the plasticizers can be enhanced under such exceptional circumstances. The possibility that plasticization preferentially perturbs a particular subset of intermolecular separation distances between the kraft lignin components is carefully investigated. The proposition that plasticization will occur more readily when a miscible low-$T_g$ polymer interacts less strongly with the kraft lignin components is subjected to decisive examination.

## Experimental Section

**Parent Kraft Lignin.** The softwood kraft lignin employed in the present work was obtained from Jack pine (*Pinus banksiana*) kraft black liquor produced by the Boise Cascade Corp. (International Falls, MN). Thus, a (7.3-fold) diluted (2.0 L) sample of the black liquor (initial pH 12.5) was filtered (VWR 417 paper) and then slowly acidified to pH 3.0 with aqueous 1.0 M HCl (0.2 mL min$^{-1}$). At pH 11.0, before kraft lignin precipitation had begun, the solution was centrifuged to remove any solid material present, whereafter acidification was resumed. The precipitate isolated at pH 3.0 was washed three times with diluted aqueous HCl at the same pH. Any colloidally suspended kraft lignin could be recovered by basifying the solution to pH 8.5 and then rapidly reacidifying to pH 3.0. The combined precipitates from the final wash were dissolved at pH 8.5 and, after standing for 12 h, the resulting aqueous solution was centrifuged (35600*g*, 30 min) to remove any suspended sulfur; it was then exhaustively ultrafiltered with triply distilled water through a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA). The retentate (pH 7.0–7.5) was concentrated 5-fold, centrifuged again to remove any colloidally suspended sulfur, and freeze-dried.

**Polydisperse Higher Molecular Weight Kraft Lignin Fraction.** A higher molecular weight kraft lignin fraction was isolated from the parent kraft lignin by ultrafiltration in aqueous (carbonate-free) 0.10 M NaOH through a $1.0 \times 10^4$ nominal molecular weight cutoff membrane (Amicon YM10, Millipore Corp., Bedford, MA) with a 20-fold larger volume of the same solution over 7 days (a period of time that would allow dissociation between the kraft lignin components to approach completion[26,27] if conformational changes in the individual molecules are rate-determining for the overall process). Ultrafiltration was then continued using the same volume of triply distilled water, after which the retentate was concentrated 5-fold (final pH 7.0–7.5), centrifuged (35600*g*, 30 min) to remove any colloidal sulfur, and freeze-dried.

**Paucidisperse Kraft Lignin Fractions.** The parent kraft lignin preparation was ultrafiltered in aqueous (carbonate-free) 0.10 M NaOH consecutively through membranes with progressively decreasing cutoffs in molecular weight to produce a series of paucidisperse fractions. Initially, a 70 g L$^{-1}$ solution of the parent kraft lignin (1.0 L) was ultrafiltered in a batch mode through a $1 \times 10^5$ nominal molecular weight cutoff (Amicon YM100, Millipore Corp., Bedford, MA) membrane. When the volume of the retentate had been reduced by a factor of 2, an equal volume of new aqueous 0.10 M NaOH was added and ultrafiltration continued. This procedure was repeated 14 more times over a 7 day period so that the individual kraft lignin components in the complexes would have sufficient opportunity to dissociate from one another[26,27] before permeating through the membrane. Then exhaustive ultrafiltration with triply distilled water was rapidly carried out in a similar way, whereupon the retentate (final pH 7.0–7.5) was freeze-dried after centrifuging (35600*g*, 30 min) to remove any colloidal sulfur.

The entire permeate from the $1 \times 10^5$ nominal molecular weight cutoff membrane was ultrafiltered through a $5 \times 10^4$ nominal molecular weight cutoff membrane (MFS, Dublin, CA) until the volume of solution retained had been reduced to 300 mL. Aqueous 1.0 M NaOH was employed to readjust the NaOH concentration in this retentate to 0.10 M, and then ultrafiltration was continued using aqueous 0.10 M NaOH and triply distilled water consecutively as before with the first membrane. Similarly, each of the successive permeate solutions was ultrafiltered through the membrane with highest remaining nominal molecular weight cutoff in the series $3 \times 10^4$, $1 \times 10^4$, $5 \times 10^3$, $3 \times 10^3$, and $1 \times 10^3$ (Amicon YM30, YM10, YM5, YM3, and YM1, respectively, Millipore Corp., Bedford, MA), and the resulting retentate solutions were freeze-dried after removing all traces of sulfur by centrifugation (35600*g*, 30 min).

The permeate from the membrane with a nominal molecular weight cutoff of $1 \times 10^3$ was subjected to a final ultrafiltration step with a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA), which should not be used with solutions of pH > 8.5. Accordingly, the pH of the permeate was adjusted to 8.0−8.2 (with aqueous 1.0 M HCl), before the solution was exhaustively ultrafiltered with triply distilled water. Sulfur tended to precipitate out from the retentate in copious quantities during the process; it was removed periodically by centrifugation (35600*g*, 30 min), and finally the solution containing the lowest molecular weight kraft lignin fraction (7.0−7.5) was freeze-dried like the others.

**Molecular Weight Determinations.** The average molecular weights of the purified kraft lignin preparations and fractions were deduced from their size exclusion chromatographic (SEC) molecular weight distributions. To this end, Sephadex G100/aqueous 0.10 M NaOH elution profiles were monitored at 320 nm using an ISCO $V^4$ detector with a ~6.6 mL $cm^{-2}$ $h^{-1}$ flow rate through a 2.5 × 100 cm column. The various samples were eluted in the presence and absence of visible high and low molecular weight markers (blue dextran and *p*-nitrophenol, respectively). The chromatographic traces were digitized and transformed to profiles of absorbance vs relative retention volume ($V_R = (V_E - V_0)/V_0$, where $V_E$ denotes elution volume, and the void volume, $V_0$, was taken as $V_E$ at the initial point of deflection from the baseline) with a Fortran 77 program. Corrections were made hereby for digitizer alignment and minor baseline drift before calculating $V_R$ on the basis of a linear change in flow rate from the beginning to the end of elution and applying a scaling factor in agreement with a standard $V_R$ value of 2.0 for *p*-nitrophenol.[28]

The SEC columns were calibrated with nine paucidisperse kraft lignin fractions collected at retention volumes evenly spaced across the breadth of the profile for the parent kraft lignin preparation. These fractions were neutralized (aqueous 1.0 M HCl) to pH 7.5−8.0 and exhaustively ultrafiltered with triply distilled water through a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA) to remove the salt before freeze-drying. They were then eluted through the analytical Sephadex G100 column in aqueous 0.10 M NaOH, whereupon the portions encompassing the upper one-third of each peak height were isolated. The profiles of these refractionated fractions were documented by reeluting some of each solution through the same SEC column. Concomitantly, they were appropriately diluted (to an absorbance at 280 nm of 0.15−0.18) with carbonate-free aqueous 0.10 M NaOH for sedimentation equilibrium measurements to determine their weight-average (and *z*-average) molecular weights in a Beckman XL-A analytical ultracentrifuge at 4 °C.[28]

