Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Degradation of Polyethylene: Effect of Phosphorylated Poly (2,6-DimethyM, 4-phenylene Oxide)

I. K. Varma[a]; Kunal Chander[a]; R. C. Anand[a]
[a] Centre for Material Science & Technology and Department of Chemistry, Indian Institute of Technology, Hauz Khas New Delhi, India

To cite this Article Varma, I. K. , Chander, Kunal and Anand, R. C.(1985) 'Degradation of Polyethylene: Effect of Phosphorylated Poly (2,6-DimethyM, 4-phenylene Oxide)', Journal of Macromolecular Science, Part A, 22: 8, 1075 — 1087
To link to this Article: DOI: 10.1080/00222338508063315
URL: http://dx.doi.org/10.1080/00222338508063315

J. MACROMOL. SCI.–CHEM., A22(8), pp. 1075-1087 (1985)

Degradation of Polyethylene: Effect of Phosphorylated Poly (2,6-Dimethyl-1, 4-phenylene Oxide)

I. K. VARMA, KUNAL CHANDER, and R. C. ANAND

Centre for Material Science & Technology and
Department of Chemistry
Indian Institute of Technology, Hauz Khas
New Delhi 110016, India

ABSTRACT

The effect of phosphorylated poly(2,6-dimethyl-1,4-phenylene oxide) (PPOP) on the stability of high-density polyethylene (HDPE) is described. One and 5% (w/w) of PPOP was melt blended with HDPE (Samples A_1 and A_5, respectively). The samples were extruded in ribbon form and irradiated with UV light for several hours. In the presence of PPOP, suppression of double bond formation in HDPE was indicated by IR spectroscopy. HDPE became very brittle after 25 h irradiation, while Samples A_1 and A_5 showed much better retention of mechanical properties. The limiting oxygen index of HDPE did not change by incorporation of PPOP. The effect of thermal aging at 100°C on the mechanical properties of HDPE and Samples A_1 and A_5 was also studied.

0022-233X/85/2208-1075$3.50/0

INTRODUCTION

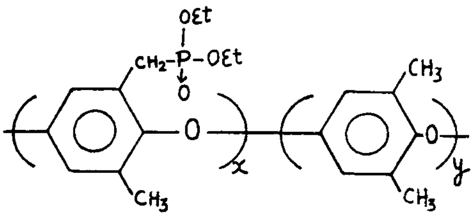
Polymeric materials are attractive for use as solar collectors due to their light weight, corrosion resistance, design flexibility, and ease of processing. However, in contrast to traditional materials, polymers are affected to a greater extent by the elements of the outdoor environment. Very few polymeric materials are available which can withstand long term aging without discoloration or embrittlement. Investigations of the aging behavior of polyolefins and the effect of additives used for improving weather resistance are important for extending the use of these large tonnage thermoplastics in the area of solar collectors.

Polyethylene (PE) is used in several other outdoor applications. A deterioration in the electrical insulation properties of this polymer is observed on long-term exposure to sunlight due to oxidation which leads to the formation of carbonyl groups. Embrittlement of polyethylene takes place due to the absorption of energy by the carbonyl group and subsequent photochemical transformations. Antioxidants (for example, phenols and amines) are added to polyethylene to provide thermal protection during processing and to maintain a low power factor. Phosphites [1, 2] and cyclic phosphates [3] have also been used for rendering polyolefins resistant to oxidation. These phosphorus-containing stabilizers are believed to function by promoting the decomposition of hydroperoxides. In the present communication the degradation of PE in the presence of phosphorylated poly(2,6-dimethyl-1,4-phenylene oxide) is reported. High molecular weight, phosphorus-containing additives are expected to impart long-term stability to polymers due to their reduced mobility and their smaller tendency to leach out.

