

Stabilization effect of potential antioxidants on the thermooxidative stability of styrene–butadiene rubber

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Abstract Effects of several heterocyclic compounds containing nitrogen, trisubstituted amines and diamines and molecules based on *N,N,N',N',N'',N''*-substituted-[1,3,5] triazine-2,4,6-triamine in preventing thermooxidative degradation of styrene–butadiene rubber (SBR) have been studied using non-isothermal DSC measurements. The aim of this study was to determine and compare the stabilizing effect of individual compounds and to select the structures with the best antioxidative properties. In order to compare the stabilizing effect of the compounds, induction periods and protection factors have been calculated. The treatment of the experimental data was carried out using a method based on a non-Arrhenian temperature function. The results show that better antioxidative properties can be assigned to heterocyclic compounds. On the other hand, molecules containing triazine structures exhibited only negligible stabilizing effect on SBR at lower temperatures and even destabilizing effect at higher temperatures.

Keywords Differential scanning calorimetry · Styrene–butadiene rubber · Antioxidants · Stability · Oxidation · Non-Arrhenian temperature function

Introduction

Organic materials exposed to oxygen undergo oxidative degradation. Oxidative degradation can occur during each stage of the polymer life cycle. In fact, it can occur already during polymerization, subsequent treatments and on storage. Thus, the stabilization of organic polymers is important since these materials are exposed to oxygen throughout their lifetime. Numerous antioxidants have been found to reduce the rate of thermal oxidation for a certain period [1].

The degradation process involves first an induction or initiation period which may range from minutes to years depending on the material, the concentrations of reactants, environmental factors and temperature. The reactions occurring during the induction period normally have only a very slight effect on the physical and chemical properties of the material. The induction period is followed by a rapid oxygen uptake; then, large changes in the properties of the material occur [2]. Thus, a prediction of the lifetime of the material is equivalent to a prediction of the length of the induction period. Prediction of the useful life of a material is frequently done by accelerated oxidation tests employing thermoanalytical methods, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG) [1]. Using DSC, the end of the induction period is determined as the oxidation induction time (OIT) in the case of isothermal measurements and as the oxidation onset temperature for non-isothermal measurements with linear heating [3]. A theory for the kinetic description of IP from non-isothermal measurements employing Arrhenius function has been outlined in [3, 4]. The theory was applied for the study of thermooxidative stability of edible oils and fatty acids methyl esters [4–6], polyolefines [3, 4, 7], pharmaceuticals

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[8], polyisoprene rubber with the addition of *p*-phenylenediamines [9, 10], determination of residual stability of polyurethane automotive coatings [11, 12], thermooxidative stability of dried milk [13], stabilization of poly(methyl methacrylate) by TiO₂/SiO₂ nanoparticles [14] and determination of residual stability of γ -irradiated polyisoprene rubber [15].

Lifetime prediction of polymeric materials undergoing thermooxidative decomposition is currently done by measuring OIT or OOT at elevated temperatures. Then an extrapolation is done to obtain the induction period at the actual use or storage temperature of the material. Using an elevated temperature inserts the uncertainty of assuming a constant activation energy over the temperature interval of the extrapolation. Extrapolation over 100–200 °C is not uncommon in current practice, and changes in the activation energy caused by the changes in the reaction mechanism over such a temperature range occur [2]. It was found that the use of Arrhenius temperature function produces high over-estimates of near room temperature lifetimes [16–19]. In our recent paper [20], it has been documented that better estimations can be obtained using non-Arrhenian temperature functions. The non-Arrhenian temperature function was applied for the study of antioxidant action of diphenyl amine-based antioxidants in styrene-butadiene rubber [21].

Our long-lasting aim is finding the relationship between the efficiency of an antioxidant and its structure in the rubber stabilization. Two criteria characterizing the stabilization effect of the studied antioxidants were proposed: protection factor (PF) and antioxidant effectiveness (AEX) [9]. The antioxidant activity of selected *N,N'*-substituted *p*-phenylenediamines (PPDs) in styrene-butadiene rubber (SBR) has been studied and the obtained values were used to compare the stabilizing effect of the same antioxidants in polyisoprene (PI) rubber [22]. It was shown that the order of stability for SBR matrix samples differs from that for PI samples and the stabilization effect of the antioxidant depends much on the polymer matrix. The results achieved in [21] 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 [21].

