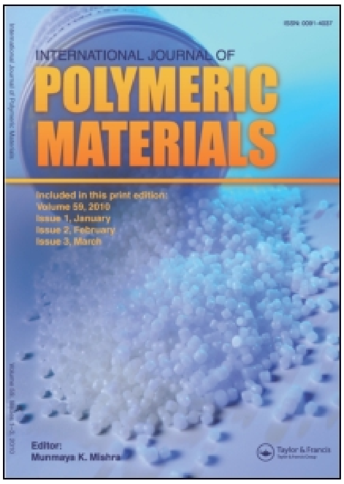

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Degradation and Stabilization of Polypentenamer

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Degradation and Stabilization of Polypentenamer

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The ageing of polypentenamers has been studied. The roles of molecular mass, of catalist used for the polymer preparation, and of antioxidants are discussed. The results of polymer ageing in the presence of various phenolic and amine-type stabilizers are described.

KEYWORDS: Polypentamer, degradation, stabilization, phenoles, amines, mechanism

The trans-polypentenamer rubber can be obtained by ring-opening polymerization of cyclopentene. This elastomer displays physical-mechanical properties similar to the natural rubber.

Stabilization of this synthetic rubber has been scarcely studied by various authors.[1,2] Owing to the particular role the use of some adequate stabilizers plays, in our paper we shall present several aspects concerning stabilization of the trans-polypentenamer rubber.

The study of thermo-oxidative degradation of the trans-polypentenamer rubber comprises: (i) determination of the influence of the average molecular mass of the polymer and (ii) determination of the influence of the catalytic system used in the synthesis.

The thermo-oxidative degradation was carried out into a glass apparatus where the polymer samples were introduced as very thin films. The behaviour during thermo-oxidative degradation was determined by measuring the induction period of oxidation which was evaluated as the time necessary for one gram of sample to absorb 10 ml of oxygen. The working temperature was chosen as to be 140°C.

In order to establish the influence of the molecular mass of the trans-polypentenamer on the behaviour during thermo oxidative degradation, samples of polymer having various molecular mass have been synthesized by using the following two catalytic systems;

I WCl_6-epichlorohydrin-iBu_3Al
II WCl_6-chloranil-iBu_3Al

The average molecular mass of the polymer samples as evaluated from the

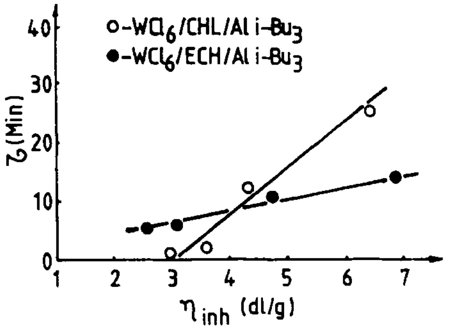

FIGURE 1 Variation of the induction period with the average molecular mass of the polymer.

inherent viscosity displayed values between 2.61–6.91 dl/g and 2.95–6.46 dl/g, respectively. The obtained data are represented in Figure 1.

As it can be observed from Figure 1, in the case of the samples synthesized with the catalytic system containing epichlorohydrin as activator, the variation of the induction period as a function of the polymer average molecular mass is small. By substituting epichlorohydrin with chloranil the measure of the induction period substantially increases with the increase of the average molecular mass of trans-polypentenamer.

Further studies on the behaviour during degradation of the trans-polypentenamer rubber containing various stabilizers in different concentration have been carried out. To compare the efficiencies of certain stabilizers the used samples were obtained from one polymerization reaction. The films resulted on evaporating the solvent in vacuum at 50°C were submitted to thermo-oxidative degradation in a drying chamber provided with air circulation at 120°C for 6 hr. At the same time these films were submitted to natural degradation at room temperature for 6 months.

The following stabilizers have been used:
Santoflex IP (N-isopropyl-*N*-phenyl-*p*-phenylenediamine)
Antioxidant H (*N*,*N*′-diphenyl-*p*-phenylenediamine)
Dinonyldiphenylamine
Antioxidant 2246 (2,2′-methylene bis(4-methyl)6-*t*-butylphenol)
Topanol OC (2,6-di-*t*-butyl-*p*-cresol)
Irganox 1076 (2,6-di-*t*-butyl-4-octadecylpropylphenol)

The efficiency of the stabilizer was determined by measuring the inherent viscosity of the polymer solution (toluene at 25°C) and the gel content. The obtained results using trans-polypentenamer rubber containing phenolic stabilizers are presented in Table I.

