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DSC STUDY OF ANTIOXIDANT ACTIVITY OF SELECTED *p*-PHENYLENEDIAMINES IN STYRENE-BUTADIENE RUBBER

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The antioxidant activity of selected N,N‘-substituted *p*-phenylenediamines (PPDs) in styrene-butadiene rubber (SBR) has been studied by differential scanning calorimetry 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. It is shown that all antioxidants under study exhibit stabilizing effect on SBR. The obtained values were used to compare the stabilizing effect of the same antioxidants in polyisoprene (PI) rubber. The order of stability for SBR matrix samples differs from that for PI samples. It is shown that the stabilization effect of the antioxidant depends much on the polymer matrix.

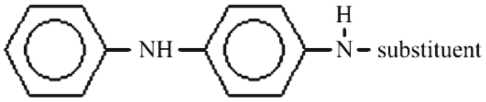
Keywords: *antioxidant effectiveness, antioxidants, DSC, induction periods, oxidation, protection factor, N,N'-substituted, p-phenylenediamines, styrenebutadiene rubber*

Introduction

Ageing of polymers is a serious problem leading to the deterioration of their physico-mechanical and chemical properties. The most common ageing causes are heat, oxygen, radiation and ozone. Elastomeric materials are especially sensitive to thermooxidative degradation. The thermal oxidation of elastomers is an autocatalytic radical chain reaction where the oxidation products are carboxylic acids, ketones, aldehydes, epoxides, etc. The rate of the oxidation can be reduced using antioxidants. Chain-breaking antioxidants, i.e., arylamines and hindered phenols, donate labile hydrogen to peroxy radicals to interrupt the propagation step [1].

The addition of antioxidants to elastomers can prolong their service life. However, the efficiency of the antioxidants depends on such factors as the type of elastomer and the type of ageing. The efficiencies of the antioxidants also greatly depend on their chemical structure. Aromatic secondary amines, particularly N,N'-substituted-*p*-phenylenediamines (PPD) represent the most important group of antidegradants used in rubber industry [2, 3] and are by far the most efficient and commonly used antioxidant and antiozonant agents.

Thermoanalytical methods are widely used to study the oxidation of polymer materials. 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 a measure of the antioxidant activity [4, 5]. Synergistic effects of antioxidants in natural rubber, including PPDs were studied by isothermal DSC [6]. A method for the evaluation of kinetic parameters of induction periods for nonisothermal processes has recent been suggested [7]. The method has been used for the kinetic description of the lengths of the oxidation induction periods for various polymer systems [8–10]. The antioxidant action of several PPDs in the thermal oxidation of polyisoprene rubber (PIR) matrix have previously been studied by DSC [11, 12]. The aim of this study was to investigate the stabilizing effect of seven compounds from the PPDs in thermooxidation of SBR and to compare the results with the results obtained for the same antioxidants in the PIR matrix. All these compounds are aryl-alkyl-*p*-phenylenediamines with various structures of the substituent:



Two of the samples, *o*-cumyl derivative of 6PPD and *p*-cumyl derivative of 6PPD are derived from 6PPD. The last one, i.e. Dusantox L, is a mixture of 6PPD and its *p*-cumyl derivative. The characteristics of antioxidants used for this work are summarized in Table 1.