**Alkylation and Acylation of Kraft Lignin Preparations.** Methylation and ethylation of 20 g $L^{-1}$ kraft lignin samples was carried out at ambient temperature in aqueous 60% dioxane with dimethyl sulfate (Aldrich, Milwaukee, WI) or diethyl sulfate (TCI America, Portland, OR) at pH 11−12 under $N_2$. The reaction was initiated by adding 2.0 mL of dialkyl sulfate/g of kraft lignin to the aqueous dioxane solution, whereupon vigorous stirring was continued for 24 h; thereafter, 1.0 mL of dialkyl sulfate/g of kraft lignin was added twice daily for a further 3 days. Whenever the pH had fallen below 11.0, it was restored to a value between 11.0 and 12.0 by adding aqueous 1.0 M NaOH. After the reaction appeared to have reached completion, it was quenched by neutralizing the solution with aqueous 1.0 M HCl, and the dioxane was removed under reduced pressure. The precipitate of alkylated kraft lignin was washed with distilled water four times, air-dried, and stored over $P_2O_5$ to remove the last traces of moisture.

On the other hand, acetylation of kraft lignin preparations was carried out with acetic anhydride in pyridine. All of the reagents used were doubly distilled; the first stages for pyridine and acetic acid involved distillation from BaO and $KMnO_4$, respectively, while acetic anhydride was allowed to stand in contact with $P_2O_5$ before being distilled for the first time. A quantity of 1.0 g of kraft lignin was completely dissolved in 2.8 mL of (carbonate-free) aqueous 0.10 M NaOH and then precipitated with 1.8 mL of acetic acid. This preliminary step facilitated complete dissolution of the sample in 100 mL of pyridine, to which 60 mL of acetic anhydride was promptly added. The resulting solution was allowed to stand for 72 h under $N_2$ in the dark, whereupon the acetylated kraft lignin was precipitated by pouring it into 500 mL of water containing 30 mL of pyridine precooled to ~0 °C. The ensuing suspension was extracted with $CHCl_3$ (3 × 150 mL), and the combined nonaqueous phase was extracted with aqueous 0.5 M $H_2SO_4$ and washed with water (five times each). After drying ($Na_2SO_4$), the $CHCl_3$ was removed under reduced pressure.

The kraft lignin derivatives obtained from the respective treatments with the dialkyl sulfates and acetic anhydride/pyridine were further methylated with $CH_2N_2$ in $CHCl_3$ (to which small quantities of dioxane or dimethyl sulfoxide (DMSO) were added as necessary to facilitate complete sample dissolution). The $CH_2N_2$ was produced by slowly adding (150 mL in 30 min) 100 g $L^{-1}$ *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich, Milwaukee, WI) in $CHCl_3$ to 60 mL of 330 g $L^{-1}$ KOH in (1:1:1 v/v/v) $CHCl_3-EtO(CH_2)_2O(CH_2)_2OH-H_2O$ at 80 °C in a distilling flask.[29] (Here the diethylene glycol monoethyl ether had been purified in the customary manner.[30]) The $CH_2N_2$ was codistilled with $CHCl_3$ through a condenser fitted with a vacuum adapter into a receiving flask. Any $CH_2N_2$ that escaped the $CHCl_3$ codistilling into this flask passed through the outlet of the vacuum adapter by way of a gas inlet tube into $CHCl_3$ being chilled in an ice bath. As a final step, more $CHCl_3$ (50 mL) was added to the reaction flask to ensure complete codistillation of the $CH_2N_2$. The $CH_2N_2$ thus produced was employed in its entirety for the 14 h methylation of each 1.0 g sample of alkylated or acylated kraft lignin dissolved in $CHCl_3$. The resulting solution was extracted five times each with aqueous 0.5 M $H_2SO_4$ and water, and after drying ($Na_2SO_4$) the $CHCl_3$ was removed under reduced pressure.

**Solvent Casting Alkylated and Acylated Kraft Lignin-Based Thermoplastics.** The alkylated and acylated kraft lignin derivatives, with and without miscible low-$T_g$ polymers, were respectively dissolved at ~50 °C in DMSO at a concentration of 130 g $L^{-1}$ overall. The plasticizing blend components, namely the miscible aliphatic polyesters, poly(ethylene glycol), and poly(ethylene glycol)−bisphenol A diglycidyl ether adduct (Aldrich, Milwaukee, WI, Scientific Polymer Products, Ontario, NY, or Polysciences, Warrington, PA), were used as received without further purification. The resulting solutions were loaded into 10 × 20 mm molds fabricated by folding and clipping together lightly scored sections of Teflon sheet. The solutions were subjected to lengthy ultrasonication under reduced pressure so that each would be completely degassed when it was subsequently placed into a wide-mouth glass bottle that was promptly filled with $N_2$ and closed (but not sealed) with a screw-cap. The bottle holding the solution housed in its mold was placed into a vacuum oven that was immediately flushed with $N_2$. The DMSO was initially allowed to evaporate at 150 °C for 36 h, after which the temperature was raised by 30 °C to remove the remaining traces of solvent uniformly under reduced pressure.

**Tensile Tests.** Alkylated and acylated kraft lignin-based thermoplastic specimens were filed into 1.0 mm thick dogbone-shaped test pieces, the narrower rectangular sections between the broader (clamped) ends of which typically measured 9.0 mm × 5.0 mm (length × width). Thus, the configuration of the specimens used for tensile testing was comparable to that specified in ASTM D638. An Instron model 4026 Test System fitted with a ±1 kN static load cell and controlled by the series IX Material Testing System software (version 6.05) was used to characterize the tensile behavior of the alkylated and acylated kraft lignin-based thermoplastic formulations. The more brittle materials were clamped in place with smooth grip faces, while serrated grips were employed with the plastic pieces that were less rigid. The sections of material held between the grip faces were softened by brief exposure to hot air from a heat gun before tightening, but then each piece and the adjoining grips were allowed to reach ambient temperature prior to the initiation of the test. Stress−strain curves were generated with a crosshead speed of 0.05 mm $min^{-1}$ and typical specimen gauge lengths of 8−9 mm. The fracture surfaces of the test pieces exhibited uniform texture upon visual examination. The data were edited to correct for any artifacts arising from initial misalignment or looseness in the mechanical couplings to the grip faces. The resulting plots were digitized using a Summagraphics MM 1812 digitizing pad and transformed with a simple Fortran program to stress−strain curves in their final form. Young's moduli (*E*) were deduced from their initial slopes on the basis of initial sample dimensions.

