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# Macroscopic Behavior of Kraft Lignin Fractions: Melt Stability Considerations for Lignin–Polyethylene Blends

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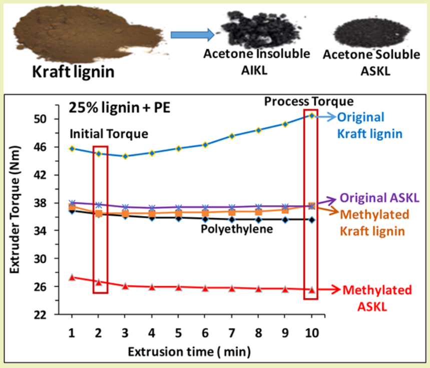
**ABSTRACT:** Questions that pertain to the behavior of softwood kraft lignin fractions as opposed to the whole lignin still prevail. In an effort to further understand such effects at a macroscopic level, we have examined the issue of melt stability of polyethylene (PE) in blends with fractionated and unfractionated softwood kraft lignin. While methylation of the phenolic OH groups significantly stabilizes any lignin/PE melt, more in depth data demonstrate that when separate, acetone soluble (ASKL) and acetone insoluble (AIKL) kraft lignin fractions behave completely differently than the original unfractionated material. The low molecular weight methylated ASKL offers unexpected plasticizing action to PE melts, possibly as a consequence of its low molecular weight and spherical configuration. The higher molecular weight AIKL offers relatively stable PE melts, possibly manifesting its rigid nature and higher glass transition temperature likely occurring due to $\pi$ stacking operating among its aromatic rings. Mixing these two fractions together creates unstable PE melts with a propensity to extensively thermally cross-link in the absence of methylation. These findings offer for the first time insight into the nonproductive cooperative action of individual fractions in softwood kraft lignin with significant technological ramifications.



**KEYWORDS:** *Softwood, Kraft lignin, Lignin fractionation, Acetone fractions of lignin, Lignin–polyethylene blends, Melt stability, NMR, $^{31}$P NMR, Melt stability, Extruder torque, $\pi$ stacking, Polymer configuration, Lignin methylation*

## INTRODUCTION

Lignin, being the second abundant component of wood, is an aromatic copolymer of phenylpropanes composed of guaiacyl (G) and syringyl (S) repeating units depending on the wood species. These units are linked to each other by mostly ether and C–C bonds that are severely altered when wood is delignified, offering a material better termed as technical lignins. The structure of technical lignins is rather heterogeneous containing a large variety of functional groups including phenolic hydroxyls.[1,2]

Since the dominant delignification process is the kraft process, such technical lignins are in a majority supply and a promising alternative for blending with synthetic polymers. Furthermore, biobased composites have gained prominence over the past two decades because of environmental and waste disposal concerns.[3] The use of lignin as a filler or reinforcement in thermoplastic materials is not new and dates back to the 1960s.[4] However, in recent years, it has been considered for incorporation in products like resins, adhesives, and polymer blends.[3,5−10] Research over the past decade has considered economic and environmental advantages of lignin as components of synthetic polymer blends. This is especially true in view of the fact that the availability of such technical lignins offers it as a viable and attractive alternative to fillers, reinforcements, or extenders for a variety of synthetic polymer applications.

While the presence of the phenolic OH in technical lignins may offer beneficial effects toward oxidation, thermal, and light stability for polymeric materials, when blended with it,[11−13] its incorporation in polymeric matrices imposes some significant difficulties. Notably, the processing of lignin is cumbersome and irreproducible at elevated temperatures due to its thermal degradation.[3−10,14] Furthermore, polymerization and eventual gelation has been shown to occur for unmodified kraft lignins when heated at temperatures near or higher than their glass transition temperature ($T_g$)[5,15] dramatically limiting their utility as thermoplastics or components in such blends. Obviously such limitations induced by the thermal instability of technical lignins inherently cause formidable melt processing and flow problems when injection molding and/or extrusion manufacturing procedures are considered. Even in the presence of softening agents, the melt spinning and extrusion processing problems of kraft lignin still occur, irrespective of them being processed alone or in blends with other polymers.[4,16] The processing and compounding difficulties of technical lignins are mounting when one considers the polar nature of the phenolic and aliphatic OH groups present in its structure offering

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incompatibility and miscibility limitations in attempts to blend them with nonpolar synthetic polymers.[3]