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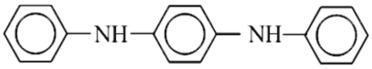
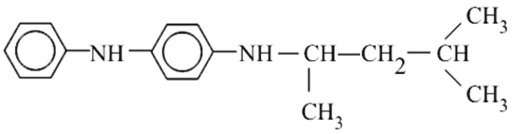
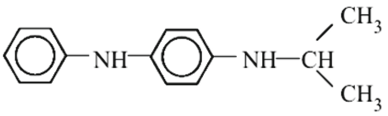
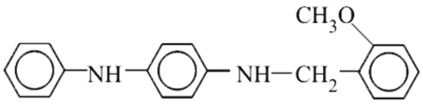
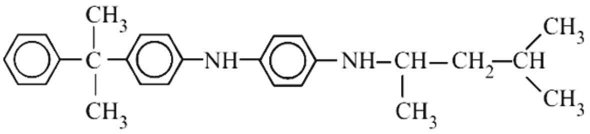
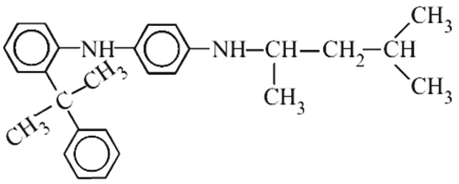
Table 1 Characteristics of antioxidants under study

Stabilizer	Structure	Summary formula	Molar mass/ g mol^{-1}
DPPD		$C_{18}H_{16}N_2$	260.3
6PPD		$C_{18}H_{24}N_2$	268.4
IPPD		$C_{15}H_{18}N_2$	226.3
MBPPD		$C_{20}H_{20}N_2O$	304.4
p-cumyl derivative of 6PPD		$C_{27}H_{34}N_2$	386.6
o-cumyl derivative of 6PPD		$C_{27}H_{34}N_2$	386.6
Dusantox L	6PPD 45%, *p*-cumyl6PPD 51%, *o*-cumyl6PPD 4%		319.5

Experimental

Antioxidants

DPPD was purchased from Aldrich and was used as received. The commercial products Dusantox IPPD and 6PPD were purified by crystallization from toluene solution. Preparation of *o*-cumyl6PPD has been previously described [13]; *p*-cumyl6PPD was isolated from Dusantox L. Preparation of MBPPD is described in [11].

Mixtures of PIR with the antioxidants

Synthetic latex was purchased from Synthos Kralupy. A solutiom of 5% casein in 0.5 N NaOH solution (15 mL) was added to 1000 mL of unstabilized latex (pH=6–7) and then the pH was adjusted to 10–11 by addition of 0.5 N NaOH solution. Subsequently, 10 mL of 10% potassium stearate and 150 mL of saturated aqueous NaCl solution was mixed with the latex. Antioxidant (stabilizer) dissolved in toluene (3 mL of toluene+antioxidant+15 mL of 10% potassium stearate) was added to the latex. The latex was added to a coagulation solution (375 mL 2% H_2SO_4+

350 mL saturated NaCl solution+2350 mL distilled water) under intense mixing. The rubber was washed three times in approx. 2.5 L of distilled water and dried at 50–60°C for 24 h. Finally, the rubber was converted to 5 mm sheet in a laboratory twin-roll. Since some of the antioxidants are not very soluble in SBR and some amount may remain in the coagulation solution, the real amount of stabilizer in the rubber was determined using HPLC. Composition of the mixtures is given in Table 2.

Differential scanning calorimetry

The calorimeter PerkinElmer 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 [7]:

$$t_\mathrm{i} = A\exp[B/T] \tag{1}$$

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):

$$\beta = \int_0^{T_\mathrm{i}} \frac{\mathrm{d}T}{A\exp[B/T]} \tag{2}$$

where β is the heating rate. 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 onset oxidation temperatures by the simplex method [14]. 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 1–3.

Table 2 Values of the kinetic parameters *A* and *B*

Antioxidant/X	A/min^{-1}	B/K
None	$2.2\cdot10^{-12}$	10030
DPPD/0.014	$5.0\cdot10^{-12}$	11550
Dusantox L/0.100	$2.2\cdot10^{-12}$	11980
IPPD/0.003	$4.0\cdot10^{-15}$	13650
MBPPD/0.147	$9.0\cdot10^{-13}$	12410
p-cumyl 6PPD/0.146	$5.6\cdot10^{-14}$	13490
o-cumyl 6PPD/0.140	$5.6\cdot10^{-16}$	14810
6PPD/0.022	$8.5\cdot10^{-14}$	12600
6PPD/0.055	$1.9\cdot10^{-15}$	14510
6PPD/0.064	$1.2\cdot10^{-13}$	13060
6PPD/0.232	$1.3\cdot10^{-12}$	12600

