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DSC study of stabilizing effect of antioxidant mixtures in styrene-butadiene rubber

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Abstract The type of cooperation between antioxidants in the binary mixtures of four substituted diphenylamines and phenotiazine in the stabilization of styrene-butadiene rubber has been tested. Thermooxidation of the samples has been studied by differential scanning calorimetry under non-isothermal conditions. The protection factors of the individual stabilizers and their mixtures were determined. The synergy factors were applied to asses the type of cooperation of antioxidants in the mixtures. From their values it can be concluded that the type of cooperation depends on temperature. The highest synergistic effect has been observed for the mixture of phenotiazine and [4-(1-methyl-1-phenyl-ethyl)-phenyl]-phenylamine.

Keywords Styrene-butadiene rubber · Antioxidants · DSC · Synergism

Introduction

Thermooxidative ageing of rubber products is one of the most serious problems in rubber industry, because it leads to considerable changes in their chemical structure and to the loss of their physico-mechanical properties. The ageing can be retarded by the addition of antioxidants. The most common ones used in rubber industry are derivatives of aromatic amines and phenols [1].

Combinations of antioxidants are frequently used in rubber products. The main reason for this is that a combination of antioxidants often exhibits a stronger stabilizing effect than either antioxidant used alone, the phenomenon known as the synergism. The synergism appears to arise either from an antioxidant effectively regenerating another one so that the latter does not become consumed or by the two antioxidants functioning by different mechanisms [2]. Sometimes the motivation to find a suitable combination of antioxidants with synergistic effects is the attempt to extend the sale of already produced commercial antioxidant.

Thermoanalytical methods are widely used to study the oxidation of elastomers. Synergistic effects of diaminic and monoaminic antioxidants in natural rubber were studied by isothermal DSC measurements [3]. The protection efficiency of antioxidant couples consisting of a classical compound (disubstituted *p*-phenylendiamines and dihydroquinoline derivatives) and compounds with a disulphide bridge resulting from diamine and phenolic structures has been tested in diene elastomers [4]. In our previous papers, the effect of *p*-phenylenediamines in preventing thermo-oxidative degradation of polyisoprene rubber [5, 6] has been investigated by non-isothermal DSC measurements. DSC measurements were also successfully employed to study the antioxidant action of several *p*-phenylenediamines, *p*-substituted diphenyl amines, heterocyclic compounds, trisubstituted amines and triazine derivatives in styrene-butadiene rubber (SBR) [7, 8].

In the rubber stabilization, combinations solely between aminic antidegradants are known, for example between derivatives of *p*-phenylenediamine and substituted diphenylamines [9]. The aim of this study is to evaluate the stabilizing effect of antioxidant binary mixtures of several

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disubstituted *p*-phenylenediamines and phenothiazine using non-isothermal DSC measurements.

Materials and methods

Preparation of the samples

The stabilizers were mixed with styrene-butadiene rubber in the Brabender-type chamber (65 cm^3, 50 rpm) at 60 °C for 5 min. The overall content of stabilizers in each sample was 0.5 parts per hundred parts of rubber (phr). Structures of the antioxidants tested and composition of the samples are given in Table 1.

Nonisothermal DSC measurements

Thermooxidation measurements were performed using Perkin Elmer DSC-7 instrument with the Pyris software. Temperature calibration of the calorimeter was carried out to the melting points of In, Sn and Pb; the enthalpy calibration to the enthalpy of In fusion. Samples of 2–4 mg were heated in the standard crimped aluminium pans where oxygen with the flow rate of 50 mL/min was used as a purge gas. In order to facilitate the contact of oxygen with the sample, the lid of each pan was perforated by seven pinholes. Heating rates of 1, 3, 5, 7, 10 and 15 K min^{-1} were used.

Results and discussion

Treatment of experimental data

Figure 1 shows examples of the DSC curves for the oxidation of the sample 2. The starting temperature of the oxidation was determined as the onset temperature of the oxidation peak. The values of onset oxidation temperatures (T_i) are summarized in Table 2.

