Improvement of the thermal stabilization of polyethylene with lignosulphonate

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The use of lignin derivatives as stabilizers for synthetic polymers was investigated by blending the additive lignin derivatives with polyethylene in a Brabender Plasticorder. The thermal stabilizing effect of lignosulphonate was observed when the blending was carried out at temperatures above 463 K. Study of the rheological properties of the polymer melt indicated that a reaction occurred during processing, which was confirmed by changes in the spin densities.

(Keywords: polyethylene; thermal stabilization; lignosulphonate)

INTRODUCTION

Many different stabilizing agents have been used for several polymers and resins in order to enhance their properties. The purpose of using stabilizers is to prevent changes in their properties during processing and also to improve the properties of the final product, for instance, its light and thermal resistance.

Polymers like polyethylene, polypropylene and poly(vinyl chloride) need to be thermally stabilized. Several kinds of stabilizing agents have been used, namely compounds with phenolic hydroxyl groups[1], aromatic amines, and organic sulphur and phosphorus compounds[2].

Szalay and Johnson[3] have shown that lignosulphonate increases the thermal stability of poly(vinyl chloride) (PVC). They proposed that the basic interaction between lignosulphonate and PVC is hydrogen bonding between the chlorine atom of PVC and the hydrogen atom of the hydroxyl group in lignosulphonate. Gul *et al.*[4] have shown the effect of lignin derivatives on polypropylene, in which the cold and u.v. light resistances are increased. The interaction between polypropylene and lignin derivatives was reported to be due to a radical reaction. Bronovitskij[5] has studied the antioxidant effect of hydroxylated lignin on polyethylene. Lignin prepared from cottonwood was hydroxylated with a catalyst in an alkaline medium. The products were fractionated into neutral and phenolic fractions. The oxygen uptake by polyethylene mixed with either one of the fractions was measured to understand the antioxidant behaviour of the fractions. Five per cent of the neutral or 10% of the phenolic fraction had to be added in order to have the same antioxidant effect on the induction period, which was detected by 0.5% of commercial antioxidant.

In this paper, the authors have investigated the effect of lignosulphonate on polyethylene and found that it caused an increase in the thermal stability of polyethylene. The similar behaviour of various lignin derivatives was studied. In addition to thermal analyses, the rheological properties of the blends were also investigated. E.s.r. measurements were used to follow the changes in the spin densities in the polyethylene–lignosulphonate mixtures with increase of temperature.

EXPERIMENTAL

The polymer blends

Low-density polyethylene was mixed with different amounts of additive as granules at room temperature and 43 g of this mixture was introduced into the roller measuring head of a Brabender Plasticorder, model PL35. The Plasticorder has a Banbury-type mixing head (volume 60 cm^3) which has two cones rotating in opposite directions. The ratio of the rotation numbers between the left and right cones was 1:1.5. The mixing head was heated electrically in a thermostat and the temperature was measured by a thermocouple detector which was calibrated in an oil bath. In order to obtain exact measurements, 34.4 g of polyethylene and 8.6 g of additive were mixed at 413 K to obtain 20% master batch (MB) blend. Then a known amount of MB was mixed with a known amount of pure polyethylene to get exact lower concentrations of additive.

Three different kinds of commercial polyethylenes manufactured by Pekema Oy, Finland, were used in this experiment, namely:

LDPE B-8015 (melt index 8.0 g/10 min),
LDPE B-4524 (melt index 4.5 g/10 min),
HDPE GD-6250.

The lignosulphonates were also of commercial origin:

Lignosulphonate 1 (LSA-1): ultrafiltrated sodium lignosulphonate (purity 95%, Rauma-Repola Oy, Finland),
Lignosulphonate 2 (LSA-2): ultrafiltrated sodium lignosulphonate (purity 80%, Rauma-Repola Oy),
Lignosulphonate 3 (LSA-3): sodium lignosulphonate (purity ~80%, G. A. Serlachius Oy, Finland),
Lignosulphonate 4 (LSA-4): low molecular weight fraction of LSA-3 (G. A. Serlachius Oy).

Kraft lignin and the lignin derivative prepared from

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lignosulphonate and sulphur[6] were both commercial products (Rauma-Repola Oy). Desulphonation of LSA-1 was carried out in an alkaline medium at 523–573 K[7].

