

Flame Retardation of Polyethylene: Effect of a Phosphorus Flame Retardant Having Both Hydrophobic and Hydrophilic Groups in the Same Molecule

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ABSTRACT: The effect of phosphorylated cashew nut shell liquid prepolymer (PCNSL), a phosphorus-based flame retardant (FR) possessing both hydrophobic and hydrophilic groups in the same molecule, on the processability, mechanical properties, thermal and flammability behavior, and aging characteristics of low-density polyethylene (LDPE) was studied. TGA showed that PCNSL enhanced the thermal stability of LDPE, whereas limiting oxygen index (LOI) values increased from 17 to 24.5. The large increase in the LOI value could most probably be due to the possibility of PCNSL acting, apart from being a normal phosphorus-containing FR, also as an antioxidant that might control the oxidative surface degradation of LDPE. The oxidative induction test (PE, 2.5 min, with 2% PCNSL, 225 min, and 2% Irganox®, 189 min) showed that the antioxidant property of PCNSL is better than that of Irganox®, a known antioxidant for polyethylene (PE) and the enthalpy of oxidation (PE 4.6 kJ/g, with 2% PCNSL 2.6 kJ/g and 2% Irganox®, 2.2 kJ/g) for the PCNSL/LDPE blend was less than that of LDPE and was comparable to that of the Irganox® system. Brabender Plasticorder traces of LDPE/PCNSL blends showed good processability and miscibility. The enhanced processability and miscibility between LDPE and PCNSL are attributed to the presence of the hydrophobic aliphatic segment in the FR. The SEM microstructure of the blend supported the above findings. Comparative evaluation with standard all-aromatic FRs such as decabromodiphenyl oxide (DBDPO) and tricresyl phosphate (TCP) was carried out and the data supported the finding that FRs having both aliphatic and aromatic moieties with hydrophobic and hydrophilic characters in the same system can give better property profiles than those without these attributes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2631–2640, 2000

Key words: flame retardants; polyethylene; phosphorylated cashewnut shell liquid prepolymer

INTRODUCTION

The vulnerability of polyethylene (PE), a commodity thermoplastic polymer with a wide range of applications, to fire is well known. Being a hydrocarbon polymer, it catches fire easily and burns with dripping. This and other problems such as high pyrolysis temperature and the tendency of PE for degra-

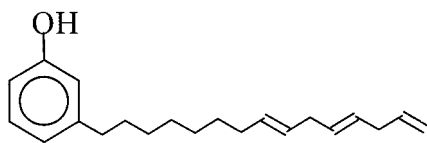
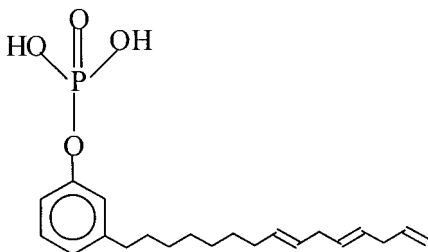
dation by surface oxidation along with the main pyrolytic chain-scission decomposition route restrict the selection of flame retardants (FRs) for PE.^{1–3} A number of phosphorus- and halogen-based FRs are recommended for PE to control its flammability.^{3–7} Although halogen FRs are rated to exhibit greater effectiveness, phosphorous compounds are recently gaining confidence as they work in the condensed phase during thermal decomposition and produce less smoke than do halogens.^{4,7} Thus, in the search for newer and better FRs,^{8–14} organic phosphorous compounds are gaining popularity.^{4,7,15} Organic

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phosphorous compounds are also expected to be more compatible than are the conventional inorganic FRs which require a high loading with consequent property deterioration.^{2,3}

Recent studies in this laboratory have shown that the selection of the structure of the FR is important in deciding the compatibility and miscibility of the FR.^{3,16-27} If the structure of the FR possesses both aromatic and aliphatic groups having substituents that can give rise to hydrophobic and hydrophilic moieties, the resulting FRs might be compatible with a wide spectrum of polymers.^{3,16} Such FRs could be called wide-spectrum FRs.³ It is shown that unsaturated long-chain hydrocarbon phenols present in cashewnut shell liquid (CNSL) possess the required structural features for transformation into such wide-spectrum FRs.^{3,16,17} Cardanol (the structures of the triene component of cardanol and the monomer of the phosphorylated cardanol prepolymer are shown in structures **I** and **II** below, respectively), the major distillation product of CNSL, can be phosphorylated at the hydroxyl group to introduce a phosphate group and polymerized to a prepolymer through the unsaturation in the side chain.¹⁶ As CNSL is technologically more potential than is cardanol by way of cost-effectiveness, CNSL was phosphorylated to get a phosphorylated CNSL prepolymer (PCNSL):^{16,22,25}

