

Thermal stability of acrylonitrile/chlorosulphonated polyethylene rubber blend

Gordana Marković · Milena Marinović-Cincović ·
Vesna Vodnik · Blaga Radovanović ·
Jaroslava Budinski-Simendić · Olivera Veljković

Received: 6 April 2009 / Accepted: 4 May 2009 / Published online: 19 June 2009
© Akadémiai Kiadó, Budapest, Hungary 2009

Abstract The properties of chlorosulphonated polyethylene (CSM) rubber, acrylonitrile rubber (NBR) and their blend (50/50 w/w) were studied. Fourier transform infrared (FTIR) studies supported that CSM/NBR rubber blend is self curable, when cross-linking takes place between acrylonitrile groups of NBR and $-\text{SO}_2\text{Cl}$ groups or in situ generated allyl chloride moieties of CSM. The thermal stability of vulcanizates was analyzed in nitrogen by thermogravimetry. It was found that the initial degradation temperature of elastomer based on CSM rubber is lower than of pure NBR rubber. By adding NBR to CSM rubbers, the degradation temperature of crosslinked material increased, indicating higher thermal stability. The activation energy for the degradation are determined using the Arrhenius equation. The activation energies for the rubber blends are higher than for elastomers based on pure rubbers. It was found that the mass loss of the blends at any temperature was between those of the pure rubbers. The differential scanning calorimetry (DSC) was used for the glass transition temperature determination. It is estimated thermodynamic immiscibility of NBR/CSM blend based on noticed two different glass transition temperatures, corresponding to CSM and NBR rubbers.

Keywords FTIR · NBR/CSM · Rubber blend · TGA · Thermal stability

Introduction

Thermal stability means the ability of a material to maintain the required properties such as strength, toughness, or elasticity at a given temperature [1]. A detailed understanding of how polymers break down on heating is important in the design of elastomeric materials with improved properties for particular application. Elastomers based on different network precursors (rubber blend) have been receiving more attention, as they are easy to prepare, once the individual network precursor are known. The blending of rubbers macromolecules has a great influence on the thermal stability of final crosslinked materials. Functionalization of polymers results in new materials with a wide spectrum of properties not available in the parent polymers. Chemical modification of rubber macromolecules either by grafting onto a polymer chain and interchain reactions or by the formation of interpenetrating networks are the subject of reviews [2]. For instance the introduction of chlorine and sulfur dioxide into the polyethylene destroys the crystallinity, thereby changing the thermoplastic into an amorphous polymer in the case of chlorosulphonated polyethylene, CSM (which contains 25–43% by weight of chlorine and 1–1.5% by weight of sulfur as $-\text{SO}_2\text{Cl}$ units). In recent years, De and associates [3] studied a series of self-cross linkable mixtures of two or more functionally reactive macromolecules that are capable of undergoing mutual cross-linking via condensation or substitution reactions at high temperatures. Such self crosslinkable rubber-rubber blends are for instance epoxidised natural rubber (ENR) and carboxylated nitrile rubber (XNBR), CSM and ENR. For

G. Marković · O. Veljković
Tigar, Pirot, Serbia

M. Marinović-Cincović (✉) · V. Vodnik
Institute of Nuclear Science VINCA, Belgrade, Serbia
e-mail: milena@vinca.rs; milena@vin.bg.ac.yu