Rheological properties

The Brabender Plasticorder used for mixing the blends was also used to study the rheological properties of the polymer melts.

The shear stress and the shear rate are linearly dependent on each other in Newtonian flow, $\tau = \eta\dot{\gamma}$. Because the polymers often differ from Newtonian behaviour, many modifications have been made to investigate the flow behaviour of polymers. Ostwald's exponential law, $\tau = K\dot{\gamma}^n$, is much used in non-Newtonian flow to show the dependence on the flow parameters: flow index n, a measure of the pseudoplasticity ($n < 1$) and the deviation from Newtonian behaviour of the polymer melt (for Newtonian liquids, $n = 1$); and parameter K, which equals the viscosity in Newtonian liquids. In order to evaluate the flow parameters exactly, the Brabender apparatus was calibrated with a Contraves rheometer. The modified equation,

$$\log M = \log[C(n)K] + n \log S$$

makes it possible to calculate the flow parameters n and K with the help of experimental values; here M is the torque and S is the rotation number. The parameter $C(n)$, which is dependent on the characteristics of the measuring apparatus, was determined by calibration.

The parameters n and K were used to estimate the flow conditions in addition to the activation energy, which was obtained from the temperature dependence of the viscosity,

$$E = R[\mathrm{d} \log \eta / \mathrm{d}(1/T)]$$

in which R is the gas constant.

The properties of polymer blends

The polymer sample was removed from the mixing head and ground to a powdery form or cut into small chips. A known weight of this substance, kept in a closed 100-mesh pouch, was extracted in boiling toluene containing 0.5% of antioxidant for 12 h. The gel fraction calculated from this test shows the degree of crosslinking.

The sample powder was also used for the measurement of melt index, which was carried out according to ASTM D1238 standard.

Thermogravimetric analyses of the samples were done using a Rigaku Thermoflex-Thermoscale (Rigaku-Denki Co., Japan). The sample weight was about 5 mg and heating rate was 10 K min^{-1}. The weight losses in air were given as a function of temperature.

Electron spin resonance measurements

Electron spin resonance spectroscopy (Varian E-4 ESR spectrometer) was used to obtain the radical contents of the blends as a function of temperature. The powders of polyethylene and lignosulphonate were mixed at room temperature. The mixture of lignosulphonate and NaCl was used as a reference for non-reactive conditions. In measuring the spin density, 0.04–0.05 g of all the samples were used. The e.s.r. signals were recorded at 279, 353, 373, 393, 413, 433, 453, 463, 473, 483 and 493 K. The samples were heated at 10 K min^{-1} in an air flow, the holding time of the samples at various temperatures being 5 min. The temperature was detected with a thermocouple which was calibrated in an oil bath. The changes in radical contents as a function of temperature were used to analyse the reaction mechanism.

RESULTS AND DISCUSSION

The addition of lignosulphonate at the temperature 463 K stabilizes the thermal degradation of polyethylene (*Figure 1*). The thermal degradation temperature is defined as the temperature when 10% weight loss occurs. Curves A and B show the degradations of polyethylene (LDPE B-8015) and lignosulphonate (LSA-1), respectively. Curve C represents the degradation of the blend when lignosulphonate (LSA-1) and polyethylene (LDPE B-8015) are blended at 433 K and it shows that no difference compared to pure polyethylene is observed. Curve D shows the effect of the addition of lignosulphonate on the thermal stabilization. If the polyethylene is blended with lignosulphonate at 463 K, the temperature of thermal degradation is 671 K.

The stabilization is investigated with two different commercial polyethylenes which are free from antioxidant. The blending of polyethylene with lignosulphonate is carried out in each case at 463 K. Although the degradation of pure polyethylene is somewhat different in each case, the thermal stabilizations by the blending of lignosulphonate appear to be the same (671 K, *Table 1*). The addition of lignosulphonate does not affect the thermal stability of high-density polyethylene presumably because of the presence of antioxidant and the different crystallinity compared to low-density polyethylene.

