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Alkylated Kraft Lignin-Based Thermoplastic Blends with Aliphatic Polyesters

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ABSTRACT: Polymeric materials solely composed of certain alkylated kraft lignin preparations can be quite similar to polystyrene in tensile behavior. They may be plasticized in forming miscible blends with aliphatic polyesters possessing methylene/carboxylate group ratios (CH_2/COO) of 2.0−4.0. The alkylated kraft lignin species in such materials range from individual molecular components to huge supramacromolecular associated complexes. The interactions between the alkylated kraft lignin components and polyester chains are most favorable when CH_2/COO falls between 2.5 and 3.0. Under these circumstances a much smaller proportion of alkylated kraft lignin in the blend is required to disrupt the crystalline domains of the polyester than if CH_2/COO were 4.0. Despite this, appreciably more aliphatic polyester is needed to plasticize the alkylated kraft lignin when CH_2/COO lies between 2.5 and 3.0: the supramacromolecular complexes tend to be dismantled to a greater extent when the plasticizer interacts more favorably with the individual kraft lignin components of which they are composed.

Introduction

The first successful formulations for thermoplastics with very high lignin contents were reported in 1997. They had been created by blending 85% softwood kraft lignin with poly(vinyl acetate) in the presence of diethylene glycol dibenzoate (1.6% overall) and indene (0.8%).[1] Despite their promising tensile properties, however, the importance of these thermoplastics lay chiefly in the feasibility of their fabrication: the constituent (underivatized) kraft lignin components still tended to dissolve to a limited extent in aqueous alkaline solution. Nevertheless, it soon proved possible to make polymeric materials composed entirely of ethylated methylated kraft lignin; indeed, the tensile behavior of these new materials was very similar to that of polystyrene.[2] Like polystyrene, such alkylated 100% kraft lignin-based polymeric materials are quite brittle, but they can be effectively plasticized by blending with suitable aliphatic polyesters.[3,4]

The foregoing developments had been preceded by altogether different approaches to producing lignin-containing polymeric materials. The earlier attempts had sought to introduce progressively larger proportions of suitable lignin derivatives into other perfectly good polymeric materials until their mechanical properties had been fatally compromised. In such a context, the effective incorporation limits for lignin derivatives in useful polymeric materials had typically fallen between 25 and 40% (w/w).[5] Representative in this regard was a series of polyurethanes obtained by reacting kraft lignin fractions with a propylene-oxide-derived polyether triol and a polymeric MDI. Whatever their molecular weights,[6] when the contents of the kraft lignin fractions exceeded 30−35%, hard brittle polyurethanes always resulted regardless of the isocyanate:hydroxyl group ratio employed.[7] However, as polyurethane constituents, the kraft lignin components had been regarded chiefly as polyols, but otherwise their physicochemical properties had not been explicitly taken into account.

Lignins occur naturally in the cell walls of all vascular plants, and as such, they represent the second most abundant group of biopolymers. They have been thought to be constituted from up to 10 different linkages between *p*-hydroxyphenylpropane units.[8] The predominant byproducts of the kraft pulping process (whereby wood chips are transformed through delignification into cellulosic fibers for making paper) are the kraft lignins, which have been modified quite extensively in relation to the native biopolymeric structure.[9] Over 25×10^6 tons of these kraft lignins is produced annually in the United States alone. There are pronounced noncovalent attractive interactions between the individual molecular kraft lignin species.[10] These engender multimodal distributions of well-defined associated complexes that extend to molecular weights between 10^3- and 10^4-fold higher than those of the individual components, even after the latter have been acetylated.[11]

Such supramacromolecular complexes might be expected to contribute to the cohesiveness of kraft lignin-based polymeric materials. Indeed, this was observed for the tensile strengths and Young's moduli of the 85% kraft lignin-based thermoplastic blends with poly(vinyl acetate) and the two plasticizers: they varied linearly with the $\bar{M}_w$'s of the kraft lignin preparations as the degree of association between the constituent molecular species was modulated.[1] Actually, at the molecular level these thermoplastics embodied two kinds of kraft lignin species, namely huge supramacromolecular complexes (measuring 0.2−0.3 μm across[12]) and the much smaller individual molecular components; both had, of course, been jointly blended with the poly(vinyl acetate).

In this connection an important insight was brought to light by kraft lignin preparations that had been fractionated to remove all the unassociated (individual) molecular components present in solution at neutral pH.[12] The resulting blends with the poly(vinyl acetate) and two plasticizers produced polymeric materials so weak that their tensile properties could not be measured.[1] Thus, compatibility between the associated kraft lignin complexes and poly(vinyl acetate) seemed to be facilitated by the presence of the individual kraft lignin components that were blended in the latter.

The presently reported work is the result of the first comprehensive attempt to characterize the recently

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developed[3,4] thermoplastic blends of ethylated and methylated kraft lignin preparations with aliphatic polyesters. The proposition that both associated kraft lignin complexes and individual kraft lignin components contribute to blend composition has been confirmed in the patterns of behavior discerned with the various miscible polyesters examined. The relative proportions of the associated and discrete kraft lignin species were clearly affected by the strengths of the intermolecular interactions between the aliphatic polyester chains and individual kraft lignin components.

Experimental Section

Underivatized Kraft Lignin Preparations. The original source of all the kraft lignin preparations used in the present work was kraft black liquor produced from Jack pine (*Pinus banksiana*) by the Boise Cascade Corp. (International Falls, MN). Although the kraft pulping conditions employed were not divulged, a ≥2 h treatment of the softwood chips at 170 °C in aqueous solution containing 45 g L^{-1} NaOH and 12 g L^{-1} or more Na_2S would traditionally have represented reasonable industrial practice.

After (7.3-fold) dilution with HPLC-grade water to 2.0 L, the black liquor (pH 12.5) was filtered through a VWR grade 417 paper to remove any fibrous materials, whereafter aqueous 1.0 M HCl was slowly added (0.2 mL min^{-1}) with vigorous stirring. At pH 11.0, the solution was centrifuged (1380*g*, 30 min) to remove any solid material that had separated, and then gradual acidification was resumed until the pH had reached 3.0. Upon being isolated by centrifugation (3100*g*, 30 min), the resulting precipitate was washed three times by resuspending in water acidified (with dilute aqueous HCl) to pH 3.0 and centrifuging. Whenever kraft lignin precipitation was incomplete during the washing procedure, the remaining suspension was basified to pH 8.5 (with carbonate-free aqueous 0.10 M NaOH) and the resulting clear solution rapidly reacidified to pH 3.0; subsequent centrifugation would then normally lead to a complete recovery of the solid kraft lignin. The combined precipitated kraft lignin portions from the third wash were finally suspended in HPLC-grade water (500 mL) and redissolved upon basification to pH 8.5. After standing for 12 h, the clear solution was centrifuged (35 600*g*, 30 min) to remove colloidally suspended sulfur and then freeze-dried to provide a stock of kraft lignin of intermediate purity.