It can be observed that of the used phenolic stabilizers, the most efficient is Antioxidant 2246. This stabilizer imports to the trans-polypentenamer a good stability during thermo-oxidative degradation for 6 hr at 120°C even in 0.20% concentration as evidenced by the constant values of inherent viscosity of the samples and by the absence of gel. By contrast, polymer samples containing Irganox 1076 in 0.20% concentration exhibited a decrease of the average

TABLE I

Behaviour of trans-polypentenamer in the presence phenolic stabilizers

Stabilizer	Antioxidant 2246			Irganox 1076			Topanol OC		
Concentration, %	0.80	0.45	0.20	0.70	0.50	0.20	0.70	0.35	0.20
η inh. initial; dl/g	3.62	3.60	3.62	3.65	3.57	3.60	3.62	3.67	3.65
η inh. 3 hr, 120°C	3.58	3.45	3.50	3.18	3.35	3.11	3.51	3.06	1.23
gel content, %	—	—	—	—	—	—	—	6	28
η inh. 6 hr, 120°C	3.56	3.45	3.50	3.61	3.53	0.59	0.79	0.64	0.51
gel content, %	—	—	—	14	16	52	52	52	68
η inh, 6 months	3.68	3.58	3.06	3.37	3.22	3.12	3.60	3.65	3.34

molecular mass after 3 hr at 120°C while after 6 hr 52% of the polymer was transformed into gel. By using the above two stabilizers in higher concentration, e.g. 0.50 and 0.70, respectively, the gel formation in small amounts is found. On the other hand, polymer samples with Topanol OC in 0.20% concentration after 3 hr at 120°C exhibited lower inherent viscosity and gel formation. However, after 6 hr within the concentration range of 0.70–0.20% an advanced net-working of the polymer and fragmentation of the molecular mass was observed.

In Table I the obtained data during natural degradation of trans-polypentenamer are presented. It may be seen that for all the concentration of Antioxidant 2246 and Topanol OC used the inherent viscosity the final polymer was similar, to that of the initial one. Only for polymer containing Irganox 1076 a small tendency in decreasing the average molecular mass was found.

The different behaviour of the trans-polypentenamer samples containing Topanol OC during thermo-oxidative and natural degradation may be assigned to the higher volatility of this stabilizer at higher temperatures as compared to other stabilizers.

The data obtained with trans-polypentenamer samples with aminic stabilizers are given in Table II.

It can be observed that of these three stabilizers only Santoflex IP imparts to the trans-polypentenamer rubber a good stability to thermo-oxidative degradation even at small concentration (e.g. 0.10%). Furthermore, the results with this stabilizer are better than those obtained with Antioxidant H. In its presence in concentration of 0.20–0.75% the trans-polypentenamer samples maintain their initial inherent viscosity during 3 hr at 120°C. However, after 6 hr the polymer

TABLE II

Behaviour of trans-polypentenamer in the presence aminic stabilizers

Stabilizer	Santoflex IP			Antioxidant H					DNDPhA		
Concentration, %	0.80	0.45	0.20	0.10	0.75	0.50	0.20	0.10	0.80	0.50	0.20
η inh, initial, dl/g	3.67	3.65	3.67	3.63	3.70	3.72	3.66	3.68	3.58	3.60	3.65
η inh, 3 hr, 120°C	3.53	3.53	3.58	3.61	3.58	3.59	3.62	2.66	3.52	2.57	3.01
gel content, %	—	—	—	—	—	—	—	20	—	12	36
η inh, 6 hr, 120°C	3.65	3.62	3.63	3.64	3.60	0.71	0.62	0.67	3.62	1.12	0.58
gel content, %	—	—	—	—	—	54	56	60	—	40	64
η inh, 6 months	3.62	3.59	3.51	3.58	3.66	3.68	3.62	0.50	3.69	3.73	3.59
gel content, %	—	—	—	—	—	—	—	80	—	4	16

reticulates forming 54–60% gel except for the sample containing the highest amount of Antioxidant H (e.g. 0.75%). It can be also seen from Table II that dinonyldiphenylamine is a similar stabilizer to Antioxidant H; it is efficient in trans-polypentenamer at thermo-oxidative degradation only in concentration of 0.80%.

By comparing these results with those obtained during natural degradation it can be observed that either the samples with Santoflex IP between 0.10 and 0.80% or Antioxidant H between 0.20–0.70% do not change their molecular mass, the values of inherent viscosity being practically constant. From Table II it can be also seen that dinonyldiphenylamine protect the trans-polypentenamer rubber at room temperature for 6 months only in concentration of 0.80% in respect to the polymer.