LSA-1 has an effect on the stabilization even with a concentration of 0.025% as shown in *Table 2*. Other lignin derivatives are also used as additives. However,

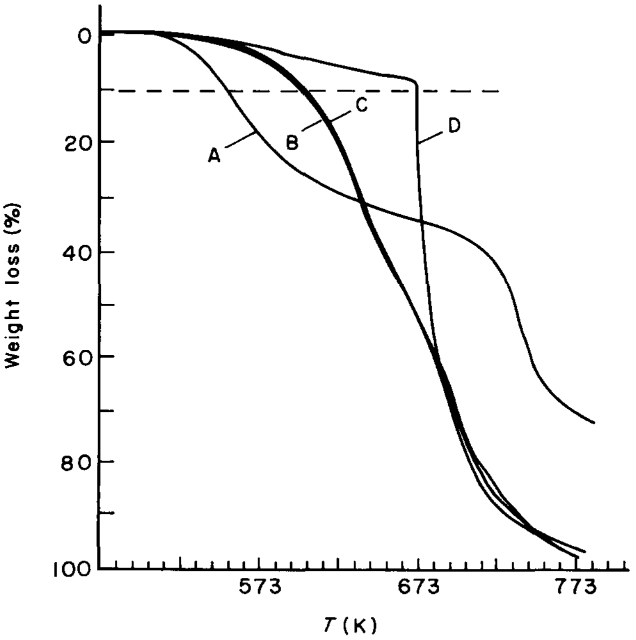

Figure 1 The stabilization effect of lignosulphonate as additive on the thermal degradation of the following samples: A, polyethylene (LDPE B-8015); B, lignosulphonate (LSA-1); C, polyethylene blended with LSA-1 at 433 K; D, polyethylene blended with LSA-1 at 463 K

Table 1 The effect of lignosulphonate (LSA-1) on the thermal degradation of various polyethylenes

Polyethylene	Additive	Thermal degradation* (K)
LDPE B-8015	None	633
	LSA-1, 1%	671
LDPE B-4524	None	593
	LSA-1, 1%	671
HDPE GD-6250	None	633
	LSA-1, 1%	633

* Temperature at 10% of weight loss by thermal degradation
LDPE B-8015: Polyethylene with melt index 8.0 g/min
LDPE B-4524: Polyethylene with melt index 4.5 g/min
HDPE GD-6250: Polyethylene with antioxidant
LSA-1: Lignosulphonate 1 (purity 95%)
Blending temperature: 463 K

Table 2 The effects of various lignin samples on the thermal degradation of polyethylene (LDPE B-8015)

Lignin	Additive (%)	Thermal degradation* (K)
LSA-1	0.025	671
	1.0	671
Kraft lignin	1.0	633
	5.0	633
Sulphur lignin	1.0	633
	5.0	633
Desulphonated lignosulphonate	1.0	633
	5.0	633

* Temperature at 10% of weight loss by thermal degradation
The abbreviations used are stated in *Table 1*
Blending temperature: 463 K

kraft lignin, desulphonated lignosulphonate and a lignin derivative prepared from lignosulphonate and sulphur do not affect the thermal stabilization as shown in *Table 2*. The blending is done in every case at 463 K. These findings strongly indicate that some structural characteristics of lignosulphonate are essential for thermal stabilization.

The thermal stabilization is dependent on the amount and the degree of purification of lignosulphonate, especially molecular weight, as shown in *Figure 2* and in *Table 3*. LSA-2 and LSA-3, which are less purified samples, have an effect on thermal stabilization only at higher concentrations. LSA-4, which is the low molecular weight fraction of LSA-3, has an effect at lower concentration. This low molecular weight fraction contains a higher degree of substitution of sulphonic groups, as generally known[8]. This indicates that the interaction between the polyethylene and lignosulphonate is dependent on the degree of sulphonation.

While blending at a constant rotation, a change in the torque was observed as a function of temperature. The maximum value of the torque in the Brabender Plasticorder is obtained when the sample is introduced in the mixing head. The torque decreases and finally becomes constant when the sample melts and the sample is distributed homogeneously in all parts of the mixing head. Changes in the torque after this may be due to crosslinking, degradation, deaeration, etc. A change occurs at about 453 K as shown in *Figure 3*. The blending must be done at temperatures higher than 453 K in order to obtain thermal stabilization.