**I****II**

It has been shown in this laboratory as well as elsewhere that a polymeric FR (a prepolymer will be preferable, as high loading will be required for the polymeric FR) is much more effective than is a monomeric FR or a simple FR compound.^{26,28} Additionally, we observed that PCNSL possesses antioxidant properties²⁷ that might control the surface oxidation of PE with consequent enhancement in flame retardance. Preliminary studies have shown that PCNSL gives compatible blends with PE, poly(vinyl chloride) (PVC), natural rubber (NR), cellulose, and polyurethane.^{16,19,21,22} Whereas PCNSL enhances the limiting oxygen index (LOI) value of NR only marginally,¹⁹⁻²¹ substantial improvement in the LOI was observed with low-density polyethylene (LDPE).²² This observation prompted us to undertake a detailed investigation of LDPE. In this article, the effect of PCNSL on the flammability, thermal, mechanical, aging, and antioxidant characteristics of LDPE is reported.

EXPERIMENTAL

Materials

LDPE in powder form (MFI value, 0.50; density, 916 kg/m³) was obtained from M/s. Mehta & Co. (Bombay, India). LDPE granules of grade Indothene 20CA002 (MFI, 0.25; density, 920 kg/m³; tensile strength, 16 MPa; and % elongation, 600) was purchased from M/s Indian Petrochemicals Corporation Ltd. (Baroda, India). Most of the experiments reported here are based on LDPE in the powder form. PCNSL was synthesized according to the patented procedure.²⁵ Toluene LR (BDH) and paraformaldehyde LR (E. Merck, Bombay, India) were used as such.

Preparation of PCNSL

PCNSL was synthesized by phosphorylation of CNSL using orthophosphoric acid. Phosphorylation was carried out in a polymerization kettle fitted with stirrer, condenser, and a vacuum connection. In a typical experiment, orthophosphoric acid (49 g), calculated to fully esterify the phenolic hydroxyl group, was added to CNSL (157.8 g) and the temperature increased to 140°C. These conditions were maintained for 3 h, during which the phosphoric acid remaining in the vessel had been reduced to below 0.01% and the hydroxyl number of the resin

Table I Properties of PCNSL

Property	Value
Color and appearance	Dark brown semisolid material
Moisture content (%)	0.09
Specific gravity	1.294
Viscosity at 30°C (million cps)	4.80
Hydroxyl no. (mg of KOH)	0.48–1.0
Iodine value (g of iodine/100 g)	90–110
Unreacted phosphoric acid content (%)	0.01–0.20
Ash content (%)	1.45
Phosphorus content (%)	7.95

exhibited a value below 1 mg of KOH (yield 99%). The properties of PCNSL as virgin resin are given in Table I.

Curing of PCNSL

PCNSL was mixed with a slurry of paraformaldehyde (10%) in toluene in a Sigma blade mixer for 30 min and the product was then oven-cured at 120°C for 30 min. The product was pulverized and sieved to obtain the required material.

Methods

LDPE was blended with PCNSL in a Brabender Plasticorder PLE 651 using a measuring mixer-type W-50 at 120°C. Torque–time plots were taken. Standard tensile specimens of size 125 × 12.5 × 3.5 mm were injection-molded using a hand injection-molding machine. Tensile properties were tested in an Instron testing machine Model 1190 at a crosshead speed of 200 mm/min. The LOI was determined using a Stanton–Redcroft flammability test analyzer with standard specimens of size 125 × 6.5 × 3.5 mm prepared from injection-molded test specimens according to ASTM D 2863-77.

Thermogravimetric analysis of the blends were carried out in a DuPont thermogravimetric analyzer 951 attached to Thermal Analyst 2000 system in nitrogen as well as in air at a purge rate of 50 mL/min and at a heating rate of 10°C/min. About 10 mg of the sample was used for each run. The temperature at 10% decomposition (T_{10}), 50% decomposition (T_{50}), and percent char at 500°C (C_{500}) were calculated from the thermogram. SEM of the blends was done using a JEOL-

35C electron microscope. Thermal aging was carried out using tensile specimens in an air oven at 80°C.

An oxidation induction test was carried out as per ASTM D3895 using a TA Instruments differential scanning calorimeter 2010. The time taken for the formation of the exothermic peak at $199 \pm 1^\circ\text{C}$ in an oxygen atmosphere was taken as the oxidation induction time.