This parent kraft lignin preparation was purified by redissolving it in distilled water, readjusting the pH to 8.5, and exhaustively ultrafiltering the resulting solution with a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA) using distilled and then triply distilled water. When the volume of permeate had exceeded 20 times that of the ultrafiltration cell, the retentate solution (final pH 7.0−7.5) was concentrated 5-fold, centrifuged (35 600*g*, 30 min) to remove any suspended sulfur, and freeze-dried.

A higher molecular weight kraft lignin fraction, retained in aqueous 0.10 M NaOH by a 1.0×10^4 nominal molecular weight cutoff membrane (Amicon YM10, Millipore Corp., Bedford, MA), was produced from the parent preparation before the latter had been fully purified. The parent preparation was dissolved in aqueous 0.10 M NaOH (under N_2) and thus exhaustively ultrafiltered for 7 days by introducing more of the same solution at a rate amounting to 20 times the volume of the ultrafiltration cell in that time period. Such a flow rate was sufficiently slow for dissociation between the kraft lignin components to approach completion under these conditions.[10,12] The process was then continued using the same overall volume of distilled water (at a similar flow rate), triply distilled water being employed for the final ultrafiltration stage to prevent the pH from falling below 7.0 and to ensure high purity in the retentate. After centrifuging (35 600*g*, 30 min) to remove any colloidally suspended sulfur, the kraft lignin species retained in solution (final pH 7.0−7.5) by the YM10 membrane were freeze-dried.

Kraft Lignin Fractionation by Consecutive Ultrafiltration. The molecular weight dependence of certain properties of the kraft lignin-based materials was considered to be central in developing a coherent basis for analyzing the most instructive results afforded by the present work. To this end, paucidisperse fractions with progressively decreasing molecular weights were prepared by consecutive ultrafiltration of the parent kraft lignin preparation through membranes with successively decreasing molecular weight cutoffs in (carbonate-free) aqueous 0.10 M NaOH.

The overall process was begun by ultrafiltering a 70 g L^{-1} parent kraft lignin solution (1.0 L) in aqueous 0.10 M NaOH through a 1×10^5 nominal molecular weight cutoff (Amicon YM100, Millipore Corp., Bedford, MA) membrane. When the retentate volume had been reduced 2-fold (to 500 mL in a 2.5 L cell), an equal volume of aqueous 0.10 M NaOH was added, whereupon ultrafiltration was resumed. This entire procedure was carried out (as were the subsequent ultrafiltration steps) 15 times during a period extending over 7 days so that sufficient dissociation of the kraft lignin components could occur from the associated macromolecular complexes in which they are usually incorporated.[10,12] Completeness of fractionation was engendered by the progressive removal of individual kraft lignin components through the ultrafiltration membrane, which in the retentate necessitated a continual readjustment of the associative−dissociative equilibrium toward dissociation.

Hereafter ultrafiltration was continued, as rapidly as possible, to completion in the same way with (triply) distilled water. Appropriate precautions were taken throughout to ensure that the solutions remained essentially carbonate-free. The retentate solution (final pH 7.0−7.5) was centrifuged (35 600*g*, 30 min) to remove any colloidal sulfur and then freeze-dried.

The permeate from the 1×10^5 nominal molecular weight cutoff membrane was then ultrafiltered through a 5×10^4 nominal molecular weight cutoff membrane (MFS, Dublin, CA). When the volume of the retentate solution held by the second membrane had reached 300 mL (in a 2.5 L cell), the NaOH concentration was adjusted to 0.10 M with aqueous 1.0 M NaOH, and ultrafiltration was continued with aqueous 0.10 M NaOH and (triply) distilled water consecutively, as described above. In the same way the respective kraft lignin permeate solutions were successively ultrafiltered through membranes with nominal molecular weight cutoffs of 3×10^4, 1×10^4, 5×10^3, 3×10^3, and 1×10^3 (respectively Amicon YM30, YM10, YM5, YM3, and YM1, Millipore Corp., Bedford, MA). Each retentate solution was freeze-dried.

The permeate from the last of these was subjected to ultrafiltration using a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA), which is not resistant to solutions with pH above 8.5. Thus, the permeate was acidified (with aqueous 1.0 M HCl) to pH 8.0−8.2 before being subjected to exhaustive ultrafiltration with distilled and triply distilled water. The quantities of sulfur precipitating out of the retentate solution under these conditions were so large that they had to be removed periodically by centrifugation (35 600*g*, 30 min). Ultimately, the water was removed from the lowest molecular weight kraft lignin fraction by freeze-drying, as it had from all the others.

Molecular Weight Distributions of Kraft Lignin Samples. The molecular weight distributions of the purified kraft lignin preparations and fractions were determined by size-exclusion chromatography. The profiles appearing in (carbonate-free) aqueous 0.10 M NaOH as a result of elution (~6.6 mL cm^{-2} h^{-1}) through a (2.5 × 100 cm) Sephadex G100 column were monitored at 320 nm with an ISCO V^4 detector. Each sample was eluted in the presence and absence of blue dextran and *p*-nitrophenol as visible high and low molecular weight internal standard markers, respectively. The chromatographic traces without the two standards were digitized, whereafter the data were transformed by a Fortran 77 program to profiles of absorbance vs relative retention volume ($V_R = (V_E - V_0)/V_0$, where V_E is elution volume and V_0 the void volume, taken as V_E at the beginning of the elution profile). The program corrected for digitizer alignment and (slight) baseline drift; then V_R was calculated assuming a linear change in flow rate from the beginning to the end of elution, the values being scaled so as to conform with a standard V_R value of 2.0 adopted for *p*-nitrophenol.[13]

