Thermochimica Acta, 123 (1988) 221–231
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STABILITY OF POLY(OXYPROPYLENE-ETHER) POLYOL *

YE SU

Research Institute for Chemical Processing and Utilization of Forest Products, Chinese Academy of Forestry, Nanjing, Jiangsu Province (People's Republic of China)

WANG WAN JIANG

Liming Research Institute for Chemical Industry, Luoyang, Henan Province, (People's Republic of China)

(Received 3 March 1987)

ABSTRACT

The thermal decomposition and thermal oxidation of poly(oxypropylene-ether) polyol (POPP) have been studied. Thermal oxidation–decomposition in air has been found to be a major factor affecting the thermal stability of POPP. The inhibiting ability of antioxidants of different structures on the thermal oxidation of POPP has been investigated by means of thermal analysis. Experimental results show that phenothiazine, 2,2′-methylene bis(4-methyl-6-tert-butyl phenol) (2246), propyl gallate and pyrogallol are more effective antioxidants. Antioxidant systems consisting of 2246 and triphenyl phosphite, 2,6-di-tert-butyl-4-methyl phenol (264) and phenothiazine, or 2246 and phenothiazine, exhibit better synergistic effects.

INTRODUCTION

Poly(oxypropylene-ether) polyol is an important raw material used to prepare both flexible and rigid polyurethane foams. The thermal stability of POPP has a direct effect on the quality of the foams. When POPP with a lower thermal endurance is used as the raw material, the core-scorching phenomenon occurs readily in the course of foaming. Madorsky and Straus [1] investigated the thermal degradation of polyoxypropylene by MS analysis. Kim Vo Van et al. [2,3] determined the kinetics of decomposition of poly(oxypropylene) glycols by TG–DSC methods. However, until now little has been reported in the way of more systematic investigation of thermal stability and potential antioxidants for POPP. The objective of this work was to study the thermal decomposition and thermal oxidation of POPP by

* Paper presented at the Sino-Japanese Joint Symposium on Calorimetry and Thermal Analysis, Hangzhou, People's Republic of China, 5–7 November 1986.

0040-6031/88/$03.50

thermal analysis, IR spectrometry and ^{1}H-NMR spectrometry, and to choose appropriate antioxidants on the basis of the thermal analysis in order to improve the thermal endurance of the material.

EXPERIMENTAL

Poly(oxypropylene-ether) triols used in this study were supplied by the Liming Research Institute for Chemical Industry. They were colourless, transparent, viscous liquids having two different molecular weights, 3000 and 4800, and acid values of less than 0.1 mg KOH g^{-1}. Commercially available antioxidants were used without further purification. The nitrogen used was of high purity (greater than 99.99%).

Thermal analysis curves were recorded using a Rigaku Standard Micro TG–DTA thermal analyzer, using samples of about 2 mg and α-Al_2O_3 as the reference material. Experiments were carried out at a heating rate of 5 °C min^{-1}.

Residues of POPP were obtained by stopping the thermal decomposition reaction in the TG–DTA apparatus at the desired weight loss. Residues obtained in flowing nitrogen at 10 ml s^{-1} and in static air will be referred to as residue 1 and residue 2, respectively. All the samples containing antioxidant were prepared by thoroughly mixing the antioxidant concerned (0.5 wt.%) with freshly synthesized neat POPP.

The oxidation induction period was determined using a Perkin-Elmer DSC-2C instrument in flowing air (25 ml min^{-1}). The size of the samples was about 5 mg. The reference material was an empty pan.

Infrared spectra were recorded for liquid films using a Perkin-Elmer 580 B spectrometer. ^{1}H-NMR spectra of the polymers were obtained using a Varian FT-80 NMR spectrometer with a deuterated chloroform ($CDCl_3$) solvent containing tetramethylsilane (TMS) as the internal standard.

RESULTS AND DISCUSSION

Typical thermal analysis curves for POPP in flowing nitrogen and in air are shown in Figs. 1 and 2, respectively. The DTA curve in nitrogen has no apparent exothermic or endothermic peak. Above 325 °C it shifts gradually to the endothermic side. At the same time, the TG (or DTG) curve also shows an appreciable weight loss. The DTA curve in air is totally different from that in nitrogen: it has a strong exothermic peak at 193.5 °C. The corresponding TG or DTG curve exhibits a rapid weight loss.