Measurement of the OH number was carried out as follows: The sample is acetylated with acetic anhydride in pyridine at the reflux temperature. The addition of water at the end converts the excess acetic anhydride to acetic acid. The total free acid is titrated with a standard sodium hydroxide solution using thymolphthalene as an indicator. A blank experiment is performed simultaneously.

RESULTS AND DISCUSSION

Processability

At ambient temperature, PCNSL was found to give a good mix with LDPE (powder form). With

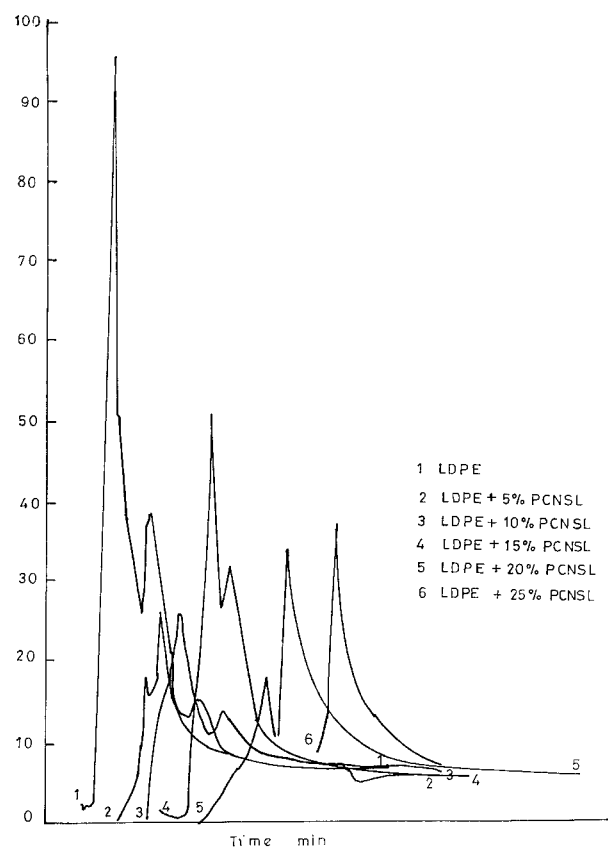


Figure 1 Torque behavior of LDPE with amount of PCNSL.

