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ANTIOXIDANT ACTIVITY OF 6PPD DERIVATIVES IN POLYISOPRENE MATRIX STUDIED BY NON-ISOTHERMAL DSC MEASUREMENTS

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The antioxidant activity of selected *N,N′*-substituted *p*-phenylenediamines derived from 6PPD in polyisoprene matrix has been studied by differential scanning calorimetry (DSC) under non-isothermal conditions. The kinetic parameters describing temperature dependence of induction period have been obtained. Protection factors and antioxidant effectiveness have been calculated to characterize the stabilizing effect of the antioxidants under study. Using both criteria, the highest antioxidant activity has been observed in the case of Dusantox L, which is a mixture of 6PPD and its *p*-kumyl derivative. Its high antioxidant efficiency can be explained by the synergistic effect of 6PPD and its *p*-kumyl derivative. The lowest antioxidant efficiency of *o*-kumylderivative of 6PPD is probably caused by the sterical effect of the bulky kumyl group.

Keywords: *antioxidants, DSC, induction periods, N,N'-substituted p-phenylenediamines, oxidation, 6PPD*

Introduction

Oxidation belongs to the main reasons of deterioration of rubber products properties. This process involves a radical chain reaction initiated by heat, light or metal ions and most antioxidants act either by preventing the formation of the initiating radicals or by breaking primary chain reactions [1]. Aromatic secondary amines, particularly *N*-phenyl-*N*'-alkyl-*p*-phenylenediamines (PPD) represent the most important group of antidegradants used in rubber industry [2, 3]. Although other classes of antioxidants are well-known, the PPDs are by far the most effective and commonly used antioxidant and antiozonant agents.

The oxidation of rubber is an exothermic process and, consequently, thermoanalytical methods are widely employed for its study. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were used to study the oxidation of ethylene/propylene rubber stabilized with several antioxidants belonging to PPDs where the onset temperature of the oxidation peak was considered as a measure of the antioxidant activity [4, 5]. Synergistic effects of antioxidants in natural rubber, including PPDs were studied recently by isothermal DSC [6]. In our previous paper [7] the antioxidant activities of six PPDs in the thermal oxidation of polyisoprene rubber matrix have been studied by DSC under non-isothermal conditions.

The efficiency of PPDs is a function of molecular structure where it depends not only on the alkyl substituent attached to nitrogen atom [8] but also on the substituent on the phenyl ring of PPD [9]. A favourable influence of the substitution in the *p*-position of PPD has been reported [10]. The substitution in *p*-position of phenyl ring was applied also in the preparation of the stabilizers mixture based on *N*-phenyl-*N*'-dimethyl-butyl-*p*-phenylenediamine (6PPD) [11]. In this study, the antioxidant activities of four antioxidants belonging to *N*,*N*'-substituted *p*-phenylenediamines in the oxidation of polyisoprene rubber (PIR) are investigated. The antioxidant activity of 6PPD, which is a commercial antioxidant widely used in the rubber industry, is taken as a standard. Two of the samples, *o*-kumyl derivative of 6PPD and *p*-kumyl derivative of 6PPD are examples of new structures, which are going to be tested. These compounds are derived from 6PPD. The last one, i.e. Dusantox L, is a mixture of 6PPD and its *p*-kumyl derivative in the mass ratio 3:2, with the low content of *o*-kumyl derivative. The main characteristics of antioxidants under study are summarised in Table 1.

In our previous paper [12] a method for the evaluation of kinetic parameters of induction periods for nonisothermal processes is suggested. The method has been employed for the kinetic description of the lengths of induction periods of rubber compounds vulcanisation [13], oxidation of edible oils [14], oxidation of polyolefines [12], oxidation of pharma-

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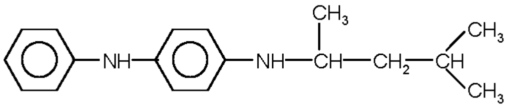
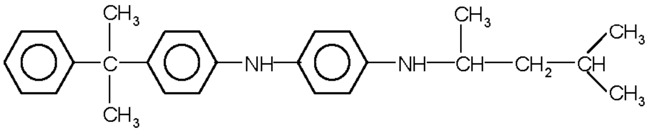
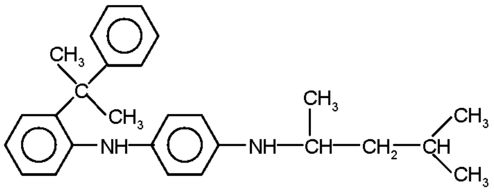
Table 1 Characteristics of the antioxidants under study