Technical lignins when blended with synthetic polymers behave as viscous or viscoelastic fluids during the melting proceses, depending on the amount of lignin in them, its structural characteristics, and process temperature.[17,18] Due to thermally induced polymerization and cross-linking processes,[5,15] a continuous increase in the melt flow index (MFI) of polyolefins, when blended with technical lignins, is apparent, and this is has been shown to continuously increase with increasing lignin content.[19] However, reduced and stable MFI indices have been reported when modified/derivatized lignin- polyolefin blends were created.[3] Such findings are in accord with our earlier work that showed that masking the phenolic hydroxyl groups of technical softwood kraft lignin by simple methylation dramatically improves and stabilizes the molecular weight distribution of the material when exposed to repeated thermal cycles as one envisaged to occur under thermoplastic processing conditions.[5,15] To further address these limitations, a number of lignin modification methods have been proposed, with some success, aimed at increasing the compatibility of technical lignins with nonpolar polymers.[3,5,10,20] However, additional complications emerge when one considers that technical lignins are highly heterogeneous materials, both in terms of molecular weight distribution and functional group content,[21,22] with individual fractions assuming different roles when it comes to the properties and functionality of the ensuing material.[23] Recent reports have revealed that the lower molecular weight fraction of kraft lignin is of a lower glass transition temperature than that of its unfractionated counterpart, indicating improved melt properties.[24]

Overall, there have been no systematic studies that correlate the melt stability of lignin/synthetic polymer blends as they are processed within the barrel of an extruder. In this work, we have embarked at resolving some of these issues by studying the torque that a twin screw extruder experiences as a function of processing time for lignin−polyethylene (PE) blends. More specifically, this was done using a raw kraft lignin material as well as its methylated (specifically directed to their phenolic OH groups) and fractionated counterparts at various PE blend charges.

## MATERIALS AND METHODS

**Materials and Chemicals.** Softwood (southern pine) kraft lignin was used as isolated via the Lignoboost process produced from a kraft pulping process operated at an approximate H factor of 1200 in a pulp mill that produces bleachable-grade pulp in a continuous Kamyr digester. The material was thoroughly washed with deionized water prior to use until the pH of the wash liquor was nearly neutral. It was then air-dried followed by drying in a vacuum oven set at 40 °C over a period of several days. Molecular weight and functional group distributions of all samples were measured by gel permeation chromatography (GPC) and quantitative $^{31}$P NMR spectroscopy as per our previously published detailed procedures.[25] The molecular weight of the initial kraft lignin sample, whose isolation is described above, was around $M_w = 6000$ and $M_n = 1500$ (PDI = 4). The amounts of phenolic and aliphatic hydroxyl groups were 4.26 and 2.24 mmol/g, respectively. A medium density of polyethylene (Equistar Co.) was used with its $T_g$, density, and melt index being 128 °C, 0.930 g/cm$^3$, and 1.2, respectively.

**Lignin Fractionation.** The original softwood kraft lignin was fractionated into two fractions using dry acetone (1 g/15 mL) and was allowed, under mild agitation, to be extracted for 10 h at room temperature. The dissolved part of the lignin was separated from the residue by filtration. The acetone soluble kraft lignin (ASKL) fraction was recovered by evaporating the solvent in a rotary evaporator followed by vacuum drying in an oven set at room temperature for 1 day. The acetone insoluble kraft lignin fraction (AIKL) was washed with acetone several times until the wash liquor was no longer colored followed by air drying and finally in a vacuum oven set at room temperature. The functional group contents, molecular weights, and $T_g$ values of all samples were determined by quantitative $^{31}$P NMR,[25] gel permeation chromatography (GPC),[15] and DSC,[22] respectively.

**Methylation of Samples with Dimethyl Sulfate.** For all lignin samples examined in this work, their phenolic OH groups were selectively methylated as per our previous publication.[26] The lignin sample was dissolved in 0.8 M NaOH solution (15 mL/g) at room temperature. An appropriate amount of 3 mmol of dimethyl sulfate per each mmol of total phenolic hydroxyl groups present in the sample was added, and the solution was stirred for 5 min at room temperature. Then, the mixture was heated to 75 °C for an additional 2 h. The pH of the mixture was controlled to around 12 with addition of excess 1 M NaOH solution.

Finally, the reaction mixture was acidified (pH 2.5) using 2 M HCl, and the solid precipitate was washed with excess deionized water, freeze-dried, and stored in a vacuum desiccators. Quantitative $^{31}$P NMR spectroscopy was used to monitor and document the complete and selective protection of the phenolic OH groups originally present in the kraft lignin.