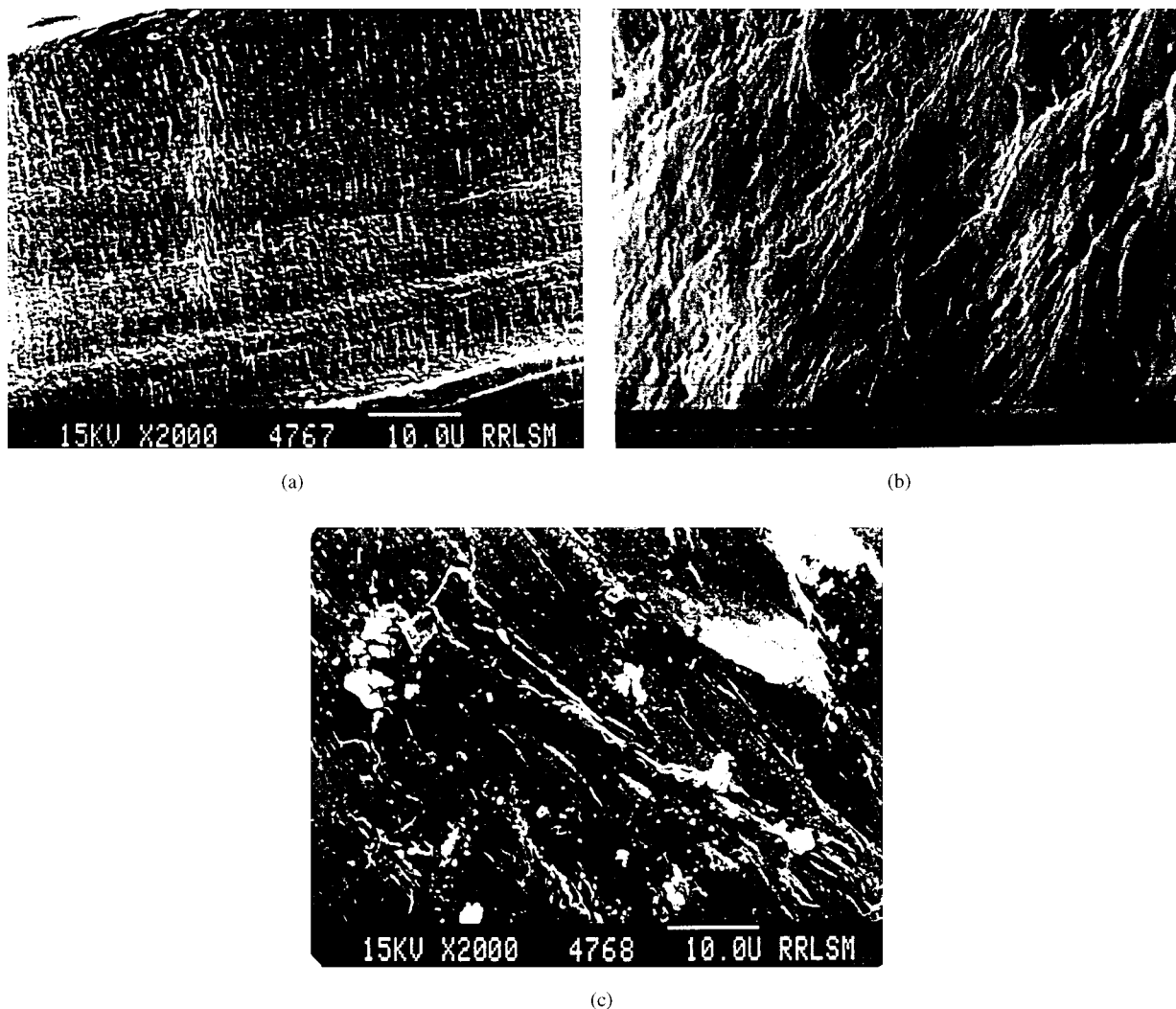


Figure 2 (a) SEM of LDPE. (b) SEM of LDPE/PCNSL blend $\times 2000$. (c) SEM of LDPE/DBDPO blend.

LDPE granules, it was found to adhere to the surface at room temperature. Both were properly mixed and blended after the melting of LDPE at $110\text{--}120^\circ\text{C}$. Figure 1 shows the blending behavior of the LDPE/PCNSL system. The torque maxima of the blend decreased from 38 Nm for PE to 25 Nm for the blend with 25% resin. The final mixing torque was about 7 Nm. The initial decrease in torque observed with increasing percentage of PCNSL might partially result from the plasticizing action of PCNSL. The final torque values indicate that there is a high level of miscibility. Although PCNSL has polar phosphate groups, the presence of a hydrocarbon segment may be responsible for the observed miscibility. In the case of cured PCNSL, the final torque increased from 8 to 12

Nm for the blend with 25% PCNSL. The results indicate that there is good miscibility of the cured resin with PE, but to a lesser extent when compared to uncured PCNSL. The observed miscibility was further confirmed by a comparison of the surface features of the SEM of the cross section of LDPE (hot-pressed in sheet form) along with the LDPE-PCNSL blend prepared under similar conditions [see Fig. 2(a,b)]. A smooth surface without a second phase can be seen in the case of the blend, indicating good miscibility. The blend of LDPE with PCNSL is thus easily processable and miscible with each other without any compatibility problems. The enhanced miscibility can be understood from the structure of the FR. II shows that the FR contains a long aliphatic moiety which permits

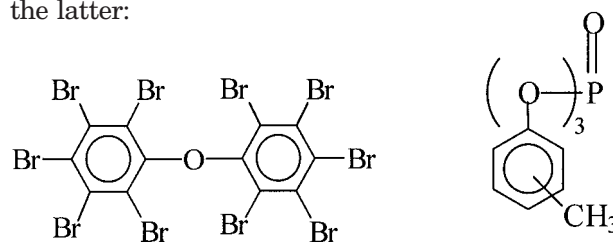
Table II Mechanical Properties of LDPE-PCNSL Blends

PCNSL (%)	Hardness (Shore D)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Percentage Elongation
0	49	8.08	62.5	152
2	53	8.0	75.0	176
5	51	7.74	29.6	144
10	45	7.02	57.8	128
15	45	6.53	62.5	160
20	45	6.43	53.12	152
25	45	6.09	35.93	152

miscibility and compatibility with LDPE. Similar behavior was observed when PCNSL was blended with NR and PVC.^{19,21} The ability of PCNSL to blend with hydrophilic polymers was experimented with, taking cellulose as an example.²⁹ The presence of the phosphate moiety enhances the compatibility with cellulose.