**Differential Scanning Calorimetry (DSC).** DSC analyses were performed using 5−6 mg samples held in aluminum crucibles that were sealed under $N_2$. A small opening was made in the lid before each crucible was loaded into the DSC30 measuring cell of a TC11 TA processor-controlled Mettler TA4000 apparatus. The measuring cell was thoroughly flushed with $N_2$ before the blend was scanned at 5 °C min$^{-1}$ between −100 and 180 °C to remove any residual traces of moisture and to create a common thermal history for each material. The glass transition temperature ($T_g$) was then taken as the midpoint of the characteristic transition in a second DSC scan. The Levenberg−Marquardt algorithm in SigmaPlot 5.0 (SPSS Science, Chicago, IL) was employed for fitting the Gordon−Taylor equation to the $T_g$−composition data for blends of the methylated polydisperse higher molecular weight kraft lignin fraction and the acetylated methylated parent kraft lignin with aliphatic polyesters or poly(ethylene glycol).

**X-ray Powder Diffraction.** A Siemens microdiffractometer operating in the transmission mode with Cu K$\alpha$ (1.542 Å) radiation was employed to obtain X-ray powder diffraction patterns of the kraft lignin derivatives and their polymer material blends. The powdered samples (pulverized with a mortar and pestle after recovery from solution through solvent removal under reduced pressure) were compressed onto a zero-background holder, and the intensity of the X-rays passing through a flat graphite monochromator positioned in the diffracted beam was measured (as a function of angle) with a Siemens area detector. Data acquisition and analysis were carried out with the Siemens General Area Detector Diffraction Software system. The Bresenham algorithm was employed to integrate the area detector frame along the Debye rings (in the $\chi$ direction) giving a plot of intensity vs $2\theta$, where $\theta$ is the angle of diffraction. These standard X-ray powder diffraction patterns for any series of alkylated kraft lignin fractions or blends were compared by scaling the area under each curve with a Fortran program to the same value. Again, SigmaPlot 5.0 (SPSS Science, Chicago, IL) was used to fit Lorentzian component peaks (in terms of the Bragg angle, $2\theta_k$, for the reflection maximum, peak height, and peak width) to the diffuse scattered intensity in these patterns.

## Results and Discussion

Blends of aliphatic main-chain polyesters with ethylated and methylated kraft lignin preparations exhibit a window of miscibility circumscribed by a particular range (2.0−4.0) of $CH_2/COO$ for the polyester.[4] In this respect they are similar to aliphatic polyester blends with poly(bisphenol A carbonate),[16] poly(bisphenol A glycerolate),[17] poly(tetramethylbisphenol A carbonate),[18] and poly(vinyl chloride),[23] in which exothermic interactions give rise to homogeneous mixtures within characteristic ranges of polyester $CH_2/COO$.

However, there are profound differences as far as the actual impact is concerned of the aliphatic polyesters as plasticizers. A necessary (but not sufficient) condition for plastic deformation in the alkylated kraft lignin-based materials is that the $T_g$ of the blend lie below ambient temperature. It is the net effect of the intermolecular polyester−lignin, lignin−lignin, and polyester−polyester forces that determines how $T_g$ varies with blend composition.[19] Empirical analyses of the ensuing $T_g$−composition curves using the Gordon−Taylor equation[31] and Kwei's equation[32] have revealed that the polyester−lignin interactions are strongest when $CH_2/COO$ for the polyester falls between 2.5 and 3.0.[4]

Such conditions have an adverse effect upon the integrity of the supramacromolecular kraft lignin complexes that play a dominant role in maintaining blend cohesion. These immense assemblies of alkylated kraft lignin components tend to undergo dissociation, releasing more individual species into the blend and hence consuming more plasticizer counterproductively. The $T_g$−composition curve for the blend thus becomes less concave[25] so that the aliphatic polyester is needed in greater proportions to plasticize the polymeric material.[4]

The situation here is at the core of the dilemma that confronts attempts to improve plasticizer efficacy. Means must be found to enhance the impact of the plasticizer without increasing the strength of its interactions at the molecular level with the lignin components. This intrinsic predicament is the primary focus of the present work.

**Low Molecular Weight Enhancers of Plasticizer Efficacy.** A plausible way of improving the efficacy of plasticizers would be to enhance their interactions selectively with the peripheral regions of the supramacromolecular kraft lignin complexes: adverse effects upon the integrity of these huge associated entities would thus be minimized. Small molecules that interact preferentially with the individual components in the peripheral regions could well facilitate such an outcome. Actually lower molecular weight lignin components themselves might be particularly effective in this regard: their short chain lengths would preclude their incorporation into the interiors of supramacromolecular complexes where they would interfere with the intrinsic pattern of interactions between the segments of much longer polymer chains.

Indeed, the manner in which the individual components of differing molecular weight contribute to overall resistance toward mechanical deformation is an important characteristic of kraft lignin-based polymeric materials. Providing that the plasticization threshold has not been reached, the Young's modulus for polymer material blends based on methylated paucidisperse kraft lignin fractions is not significantly affected by the molecular weight of the constituent kraft lignin components (Figure 1). On the other hand, the tensile strength of these materials approaches an asymptotic limit[33] as it increases with the number-average molecular weight ($\bar{M}_n$) of the same discrete species (Figure 1). This agrees with early ideas about fracture in polymeric materials obligatorily being initiated at the "ends" of molecules; thus, the probability of failure should somehow depend on the number of such molecular "ends",[34] which in turn would be related to $1/\bar{M}_n$.[33]

Another important feature of Figure 1 lies in the quantity of miscible low-$T_g$ polymer needed to plasticize the different methylated kraft lignin preparations. The amount is significantly affected by the polydispersity of the alkylated lignin. After blending with 30% (w/w) poly(butylene adipate), both the methylated parent kraft lignin preparation and a polydisperse higher molecular weight fraction produced from it have exceeded the plasticization threshold, while the corresponding blends involving the paucidisperse kraft lignin fractions have not been plasticized. This is presumably related to the extent to which the available kraft lignin components can fill in the supramacromolecular domains of the associated complexes. Reducing the number of inter-

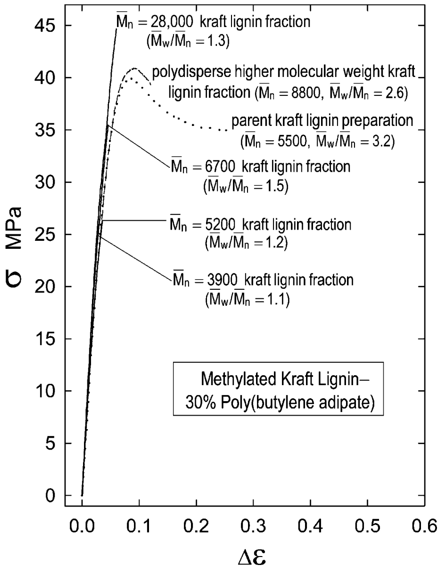

**Figure 1.** Tensile behavior of methylated kraft lignin-based blends with 30% poly(butylene adipate): effect of kraft lignin polydispersity. Young's modulus (1.00 ± 0.06 GPa) for materials based on paucidisperse fractions is independent of kraft lignin molecular weight.