For molecular weight calibration purposes, paucidisperse (~18 mL) fractions were consecutively collected seven times at each of nine selected retention volumes that were evenly distributed across the purified parent kraft lignin profile generated by elution through a preparative (5.0 × 100 cm) aqueous 0.10 M NaOH/Sephadex G100 column. The respective fractions were combined and neutralized with aqueous 1.0 M HCl to pH 7.5−8.0 and then desalted by ultrafiltration through a 500 nominal molecular weight cutoff membrane (Amicon YC05, Millipore Corp., Bedford, MA) with a quantity of (triply) distilled water equal to 20 times the ultrafiltration cell volume. Prior to absolute molecular weight determinations, these fractions were eluted in aqueous 0.10 M NaOH through the analytical Sephadex G100 column, and the portions corresponding to the sections of each profile above two-thirds of the peak height were collected. The profiles of these refractionated fractions were recorded by re-elution through the same size-exclusion chromatographic column. Then each was suitably diluted with carbonate-free aqueous 0.10 M NaOH (to a concentration for which the absorbance at 280 nm fell between 0.15 and 0.18) before being introduced into Beckman XL-A analytical ultracentrifuge cell assemblies (incorporating double-sector charcoal-filled Epon centerpieces) for subsequent sedimentation equilibrium measurements at 4 °C.[13,14]

Alkylated Kraft Lignin Preparations. The kraft lignin preparations were alkylated at 20 g L^{-1} concentrations with dimethyl sulfate (Aldrich, Milwaukee, WI) or diethyl sulfate (TCI America, Portland, OR) at pH 11−12 in aqueous 60% dioxane (to maintain homogeneous reaction conditions) under N_2 at ambient temperature. A quantity of 2.0 mL of dialkyl sulfate/g of kraft lignin was initially added to the aqueous dioxane solution, and the reaction was allowed to proceed with vigorous stirring for 24 h; then additional quantities of 1.0 mL/g of kraft lignin were added twice a day 8−16 h apart for another 3 days altogether. Aqueous 1.0 M NaOH was added to restore the pH to a value between 11.0 and 12.0 whenever it had dropped below 11.0. After the reaction was deemed to be complete, the solution was neutralized with aqueous 1.0 M HCl and the dioxane removed by evaporation under reduced pressure. The resulting alkylated kraft lignin precipitate was washed four times by resuspending in distilled water and centrifuging (1380*g*) whereafter it was air-dried, the final traces of moisture being removed over P_2O_5.

The alkylated kraft lignin preparations thus obtained were further methylated with diazomethane in chloroform, to which a small amount of dioxane or DMSO had been added to facilitate complete dissolution of the sample. The diazomethane was slowly generated by gradually adding (150 mL in 30 min) 100 g L^{-1} *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich, Milwaukee, WI) in chloroform to 60 mL of 330 g L^{-1} KOH in a (1:1:1 v/v/v) chloroform−2-(2′-ethoxyethoxy)ethanol−water mixture at 80 °C in a distilling flask,[15] which was connected through a condenser fitted with a vacuum adapter to a receiving flask. To trap the diazomethane that was not captured by the chloroform codistilling into this flask, the outlet of the adapter was attached to a gas inlet tube, the tip of which was immersed below the surface of chloroform contained in an Erlenmeyer flask standing in an ice bath. Finally, 50 mL of chloroform was slowly added to the reaction flask to ensure that all the diazomethane would be completely codistilled.

The entire quantity of diazomethane formed was used to methylate each 1.0 g of alkylated kraft lignin sample in chloroform solution by a reaction that was allowed to proceed for 14 h. After extracting five times each with aqueous 0.5 M H_2SO_4 and distilled water, the resulting chloroform solution was dried with Na_2SO_4, filtered through a medium-porosity fritted disk glass funnel, and centrifuged (1380*g*, 30 min) in glass bottles. Last, the chloroform was removed under reduced pressure.

Solvent Casting Alkylated Kraft Lignin-Based Thermoplastics. The alkylated kraft lignin samples, with and without miscible aliphatic polyesters, were dissolved at 130 g L^{-1} overall concentrations in dimethyl sulfoxide (DMSO) at around 50 °C. The aliphatic polyesters (Aldrich, Milwaukee, WI, or Scientific Polymer Products, Ontario, NY), which were capable of plasticizing the alkylated kraft lignin-based materials, were used as supplied without further purification. The resulting solutions were transferred to 10 × 20 mm Teflon molds constructed by appropriately folding sections of Teflon sheet along lightly scored lines. To avoid bubble formation during subsequent solvent evaporation, each solution was degassed in its respective mold under reduced pressure while being subjected to ultrasonication. The Teflon mold containing the degassed sample solution was placed into a wide-mouth glass bottle, which was promptly filled with N_2 and closed with a screw-cap that was not tightened fully. The bottle with its contents was transferred into a vacuum oven which was flushed with N_2. To prevent bubbles from forming within the sample, the DMSO was allowed to evaporate for 36 h at 150 °C (well below its 189 °C boiling point) whereafter the temperature was raised to 180 °C for the final traces of solvent to be evenly removed under reduced pressure.

The specimens for tensile testing were fashioned into a form comparable to the specifications given in ASTM D638. Thus, the 1.0 mm thick solid samples were filed into dogbone-shaped specimens, the dimensions of the narrower rectangular sections between the broader ends being typically 9 mm long and 5 mm wide.

Tensile Tests. The tensile behavior of the alkylated kraft lignin-based thermoplastics (in the form of dogbone-shaped test pieces) was characterized with 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). Smooth grip faces were employed to hold the more brittle materials firmly enough to prevent slippage, while serrated grip faces were used to hold the less rigid test pieces. In both cases the sections of material placed between the grip faces were softened by heating briefly before tightening; thereafter, the temperature of each specimen and the adjoining grips was allowed to fall to that of the surroundings before the test was initiated.

A crosshead speed of 0.05 mm min^{-1} was employed with typical specimen gauge lengths of 8−9 mm. The Young's modulus (E) was deduced from the initial slope of the stress−strain curve on the basis of initial sample dimensions. The resulting plots of stress−strain data were corrected for any artifacts due to initial misalignment or looseness in the mechanical couplings to the grip faces; they were then digitized with a Summagraphics MM 1812 digitizing pad and transformed to the final stress−strain curves using a simple Fortran program.

Differential Scanning Calorimetry (DSC). DSC analyses were carried out with a Mettler TA4000 instrument equipped with a DSC30 measuring cell and controlled by a TC11 TA processor. Each sample (5−10 mg) was placed into an aluminum crucible under N_2 and sealed; a small opening was made in the lid of the crucible before loading into the measuring cell, which was flushed thoroughly with N_2. The samples were scanned at 5 °C min^{-1} in the temperature range of interest (typically −20 to 180 °C) to remove any traces of moisture and to establish the same thermal history for each. A second scan was then performed, and the glass transition temperature (T_g) was taken to be at the midpoint of the characteristic transition in the DSC curve.