To show that the aliphatic segment in PCNSL is contributing positively to enhance the miscibility with LDPE, a fully aromatic FR, decabromodiphenyl oxide [DBDPO (III)], which is used frequently for flame retardation of PE,² was blended with LDPE under similar conditions for comparison. Figure 2(c) shows the SEM of the cross section of the LDPE-DBDPO blend. The existence of separate particles in Figure 2(c) in comparison to Figure 2(a,b) possibly suggests inadequate mixing. The Brabender curves for the blending operations in the case of the LDPE-DBDPO system also have given higher values of torque, indicating not so good miscibility for the system in comparison to the LDPE-PCNSL blend. The improved processability of the LDPE-PCNSL system was further confirmed through studies with tricresyl phosphate [TCP (IV)] replacing PCNSL. The Brabender curves of the LDPE-TCP blend, although similar to that of the LDPE-PCNSL system, registered higher torque than

that of the latter, indicating better processability for the latter:



III

IV

Mechanical Properties

The mechanical properties of LDPE/PCNSL and LDPE/cured PCNSL blends are given in Tables II and III, respectively. The decrease in tensile properties even up to 25% addition of PCNSL brought out only a 25% reduction in tensile strength. This is significant because addition of halogen-free FRs to PE is reported to bring about a reduction of tensile strength up to 55%.² The deterioration in tensile property of the LDPE-DBDPO blend was much more than that of the LDPE-PCNSL blend.

Table III Mechanical Properties of LDPE-cured PCNSL Blends

Cured PCNSL (%)	Hardness (Shore D)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)
0	49	8.08	62.5	152
2	52	8.06	125	176
5	54	8.28	45.83	108
10	55	8.04	53.12	64
15	54	8.34	87.5	56
20	54	7.28	79.1	48
25	56	7.24	50.0	24

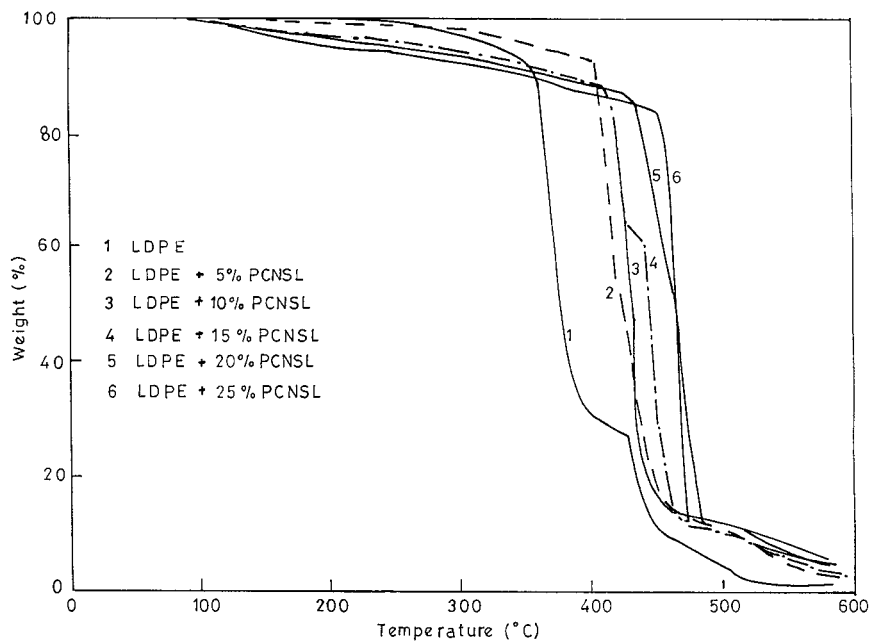


Figure 3 Thermogram of LDPE-PCNSL blends.

In the case of natural rubber, the tensile strength and tensile modulus were found to increase with increase in the percentage addition of PCNSL.^{19,21} This has been attributed to the ability of PCNSL to become crosslinked to the NR molecules during vulcanization. This capability can be used to impart better strength to the LD-

PE-PCNSL blend if curing is initiated through the side chain during or after blending.