EXPERIMENTAL

Materials

High-density polyethylene (Hostalen G Grade GD 7250) was used. Phosphorylated poly(2,6-dimethyl-1,4-phenylene oxide) was prepared according to the method reported elsewhere [4]. The polymer had a phosphorus content of 9.8% and an intrinsic viscosity of 0.3 dL/g in chloroform at 30 °C. The following structure can be assigned to PPOP on the basis of its phosphorus content:



Methods

A Betol (Model BM 1820) single screw extruder was used for melt blending of dried HDPE and PPOP. The temperatures of zones, I, II, III, and the dye zone of the extruder were maintained at 170, 180, 190, and 190°C, respectively. The speeds of the feed-up and take-up rollers were 5.75 and 24.5 m/min, respectively. Samples A_0, A_1, and A_5 (ribbon-shaped tapes) were obtained by blending HDPE with 0, 1, and 5% (by weight) of PPOP, respectively.

Photoirradiation

Five samples (20 cm long) of Specimens A_0, A_1, and A_5 were mounted on a thick, flexible sheet of paper and placed in a dark chamber equidistant (15 cm) from a high-pressure mercury lamp (Philips 125 W). These samples were irradiated for periods of 25, 50, 75, and 100 h in an air atmosphere.

Thermal Aging

Samples A_0, A_1, and A_5 were heated at 100°C in an air oven. Thermal degradation was followed by measurement of the loss in weight of the samples after intervals of 25, 50, 75, and 100 h.

Characterization

A Perkin-Elmer Model 580B Spectrophotometer was used to record changes in the IR spectra of various polymer samples. Yield stress, % elongation, and 1% secant modulus were determined by using a table Instron machine. Load vs extension curves were obtained by using a gauge length of 5 cm and a cross-head speed of 2 cm/min.

A Norelco Type 120-101-85 Philips X-Ray Generator was used for recording the x-ray diffraction patterns. The generator was operated at 40 kV and 30 mA. Polymer samples (as tapes) were exposed to nickel filtered CuK_α x-ray radiation. A scanning speed of one minute per degree of 2θ was used.

A Stanton Red Croft Flammability Tester was used for evaluating the oxygen index according to ASTM D-2863.

Thermal behavior of various specimens was obtained by using a Du Pont 1090 Thermal Analyzer having a 910-DSC module. A heating rate of 10°C/min was used.

RESULTS AND DISCUSSION

In the IR spectrum of HDPE (A_0), bending absorptions due to the $>CH_2$ group were observed at 1370 and 1355 cm^{-1}. The presence of a shoulder at 1380 cm^{-1}, which may be due to $-CH_3$ bending vibrations, indicates a small amount of branching in the polymer. In the spectra of A_1 and A_5, characteristic bands were observed at 1260 (P=O) and 1060, 1030, 965 cm^{-1} (=P–O–C) (Fig. 1). In Sample A_0, weak absorptions at 912 and 990 cm^{-1} were observed which may be due to trace amounts of vinylic double bonds in the polymer.

On irradiation of Samples A_0 and A_1, the intensity of vinylic absorption increased with time, but in Sample A_5, no significant change was observed (Figs. 1-3).

The relative increase in the unsaturation by irradiation of HDPE samples was calculated by measuring the intensity of absorption at 912 cm^{-1} (due to vinyl-type unsaturation) and 1370 cm^{-1}. Semiquantitative information regarding the appearance of double bonds on irradiation of HDPE can be obtained by evaluation of this ratio (Table 1). A significant increase in this ratio was obtained when HDPE was irradi-