Employing the Levenberg−Marquardt algorithm in SigmaPlot 5.0 (SPSS Science, Chicago, IL), the Gordon−Taylor equation and Kwei's equation were respectively fitted to the sets of T_g−composition data for the blends of ethylated methylated and methylated kraft lignin preparations with various miscible aliphatic polyesters, as described in Results and Discussion.

X-ray Powder Diffraction. X-ray powder diffraction patterns were obtained with a Siemens microdiffractometer operating in the transmission mode using Cu Kα radiation with a flat graphite monochromator in the diffracted beam and employing a Siemens area detector for measuring the diffracted X-rays. Data were acquired and analyzed using the Siemens General Area Detector Diffraction Software (GADDS) system. By integrating the area detector frame in the χ direction (along the Debye rings), a standard "powder pattern" (plot of intensity vs 2θ, where θ is the angle of diffraction) could be obtained. To compare the X-ray diffraction patterns for a series of blends, the plots were scaled by a Fortran program in such a way that the area under each curve would be the same.

Results and Discussion

The feasibility of making a polymeric material exclusively composed of a simple lignin derivative was first established with two ethylated methylated kraft lignin samples. These were produced by alkylating (consecutively with diethyl sulfate and diazomethane) a parent Jack pine kraft lignin preparation and a higher molecular weight fraction derived therefrom by ultrafiltration in aqueous 0.10 M NaOH through a 1.0×10^4 nominal molecular weight cutoff membrane.[2] The two underivatized preparations represented the starting materials from which the thermoplastic blends examined during the present work were created. They differed from one another in that there were substantial proportions of kraft lignin components with molecular weights below 3.0×10^3 in the parent preparation but not in the higher molecular weight fraction. The differences were readily evident in aqueous 0.10 M NaOH/Sephadex G100 size-exclusion chromatographic elution profiles.[2] The upper bounds to these molecular weight distributions lay in modest excluded peaks with weight-average molecular weights of 5.0×10^4. However, when not dissolved in aqueous alkaline solutions (with pH's above ~11.5), the individual molecular components in both kinds of kraft lignin preparation undergo extensive, but not complete, association to form huge supramacromolecular complexes with molecular weights that can exceed 2×10^7. This occurs whether[11] or not[12] the hydroxyl groups on the kraft lignin components have been acetylated, so that the associative processes are not governed by hydrogen bonding.

The Young's modulus (1.9 GPa), tensile strength (37 MPa), and ultimate strain (2.2%) of the ethylated methylated higher molecular weight kraft lignin-based material were not much larger than the respective values (1.5 GPa, 25 MPa, and 1.8%) for the corresponding alkylated parent preparation (Figures 1 and 2).[3] The similarity in the two sets of numbers was surprising in view of the marked difference between the proportions of lower molecular weight components in the two samples; it presumably arises from the fact that the prevalent species in both materials are supramacromolecular complexes with very high molecular weights.[11]

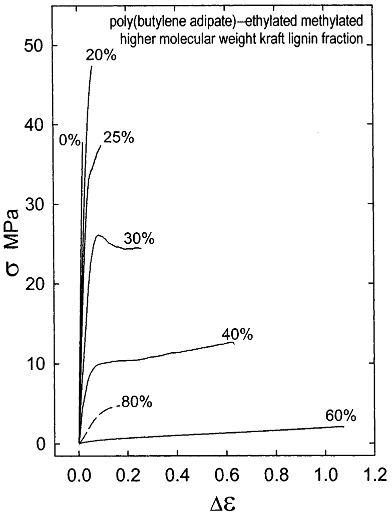

Figure 1. Progressive plasticization of ethylated methylated higher molecular weight kraft lignin-based polymeric material (EtKL(10K)) by poly(1,4-butylene adipate) (PBA) (stress−strain σ−ϵ curves delineated by Instron model 4026 Test System employing 0.05 mm min^{-1} crosshead speed with 9 mm specimen gauge lengths).

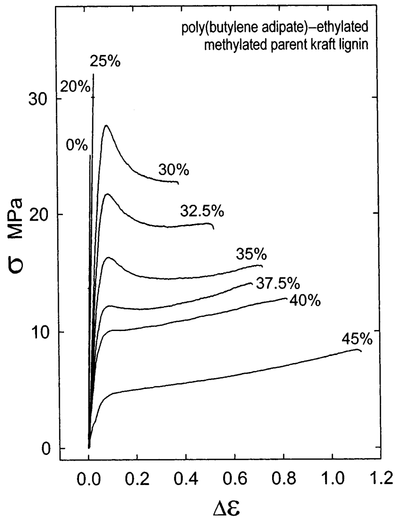

Figure 2. Progressive plasticization of ethylated methylated parent kraft lignin-based polymeric material (EtKL(par)) by poly(1,4-butylene adipate) (PBA) (stress−strain σ−ϵ curves delineated by Instron model 4026 Test System employing 0.05 mm min^{-1} crosshead speed with 9 mm specimen gauge lengths).

The tensile behavior exhibited by the two alkylated kraft lignin-based thermoplastics was remarkably similar to that of unplasticized polystyrene,[2] and indeed these materials were quite brittle. However, they could be effectively plasticized by a range of aliphatic polyesters with which they are miscible.[3,4] As shown in Figures 1 and 2, the materials based on the ethylated methylated higher molecular weight kraft lignin fraction and similarly alkylated parent kraft lignin both exhibited progressively more plasticity as a result of blending with poly(1,4-butylene adipate) at levels extending to 40−45% (w/w). Initially, appreciable increases in the measured tensile strength were achieved with a poly(butylene adipate) content of 20%. Then, at a 30% polyester incorporation level, the two materials exhibited stress yielding between 26 and 28 MPa, after which some strain softening occurred before the onset of substantial plastic deformation. On the other hand, the blend compositions with 40−45% poly(butylene adipate) contents displayed detectable strain hardening after the onset of plastic deformation. Notably, when the threshold in polyester content for plastic deformation had been exceeded, the tensile behavior of the alkylated parent kraft lignin-based blends was quite similar to that of the thermoplastics produced from the alkylated higher molecular weight kraft lignin fraction. The ultimate strains exhibited by the former were invariably greater, but the ultimate stresses observed for the same blend composition were almost identical (Figures 1 and 2). Again, the close correspondence in these values was probably determined by the fact that very high molec-