The flow behaviours of LDPE B-8015 and LDPE B-4524 blended with lignosulphonate (LSA-1, 5%) are shown in *Figure 4*. The flow behaviour becomes more ideal with increase of temperature for both the pure polyethylene and the polyethylene blended with lignosulphonate. Five per cent of lignosulphonate does not seem to affect the flow behaviour. A similar result can be observed with the flow parameters (*Table 4*). The increase of n and the decrease of K with increase of temperature in the case of pure polyethylene as well as in

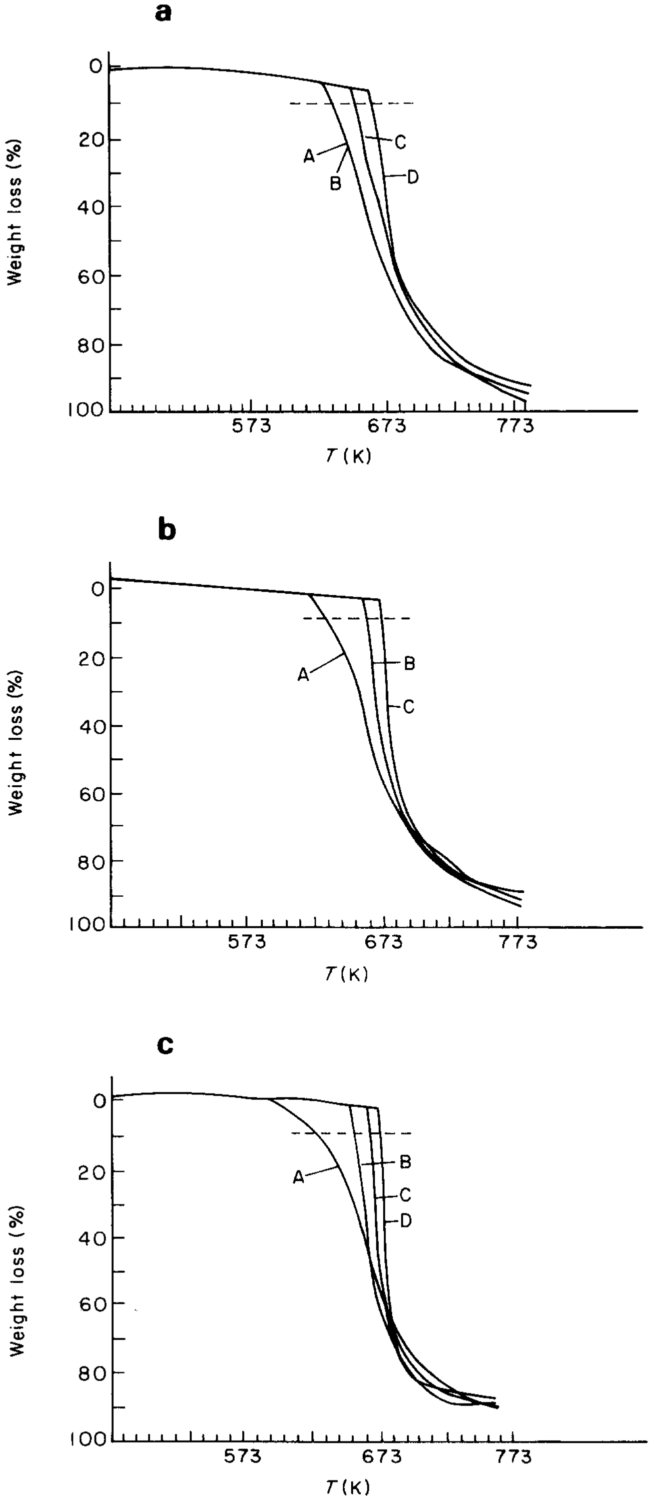

Figure 2 The thermal degradations of polyethylene (LDPE B-4524) and polyethylene–lignosulphonate blends: (a) LSA-2, (b) LSA-3 and (c) LSA-4. Curves A–D are as in *Figure 1*

Table 3 Thermal degradation of polyethylene and polyethylene–lignosulphonate blends

Additive		Thermal degradation*	Symbol in
Lignosulphonate	(%)	(K)	*Figure 2*
None	–	633	(a)–A
LSA-2	1.0	633	(a)–B
	5.0	653	(a)–C
	20.0	663	(a)–D
LSA-3	0.1	633	(b)–A
	1.0	658	(b)–B
	5.0	671	(b)–C
LSA-4	0.025	633	(c)–A
	0.1	653	(c)–B
	1.0	663	(c)–C
	5.0	671	(c)–D

* Temperature at 10% of weight loss by thermal degradation
LSA-2: Lignosulphonate 2 (purity 80%, Rauma-Repola Oy)
LSA-3: Lignosulphonate 3 (purity 80%, G. A. Serlachius Oy)
LSA-4: Low molecular weight fraction of LSA-3
Blending temperature: 463 K