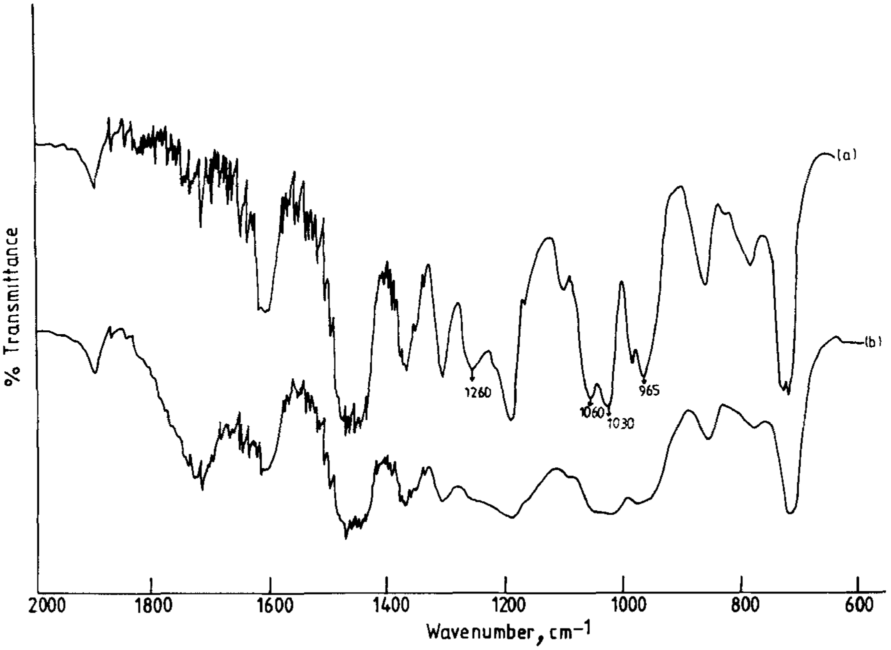


FIG. 1. IR spectra of Sample A_5 irradiated for (a) 0 h and (b) 25 h as a thick film.

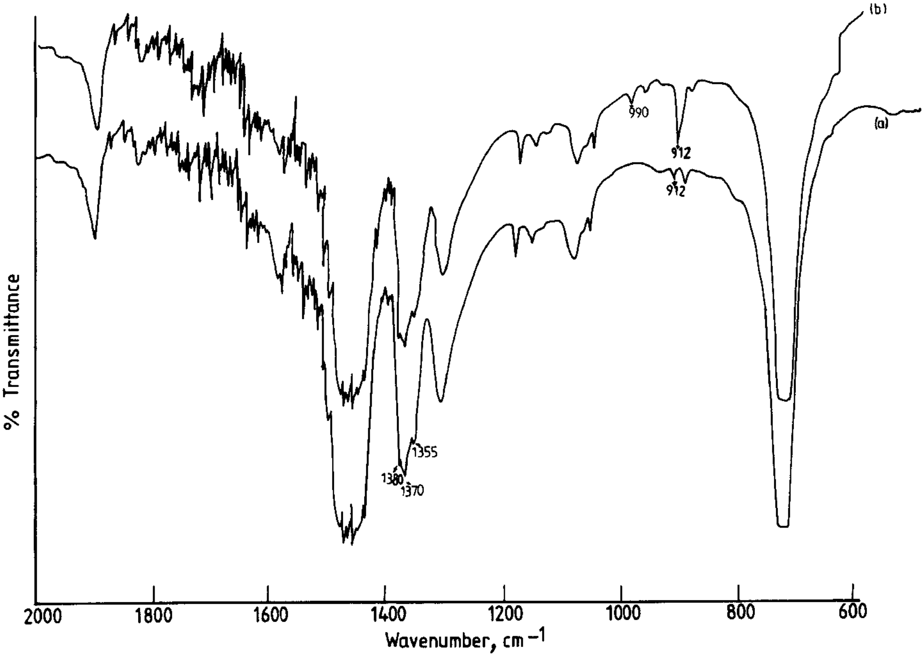
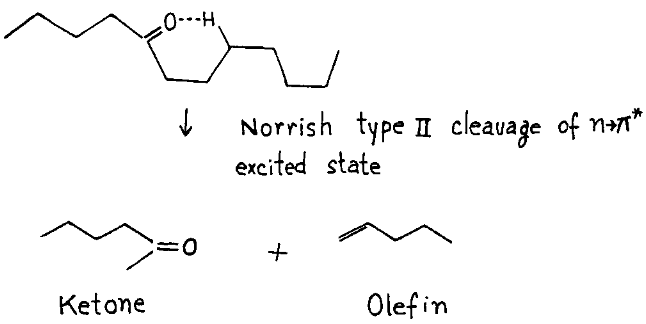


FIG. 2. IR spectra of Sample A_0 irradiated for (a) 0 h and (b) 25 h.