This work is focused on the study of thermooxidative stability of styrene-butadiene rubber (SBR) in the presence of several potential antioxidants with the aim to evaluate their antioxidant effect on SBR and to select the best structures. The group of studied molecules consists of heterocyclic compounds containing nitrogen atom, phenoxazine, phenothiazine, trisubstituted amines and diamines and molecules based on *N,N,N',N',N'',N''*-substituted-[1,3,5]triazine-2,4,6-triamine.

Experimental

Preparation of the samples

Potential stabilizers were mixed with styrene-butadiene rubber in the Brabender type chamber (65 cm³, 50 rpm) at 60 °C for 5 min. Content of the stabilizer was 0.5 wt%. Notation and structures of the studied molecules are given in Table 1.

DSC measurements

Thermooxidative stability of the samples was studied using the power-compensated calorimeter Perkin Elmer DSC-7 under nonisothermal conditions. Temperature calibration was carried out to the melting points of In, Sn, and Zn; the enthalpy calibration to the heat of fusion of In. The measurements were carried out at heating rates 1, 3, 5, 7, 10, and 15 K min⁻¹ under oxygen atmosphere. Samples of 2–4 mg were placed in standard aluminium pans. The lid of each pan was perforated by seven pinholes. The onset temperatures of the oxidation peaks were taken as the starting temperatures of the samples oxidation.

Theory

In order to describe the kinetics of the processes occurring during induction period, methods based on the single-step approximation are often used [23] where it is assumed that the rate of the complex process can be formally described as:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

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 . As it has been shown in our previous work better estimations of room temperature lifetimes can be obtained using following temperature function [20, 24]:

$$k(T) = A' \exp(DT) \quad (2)$$

Combination of Eqs. 1 and 2, separation of variables and integration under the assumption that the conversion corresponding to the end of the IP is constant gives the result:

$$1 = \int_0^{t_i} \frac{dt}{A \exp(-DT)} \quad (3)$$

where t_i is the length of IP, A and D are kinetic parameters. The parameter A in Eq. 3 is given as:

$$A = \frac{F(\alpha_i) - F(0)}{A'} \quad (4)$$

Table 1 Chemical structures of potential stabilizers under study

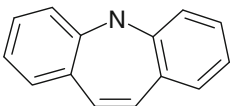
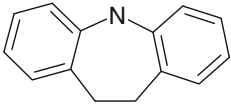
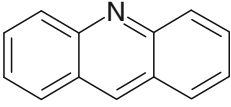
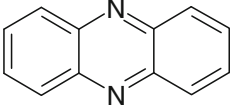
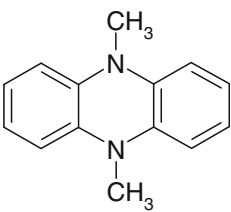
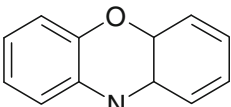
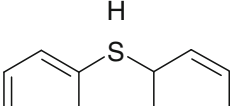
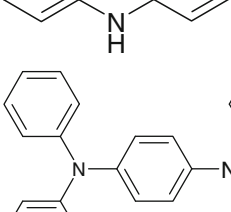
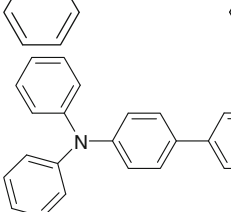
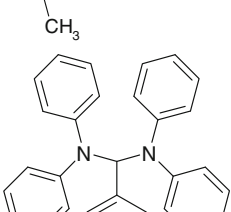
Sample	Formula	$M/g \text{ mol}^{-1}$
2		193.25
3		195.27
4		179.22
5		180.21
6		210.28
7		185.23
8		201.29
9		412.54
10		440.59
11		426.57