In our previous papers, a method for the evaluation of the lengths of oxidation induction periods using non-Arrhenian temperature function has been described [10]. At the end of induction period, also a sudden change in material characteristics mostly takes place so that the length of induction period is often considered a relative measure of material stability. It has been shown that the dependence of the induction period on the temperature can be expressed as follows [10]:

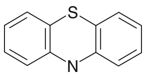
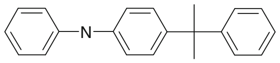
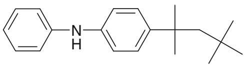
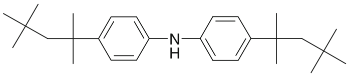
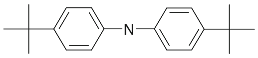
$$t_i = A\exp(-DT) \tag{1}$$

where A and D are kinetic parameters and T is the absolute temperature. In the case of DSC measurements with constant heating rate, β, the parameters A and D can be obtained from Eq. 2 [10]:

$$T_i = \frac{1}{D}\ln(AD\beta + 1) \tag{2}$$

The values of the kinetic parameters A and D have been obtained from dependences T_i versus β by the non-linear

Table 1 Characteristics of the antioxidants and their mixtures

Sample	Antioxidant				Ratio in mixtures w/w
	Code	Name	Structure	M/ g mol^{-1}	
1	–	–	–	–	–
2	A_1	Phenothiazine		199.28	–
3	A_2	[4-(1-Methyl-1-phenyl-ethyl)-phenyl]-phenylamine		287.41	–
4	A_3	Phenyl-[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-amine		281.44	–
5	A_4	Bis-[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-amine		393.66	–
6	A_5	Bis-(4-*tert*-butyl-phenyl)-amine		281.44	–
7	$A_1 + A_2$	–	–	–	1:1
8	$A_3 + A_5$	–	–	–	1:1
9	$A_4 + A_5$	–	–	–	1:1
10	$A_1 + A_5$	–	–	–	1:1

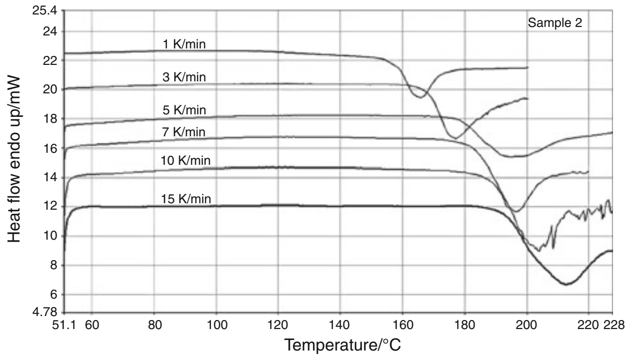


Fig. 1 DSC records of thermal oxidation of sample 2 obtained for different heating rates

least squares method using Eq. 2. Their values are summarized in Table 3. The coefficient of variability of the parameter A was about 150%, the one of the parameter D about 10%. The agreement between the calculated and experimental values of the onset oxidation temperatures for individual heating rates is demonstrated in Fig. 2 for the case of samples 1, 2, 3 and 7. For the rest of the samples, the agreement between the experimental and fitted values was also very good.

Protection factor

From the values of kinetic parameters A and D the lengths of the induction periods for temperatures 25 and 130 °C were evaluated using Eq. 1. The first chosen temperature represents a room temperature and the second one is the average temperature of rubber processing. To characterize the stabilizing effect of individual antioxidants and their mixtures, the protection factors, PFs, have been calculated. The protection factor was defined in our previous article as the ratio of the lengths of induction period of stabilized and unstabilized material [5]:

$$\mathrm{PF} = \frac{t_i(\mathrm{stab.})}{t_i(\mathrm{unstab.})} \tag{3}$$

Since the length of induction period depends on the temperature, the protection factor is temperature-dependent as well. Values of the protection factors for 25 and 130 °C are given in Table 3.