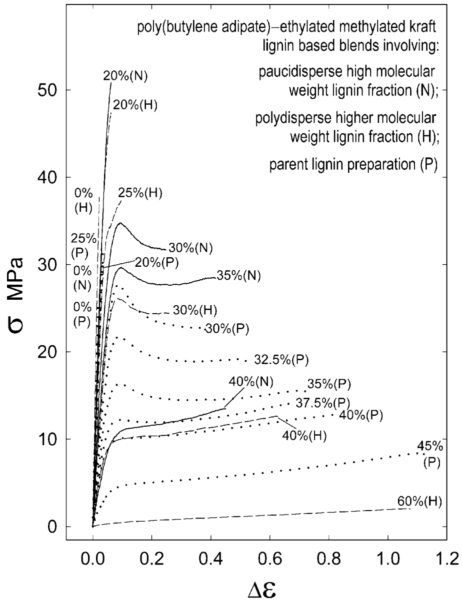

**Figure 2.** Progressive plasticization of ethylated methylated kraft lignin-based polymeric materials by poly(butylene adipate): effect of lower molecular weight kraft lignin components on plastic deformation. Paucidisperse high molecular weight fraction: $\bar{M}_w = 36.0 \times 10^3$, $\bar{M}_n = 28.0 \times 10^3$; polydisperse higher molecular weight fraction:[4] $\bar{M}_w = 23.0 \times 10^3$, $\bar{M}_n = 8.8 \times 10^3$; parent preparation:[4] $\bar{M}_w = 18.0 \times 10^3$; $\bar{M}_n = 5.5 \times 10^3$.

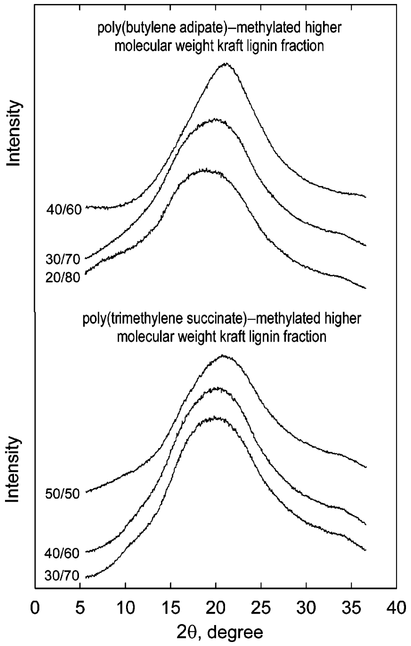

**Figure 3.** Wide-angle X-ray diffraction diagrams for blends of methylated polydisperse higher molecular weight kraft lignin fraction with poly(butylene adipate) and poly(trimethylene succinate).

stices and accessible macromolecular chains would lower the net frequency of interactions with the low-$T_g$ polymer molecules, which thus will be able to act more exclusively in their plasticizing capacity.

Concomitantly, when the threshold of plasticization has been exceeded in these formulations, the presence of lower molecular weight lignin components in the alkylated kraft lignin-based materials allows greater tensile strains to be attained before fracture occurs. This pattern is clearly evident in Figure 2 where the progressive plasticization of polymeric materials based on ethylated methylated paucidisperse and polydisperse[4] high molecular weight kraft lignin fractions is compared with the analogous effect in formulations with the parent[4] kraft lignin preparation. The materials based on the high molecular weight paucidisperse fraction ($\bar{M}_n$ = 28 000) exhibit similar behavior to those containing the polydisperse fraction ($\bar{M}_n$ = 8800), although the former are somewhat stronger. However, at ≥30% (w/w) poly(butylene adipate) levels (i.e., above the plasticization threshold), the alkylated parent kraft lignin-based materials sustain elongations to break, beyond the onset of plastic deformation, that are ~30% greater than those borne by the equivalent blends containing the higher molecular weight fractions. Thus, the lower molecular weight components in the ethylated methylated parent kraft lignin preparation are seen to enhance the effect of plasticization by miscible low-$T_g$ polymers. In a general way, this is reminiscent of the synergy in the effects of tributyl phosphate and water on the thermal softening temperature of softwood thiolignin.[35]

**X-ray Diffraction Studies.** In blends with successively larger proportions of plasticizing aliphatic polyester, the overall maximum in the intensity of the characteristic amorphous halo in the X-ray diffraction diagram obtained from alkylated kraft lignin-based materials is progressively displaced toward larger scattering angles (Figure 3), i.e., smaller *d*-spacings. The precise effect of the polyester upon the diffuse scattered intensity cannot be predicted in a simple way: the miscible low-$T_g$ polymer contributes appreciably to the diffraction pattern, even if much less strongly than the aromatic lignin components themselves. Hence, the underlying determinants of the observed trend may be more clearly apprehended from a series of alkylated kraft lignin preparations that exhibit a comparable result without the introduction of any other blend components. Such an effect is encountered with paucidisperse methylated kraft lignin fractions of progressively decreasing molecular weight in the absence of any added aliphatic polyester (Figure 4). That a similar

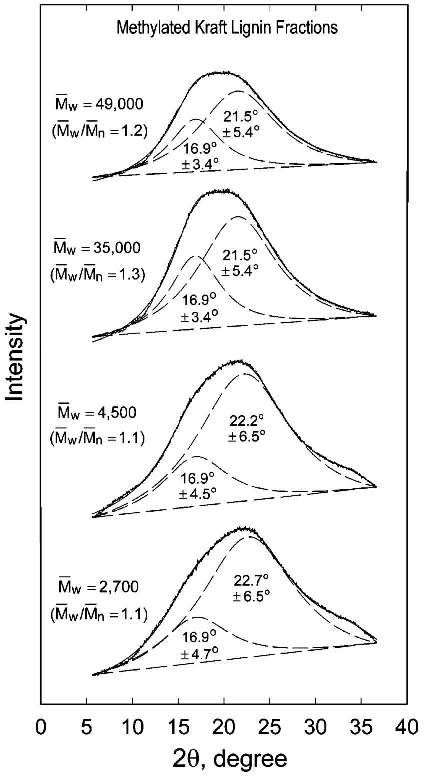

**Figure 4.** Fits of two principal Lorentzian functions to diffuse scattered intensity in the X-ray diffraction patterns of methylated paucidisperse kraft lignin fractions.

trend is observed in this context may not be surprising in view of the fact that alkylated low molecular weight kraft lignin components can enhance the efficacy of miscible low-$T_g$ aliphatic polyesters as plasticizers (vide supra: Figure 2).

