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DSC study of the influence of *p*-subtituted diphenyl amines on the thermooxidative stability of styrene-butadiene rubber

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Abstract Effect of several *p*- and *p*,*p*′-substituted diphenyl amines on the thermooxidative stability of styrene-butadiene rubber (SBR) has been studied using non-isothermal DSC measurements with the aim of exploring the relation between the structure of the compound and its antioxidative performance. The treatment of the experimental data was carried out by applying a new method based on a non-Arrhenian temperature function. In order to compare the stabilizing effect of the compounds, protection factors have been calculated from the oxidation induction times. The results achieved document that some functional groups in substituted diphenyl amines modify greatly the antioxidative performance. The groups having a positive mesomeric effect increase dramatically the antioxidant efficiency; the highest increase exhibited the nitroso group. On the other hand, the nitro group with the negative mesomeric effect is responsible for the loss of antioxidative properties. In general, the protection factors of the compounds depend on temperature.

Keywords Styrene-butadiene rubber · Thermooxidation · Stability · Induction period · Protection factor · Non-Arrhenian temperature function

Introduction

Thermooxidative degradation is one of the most common reasons causing a rapid failure of elastomer properties. In order to retard the thermooxidative degradation of elastomers during their processing, storage and use, various antioxidants are used. Thermooxidative degradation generally occurs in two steps [1]. The first one is the induction period (IP), where seemingly no chemical reaction takes place. At the end of the induction period, the second process, i.e. the oxidation, begins. At the end of IP, a sudden change in the material properties mostly occurs and, therefore, the length of IP is often considered a measure of the material stability [1, 2]. In order to estimate the stability of the materials, accelerated oxidation tests are frequently used employing thermoanalytical methods. Regarding the differential scanning calorimetry (DSC), the end of the induction period is determined as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of non-isothermal measurements with linear heating [2]. The standard accelerated tests are usually carried out under isothermal conditions. In our previous papers, it has been shown that the onset of the oxidation peak can mostly be determined more accurately from the non-isothermal DSC records than from the isothermal ones [1, 2]. A theory for the kinetic description of IP from non-isothermal measurements has been outlined in [1, 2]. The theory was applied for the study of thermooxidation of edible oils and fatty acids methylesters [1, 3, 4], thermooxidation of polyolefines [1, 2, 5], thermooxidative stability of pharmaceuticals [6], evaluation of antioxidant activity of *p*-phenylenediamines in polyisoprene rubber [7, 8], determination of residual stability of polyurethane automotive coatings [9, 10], thermooxidative stability of dried milk

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[11], stabilization of poly(methyl methacrylate) by TiO_2/SiO_2 nanoparticles [12] and determination of residual stabilty of γ-irradiated polyisoprene rubber [13].

The oxidative induction time (OIT) test was developed by former Bell Telephone Laboratories researchers as a rapid screening test for the relative effectiveness of stabilizer packages for olefinic cable jackets [14]. Later, it was discovered that due mainly to the curvature in the Arrhenius activation energy plots, gross over-estimates of near room temperature lifetimes were encountered [14–17]. The aim of most stability studies is to extrapolate the data obtained from the accelerated tests to lower temperatures. In our recent paper [18], it has been documented that the extrapolation from high-temperature data to ambient temperature based on the Arrhenius temperature function very often leads to unrealistic estimations of the material stability. Better estimations can be obtained using non-Arrhenian temperature functions [18].

Diphenyl amine-based antioxidants are commercialized for long time (see, for example, the compound 2 in Table 1). In order to develop new antioxidants, it would be advisable to recognize the relation between structure of the antioxidants and their efficiency. In this pilot work, the antioxidant effects of diphenyl amine and 11 p- and p,p'-substituted diphenyl amines on the thermooxidative stability of styrene-butadiene rubber (SBR) are tested with the aim to assess the effect of the substituents on the protection factor of the substituted diphenyl amines. The evaluation of experimental results and kinetic description of the induction periods are carried out employing a non-Arrhenian temperature function.

Theory

In order to describe the kinetics of the processes occurring in condensed phase, methods based on the single-step approximation are often used [19, 20] where the rate of the complex process can be formally described as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is the temperature function depending only on temperature T and $f(\alpha)$ is the conversion function depending only on the conversion of the process, α.