**Melt Stability.** During this work, blends of the original kraft lignin as well as its methylated counterparts and its fractions were created with polyethylene in order to investigate their processing characteristics, their melt stability within an extruder, and the mechanical properties of the ensuing blends. A laboratory-scale extruder (DSM Xplore Micro 15 cm$^3$ Twin Screw Compounder) was used for these purposes. The lignin contents in the PE blends were varied from 5% to 25%. The physical mixtures of PE and lignin were manually introduced into the feeder of the extruder (14 g of each blend), and then, the material was injected into the extruder whose chamber was preheated at 170 °C with the speed of the twin screw arrangement being set at 100 rpm. After 2 min, the torque of the twin screws the extruder experienced were continuously recorded using the build-in sensors and the computing software of the system over a period of 10 min. More specifically, the system accumulated torque values every 10 s. The values obtained at each minute interval were separately recorded and averaged over the span of 10 min to obtain the incremental “extruder torque” values used in this work.

The changes and variations in the torque, recorded during the process, were then examined and compared among the various blends, being indicative of the melt stability. Notably, due to the high $T_g$ of the acetone insoluble kraft lignin fraction (AIKL) (170 °C), we examined two extruder temperatures, namely, 170 and 190 °C. Interestingly, the data obtained for this fraction was similar irrespective of whether 170 or 190 °C were used for its compounding with polyethylene. The melt processing a pure polyethylene was done at 170 °C, and this condition was used as the blank for comparison with all the lignin blends.

**Quantitative $^{31}$P NMR.** Quantitative $^{31}$P NMR spectra for all lignins were acquired using a Bruker 300 MHz spectrometer in accordance to previously published procedures.[25] An accurately known amount of 40 mg of a dried lignin sample was dissolved in 600 $\mu$L of an anhydrous pyridine/CDCl3 mixture (1.6:1, v/v). A total of 200 $\mu$L of an endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/mL) was then added, and it was used as the internal standard. Then, 50 $\mu$L of a chromium(III) acetylacetonate solution (5.6 mg/mL) in the above pyridine/$CDCl_3$ solvent were added, serving as the spin−lattice relaxation agent. Finally, 100 $\mu$L of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) were added. The mixture was then transferred into a 5 mm NMR tube for subsequent $^{31}$P NMR acquisitions (256 scans with 5 s delay time using an inverse-gated decoupling pulse sequence).

Table 1. Functional Groups, Molecular Weight, and $T_g$ Values of Original, Fractionated, and Methylated Samples

| lignin | aliphatic−OH (mmol/g) | phenolic−OH (mmol/g) | COOH (mmol/g) | $M_w$ (g/mol) | PDI ($M_w/M_n$) | $T_g$ (°C) |
|---|---|---|---|---|---|---|
| original lignin (KL) | 2.24 | 4.25 | 0.42 | 6000 | 4 | 153 |
| methylated KL | 1.98 | 00.00 | 0.41 | | | 110 |
| original ASKL | 1.63 | 5.70 | 0.57 | 3500 | 3.5 | 114 |
| methylated ASKL | 1.59 | 00.00 | 0.48 | | | 101 |
| original AIKL | 2.74 | 3.56 | 0.35 | 14000 | 6.6 | 170 |
| methylated AIKL | 2.71 | 00.00 | 0.33 | | | 162 |

## RESULTS AND DISCUSSION

Due to the documented importance that lignin homogeneity offers on most of its properties,[21,27,28] we fractionated softwood kraft lignin using acetone as per our earlier efforts.[29] The functional group profiles, molecular weights, $T_g$ values for the original unfractionated kraft lignin and its fractions as well as its methylated and nonmethylated counterparts are presented in Table 1.

The initial unfractionated kraft lignin was found to contain about 65% of acetone soluble material (ASKL) (35% acetone insoluble fraction, AIKL). The molecular weight of the lower molecular weight fraction (or ASKL) was determined to be about 3500 g/mol ($M_w$) and its PDI was 3.5, while its acetone insoluble counterpart was of significantly higher molecular weight ($M_w$ = 14000) and of wider molecular weight distribution (PDI = 6.6). Notably, the molecular weight and PDI of the initial unfractionated lignin was 6000 g/mol and 4, respectively. Our $^{31}$P NMR determinations of the various hydroxyl functional groups present showed that the low and high molecular weight fractions of kraft lignin are significantly different in functional group composition. Specifically, the ASKL fraction has a higher phenolic OH content (5.70 mmol/g) and a lower aliphatic OH content (1.60 mmol/g) than the AIKL fraction (3.56 and 2.74 mmol/g, respectively).

