Value-Added Derivatives of Soda Lignin Alfa Grass (*Stipa Tenacissima*). II. Uses as Lubricants in Plastic Processing

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ABSTRACT: Esparto (*Stipa tenacissima*) grass, also called Alfa is the raw material for the manufacture of paper pulp in North Africa. To add value to one of its processing by-products, we aimed to develop lubricants from modified Soda-Lignin (SL), which could eventually compete with industrial lubricants such as zinc stearates. Linear low density polyethylene mixed formulations prepared with zinc stearate and each modified lignin was studied by rheological tests using a rotational parallel plate system to investigate the effects of such esterified SL additives. One type, made up of SL esterified with 100% stearic anhydride (W/W) was found to promote excellent external lubrication. The same result was confirmed by contact angle and thermal analysis. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3003–3007, 2009

Key words: polyethylene; modification; biopolymers; renewable resources; rheology

INTRODUCTION

Alfa (*Stipa tenacissima*) is a native species of North Africa. It is estimated that 7 million ha of land of this region is used for its culture. Besides producing paper pulp, the industry also generates massive amounts of Soda-lignin (SL) residues.[1] However, the lignin extracted during the pulping process has, so far, not been investigated for its usefulness. In industry, importance of the Alfa, also called esparto, resides in the use of its sheets fibrils in the manufacture of the paper pulp.[2]

The major problem caused by the paper industry is the strong pollution of the rivers which receive its black liquor.[3] Currently, about 750,000 tons of lignins are used annually worldwide for various industrial purposes. Most of it is used in the form of water-soluble lignosulfonates, utilizing the dispersing, binding, complexing, and emulsion stabilizing properties of such lignins. Despite the extensive research, attempts to expand the use of lignins into other areas have not been very successful.[4]

One possible application area which has attracted a considerable interest is the use of SL or SL derivatives as polymeric components in thermosets like phenolic resins and polyurethanes.[5]

The present work is part of an investigation on the performance of SL compounds as a component in formulation systems of linear low density polyethylene (LLDPE) thermoplastics. Thus, the objective of the present investigation was to clarify the effects of SL modified as a lubricant or as a substitute in the thermoplastic lubricant industry for zinc stearates.[6]

Our objective is thus a partial esterification, to increase the hydrophobicity of the SL and to use it like an external lubricant without considerably increasing its cost. Indeed, the lignin is fairly hydrophobic to start with, and does not mix with polyolefins.[7] Lubricants are added to improve the ease of processing of thermoplastics. A typical lubricant for wire and cable manufacturing is stearic acid (added to PVC) and zinc stearate (added to PE or PP). Lubricants help provide a consistent, flawless surface finish and make it possible to produce long lengths of wire at high line speed.[8] They are also used in wood plastic composites.

In this study, we assessed the effects of esterification of SL by stearic anhydride and use of such derivatives as lubricants in LLDPE processing.

The modified SL was characterized by different methods of analysis in previous work.[9] The comparative or reference product is TPW104 (industrial lubricant) from Struktol Company of America (Ohio). Finally, the rheological, surface tension, and thermal properties were examined.[10]

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Sample	Description
SL	Not modified
LM1	SL modified by 10% of SA
LM2	SL modified by 30% of SA
LM3	SL modified by 100% of SA

EXPERIMENTAL

Raw materials

Alfa soda lignin was isolated from industrial Soda black liquor by acid precipitation. The pH of the black liquor was 12.3 and its density 1.02 g/mL. The soda lignin was precipitated from the concentrated black liquor by acidification to pH = 4 using sulfuric acid at 72%. A detailed description of the isolation procedure was presented elsewhere.[11]

The LLDPE supplied by ESSO Chemical Canada (ESCORENE) (ON, Canada) is an ethylene-butene copolymer with a density of 0.9225 g/cm^3, a melt flow index of 4.2 g/10 min, an average molecular weight of $\sim$ 85 kg/mol with $M_w/M_n = 4$. The melting point of the LLDPE is around 120°C.