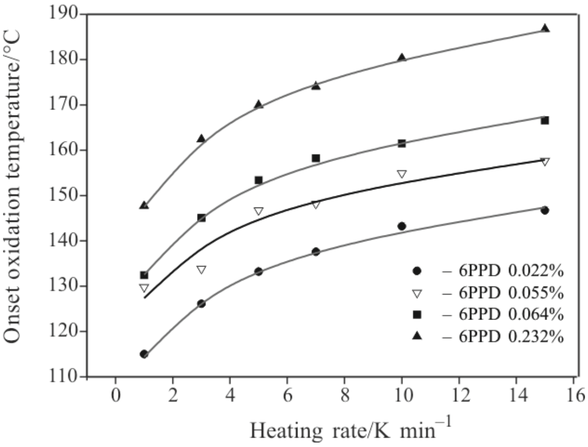


Fig. 1 Experimental and fitted dependences of the onset oxidation temperatures on the heating rates for SBR stabilized with 6PPD

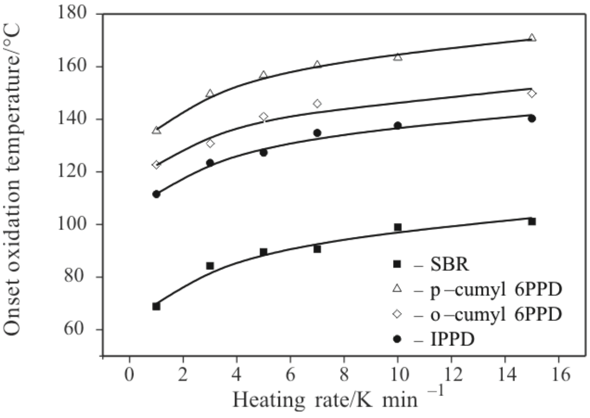


Fig. 2 Experimental and fitted dependences of the onset oxidation temperatures on the heating rates for pure SBR and SBR stabilized with IPPD, *p*-cumyl derivative of 6PPD and *o*-cumyl derivative of 6PPD

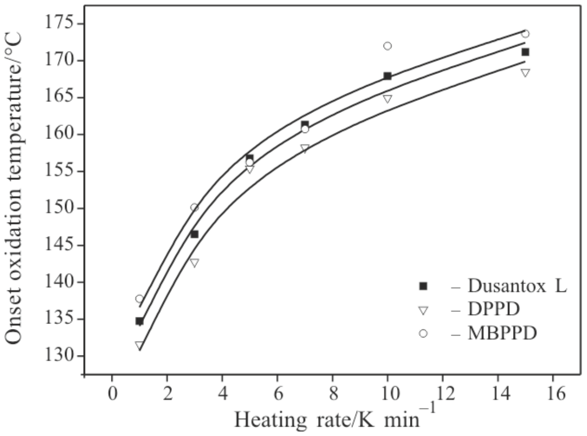


Fig. 3 Experimental and fitted dependences of the onset oxidation temperatures on the heating rates for SBR stabilized with DPPD, MBPPD and Dusantox L

Protection factor, antioxidant effectiveness

In order to evaluate the antioxidant effectiveness, the protection factor (PF) was calculated [11]:

$$PF=\frac{t_i\,(SBR+AOx)}{t_i\,(SBR)} \qquad (3)$$

where t_i(SBRstab) and t_i(SBR) are the induction periods of stabilized and non-stabilized SBR, respectively. If the value of PF is greater than one, the additive has a stabilizing effect on styrene-butadiene rubber. Otherwise, the additive exhibits a destabilizing effect. The greater 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 are depicted in Figs 4 and 5. These dependences exhibit increasing tendency with decreasing temperature and with increasing the content of antioxidant.