IR and ^{1}H-NMR spectra of POPP and its decomposition residues are presented in Figs. 3 and 4, respectively. A comparison of the IR spectra for the original sample and residue 1 shows that two new peaks appear in the

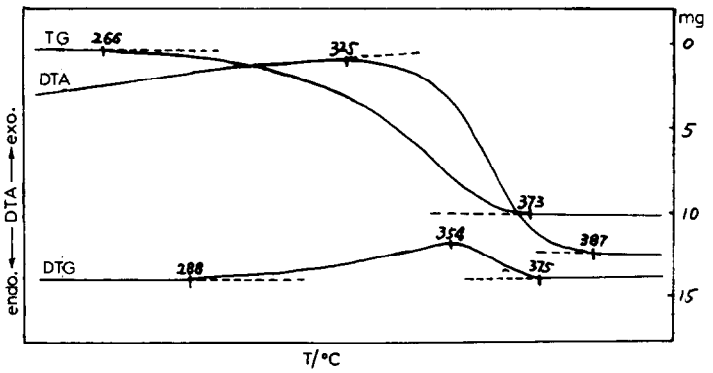

Fig. 1. Thermal analysis of POPP in flowing nitrogen: heating rate, 5 °C min^{-1}.

latter at 1720 cm^{-1} (C=O stretch) and 1670 cm^{-1} (C=C stretch). From the ^{1}H-NMR spectra of residue 1 it may be observed that new peaks appear at δ4.15 and δ2.16, and that there are some small changes at δ2.6 and δ1.85: these relate to the appearance of carbonyl groups. To sum up, it is thought that the thermal decomposition of POPP at higher temperature in flowing nitrogen mainly results in the cleavage of ether bonds to yield carbonyl groups of ketones and esters, accompanied by the cleavage of C–C bonds, dehydrogenation and dehydration which together lead to the formation of double bonds.

Figure 3 shows that the C=O stretch at 1720 cm^{-1} for residue 1 shifts to a higher region (1728 cm^{-1}) for residue 2. The new peak at 1728 cm^{-1} is characteristic of an aldehyde carbonyl group. The higher the heating temperature, the greater the intensity of this peak. One can also see that the intensity of the hydroxyl absorption peak at 3440 cm^{-1} increases with an

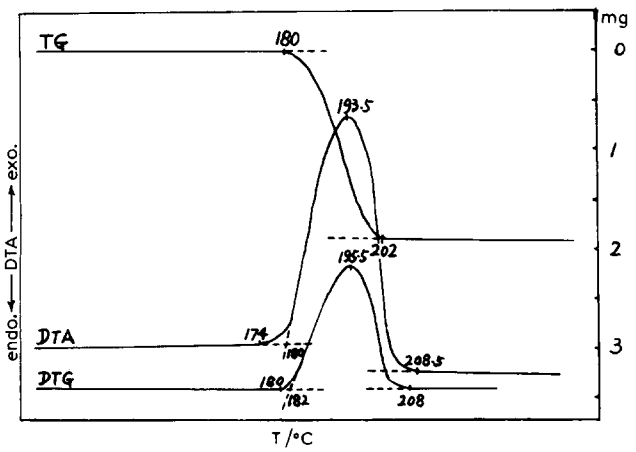

Fig. 2. Thermal analysis of POPP in air: heating rate, 5 °C min^{-1}.

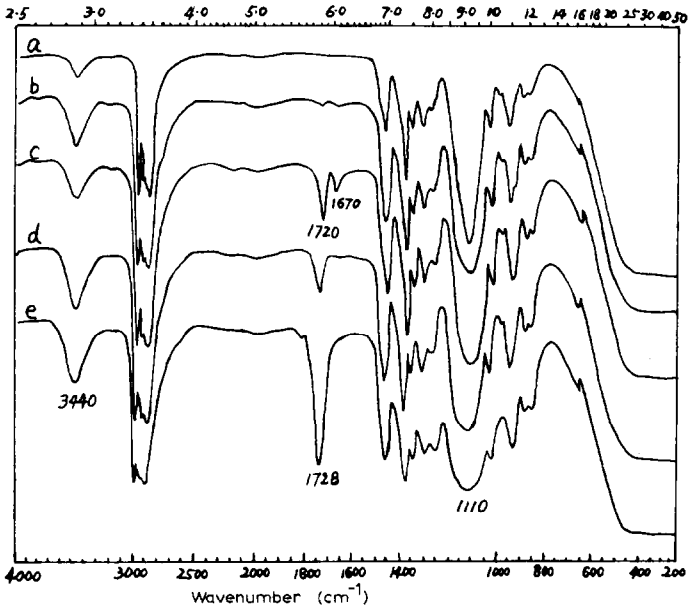

Fig. 3. IR spectra of POPP and of residues obtained in flowing nitrogen or in air for various weight losses: (a) POPP; (b) 10%, in nitrogen; (c) 50%, in nitrogen, (d) 10%, in air; (e) 50%, in air.

