THE INFLUENCE OF THE METHOD OF BUTADIENE RUBBERS CROSS-LINKING ON THEIR THERMAL PROPERTIES

G. Janowska[*] *and A. Kucharska*

Faculty of Chemistry, Institute of Polymers and Dye Technology, Technical University of Łódź, Łódź, Poland

The paper presents results of thermal properties measurements of *cis*-1,4-polybutadienes with different contents of *cis*-1,4 mers before and after their conventional cross-linking with the use of dicumyl peroxide and non-conventional cross-linking by means of iodoform. The measurements were carried out under the atmosphere of neutral gas using a micro-calorimeter, DSC and thermogravimetry, TG. The thermal curves have been interpreted from the point of view of phase transitions and chemical reactions of investigated elastomers.

Keywords: conventional cross-linking, crystallization, DSC, glass transitions, non-conventional cross-linking, polybutadienes, TG, thermal analysis, thermal curves, thermal cross-linking, thermal properties

Introduction

The main structural parameter of elastomers responsible for their thermal stability is the energy of valence bonds in the macromolecule skeleton [1–3]. The cross-linking of elastomer generally increases its thermal stability, mainly due to the limitation of fluctuation amplitude of macromolecules. In the case of low-density elastomer lattices, this effect however is not clear. Besides, the energy of chemical bonds in some types of lattice points is lower than that in the main chain. Thus, it is particularly difficult to assess the influence of cross-linking substances on thermal stability as some of them undergo thermal decomposition, while the resultant low-molecular radical, often with a high activity, initiate various reactions of macromolecules.

The paper presents the results of the thermal properties studies of commonly used in the rubber industry butadiene rubbers before and after their conventional and non-conventional cross-linking.

Experimental

Under our investigation were two butadiene rubbers: *cis*-1,4-polybutadiene, SKDII and *cis*-1,4-polybutadiene, BR1220 (Table 1). They were examined also after their conventional cross-linking by means of dicumyl peroxide, DCP [4–6] and non-conventional cross-linking with the use of iodoform, CHI$_3$.

Viscosity-average molecular mass, M_v, was determined using the Ubbelohde viscometer and toluene as the solvent. The temperature of measurements was 30°C. The following values of constants were used: K·10^3[mL g^{-1}]=33.9; α=0.688 [7].

The composition of the conventional elastomer mixture was as follows: 100 parts by mass of SKDII or BR 1220, 0.2 phr (parts by mass per hindered parts by mass of rubber) dicumyl peroxide (purity 95%) of Merck-Schuchard and 5 phr ZnO. Non-conventional elastomer mixture consisted of 100 parts by mass SKDII or BR1220 and 5 phr iodoform of Aldrich Chemical Company.

Table 1 Characteristic of butadiene rubbers

Trademark	Producer	Percentage of *cis*-1,4 mers*	Composition/** %	Molecular mass, M_v
SKDII	Russia	87–93	C=88.60 H=10.79 S=0.51 O=0.10***	243 000
BR1220	The Dow Chemical Company	min 95	C=88.46 H=10.74 S=0.30 O=0.50	312 931

*based on data from producer;**results of elemental analysis;***make a complement to 100%

* Author for correspondence: janowska@p.lodz.pl

Rubber compounds prepared with the use of a laboratory rolling mill at room temperature were vulcanised in an electrical press at 160°C. The optimal time of vulcanization was found by means of a WG-02 vulcameter according to PN-ISO 3417:1994.

The thermal analysis of elastomers [8] was carried out in inert atmosphere by means of differential scanning calorimetry of Netzsh, DSC-204 and thermogravimetry of Netzsch, TG-209, using portions of about 5 mg at heating rate of 10°C min⁻¹ within temperature range 20÷–150 and –150÷500°C in the case of DSC measurements and 20÷500°C in the case of TG measurements.