Since the presence of phenolic OH groups within the lignin structure is a documented characteristic affecting its oxidative,[12] thermal and light stability contributions to polymeric materials when blended with it,[12,13] such differecnes are of major significance. This is further compounded with recent literature accounts that have demonstrated that the phenolic hydroxyl groups of lignin are of vital importance in inducing thermal cross-linking reactions,[14,15] which are anticipated to occur during thermal processing when blended with polyethylene. Furthermore, the polar nature of the phenolic OH groups promotes the lignin's incompatibility with nonpolar synthetic polymers.[3,4]

Consequently, in an effort to delineate the complex effects of the phenolic hydroxyl groups on the properties of lignin, their selective methylation was carried on the fractionated and the initial unfractionated lignin. The data of Table 1 shows that the methylation reaction, carried out in accordance to previously published procedures, was highly selective in targeting the phenolic hydroxyl groups.[26] As such, the thermal stability data that follows may offer answers related to the role of the lignin's phenolic OH groups because they are selectively masked while their aliphatic counterparts remain free.

**Melt Stability of Kraft Lignin Blends with Polyethylene and Effect Of Methylation.** Processing kraft lignin in a twin screw extruder is a complex task due to its thermal instability and cross-linking behavior at elevated temperatures.[4,15] Polymerization and cross-linking severely affects the ability of the material to flow and eventually to emerge as a stable melt through the nozzle of the extruder. Our work showed that the addition of lignin into polyethylene altered the initial torque the extruder experienced during melting, most likely due to the large differences between the melt fellow indices (MFI) of the polyethylene and the lignin. Further processing of the melt of the combined polymers induced large increases in the torque due to the lignin's thermal polymerization and cross-linking events discussed above.

For clarity purposes, and from this point on, we adopt the following two terms: initial torque, indicating the force the extruder experiences once in contact with the material at the preset elevated temperature as averaged between time zero and 2 min, and "processing torque", reflecting the behavior of the material in the extruder barrel beyond the already defined initial regime.

Figure 1A and B shows the initial and processing torque values as accumulated during 5 and 10 min of heating for unfractionated original and fully methylated lignin samples as a function of lignin content for various polyethylene blends. More specifically, pure polyethylene is seen to exert in the

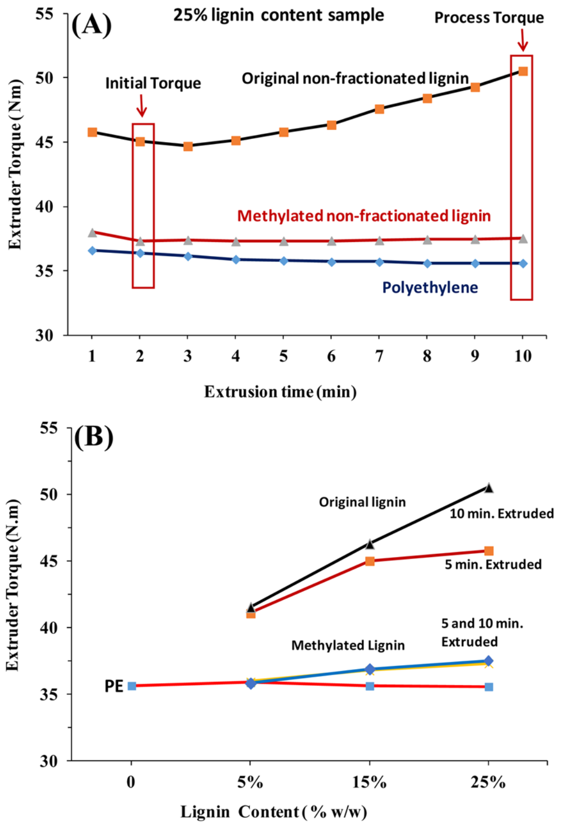

Figure 1. (A) Effect of original and methylated nonfractionated kraft lignin on the extruder torque as a function of time (for 25% lignin content). (B) Processing torque values as a function of lignin content in PE blends at two processing times 5 and 10 min.

extruder a torque value ranging between 36 to 36.5 N m similar in magnitude to literature accounts.[30] This value was stable during the 10 min of heating at 170 °C in effect defining a stable melt (Figure 1 A). Blending PE, however, with nonfractionated lignin at levels of 5%, 15%, and 25% showed significantly increased values of initial and processing torque. Adding only 5% of unfractionated original lignin in the PE blend was seen to increase the initial torque by about 15% compared to pure PE followed by an approximate subsequent increase in the torque of about 3% lasting over the ensuing 10 min of processing. When the lignin content in the PE blend was increased to 10%, the initial torque was increased by 23% (compared to pure PE) and ended higher by an additional 28% after 10 min of processing. Further increases in the unmodified lignin content to 25% (w/w) showed the initial torque value to increase by 25% and the processing torque by 40%, always compared to pure PE. Such continuous increases in the melt flow index (MFI) value of polyolefin/lignin blends have been reported in the literature as a function of lignin content.[19]