The rate of degradation processes under application conditions is usually too slow to be measured. In order to estimate the stability of materials, a sample is mostly subjected to an accelerated test under standardized conditions where heating is the most common means of accelerating the oxidation. As it has been noted above, the principal goal of stability studies is to extrapolate the kinetic data, obtained from accelerated stability tests, to the application conditions. The prediction of long-term durability by extrapolation is a very difficult task since many fundamental scientific problems in this field remain unsolved. The Arrhenius extrapolation mostly gives unrealistically long estimates of thermooxidative stability. In [18], it has been documented that the most realistic estimates of the material durability under thermooxidative conditions are obtained when a non-Arrhenian temperature function is applied instead of the Arrhenius equation. Hence, the dependence of the oxidation onset temperature on the heating rate is treated using the relationship

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

where T_i is the oxidation onset temperature, β is the heating rate, A and D are adjustable kinetic parameters without clear physical meaning [21]. Knowing the values of kinetic parameters, the oxidation induction time for a chosen temperature, T, can be calculated as

$$t_i = Ae^{-DT}. \tag{3}$$

Experimental part

Thermooxidative degradation of the samples has been studied using power compensated calorimeter Perkin Elmer DSC-7 with the Pyris software. The temperature scale of the calorimeter was calibrated to the fusion points of In and Zn; the enthalpy scale was calibrated to the enthalpy of fusion of In. Samples of 2–4 mg were placed in standard aluminium pans where the lid of each pan was perforated by 7 pinholes to facilitate the contact of the sample with oxygen. The samples were measured at heating rates 1, 3, 5, 7, 10 and 15 K/min. The onset temperatures of the oxidation peaks were taken as the starting temperatures of the samples oxidation.

The unstabilized SBR was prepared by coagulation from an unstabilized latex E-SBR 1500 (Synthos Kralupy, Czech Republic). The coagulate was dried in mild conditions at 40 °C for 120 h.

Preparation of the samples

The samples were prepared in a Brabender type mixing chamber (65 cm^3, 50 rpm) from the unstabilized SBR and 0.5 wt% of the antioxidant at 60 °C for 5 min. Description of the samples, the antioxidants used, their formulas, sources and purity are given in Table 1.

Results and discussion

From the non-isothermal DSC records, the oxidation onset temperatures, T_i, were read; their values are summarized in

Table 1 Names, formulas, sources and purity of the substituted *p*-diphenyl amines under study

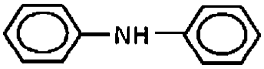
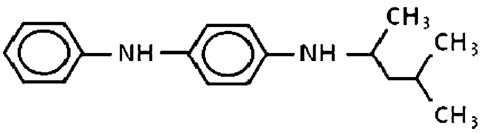
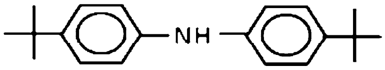
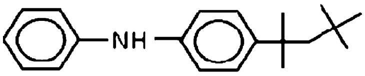
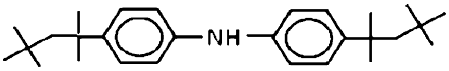
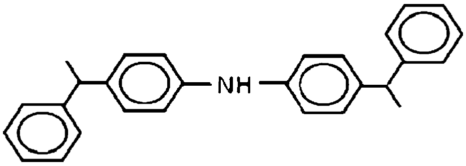
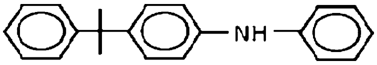
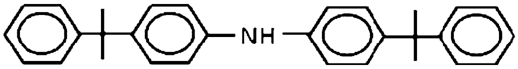
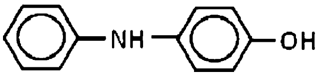
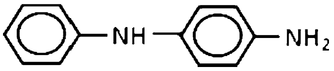
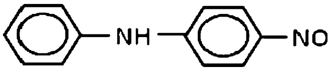
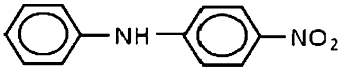
No.	Name	Formula	Source	Purity/ %
0	SBR without additive	–		
1	Diphenyl-amine		Duslo Šaľa, Slovakia (intermediate product)	99.5
2	*N*-(1,3-Dimethyl-butyl)-*N*′-phenyl-benzene-1,4-diamine (6PPD)		Duslo Šaľa, Slovakia (Dusantox 6PPD)	98.5
3	Bis-(4-tert-butyl-phenyl)-amine		VUCHT and FCHPT	98.5
4	Phenyl-[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-amine		VUCHT	98.3
5	Bis-[4-(1,1,3,3-tetramethyl-butyl)-phenyl]-amine		VUCHT (Dusantox ODPA HP)	98
6	Bis-[4-(1-phenyl-ethyl)-phenyl]-amine		VUCHT and FCHPT (Dusantox 80)	98.5
7	[4-(1-Methyl-1-phenyl–ethyl)-phenyl]-phenyl-amine		VUCHT	93
8	Bis-[4-(1-methyl-1-phenyl-ethyl)-phenyl]-amine		VUCHT (Dusantox CDPA HP)	98
9	4-phenylamino phenol		VUCHT	95
10	*N*-Phenyl-benzene-1,4-diamine		Duslo Šaľa, Slovakia (intermediate product)	98.9
11	(4-Nitroso-phenyl)-phenyl-amine		VUCHT	98
12	(4-Nitro-phenyl)-phenyl-amine		Chemie Brunschwig AG, Switzerland	97