Antioxidant	Formula	Summary formula	Molar mass/ g mol^{-1}
6PPD		$C_{18}H_{24}N_2$	268.4
p-kumyl derivative of 6PPD		$C_{27}H_{34}N_2$	386.6
o-kumyl derivative of 6PPD		$C_{27}H_{34}N_2$	386.6
Dusantox L	6PPD 60% *p*-kumyl 6PPD 40%	–	306.0

ceuticals [15] and thermal oxidation of polyisoprene rubber in the presence of six PPDs [7] under non-isothermal conditions. Advantage of the method is that it provides kinetic parameters describing the length of induction period under any temperature regime. It has been verified that the induction periods determined by the method [12] are free of systematic errors and, in many cases, the calculated isothermal induction periods coincide with the measured isothermal values. At the end of induction period, antioxidants lose their protective effect and the material properties suddenly deteriorate. In this paper, the method is applied for the study of the four PPDs antioxidants in polyisoprene rubber matrix. The aim of the study is to explore the antioxidant activity and the dependence between the structure of the substituent in 6PPD molecule and the antioxidant effectiveness.

Experimental

Antioxidants

The commercial product 6PPD was purified by crystallization from toluene solution. Preparation of *o*-kumyl 6PPD is described in [16]; *p*-kumyl 6PPD was isolated from Dusantox L by column chromatography as described in [16].

Mixtures of PIR with the antioxidants

Synthetic polyisoprene was purchased from Aldrich. In the preparation of the samples, PIR and the appropriate amount of antioxidant were dissolved in toluene, poured on Petri dish and the solvent was evaporated in a vacuum oven at ambient temperature. Composition of the mixtures is given in Table 2.

Table 2 Values of the kinetic parameters *A* and *B* and their standard deviations

Antioxidant/phr	A/min	$B\cdot10^{-3}$/K
none	$(3.0\pm4.5)\cdot10^{-10}$	10.50±0.72
6PPD/0.1	$(0.7\pm1.3)\cdot10^{-12}$	12.26±0.97
6PPD/0.2	$(0.5\pm1.1)\cdot10^{-12}$	12.62±0.81
p-kumyl 6PPD/0.1	$(2.0\pm1.4)\cdot10^{-12}$	13.89±0.73
p-kumyl 6PPD/0.2	$(2.0\pm2.0)\cdot10^{-12}$	14.10±1.10
o-kumyl 6PPD/0.1	$(2.0\pm1.3)\cdot10^{-13}$	14.70±0.69
o-kumyl 6PPD/0.2	$(6.0\pm5.0)\cdot10^{-14}$	15.60±0.90
Dusantox L/0.1	$(4.0\pm1.9)\cdot10^{-14}$	15.80±0.52
Dusantox L/0.2	$(4.0\pm4.7)\cdot10^{-14}$	16.0±1.30

Differential scanning calorimetry

The calorimeter Perkin Elmer DSC-7 was employed to study the thermooxidative stability of the samples. The temperature scale was calibrated using In, Sn and Zn, the enthalpy calibration has been carried out to the heat of fusion of In. The samples of 2–4 mg were placed in crimped standard aluminium pans, where the lid of each pan was perforated by ten pinholes. Heating rates were 1, 3, 5, 7, 10 and 15 K min^{-1}. The purge gas forming the reaction atmosphere was oxygen. The starting temperature of oxidation was determined as the onset temperature of the oxidation peak.