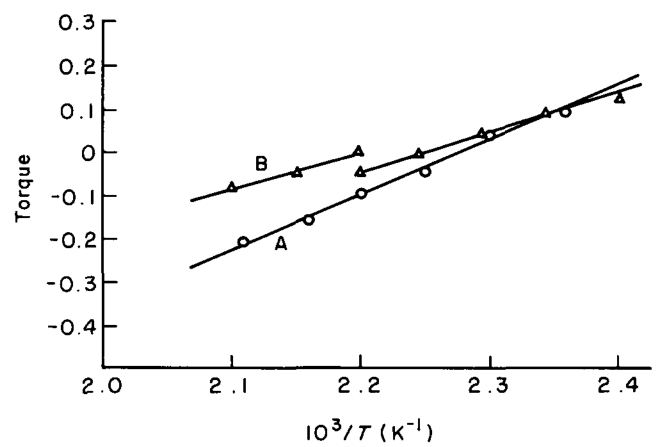

Figure 3 The relationship between the torque value and temperature: A, polyethylene (LDPE B-4524); B, polyethylene (LDPE B-4524)–lignosulphonate (LSA-1) (95:5) blend. The abbreviations are stated in *Table 1*

the case of polyethylene blended with lignosulphonate indicates that lignosulphonate does not affect the flow behaviour. Kubat[9] studied the flow behaviour when lignosulphonate (10–50%) was blended with polyethylene by extrusion. The changes in flow parameters obtained by a capillary viscosimeter were small compared to those of pure polyethylene.

The activation energy of flow decreases with the amount of lignosulphonate (*Table 5*). The decrease of activation energy with increasing amount of lignosulphonate has been observed with polypropylene[10]. It can be assumed that the decrease of the activation energy is due to increased branching by the incorporation of large lignosulphonate molecules.

The melt index values for pure polyethylene are observed to decrease with temperature (*Table 5*). The melt index shows the amount of substance which goes through the capillary at a certain temperature with a standard weight. In general, the crosslinking results in a decrease of the melt index. The differences in the melt index values are small between the pure polyethylene and the polyethylene–lignosulphonate blend, both of which are blended at the same temperature, and this difference may be due to the blending duration as well as to slight crosslinking. The melt index for polyethylene with 0.025% lignosulphonate is smaller than that of polyethylene. The melt index values for polyethylene blends including larger amounts of lignosulphonate are larger than those for polyethylenes without additives. This indicates that lignosulphonate causes crosslinking at the initial stage of reaction and an increasing amount of lignosulphonate causes branching that results in an increase in the melt index.

