THERMAL PROPERTIES OF SWOLLEN BUTADIENE-ACRYLONITRILE RUBBER VULCANIZATES

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Abstract

The present paper discusses the results of assessing thermal properties of nitrile rubber, Perbunan NT 3945 and its peroxide vulcanizates, before and after their swelling in solvents such as benzene, toluene and dimethylformamide. The measurements were carried out by means of differential scanning calorimetry (DSC) and thermogravimetry (TG) under nitrogen. It has been found that a slight rise in the glass transition temperature due to the elastomer cross-linking is clearly revealed under the influence of its vulcanizates swelling in solvents whose solubility parameters considerably differ from the solubility parameters of the polymer. The thermal curves of swollen samples reveal processes resulting from polymer–solvent interactions and thermodesolvation processes, which accompany the initial stage of solvent evaporation.

Keywords: glass temperature, nitrile rubber, swollen vulcanizates, thermal stability, thermal transitions

Introduction

In the recent years one can observe a considerable interest in polymeric materials with special properties being resistant to very low or elevated temperature, flame-retardant and characterized by appropriate mechanical strength. This group of polymers includes technical rubber products made of butadiene-acrylonitrile rubber, which are commonly used under conditions of prolonged and simultaneous action of many external factors and agents such as low or elevated temperature in various technical liquids, subjected to mechanical stresses.

The present paper shows the results of the testing thermal properties of peroxide vulcanizates of butadiene-acrylonitrile rubber swollen in various organic solvents. This problem is of importance from both cognitive and practical points of view, considering that only few studies on the thermal analysis of swollen polymeric gels are available in [1–5].

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Object of studies

Our investigation was focused on butadiene-acrylonitrile rubber containing 39% of acrylonitrile units, Perbunan NT 3945 (NBR 39) of Bayer and its vulcanizates with different densities of cross-linking. NBR 39 was cross-linked with dicumyl peroxide: 0.8 phr (W1) and 1.3 phr (W2), in the presence of zinc oxide: 5.0 phr and stearic acid: 1.0 phr.

Testing methods

The rubber compounds prepared by means of a laboratory mixing rolls were vulcanized in an electric press at a temperature of 160°C. The optimal time of vulcanization, $\tau_{0.9}$, was determined by means of a WG-02 vulcameter.

The cross-linking density of NBR 39, υ, was determined by the method of equilibrium swelling in dimethylformamide, based on Flory–Rehner's equation [6, 7] and the parameter of polymer–solvent interaction found by us previously [8].

The thermal analysis of vulcanizates was carried out under nitrogen by the method of scanning dynamic calorimetry and thermogravimetry by means of a DSC-204 micro-calorimeter of Netzsch and a TG 209 thermobalance of Netzsch, using weighed portions of 5–7 mg. The heating rate was 10°C min^{-1}. TG curves were recorded within the temperature range from 30 to 500°C and DSC curves within 20–90 and –90–500°C. The DSC analysis of swollen samples in benzene (B), toluene (T) and dimethylformamide (DMF) at 25°C for 24 h was performed within the temperature ranges from 20 to –140°C and from –140 to 500°C. After each cooling step of all samples, they were stored under isothermal conditions for 5 min.

Results and discussion

The glass-transition temperature of butadiene-acrylonitrile rubbers depends of the acrylonitrile unit content in the elastomer macromolecules [9–11]. The nitrile rubber under investigation becomes glassy at a temperature of –27.6°C during cooling and –20.8°C during heating (Fig. 1). At a temperature of 255°C, polymer cross-linking processes are initiated, whose maximal rate takes place at 361.0°C The final stage of elastomer cross-linking is accompanied by the sample mass loss reaching 18% (Fig. 2). An intensive thermal decomposition of the cross-linked rubber starts at a temperature of 424°C (Figs 1 and 2).