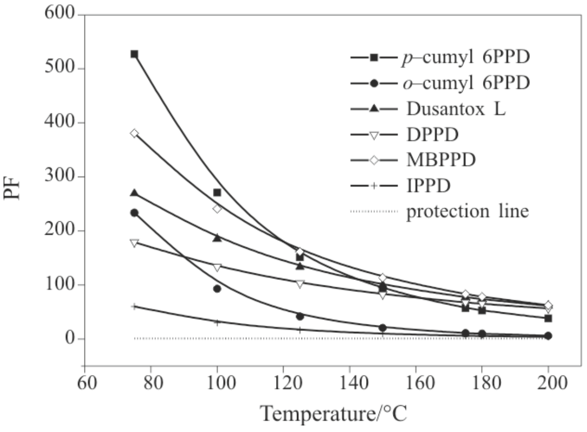


Fig. 4 Temperature dependences of the protection factors for DPPD, IPPD, Dusantox L, *p*-cumyl derivative of 6PPD, *o*-cumyl derivative of 6PPD and MBPPD

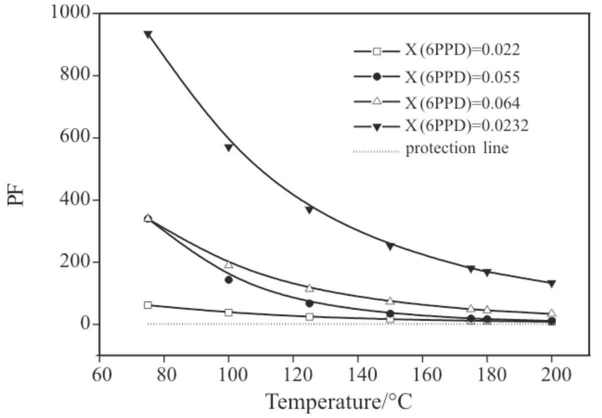


Fig. 5 Temperature dependences of the protection factors for 6PPD

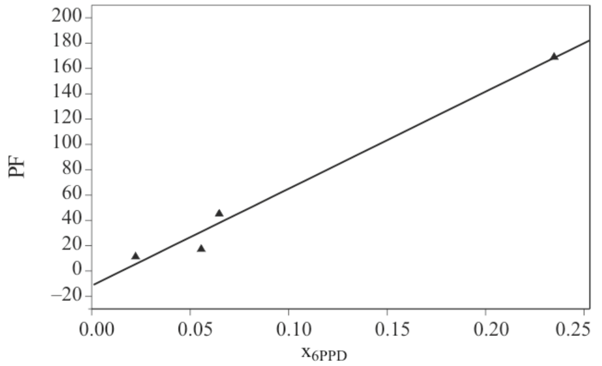


Fig. 6 Dependence of the PF on the mass fraction of 6PPD

Table 3 Antioxidants effectiveness at temperature 180°C

Stabilizer	AEX	
	SBR matrix	PI matrix
DPPD	4579	283
IPPD	1467	78
Dusantox L	726	129
6PPD	626	103
MBPPD	524	50
p-cumyl 6PPD	351	97
o-cumyl 6PPD	62	68

The horizontal line depicted in Figs 4 and 5 is called the protection line and its value is equal to one. Above this line the antioxidant exhibits a stabilizing effect. The values of protection factors were greater than 1 for all studied antioxidants. It means that all of the investigated compounds exhibit a stabilizing effect on SBR.

It may be seen from Fig. 6 that the dependence of protection factor on the relative mass fraction of antioxidant 6PPD is almost linear. This fact permits a calculation of antioxidant effectiveness, AEX as a slope of the dependence PF=*f*(*X*) [11]:

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

where X is concentration of antioxidant in mass%. The values of AEX may be used to compare the stabilization effect of the antioxidants under study. The physical meaning of AEX is that it expresses the additional stability brought about by a stabilizer, normalized per mass unit of the stabilizer.