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Table 2. The kinetic parameters *A* and *D* describing the length of oxidation induction period have been obtained from the dependences of oxidation onset temperature versus heating rate applying Eq. 2. The data treatment was carried out using the non-linear least squares method in the program ORIGIN. As seen in Fig. 1 for the case of 6PPD, a satisfactory agreement between the experimental and calculated values of T_i has been reached for all samples under

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

β/K min^{-1}	Sample no.												
	0	1	2	3	4	5	6	7	8	9	10	11	12
1	70.9	125.3	152.4	139.9	120.8	120.0	116.7	123.2	116.1	148.3	149.6	157.1	98.5
3	81.5	137.8	166.1	150.1	130.0	128.6	123.8	131.6	132.2	163	159.8	172.7	110.3
5	87.1	140.2	175.2	152.8	139.1	133.8	134.0	140.0	138.8	173.9	167.7	177.7	117.1
7	96.2	142.7	177.3	160.6	141.7	141.3	136.6	143.0	142.2	180.3	169.8	181.5	119.5
10	99.5	147.2	181.8	165.6	146.0	146.9	137.2	146.8	148.5	182.9	174.7	187.0	123.1
15	99.3	155.7	190.6	168.9	154.2	150.0	144.6	154.2	155.1	187.6	180.0	190.0	126.5

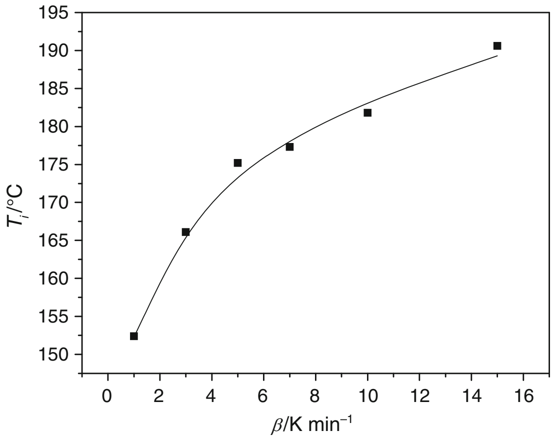

Fig. 1 Dependence of the onset oxidation temperature, T_i, on the heating rate β for SBR with the addition of 0.5 wt% 6PPD

Table 3 Kinetic parameters obtained from the treatment of experimental data presented in Table 2 by using Eq. 2

Sample	A/min	D/K^{-1}
0	8.37E13	0.086
1	5.90E17	0.097
2	4.44E14	0.073
3	1.81E17	0.091
4	1.40E15	0.083
5	4.31E15	0.086
6	2.75E17	0.097
7	1.58E16	0.088
8	1.32E13	0.071
9	2.00E13	0.066
10	2.34E17	0.089
11	2.41E16	0.082
12	2.84E16	0.096

study. The resulting values of A and D are listed in Table 3. The coefficient of variability of the parameter A was about 100%, the one of the parameter D about 10%.