The character of the polymer thermal transition does not change under the influence of its cross-linking and the low exothermic peak recorded at 183.3°C is connected with the presence of decomposition products of dicumyl peroxide used as a cross-linking agent (Fig. 3). The cross-linking of the elastomer exerts a slight influence on its glass transition temperature, T_g (Table 1), seen during the process of sample cooling segment. Both before and after the nitrile rubber cross-linking, its transition from the elastic into glassy state proceeds at a clearly lower temperature than its

Table 1 The result of thermal analysis of NBR 39

Sample	Cooling process		Heating process			
	$T_g/°C$	Temperature range of glass process/°C	$T_g/°C$	Temperature range of glass process/°C	$T_c/°C$	$T_{dk}/°C$
E	−27.8	−34.1 ÷ −21.4	−20.8	−22.8 ÷ −18.8	360.6	449.1
W1	−27.1	−37.1 ÷ −20.3	−19.1	−21.2 ÷ −17.0	361.8	449.8
W2	−25.1	−28.9 ÷ −21.3	−19.0	−21.5 ÷ −16.6	363.3	442.1
W1-B	−58.9	−68.3 ÷ −49.5	−53.6	−61.4 ÷ −45.7	361.6	445.0
W2-B	−49.2	−62.1 ÷ −36.4	−48.1	−53.7 ÷ −42.4	361.1	444.1
W1-T	−102.1	−110.1 ÷ −93.4	−96.6	−101.6 ÷ −92.0	362.0	446.3
W2-T	−92.0	−96.6 ÷ −87.4	−89.3	−94.5 ÷ −84.1	362.3	448.8
W1-DMF	−140.8	−144.0 ÷ −136.9	–	–	363.1	454.6
W2-DMF	−139.0	−143.0 ÷ −135.9	–	–	364.2	455.5

E – uncross-linked NBR 39
W1 – peroxide vulcanizate of NBR 39, $\upsilon=0.153 \cdot 10^{-4}$ mol cm^{-3}
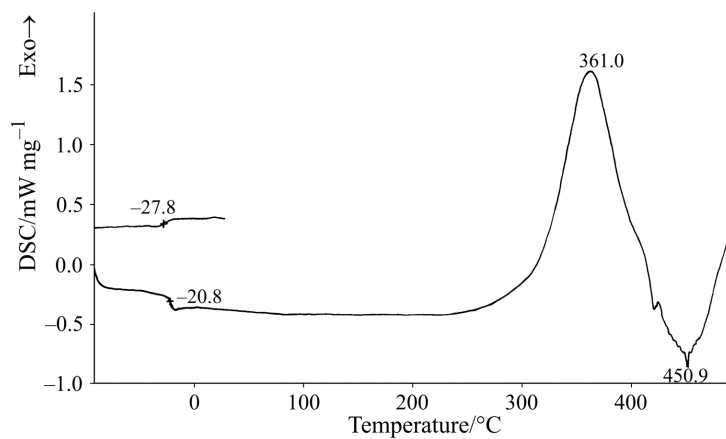W2 – peroxide vulcanizate of NBR 39, $\upsilon=0.407 \cdot 10^{-4}$ mol cm^{-3}
W1, W2-B – vulcanizates swollen in benzene
W1, W2-T – vulcanizates swollen in toluene
W1, W2-DMF – vulcanizates swollen in dimethylformamide
T_c – cross-linking temperature
T_{dk} – destruction temperature
The temperatures placed in the table have been determined from DSC curves using the Taa computer program of Netzsch.

