

EFFECT OF *TRANS*-POLYOCTENAMER ON THERMAL STABILITY OF RUBBERS DETERMINED BY THERMAL ANALYSIS

T. Kleps¹, M. Piaskiewicz¹, W. Parasiewicz¹ and L. Ślusarski²

¹The Rubber Research Institute "Stomil" 05-820 Piastów by Warsaw, ul. Harcerska 30

²Technical University, Institute of Polymers 90-530 Łódź, ul. Żeromskiego 116, Poland

Abstract

An effect of a cyclic low molecular-weight polymer *trans*-polyoctenamer rubber (TOR) on the thermal stability of diene rubbers and their vulcanizates was investigated. The investigation was carried out in the air and nitrogen atmospheres using thermogravimetry, DSC and simultaneous thermoanalytical methods. The thermal stability indexes: T_5 , T_{max} and activation energy of degradation (ΔE), as well as T_g and T_m values, have been determined.

It was found that *trans*-polyoctenamer (TOR) increases of the thermal stability indices of raw diene rubbers and their vulcanizates. The results show that the thermal degradation of diene rubbers occurred at higher temperature if they were blended with TOR. In our opinion, intermolecular structures formed between the cyclic low-molecular weight polymer and some linear rubber molecules may be the reason for the higher thermal stability of these rubber blends.

Keywords: polymers, rubbers, thermal stability, *trans*-polyoctenamer

Introduction

Thermal stability of rubbers is one of the most important factors determining areas of their application. Constant development of technology creates a demand for very sophisticated rubber goods and, therefore, it is necessary to find the ways to improve their thermal resistance. The high thermal stability of rubbers and rubber materials gives a longer life cycles and a great advantage in economy and ecology.

According to present knowledge the thermal stability of polymers (rubbers) first of all is related to their chemical composition and structure [1-3]. It depends on different factors such as the energy of valence bonds in the main chains and in the network crosslinks, molecular interactions, flexibility of chains, ability to crystallize and so on. However, a mechanism of chemical reactions and physical transformations occurring at elevated temperature on molecular level is not well enough recognized.

It is known that different chemicals added to the rubber can exert an effect on the thermal behaviour and stability of rubbers and their vulcanizates. For examples, Sircar [4] has detected an effect of sulphur content and Brazier and Schwartz [5] noted an influence of accelerators on thermal properties of the polyisoprene. In our

earlier work, we have observed the strong effect of zinc oxide on the thermal degradation of polychloroprene [6].

The influence of polymer substances on thermal stability of rubbers is not well understood. It has been reported that macrocyclic polymers like *trans*-polyoctenamer (TOR) effect positively on the compatibility of rubbers as well as processability property of their compounds and also influence the physical properties of rubber vulcanizates in their hardness, elasticity, tensile strength [7–11]. We have assumed TOR should also influence on thermal properties of rubbers.

TOR is an oligomer containing above 25 wt% of the ring structures (Fig. 1) with the rest consisting of linear structures [8–10]. Because of its double bond content, it can be crosslinked with sulphur systems. TOR is distinguished by very high crystallinity, low molecular weight, low melting point and low viscosity above the melting temperature [9, 10]. Recently published works report an effect of high crystalline TOR on a rate and extent of NR and SBR cure with different systems [12, 13]. In our previous work, we have found that TOR advantageously influences the cross-linking rate of NR and the vulcanizates show higher resistance to cross-linking reversion of natural rubber when TOR was added [14].

The thermal properties of polymers blended with TOR are not well enough recognized. Setiawan and others [15] have studied the blends of NR/EPDM/TOR by DSC method. In the present work, the effect of *trans*-polyoctenamer on the thermal stability of diene rubbers and their vulcanizates has been studied by means TG, DSC and derivatography methods.

Experimental

Materials

Polymers

Macrocyclic polymer *trans*-polyoctenamer (TOR) with partially linear structure: Vestenamer 8012, produced by Hüls (Fig. 1, Table 1).

Linear polymers-diene rubbers: natural rubber (NR)-RSS-1, high *cis* polybutadiene (BR)-Buna *cis* 132, emulsion styrene-butadiene rubber (SBR)-Ker 1500, nitrile rubber with high ACN content (NBR)-Nipol N-41, terpolymer ethylene-propylene-diene (EPDM)-Keltan 512 and chloroprene rubber (CR)-Denka S-40.