ated for 100 h. In Sample A_1, the peak due to vinylic unsaturation developed at a decreasing rate while in Sample A_5 a significant reduction in the intensity of 912 cm^{-1} band was observed. Chain scission reactions (Norrish type II) are generally responsible for the development of vinylic unsaturation in polyethylene:



(1)

PPOP may be involved in the quenching of the excited triplet state of the ketonic group by energy transfer (Eq. 2), thus retarding Norrish

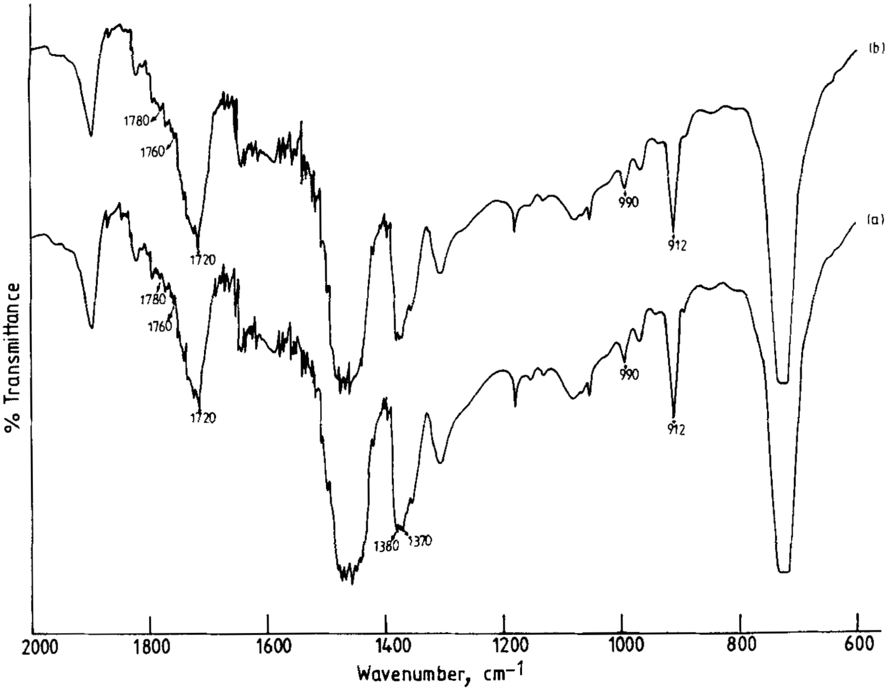


FIG. 3. IR spectra of Sample A_0 irradiated for (a) 50 h and (b) 100 h.

TABLE 1. Effect of PPOP on Development of Unsaturation in HDPE on Irradiation

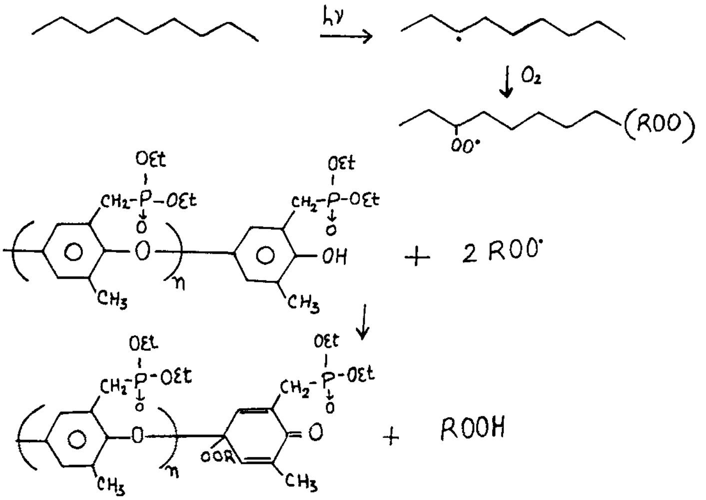
	Absorbance ratio 912 cm^{-1}/1370 cm^{-1}		
Exposure time, h	A_0	A_1	A_5
0	0.016	0.0078	0.005
25	0.084	0.064	0.010
50	0.287	0.162	0.065
75	0.260	0.259	0.033
100	0.216	0.234	0.026

type II reactions. Another possibility is the reduction in the rate of carbonyl group generation in the presence of PPOP.