B. Radovanović
Faculty of Science, Niš, Serbia

J. Budinski-Simendić
Faculty of Technology, Novi Sad, Serbia

example, the powder mixture of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) behaves very differently as a film cast and as a solution [4]. The degree of dispersion is important because of the type of reaction which can occur during the degradation of the final crosslinked materials, which, in turn, depends on the interaction between the individual network precursors [5]. Several methods have been developed in order to investigate the thermal stability of rubbers [6]. Today, thermal analysis is carried out with the aid of commercially available equipment, allowing the elegant investigation of the materials thermal behavior. Both thermogravimetry and DSC will provide information about the nature and extent of degradation of the material. Thermal properties of three binary blends PVC/poly(ethylene-*co*-vinyl acetate), PVC/poly(styrene-*co*-acrylonitrile), and poly(ethylene-*co*-vinyl acetate)/poly(styrene-*co*-acrylonitrile) have been extensively reported by Lizymol and Thomas [7] using thermogravimetric analysis. Cowie and co-workers [8] studied the decomposition of blend based on poly(ethylene-*co*-acrylic acid) and ENR by thermogravimetry and DSC method. In the case of rubber vulcanizates, the stability depends on environment, because network stability is primarily dependent on thermal or thermo-oxidative degradation, or both. The structure of the main network chains, the energy of main chain bonds, the nature of cross-links, and the presence of additives in polymer network can affect the thermal stability of final materials. A number of studies on the degradation of different elastomers by using thermal analysis and other conventional techniques have already been reported [9, 10]. Podina et al. [11, 12] extensively studied the thermal degradation of IIR, EPDM, and its blends with and without compounding ingredients. Quantitative analysis of SBR/BR blends by thermogravimetric analysis has been carried out by Lee et al. [13]. The thermal stability of the aged vulcanizates of silicon rubber, EPDM, and its blends has been reported based on no isothermal thermogravimetric measurements [14]. Thermogravimetric analysis (TG) has proved itself as a successful technique in determining the thermal stability of polymers and polymer blends [15]. Several studies have been conducted about degradation of rubber blend based materials. However, to date, the degradation studies of elastomers based on NBR/CSM rubber blend have not been reported. Differential scanning calorimetry (DSC) is another method where the heat flow rate associated with a thermal event is measured as a function of time and temperature, allowing us to obtain quantitative information about the melting and phase transitions and can be used as an effective tool for evaluating the polymer blend compatibility [16]. The chemical nature of the thermal decomposition of polymers varies from material to material. The simplest and readily identifiable product is often the monomer. On the other hand, complex mixtures of products

are also obtained. There are three types of thermal degradation products. First types are substances in which the molecular dimensions are similar to monomer thus the detailed analysis can be made. Second are substances which are volatile at the degradation temperature but non volatile at ambient temperature. These are usually polymer-chain fragments which are larger than the monomer. Although they may be referred to as dimeric, trimeric, and so forth, their precise chemical structure usually was not determined. Third type's substances are the in volatile residue which often remains insoluble (although knowledge of the mechanism of degradation reaction combined with spectral data can give some information about its structure). The relative amount of these three types of degradation product can vary with the temperature of degradation [17, 18]. The aim of this work was to study thermal properties of pure NBR and CSM rubbers and its blend NBR/CSM by thermogravimetry and differential scanning calorimetry. Attempts have been made to understand how rubber blending influences the thermal stability of the elastomeric materials.

Experimental

Materials

The chlorosulphonated polyethylene (CSM, Hypalon-40, DuPont de Nemours, U.S.A.) which contained 35 mass% of chlorine and 1 mass% of sulphur. The acrylonitrile rubber (NBR, Krynac-3345, Polysar Canada) containing 33 mass% of acrylonitrile.

Blend preparation

The rubber compounds based on CSM, NBR and CSM/NBR (50/50 w/w), were prepared on a laboratory size (300 × 600 mm) two-roll mixing mill having a friction ratio of 1:1.4 according ASTM D-15-627. The temperature of the rollers of the mill was kept at 313 K by the circulation of cold water. The pure rubbers were separately milled for about 1 min each, keeping a tight nip gap (0.8 mm), and subsequently mixed for 3 min. The compounding recipes of the blends are given in Table 1. The compounds were compression molded at 433 K under a pressure of 10 MPa, for the optimum cure time. The molded samples were taken out after cooling them to room temperature under pressure by circulating cold water through the platens of the press.