Results and discussion

Treatment of experimental data

Dependence of the induction period on temperature can be expressed by an Arrhenius-like relationship [12, 17]:

$$t_{\mathrm{i}} = A\exp\left(\frac{B}{T}\right) \tag{1}$$

where A and B are constants and T is the absolute temperature. In the case of linear increase of temperature, the parameters A and B in Eq. (1) can be obtained from Eq. (2):

$$\beta = \int_{0}^{T_{\mathrm{i}}} \frac{\mathrm{d}T}{A\exp\left(\frac{B}{T}\right)} \tag{2}$$

From the non-isothermal measurements, the kinetic parameters A and B in Eq. (2) have been obtained by minimizing the sum of squares between experimental and theoretical values of heating rates by the simplex method [18]. The integration indicated in Eq. (2) was carried out by the Simpson method. The values of A and B for all samples are listed in Table 2. The agreement between the calculated and experimental values of the onset oxidation temperatures for individual heating rates is demonstrated in Figs 1 and 2.

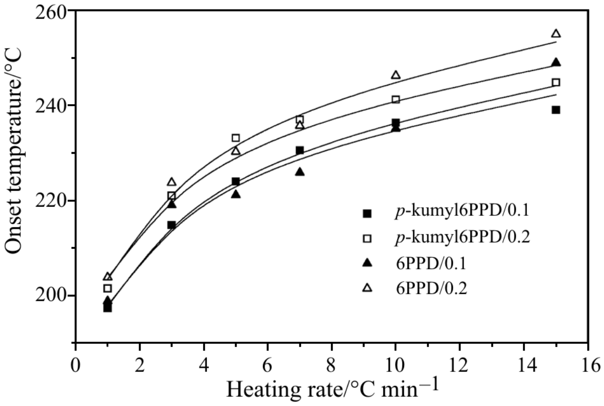


Fig. 1 Experimental and fitted dependences of the oxidation onset temperatures on the heating rates for PIR stabilized with 6PPD and its p-kumyl derivative

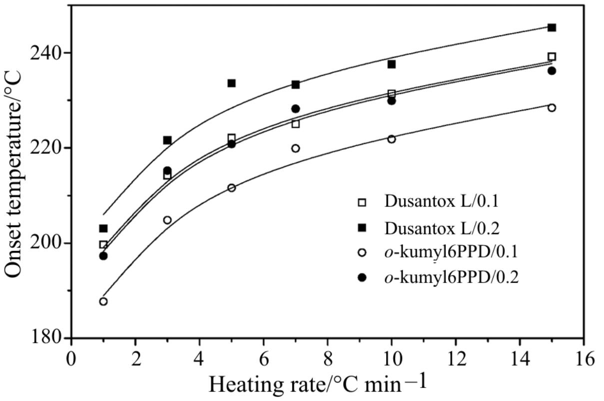


Fig. 2 Experimental and fitted dependences of the oxidation onset temperatures on the heating rates for PIR stabilized with o-kumyl derivative of 6PPD and Dusantox L

Protection factors

The temperature range of accelerated DSC stability tests differs significantly from the temperature range where the stability of the polymer materials should be predicted. The temperature change can lead to the change of the reaction mechanism, i.e. to the change of the kinetic parameters A and B. Thus, extrapolation of absolute values of the lengths of induction periods can lead to non-realistic estimations. A better estimation of the stabilizing effect can be obtained using the ratio of the lengths of the induction periods of stabilized and unstabilized polymer since the stability or non-stability of the polymer is brought about the same structural units both in stabilized and unstabilized polymer. This ratio is called the protection factor (PF):

$$PF = \frac{t_{\mathrm{i}}\,(\mathrm{PIR} + \mathrm{AOx})}{t_{\mathrm{i}}\,(\mathrm{PIR})} \tag{3}$$

Another advantage of using the protection factor for the evaluation of the stabilizing effect of antioxidants is that objectionable effects of the sample preparation are eliminated. For example, supposable effects of toluene residues on PIR stability are cancelled since the protection factor is a ratio of the induction periods and the samples are prepared in the same way.

If the value of PF is greater than one, the additive has stabilizing effect on polyisoprene. Otherwise, the additive exhibits destabilizing effect. The greater is the value of PF, the higher is the antioxidant effectiveness of the additive. It follows from Eq. (1) that the length of induction period depends on temperature; hence, the protection factor depends on temperature as well.