$$\begin{tikzcd} P^* + \text{stabilizer} \arrow[r] & P + \text{stabilizer} \arrow[d, squiggly] \\ & \text{stabilizer} \end{tikzcd} \qquad (2)$$

In Sample A_0, the band associated with the carbonyl group (1800-1675 cm^{-1}) was obvious after 25 h irradiation. The intensity of this absorption band increased significantly on further exposure (Figs. 2 and 3). The main band at 1720 cm^{-1} was due to ketone-type carbonyl. However, small shoulders at 1760 and 1780 cm^{-1} appeared on prolonged exposure to UV light. These bands have been attributed to per-esters and per-acids, respectively [5, 6]. Absorptions due to the carbonyl group were observed in Samples A_1 and A_5, but the increase in the intensity of these bands with the duration of exposure was not as pronounced.

Samples A_1 and A_5, which were initially slightly yellow in color, developed a deeper yellow color on irradiation. This could be due to the formation of a quinoid structure. The terminal hydroxyl group of PPOP may react with peroxy radicals to give a quinoid structure (Eq. 3) as is the case with hindered phenols [7].



(3)

These spectral studies thus indicate a significant reduction in vinylic unsaturation and a marginal decrease of carbonyl groups in HDPE in the presence of PPOP.

MECHANICAL PROPERTIES

Up to 25 h irradiation, PPOP was a very effective stabilizer for HDPE as can be seen from the % elongation data (Table 2). Pure PE failed at 28% elongation whereas Sample A_5 did not break even at 700% elongation. After 50 h irradiation, Sample A_0 showed a 2% elongation only, while Sample A_5 had a relatively high % elongation (26%).

Similarly, PPOP has a dramatic effect on the yield stress of HDPE (Table 3). About a 38% reduction in yield stress was observed in HDPE (Sample A_0) after 50 h of irradiation, while in Sample A_5, containing 5% PPOP, only an 18% reduction was observed. The fractional retention of yield stress was calculated for the various samples by dividing the yield stress obtained at any given time of exposure with the original yield stress of the sample. These results are plotted in Fig. 4. Better retention of yield stress was observed in Sample A_5. In Samples A_0 and A_1, a slight increase in yield stress was observed during the first 25 h of irradiation, followed by a decrease in the second 25 h. This decrease may be due to the chain scission reaction which becomes significant in the second 25 h. Further irradiation may bring about some crosslinking, leading to an improvement in yield stress.

Stress at 1% elongation (1% secant modulus) was also calculated. Incorporation of PPOP in HDPE resulted in an increase in modulus (Table 4). However, when these samples were irradiated, a decrease was observed in Samples A_1 and A_5. Fractional retention values of the 1% secant modulus as a function of exposure time are given in Fig. 5.

TABLE 2. Effect of Irradiation on % Elongation of HDPE Samples Containing PPOP

Time of exposure, h	A_0	A_1	A_5
0	>700	>700	>700
25	28	70	>700
50	2.0	2.0	25.9
75	2.0	2.0	14.5
100	3.1	2.9	13.1

TABLE 3. Effect of Irradiation on Yield Stress of HDPE Containing PPOP

	Yield stress, kg/cm^2		
Time of exposure, h	A_0	A_1	A_5
0	157	161	165
25	177	169	162
50	95	77	135
75	97	86	142
100	115	97	153