In describing the shapes of the peaks that contribute to the halos typically obtained from amorphous polymers, adequate fits with few adjustable parameters are given by Lorentzian functions:[36]

$$I(x) = I(0)/(1 + x^2/(\text{hwhm})^2), \quad x = 2\theta - 2\theta_k$$

where $I(x)$ is the scattered intensity at distance $x$ from the Bragg angle $2\theta_k$ for the reflection, $2\theta$ is the scattering angle, and hwhm is the half-width at the half-maximum of the peak. Thus, a sum of two Lorentzian component peaks (centered at $2\theta = 16.9°$, $d = 5.25$ Å and $2\theta = 22.1 \pm 0.6°$, $d = 4.0 \pm 0.1$ Å) is necessary to describe the diffuse scattered intensity in the $2\theta = 5-35°$ (Cu Kα) range of the X-ray diffraction patterns from the methylated paucidisperse kraft lignin fractions (Figure 4). This suggests that there is some degree of short-range order in these noncrystalline materials. The two major peak maxima occur at the same scattering angles as reported earlier for a methylated softwood (cedar) dioxane lignin sample, although in the latter instance an inner halo centered at $d = 8.5$ Å was also observed.[37] A basis for proposing reasonable assignments can be inferred from the legacy of pertinent examples furnished by the literature.

Usually the diffuse scattered intensity in the X-ray diffraction pattern of an amorphous polymeric material is not easy to interpret. In these materials short-range order is inevitably anisotropic (even though there is no long-range three-dimensional order) because dense packing of macromolecular chain segments cannot be achieved without some correlation between their relative positions and orientations.[38] Anisotropic short-range order in such cases may be treated through the autocorrelation function of the electron density distribution in physical space and the corresponding scattered intensity distributions in reciprocal space.[38] From the electron density distribution, a radial atomic distribution function can be obtained that yields information more directly on molecular structure, but the scattered intensity distributions provide a clearer picture of intermolecular arrangements.[38]

Thus, the amorphous scattering from atactic polystyrene has been characterized by two Lorentzian peaks centered at well-separated $d$-spacings ($2\theta = 10°$, $d = 8.9$ Å and $2\theta = 19°$, $d = 4.6$ Å).[39] A radial distribution function analysis suggested that 87% of the amorphous peak centered at 4.6 Å arises from two kinds of spacing: intermolecular separations between benzene rings and intramolecular distances between aromatic ring and chain atoms.[40] On the other hand, the 8.9 Å peak was attributed largely to intermolecular distances[39] since it was shifted to smaller angles at temperatures above $T_g$[41] while the 4.6 Å peak was unaffected. Interestingly, it was first reported almost 70 years ago that liquid styrene exhibits an amorphous halo centered at 4.6 Å, although there is no 8.9 Å subsidiary maximum in the diffuse scattered intensity.[42]

A comparable yet contrasting situation was encountered in the X-ray diffraction pattern emanating from the amorphous phase of partially crystalline poly(ethylene terephthalate), which also required two Lorentzian functions (centered at $2\theta = 17.5°$, $d = 5.1$ Å and $2\theta = 23.5°$, $d = 3.8$ Å) to fit the amorphous halo.[43] On the basis of the proximity of these amorphous peaks to two characteristic reflections from the crystalline poly(ethylene terephthalate) domains, the 3.8 Å peak was attributed to intermolecular distances perpendicular to the aligned aromatic rings, while the 5.1 Å peak was assumed to embody contributions from two other series of intermolecular distances, viz. those in the planes of the aromatic rings and those between randomly oriented chains.[43] Here the correspondence between the amorphous peaks and the reflections from crystalline domains in the same partially crystalline polymeric material was central to the interpretation.

Unfortunately, lignins and lignin derivatives are not crystallizable polymers. Consequently, assignments of the Lorentzian component peaks centered at $2\theta \approx 17°$ and 22° in the amorphous halos from methylated kraft lignin fractions (Figure 4) and methylated softwood dioxane lignin[37] cannot be established by comparison with reflections from crystalline domains in the same kinds of materials. The dominant contributions to the X-ray diffraction patterns of lignins are expected to come from the interacting aromatic rings; that their relative placement can conform with a number of possible geometries is evident from the crystal structures of several dimeric and (in one case) trimeric lignin model compounds. On one hand, nonbonded orbital interactions will be significant between cofacial aromatic rings that descend to an energy minimum at small ($\leq 3.4$ Å) separation distances.[44] Such a situation has been encountered in the crystal structures of divanillyltetrahydrofuran[45] and a 5−5′,8−$O$−4″ linked trilignol derivative.[46] On the other hand, when nonbonded orbital interactions fail to compensate for $\pi$-electron repulsion, face-to-face placement of two aromatic rings is unfavorable; instead, there is a continuum of favorable geometries extending from a parallel offset arrangement to an edge-on relationship.[47] The former is essentially what prevails at ~4.6 Å intermolecular separation distances in the crystal structure of a typical (phenolic) 8−5′ linked dilignol,[48] while the latter is a reasonable representation of what occurs at ~5.3 Å intermolecular separations in the crystal structure of a standard (nonphenolic) 8−*O*−4′ linked dilignol.[49]

Thus, the *d*-spacings between approximately parallel aromatic rings in these di- and trimeric lignin model compounds vary between 3.4 and 4.6 Å (with an average of ~4.0 Å), while those between aromatic rings bearing an edge-on relationship to one another are centered around ~5.3 Å. The similarities between these values and those for the two component Lorentzian peak maxima at 4.0 Å and 5.25 Å in the amorphous halos of the methylated lignin preparations (Figure 4) are quite striking. The demands of packing small molecules into crystalline domains are, of course, different from the corresponding requirements of macromolecules in amorphous domains. Nevertheless, in view of the close agreement between the diffuse scattering from liquid styrene[42] and amorphous polystyrene[39] (vide supra), there should be meaningful correlations between the X-ray diffraction patterns of di- and trilignols, on one hand, and those of polymeric lignin derivatives, on the other. Hence the 4.0 and 5.25 Å component peak maxima in the amorphous halos arising from the methylated kraft (Figure 4) and dioxane[37] lignins may be provisionally assigned, in part, to arrangements of aromatic rings that are respectively parallel and edge-on in relation to each other.