Results and discussion

Cis-1,4-polybutadiene, SKDII, during cooling passes from the elastic to the glassy state at $T=$ –113.50°C (Fig. 1, Table 2). Its transition from the glassy to the elastic state takes place during heating at T= –106.0°C. The temperature range associated with this phase transition is considerably narrower during its heating than during cooling. At $T=$ –55.5°C, a small exothermic peak is recorded in the DSC curve connected with the polymer crystallisation. Taking into account the change of enthalpy of this process (Fig. 1, Table 2), it proceeds with a slight yield. The processes of thermal crystallisation of elastomers proceed with difficulty as due to a high segmental mobility of their macromolecules, the life-period of ordered areas is very short and only few of them are transformed into thermodynamically stable crystallisation nuclei. The crystalline phase is melted at $T=$ –23.7°C. At $T=269.9$°C the DSC curve shows the beginning of a great exothermic transition brought about by the thermal cross-linking of rubber SKDII (Fig. 1), with its maximum rate being at $T=372.5$°C. The considerable change in the enthalpy of these processes shows that they proceed with a high yield as it is a radical polymerisation of butadiene mers [9–13]. The final stage of thermal cross-linking

is accompanied by commencing destruction processes (Fig. 3). The sample weight loss after the termination of thermal cross-linking processes amounts to 5%. The temperature of maximum destruction rate of the thermally cross-linked SKDII is observed at 475.1°C.

The crystallisation processes of BR1220 take place during its cooling as manifested by the exothermic peak at $T=$ –43.7°C (Fig. 2). Taking into consideration the change of enthalpy brought about by this transition, one should state that the crystallisation of BR1220 proceeds with a clearly higher yield than that of SKDII (Table 2). This results from the higher content of mers with *cis*-1,4 structure, which in the case of BR1220 amounts to min. 95% according to the manufacturer's data (Table 1). The crystalline phase-containing rubber passes into the glassy state at $T=$ –113.1°C. The glass transition temperatures of SKDII and BR1220 are the same and included within the same range, but the change in position of the base-line brought about by the change in the thermal capacity of BR1220 is considerably less clear than in the case of SKDII. This is undoubtedly due to the sooner development of the crystalline phase in BR1220. The transition from the glassy to the elastic state of this rubber takes place at $T=$–106.9°C and then at $T=$–65.9°C the crystalline phase begins to melt, which is continued within a wide temperature range (Fig. 2, Table 2), which is considerably wider than that of its crystallisation. A wide temperature range of this phase transition indicates the presence of areas with different degrees of order and different contents of defects.

The processes of thermal cross-linking of BR1220 start at a higher temperature as compared with SKDII, but the change of enthalpy clearly indicates that they proceed with a comparable yield. A considerably higher yield of the thermal cross-linking of BR1220 is observed after its extraction with acetone (Table 2, sample BR1220e).

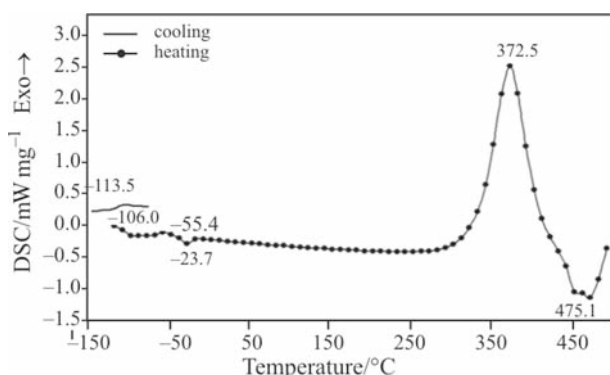The cross-linking of *cis*-1,4-polybutadiene, SKDII, by means of dicumyl peroxide (DCP) does not change
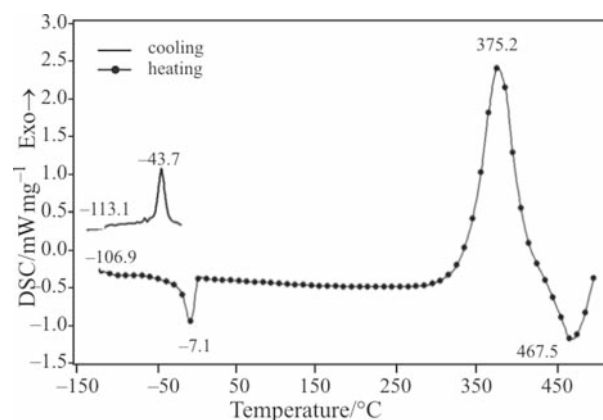