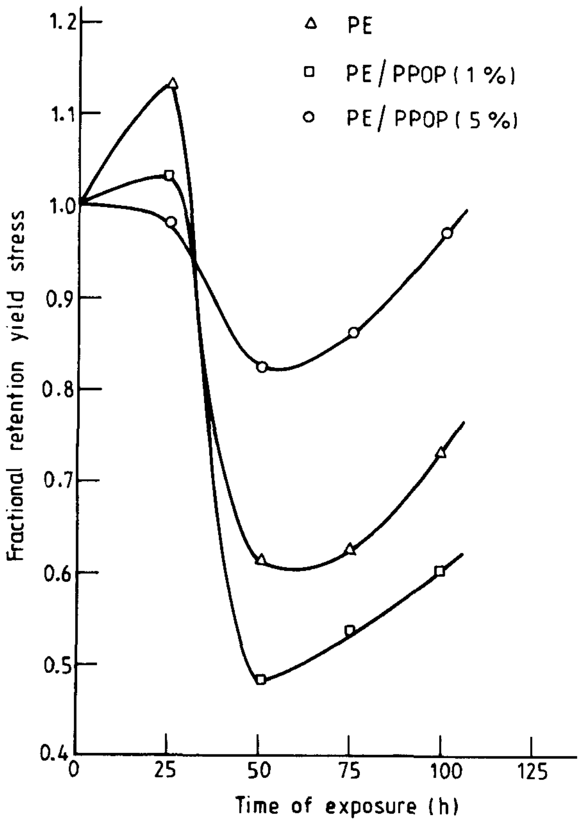


FIG. 4. Plot of fractional retention yield stress vs exposure time.

TABLE 4. Effect of Irradiation on 1% Secant Modulus of HDPE Containing PPOP

Time of exposure, h	1% Secant modulus, kg/cm^2		
	A_0	A_1	A_5
0	4648	5895	6310
25	2768	5490	5926
75	3780	4079	3985
100	4434	3856	3576

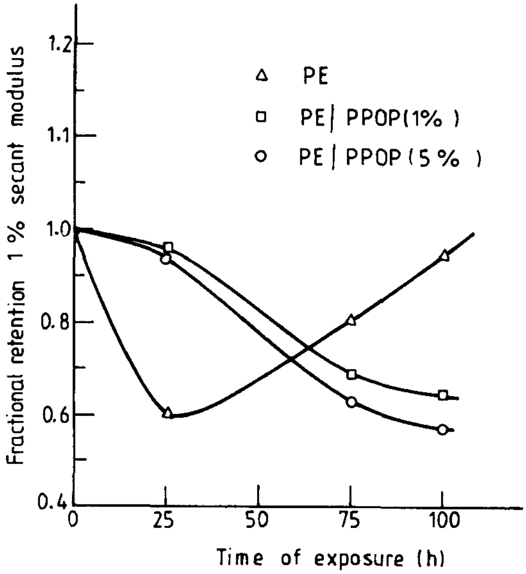


FIG. 5. Plot of fractional retention 1% secant modulus vs exposure time.

Crystallinity

Percent crystallinity was calculated from the normalized x-ray diffraction curves. The original x-ray curves were normalized at all values of θ by employing the expression

$$S = \frac{2 \sin \theta}{\lambda} \qquad (\lambda = 1.54 \text{ Å})$$

A curve was plotted for IS^2 values vs 2θ. A tentative amorphous curve was drawn, and crystallinity was evaluated from the equation

$$\% \text{ Crystallinity} = \frac{\text{area under crystalline region}}{\text{total area}} \times 100$$

The % crystallinity of HDPE (39.8%) increased slightly upon incorporation of PPOP (46.9% in Sample A_5). These results indicate that PPOP induces crystallization in HDPE. A significant increase in crystallization was observed in HDPE upon irradiation for 100 h (48.7% crystallinity). A slight increase was also observed in Samples A_1 and A_5 (48.9%).

Some information about the crystallinity of these polymers can also be obtained from the heat of fusion as determined by DSC. In Sample A_0, the heat of fusion increased with the exposure time (Table 5), while in Sample A_5 only a slight improvement in ΔH values was noticed. The melting point of the polymers did not change with exposure and was 128.4 ± 0.3°C in HDPE (A_0) (Fig. 6).

The limiting oxygen index of HDPE (19.3) did not change upon incorporation of PPOP.

