

THERMAL PROPERTIES OF CIS-1,4-POLY(BUTADIENE)

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Abstract

Thermal properties of *cis*-1,4-poly(butadiene), Europrene *cis*, were investigated by means of thermal analysis and complementary methods. Thermal analysis of polymer was carried out both in air and inert atmosphere with a derivatograph, DSC and internal TG-FTIR coupling system as well as internal TG, DTA-MS coupling system. It was found that investigations in air atmosphere the method of the sample preparation of *cis*-1,4-poly(butadiene) influences the results of thermal analysis, which is connected with the rate oxygen diffusion into the reaction zone. Taking into consideration both the method of the sample preparing and atmosphere of thermal studies, the values of activation energy of destruction of *cis*-1,4-poly(butadiene) were determined. Using TG-FTIR and TG-MS methods, some products of thermal destruction of elastomer were determined.

Keywords: DTA, DTA-MS, DSC, elastomer, polybutadiene, TG, TG-FTIR, TG-MS, thermal properties, thermal stability

Introduction

It was found that energy of valence bonds, generally considered as the main parameter of elastomer structure determining their thermal stability [1–3], is not always the most important factor. Our investigations have proved that differences in the thermal stability of elastomers mainly result from the character of their chemical reactions at elevated temperature [4, 5]. The elastomers able to crosslink as a result of their heating prove greater thermal stability because entanglement of macroradicals generated in the increased crosslink density zone favours their stabilization. Thermally initiated cross-polymerization of monomer units also decreases the fluctuation of macromolecules and a rate of oxygen diffusion to the reaction zone is locally restricted [5].

One of the elastomers able to crosslink during its heating is *cis*-1,4-poly(butadiene). In this work the thermal properties of this polymer, commonly used in rubber industry, has been presented.

Experimental

Materials

The object of investigations was *cis*-1,4-poly(butadiene), Europrene *cis*, containing 93% of *cis*-1,4 units, with molecular mass, $M_v=373\ 000$ [6].

Methods

The thermal analysis of polymer was carried out with the following apparatus: derivatograph (MOM-Hungary; DSC 204 (Netzsch)); Biorad 175C spectrometer (FTIR); internal TG-FTIR coupling system (Netzsch, Bruker instruments); internal TG, DTA-MS coupling system (TA instruments).

The samples for simultaneous thermal analysis were prepared by cutting out disks of the pressed elastomer, having the diameter of 16 ± 0.05 mm, equal to the diameter of the platinum plate of the apparatus. The thickness of the disks was 0.5 ± 0.05 mm. At the same time, using microtome, samples prepared by disintegration of elastomer into small cubes about 1 mm in size were also tested. The analysis was carried out under the following conditions: air atmosphere, standard substance Al_2O_3 , temperature range 25–800°C, sample mass 90 mg, heating rate 7.9°C min⁻¹.

DSC analysis was carried out in nitrogen atmosphere, temperature range 20÷–130 and –130÷+500°C, sample mass 6.9 mg, heating rate 10°C min⁻¹.

FTIR analysis was made before and after heating of poly(butadiene) in the form of film on KBr.

TG–FTIR analysis was carried out in nitrogen, temperature range 30÷550°C, sample mass 21.5 mg, heating rate 8.0°C min⁻¹.

TG–MS analysis was carried out in helium, temperature range 20÷550°C, sample mass 27 mg, heating rate 8°C min⁻¹.

The cross-link densities were determined by the equilibrium swelling method in toluene at 25°C. The activation energies of destruction of polybutadiene were calculated by Freeman–Carroll method [7]. The elemental analysis was also used.

Results and discussion

The chemical reactions of *cis*-1,4-poly(butadiene) in air atmosphere start after its heating to temperature of 190°C (Fig. 1). The observation is also of practical importance because some rubber goods containing *cis*-1,4-poly(butadiene) e.g. tyres are vulcanized at temperature as high as 200°C. The first exothermic peak at 220°C is a symptom of thermooxidative reactions. The small mass gained in the temperature range of 190÷220°C, visible both on TG and DTG curves, is connected with the increasing concentration of hydroperoxide groups [6, 8]. Decomposition of these groups generates radicals initiating cross-polymerization of butadiene monomer units, which brings about the elastomer crosslinking, independently of the method of sample preparation for investigation (Table 1) [4–6]. Temperature of 200°C is the limit of thermal