Fig. 1 DSC curve of SKDII

Fig. 2 DSC curve of BR1220

Table 2 The results of thermal analysis of butadiene rubbers elastomers in nitrogen atmosphere

Sample	Cooling										Heating						
	T_g/°C	ΔT_g/°C	T_c/°C	ΔT_c/°C	ΔH_c/Jg⁻¹	T_g/°C	ΔT_g/°C	T_c/°C	ΔT_c/°C	ΔH_c/Jg⁻¹	T_m/°C	ΔT_m/°C	ΔH_m/Jg⁻¹	T_{tc}/°C	ΔT_{tc}/°C	ΔH_{tc}/Jg⁻¹	T_d/°C
SKDII	−113.5	−108.9÷ −118.0	—	—	—	−106.0	−108.2÷ −103.8	−55.4	−76.6÷ −42.6	6.11	−23.7	−42.6÷ −15.8	−7.9	372.5	269.9÷ 430.9	931.2	475.1
SKDII DCP	−113.2	−106.7÷ −119.8	—	—	—	−107.4	−110.7÷ −104.1	−57.8	−77.0÷ −43.5	3.85	−29.8	−43.5÷ −22.3	−4.9	375.0	257.1÷ 431.1	780.0	472.0
SKDII I	−109.7	−102.4÷ −117.0	—	—	—	−102.0	−103.1÷ −101.0	—	—	—	—	—	—	286.5	158.6÷ 402.2	943.0	469.9
BR1220	−113.1	−110.2÷ −115.9	−43.7	−26.2÷ −60.9	45.7	−106.9	−109.7÷ −104.1	—	—	—	−7.1	−65.0÷ 1.8	−50.0	375.0	281.8÷ 430.6	914.7	467.5
BR1220 e	−110.8	−106.2÷ −115.5	−45.6	−33.7÷ −73.6	45.3	−105.6	−108.2÷ −103.1	—	—	—	−7.7	−49.5÷ 1.1	−48.8	376.0	268.5÷ 435.0	1025.0	470.9
BR1220 DCP	−113.1	−115.1÷ −112.7	−48.3	−30.2÷ −65.8	40.7	−109.9	−114.3÷ −106.6	—	—	—	−17.4	−63.6÷ −5.9	−41.2	373.0	264.5÷ 432.5	909.0	469.0
BR1220 I	−111.3	−105.8÷ −116.4	−62.7	−47.9÷ −85.3	7.4	−105.1	−107.7÷ −102.4	−55.5	−80.1÷ −36.0	12.2	−21.6	−36.0÷ −11.0	−14.7	284	183.4÷ 410.7	1055	468.9

SKDII – non cross-linking rubber; SKDII DCP – rubber SKDII cross-linking by DCP; SKDII I – rubber SKDII cross-linking by CHI3; BR1220 – non cross-linking rubber; BR1220 e – rubber BR1220 extract by acetone in $t=48$ h; BR1220 DCP – rubber BR1220 cross-linking by DCP; BR1220 I – rubber BR1220 cross-linking by CHI3; T_g – glass transition temperature; ΔT_g – temperature range of glass transition; T_c – temperature of crystallization; ΔT_c – temperature range of crystallization; ΔH_c – change of crystallization enthalpy; T_m – melting point; ΔT_m – temperature range of melting point; ΔH_m – change of melting enthalpy; T_{tc} – temperature of thermal cross-linking; ΔT_{tc} – temperature range of thermal cross-linking, max. rate; ΔH_{tc} – change of thermal cross-linking enthalpy; T_d – temperature of destruction max. rate.

the character of its thermal transitions under the atmosphere of neutral gas. The glass transition temperatures of this elastomer before and after its cross-linking are comparable. On the other hand, under the influence of cross-linking its crystallisation temperature and yield are decreased (Table 2). This is due to the processes of cis-trans isomerisation, which proceed during elastomer vulcanisation at T=160°C. The cross-linking of polymer decreases also the melting point of the SKDII crystalline phase. The enthalpy of this transition is also lower. From the analysis of enthalpy values connected with thermal cross-linking it clearly follows that the cross-linking of SKDII with the use of DCP limits the processes of polymer thermal cross-linking (Table 2). Also in this case, the final stage of cross-linking processes is accompanied by a thermal decomposition reaching 7% (Fig. 3).