Temperature dependences of PFs for antioxidants under study were calculated from the data of Table 2 using Eqs (1) and (3) and are depicted in Figs 3 and 4. These dependences exhibit increasing tendency with decreasing temperature and with increasing the content of antioxidant. The horizontal line depicted in Figs 3 and 4 is called the protection line and its value is equal to one. Above this line the

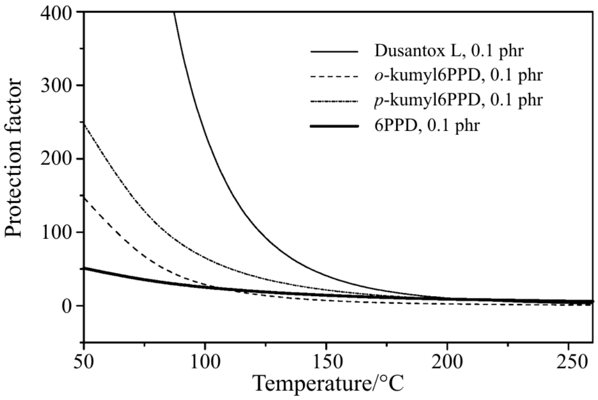


Fig. 3 Temperature dependences of the protection factors for 6PPD, *p*-kumyl derivative of 6PPD, *o*-kumyl derivative of 6PPD and Dusantox L in the relative mass ratio 0.1

antioxidant exhibits a stabilizing effect. It can be seen that the values of *PF*s are greater than one in the temperature range of PIR practical use. The highest values of *PF*s were obtained for the mixture of 6PPD and its *p*-kumylderivative (Dusantox L). The results also show that the new derivatives exhibit higher antioxidant activities than 6PPD at lower temperatures. With increasing temperature the values of the *PF*s of 6PPD decrease less rapidly and above approx. 200°C are greater than *PF*s of its derivatives.

Antioxidant effectiveness

In our previous paper [7] it was shown that the dependences of protection factors of PPDs on their relative mass ratios are almost linear. This fact enables to define a criterion characterizing the antioxidant effectiveness, *AEX*, as a slope of the dependence *PF=f*(*X*)

$$AEX = \frac{PF - 1}{X} \quad (4)$$

where *X* is expressed in phr. In a molar scale, the effectiveness *AEM* can be defined as follows:

$$AEM = \frac{PF - 1}{m} \quad (5)$$

where *m* is the concentration of antioxidant in polymer matrix expressed in mol kg^{-1}. Both criteria bring about a normalization of the protection factor so that the values of *PF* for various stabilizer content can be mutually compared. Similarly as *PF*, also both *AEX* and *AEM* depend on temperature. From Eqs (4) and (5) it is obvious that a relationship exists between *AEX* and *AEM*:

$$AEM = 10M \cdot AEX \quad (6)$$

where *M* is the molar mass of the antioxidant expressed in mol kg^{-1}.

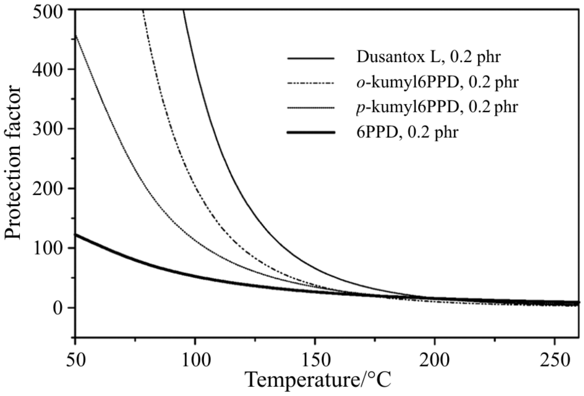


Fig. 4 Temperature dependences of the protection factors for 6PPD, *p*-kumyl derivative of 6PPD, *o*-kumyl derivative of 6PPD and Dusantox L in the relative mass ratio 0.2

Since *PF* depends on temperature, also both *AEX* and *AEM* are functions of temperature. The antioxidant effectiveness of individual stabilizers for the temperature 180°C are listed in Table 3. This temperature was chosen since it is a standard temperature for isothermal stability tests and it was used also by other authors [5]. *AEX* expresses the antioxidant effectiveness in units better understandable for practitioners whereas *AEM* gives a picture on the antioxidant effect per an antioxidant molecule. The order of antioxidant effectivenesses, using *AEX*, is Dusantox L>6PPD> *p*-kumyl derivative of 6PPD>*o*-kumyl derivative of 6PPD and using *AEM*, is Dusantox L>*p*-kumyl derivative of 6PPD>6PPD>*o*-kumyl derivative of 6PPD. The highest ranking of Dusantox L indicates that a synergism exists between 6PPD and its *p*-kumyl derivative. Although these secondary diamines include formally identical stabilizing group –NH– in their molecules, they differ in relative antioxidant efficiencies. The final integral effect becomes greater than the sum of individual antioxidant efficiencies.