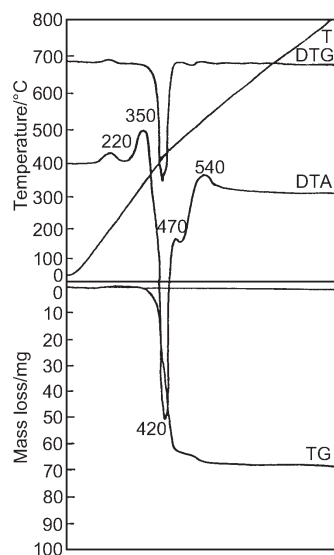


Fig. 1 The thermal curves of *cis*-1,4-poly(butadiene) (sample in the form of film) in air atmosphere

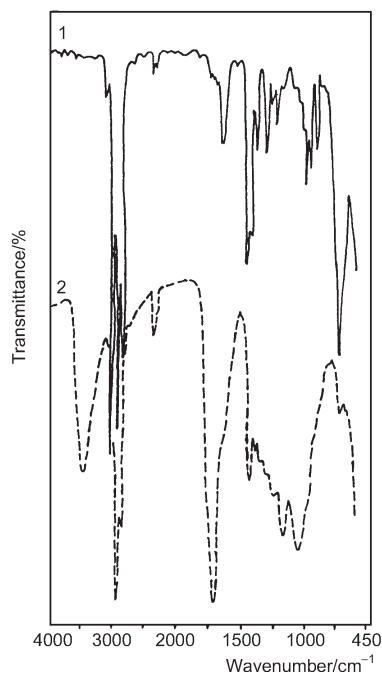


Fig. 2 FTIR spectrum of *cis*-1,4-poly(butadiene). 1 – before heating, 2 – after heating to temperature of 220°C in the derivatograph furnace in the form of film on sodium chloride plate

stability of diene elastomers in air atmosphere [9]. We have stated that heating of poly(butadiene) in the form of film on sodium chloride plate in the derivatograph furnace to 220°C causes significant changes in the FTIR spectrum (Fig. 2). Nearly total disappearance of bands at 912, 967, 994 and 1654 cm⁻¹ corresponds to the reaction of double bonds with free radicals [4, 10] which leads to the crosslinking of polymer (Table 1). Transmittance increasing in the range of 1000–1400 cm⁻¹ and new bands appearing in 1062 and 1180 cm⁻¹ proceeds from C–O bonds in alcohols, ethers or esters. New bands in 1718 and 3454 cm⁻¹ indicate the presence of C=O and OH groups, respectively. Therefore, heating of *cis*-1,4-poly(butadiene) at 200°C in air leads to the formation of mixture of products containing alcohol, aldehyde, ketonic or ester groups. Esters can be formed as a result of recombination of radicals and they are the secondary products of oxidation of polybutadiene [11].

Processes of thermal crosslinking of polybutadiene also occur in the range of the second exothermic transition. They are accompanied by cyclization and destruction of macromolecules [12]. Reactions of destruction take place particularly clearly in the case of the disintegrated sample (Table 1).

Table 1 The results of thermal analysis of *cis*-1,4-poly(butadiene)

	Sample			
	in form of film		disintegrated	
Temperature of transition/°C	220	350	220	360
Mass loss of the sample/%	0	0.9	0	2.1
Elementary analysis/%	C=87.29	C=88.17	C=86.79	C=88.21
	H=11.48	H=10.65	H=10.99	H=10.70
	O= 1.23	O= 1.18	O= 2.22	O= 1.09
Crosslink density, $\nu \cdot 10^5$, mol cm ⁻³	2.19	3.90	2.19	6.8
Activation energy of destruction/kJ mol ⁻¹		268.8		246.2

The results of elementary analysis of the sample before heating: C=87.97%, H=11.02%, O=1.01%.
Calculated values: C=89.89%, H=11.11%

The thermal decomposition of *cis*-1,4-poly(butadiene) in air starts at 360°C (Fig. 1). The negative thermal effect of these transitions indicates that decomposition products of elastomer are not oxidized in a significant grade because of insufficient oxygen diffusion rate in the reaction zone. The exothermic peak on DTA curve at 540°C is a symptom of combustion of small residue after thermal decomposition of polymer.