In the scientific literature one can find only few studies concerning thermal properties of non-conventionally cross-linked elastomers by means of iodoform, one of the oldest antiseptics [14–16]. The investigations carried out at the Institute of Polymer and Dye Technology (Technical University of Łódź) have not resulted as yet in the ultimate explanation of the mechanism of elastomer cross-linking with the use of this compound. It is known, however, that this mechanism may be ionic as well as radical and similarly as in the case of DCP, it leads to the formation of C–C lattice points, which is accompanied by the cis-trans isomerisation and the modification of rubber macromolecules with either iodoform or products of its decomposition [15, 16]. The cross-linking of SKDII with iodoform changes the thermal properties of the polymer (Fig. 4, Table 2) and considerably increases its T_g during sample heating as well as cooling. In our opinion, it is a symptom of intensified interactions of macromolecules resulting from their modification with iodine compounds [14]. SKDII cross-linked with iodoform does not crystallise, which results from the
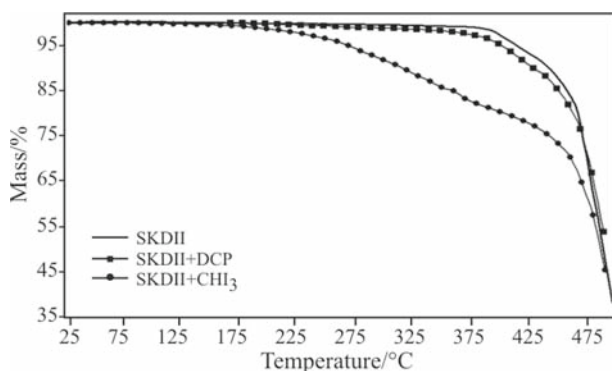
mentioned above cis-trans isomerisation processes, whose contribution to the vulcanisation of diene rubbers in the presence of iodoform is considerable [14]. The cross-linking of SKDII with the use of iodoform considerably decreases the temperature of elastomer cross-linking processes (Fig. 4, Table 2). They start already at T=158.6°C, while their maximum rate is observed at T=286.5°C. From the analysis of DSC curve it follows that the thermal cross-linking of the non-conventionally cross-linked SKDII proceed in two stages (Fig. 4). In our opinion, the first stage at ΔT=(158.6÷286.5)°C is brought about by the presence of products of both homo- and heterolytic decomposition of CHI_3, while the clear notch in the sloping part of exotherm at T=348.5°C results from the thermally initiate polymerisation of diene mers. Therefore, the processes of thermal cross-linking proceed within a wide temperature range and the accompanying processes of thermal decomposition bring about an 18% loss of initial sample mass (Fig. 3).

The non-conventional cross-linking of BR1220 with the use of iodoform considerably limits its ability to crystallisation that proceeds in two stages. The first stage takes place during sample cooling at T= –62.7°C and the second stage during its heating at T= –55.5°C, after the transition of polymer from the glassy to the elastic state (Fig. 5, Table 2). In our opinion, the thermal modification of BR1220 macromolecules during the vulcanisation in the presence of iodoform proceeds to a clearly lesser extent than that of SKDII. This is also confirmed by the higher temperature at which begins the thermal cross-linking of BR1220 initially proceeding with the contribution of CHI_3 products. On the other hand, the thermally initiated polymerisation of diene mers begins, similarly as in the case of SKDII, at T=350°C (Figs 4 and 5, Table 2). The sample mass loss accompanying the processes of thermal cross-linking of BR1220 amounts to 18%.