increase in heating temperature, while the intensity of the peak characteristic of the ether bond at 1110 cm^{-1} apparently decreases. The absorption peak of the double bond at 1670 cm^{-1} is absent in the spectrum of residue 2. ^{1}H-NMR spectra of residue 2 show that new peaks appear at δ4.15, δ2.16, δ2.07 and δ8.0; the last two of these chemical shifts do not occur in the case of residue 1. This is due to the fact that POPP can readily be attacked by the oxygen in air to form unstable hydroperoxides, which rapidly decompose when heated forming free radicals and initiating chain decomposition reactions. A great many ether and C–C bonds are cleaved by oxidation. In consequence, aldehyde, ketone and ester carbonyl groups result, which can also be oxidized further into acid carbonyl groups. The thermal oxidation is an autocatalytic process. The reaction starts at a lower temperature and proceeds intensely, evolving a large amount of heat. The mechanisms of thermal decomposition in air differ totally from that in nitrogen.

From the above discussion, it can be seen that the thermal stability of POPP is lower because it decomposes more easily by thermal oxidation in air. In order to improve the thermal stability of POPP, various antioxidants are generally added to it. The main function of the antioxidant is to prevent radical formation in the course of thermal oxidation of the polymer. This special ability of the antioxidant is ascribed to its particular structure, which generally gives rise to more steric hindrance and greater electron withdrawal

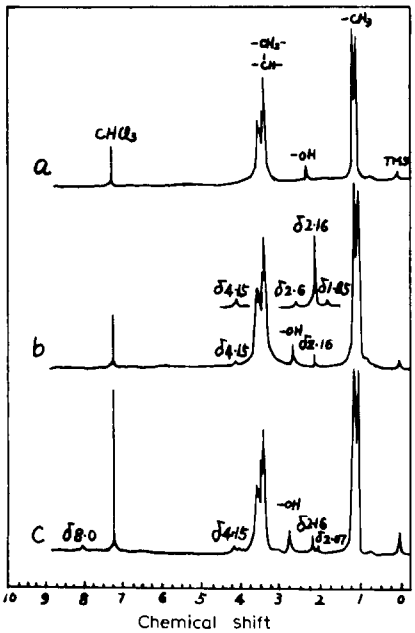

Fig. 4. ^{1}H-NMR spectra of POPP and of residues obtained in flowing nitrogen or in air at 50% weight loss: (a) POPP; (b) in nitrogen; (c) in air.

[4]. The precise thermal oxidation mechanisms of polymers change with the structures themselves. Only if an antioxidant is adapted to the structured characteristics of the polymer concerned will it be efficient.

One of the more recent methods for selecting antioxidants is thermal analysis. As has been mentioned before, the DTA curve of POPP in air exhibits a regular exothermic peak due to thermal oxidation. This exotherm shifts to higher temperatures in the presence of antioxidant, and this shift can be regarded as a measure of the inhibiting ability of the antioxidant. Therefore, the inhibiting abilities of antioxidants with various structures on the thermal oxidation of POPP can be evaluated on the basis of the initial temperature of the oxidative exothermic peak.

TG–DTA results for POPP samples containing various antioxidants are summarized in Table 1. It can clearly be seen that the sixteen antioxidants investigated can roughly be divided into three groups. The first group contains the most effective antioxidants, with inhibiting abilities in the following descending order: phenothiazine > 2246 > propyl gallate > pyrogallol. The second group includes M-4426-S, 1010, MB, DOD, bisphenol A, 264, DMP-30; these substances are reasonably effective. The third group is poor, and includes 8-hydroxy quinoline, triphenyl phosphite, DDS, TCP and dimethylbenzylamine.