The $2\theta = 16.9°$ maximum of the peak encompassing the (~5.25 Å) *d*-spacings between the edge-on pairs of aromatic rings in the methylated paucidisperse kraft lignin fractions does not change with the molecular weight of the components, but the width of the peak is about 40% greater for the lower molecular weight preparations (Figure 4). The effect presumably arises from the fact that the higher molecular weight kraft lignin components are largely incorporated in supramacromolecular associated complexes[4,6,26] where there is less opportunity for variations in intermolecular registration. The $2\theta = 21.5°$ maximum of the peak embracing contributions from parallel aromatic rings in the methylated kraft lignin complexes corresponds to a *d*-spacing of 4.1 Å. This peak is shifted to slightly higher scattering angles ($d = 3.9$−$4.0$ Å) and is broadened significantly (by ~20%) for the lower molecular weight methylated kraft lignin fractions, which can accommodate greater freedom as far as relative placement of the aromatic rings is concerned (Figure 4).

The foregoing methylated paucidisperse kraft lignin fractions differ in a fundamental way from the corresponding polydisperse higher molecular weight fraction included in Figure 1. The latter was isolated (before alkylation) by ultrafiltration in aqueous 0.10 M NaOH through a $1 \times 10^4$ nominal molecular weight cutoff membrane, and most of the constituent components have been incorporated into supramacromolecular complexes that are in a more completely assembled state than in the paucidisperse fractions. These immense associated assemblies are built in a well-defined manner from thousands of discrete components embracing quite a broad range of molecular weight.[6,26] The conditions under which the higher molecular weight polydisperse kraft lignin fraction was prepared facilitated virtually complete removal of those species that were not trapped in these associated complexes.

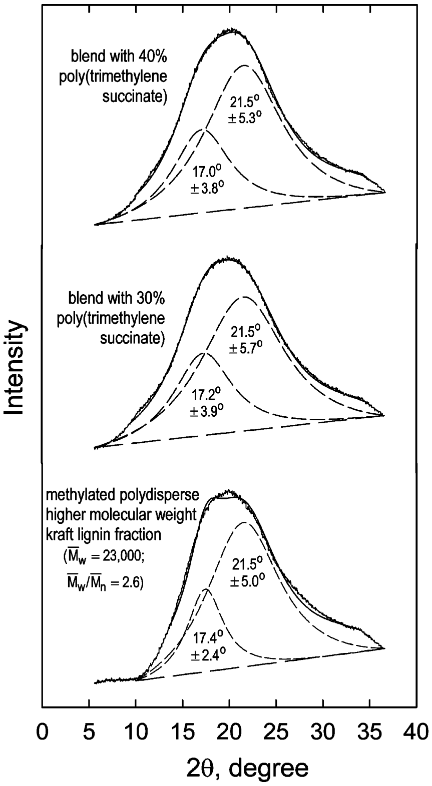

**Figure 5.** Fits of two principal Lorentzian functions to diffuse scattered intensity in the X-ray diffraction patterns of the methylated polydisperse higher molecular weight kraft lignin fraction and its blends with poly(trimethylene succinate).

The ($2\theta = 21.5 \pm 5.0°$) Lorentzian peak which embodies the diffuse scattering from parallel aromatic rings in the methylated polydisperse higher molecular weight kraft lignin fraction (Figure 5) is centered at the same *d*-spacing (4.1 Å) as observed for the paucidisperse high molecular weight fractions (Figure 4). On the other hand, the maximum of the Lorentzian peak ($2\theta = 17.4 \pm 2.4°$) that includes reflections from the aromatic rings in edge-on orientations with respect to one another (Figure 5) is displaced to a slightly smaller *d*-spacing (5.1 Å) than found with the methylated paucidisperse high molecular weight kraft lignin fractions; furthermore, the width of the peak is ~30% narrower (Figure 5). This presumably reflects the fact that the associated complexes in the polydisperse higher molecular weight kraft lignin fraction are in a more complete state of assembly (vide supra) than in the paucidisperse high molecular weight fractions.

The two Lorentzian peaks centered at *d*-spacings of 4.1 and 5.1 Å in the amorphous halo emanating from the methylated polydisperse higher molecular weight kraft lignin fraction are broadened by ~10% and 60%, respectively, as a result of blending with 30−40% poly(trimethylene succinate). The reflections to which the poly(trimethylene succinate) chains contribute are integrated into the X-ray diffraction patterns of the blends in a way that is not predictable a priori: the effects of adding the polymeric plasticizer are not entirely systematic (Figure 5). Nevertheless, it is evident that there is a far greater broadening in the distribution of separations between edge-on than between parallel aromatic rings among the methylated kraft lignin

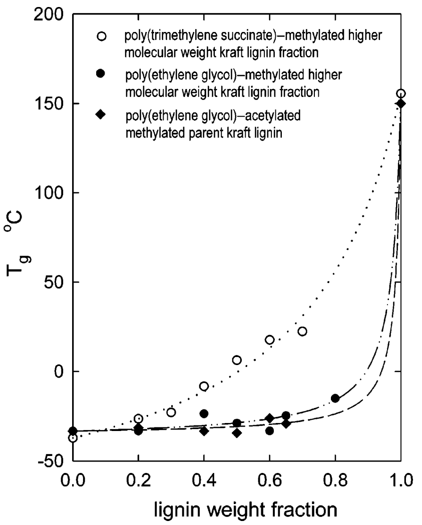

**Figure 6.** Variation of $T_g$ with composition for blends of methylated polydisperse higher molecular weight kraft lignin fraction with poly(trimethylene succinate) and poly(ethylene glycol), and of acetylated methylated parent kraft lignin with poly(ethylene glycol).

components. The contrast would be in accord with intuitive expectations if the interactions between the edge-on aromatic rings (which are separated by greater distances) are weaker than those between the parallel rings. There are obvious qualitative similarities between the effects on the X-ray diffraction diagrams of adding poly(trimethylene succinate) (Figure 5) and reducing the molecular weight of the kraft lignin components (Figure 4); this is consistent with the fact that the presence of the lower molecular weight components enhances the plasticization of alkylated kraft lignin-based polymeric materials by the miscible aliphatic polyesters (Figure 2).