DSC curves of *cis*-1,4-poly(butadiene) obtained in inert atmosphere are presented in Fig. 3. During cooling of elastomer in the temperature range of 20÷–130°C its glass transition can be observed at –109°C (curve 1, Fig. 3). The glass transition of polybutadiene heated from –130 to 500°C occurs at –104 and next at –53°C polymer crystallizes. The small endothermic peak at –23°C is connected with melting of the crystalline phase. The great exothermic transition on DSC curve at 370°C is connected with crosslinking, degradation, and cyclization processes [4, 12, 13]. The thermal decomposition of polymer in inert atmosphere starts at 400°C (Fig. 4). The value

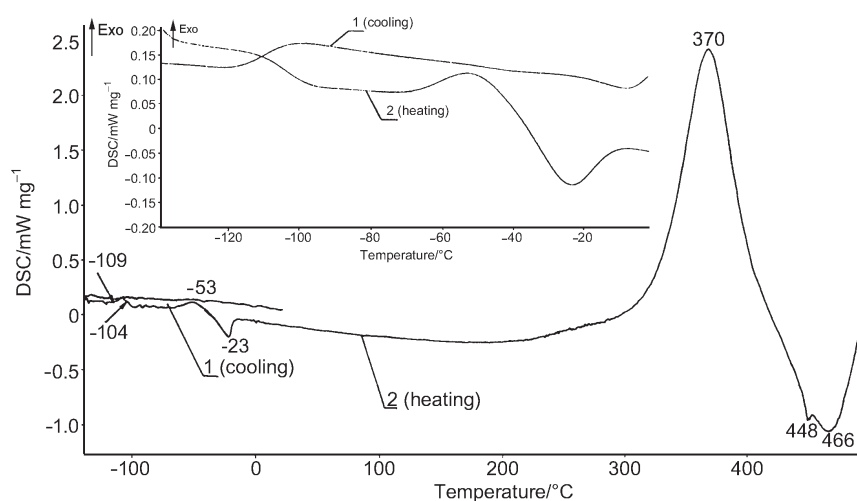


Fig. 3 DSC curves of *cis*-1,4-poly(butadiene) in inert atmosphere

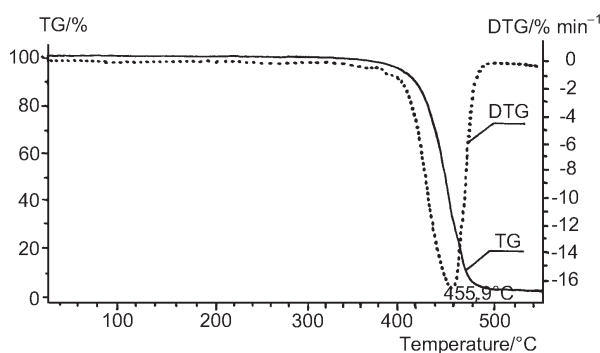


Fig. 4 TG, DTG curves of *cis*-1,4-poly(butadiene) in inert atmosphere

of activation energy of destruction of polybutadiene in inert atmosphere is greater than in air atmosphere and it is equal to $E_a=344 \text{ kJ mol}^{-1}$.

Figures 5 and 6 show the results of TG-FTIR analysis of *cis*-1,4-poly(butadiene). Taking into consideration the first curve (Fig. 6) it could be deduced that at 400 °C the mixture of volatile products is formed containing monomer-bands in the range of 900–667 cm^{-1} and other hydrocarbons – 2926, 2863 and 1456 cm^{-1} . Bands in 1456 and 1368 cm^{-1} can be connected with the presence of the methane and ethane [14]. The composition of volatile products formed at 425 and 445 °C is quite similar (curves 2 and 3, Fig. 6). The mixture of hydrocarbons with a little amount of monomer is formed at 470 °C. The results of TG-MS analysis stated that bands in the range 900–667 cm^{-1} are connected with the presence of 1,3-butadiene and 1,2-butadiene (Fig. 7). The bands in 2926, 2863 and 1450 cm^{-1} are connected among other with the presence of methane, ethane, propylene, methylcyclohexane and toluene.