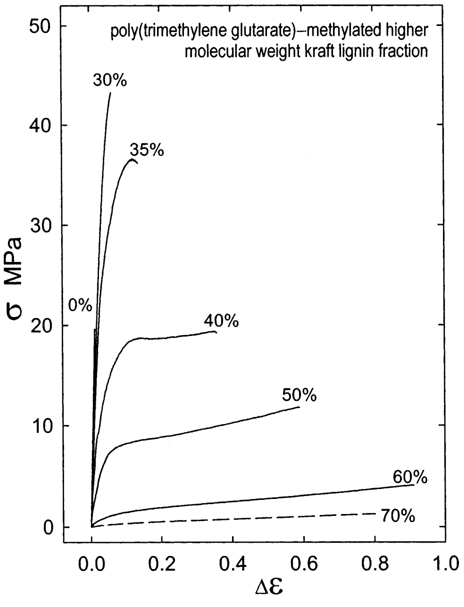

Figure 3. Progressive plasticization of methylated higher molecular weight kraft lignin-based polymeric material (MeKL-(10K)) by poly(trimethylene glutarate) (PTMG) (stress−strain $\sigma-\epsilon$ curves delineated by Instron model 4026 Test System employing 0.05 mm min^{-1} crosshead speed with 9 mm specimen gauge lengths).

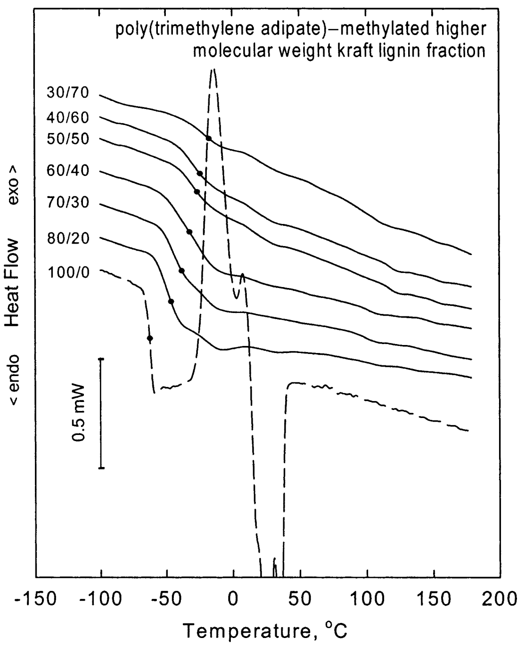

Figure 4. Differential scanning calorimetric (DSC) curves (5 °C min^{-1}) for blends of methylated higher molecular weight kraft lignin-based polymeric material (MeKL(10K)) and poly(trimethylene adipate) (PTMA). The symbols ● indicate the T_g's of these blends.

ular weight supramacromolecular associated complexes are the predominant entities in both kinds of preparation.[11] It should be borne in mind that the poly(butylene adipate) itself did not possess any measurable strength under the testing conditions employed.

Naturally, the tensile behavior of the alkylated kraft lignin-based thermoplastics depended on the identity of the alkyl substituents and the configuration of the polyester. The tensile strength of the material produced from the methylated higher molecular weight kraft lignin fraction (Figure 3) was around half of that made from the corresponding ethylated methylated fraction (Figure 1). Blends of the methylated higher molecular weight fraction with 30% (w/w) poly(trimethylene glutarate) exhibited an over 2-fold greater tensile strength than the unblended material, but appreciable stress yielding first appeared in blends incorporating 35% levels of poly(trimethylene glutarate). Substantial plastic deformation with perceptible strain hardening was evident in blends containing 40% of this polyester (Figure 3), but here the ultimate stress was 1.6-fold larger than that for the blend of the corresponding ethylated methylated kraft lignin fraction with 40% poly(butylene adipate) (Figure 1).

The plasticization of the alkylated kraft lignin-based polymeric materials by aliphatic polyesters was accompanied by a marked reduction in glass transition temperature (T_g). Concomitantly, the presence of alkylated kraft lignin increased the T_g of the aliphatic polyesters, as illustrated in Figure 4 for blends of poly(trimethylene adipate) with the methylated higher molecular weight kraft lignin fraction. It can be seen that the prominent endothermic melting peak of the polyester was no longer visible in the blend containing 80% (w/w) poly(trimethylene adipate), and indeed the exothermic (two-component) cold crystallization peak was absent also.

In general, the formation of miscible binary polymer blends depends on the occurrence of exothermic interactions between the two components being mixed.[16] The manner in which the glass transition temperature (T_g) varies with blend composition is reflective of the relative strengths of these intermolecular interactions. Thus, the latter govern the observed relationship between the T_g of the blend and those of the two constituent polymers,[16] namely, the aliphatic polyester and alkylated kraft lignin as far as the present work is concerned. However, it has not been possible to measure the T_g's of the alkylated parent kraft lignin preparations and corresponding higher molecular weight fractions. This is presumably due to the fact that the majority of the individual kraft lignin components are incorporated into supramacromolecular associated complexes.[11]

To the extent that these associated entities are disassembled in blends with aliphatic polyesters, an estimate is needed for the T_g that the individual alkylated kraft lignin components would exhibit if they were not confined within such complexes. A reasonable approximation to this value may be deduced by examining lower molecular weight paucidisperse alkylated kraft lignin fractions that have been prepared by means of consecutive ultrafiltration of the *underivatized* parent preparation through membranes with progressively lower molecular weight cutoffs (Figure 5). The T_g's of these fractions increased with their molecular weight before the transition was lost altogether as the proportion of associated complexes grew in the series of samples being considered (Figure 6). Such studies suggested that a T_g of ~160 °C is reasonable for the preponderant higher molecular weight ethylated methylated kraft lignin components, and a very similar estimate emerged for the corresponding methylated kraft lignin components also.