To further understand melt stability and quantify the effect and the role of the lignin's phenolic OH group on the torque it exerts on the extruder when blended with PE, these reactive functional groups were selectively methylated. Figure 1 shows that such derivatization dramatically increased the melt stability of the lignin PE blends. Even at a level of 25%, the use of methylated unfractionated lignin when blended with PE, showed a nearly stable torque profile experienced by the extruder during the processing of the blend over a period of 10 min at 170 °C. The initial torque recorded was seen to increase by only 4% at the elevated 25% methylated lignin content present in the blend. This was about 36% lower than the same data obtained for the original, unmodified, and unfractionated lignin sample. The significantly more stable melt viscosity, apparent after methylation, is in accordance with our earlier findings that showed no molecular weight increases when methylated lignins were heated for a prolonged time and in various processing cycles above its $T_g$.[15] This amply demonstrates that if kraft lignins are to be thermally processed, thermal stability considerations need to be taken into account.[31] As per our earlier work, most likely free radical polymerization and cross-linking induced within the lignin have dramatic negative effects on the melt stability of its blends with polyethylene and by extension with most polyolefins and other synthetic polymers.[15] The use of methylated lignin derivatives as directed at altering its phenolic OH content may be a way to overcome the documented melt stability considerations. It is important to note at this juncture that oxypropylation of lignin did not offer the same stability in the molecular weight profiles as simple methylation.[15] As such, one needs to be acutely aware that not all lignin derivatives will offer the sought melt stability and that this issue needs to be examined on a case by case basis.

**Effect of Lignin Fractionation.** To understand the effect of the lignin's molecular weight, polydisperity index, and functional group distributions on its melt stability, fractionated kraft lignin was then used using acetone as the solvent since the acetone soluble fraction of the lignin (ASKL) was of lower molecular weight, narrower distribution, and higher phenolic OH content than its acetone insoluble counterpart (AIKL).[27,29] Furthermore, we methylated both fractions in an effort to further elucidate the effect of modification on the melt stability.

**Acetone Soluble Fraction and Its Effect on Melt Stability.** Figure 2 shows the extruder torque as a function of processing time for the methylated and unmethylated acetone soluble fraction (ASKL) of softwood kraft lignin at different charges in the PE blends.

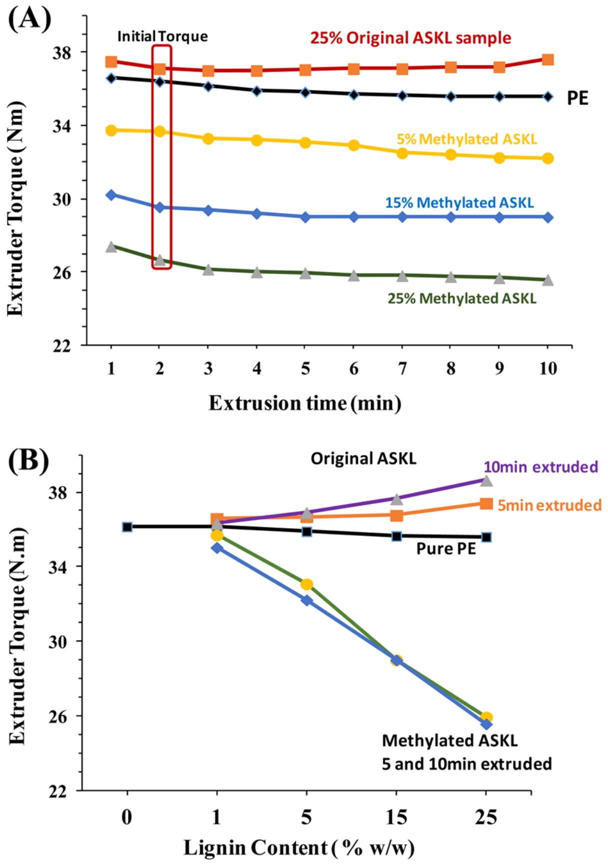

**Figure 2.** Effect of original and methylated acetone soluble fraction (ASKL) of kraft lignin on the extruder torque as a function of time (A) and lignin content (B) in PE blends at two processing times of 5 and 10 min.