As regards structural features, 2246 and DOD are bisphenolic antioxidants, but 2246 is sterically hindered, has more branched chains in the

TABLE 1

Comparison of the inhibiting ability of various antioxidants on thermal oxidation of POPP

No.	POPP + antioxidant	Colour of sample	Oxidation temperature (°C)	
			DTA	TG
1	Phenothiazine	red–brown	224	223.5
			221	219.5
			228	227.5
2	2,2′-Methylene bis(4-methyl -6-*tert*-butyl phenol) (2246)	light yellow	204.5	208
			201.5	203.5
			199.5	205
3	Propyl gallate	yellow	200	207
			200	207.5
4	Pyrogallol	yellow	198	203.5
			195	205
5	Bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) sulphide (M-4426-S)	yellow	178	185.5
			175	185.5
6	Tetra(β-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-pentaerythritol propionate (1010)	colourless	175.5	191.5
			182	192
7	2-Mercaptobenzimidazole (MB)	light yellow	179	185
			170.5	179
8	4,4′-Dihydroxydiphenyl (DOD)	colourless	171	191.5
			173	192.5
9	2,2′-Di-p-hydroxyphenylpropane (bis-phenol A)	colourless	153	179
			153	178
10	2,6-Di-*tert*-butyl-4-methyl phenol (264)	colourless	145	157.5
			149	154
11	2,4,6-Tri(dimethylamino)phenol (DMP-30)	light yellow	135	170
			153	169
12	8-Hydroxyquinoline	yellow	134	151
			130	152.5
13	Triphenyl phosphite	colourless	132	152.5
			109	149
14	4,4′-Diaminodiphenyl sulfone (DDS)	colourless	127	155.5
			133	157
15	Trimethylphenyl phosphate (TCP)	colourless	126	156
			125	149
16	Dimethylbenzylamine	colourless	122	141
			112	143.5

ortho-substituting group, and has the electron-donating methyl group para to the phenolic group. Consequently, the antioxidation ability of 2246 is considerably greater than that of DOD. The structure of propyl gallate is analogous to that of pyrogallol, but the former has an ester group in the para position so that the steric hindrance is greater. The stability of the phenoxy radical increases and the chance of reaction due to oxygen attack

TABLE 2

Synergistic effect of primary and subsidiary antioxidants

No.	Antioxidant (%)		Colour of sample	Oxidation temperature (°C)	
	Primary	Subsidiary		DTA	TG
1	264 (0.3)	Triphenyl phosphite (0.3)	colourless	147.5	159
2	2246 (0.3)	Triphenyl phosphite (0.3)	light yellow	204	206.5
3	DOD (0.3)	Triphenyl phosphite (0.3)	colourless	178	190
4	264 (0.3)	Phenothiazine (0.05)	yellow	205	204
5	2246 (0.3)	Phenothiazine (0.05)	violet	204	204

decreases; therefore, the antioxidation ability of propyl gallate is higher than that of pyrogallol. In general, according to their mechanisms of operation, antioxidants may be divided into primary antioxidants (chain stoppers) and subsidiary antioxidants (agents that decompose hydroperoxide). Subsidiary and primary antioxidants often have a synergistic effect; when both are used in combination, the overall antioxidation ability can be considerably strengthened. Using 264, 2246 or DOD as primary antioxidant, and phenothiazine or triphenyl phosphite as subsidiary antioxidant, respectively, it may be observed from Table 2 that systems consisting of 2246 + triphenyl phosphite, or 264 + phenothiazine, or 2246 + phenothiazine have improved synergistic effects. When the 264 + phenothiazine system is used, the colour of the solution formed is yellow.

The activation energies for the oxidation reaction have been computed by the Ozawa method [5] for POPP and for POPP + phenothiazine and POPP + 2246, according to the temperature at which an equal weight loss occurs under various heating rates. The results are presented in Table 3. The data

TABLE 3

Activation energy of oxidation reaction

No.	Weight loss (%)	Activation energy (kJ/mol)		
		Neat POPP	POPP + phenothiazine	POPP + 2246
1	10	93.19	116.50	145.04
2	20	95.54	114.77	139.83
3	30	97.40	113.30	137.29
4	40	98.67	112.46	135.22
5	50	100.11	111.76	133.08
6	60	100.95	111.29	130.93
7	70	101.34	112.46	129.11
8	80	101.72	112.75	128.67
9	90	101.22	112.04	128.18