Fourier transform infrared spectra (FTIR-ATR)

Fourier transform infrared spectra (FTIR) were recorded on a Bruker IFS-66 spectrometer with an attenuated total reflection (ATR) attachment. A minimum of 500 scans was

Table 1 Formulation of compounds based on pure rubbers (NBR, CSM) and its blend (NBR/CSM)

Components (phr)	Compound		
	1-NBR	2-CSM	3-NBR/CSM
NBR	100	–	50
CSM	–	100	50
ZnO	5	–	2.5
Stearic acid	2	2	2
Magnesium oxide	–	4	2
TMTD*	2.5	2	2.5
CZ**	2	–	1
Sulfur	0.5	1	0.75

* TMTD—tetra methyl thiuram disulphide

** CZ-*N*-cyclohexyl-2-benzothiazole sulphonamide

signal-averaged at a resolution of 4 cm⁻¹. For FTIR-ATR measurements, the spectrometer was equipped with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. The internal reflection element (IRE) chosen was a 45° KRS-5. Samples for measurements were approximately 0.3 mm thick sheets, prepared by compression molding between two teflon films at temperature of 373 K (for uncured rubber blend). For cured rubber blend samples melting times were 2 min.

Cross-linking density determination

The crosslink density, v_{EANC} (concentration of elastically active chains) of the elastomers was determined by the swelling method [19]. The samples were allowed to swell in toluene and the equilibrium uptake is noted. The molecular mass between the crosslink’s is calculated using the following equation:

$$M_c \equiv -V_1 \rho_p \frac{(\phi_p^{1/3} - \frac{\phi_p}{2})}{\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2} \tag{1}$$

where ρ_p , density of sample; V_s , molar volume of solvent; ϕ , volume fraction of polymer in the swollen mass; χ , interaction parameter. ϕ and χ are given by the following equations:

$$\phi = \frac{\frac{W_1}{\rho_1}}{\left(\frac{W_1}{\rho_1} + \frac{W_2}{\rho_2}\right)} \tag{2}$$

where W_1 is mass of crosslinked sample, ρ_1 is density of crosslinked sample, W_2 is mass of solvent at equilibrium and ρ_2 is density of solvent.

$$\chi = 0.34 + \frac{V_s}{RT}(\delta_A + \delta_B)^2 \tag{3}$$

where δ_A are δ_B are solubility parameter of solvent and polymer, respectively. From the molecular mass of

network chains between crosslink’s M_c , the crosslinking density, is calculated using the following equation

$$v = \rho / 2M_c \tag{4}$$

Thermogravimetric analysis

The measurements were made at a heating rate of 10 K min⁻¹, at a temperature range 303–1073 K, using Perkin Elmer TGS-2 Thermogravimetric system. The experiments were done in nitrogen atmosphere. About 5–8 mg of the sample was used for the analysis.

Differential scanning calorimetry (DSC)

The differential scanning calorimetry (DSC) was performed on a DSC 2910 (DuPont instrument) for the determination of the glass transition temperatures. The samples were inserted into the apparatus at room temperature and heated immediately to 473 K at a rate of 283 K min⁻¹ and kept for 1 min at this temperature in order to remove the volatile impurities. They were then quenched to 193 K and the DSC scan was taken from 353 to 393 K at a heating rate of 283 K min⁻¹ in helium atmosphere.