Fig. 1 DSC curves of NBR 39
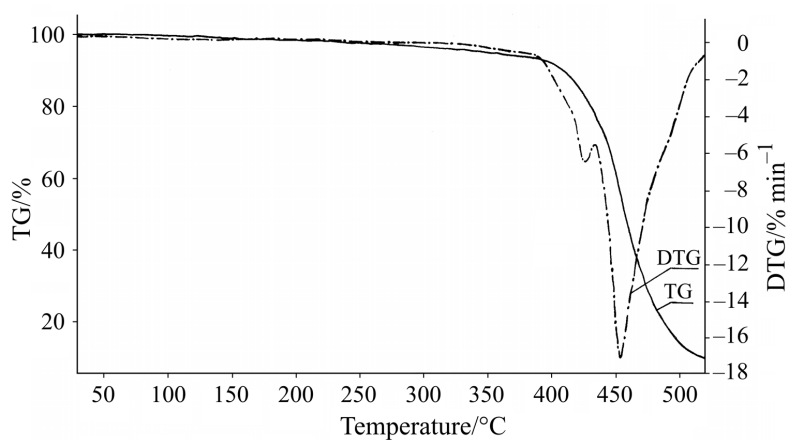
Fig. 2 TG and DTG curves of NBR 39
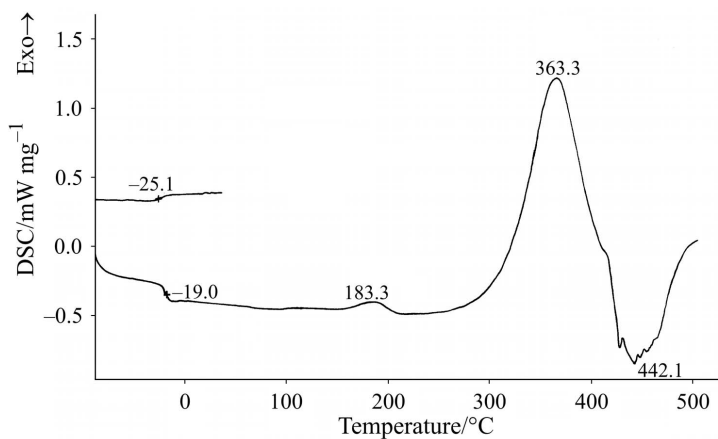
Fig. 3 DSC curves of vulcanizate W2

transition from the glassy into elastic state. It should be also underlined that the temperature range of polymer glass transition determined from the curve of sample cooling is considerably wider than that determined from the heating curve.

As expected, due to the presence of solvent molecules, we have found that the glass transition temperature of the cross-linked rubber is considerably lowered under the influence of its swelling (Figs 4–6, Table 1). The lowest glass transition temperature is shown by the samples of vulcanizates swollen in DMF, in which the examined rubber dissolves completely [12]. In this case, T_g was determined only from the cooling curve as the DSC used by us can provide the proper course of heating only from the temperature –120°C irrespective of the programmed time of the isothermal segment (Fig. 6, Table 1). On the other hand, a clear effect of cross-linking density of nitrile rubber on its glass transition temperature is revealed as a result of peroxide vulcanizate swelling in solvents such as benzene or toluene, in which the elastomer
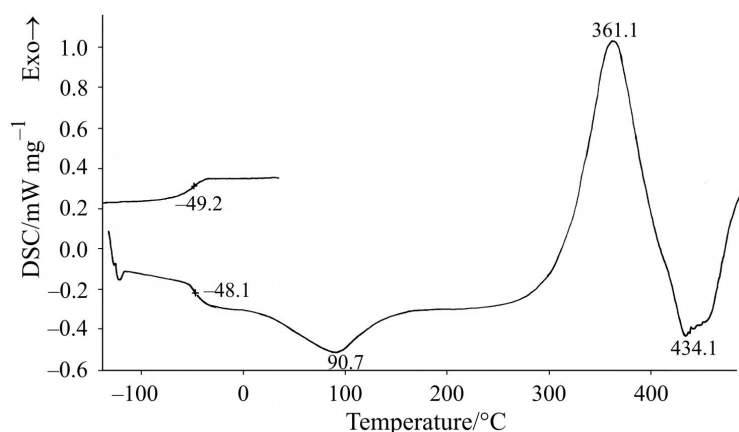

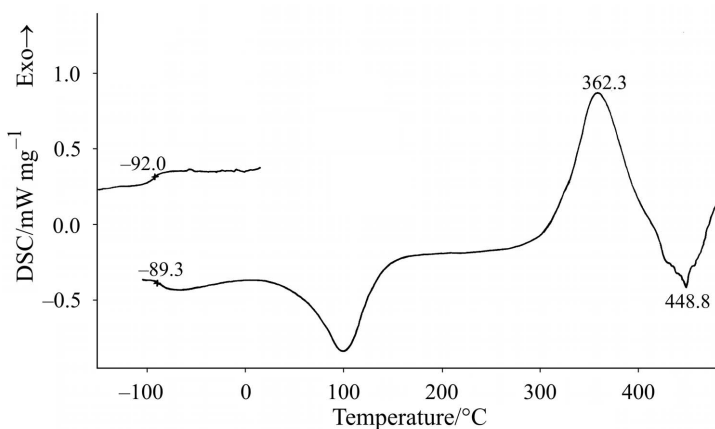**Fig. 4** DSC curves of vulcanizate W2 swollen in benzene