Compared to the data of Figure 1 (where the same data is displayed for the unfractionated lignin), the data for ASKL is dramatically different. Blends of polyethylene with ASKL showed only a minor increase in the extruder torque when blended with PE at charges varying from 1%−25% by weight. Furthermore, for all charges, the initial torque increases (in the presence of the lignin fraction) were almost negligible. This large difference in melt stability between unfractionated and fractionated lignin is surprising. On the basis of thermal cross-linking considerations induced by the presence of phenolic OH, one would have thought that ASKL would be more prone to promoting such events since its phenolic OH content of 5.7 mmol/g would offer more such possibilities than its unfractionated counterpart containing only 4.2 mmol/g of phenolic OH (Table 1). Since this is not the case, then it is likely that an additional factor that affects melt stability is operational here. This is likely to be molecular weight and its distribution. The molecular weight determined for ASKL was 3500 g/mol (PDI = 3.5), and for the unfractionated lignin, it was 6000 g/mol (PDI = 4.0). The significantly lower molecular weight of ASKL, despite containing about 25% more phenolic content, seems to offer less possibilities for cross-linking in the melt, inducing eventual extruder torque changes. Larger molecular weights with smaller amounts of phenolic OH seem to induce greater changes in the melt as evidenced by the behavior of the unfractionated lignin documented in Figure 1.

At a qualitative molecular level, the data seems to validate the traditional Flory–Stockmayer polymer view that larger preformed chains need a smaller number of cross-linking events to create a network structure.[32−34]

By completely eliminating the possibility of cross-linking events from within ASKL, via methylation of its phenolic–OH, the possibility of cross-linking is also eliminated as evidenced by the data of Figure 2. In actual fact, the presence of methylated ASKL in PE seems to be offering a significant plastizing effect on the blends. The initial torque (2 min) experienced by the extruder twin screws was seen to be reduced by 8%, 18%, and 26%, respectively, at the 5%, 15%, and 25% (w/w) loadings of methylated ASKL in blends with PE. This significant plastizing action was seen to be maintained at extended processing times as evidenced by the data provided in Figure 2 for the 10 min processing regimes at all methylated ASKL loadings.

Once again, this data can be rationalized by resorting to the polymer material considerations of the kraft lignin. The Kuhn–Mark–Houwink–Sakurada (KMHS) equations for kraft lignin, based on absolute molecular weights (low-angle laser light scattering), showed that the exponential factors of such materials were averaged to be 0.12 in dimethylformamide (DMF).[35] Such a minute dependency of the lignin's intrisic viscocity on molecular weight ($M_w$) offers a spherical particle solution configuration for kraft lignin. This configuration seems to be having a significant plasticizing action even in the solid state when methylated ASKL is applied to PE blends at charges extending up to 25% (w/w).

**Acetone Insoluble Fraction and Its Effect on Melt Stability.** In an effort to further understand the effects of the different fractions of softwood kraft lignin on the melt flow and stability of blends with PE, we examined the behavior of the acetone insoluble fraction (AIKL). The data of Table 1 shows that this fraction is of significantly higher molecular weight ($M_w$ = 14000 mol/g) and of a somewhat lower phenolic OH content (3.5 mmol/g) compared to the initial unfractionated lignin and its acetone soluble counterpart.[27,29] Table 1 also signifies that the $T_g$ of AIKL was 170 °C, the highest among all the samples examined. Since it is customary to run extrusion experiments 20 degrees above the $T_g$ of the component that shows the highest $T_g$, AIKL and its blends were examined initially at 170 °C, but the same experiments were also repeated at 190 °C (20 °C above the AIKL's $T_g$). Interestingly, the data obtained for the two temperatures were identical, and the data for 170 °C is plotted in Figure 3 so as to be consistent with the overall effort.

Figure 3 shows the actual extrusion data accumulated for original and methylated AIKL. Blending the original AIKL at a 25 wt % level with PE showed an increase in the initial torque (relative to pure PE) of about 13%. This value is significantly higher when compared with the same data obtained for ASKL (Figure 2). In a manner similar to ASKL, the AIKL and its methylated counterpart offered a relatively stable melt viscosity as evidenced by the torque profile plotted over the 10 min processing time (Figure3A). This was certainly not the case for the nonfractionated original lignin (Figure 1A), where at the same 25% loading a progressive dramatic increase in the torque was apparent.

The enumerated differences discussed so far become evident in the data of Figure 4, where a direct comparison of the processing torque can be made for the nonfractionated lignin, its two fractions (Figure 4A), and all methylated derivatives (Figure 4B). For nonmethylated lignins, Figure 4A shows the dramatically different processing torque profiles of original, ASKL, and AIKL, at all blend levels with PE. At this point, therefore, one arrives at the conclusion that the lignin fractions when blended with PE and extruded behave completely different than the original nonfractionated lignin. It is, therefore, likely that complex (yet unknown) interactions occur when the two fractions are intimately mixed within the original lignin. As already discussed earlier, methylation offers opportunities for melt stabilization (Figure 4B), as with outstanding plasticization, effects are apparent for methylated ASKL.