TPW104, a commercial lubricant, was provided by Struktol Company of America (Stow, OH). This compound is based on zinc stearate. Usually, this product is used to reduce friction between components and equipment, which eases processing. The lignins used in this work are the SL and three other modified SL as presented in Table I. Also, the various prepared formulations are described in Table I. The modification consisted in esterifying the hydroxyl function by SA.[9]

Esterification of soda lignin

The esterification reactions were performed using the catalyst 1methyl-imidazol (1MIM; liquid state). Stearic anhydride (SA; solid state) was chosen as reactant since stearates are widely used in plastic processing industry as lubricants. The 1,4-dioxane was used as solvent for the SL with the pure stearic compounds SA. As the modification reaction progressed, all derivatized lignins remained completely soluble in the reaction mixture using 1-4dioxane as solvent.

All chemical modifications were performed at 50°C, under closed nitrogen atmosphere while stirring vigorously. Although there is evidence that reactions went to completion within 2 h, they were left to react overnight to ensure complete conversion.

The reaction mixture was made up of 1 g of 1MIM and 20 mL of 1,4-dioxane per g of SL added. A total of 5 mL of 1MIM in 100 mL of 1,4-dioxane mixture was added to catalyze the reaction.

Ethyl ether addition quenched the reaction. This mixture was then washed three times with bidistilled water. The aqueous phase was drained which removed all 1MIM. Some derivatized lignins were found to form granular sediment in the ethyl ether phase due to limited solubility. Cyclohexane was subsequently added to the ether phase to precipitate the derivatized SL. The SL granular precipitate was recovered by filtration and dried under vacuum for 24 h. Quantities used in the extraction process per 100 mL of reaction mixture are 200 mL of ethyl ether, 3 × 200 mL of water, and 200 mL of cyclohexane.

This stearic acid modified SL was recovered by addition of a 10-fold amount of water to the reaction mixture, followed by centrifugation, filtration, and vacuum-drying for 24 h. All modified SL (LM1, LM2, and LM3), esterified by stearic anhydride (10, 30, and 100%, respectively) were mixed with LLDPE.[12]

Sample preparation

The lignins (SL & modified SL) were first dried and stored at 105°C during 24 h to eliminate moisture before further use. The LLDPE blends were then compounded at 1% weight for each sample[13] (SL, LM1, LM2, LM3, TPW104) in an internal batch mixer (Haake, Rheomix) at 40 rpm and 160°C for 15 min to obtain well dispersed materials (constant torque readings). While processing, the polymer was introduced first until the mixing torque reached a constant value (generally after 2 min). At this point, the additive was introduced for a total preparation time of 15 min. The compounds were then compression molded at 150°C under 3 tons of pressure for 5 min in a mold having dimensions of 150 × 150 × 1.55 mm, resulting in nine circular disks with dimensions of 25 × 1.55 mm.

Thermogravimetric analysis

A Mettler–Toledo (TGA/SDTA851e) thermogravimetric analyzer was used to evaluate the thermal properties of lignins. The heating rate was set at 10°C/min over a temperature range of 25–700°C. Measurements were carried out in an air atmosphere, with a rate of air flow of 50 cm^3/min. For each measurement, 7 mg of the oven-dry sample was used to determine the weight loss of material as a function of temperature and time. The results obtained by TGA (dynamic and isothermal modes) are useful to study the applicability and thermal stability of different lignin samples in various composite materials (Fig. 1).

Rheological analysis

Because of the limited amount of material, the rheological analysis is limited here to low amplitude
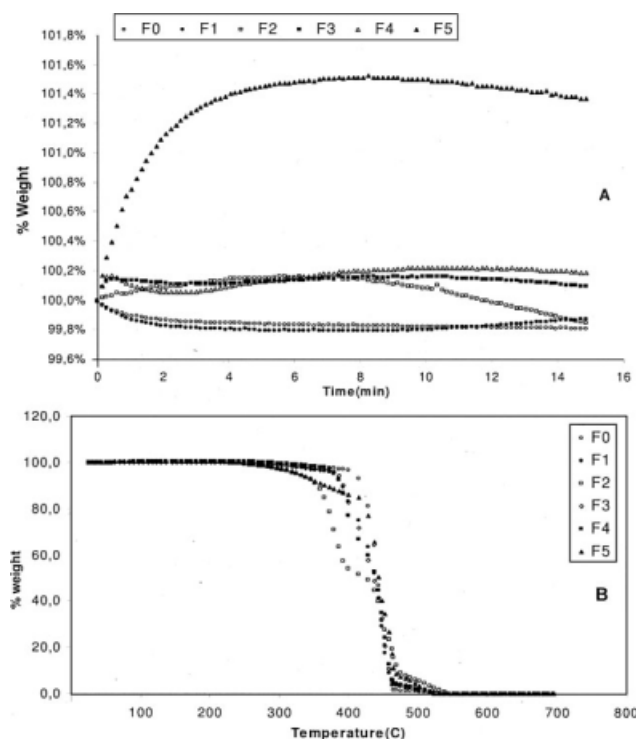
Figure 1 Thermal behavior of LLDPE formulations with 1% of each sample. (A) Isothermal mode at 200°C and (B) Dynamic mode between 25°C and 700°C.