Thermal and Flammability Behavior

The thermogravimetric traces of the LDPE/PCNSL blends are given in Figures 3 and 4 and the thermal

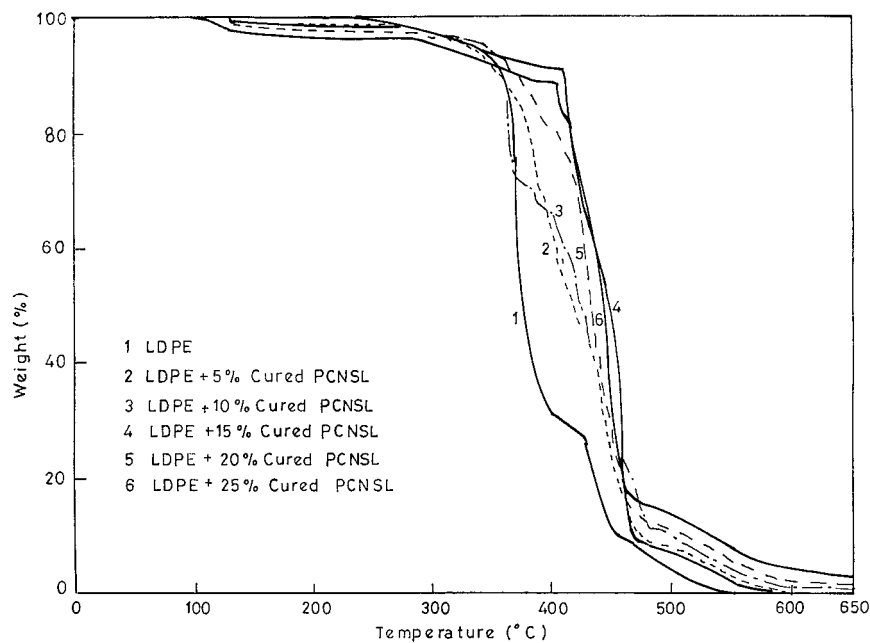


Figure 4 Thermogram of LDPE-cured PCNSL blends.

Table IV Thermal Stability and Flammability Parameters for LDPE-PCNSL System

PCNSL (%)	T_{10} (°C)	T_{50} (°C)	C_{500} (°C)	LOI
0	358.9	376.3	4.5	17.0
5	407.8	425.0	10.2	20.0
10	360.2	432.5	11.4	22.0
15	373.2	442.8	10.3	22.5
20	380.3	466.0	10.2	23.5
25	366.9	467.7	11.7	24.5

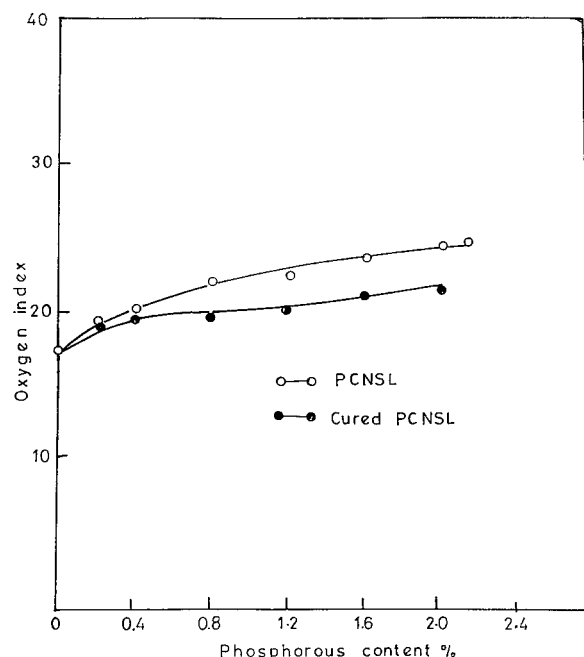
data are given in Tables IV and V. These data indicate that addition of both PCNSL and cured PCNSL enhances the thermal stability of LDPE. The difference in behavior observed between PCNSL and cured PCNSL might be due to the lower P content of cured PCNSL, as 10% paraformaldehyde has been added as the curing agent. Moreover, with PCNSL, the mixing is more intimate, so that the availability of phosphorus is closely assured.

Flame-retardant Behavior

As observed generally with phosphorous FRs, addition of PCNSL increases the LOI values of LDPE. In contrast to TCP which increases the LOI value of LDPE by 2–3 units only, the increment in the value of LOI for PCNSL is 7.6 units (see Fig. 5) at 25% addition. The cured PCNSL, on the other hand, gave only an increment of 4.5 at the same add-on value. Table VI compares the values for the oxygen index slope^{1,22} for a number of FRs with that of PCNSL. The value of the oxygen index slope for the PCNSL-LDPE system is comparable to those of some of the most effective halogen FRs and is much superior to that of TCP. It is generally known that halogen FRs that function in the vapor phase are more effective for

Table V Thermal and Flammability Parameters for LDPE-cured PCNSL System

Cured PCNSL (%)	T_{10} (°C)	T_{50} (°C)	C_{500} (°C)	LOI
0	358.9	376.3	4.5	17.0
5	354.6	420.3	7.5	19.5
10	355.4	425.1	9.6	19.5
15	356.0	450.0	9.8	20.5
20	371.4	453.9	10.7	21.0
25	364.0	445.3	13.4	21.5


Figure 5 Effect of PCNSL on the flammability of LDPE.