Table 1 continued

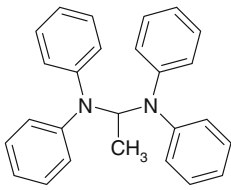
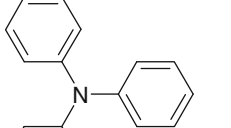
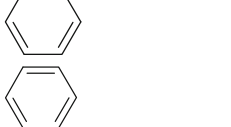
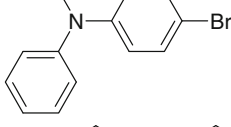
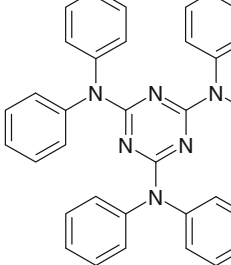
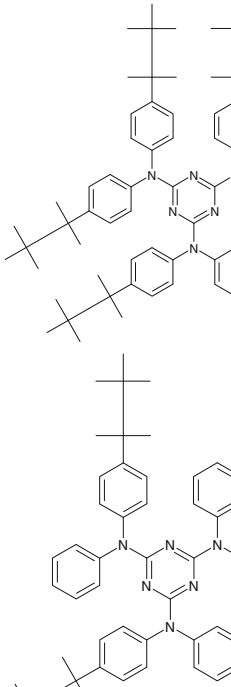
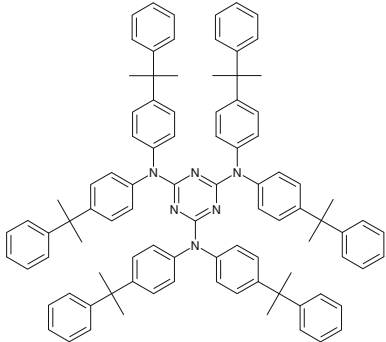
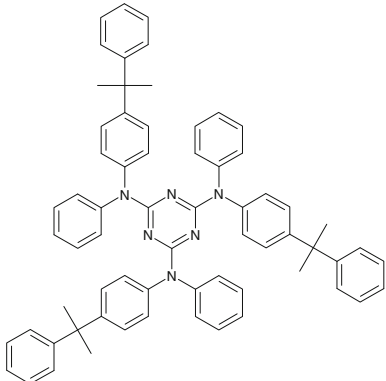
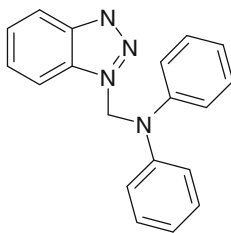
Sample	Formula	$M/g \text{ mol}^{-1}$
12		364.49
13		245.33
14		324.22
15		582.71
16		1256.01
17		919.26

Table 1 continued

Sample	Formula	$M/g \text{ mol}^{-1}$
18		1291.79
19		937.25
20		302.38

For isothermal conditions, from Eq. 3, the length of the induction period can be simply obtained [20, 23, 24]:

$$t_i = A \exp(-DT) \quad (5)$$

For the DSC measurements with constant heating rate, β , from Eq. 3, it can be obtained [20, 23, 24]:

$$T_i = \frac{1}{D} \ln(AD\beta + 1) \quad (6)$$

Equation 6 represents dependence of the onset oxidation temperature, T_i on the heating rate, β .

Results and discussion

Treatment of the experimental results

From the nonisothermal measurements, onset oxidation temperatures, T_i , have been obtained and their values are

listed in Table 2. The dependences of T_i on the heating rates, β , were treated using Eq. 6, where the parameters A and D were obtained by the non-linear least squares method in the program ORIGIN. As it is demonstrated in Fig. 1, a very good agreement between the calculated and experimental values of T_i has been reached for all samples under study. The values A and D for all studied samples are given in Table 3. The coefficient of variability of the parameter A was about 150%, the one of the parameter D about 10%.

Induction periods and protection factors

As it has been already mentioned, the length of the induction period, t_i , is often taken as a measure of the material stability. The kinetic parameters enabled to calculate the values of t_i according to Eq. 5. The values of t_i have been calculated for two different temperatures: 25 and 130 °C. The first one represents a storage temperature of SBR and obtained values of IPs represent an extrapolation far from the measured values. The second temperature chosen corresponds to the temperature of SBR processing.