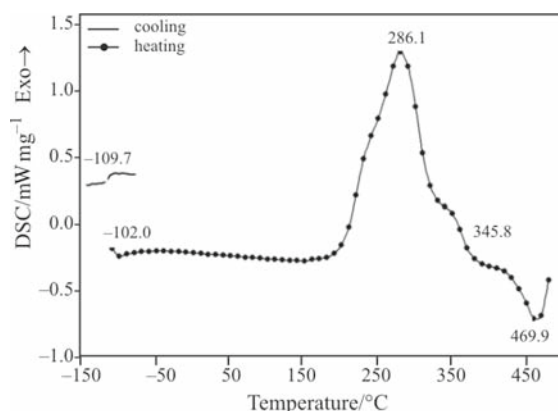**Fig. 3** TG curves of SKDII after conventional and non-conventional cross-linking

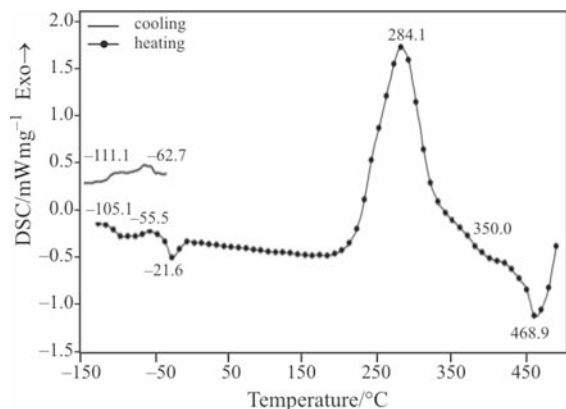**Fig. 4** DSC curve of SKDII after non-conventional cross-linking by CHI_3

Fig. 5 DSC curve of BR1220 after non-conventional cross-linking by CHI₃

Conclusions

The method of cross-linking of investigated *cis*-1,4-polybutadienes has a significant influence on their thermal transitions.

Crystallization processes of SKDII proceed with a slight yield during its heating. BR1220 rubber, despite its higher molecular mass as compared to that of SKDII, undergoes crystallisation, during its cooling, to a greater extent.

The non-conventional cross-linking of BR1220 with the use of iodoform decreases its ability to crystallisation and in the case of SKDII it brings about a loss of elastomer capability to crystallise.

The conventional cross-linking by means of dicumyl peroxide limits the thermal cross-linking processes of both elastomers.

The thermal cross-linking of the non-conventionally cross-linked polymers proceeds in two stages within the range of lower temperatures.

References

1 L. Reich and S. S. Stivilla, Elements of Polymer Degradation, McGraw – Hil Book Co., New York 1971.
2 Z. Jedliński, Advances in the Chemistry Stable Polymers, Polish. Sci. Publ., Warszawa 1977.
3 W. Schnabel, Polymer Degradation, Akademie-Verlag, Berlin 1981.
4 K. W. Wu, H. Y. Hou and C. M. Shu, J. Therm. Anal. Cal., 83 (2006) 41.
5 H. Y. Hou, T. S. Liao, Y. S. Duh and C. M. Shu, J. Therm. Anal. Cal., 83 (2006) 167.
6 A. Miyake, K. Nomura, Y. Mizuta and M. Sumito, J. Therm. Anal. Cal., 92 (2008) 407.
7 R. Endo, J. Rubber Ind. Jpn., 34 (1961) 522.
8 B. Wunderlich, J. Therm. Anal. Cal., 89 (2007) 321.
9 G. Janowska and T. Janczak, J. Thermal Anal., 36 (1990) 901.
10 G. Janowska and L. Ślusarski, J. Therm. Anal. Cal., 65 (2001) 205.
11 G. Janowska, P. Rybiński and R. Jantas, J. Therm. Anal. Cal., 87 (2007) 511.
12 G. Janowska and P. Rybiński, J. Therm. Anal. Cal., 91 (2008) 697.
13 P. Rybiński, G. Janowska, W. Antkowicz and S. Krauze, J. Therm. Anal. Cal., 81 (2005) 9.
14 G. Janowska, P. Rybiński and S. Krauze, Polimery, 51 (2006) 735.
15 A. Popińska, D. Bieliński and L. Ślusarski, Materiały Konferencji PTChem, Cracow 2002, s. 579.
16 D. Bieliñski, L. Ślusarski, Affrossman S., S. O'Neil and R. Pethrick, J. Appl. Polym. Sci., 64 (1997) 1927.