**Miscible Polymers with Heightened Plasticizing Capability.** The proportion of a miscible low-$T_g$ polymer required to bring the plasticization threshold of an alkylated kraft lignin-based blend to ambient temperature is related phenomenologically to the concavity of the corresponding $T_g$–composition curve.[25] Analysis of the latter in terms of the Gordon–Taylor equation,[31] for example, indicates that this is equivalent to reducing the net strength of the intermolecular forces between dissimilar blend components.[4] Thus, the plasticizing capability of a low-$T_g$ polymer will be greater when its interactions with the alkylated kraft lignin components are weaker—providing that the blend remains miscible. This is consistent with the need to preserve the integrity of the supramacromolecular complexes which largely govern the mechanical properties of kraft lignin-based materials.

The differing $T_g$–composition curves (Figure 6) for blends of the methylated polydisperse higher molecular weight kraft lignin fraction with poly(trimethylene succinate) and poly(ethylene glycol) effectively illustrate the point. In the poly(ethylene glycol) blends, $T_g$ initially increases only very gradually with lignin content; there is very little change when the level of the methylated kraft lignin fraction remains below 65% (w/w). On the other hand, the $T_g$ of the blends with poly(trimethylene succinate) has increased by over 50 °C when similar proportions of components in these materials have been mixed together.

**Table 1. Fits of Gordon–Taylor Equation to Selected Blend $T_g$–Composition Data**

| low-$T_g$ polymer blend with kraft lignin derivative[a] | $k'$ in Gordon–Taylor equation |
|---|---|
| PTMS-methylated higher mol wt fraction | 0.24[b] |
| PBA-methylated higher mol wt fraction | 0.17[b] |
| PEG-methylated higher mol wt fraction | 0.025 |
| PBA-acetylated methylated parent preparation | 0.014 |

[a] PBA = poly(butylene adipate); PEG = poly(ethylene glycol); PTMS = poly(trimethylene succinate). [b] Analysis[4] of previous data included for comparative purposes.

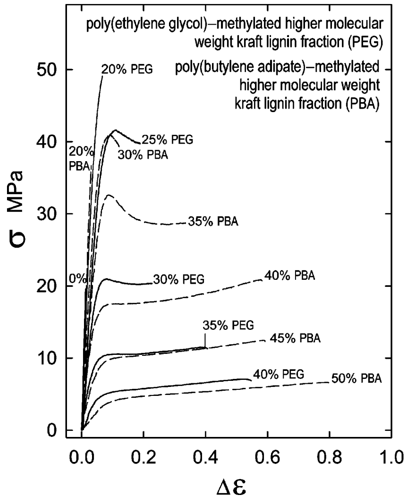

**Figure 7.** Progressive plasticization of methylated polydisperse higher molecular weight kraft lignin fraction in blends with poly(ethylene glycol) and poly(butylene adipate).

The distinction is reinforced by analyses of the data with the Gordon–Taylor equation[31] (Table 1):

$$T_{gm} = \frac{w_1 T_{g1} + k' w_2 T_{g2}}{w_1 + k' w_2}$$

Here $k'$ increases with the strength of the intermolecular forces between dissimilar components in the blend and thus can be taken qualitatively as a relative measure of their magnitude. As shown in Table 1, the $k'$ value for the blends of the methylated polydisperse higher molecular weight kraft lignin fraction with poly(ethylene glycol) is 10-fold smaller than that for the corresponding poly(trimethylene succinate) blends; it is 7-fold smaller, even, than the $k'$ value characterizing the blends with poly(butylene adipate) which, with a polyester $CH_2/COO$ of 4.0, are near the boundary of the miscibility window for such alkylated kraft lignin-based materials.[4]

These observations are consistent with the fact that significantly less poly(ethylene glycol) is required (<25% w/w) to plasticize methylated kraft lignin blends (Figure 7) than the 30% and 35% levels needed with poly(butylene adipate) and poly(trimethylene succinate), respectively. (The effect of poly(trimethylene succinate) is very similar to that of poly(trimethylene glutarate).[4]) It can be seen that, once the plasticization threshold has been exceeded, the tensile strengths of the methylated polydisperse higher molecular weight kraft lignin blends decrease much more rapidly with increasing content of poly(ethylene glycol) than that of poly(butylene adipate). The difference in behavior arises from the mechanical properties of the low-$T_g$ polymers:

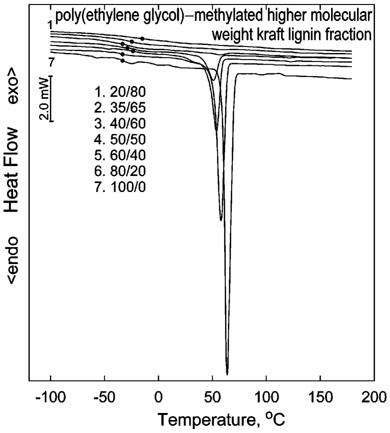

**Figure 8.** Differential scanning calorimetric curves (5 °C $\mathrm{min}^{-1}$) for blends of methylated polydisperse higher molecular weight kraft lignin fraction with poly(ethylene glycol). The $T_g$'s of the blends are denoted by ●.

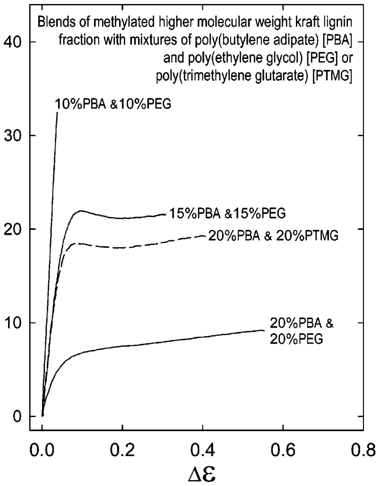

**Figure 9.** Tensile behavior of methylated polydisperse higher molecular weight kraft lignin fraction in blends with mixtures of poly(butylene adipate) and poly(ethylene glycol) or poly(trimethylene glutarate).

with a molecular weight of ~1.0 × $10^4$, poly(ethylene glycol) is a waxlike material so weak that its tensile behavior cannot be documented under ambient conditions.[50]

Even though the interactions between poly(ethylene glycol) and the methylated kraft lignin components are very weak (Table 1 and Figure 6), the melting point of the low-$T_g$ polymer is depressed by 13 °C (Figure 8) when the proportion of the methylated higher molecular weight kraft lignin fraction in the mixture has been increased to 50% (w/w). Thus, the blends are still homogeneous, and indeed, at 60% levels of these methylated kraft lignin components, the melting transition of the poly(ethylene glycol) is no longer detectable (Figure 8).