Since PF depends on temperature, also AEX is a function of temperature. The antioxidant effectiveness of individual stabilizers at 180°C are listed in Table 3 together with values of AEX for PIR samples taken from previous reports [11, 12]. This temperature was chosen since it is a standard temperature for isothermal stability tests and it has also been used to characterize the stabilization effect of these compounds in PIR [11, 12].

The order of antioxidant effectiveness for SBR samples is DPPD>IPPD>Dusantox L>6PPD> MBPPD>*p*-cumyl derivative of 6PPD>*o*-cumyl derivative of 6PPD. For the PI samples the order of AEX was different: DPPD>6PPD>Dusantox L>*p*-cumyl derivative of 6PPD>IPPD>*o*-cumyl derivative of 6PPD> MBPPD. Similar values of AEX were obtained only for *o*-cumyl derivative of 6PPD for both PI and SBR matrices. The highest values of AEX for DPPD in both matrices are not surprising since its high antioxidant efficiency is well known. The high value for Dusantox L indicates that a synergism exists between 6PPD and its *p*-cumyl derivative. The integral AEX value of these stabilizers becomes greater than the sum of individual antioxidant efficiencies. Surprisingly, totally different values have been calculated for MBPPD and 6PPD. While MBPPD mixed with SBR exhibits good stabilizing effect, this not the for MBPPD on a PI matrix. In this case, MBPPD exhibited the lowest stabilizing effect.

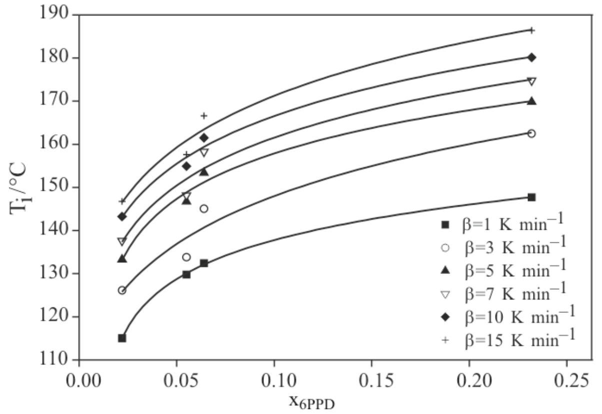


Fig. 7 Dependences of the onset oxidation temperatures on the mass ratio of 6PPD

Concentration dependences

In the case of 6PPD sample, the effect of the sample concentration has been investigated. Dependence of the onset oxidation temperatures on the mass ratio of antioxidant 6PPD is shown in Fig. 7. It can be seen that the values of onset oxidation temperatures exhibit a logarithmic tendency. Similar dependences have been observed in the case of the PIR matrix [11].

Conclusions

In this study, the antioxidant effectiveness of seven *p*-phenylenediamines in styrene-butadiene rubber was studied by non-isothermal DSC measurements. For the treatment of experimental results, a previously developed method for the description of the lengths of induction periods [7] was employed. Two criteria characterizing the stabilization effect of the studied compounds were used: protection factor (PF) and antioxidant effectiveness (AEX). The values of protection factors were greater than 1 for all antioxidants under study, what means that they exhibit stabilizing effect on SBR. The values of AEX permitted an establishment of the order of stabilization on SBR and comparison with the stabilization effect on PI. From the obtained values it can be seen that the highest stabilization effect on SBR is shown by DPPD and the lowest stability was observed in the case of SBR mixed with *o*-cumyl derivative of 6PPD. In the case of PI rubber the order was different: the highest values of AEX were obtained for DPPD and the lowest for MBPPD. As the data in Table 3 show, the antioxidant effectiveness depends substantially on the polymer matrix.

DSC appears to be a powerful and a fast technique for studying the oxidation of elastomers and to evaluate the efficiency of various antioxidants in retarding thermooxidative degradation.

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