Table 3 Antioxidants effectiveness for the temperature of 180°C

Stabilizer	*AEX*	*AEM*
6PPD	103	277
p-kumyl 6PPD	97	375
o-kumyl 6PPD	68	263
Dusantox L	129	395

Using *AEX*, the antioxidant efficiency of 6PPD is higher than that of its *p*-kumyl derivative. In the case of *AEM*, the inverse order of 6PPD and its *p*-kumyl derivative is caused by greater molar mass of the derivative. The lowest antioxidant effectiveness of *o*-kumyl 6PPD is probably caused by the sterical effect of bulky kumyl group.

Conclusions

The antioxidant effectiveness of *p*-phenylene diamines derived from 6PPD in polyisoprene rubber has been studied by non-isothermal DSC measurements. For the treatment of experimental data, our method for the description of the lengths of induction periods [8] was employed. DSC appeared powerful and fast technique for studying the oxidation of elastomers and to evaluate the efficiency of various antioxidants in retarding the thermooxidative degradation.

The values of protection factors increase with decreasing temperature and increasing concentration of the antioxidant. Two criteria characterizing the antioxidant effectiveness are employed. Using both criteria, the synergistic effect of 6PPD and its *p*-kumyl derivative in Dusantox L is indicated. The results obtained in this study show that the new secondary amines tested have a promising potential as antioxidant additives.

The thickness of the samples used in measurements is about 0.1 mm. So, the sample is very thin and the diffusion of oxygen plays no role in the determination of antioxidant effectiveness. The experimental results thus reflect pure effects of the structure and concentration of antioxidant on its effectiveness.

References

1 A. E. Somers, T. J. Bastow, M. I. Burgar, M. Forsyth and A. J. Hill, Polym. Degrad. Stab., 70 (2000) 31.
2 F. Cataldo, Eur. Polym. J., 38 (2002) 885.
3 F. Cataldo, Polym. Degrad. Stab., 72 (2001) 787.
4 M. M. Abdel-Aziz and A. A. Basfar, Nucl. Instr. Meth. Phys. Res. B, 185 (2001) 346.
5 M. M. Abdel-Aziz and A. A. Basfar, Polym.Testing, 19 (2000) 591.
6 D. F. Parra and J. do Rosario Matos, J. Therm. Anal. Cal., 67 (2002) 287.
7 Z. Cibulková, P. Šimon, P. Lehocký and J. Balko, Polym. Degrad. Stab., 87 (2005) 479.
8 G. Bertrand and J. Lebouc, Rev. Gen. Caout. Plast, 52 (1975) 919.
9 G. Bertrand and E. Leleu, Rubber World, 192 (1985) 32.
10 Th. Kempermann, Kautsch. Gummi Kunstsoffe Asbest, 15 (1962) 422.
11 Patent SK 279 532
12 P. Šimon and Ĺ. Kolman, J. Therm. Anal. Cal., 64 (2001) 813.
13 P. Šimon and A. Kučma, J. Therm. Anal. Cal., 56 (1999) 1107.
14 P. Šimon, Ĺ. Kolman, I. Niklová and Š. Schmidt, J. Amer. Oil Chem. Soc., 77 (2000) 639.
15 P. Šimon, M. Veverka and J. Okuliar, Int. J. Pharm., 270 (2004) 21.
16 I. Sigmundová, J. Uhlár and Š. Toma, Synth. Commun., 34 (2004) 3667.
17 P. Šimon, J. Therm. Anal. Cal., 76 (2004) 123.
18 J. A. Nelder and R. Mead, Computer J., 7 (1965) 308.