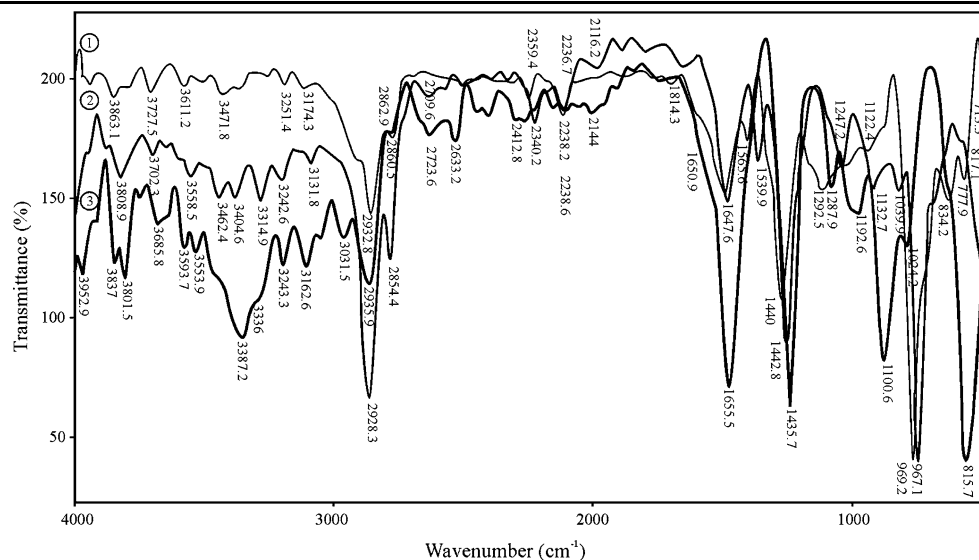
Results and discussion

The minimum torque can be taken as a measure of the viscosity of the masticated rubber. Whenever there is excessive mastication, the viscosity registers a sharp decrease. Normally the maximum torque can be taken as the maximum viscosity of the rubber compound and is an approximate measure of the cross link density in the sample [20]. All curing characteristics estimated by the Monsanto rheometer (i.e. vulcameter) for rubber compounds based on NBR and CSM rubber and its blend are given in Table 2. It is obvious that the optimum curing time (t_{c90}) for CSM rubber is significantly longer than for NBR and NBR/CSM

Table 2 The curing characteristics of compounds based on pure rubbers or rubber blends

Curing characteristics	Compound		
	NBR	CSM	NBR/CSM
Rmin (dNm)	2	3	3
Rmax (dNm)	34	32	38
ΔR (dNm)	32	29	35
t_{s2} (min)	2.3	6.5	2.5
t_{c90} (min)	6.4	50.2	6.1
CRI (100/ $t_{c90} - t_{s2}$)min ⁻¹	25	2	17

Fig. 1 FTIR-ATR spectrum of elastomers: (1) NBR; (2) CSM; (3) NBR/CSM



blend. The shorter cure time is extremely beneficial because it increases the production rate.

Figure 1 (spectrum 1 and 2) represents the FTIR spectra of elastomer based on NBR and CSM rubber, respectively. The assignment of the principal bands is presented in Table 3.

The absorption band at 2238 cm^{-1} , which is attributed to C=N stretching mode [21] is strongly attenuated by self-cross-linking of the rubber blend macromolecules. This indicates a significant loss or conversion of cyanide groups, which may be due to cyanide/cyanide reaction [22] or even hydrolysis of cyanide groups. Hence, it is logical to infer that NBR/CSM do not contain any side products due to cyanide/cyanide reactions. The decrease of the -CN group concentration is therefore attributed to a partial hydrolysis of cyanide groups by the split-out HCl gas from CSM during high-temperature heating in the presence of inherent moisture in the materials. Similar observations were made by Ismail et al. with reference to the thermally induced self-cross-linking PVC/NBR, as well as the PVC/HNBR [23]. A controlled HCl liberation from PVC favors the self-cross-linking by bringing the hydrolysis of a cyanide groups to amides and acids. In situ generated amides and carboxylic acids are capable of reacting with the allylic sites of degraded PVC [23, 24].

The absorption bands at 1100 and 1292 cm^{-1} in the crosslinked CSM rubber are assigned, respectively, to the symmetric and asymmetric stretching modes of SO_2 of $-\text{SO}_2\text{Cl}$ groups. These two characteristic bands of CSM totally vanish in the spectrum of self-cross-linked material. The difference spectrum (spectrum 3, Fig. 1) also illustrates the loss of $-\text{SO}_2\text{Cl}$ groups. An inspection of spectrum 3 (Fig. 1) reveals a new absorption band centered at 1539 cm^{-1} . New absorption could be assigned to the amide II band, which is due to a motion combining both the N-H