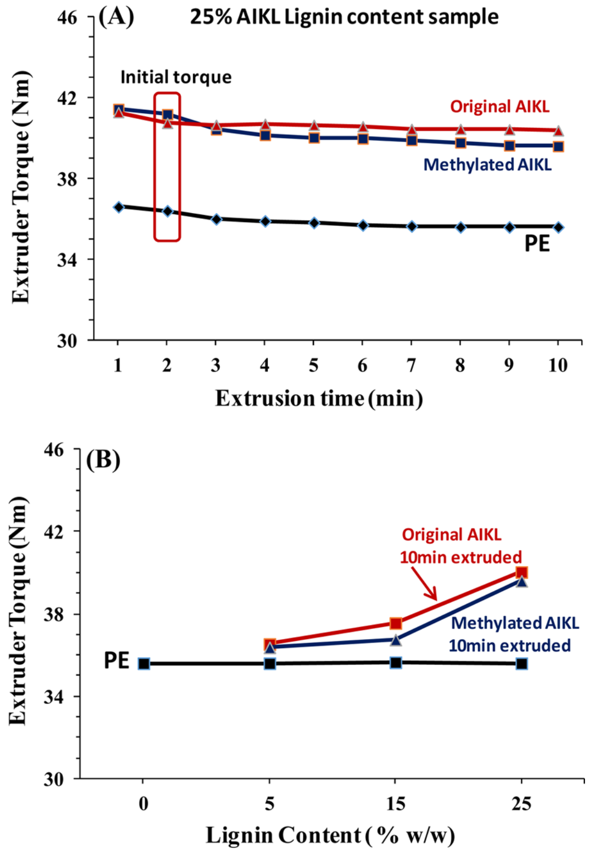

**Figure 3.** Effect of original and methylated acetone insoluble fraction (AIKL) of kraft lignin on the extruder torque at 170 °C as a function of time (for 25% lignin content, A) and on the processing extruder orque at different levels of lignin content in PE blends at a processing times of 10 min (B) .

**Molecular Rationalizations for the Observed Effects.** Further discussion to rationalize the accumulated data needs now be made. The unexpected plasticization effects of ASKL can be rationalized on the basis of it being lignin fragments of low molecular weight and of an extreme spherical polymeric configuration[35] even in the solid state. Their higher phenolic OH content (Table 1) seems inadequate to promote high enough concentrations of phenoxy radicals to cause any cross-linking in the melt in view of the fact that their molecular weight is low. Gelation via cross-linking of preformed polymer chains is known to be pronounced when the molecular weight of the initial preformed polymer chains is high.[32−34] Methylation of the phenolic OH further eliminates such possibilities offering additional plasticization effects and melt stability (Figure 2A, B).

The higher molecular weight apparent for AIKL can be viewed as a manifestation of extensive π stacking within this

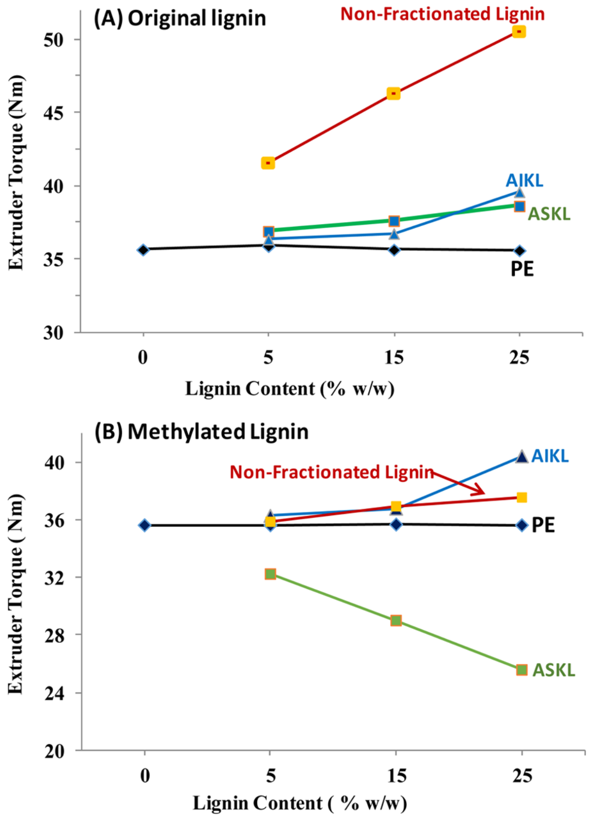

**Figure 4.** Effect of original and methylated nonfractionated lignin and its acetone soluble (ASKL) and insoluble (AIKL) fraction in blends with PE on the processing torque (10 min).