oscillatory measurements (linear viscoelastic regime). In this case, the parameters of interest are the complex viscosity (η^*) and the dynamic moduli G' (storage modulus) and G'' (loss modulus).

The measurements were performed on an ARES rheometer from Rheometric Scientific. At first, strain sweeps were done at a frequency of 1 rad/s to determine the limits of the linear viscoelastic zone of the samples. Following this, frequency sweeps between 0.5 and 315 rad/s at a strain of 30% were made for each sample using gaps between 1.2 and 1.5 mm. All the rheological characterization was done at three temperatures (130, 145, and 160°C) for a complete analysis (frequency and temperature effects).

Contact angle

Similar samples prepared for the rheological tests were used to obtain water- contact angle. Static contact angles were measured using a KSV CAM 200 computer-controlled video based instrument (KSV Instruments, Finland). The instrument includes a CCD video camera, a frame grabber, an adjustable sample stage, and a LED light source. A distilled water drop (14 µL ± 7%) was allowed to fall onto the solid from a syringe tip to produce a sessile drop. Images were captured at a rate of 3/s for 15 s. The contact angles were calculated by curve fitting of the captured drop profile to the theoretical shape

predicted by the Young-Laplace equation. The software (CAM200) fits the Young–Laplace equation to the shape of the drop using all points on the drop profile. The tangent to the curve assigned where the curve intersects the baseline. The angle between this tangent and the baseline is the contact angle within ± 0.1°.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The first mixed formulation (LLDPE + SL) (F_1) has slightly decreased stability compared to LLDPE (F_0) alone (Fig. 1), about 0.2% additional weight loss after 2 min at 200°C. Formulation (LLDPE + LM2) (F_3) is the most stable formulation thermally and chemically as it did not undergo oxidation during a scan in isothermal mode (200°C during 15 min).

Formulation (LLDPE + TPW104) (F_5) shows an increase in mass of about 1.4%, which is clear evidence of oxidation compared to the other formulations [Fig. 1(A)]. In the industrial processes, there are always antioxidants presents at the time of the application of the formulations to prevent light oxidation, which can be seen in Figure 1. We can state that the modified lignin with formulations (LLDPE + LM2) (F_3) and (LLDPE + LM3) (F_4) have an important effect on the stability towards oxidation in a more interesting way, showing a better stability (thermal and capacity antioxidant).

About the thermal behavior in TGA Dynamic mode [Fig. 1(B)] until 250°C, there is no difference between the various formulations. The formulation (LLDPE + LM2) (F_3) loses 5% of its mass in the final state around 386°C. On the basis of this test, it seems that this formulation is the most thermally stable.

The least stable formulation is (LLDPE + LM1) (F_2), which loses 5% of weight at 325°C, while the last formulation which loses 50% of its mass is formulation (LLDPE + LM3) (F_4) around 436°C. Formulation (LDPE + LM1) (F_2) especially shows the existence of two different products, where the first decomposition step is due to the modified lignin around 372°C and the second step to LLDPE at about 450°C.