Table 4 Calculated oxidation induction times and protection factors for temperatures 25 and 130 °C

Sample	$t_{i(25\ °C)}$/year	$t_{i(130\ °C)}$/min	PF$_{(25\ °C)}$	PF$_{(130\ °C)}$
0	0.0011	0.068	–	–
1	0.315	6.13	286	90
2	0.282	67	256	985
3	0.624	21	567	309
4	0.055	4.11	49.6	60
5	0.064	3.78	58.6	56
6	0.131	2.86	119	42
7	0.109	6.18	99.2	91
8	0.017	4.89	15	72
9	0.102	55.6	93	818
10	1.33	61.2	1200	900
11	1.11	106	1000	1560
12	0.023	0.44	21	6

The kinetic parameters have no physical meaning; however, they enable to calculate the lengths of isothermal induction periods for any temperature [2, 18]. In fact, the isothermal induction period is identical with OIT [2]. We have chosen two temperatures for the evaluation of OIT. The first one is 130 °C which is the temperature from the range of T_i values. The other temperature chosen is 25 °C which represents an extrapolation far from the measured values of T_i. In order to characterize and compare the stabilizing effect of the compounds, the protection factor (PF) has been calculated which is defined as a ratio of the length of induction periods of the stablized and unstabilized SBR [7, 8]:

$$\mathrm{PF} = \frac{t_i(\mathrm{stab.})}{t_i(\mathrm{unstab.})}. \tag{4}$$

The values of OITs and PFs calculated for the both temperatures are summarized in Table 4. It can be seen that the values of *PF*s are >1 for all compounds under study, i.e. the compounds exhibit stabilizing effect on SBR.

First, we will discuss the data in Table 4 calculated for the temperature 130 °C. This temperature is within the range of OOTs measured so that no extrapolation of the results measured is performed. The calculated data of OITs and protection factors represent a transformation of the measured OOT data into OIT values through the kinetic parameters comprised in Eqs. 2 and 3. The values of the protection factors point out that the order of the stability should be $11 > 2 > 10 > 9 > 3 > 7 \approx 1 > 8 > 4 > 5 > 6 > 12$. The higher is the thermooxidation stability of the samples, the higher is OOT [2]; hence, the same order of stabilities is pointed out from the data of Table 2. The compounds 2, 9, 10 and 11 have extremely high protection factors, higher by an order of magnitude than diphenyl amine itself. The functional groups comprised in these compounds have a positive mesomeric effect so that they increase the electron density on the adjacent benzene ring. On the other hand, the lowest protection factor is observed for the compound 12 containing a functional group with the negative mesomeric effect. The compound 3 also exhibits a protection factor much higher than diphenyl amine itself. The protection factor of the compounds 4–8 is of the same order than that of diphenyl amine so that the substituents incorporated in these compounds do not have much influence on the antioxidant performance.

The protection factor (Eq. 4) represents the ratio of OITs for the stabilized and unstabilized samples. From Eq. 3, it follows that OIT depends on temperature so that the protection factor should depend on temperature as well. The comparison of protection factors for 25 and 130 °C in Table 4 suggests that the factor could increase with temperature for the compounds 2, 8, 9 and 11 and could decrease for the compounds 1, 3, 6, 10 and 12. The temperature dependence seems negligible for the compounds 4, 5 and 7.

It has already been underlined that the temperature of 25 °C represents an extrapolation very far from the range of the measured values of OOTs. Taking into account great values of the coefficients of variability of the kinetic parameters (Table 3), one should be very careful to draw trustworthy conclusion from the values of protection factors for this temperature. From the point of view of their antioxidant efficiency, it seems reasonable to divide the compounds into three groups. The group of highly efficient stabilizers involves the compounds 10, 11, 3, 1 and 2. The compounds 6, 7, 9, 5 and 4 belong to the group of compounds with a medium antioxidative performance. The antioxidant effeciency of the compounds 9 and 12 is low.