At 130 °C, among the individual antioxidants, phenothiazine (A_1) exhibits the highest protective effect, higher by an order of magnitude than derivatives of diphenylamine. There are only small differences in the protective effects of diphenylamine structures in A_2, A_3,

Table 2 Oxidation onset temperatures (in °C) as a function of the heating rate for individual samples

β/K min^{-1}	Sample no.									
	1	2	3	4	5	6	7	8	9	10
1	73.9	153.8	123.0	127.8	123.2	127.7	148.2	127.8	132.2	144.9
3	85.9	167.3	132.5	141.1	132.0	137.0	162.7	136.7	139.7	156.7
5	90.1	176.9	141.4	146.3	139.5	141.0	167.7	143.0	146.8	163.0
7	97.5	180.9	144.3	148.9	143.7	147.7	172.8	147.6	152.0	164.8
10	100.0	184.5	148.1	152.6	146.0	150.4	177.0	152.9	154.7	172.8
15	101.2	188.6	154.0	155.2	147.1	156.2	181.1	155.2	160.2	176.9

Labelling of the samples—see Table 1

Table 3 Kinetic parameters, lengths of the induction periods and protection factors for 25 and 130 °C

Sample	A/min	D/K^{-1}	$t_{\mathrm{i}(25\ °\mathrm{C})}$/year	$t_{\mathrm{i}(130\ °\mathrm{C})}$/min	PF$_{(25\ °\mathrm{C})}$	PF$_{(130\ °\mathrm{C})}$
1	1.39×10^{15}	0.0936	0.00204	0.0577	–	–
2	1.33×10^{15}	0.0755	0.430	81.7	210	1420
3	8.69×10^{15}	0.0867	0.0995	5.82	48.8	101
4	1.25×10^{18}	0.0979	0.508	9.16	249	159
5	1.24×10^{19}	0.105	0.573	4.81	281	83.3
6	3.40×10^{17}	0.0951	0.314	7.58	154	131
7	1.23×10^{16}	0.0819	0.586	56.6	287	981
8	2.32×10^{17}	0.0941	0.293	7.87	143	136
9	3.09×10^{17}	0.0939	0.414	11.4	203	197
10	2.55×10^{16}	0.0846	0.544	39.6	267	687

Labelling of the samples—see Table 1

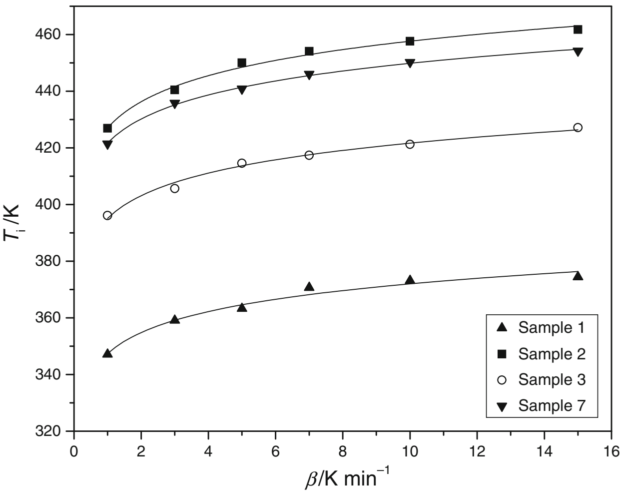


Fig. 2 Experimental and fitted dependences of the onset oxidation temperatures, T_i, on the heating rates, β, for unstabilized SBR and SBR stabilized with antioxidants A_1, A_2 and $A_1 + A_2$

A_4 and A_5 comparing to that of phenothiazine. Among them, the highest value can be assigned to A_3. In the case of mixtures, presence of phenothiazine (A_1) in the mixtures (samples 7 and 10) led to the higher values of their PFs.

The situation is different in the case of the lower temperature. The effect of phenothiazine is comparable to the stabilizing effect of the diphenylamine derivatives. The weakest protective effect can be observed in the case of the diphenylamine structure in A_4.

The values of PFs for 25 and 130 °C in Table 3 indicate that the compounds A_1 and A_2 perform better stabilizing effect at higher temperatures. Similar trends can be observed in the couples containing A_1 (samples 7 and 10). On the other hand, protection factor decreases with temperature for the compounds A_3 and A_4. The temperature dependence of PF is negligible for the antioxidant A_5 and for the mixtures $A_3 + A_5$ and $A_4 + A_5$.