Rheological analysis

At first, a viscosity master curve can be constructed using the time–temperature superposition.[14] Using the data obtained at three different temperatures (130, 145, and 160°C), a master curve can be obtained by using a shifting factor a_T defined as:

$$a_T = \frac{\eta_0(T)}{\eta_0(T_0)} \tag{1}$$

TABLE II
Temperature Shift Factor (a_T) for the Prepared Samples
($T_0 = 160$ °C)

LLDPE with 1%	130°C	145°C
–	1.78	1.30
SL	1.81	1.30
LM1	1.92	1.36
LM2	1.95	1.38
LM3	1.89	1.32
TPW104	2.64	1.62

TABLE III
Parameters for the Carreau Viscosity Equation

LLDPE with 1%	η_0 (Pa s)	λ (s/rad)	a (–)	b (–)
–	686	3.22×10^{-4}	0.573	4.35
SL	678	1.60×10^{-3}	0.596	1.97
LM1	755	1.42×10^{-4}	0.457	5.50
LM2	729	3.61×10^{-5}	0.426	9.18
LM3	635	2.22×10^{-3}	0.563	1.71
TPW104	461	8.37×10^{-4}	0.504	2.37

where η_0 is the zero shear viscosity and T_0 the reference temperature taken as 160°C here. From the definition of the shift factor, $a_T = 1$ for $T = 160$°C. Table II presents the variation of a_T with temperature for each sample.

Within the experimental uncertainty, there was very little effect of adding SL, LM1, and LM2 to LLDPE in terms of viscosity. For the sake of clarity, Figure 2 presents only the dynamic viscosity results for LLDPE, LM3, and TPW104 compounds. On the basis of the viscosity master curves, the data can be fitted to a modified Carreau (Carreau-Yasuda) equation of the form:

$$\frac{\eta}{\eta_0} = [1 + (\lambda\omega)^a]^b \qquad (2)$$

where λ is a characteristic time of the fluid and a and b are the power-law indices. Performing non-linear data regression using SigmaPlot 8.0 from SPSS, the four parameters of eq. (2) are presented in Table III.

From Figure 2 and Table III, it is clear that for a temperature of 160°C, presence of LM3 reduces the LLDPE zero shear viscosity (about 7%) but not as much as TPW104 (33%).
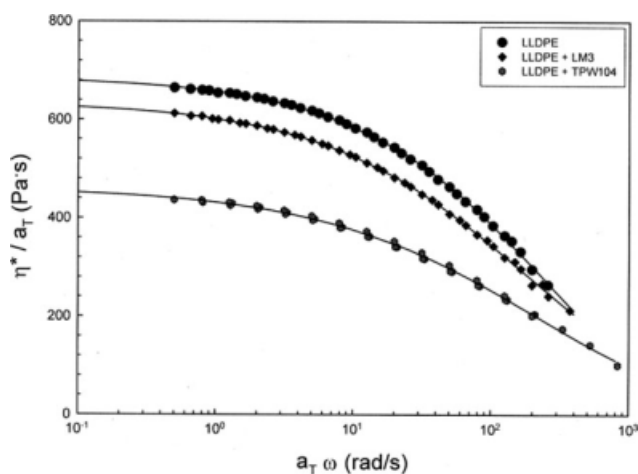
Nevertheless, LM3 seems to act as a lubricant as viscosity reduction is observed over the whole range of frequency tested. Further information can also be obtained by analyzing the dynamic moduli data. As presented in Figure 3, adding LM3 did not change significantly the loss and storage moduli of LLDPE. Once again, similar results were obtained for SL, LM1, and LM2. On the other hand, a slight decrease of both moduli (around 30%) was observed for TPW104 samples.

Finally, the rheological data must be analyzed in terms of temperature dependence. On the basis of the viscosity curves and the eqs. (1) and (2), the effect of temperature can be taken into account via an Arrhenius type of equation as:

$$a_T = \frac{\eta_0(T)}{\eta_0(T)} = \exp\left[\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad (3)$$

where E_A is the flow activation energy and R is the gas constant. On the basis of eq. (3), a plot of $\mathrm{Ln}(a_T)$ versus $(1/T - 1/T_0)$ should give a strait line going through the origin with a slope of E_A/R. This was the case for our samples and the results are presented in Table IV.
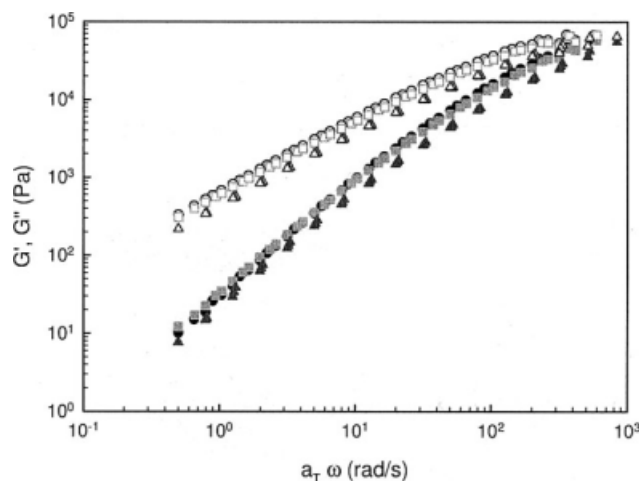

Figure 2 Dynamic viscosity master curve (reference temperature of 160°C) as a function of frequency. The lines are fitted using eq. (2) with the parameters reported in Table III.