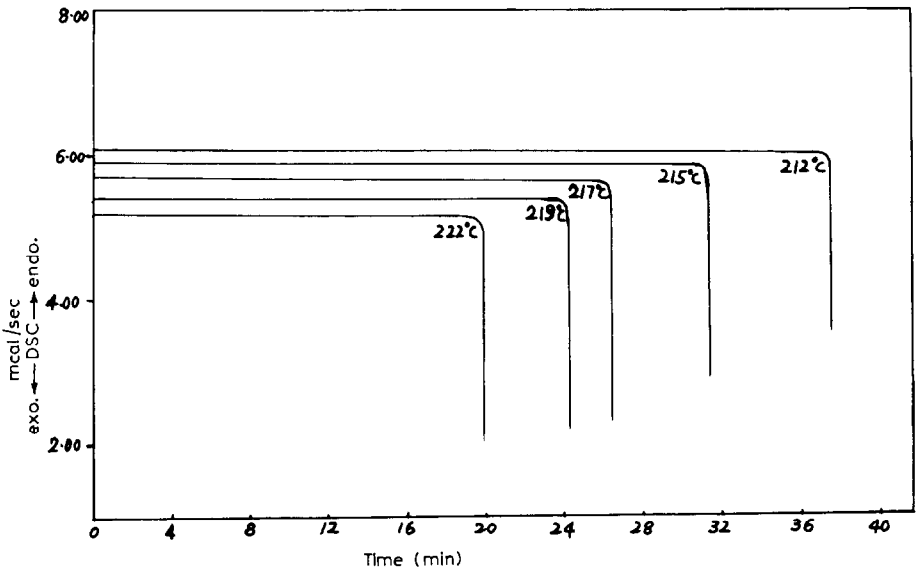

Fig. 5. Oxidation induction period for POPP in the presence of phenothiazine.

indicate that, in the presence of antioxidant, the initial temperature of oxidative decomposition is "postponed" to a higher one and that the activation energy becomes greater.

In order to make a further appraisal of antioxidation ability for the compounds studied, the oxidation induction period for the three above samples were determined by isothermal DSC. The oxidation induction period is an indicator of the inhibiting ability of the antioxidant: it is frequently used to judge the thermal oxidation stability of polymers [6]. The results shown in Fig. 5 demonstrate that an increase in temperature leads to a shortening of the induction period. The Arrhenius plot of induction time vs. temperature can be used to calculate oxidation induction period at any temperature (Fig. 6). As the mechanisms of thermal decomposition is more complex, and at higher temperature it may actually be different from that observed at room temperature, it is inappropriate to extrapolate results obtained at higher temperatures to room temperature. The measured results also confirm that phenothiazine and 2246 are better antioxidants for POPP. This coincides with results obtained by non-isothermal DTA.

Antioxidants are also easily oxidized by oxygen to form active radicals; if an excess is added they cease to act as antioxidants and actually accelerate the chain decomposition reaction. This phenomenon is called the "oxidation intensifying effect" [4]. In order to select an appropriate quantity of antioxidant, the effects on the oxidation temperature of POPP have been investigated for various quantities of the three antioxidants concerned. Figure 7 shows the quantity of antioxidant required in order to achieve a given level

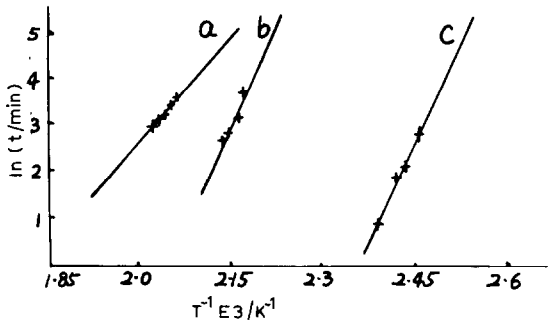

Fig. 6. Arrhenius plot of induction time vs. temperature: (a) phenothiazine; (b) 2246; (c) POPP.

of thermal oxidation property in POPP. For example, if it is desirable that the oxidation temperature is 170 °C, then either 200 ppm phenothiazine or 2000 ppm 2246 antioxidant should be added. For 264, even if a greater amount is added, the thermal endurance of POPP shows no significant improvement.