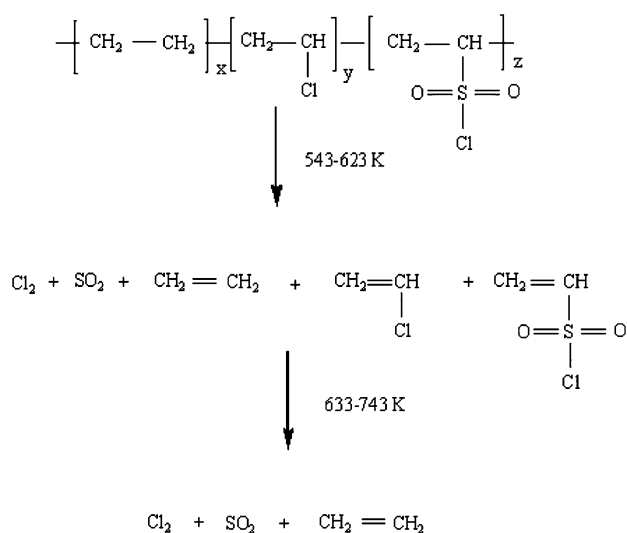
bending and C-N stretching vibrations of -CONH groups. Amide I band, which is ascribed to the C=O stretching mode of the amide group, generally occurs at the $1680\text{--}1630\text{ cm}^{-1}$ region [25, 26]. In the present material, the amide I band cannot be detected because of the interference from the C=C stretching in the same region. It is also noteworthy that the amide present in the NBR/CSM self-cross-linked blend is likely to be a secondary amide because the amide II band of the primary amide (in the condensed phase) occurs at $1650\text{--}1620\text{ cm}^{-1}$, while the corresponding absorption due to a secondary amide (solid) takes place at $1570\text{--}1515\text{ cm}^{-1}$. This indicates a chemical reaction between in situ generated primary amides and allyl chlorides. The mechanism of random scission of the polymer chains that can occur at high temperature is shown in Schemes 1 and 2. A thermal treatment of crosslinked NBR rubber, also results in an internal cyclization reaction of a nitride group (polyimide formation), followed by dehydrogenation to form a highly conjugated structure [27].

In the Fig. 2 are presented TG curves for elastomers based on pure rubbers (NBR, CSM) or NBR/CSM rubber blend. In the Fig. 3 are presented DTG curves for elastomers. Two regions of degradation are observed. The first step was started at 543 K and was completed at 623 K . The second degradation stage occurred in the temperature region of $633\text{--}743\text{ K}$. The mass losses observed during the first and second stages were 23.25 and 51.58% , respectively. A residue of 26.23% remained at 1035 K . In the DTG curve, the major peak is observed at 697 K , which corresponds to the degradation of saturated and unsaturated carbon chains in CSM rubber macromolecules. The former stage of degradation is due to the elimination of ethylene, chloroethylene, sulphochloroethylene and so forth from the chain and the later stage is due to the main chain scission.

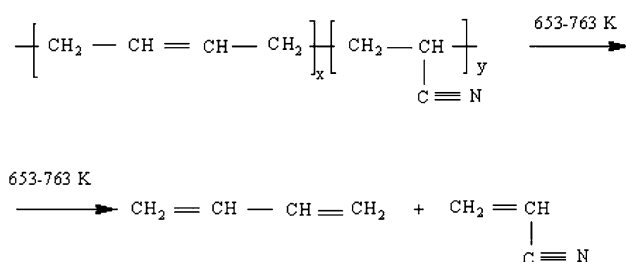
Table 3 FTIR-ATR spectroscopic data for crosslinked acrylonitrile-butadiene rubber, chlorosulphonated polyethylene rubber and its blend NBR/CSM (50/50 w/w)