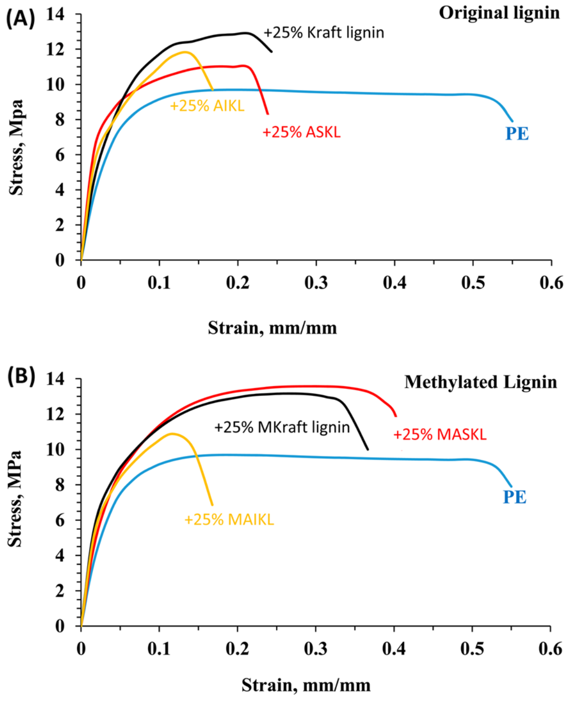

**Figure 5.** Stress−strain curves of 25 weight % blends of non-methylated (A) and methylated (B) lignin and their acetone fractions with PE.

fraction.[36,37] Such effects may be offering a rigid structure to the polymer, and this rigidity could explain the observed initial torque increase (Figure 3A, manifested mainly at 25% w/w lignin content). However, the demonstrated melt stability could be likely due to the rigidity offered by these forces being in place precluding the lignin molecules from thermally cross-linking and causing gelation. Obviously, higher AIKL contents in the blend may cause small amounts of otherwise unavoidable cross-linking, as manifested in the minor torque increases observed (Figure 3B).

Finally, the intimate mixing of ASKL and AIKL in the original lignin could likely be dramatically reducing the possibility of $\pi$ stacking among the aromatic groups in AIKL. The presence of ASKL is the factor that interferes with it due to the spherical configuration of these particles, and their compatibility with the AIKL components that could otherwise form rigid $\pi$ stacked structures. Consequently, the intimate mixture behaves as a polydisperse random polymer, where the statistics of polymer gelation freely operate even when diluted with PE (Figure 1).

**Mechanical Properties of Original and Methylated Lignin−Polyethylene Blends.** Possible macroscopic effects of original and modified kraft lignin and its fractions on the stress−strain curves of its blends (at 25 wt %) with polyethylene were investigated using appropriately molded dog bone samples (Figure 5). The elongation at break behavior was seen to be significantly reduced for all samples and fractions when compared to neat polyethylene irrespective of whether they were methylated or not in a manner similar to previous accounts.[38] It is important to note, however, that overall blending PE with methylated samples (in particular, methylated ASKL) showed somewhat more improved elongation at break most likely due to the better compatibility between the polyolefin and the lignin structure induced by the methylation of the phenolic hydroxyl groups[4,13] These data results confirm the effect of methylated ASKL as a plastisizer for PE.

## ■ CONCLUSIONS

The effects of lignin fractionation and methylation on the torque of a twin screw extruder for the processing of lignin−polyethylene blends were investigated. The original non-fractionated softwood kraft lignin showed significant increases in the initial torque and melt cross-linking demonstrating the documented difficulties in processing such materials. However, the lower molecular weight (ASKL) and higher molecular weight (AIKL) fractions of the same kraft lignin showed lower initial torque increases and considerably better melt stability. The selective methylation of the phenolic OH groups in softwood kraft lignin and its fractions demonstrated that it can offer thermally stable melts. Furthermore, dramatic reductions in torque and consequently melt viscosities were observed when methylated ASKL was blended with PE, offering augmented plasticization effects. Overall, the data amply demonstrate the different behaviors of softwood kraft lignin fractions with significant commercial ramifications.

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### Notes

The authors declare no competing financial interest.

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