As poly(butylene adipate) is replaced by poly(ethylene glycol) in blends of the methylated polydisperse higher molecular weight kraft lignin fraction containing 30–40% (w/w) polymeric plasticizer altogether, there is a 2–3-fold reduction in tensile strength (Figure 7). The majority (85–90%) of the effect occurs when only half of the aliphatic polyester has been replaced by the other low-$T_g$ polymer (Figure 9). Since the methylated kraft lignin species interact at the molecular level much more strongly with the poly(butylene adipate) components (Table 1), the dominant effect of the poly(ethylene glycol) probably lies in its impact upon the mechanical properties of the polymeric plasticizer mixture. Thus, there is, in contrast, very little change in the tensile strength of the blend containing a total of 40% (w/w) polymeric plasticizer (Figure 7) when half of the poly(butylene adipate) has been replaced by poly(trimethylene glutarate)[4] (Figure 9).

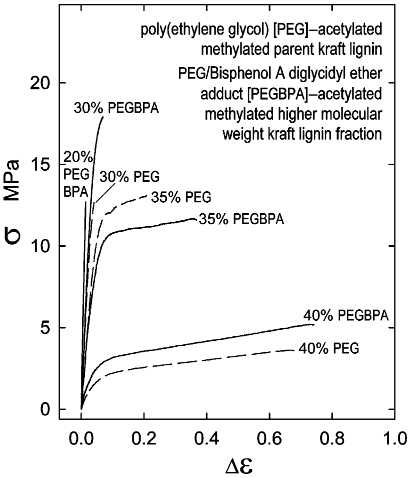

**Figure 10.** Plasticization of acetylated methylated kraft lignin preparations in blends with poly(ethylene glycol) or its bisphenol A diglycidyl ether adduct.

**Acetylated Kraft Lignin-Based Polymeric Materials.** Acylated kraft lignin derivatives give rise to materials that are weaker and more brittle than those based on alkylated kraft lignins. Nevertheless, acetylated methylated kraft lignin preparations can be toughened and plasticized by poly(ethylene glycol) and its adduct with bisphenol A diglycidyl ether (Figure 10). The plasticization threshold lies between 30% and 35% (w/w) levels of poly(ethylene glycol) or the adduct in blends with the acetylated methylated parent kraft lignin preparation or higher molecular weight fraction derived from it. However, introduction of additional poly(ethylene glycol) or the adduct beyond this point brings about a rapid reduction in the tensile strengths of the resulting acetylated methylated kraft lignin-based blends (Figure 10). Indeed, the variation of $T_g$ with blend composition (Figure 6) indicates that poly(ethylene glycol) interacts more weakly with kraft lignin components that have been acetylated and methylated than those that have just been methylated. The value of $k'$ in the Gordon–Taylor equation is almost 2-fold smaller for the acetylated methylated kraft lignin-based blends with poly(ethylene glycol) than for similar methylated kraft lignin-based materials (Table 1).

Be that as it may, the acetylated methylated kraft lignin-based blends with poly(ethylene glycol) seem to be homogeneous; the melting point of this low-$T_g$ polymer is depressed by 9 °C when the proportion of acetylated methylated kraft lignin components is 50% (w/w) (Figure 11). The melting transition disappears completely only when the acetylated methylated kraft lignin level reaches 65%. Comparison with the corresponding blends based on the methylated polydisperse higher molecular weight kraft lignin fraction (Figure 8) affirms that these findings are in qualitative accord with the $T_g$ data (Figure 6). The melting point of the poly(ethylene glycol) is depressed by 13 °C when blended with 50% levels of the methylated kraft lignin components, and the melting transition is no longer visible when the proportion of the methylated higher molecular

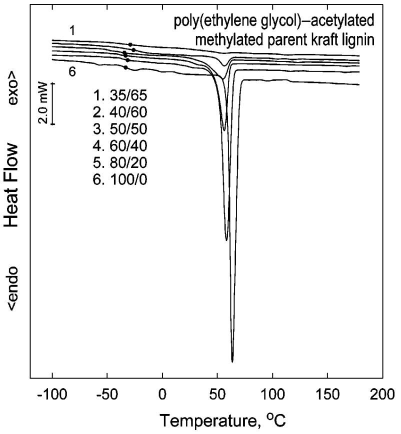

**Figure 11.** Differential scanning calorimetric curves (5 °C min$^{-1}$) for blends of acetylated methylated parent kraft lignin preparation with poly(ethylene glycol). The $T_g$'s of the blends are denoted by ●.

weight kraft lignin fraction has reached 60%. Only part of this disparity could arise from the fact that, merely by virtue of the differences in derivatization, the molecular weights of the acetylated methylated kraft lignin components are ~20% greater than those of the methylated components. As reflected in the way in which $T_g$ varies with blend composition (Figure 6 and Table 1), the acetylated methylated kraft lignin components interact less strongly than the methylated kraft lignin components with the poly(ethylene glycol) chains.

## Conclusions

There are some singular aspects to the trends manifested in the mechanical properties of homogeneous polymer blends based on alkylated kraft lignins. They arise from the fact that the behavior of simple kraft lignin derivatives is largely governed by well-defined supramacromolecular complexes containing many thousands of individual components.[6,25] Thus, the strengths of kraft lignin-based materials depend palpably on the extent to which these very high molecular weight species have been preserved intact.

As far as plasticizing activity is concerned, miscible low-$T_g$ polymers are more efficient when their interactions with the alkylated kraft lignin components are minimized. Beyond the plasticization threshold, small proportions of low molecular weight alkylated kraft lignin components have little impact on tensile strength, and yet their presence extends the amount of plastic deformation that can occur before fracture. The action of the low molecular weight components is presumably restricted to the peripheral regions of the supramacromolecular associated kraft lignin complexes. The character of the kraft lignin derivative is important: acylated preparations are plasticized by poly(ethylene glycol) and some of its adducts, but the resulting blends are less strong than those based on their alkylated counterparts.

The X-ray powder diffraction diagrams of alkylated kraft lignin-based materials are dominated by two overlapping Lorentzian peaks that reflect different distributions of separation distances between the constituent aromatic rings. One may be ascribed to rings that are cofacially positioned in roughly parallel orientations but offset to varying degrees. The other is attributable to aromatic rings that bear more-or-less edge-on relationships to one another over a range of angles about the perpendicular. The polymeric plasticizer primarily affects the latter distribution of inter-aromatic-ring distances, which is broadened substantially even though there is little movement in the position of the Lorentzian peak maximum. The effect is quite comparable to the immediate outcome of cleaving the kraft lignin chains themselves. This is consistent with the fact that the lower molecular weight components will enhance the extent to which alkylated kraft lignin-based polymer blends of a given composition are plasticized.

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