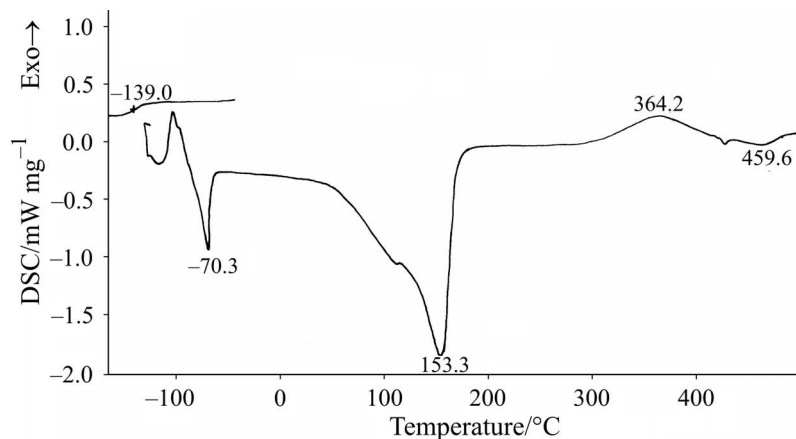**Fig. 5** DSC curves of vulcanizate W2 swollen in toluene

Fig. 6 DSC curves of vulcanizate W2 swollen in DMF

under investigation is only partly dissolved. From the DSC curves of the examined solvents it follows that under the conditions of measurements, except for toluene, they are crystallized during cooling (Figs 7 and 9), while the melting and evaporation processes are recorded in the heating curves (Figs 7–9). Thus, one can assume that the crystallization of toluene under the examination conditions used proceeds during the 5 min-isothermic segment programmed at –140°C. The curves of vulcanizates swollen in benzene or toluene show no transitions connected with the solvent crystallization and melting (Figs 4 and 5). This is probably due to the rather low quantity of solvent present in the swollen sample and the fact that the solvent is strongly entangled in the elastomer network structure.

The crystallization and melting processes of solvent are recorded in the DSC curves connected with the heating of vulcanizate samples swollen in DMF at –104 and –70°C, respectively. Both the crystallization and melting of DMF included in the
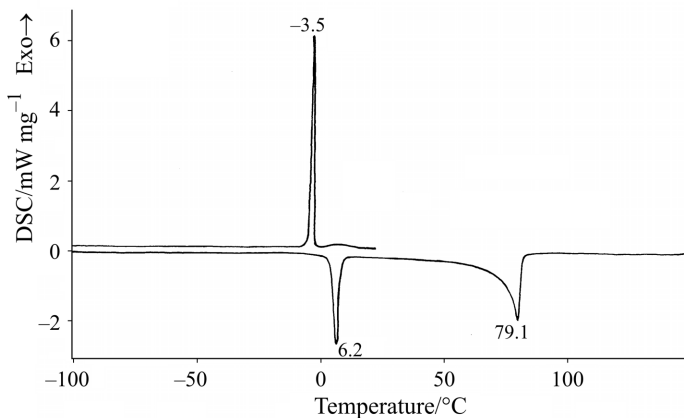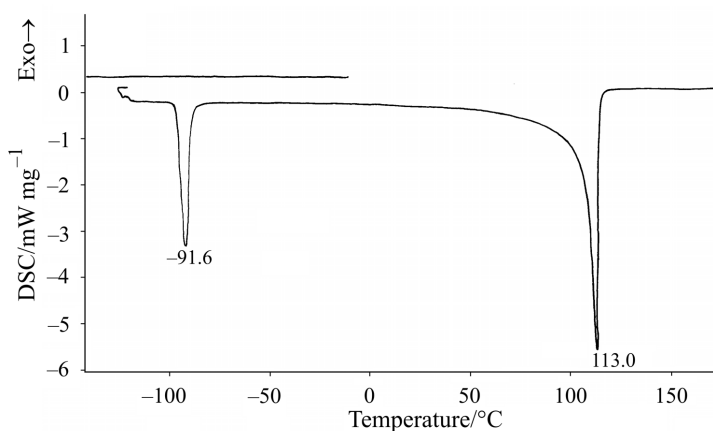