Conclusions

The results achieved document that some functional groups in substituted diphenyl amines modify greatly the antioxidative performance. The groups having a positive mesomeric effect increase dramatically the antioxidant efficiency. The highest increase exhibited the nitroso group. On the other hand, the nitro group with the negative mesomeric effect is responsible for the loss of antioxidative properties. In general, the protection factors depend on temperature.

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References

1. Šimon P, Kolman L. DSC study of oxidation induction periods. J Therm Anal Calorim. 2001;64:813–20.
2. Šimon P. Induction periods—theory and applications. J Therm Anal Calorim. 2006;84:263–70.
3. Šimon P, Kolman L, Niklová I, Schmidt Š. Analysis of the induction period of oxidation of edible oils by differential scanning calorimetry. J Am Oil Chem Soc. 2000;77:639–42.
4. Polavka J, Paligová J, Cvengroš J, Šimon P. Oxidation stability of methyl esters studied by differential thermal analysis and Rancimat. J Am Oil Chem Soc. 2005;82:519–24.
5. Gregorová A, Cibulková Z, Košíková B, Šimon P. Stabilization effect of lignin in polypropylene and recycled polypropylene. Polym Degr Stab. 2005;89:553–8.
6. Šimon P, Veverka M, Okuliar J. New screening method for the determination of stability of pharmaceuticals. Int J Pharm. 2004;270:21–6.
7. Cibulková Z, Šimon P, Lehocký P, Balko J. Antioxidant activity of *p*-phenylenediamines studied by DSC. Polym Degr Stab. 2005;87:479–86.
8. Cibulková Z, Šimon P, Lehocký P, Balko J. Antioxidant activity of 6PPD derivatives in polyisoprene matrix studied by non-isothermal DSC measurements. J Therm Anal Calorim. 2005;80:357–61.
9. Fratričová M, Šimon P, Schwarzer P, Wilde HW. Residual stability of polyurethane automotive coatings measured by chemiluminescence and equivalence of Xenotest and Solisi ageing tests. Polym Degr Stab. 2006;91:94–100.
10. Šimon P, Fratričová M, Schwarzer P, Wilde HW. Evaluation of the residual stability of polyurethane automotive coatings by DSC—equivalence of Xenotest and desert weathering tests and the synergism of stabilizers. J Therm Anal Calorim. 2006;84:679–92.
11. Šimon P, Polavka J. Thermooxidative degradation of dried milk studied by non-isothermal thermogravimetry. J Food Nutr Res. 2006;45:166–70.
12. Šimon P, Zhong W, Bakoš D, Hynek D. Thermooxidative stability of polymethyl methacrylate containing nanoparticles of silica/titania and silica/zirconia. Chem Pap. 2008;62:176–80.
13. Cibulková Z, Polovková J, Lukeš V, Klein E. DSC and FTIR study of the gamma radiation effect on cis-1,4-polyisoprene. J Therm Anal Calorim. 2006;84:709–13.
14. Woo L, Khare A, Blom HP, Sandford C, Ding SY. Application of the oxidative induction test to depolymerizing systems. Thermochim Acta. 2001;367:113–8.
15. Gillen KT, Bernstein R, Derzon DK. Evidence of non-Arrhenius behaviour from laboratory aging and 24-year field aging of polychloroprene rubber materials. Polym Degr Stab. 2005;87:57–67.
16. Gillen KT, Bernstein R, Celina M. Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials. Polym Degr Stab. 2005;87:335–46.

17. Celina M, Gillen KT, Assink RA. Accelerated aging and lifetime prediction: review of non-Arrhenius behaviour due to two competing processes. Polym Degr Stab. 2005;90:395–404.
18. Šimon P, Hynek D, Malíková M, Cibulková Z. Extrapolation of accelerated thermooxidative tests to lower temperatures applying non-Arrhenius temperature functions. J Therm Anal Calorim. 2008;93:817–21.
19. Šimon P. The single-step approximation—attributes, strong and weak sides. J Therm Anal Calorim. 2007;88:709–15.
20. Šimon P. Single-step kinetics approximation employing non-Arrhenius temperature functions. J Therm Anal Calorim. 2005;79:703–8.
21. Šimon P. Considerations on the single-step kinetics approximation. J Therm Anal Calorim. 2005;82:651–7.