Figure 3 Dynamic moduli master curve (reference temperature of 160°C) as function of frequency. Open symbols are the loss modulus G'' and closed symbols are for the storage modulus G'. Circles: LLDPE, squares: LLDPE + LM3, and triangles: LLDPE + TW104.

On the basis of the results of Tables II and IV, a more important temperature dependence is observed for the commercial lubricant (TPW104) than for LM3 due to its higher flow activation energy. Actually, the viscosity difference between LM3 and TPW104 decreases as temperature decreases up to a point (around 130°C) where both products have similar rheological behavior; i.e., dynamic viscosity and G' and G'' moduli.

Contact angle

On all LLDPE formulations with modified lignin at 1% (w/w), water has a higher contact angle than on pure LLDPE. The addition of 1% of SL decreases the water-contact angle, while the modified SL increases the contact angle, which is an evidence of higher hydrophobicity in this new material.

This contact angle reaches 80° in formulation (LLDPE+LM2) (F$_3$) and 86° in formulation (LLDPE +LM3) (F$_4$), which clearly exceeds the value achieved with same addition of industrial lubricant TPW104 (refer Fig. 4).

The comparison of the contact angles at the starting time of damping (beginning of the stability of the drop after the fall in FTA200) shows that the formulation (LLDPE + LM3) (F$_4$) is better than formulation (LLDPE + TPW104) (F$_5$).

CONCLUSION

Partial esterification of SL was confirmed by our previous work[9] and other lignins accordingly to literature.[15–17]

It has been shown that the lubrication effects of additives in LLDPE can be identified through rheological analysis. The esterified lignins has been shown to be highly effective in promoting excellent external lubrications. Also, the evidence for the external lubricating role of modified SL is also provided. At lower temperature it would be better to use LM3. Morphology and more dedicated rheology studies are necessary for further understanding the role of SL modified lubricating system in composites plastics.

The test showed that the modified SL of the formulations (LLDPE + LM2) (F$_3$) and (LLDPE + LM3)

TABLE IV
Flow Activation Energy (E_A/R) of the Samples

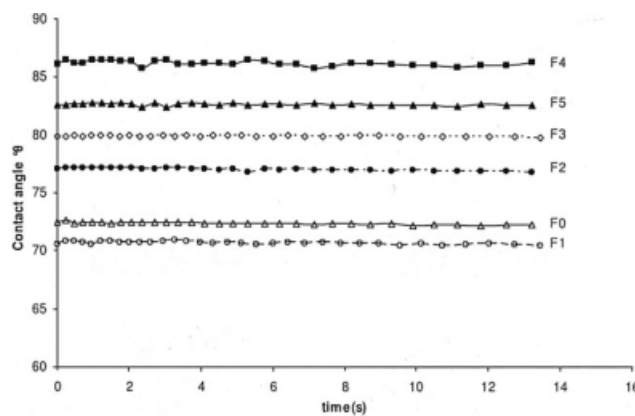| LLDPE with 1%	E_A/R (mol K)
–	3340
SL	3410
LM1	3791
LM2	3884
LM3	3615
TPW104	5673

Figure 4 Contact angle for F0 and F0 mixed at 1% of each sample (F1, F2, F3, F4, and F5) during 15 s.

(F$_4$) thanks to their thermal stability in the two modes, isothermal and dynamic, can be a good replacement for industrial lubricant TPW104. The same observation is confirmed by the hydrophobicity of the formulations assessed by the water-contact angle measurements by the FTA200. In the processing temperature zone of LLDPE (around 140°C) LM3 is the best lubricant which will be able to substitute the industrial lubricant TPW104 which is taken as reference during all the test of comparison. Thus, we have shown that lignin from industrial origin is far from being as a simple industrial waste.

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