Antioxidant effectiveness and antioxidant synergism

Based on the obtained values of PFs, it is possible to calculate antioxidant effectiveness AEX [5]:

$$\mathrm{AEX} = \frac{\mathrm{PF} - 1}{X} \tag{4}$$

where X is expressed in parts per hundred parts of rubber (phr). Physical meaning of AEX is that it expresses the additional stability brought about by a stabilizer, normalized per a mass unit of the stabilizer. The values of stabilizer effectiveness are summarized in Table 4. The stabilizer effectiveness introduced by Eq. 4 offers the possibility of quantitative characterization of the stabilizer synergism. If there is no interaction between the stabilizers in the mixture, the resulting stabilizer effectiveness should be a weighed average mean of the effectiveness of single stabilizers [11]. Thus, the calculated stabilizer effectiveness, $\mathrm{AEX_{calcd}}$, can be expressed as follows:

$$\mathrm{AEX_{calcd}} = \sum_i w_i \mathrm{AEX}_i \tag{5}$$

A type of cooperation between the antioxidants (synergism, antagonism or additive effect) was estimated using S-factors [11]. The S-factors of antioxidants in the mixtures have been evaluated using equation [11]:

$$S = \frac{(\mathrm{AEX} - \mathrm{AEX_{calcd}})}{\mathrm{AEX_{calcd}}} 100\% \tag{6}$$

If the value of S is positive, antioxidants in the mixture exhibit synergistic effect, for the value of $S < 0$, the effect is antagonistic and in the case of $S = 0$ the cooperation is additive. The values of S are listed in Table 5.

From the values of S it can be seen that the type of cooperation between individual stabilizers strongly depends on temperature. At 130 °C, the highest synergistic effect can be observed in the couple $A_4 + A_5$. Synergism was produced also by the $A_1 + A_2$ blend. Antioxidant blends in the samples 8 and 10 exhibited almost additive

Table 4 Measured and calculated values of antioxidant effectiveness for 25 and 130 °C

Sample	$\mathrm{AEX}_{(25\ ^\circ\mathrm{C})}$	$\mathrm{AEX}_{(130\ ^\circ\mathrm{C})}$	$\mathrm{AEX}_{(25\ ^\circ\mathrm{C})\mathrm{calcd}}$	$\mathrm{AEX}_{(130\ ^\circ\mathrm{C})\mathrm{calcd}}$
2	420	2840	–	–
3	97.6	202	–	–
4	498	318	–	–
5	562	167	–	–
6	308	262	–	–
7	574	1960	259	1520
8	286	272	403	290
9	406	394	435	214
10	534	1370	364	1550

Labelling of the samples—see Table 1

Table 5 Values of *S*-factor in % calculated for 25 and 130 °C

Sample	Antioxidants	$S_{(25\ °C)}$	$S_{(130\ °C)}$	Type of cooperation
7	$A_1 + A_2$	122	29	Synergy
8	$A_3 + A_5$	−29	−6	Antagonism/additivity
9	$A_4 + A_5$	−7	84	Additivity/synergy
10	$A_1 + A_5$	47	−11	Synergy/additivity

type of cooperation. A different situation occurs at 25 °C, where the highest synergistic effect can be assigned to the combination of the compounds A_1 and A_2. Synergy can be observed also for the antioxidants in the sample 10 ($A_1 + A_5$). Decreasing temperature leads to the extinction of the synergistic effect in the couple $A_4 + A_5$. The couple $A_3 + A_5$ shows slightly antagonistic type of cooperation.

The best results have been obtained for the mixture of $A_1 + A_2$, where the synergism can be observed at both temperatures. The worst combination appeared to be $A_3 + A_5$ in the sample 8, where the antagonistic effect has been observed for the lower temperature and at higher temperatures the type of cooperation was only additive.

Conclusions

In this work, the stabilization effect of individual antioxidants and their mixtures in the thermal oxidation of SBR has been studied. It is shown that the antioxidant effect is strongly dependent on temperature. At higher temperatures, the protective effect of phenothiazine is higher than the protective effects of the compounds with diphenylamine structure. At lower temperatures the effects of the antioxidants are comparable.

Among the mixtures, the best stabilizing properties has been observed for the mixture $A_1 + A_2$. On the other hand, the lowest protective effect has been obtained for the combination $A_3 + A_5$.

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