TABLE 5. Effect of Irradiation of Samples A_0 and A_5 on Heat of Fusion

Exposure time, h	A_0	A_5
0	136	132
50	152	134
100	175	140

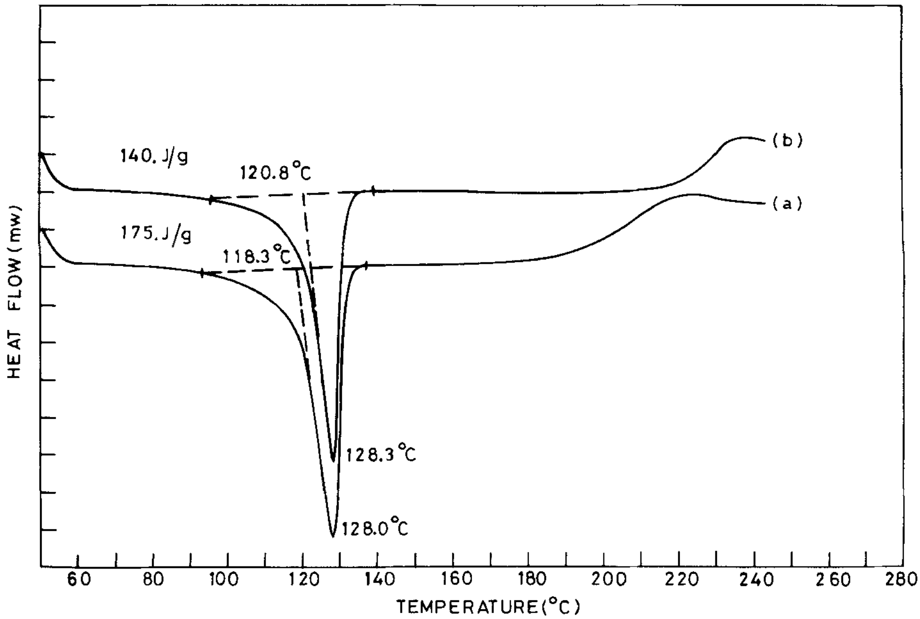


FIG. 6. DSC thermograms of (a) Sample A_0 irradiated for 100 h and (b) Sample A_5 irradiated for 100 h.

TABLE 6. Change in Mechanical Properties of HDPE after Thermal Aging at 100°C for 100 h

Property	A_0	A_1	A_5
Weight loss, %	0	0	0
Yield stress, kg/cm^2	203	154	164
% Elongation	>700	>700	>700
1% Secant modulus, kg/cm^2	12,040	5,200	5,175
% Crystallinity	45.6	45.3	46.0

Effect of Heat on Mechanical Properties of HDPE

No change in the weight of HDPE (Samples A_0, A_1, and A_5) was observed on heating at 100°C for 100 h. Thermal aging did not influence the % elongation. The yield stress of HDPE increased on aging. No significant change in the mechanical properties of heat-aged HDPE containing PPOP was observed (Table 6).

CONCLUSION

These results indicate that phosphorylated polyphenylene oxide reduces the oxidation of HDPE. Better retention of mechanical properties of HDPE on irradiation is obtained by incorporation of PPOP. Embrittlement of HDPE was considerably reduced in the presence of phosphorylated polyphenylene oxide.

REFERENCES

[1] B. A. Hunter, Ind. Eng. Chem., 46, 1524 (1954).
[2] P. A. Kirpichanikov and N. A. Mukmeneva, in The Ageing and Stabilisation of Polymers (A. S. Kisminkii, ed.), Elsevier, Amsterdam, 1971, p. 200.
[3] K. J. Humphris and G. Scott, U.S. Patent 3,920,607 (1975).
[4] K. Chander, R. C. Anand, and I. K. Varma, J. Macromol. Sci.–Chem., A20(7), 697 (1983).
[5] W. H. T. Davison, J. Chem. Soc., p. 2456 (1951).
[6] J. P. Luongo, J. Polym. Sci., 42, 139 (1960).
[7] N. M. Emaniel, E. Denisor, and Z. K. Maizus, The Chain Oxidation of Hydrocarbons in Liquids, Nauka, Moscow, 1965. Translated into English by Plenum Press, 1967.

Accepted by editor April 4, 1984
Received for publication April 20, 1984