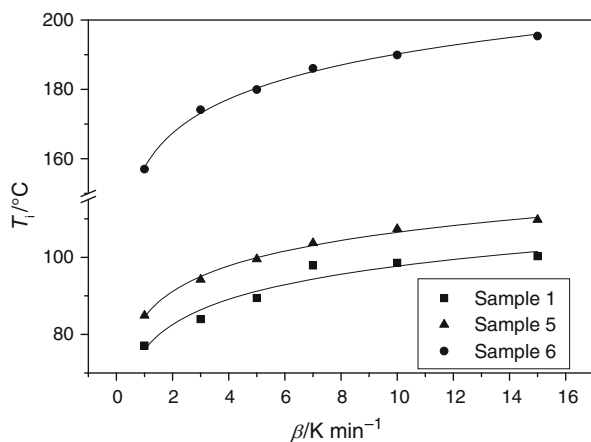
In our previous papers protection factor, PF, has been introduced [9, 10]. It is defined as a ratio of the length of IPs of stabilized and unstabilized SBR. PF enables to compare the stabilizing effect of various stabilizers. The higher the value of PF, the greater is the stabilization effect of the potential antioxidant on SBR. Again, the values of PFs were calculated for both above mentioned temperatures. Their values together with the lengths of IPs are summarized in Table 4. The values of PFs indicate that the order of samples stability is different for the chosen temperatures.

First, we will discuss the results obtained for 25 °C. These results represent an extrapolation of the measured data far from the range of the measured values of T_i . The values of PFs indicate that the stabilization effect of the studied additives compounds in the following order: 3 > 7 > 12 > 2 > 6 \approx 11 > 8 > 16 \approx 18 \approx 14 > 17 \approx 19 > 20 > 5 \approx 4 \approx 15 > 13 \approx 10 \approx 9. The highest value of protection factor has been obtained for the sample 3. The compounds 7, 12, and 2 also exhibit high values of PFs and can act as antioxidants in SBR. Very low values have been observed for the compounds in the samples containing triazine structures (15, 16, 17, 18, 19). Their protective effect at 25 °C is almost negligible. In the case of trisubstituted amines and diamines in the samples 9, 10, and 13 no stabilization effect has been observed. Generally, we can conclude that molecules consisting of heterocyclic structures appear to have better antioxidative properties in preventing thermal oxidation of SBR than trisubstituted triazine and trisubstituted amine/diamine structures at lower temperatures.

The order of antioxidant efficiency at 130 °C is: 2 > 6 > 7 > 8 > 3 > 11 > 12 > 16 > 4 > 9 \approx 5 \approx 13 >

Table 2 Values of onset oxidation temperatures, T_i , for the samples under study

Sample	$T_i/^\circ\text{C}$ ($\beta = 1 \text{ K min}^{-1}$)	$T_i/^\circ\text{C}$ ($\beta = 3 \text{ K min}^{-1}$)	$T_i/^\circ\text{C}$ ($\beta = 5 \text{ K min}^{-1}$)	$T_i/^\circ\text{C}$ ($\beta = 7 \text{ K min}^{-1}$)	$T_i/^\circ\text{C}$ ($\beta = 10 \text{ K min}^{-1}$)	$T_i/^\circ\text{C}$ ($\beta = 15 \text{ K min}^{-1}$)
1	77.1	83.96	89.44	97.89	98.58	100.3
2	159.75	174.92	180.77	185.92	193.54	194.59
3	142.61	148.58	153.37	162.32	163.02	166.27
4	86.45	98.93	105.73	107.24	110.3	114.17
5	84.91	94.23	99.52	103.71	107.37	109.74
6	156.98	174.12	179.93	186.04	189.92	195.38
7	149.95	160.58	163.49	168.95	175.65	181.64
8	150.41	168.58	177.1	186.17	188.86	195.99
9	79.83	94.69	98.58	103.97	105.45	107.50
10	95.16	105.2	110.89	115.32	117.55	123.69
11	133.70	148.89	152.75	157.36	161.31	165.56
12	132.38	142.57	147.87	150.73	154.55	160.22
13	79.66	88.34	95.19	97.02	101.09	105.67
14	80.59	87.00	90.12	95.33	97.53	100.47
15	78.21	88.29	92.53	95.18	99.84	101.15
16	102.94	116.85	123.53	127.22	129.01	133.34
17	81.69	87.52	94.00	95.86	99.47	104.46
18	82.19	89.23	93.48	97.27	100.67	102.05
19	78.39	87.58	90.59	94.77	97.35	99.79
20	79.27	87.16	90.08	93.05	97.18	101.95