Blends

Blends of the following rubbers: NR, BR, SBR, NBR, EPDM, CR with TOR were mixed:

- I series: 90 wt. p. rubber/10 wt. p. TOR
- II series: 80 wt. p. rubber/20 wt. p. TOR
- III series: 70 wt. p. rubber/30 wt. p. TOR

In the case of NR and EPDM additionally blends: 90/10, 80/20, 60/40, 40/60 and 20/80 NR/TOR or EPDM/TOR were prepared.

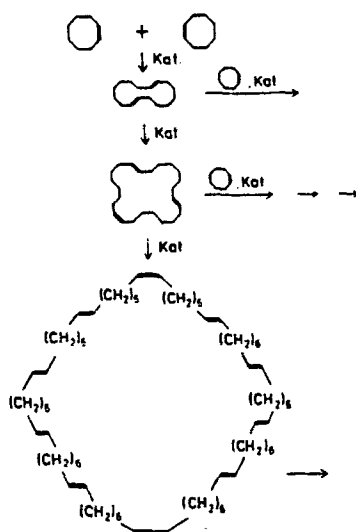


Fig. 1 TOR synthesis from cyclooctadiene [8]

Table 1 Typical physical properties of TOR [8-10]

TOR grade:	Vestnamer 8012
Density/g ml ⁻¹	0.91
Melting point/°C	54
Mooney viscosity ML (1+4) at 100°C	<10
Crystallinity at 23°C/% (ca.)	27
Molecular weight, MW (ca.)	100 000
Glass transition temperature, T_g /°C	-65
<i>Trans</i> -/ <i>cis</i> -ratio of double bonds	80/20

Vulcanizates

Vulcanizates of the above mentioned rubbers with 20 wt. p. TOR/100 wt. p. rubber were cross-linked by sulphur systems and CR by ZnO, MgO, ethylenetiocarbamide system.

Methods

1. Thermogravimetric investigations were performed using a Perkin-Elmer Thermobalance TGS-1 under the following conditions: atmosphere air or nitrogen, sample size about 5 mg, temperature range 25–800°C, heating rate 10°C min⁻¹. The mass loss TG and DTG curves were recorded. The thermal stability index T_5 at a temperature of 5 wt% mass loss was determined.

2. The thermoanalytical investigations were also carried out by means of Derivatograph C in an air using 20 mg samples, at a heating rate of $10^{\circ}\text{C min}^{-1}$.

3. The DSC investigation were carried out with Perkin-Elmer Differential Scanning Calorimeter DSC-1B in an inert atmosphere using 10 mg samples, at the heating rate $8^{\circ}\text{C min}^{-1}$ in the temperature range: -80 to $+200^{\circ}\text{C}$.

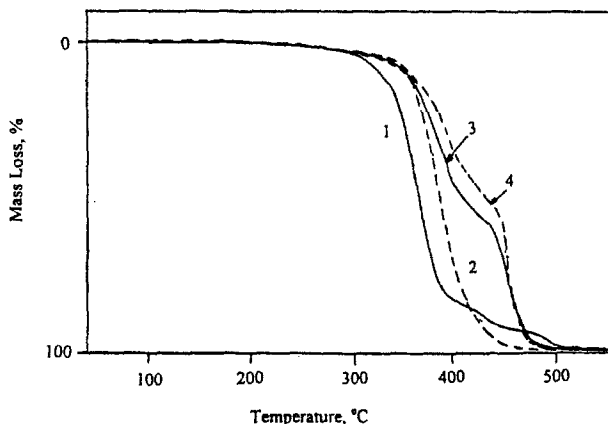


Fig. 2 TG curves of NR (1, 2) and NR/TOR (80/20) blends (3, 4): in air atmosphere (1, 3), in nitrogen (2, 4). Heating rate $10^{\circ}\text{C min}^{-1}$