Owing to its importance in determining the phase behavior of polymer blends, enthalpy was the thermodynamic variable employed by Lu and Weiss[16] to derive a general expression (containing no adjustable parameters) for the T_g of a binary polymer mixture (T_{gm}) in terms of the glass transition temperatures of the two

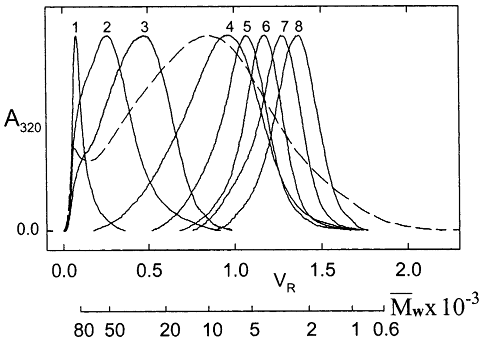

Figure 5. Molecular weight distributions of paucidisperse kraft lignin fractions resulting from consecutive ultrafiltration of parent preparation (dashed line) through a series of membranes with nominal molecular weight cutoff (1) 100, (2) 50, (3) 30, (4) 10, (5) 5, (6) 3, and (7) 1 kDa in aqueous 0.10 M NaOH and (8) 0.5 kDa in water. Aqueous 0.10 M NaOH/ Sephadex G100 elution profiles calibrated by ultracentrifuge sedimentation equilibrium analyses.[13,14]

constituent polymers, T_{g1} and T_{g2}. The enthalpy of mixing for the blend (ΔH_m) was related to the Flory–Huggins interaction parameter (χ) through the van Laar relationship $\Delta H_m = \chi RT\phi_1\phi_2$, where R is the gas constant, T the temperature, and ϕ_i the volume fraction of component i; χ was assumed to be a quadratic function of composition. Moreover, the isobaric specific heat of the mixture (c_{pm}) was assumed to have the form $x_1c_{p1} + x_2c_{p2} + x_1x_2\delta c_p$, where x_i is the mole-fraction of polymer i, c_{pi} the isobaric specific heat of component i, and δc_p the change in specific heat due to mixing (which is negative for a miscible blend).[17] The foregoing assumptions led to the following equation:[16]

$$T_{gm} = \frac{w_1T_{g1} + kw_2T_{g2}}{w_1 + kw_2} + \frac{Aw_1w_2}{(w_1 + kw_2)(w_1 + bw_2)(w_1 + cw_2)^2}$$

$$k = \frac{\Delta c_{p2} - w_1\delta c_p^l}{\Delta c_{p1} - w_2\delta c_p^g} \qquad A = \frac{-\chi R(T_{g1} - T_{g2})c}{M_1\Delta c_{p1}}$$

where $b = M_2/M_1$ (M_i is the molecular weight per chain segment of polymer i), $c = \rho_1/\rho_2$ (ρ_i is the density of polymer i), w_i is the weight fraction of polymer i, and $\Delta c_{pi} = c_{pi}^l - c_{pi}^g$ at T_{gi}, the superscripts l and g denoting the liquid and glassy states, respectively.

The direct application of the Lu–Weiss expression to blends of alkylated kraft lignins with aliphatic polyesters would require the evaluation of parameters that were beyond the scope of the present work. However, when the interactions between the miscible polymer blend components are relatively weak, the effect of k is greater than that of A,[16] and the expression is simplified into the Gordon–Taylor equation:[18]

$$T_{gm} = \frac{w_1T_{g1} + k'w_2T_{g2}}{w_1 + k'w_2} \quad \text{where } k' = k + A/(T_{g2} - 1)$$

Here k' can be employed qualitatively as a relative measure of the intermolecular interactions in the blend since it increases with their strength.[16]

On the other hand, when the miscible polymer blends are characterized by strong specific intermolecular interactions, A is large.[16] Under such circumstances, the magnitudes of k, b, and c may allow T_{gm} to be approximated as Kwei's equation:[19]

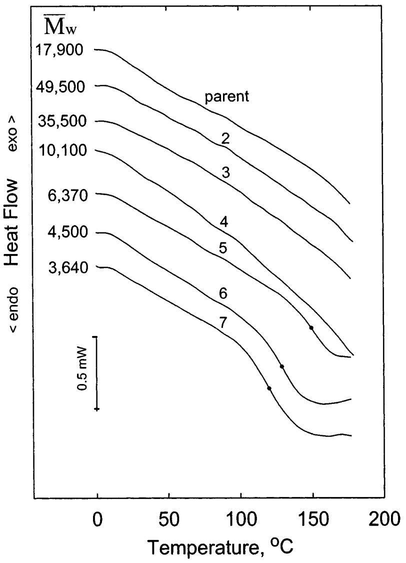

Figure 6. Differential scanning calorimetric curves (15 °C min^{-1}) for ethylated methylated parent kraft lignin preparation (EtKL(par)) and fractions derived therefrom before alkylation by consecutive ultrafiltration in aqueous 0.10 M NaOH through a series of membranes with nominal molecular weight cutoff 100, (2) 50, (3) 30, (4) 10, (5) 5, (6) 3 and (7) 1 kDa. $\overline{M}_w$'s were calculated from calibrated aqueous 0.10 M NaOH/ Sephadex G100 elution profiles.

$$T_{gm} = \frac{w_1T_{g1} + kw_2T_{g2}}{w + kw_2} + Aw_1w_2 \quad \text{where } k = \frac{\Delta c_{p2}}{\Delta c_{p1}}$$

In this case, A may be qualitatively regarded as a relative measure of the interactions between the polymer components, assuming that the Flory–Huggins interaction parameter is independent of blend composition.

It is not possible to decide a priori whether the intermolecular interactions in the alkylated kraft lignin-based blends with aliphatic polyesters are relatively weak or strong in the context developed by Lu and Weiss.[16] Nevertheless, the T_g–composition curves all exhibited markedly negative deviations from what would have been expected from the straightforward rule of mixtures. With regard to the polyester being employed, there were clear differences in the way in which the T_g's of these thermoplastics varied with alkylated kraft lignin content. For blends of the methylated higher molecular weight kraft lignin fraction and poly(trimethylene adipate), for example, T_g increased only modestly with increasing alkylated kraft lignin content (Figure 7); Kwei's equation provides a better empirical curve fit to the data than does the Gordon–Taylor equation, but this may be due to the fact that the former embodies two adjustable parameters rather than one. On the other hand, when poly(trimethylene glutarate) was mixed with the methylated higher molecular weight kraft lignin fraction, T_g increased more rapidly with alkylated kraft lignin content (Figure 8); here the Gordon–Taylor equation and Kwei's equation both provide equally good empirical curve fits to the experimental points.