**Fig. 1** Experimental and fitted dependences of the onset oxidation temperatures on the heating rates

$15 > 17 > 10 > 18 > 20 \approx 19 > 14$. Again, higher stabilization effects can be observed in the case of heterocyclic structures. As the values in Table 4 indicate, high stabilization effects can be assigned to molecules in the samples 3, 7, 8, and 9. Trisubstituted amines show only low antioxidant efficiencies. The PF values smaller than 1 were calculated for the samples consisting of triazine structures.

Table 3 Values of the kinetic parameters A and D obtained from the treatment of experimental data using Eq. 6

Sample	A/min	D/K
1	1.25×10^{17}	0.106
2	1.28×10^{15}	0.074
3	1.42×10^{20}	0.107
4	2.25×10^{16}	0.098
5	1.97×10^{17}	0.105
6	2.32×10^{14}	0.071
7	9.64×10^{16}	0.087
8	1.06×10^{12}	0.059
9	6.03×10^{15}	0.0958
10	8.22×10^{17}	0.112
11	1.84×10^{16}	0.0859
12	3.07×10^{18}	0.0994
13	7.81×10^{16}	0.104
14	1.38×10^{21}	0.132
15	2.63×10^{18}	0.114
16	3.97×10^{15}	0.0888
17	1.66×10^{19}	0.119
18	6.25×10^{20}	0.129
19	8.25×10^{19}	0.125
20	4.75×10^{19}	0.123

Table 4 Values of the lengths of induction periods and protection factors for 25 and 130 °C

Sample	t_i (25 °C)/year	t_i (130 °C)/min	PF (25 °C)	PF (130 °C)
1	0.00448	0.0345	–	–
2	0.638	142	143	4100
3	3.77	26.2	843	759
4	0.00875	0.156	1.96	4.53
5	0.00950	0.0814	2.12	2.36
6	0.283	86.0	63.2	2490
7	0.996	56.4	223	1640
8	0.0462	49.6	10.31	1440
9	0.00452	0.102	1.01	2.95
10	0.00492	0.0202	1.10	0.585
11	0.264	16.8	59.0	487
12	0.787	12.1	176	351
13	0.00508	0.0483	1.13	1.40
14	0.0213	0.0107	4.75	0.310
15	0.00867	0.0289	1.94	0.836
16	0.0240	1.13	5.36	32.6
17	0.0123	0.0243	2.76	0.703
18	0.0235	0.0162	5.26	0.470
19	0.0119	0.0131	2.65	0.380
20	0.0107	0.0138	2.39	0.401

The comparison of protection factors for 25 and 130 °C in Table 4 suggests that the factor increases with temperature for the compounds 2, 4, 6, 7, 8, 9, 11, 12, 16 and decreases for the compounds 10, 14, 15, 17, 18, 19, and 20. The temperature dependence is negligible for the compounds 3, 5 and 13.

Conclusions

In this study, the antioxidant effectiveness of 19 compounds in styrene–butadiene rubber was studied by non-isothermal DSC measurements. For the treatment of the experimental results and kinetic description of induction periods a non-Arrhenian temperature function has been employed. The results achieved show that the antioxidant performance depends on temperature. Generally, higher stabilization effect can be assigned to heterocyclic compounds for both temperatures. Triazine structures and trisubstituted amines/diamines exhibited only weak antioxidant effect at 25 °C. For 130 °C, triazine compounds even destabilized styrene–butadiene rubber.

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