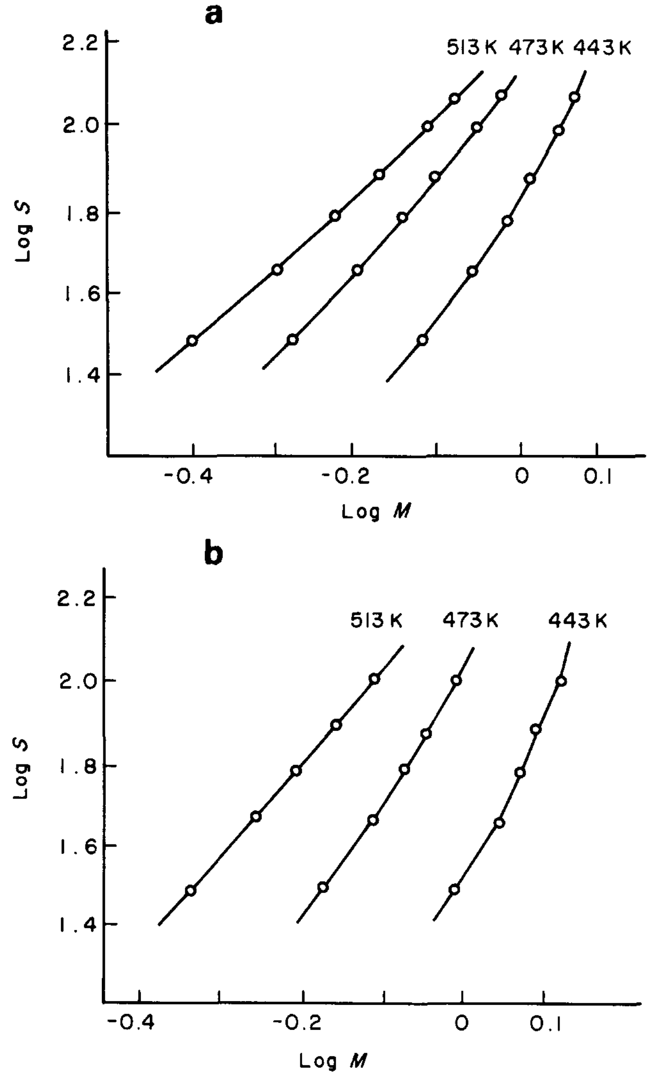

Figure 4 The flow behaviours (log S vs. log M) of (a) polyethylene (LDPE B-8015) and (b) polyethylene–lignosulphonate (LSA-1, 5%) at various temperatures. The abbreviations are stated in *Table 1*

Table 4 The flow parameters n and K for polyethylene (LDPE B-8015) and polyethylene (LDPE B-4524) blended with lignosulphonate (LSA-1, 5%)

Polyethylene	Additive	Processing temperature (K)	n	K ($\times 10^4$)
LDPE B-8015	–	433	0.30	2.78
LDPE B-8015	–	473	0.43	1.24
LDPE B-8015	–	513	0.57	0.55
LDPE B-4524	–	433	0.28	3.42
LDPE B-4524	LSA-1, 5%	433	0.24	4.40
LDPE B-4524	LSA-1, 5%	473	0.31	2.48
LDPE B-4524	LSA-1, 5%	513	0.44	1.06

The abbreviations used are shown in *Tables 1* and *3*

The possible crosslinking is followed by hot toluene extraction of the gel phase. The gel contents of polyethylene with or without an additive at various temperatures are shown in *Table 6*. The crosslinking of polyethylene (LDPE B-8015) occurs when the sample is processed at higher than 473 K as shown by the increase of the gel contents. The effect of lignosulphonate on the gel contents is shown in *Table 6*. The gel content is slightly increased (3%) in the presence of lignosulphonate, but does not increase further with the amount of lignosulphonate. Similar results for a slight crosslinking were observed above with melt index measurements.

All the above results indicate that a reaction between lignosulphonate and polyethylene occurs above 453 K, and increasingly affects the thermal degradation of polyethylene. In order to investigate the reaction, the relative spin densities were measured at different temperatures (*Figure 5*). Radical formation by the mechanical treatment is not observed in these experiments. The spin density of lignosulphonate increases over the temperature range 373–453 K and at higher temperatures (higher than 453 K) the spin density is almost stable (*Figure 6*, curve A). Domburg[11] has shown that the ether linkages can be cleaved at higher temperatures with the formation of phenoxy radicals, and that the other bonds may also be cleaved with radical mechanisms at even higher temperatures. Steelink[12] has shown that in alkaline treatment the phenoxy radicals are formed via quinonoic structures (*o*-quinone and quinone methide structures). The measurements of spin density were done in sodium chloride (NaCl) in order to prevent radical coupling among the lignin radicals. The relative spin density is higher in polyethylene–lignosulphonate mixtures at temperatures below 453 K (curve B) because of the radicals formed during oxidative degradation of polyethylene. The degradation of polyethylene is known to be a chain reaction which occurs by a radical mechanism[13]. The spin density of lignosulphonate–polyethylene mixtures starts to decrease clearly at temperatures above 453 K (curve B). This proves the stabilization reaction above 453 K, which was also shown in the earlier experiments, and shows that the radical reaction mechanism is involved in thermal stabilization.

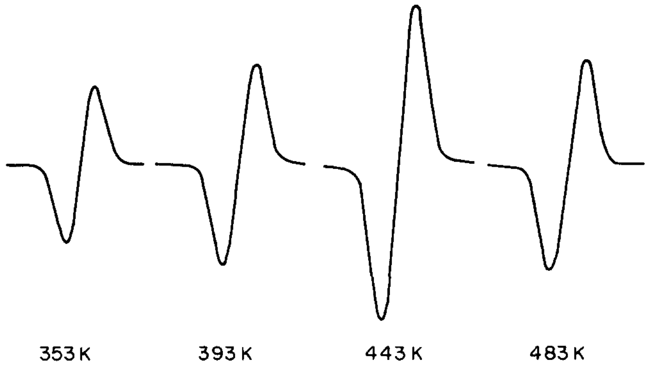

Figure 5 E.s.r. spectra of polyethylene (LDPE B-8015)–lignosulphonate (LSA-1) blend (97:3)