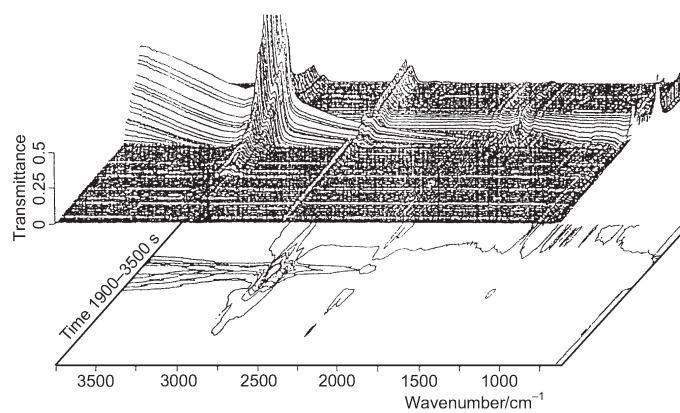


Fig. 5 Contour diagram of the volatile products of thermal decomposition of *cis*-1,4-poly(butadiene)

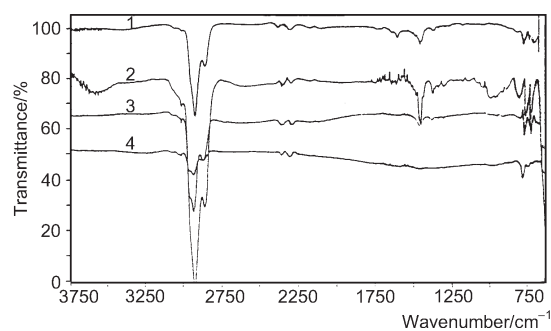


Fig. 6 FTIR curves of the volatile products of thermal decomposition of *cis*-1,4-poly(butadiene): 1 – $T=400^{\circ}\text{C}$, 2 – $T=426^{\circ}\text{C}$, 3 – $T=444^{\circ}\text{C}$, 4 – $T=455^{\circ}\text{C}$

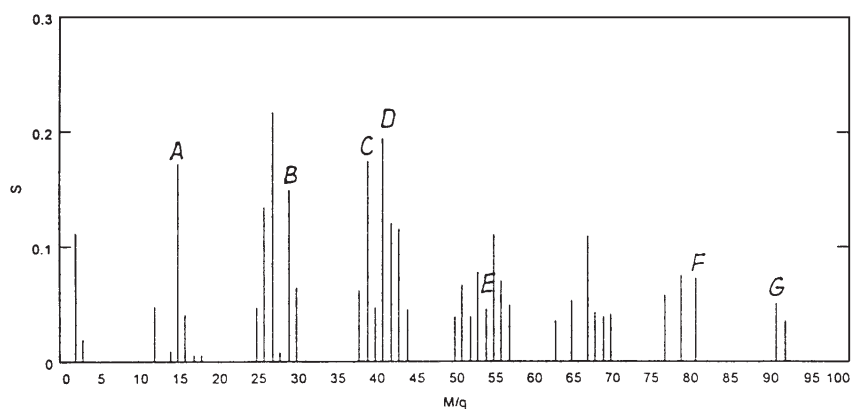


Fig. 7 The results TG, DTA-MS analyse of *cis*-1,4-poly(butadiene). Mass spectrum obtained at temperature of 444°C . M/q =mass/charge. A – methane, B – ethane, C – 1,3-butadiene, D – propylene, E – 1,2-butadiene, F – methylcyclohexene, G – toluene

(R_1) (R_2) and (R_3) macroradicals initiate crosslinking, cyclization and depolymerization processes of polymer.

Conclusions

1. In air atmosphere the method of the sample preparation of *cis*-1,4-poly(butadiene) affects the results of thermal analysis, which is connected with the rate of oxygen diffusion into the reaction zone.
2. Because of great reactivity of *cis*-1,4-poly(butadiene) to oxygen, particularly at elevated temperature, its thermal reactions prove greater efficiency and smaller destruction activation energy in air than in inert atmosphere.
3. Thermal decomposition of *cis*-1,4-poly(butadiene) proceeds through series of parallel and consecutive reactions. Therefore, using TG-FTIR and TG-MS methods to study compositions of products of thermal destruction of elastomers requires the preliminary separation of these products.

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