Thus, a comparison of the data from the respective sets of blends with poly(trimethylene adipate) and poly(trimethylene glutarate) suggests that neither the

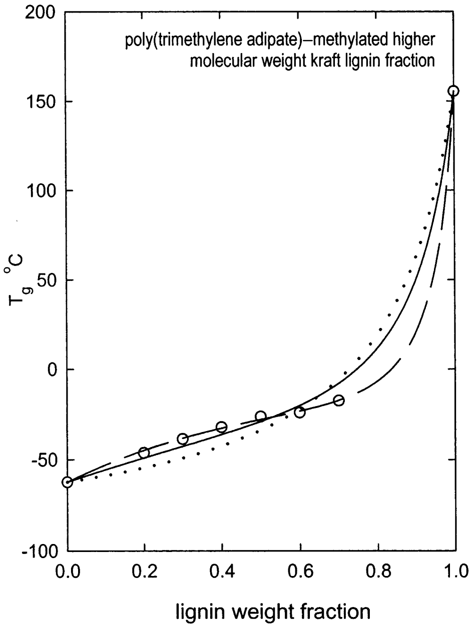

Figure 7. Variation of T_g with composition for blends of the methylated higher molecular weight kraft lignin fraction (MeKL(10K)) and poly(trimethylene adipate) (PTMA) with fits to Gordon−Taylor equation (dotted line), Kwei's equation having unrestricted k and A (dashed line), and Kwei's equation having k set at the empirical average value of 0.11 (solid line).

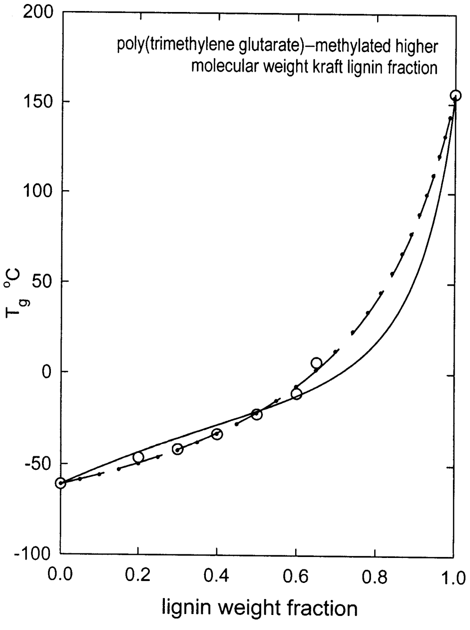

Figure 8. Variation of T_g with composition for blends of the methylated higher molecular weight kraft lignin fraction (MeKL(10K)) and poly(trimethylene glutarate) (PTMG) with fits to Gordon−Taylor equation (dotted line), Kwei's equation having unrestricted k and A (dashed line), and Kwei's equation having k set at the empirical average value of 0.11 (solid line).

Gordon−Taylor equation nor Kwei's equation possesses an appropriate analytical form for complete consistency in treating the variation of T_g with the composition of these thermoplastics. Nevertheless both equations can be applied empirically to obtain relative measures of the strengths of the intermolecular interactions between the polymer components in the materials.[16]

During the course of the present work, it was found that the blends formed between alkylated kraft lignins and aliphatic polyesters were miscible when the methylene/carboxylate group (CH_2/COO) ratios of the latter fell between 2.0 and 4.0. The values of k' in the Gordon−Taylor equation and A in Kwei's equation are listed in Table 1 for the corresponding curve fits to the variations of T_g with the compositions of these thermoplastic materials. The two sets of numbers reveal similar trends in that k' and A both achieve their largest values when CH_2/COO for the aliphatic polyester is 2.5−3.0, namely near the middle of the miscibility range. Here the net effect of the intermolecular interactions between the blend components was the most favorable, and thus the macromolecular alkylated kraft lignin complexes tended to undergo dissociation to a greater extent in response to the presence of these polyester molecules. Under such circumstances the T_g of the thermoplastic increased more rapidly with alkylated kraft lignin content (cf. Figure 8 where CH_2/COO = 3.0): on a w/w basis, the polyester molecules interact much more strongly with individual alkylated kraft lignin components than with the associated complexes (since the latter embody so many of the former). On the other hand, when the intermolecular interactions with the polyester were weaker, the alkylated kraft lignin components exhibited less of a tendency to dissociate from the macromolecular complexes, so that T_g increased more slowly with alkylated kraft lignin content (cf. Figure 7 where CH_2/COO = 3.5).

Table 1. Values of Adjustable Parameters for Fits of Semiempirical Equations to Blend T_g−Composition Data

blend[a]	polyester CH_2/COO	k' in Gordon−Taylor equation	A in Kwei's equation when $k = 0.11$[b]
EtKL(10K)-PBA	4.0	0.18	65
MeKL(10K)-PBA	4.0	0.17	56
MeKL(10K)-PTMA	3.5	0.15	47
EtKL(par)-PTMG	3.0	0.24	83
MeKL(10K)-PTMG	3.0	0.22	75
MeKL(10K)-PTMS	2.5	0.24	78
MeKL(10K)-PES	2.0	0.12	13

[a] KL = kraft lignin; Et = ethylated methylated; Me = methylated; 10K = fraction retained by 10 kDa nominal molecular weight cutoff membrane; par = parent preparation; PBA = poly(butylene adipate); PTMA = poly(trimethylene adipate); PTMG = poly(trimethylene glutarate); PTMS = poly(trimethylene succinate); PES = poly(ethylene succinate). [b] Calculated with k fixed at an average value of 0.11 initially determined from curve fits of Kwei's equation where both k and A were taken to be adjustable. The CH_2/COO range over which A is close to its maximum value was not very sensitive to the magnitude of k.

Whether the interactions between the alkylated kraft lignin and aliphatic polyester components were relatively weaker (Figure 7) or stronger (Figure 8), the composition dependence of T_g for the blends exhibited markedly negative deviations from a simple weighted average of the T_g's of the two constituent polymers. This was a direct consequence of the fact that the thermoplastic materials contained more than one kind of alkylated kraft lignin species, ranging from individual components to supramacromolecular complexes,[11] all blended with the aliphatic polyester. A similar situation had been encountered in the thermoplastics composed of 85% kraft lignin and 12.6% poly(vinyl acetate) with two plasticizers;[1] here it was the individual kraft lignin components dispersed in the poly(vinyl acetate) that rendered the latter compatible with the supramacromolecular associated kraft lignin complexes in the blend.