PE and similar olefinic polymers than are phosphorous-based FRs that are active in the condensed phase.² So, the enhanced performance of PCNSL, which is similar to that of FRs that function by a vapor-phase mechanism, might give rise to the idea that PCNSL or a phosphorus-containing decomposition product may be going to the vapor phase for interfering with the vapor phase free-radical degradation processes. The TGA and the DTA (unpublished results) of PCNSL, however, do not support vaporization at this stage and, therefore, one possibility could most proba-

Table VI Comparison of Oxygen Index Slopes for Various FR-PE Combinations¹

FR	Oxygen Index Slope
Tris(tribromophenyl)phosphite	3.6
Hexachlorocyclopentadiene dimer + Sb_2O_3	0.2
Chlorinated polyisobutylene + Sb_2O_3	1.3
Poly(<i>b</i> -tribromoethyl methacrylate)	0.2
Tris(tribromoneopentyl)phosphite	1.0
Tris(bromophenyl)phosphate	1.7
Tricresyl phosphate	1.0
Chlorinated polyisobutylene	0.2
PCNSL	3.0

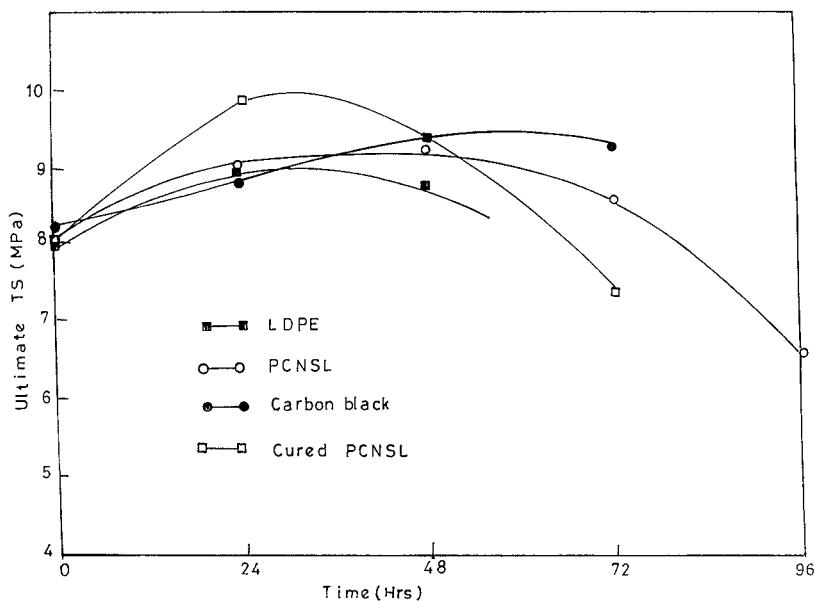


Figure 6 Effect of 2% resin on the aging properties of LDPE compared with carbon black at 80°C.

bly be the functioning of PCNSL as an antioxidant as well. The antioxidant property of PCNSL was shown in an earlier experiment when used along with NR.²⁷ The antioxidant activity was maximum for the formulation containing 2% PCNSL. The aging characteristics of the LDPE-PCNSL system was studied and the results are given

in Figure 6. It can be seen that at a 2% level of addition of PCNSL (LDPE-carbon black system is shown for comparison), there is an increase, instead of the expected decrease, in tensile strength, indicating possible antioxidant activity.