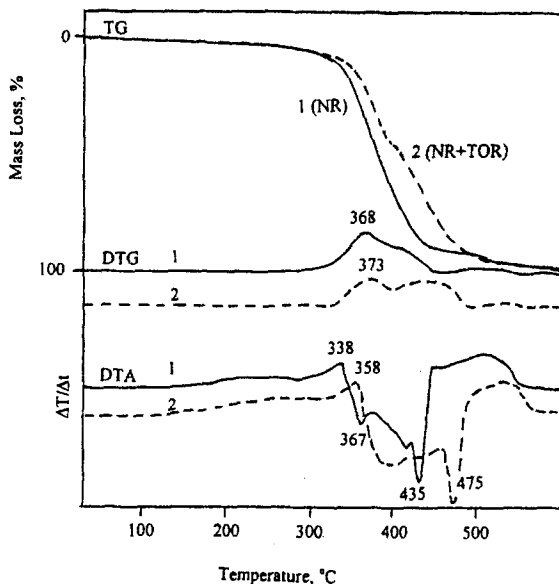


Fig. 3 Thermoanalytical curves of NR (1) and its blend (80/20) with TOR (2) in air. Heating rate $10^{\circ}\text{C min}^{-1}$

Results and discussion

The thermoanalytical investigations show that macrocyclic polymer – TOR – blended with linear diene rubbers does not change the shape of their thermal decomposition curves, although it affects on the characteristic decomposition temperatures. In Fig. 2, as an example, the TG plot of the natural rubber, RSS-1 and its blend with TOR heated in air and nitrogen atmospheres, has been demonstrated. For the NR/TOR blend thermal curves two steps of the mass loss could be seen. The first one related to natural rubber and the second (above 450°C) to TOR decomposition. The destruction of NR in the blends are evidently shifted toward the higher temperatures in comparison to NR alone. As was expected, the thermal decomposition of the rubbers and blends in an inert atmosphere takes place at higher temperature than in the air. The complete thermal characteristics of polymers studied could be deduced from derivatographic curves TG, DTG and DTA. As an example of NR/TOR in Fig. 3 is presented. As can be seen, the peaks on DTG and DTA curves for the blend are also shifted toward the higher temperatures.

T_5 index is an important indicator of the polymer thermal stability and because the initial, T_0 temperatures of the first symptom of the polymer destruction are not

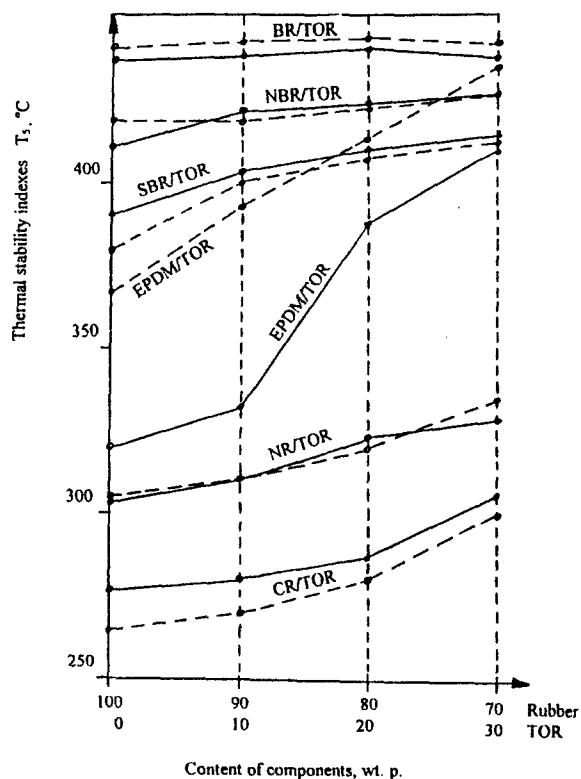


Fig. 4 The thermal stability indexes – T_5 of rubber/TOR blends: in air atmosphere (—) in nitrogen (- - -)

exactly readable. The values of T_5 for all studied rubbers and their blends containing 10, 20 and 30 wt. p. of TOR tested in air and nitrogen are compared in Fig. 4. The data from these diagrams show evidently that TOR increases the thermal stability of all rubbers to different degrees. We have observed that the values of T_5 increase with larger amount of TOR in the blends, but the level of the changes depends probably on structure of rubber itself. It is very interesting that the thermal stability of polybutadiene increases very little, while natural rubber, polychloroprene and particularly EPDM rubbers, are affected to much higher extent. The effect could be seen very clearly in the Fig. 5 where T_5 values for EPDM and NR blends with TOR v/s total composition are demonstrated.