Indeed, efficient plasticization of alkylated kraft lignin-based polymeric materials has to contend with two

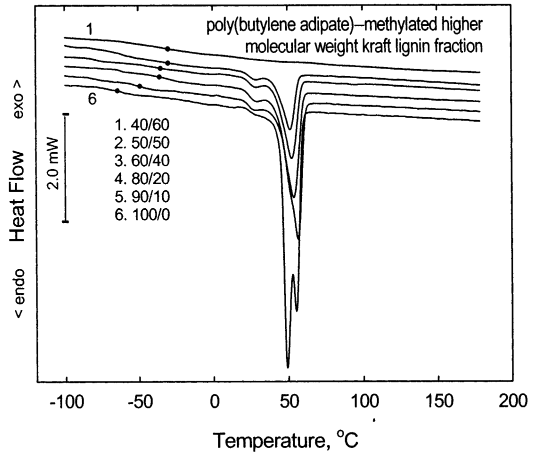

Figure 9. Differential scanning calorimetric curves (5 °C min^{-1}) for blends of methylated higher molecular weight kraft lignin fraction (MeKL(10K)) with poly(1,4-butylene adipate) (PBA). The T_g's of the blends are denoted by ●.

opposing tendencies. Intermolecular attraction toward the polyester must be strong enough for blend formation to involve the individual components in the peripheral regions of the associated kraft lignin complexes. On the other hand, access to the interiors of these huge supramacromolecular assemblies would be detrimental since it would be counterproductive for them to dissociate extensively under the influence of powerful intermolecular interactions with the polyester components.

There were other indications of miscibility between the alkylated kraft lignin and aliphatic polyesters in these thermoplastic blends. When the polyester exhibited a well-defined melting point, it was depressed as the alkylated kraft lignin content increased. Such an effect is illustrated in Figure 9 for blends of the methylated higher molecular weight kraft lignin fraction with poly(butylene adipate). Here the pure polyester exhibited two partially overlapping endotherms;[20] the lower of the two (representing the less stable crystalline domains) disappeared quickly when even small quantities (<10%) of alkylated kraft lignin had been introduced. This was similar to the behavior of poly(trimethylene adipate), the melting point of which was no longer detectable in the presence of 20% (w/w) levels of the methylated higher molecular weight kraft lignin fraction (Figure 4).

In contrast to poly(trimethylene adipate), the poly(butylene adipate) did not manifest an exothermic cold crystallization peak. Nevertheless, the poly(butylene adipate) did contain appreciable proportions of noncrystalline domains that exhibited T_g's which had increased by more than 30 °C when the alkylated kraft lignin content in the blend reached 60% (Figure 9). Among the crystalline domains, on the other hand, it was the more stable of the two (the one with the higher melting endotherm[20]) that exhibited a melting point depression: as the proportion of the methylated higher molecular weight kraft lignin fraction in the blend increased from 10% to 60%, the melting point was depressed by over 5 °C (Figure 9).

The effects of miscibility were also evident in wide-angle X-ray powder diffraction analyses of alkylated kraft lignin–aliphatic polyester blends. Lignin derivatives typically exhibit diffuse halos in their X-ray powder diffraction patterns,[21] which appear as broad peaks in diagrams of diffracted intensity vs 2θ (where θ is the angle of diffraction); such features are typical of amorphous polymers. In the X-ray powder diffraction diagrams for blends of the methylated higher molecular weight kraft lignin fraction with poly(butylene adipate), the threshold for the appearance of the characteristic crystalline pattern of the latter occurred at a polyester content around 55% (Figure 10). However, in blends of the same methylated higher molecular weight kraft lignin fraction with poly(trimethylene succinate), the characteristic crystalline pattern first materialized at a polyester content above 70% (data not shown).

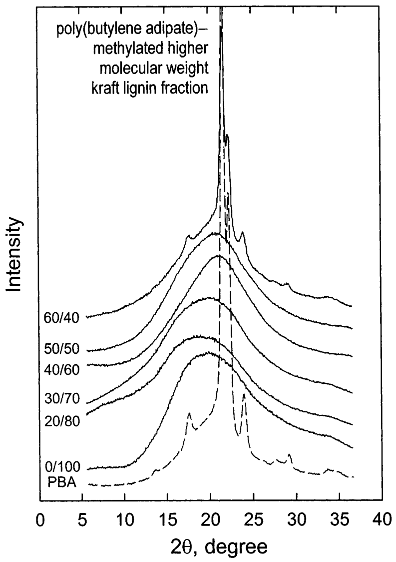

Figure 10. Wide-angle X-ray diffraction diagrams for blends of methylated higher molecular weight kraft lignin fraction (MeKL(10K)) with poly(1,4-butylene adipate) (PBA).

Thus, the crystalline domains of the poly(trimethylene succinate) exhibited a greater tendency than those of poly(butylene adipate) to be disrupted by methylated kraft lignin components. This is consistent with differential scanning calorimetric analyses (Table 1) which indicated that the intermolecular interactions of the alkylated kraft lignin species with poly(trimethylene succinate) (for which $CH_2/COO = 2.5$) were stronger than those with poly(butylene adipate) (for which $CH_2/COO = 4.0$). Thus, the T_g of poly(trimethylene succinate) rose more quickly than that of poly(butylene adipate) during the course of blending with progressively greater proportions of the methylated higher molecular weight kraft lignin fraction. Concomitantly, a larger amount (over 5%—data not shown, but cf. Figures 1 and 3) of poly(trimethylene succinate) than poly(butylene adipate) was required to attain plastic flow in these alkylated kraft lignin blends under ambient conditions.

Conclusions

For many years it looked as though useful lignin-containing polymeric materials could only be formed by incorporating lignin derivatives into other polymers that uphold respectable mechanical properties in their own right. However, this view has been refuted by the creation of promising thermoplastic blends from simple alkylated kraft lignin derivatives and aliphatic polyesters with low T_g's. Such blends are miscible when the CH_2/COO ratio of the polyester lies between 2.0 and 4.0. This window of miscibility exists presumably because the rate of change in the intermolecular polyester–

polyester interactions varies more quickly with carboxylate group frequency along the macromolecular chain than that between the polyester and lignin components.

The net effect of the intermolecular interactions between the blend components is the most favorable when the CH_2/COO ratio for the aliphatic polyester falls between 2.5 and 3.0. Yet under these circumstances appreciably more of the low-T_g polymer is needed in order for the alkylated kraft lignin-based blends to exhibit plastic deformation. Thus, the most effective plasticizers are aliphatic polyesters that interact sufficiently but not too strongly with the alkylated kraft lignin species: intermolecular attraction should be powerful enough to compete for the kraft lignin components in the peripheral regions of the supramacromolecular complexes, but not so strong as to dismantle these huge associated entities significantly.

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