The data presented in Table I and II suggest that of the studied stabilizers only Antioxidant 2246 and Santoflex IP are efficient during thermo-oxidative degradation even in low concentration of 0.20%. From the obtained results during natural ageing for 6 months the Antioxidant 2246 and Topanol OC on one side and the Santoflex IP and Antioxidant H on the other contribute satisfactorily to maintaining the physical-chemical characteristics of the trans-polypentenamer rubber.

In order to point out the structural changes of the trans-polypentenamer, polymer samples as films containing 0.2% stabilizer were submitted to thermo-oxidative degradation at 120°C. The films were analized spectrophotometrically by IR method.

To identify the functional groups having oxygen, the IR spectra of both the initial and degraded film were recorded. In this way it could be found that in the films treated thermo-oxidatively certain wide bands in the region 1600–1800 cm^{-1} corresponding to C=O groups as well as in the region 3300–3600 cm^{-1} corresponding to —OH and —OOH groups appear.

In Figure 2 the IR spectrum of the initial and degraded sample is represented.

Parallel studies by differential calorimetric method have been carried out in view of obtaining further data on the efficiency of various stabilizers used in trans-polypentenamer. This method allowed also to compare the thermal stability of the unstabilized trans-polypentenamer rubber with that of other unstabilized synthetic rubber. The results obtained are given in Table III.

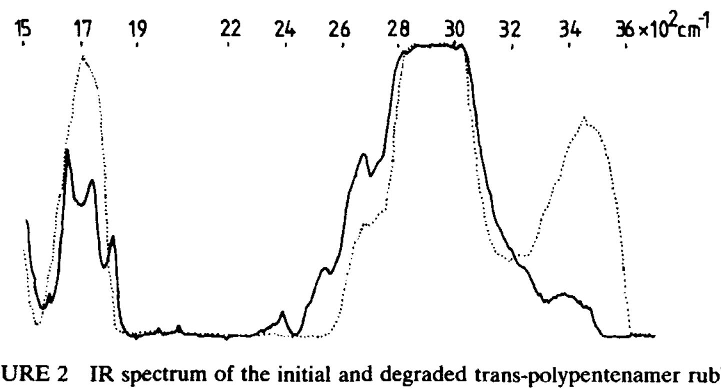

FIGURE 2 IR spectrum of the initial and degraded trans-polypentenamer rubber.

TABLE III

Initial temperature and heat of oxidation of some synthetic rubbers

Rubber	T_i, °C	ΔH_{OX}, KJ/Kg	References[a]
cis-1,4-polybutadiene	133	5016	4186
cis-1,4-polyisoprene	134	3177	
trans-polypentenamer	146	4598	

[a] V. Gonzales, *Rubber Chem. Technol.* **54**, 134 (1980).

As it can be seen the value of the heat of oxidation of the trans-polypentenamer ranges between that of cis-1,4-polybutadiene and cis-1,4-polyisoprene. It is remarkable that for cis-1,4-polybutadiene a higher value than that reported by Gonzales (e.g. 4186 KJ/Kg,[3]) has been obtained, probabily due to the fact that the thermo-oxidative process has been more advanced in this case.

Analysis by DSC of the trans-polypentenamer samples containing different stabilizers is presented in Table IV. (Both the initial thermo-oxidation temperatures and the activation energies are given.)

As it can be observed from Table IV, addition of a stabilizer even at small concentration increases the temperature at which the oxidation exotherm appears and the activation energy. These data indicate that Antioxidant 2246 is similar to Irganox 1076 for the trans-polypentenamer rubber.

In Table V results obtained by DSC using aminic stabilizers are presented.

It can be readily seen that Santoflex IP is the most efficient amine stabilizer even at low concentration of 0.20%.

In order to compare the obtained results, the DSC thermograms of unstabilized and stabilized trans-polypentenamer rubber are represented in Figure 3. The trans-polypentenamer rubber was stabilized with 0.80% of the following stabilizers: dinonyldiphenylamine, Antioxidant H, Irganox 1076 Antioxidant 2246, Santoflex IP.

As it can be observed degradation of the samples stabilized with 0.80% Santoflex IP or Antioxidant 2246 appears at highest temperature.

The effect of concentration of various stabilizers on the initial thermo-oxidative temperature is represented in Figure 4.