The values of all thermal destruction indices for the individual rubbers, blends with TOR and vulcanizates are presented in Table 2. These data show higher T_5 indexes, higher values of the activation energy of decomposition, ΔE , and lower rates of mass loss, dm/dt , which evidence higher thermal stability when TOR is present in the blends or vulcanizates. However lower improvement of the thermal stability was observed for the vulcanizates than blends. It is probably because of an effect of

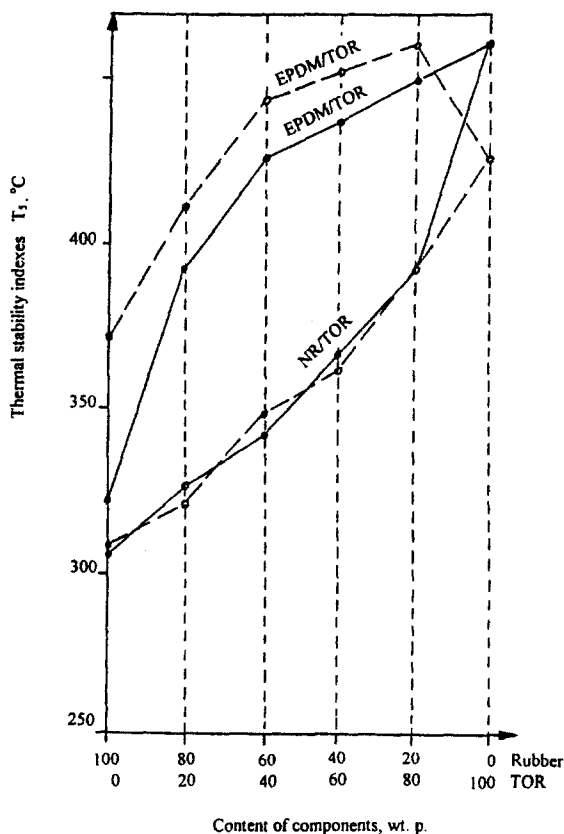


Fig. 5 The thermal stability indexes – T_5 of EPDM/TOR and NR/TOR blends: in air atmosphere (—) in nitrogen (- - -)

Table 2 Comparison of thermoanalytical data for TOR and diene rubbers and their blends (B) (80/20) as well vulcanizates (V) in an air. Heating rate 10°C min⁻¹

Sample	T_g / °C	ΔE / kJ min ⁻¹	dm/dt/ % wt min ⁻¹	T_{DTGmax} / °C	T_{DTAmax} / °C
TOR	450	645.2	4.19	459	465
NR	303	143.4	4.07	371	365
B NR/TOR	323	176.6	2.43	380	463
V NR	305	158.7	2.32	368	338
V NR/TOR	325	179.4	1.73	373	448
SBR	400	172.8	3.30	408	427
B SBR/TOR	410	220.2	3.33	417	430
V SBR	395	137.8	2.54	408	457
V SBR/TOR	408	136.7	2.27	405	464
NBR	411	186.6	3.33	427	458
B NBR/TOR	424	209.6	2.18	435	445
V NBR	420	150.9	2.43	420	463
V NBR/TOR	435	169.8	2.09	424	466
EPDM	320	168.0	3.26	468	
B EPDM/TOR	414	331.1	3.51	471	
V EPDM	315	374.0	3.19	469	
V EPDM/TOR	340	367.9	1.63	477	
CR	277	159.7	1.90	360	460
B CR/TOR	287	140.2	2.11	355	453
V CR	310	709.6	9.11	308	
V CR/TOR	320	516.0	4.35	311	466
				442	455
				341	365
				340	362
				338	367
				358	402
				393	410
				398	417
				385	410
				400	414
				456	404
				364	406
				355	403
				359	405
				380	455
				417	453
				450	469
					482
				362	462
				355	441
				308	445
				312	445
					474
					522