In practical applications, the kind and quantity of antioxidant in POPP depend upon the final uses to which the products will be put. In general, it is necessary to take into account toxicity, volatility, colour, extractability, physical form, smell, compatibility, price, and so on. For example, the inhibiting ability of phenothiazine on the thermal oxidation of POPP is very strong; however, when phenothiazine is added to POPP, the mixture is at

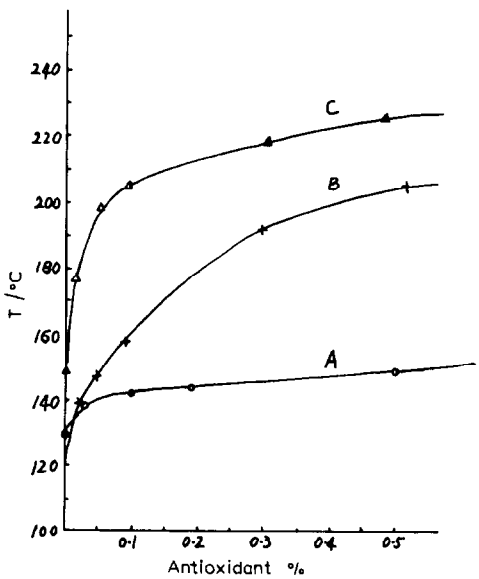

Fig. 7. Effect of quantity of antioxidants on oxidation temperature for POPP: A, 264; B, 2246; C, phenothiazine.

TABLE 4

Effect of potassium ion content on thermal oxidation for POPP

No.	Potassium ion content (ppm)	Phenothiazine content (%)	Oxidation temperature (°C)	
			DTA	TG
1	0	0	139	163.5
			137	158
2	115.7	0	105.5	143
			105	144.5
3	0	0.5	223	223
			220.5	221
4	115.7	0.5	218	219
			222	220.5
			223	224

first light green in colour, turning to red–brown after several days in air. Thus, products using phenothiazine as antioxidant may have a darker colour and the method described above is clearly unsuitable for use in the formulation of light-coloured products. The inhibiting ability of 264 alone on thermal oxidation is not very strong, but then the synergism of 264 with phenothiazine is more effective, the colour of stabilized POPP containing them is lighter, so that the method can be used in the formulation of lighter-coloured products.

In the course of synthesizing POPP, potassium hydroxide is usually used as a catalyst; consequently, potassium ions may be present in the product resins. The data in Table 4 illustrate that, if the content of potassium ions is too great, the thermal stability of POPP falls; thus, the addition of sufficient antioxidant to POPP containing potassium ions is helpful in eliminating such unwanted effects. The difference in initial temperatures of oxidation arising from different contents of potassium ions disappears after such treatment. This suggests that potassium ions play some catalytic role in the decomposition of hydroperoxides. In the presence of antioxidant, free-radical formation during decomposition is quickly stopped, so that it cannot initiate any further chain decomposition reaction.

The antioxidation process is closely related to the thermal properties of the antioxidant concerned. It may be seen from the thermal analysis curves of phenothiazine, 2246 and 264 that the endotherms at 183, 129, and 71.5 °C are the melting peaks of the three compounds, respectively. After melting, weight losses gradually occur as part of the sample evaporates. The endotherms at 261 and 170 °C are due to the boiling of phenothiazine and 264, respectively, while the exotherm at 279 °C is the decomposition peak of 2246. This shows that the thermal stability of 2246 is less than that of phenothiazine, while the melting point and boiling point of 264 are both

lower; bearing in mind its greater volatility, the amount of 264 used as antioxidant should be suitably increased.

ACKNOWLEDGMENTS

We thank Hu Zhong Wei and Yang Qing for helpful discussions and for supplying the samples, Guo Li Hua for the measurements of IR spectra and Cheng An Tai for NMR analysis; all of them are from the Liming Research Institute for Chemical Industry; we also thank Yu Shou Zhi and Zhu Yan of the Henan Chemical Research Institute for determining the oxidation induction period.

REFERENCES

1 S.L. Madorsky and S. Straus; J. Polym. Sci., 36 (1959) 183.
2 Kim Vo Van, S.L. Malhotra and L.P. Blanchard, J. Macromol. Sci. Chem., 8(5) (1974) 843.
3 Kim Vo Van, S.L. Malhotra and L.P. Blanchard, J. Appl. Polym. Sci., 18(9) (1974) 2671.
4 Hu Xingjun; Ageing Application, 4 (1980) 15.
5 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
6 D.I. Marshall, E.J. George and J.M. Turnipseed, Polym. Eng. Sci., 13(6) (1973) 415.