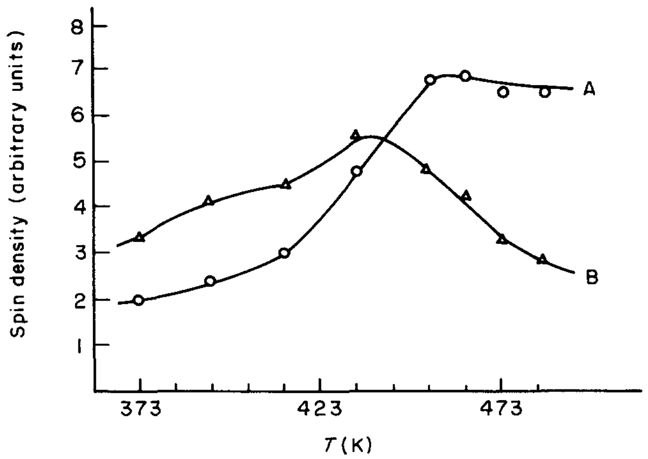

Figure 6 The relationship between the spin density and temperature: A, lignosulphonate (LSA-1)–NaCl blend; B, polyethylene (LDPE B-8015)–lignosulphonate (LSA-1) blend (97:3)

Table 5 The activation energies and melt indexes of polyethylene and polyethylene–lignosulphonate blends

Additive	Processing temperature (K)	Activation energy (kcal/mol)	Melt-index (g/10 min) LDPE B-8015 (463 K)	Melt-index (g/10 min) LDPE B-4524
None	–	–	6.9	4.2
None	423–473	5.63	2.6	0.8
LSA-1, 0.01%	423–473	4.87	1.2	–
LSA-1, 0.25%	423–473	3.80	–	–
LSA-1, 1.00%	473	–	–	0.9
LSA-1, 5.00%	473	–	–	1.2

The abbreviations used are shown in *Table 3*

Table 6 The gel contents of polyethylene and polyethylene–lignosulphonate blends

Additive	Processing temperature (K)	Gel content (%)
None	433	0.37
None	463	0.94
None	473	1.03
None	513	7.58
None	523	13.52
LSA-1, 0.025%	473	3.46
LSA-1, 1.10%	473	3.18
LSA-1, 2.75%	473	2.58
LSA-1, 5.00%	473	2.93

Polyethylene used in this experiment is LDPE B-8015
The abbreviations used are shown in *Tables 1* and *3*

CONCLUSIONS

The thermal analysis of polyethylene–lignosulphonate blends shows that the thermal degradation of polyethylene is raised from 593–633 K to 671 K. The thermal stabilization occurs only when blending is done at temperatures above 463 K. A change in torque values is observed at 453 K, which is the reaction temperature. The changes in spin densities measured by e.s.r. spectroscopy show that the reaction begins at the same temperature. Thermal stabilization was obtained when blending was done at temperatures over 463 K, i.e. when the observed reaction has completed.

The flow behaviour of the blends is almost the same as the flow behaviour of pure polyethylene with increase of temperature. The flow behaviour in the indicated reaction temperature region must be studied more exactly with varying lignosulphonate concentration. A slight crosslinking might be present to account for the increasing pseudoplasticity. The increasing amount of lignosulphonate after a slight crosslinking may contribute to increased branching in the chains and thus cause more ideal flow behaviour.

The effect of lignosulphonate on the thermal stabilization is dependent on the quality of lignosulphonate, and it occurs by the addition of more than 0.025% of the most purified lignosulphonate. The improvement in the thermal stability is dependent on the amount of sulphonic groups. During processing at temperatures above 463 K, the stabilization effect can be explained as follows. The phenoxy radicals are newly formed in lignosulphonate itself. At the same time, free radicals are also formed in polyethylene by oxidation. Thus the lignin radicals would inhibit the thermal degradation of polyethylene because of the coupling reaction with polyethylene radicals. The effect of the amount of additive on the mechanical properties and on the electrical resistance was discussed and no differences compared to the effects of commercial agents were observed.

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