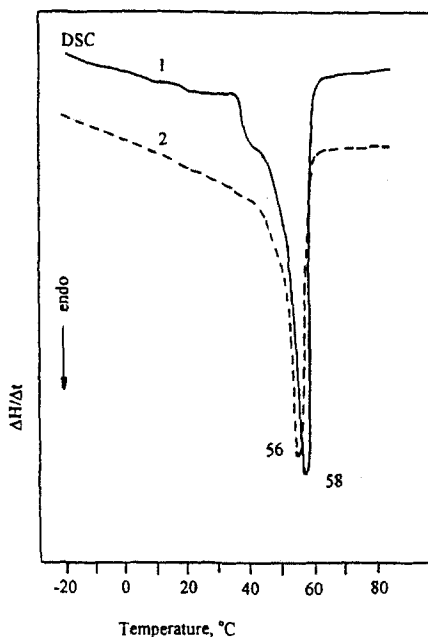


Fig. 6 DSC curves for TOR in nitrogen, the first heating (1) the second heating (2). Heating rate $8^{\circ}\text{C min}^{-1}$

low molecular weight unpolymeric components present in the rubber compounds, which decompose at lower temperature.

Differential scanning calorimetry studies show the very weak glass transition T_g of TOR at -65°C and the sharp endotherm transition T_m at 56°C corresponding to the melting of TOR crystalline phase. This transition is preceded by a lower endothermic transition in the range of 40°C probably associated with the solid – solid transformation of microcrystalline phase of TOR (Fig. 6). As we can see, during the repeated heating of the same sample of TOR, this transition could not be observed. DSC studies of the blends show no clear effect of TOR on the glass transition temperatures of the rubber. It has been also observed any distinct change in the character of thermal curve and melting temperature of TOR blended with diene rubbers.

Conclusions

Such significant effects of macrocyclic polymer (TOR) on thermal stability of EPDM and NR as measured by TG method could indicate some specific interaction in these systems on the molecular level. It is expected the formation of the special kind of intermolecular structures leading katenane or rotaxane structures which diminish the amplitude of fluctuation of linear macromolecules and consequently decrease the tendency to their thermal degradation.

Such hypothesis is confirmed by results of earlier investigations [14] indicating increase of crosslink density of NR and decrease of destruction of vulcanizates network (reversion) in the presence of TOR. The results of NMR tests made recently [16] confirm this assumption. ^1H NMR indicator which determines the distribution of crosslink concentration of double bonds in diene rubbers calculated for NR/TOR blends point out that these rubbers with addition of TOR show much lower thermal degradation. The research is continued, the results will be prepared for publication in the next future.

* * *

The work was supported by State Committee for Research, Poland. Grant No. 7.T08 E 032-08.

References

- 1 L. Reich and S. S. Stivlla, *Elements of Polymer Degradation*, Mc Graw Hill Book Co., New York 1971.
- 2 G. Geuskens, *Degradation and stabilization of polymers*, Applied Science Publishers Ltd., London 1975.
- 3 L. Ślusarski, *J. Thermal Anal.*, 29 (1984) 205.
- 4 A. K. Sircar, *Rubber Chem. Technol.*, 50 (1977) 71.
- 5 D. W. Brazier and N. V. Schwartz, *Rubb. Chem. Technol.*, 51 (1978) 1060.
- 6 T. Kleps, D. Jaroszynska and M. Piaskiewicz, *J. Thermal Anal.*, 36 (1990) 1213.
- 7 H. G. Braun and G. Rehage, *Macromol. Chemie*, 131 (1985) 107.
- 8 J. Lohmar, *Kautschuk, Gummi Kunstst.*, 39 (1986) 1065.
- 9 Vestenamer Product Information of Hüls AG. 2247/ 109 (1984).
- 10 K. M. Diedrich, G. Huhn and K. Zur Nedden, The technology of polyoctenamers in blends with natural rubber, "Elastomery '90" Scientific Conference, Piastów, Poland 1990.
- 11 S. Akhtar and S. K. De, *Kautschuk, Gummi Kunstst.*, 39 (1986) 327.
- 12 P. P. Chattaraj, R. Mukhopadhyay and D. K. Tripathy, *J. Elast. Plast.*, 26 (1994) 74.
- 13 P. P. Chattaraj, A. K. Kalidaha and R. Mukhopadhyay, *J. Elast. Plast.*, 28 (1966) 14.
- 14 M. Piaskiewicz, W. Parasiewicz and L. Ślusarski, *Polimery*, 38 (1993) 458.
- 15 L. Setiawan, D. Schönherr, B. Roß and A. Böhme, *Kautschuk, Gummi Kunstst.*, 45 (1992) 820.
- 16 Unpublished works of Research Rubber Institute, Poland.