TABLE IV

Efficiency of the phenolic stabilizers for trans-polypentenamer

Stabilizer	Antioxidant 2246			Irganox 1076			Unstab.
Concentration, %	0.80	0.45	0.20	0.70	0.50	0.20	—
T_i, °C	189	184	163	179	171	163	146
E_2, KJ/mol	104.4	94.5	84.7	103.5	97	85.6	83.2

TABLE V

Efficiency of the amine stabilizers

Stabilizer	Santoflex IP			Antioxidant II			DNDPHA		
Concentration, %	0.80	0.45	0.20	0.75	0.50	0.20	0.80	0.50	0.20
T_i, °C	186	183	173	162	158	156	171	162	148
E_a, KJ/mol	138	135	128	162	95.4	89.9	100	91.2	84

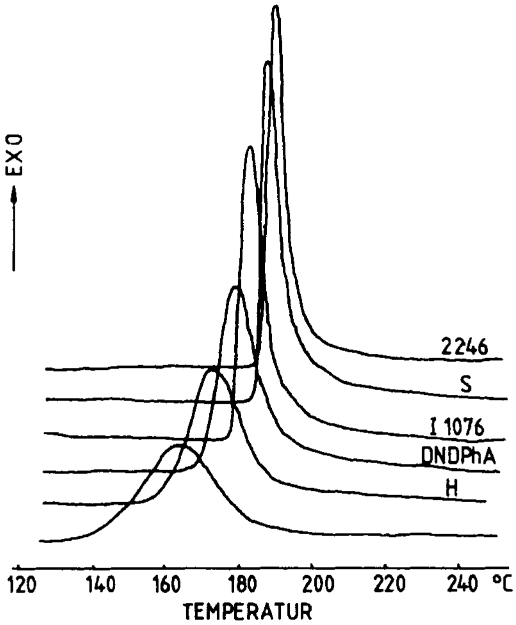

FIGURE 3 DSC thermograms of unstabilized and stabilized trans-polypentenamer rubber.

The figure shows that the efficiency of stabilizer Santoflex IP is similar to Antioxidant 2246 while that of the other stabilizers decreases in the following order:

Irganox 1076 > dinonyldiphenylamine > Antioxidant H

Determination of the activation energies was carried out by the Kissinger–Ozawa method.[4] In Figure 5 the effect of the concentration of stabilizer as a function of the activation energy is represented.

In conclusion, degradation of the trans-polypentenamer rubber in the presence

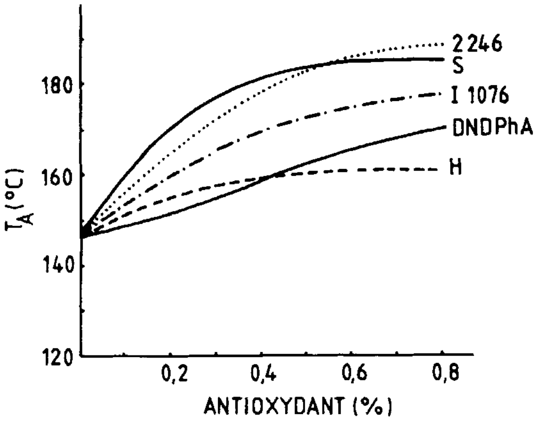

FIGURE 4 Variation of the initial degradation temperature with stabilizer concentration.

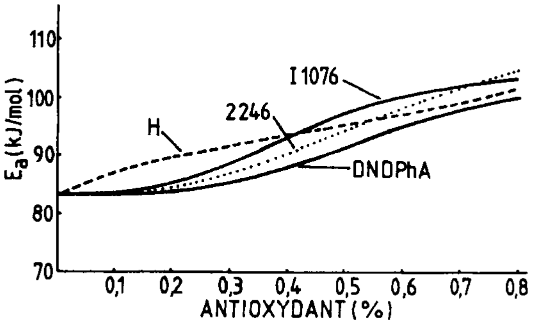

FIGURE 5 Variation of activation energy with stabilizer concentration.

of various phenolic and aminic stabilizers was examined. From the presented data it follows that of the above stabilizers the most efficient are Santoflex IP and Antioxidant 2246 but other ones can also be used in a higher amount in respect to the polymer.

References

1. K. B. Piotrovski and V. T. Smirnova, *J. Prikl. Him.* **50**, nr. 11, 2613 (1978).
2. V. T. Smirnova, T. D. Escenko, Iu. A. Lvov and B. D. Babiţki, *Prom. Sint. Kauc. nr.*12, 7 (1984).
3. V. Gonzalez, *Rubber Chem. Technol.* **54**, 134 (1980).
4. T. Ozawa, *J. Therm. Anal.* **9**, 369 (1976).