Fig. 7 DSC curves of benzene
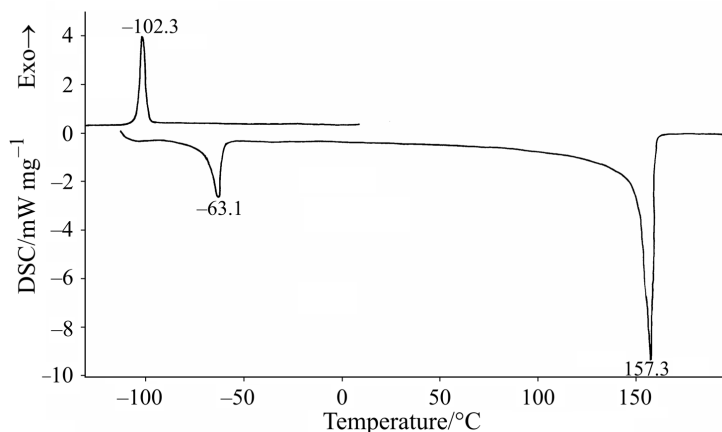
Fig. 8 DSC curves of toluene

Fig. 9 DSC curves of dimethylformamide

swollen sample proceeds at a temperature lowered by 2 and 8°C, respectively, in relation to the pure solvent (Figs 6 and 9).

The DSC curves associated with the heating of the swollen vulcanizate samples show that a broad endothermic peak starts at a temperature of about 25°C. We believe that its beginning, connected with the descending portion of the endotherm, is due to the changes in interactions, first of all, in the polymer–solvent interactions, thermodesolvation of molecules and gradual evaporation of solvent. The second portion of the mentioned transition, indicated by the ascending portion of the endotherm, is associated mainly with the evaporation of solvent. It is clearly seen in the case of the vulcanizate swollen in DMF (Fig. 6). The inflexion at a temperature of 110°C seen in the endotherm of the transition under discussion corresponds to the temperature, in which the evaporation of pure DMF begins (Figs 6 and 9).

The transitions associated with the thermal cross-linking of the elastomer followed by its destruction are recorded in the DSC curves of the swollen samples at a temperature over 300°C (Figs 4–6).

The thermal stability of elastomer is defined by the temperature range, ΔT, in which the elastomer retains its specific elastic properties:

$$\Delta T = T_p - T_k$$

where T_p – initial temperature of the elastic state range determined by the glass transition temperature of elastomer, T_g, or the temperature of its crystallization, T_k; T_k – final temperature of the elastic state range determined by the elastomer flow temperature, T_f, degradation temperature, T_d, thermal cross-linking temperature, T_c, or destruction temperature, T_{dk}.

In the case of butadiene-acrylonitrile rubber, T_p is determined by its glass transition temperature and T_k is determined by its cross-linking temperature. The solvents used by us and included in the swollen vulcanizates exert no significant influence on T_k, while they considerably lower T_g, which widens the range of its elastic state. The highest value of ΔT is reached by the peroxide NBR 39 vulcanizate swollen with DMF.

The Institute of Polymers at the Technical University of Łódż continues to perform the examinations of the effects of macromolecule chemical structure, cross-linking density, network structure and fillers on the thermal properties of swollen vulcanizates.

Conclusions

- The retardation of segmental mobility of NBR 39 macromolecules, both before and after their cross-linking, proceeds in a wider temperature range than its initiation.
- A slight increase in the glass transition temperature, T_g, due to the nitrile rubber cross-linking manifests itself in the cooling process. On the other hand, the rise in the glass transition temperature resulting from the increased cross-linking density of NBR 39 is clearly due to the swelling with solvents that are characterized by a low thermodynamical affinity to the polymer, i.e. benzene or toluene.
- The changes resulting from the polymer–solvent interactions, thermodesolvation and evaporation of solvent are revealed in the broad endothermic peak recorded in the DSC curves of swollen vulcanizate samples within the temperature range from 20 to 170°C.

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