The increase in char value (see Table IV) and thermal stability with increase in the LOI of

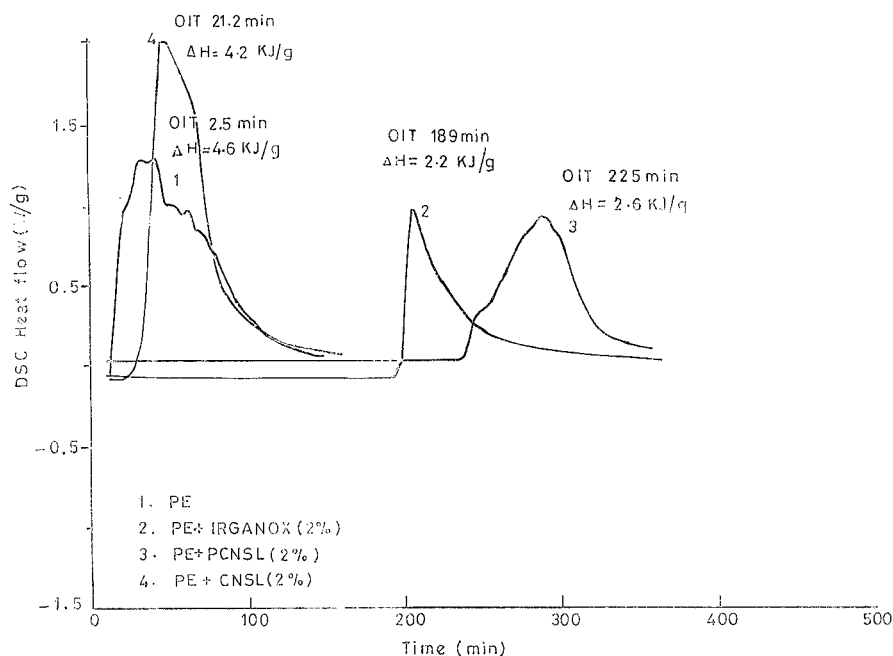


Figure 7 DSC traces of oxidation induction test.

LDPE on addition of PCNSL suggests that the mode of action of phosphorus might be at the condensed phase. Additionally, as explained above, the action of PCNSL as an antioxidant might further control the degradation process to register an improvement in the LOI. Surface oxidation, in general, may follow a peroxy initiation and the early decomposition products will be carbonyl-bearing compounds.³⁰ The formation of the carbonyl-bearing moieties can be detected if the IR spectrum of the char at the appropriate temperature is measured.^{30,31} The IR spectra of the char of LDPE and LDPE-PCNSL systems exposed to isothermal conditions at 350 and 450°C revealed a reduction in the intensities of the carbonyl group of charred LDPE in the presence of PCNSL, indicating possible involvement of PCNSL in controlling the surface oxidation of PE.

Antioxidant Properties

DSC traces obtained for the oxidation induction test at $199 \pm 1^\circ\text{C}$ are shown in Figure 7. Virgin PE took 2.5 min, whereas with 2% PCNSL, it was increased to 225 min compared to 189 min, with 2% Irganox®. NSL, being a phenol, is expected to contribute to the antioxidant activity. The DSC trace [Fig. 7(4)] for the blend of 2% CNSL alone with LDPE gave a value of oxidation induction time of only 21.2 min. This shows that the contribution from free CNSL to the antioxidant activity is only marginal. Analytical data shown earlier in the Experimental section also indicate that the presence of free CNSL in PCNSL is negligible. So, it may be seen that the antioxidant activity observed is solely due to PCNSL. There are also certain earlier reports³² stating that phosphates also exhibit antioxidant activity, although it is generally believed not to exhibit such properties. The enthalpy of oxidation observed for the primary oxidation exotherm of LDPE was 4.6 kJ/g compared to 2.2 kJ/g for the PE/Irganox® system and 2.6 kJ/g for the PE/PCNSL system. This showed a decreasing trend as reported with antioxidant-added systems.^{33,34} The enthalpy of oxidation observed for the PE/CNSL system was only 4.2 kJ/g, which also indicated that the antioxidant activity of CNSL was only marginal when compared to PCNSL.

CONCLUSIONS

In conclusion, it can be said that PCNSL improves the processability of LDPE by acting as a

processing aid and gives miscible and compatible blends with LDPE. Similar effects were observed with other hydrocarbon polymers such as NR. PCNSL also showed good compatibility with polymers having a pronounced hydrophilic character such as cellulose. The presence of both hydrophobic and hydrophilic groups in the same molecule thus makes PCNSL an ideal FR that is compatible with a wide spectrum of polymers. Although addition of PCNSL improves the LOI of NR only marginally, it enhances the LOI of LDPE substantially, due possibly to its action as an antioxidant as well. Comparison with all-aromatic FRs such as DBDPO and TCP supports the finding that the presence of aliphatic and aromatic moieties in the same molecule with hydrophobic and hydrophilic characteristics gives a better property profile than do those FRs without such attributes. PCNSL also showed better antioxidant properties in PE compared to commercial antioxidants like Irganox®.

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