Wave number (cm ⁻¹)	Group	Assignment
Acrylonitrile-butadiene rubber		
2932	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
2860	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
2238	-CN	ν (-C=N)
1647	-CH=CH-	ν (-C=C)
1440	-CH ₂ -	δ (-C-H)
1287	-CH ₂ -	γ (CH ₂)
969	trans -CH=CH-	δ (=C-H)
967	CH ₂ =CH-	δ (CH ₂)
Chlorosulphonated polyethylene rubber		
2935	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
2862	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
1435	-CH ₂ -	δ (-C-H)
1292	-SO ₂ Cl	ν (SO ₂) _{asym.}
1192	-CH ₂ -	γ (CH ₂)
1100	-SO ₂ Cl	ν (SO ₂) _{sym.}
815	-CH ₂ -	γ (CH ₂)
NBR/CSM (50/50 w/w) rubber blend		
2928	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
2854	CH ₃ -, -CH ₂ -, >CH-	ν (-C-H)
-	-CN	ν (-C=N)
1650	-CH=CH-	ν (-C=C)
1680-1630	-CONH	δ (C=O) amide I interference by ν (-C=C)
1539	-CONH	δ (>N-H) amide II
1247	-CH ₂ -	δ (-C-H)
-	-SO ₂ Cl	ν (SO ₂) _{asym.}

ν, stretching vibrations; δ, bending vibrations in plain; γ, bending vibrations out-of-plane

**Scheme 1** Degradation mechanism of elastomer based on CSM

This results in the formation of volatile monomer along with some amount of impurities. The structural changes that occur upon heating CSM in nitrogen or in vacuum

**Scheme 2** Degradation mechanism of elastomer based on NBR

have been studied by several authors [24, 28]. Under these conditions, CSM undergoes cross-linking and chain scission following with extensive mass loss. The mechanism of random scission of the polymer chains that can occur at high temperature is shown in Scheme 1.

The thermal decomposition of NBR (presented in Fig. 2) has two regions. The degradation started at 653 K and was completed at 763 K. The former stage of degradation is due to the elimination of acrylonitrile and butadiene from the NBR chain and the later stage is due to the main chain scission [25, 28]. Possible mechanism of

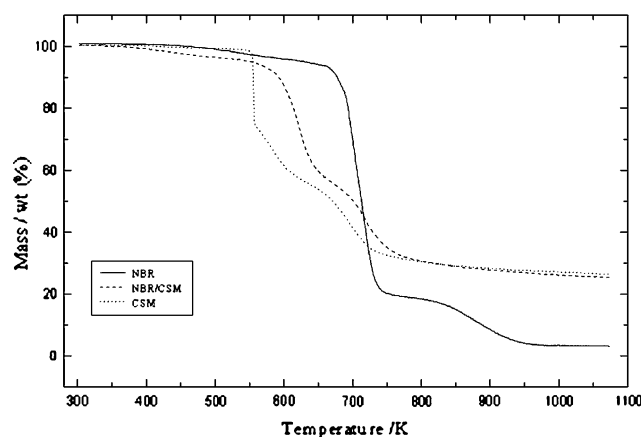


Fig. 2 TG curves for elastomers based on pure rubbers (NBR, CSM) or its blend (NBR/CSM)

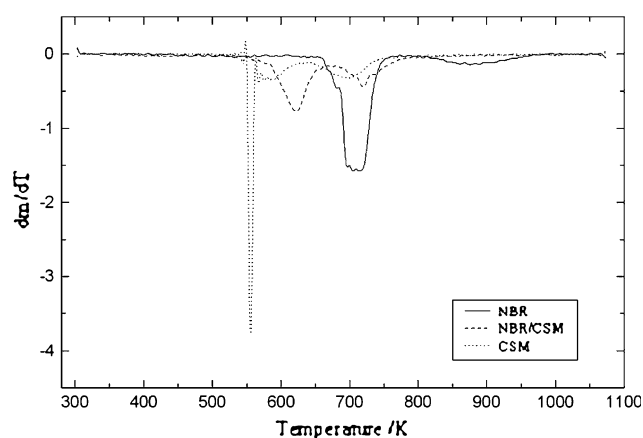


Fig. 3 DTG curves for elastomers based on pure rubbers (NBR, CSM) or its blend (NBR/CSM)

degradation process that occurred in NBR is shown in Scheme 2. The mass loss observed during the degradation was 50.63%. About 3.79% remained as residue at 968 K. The total mass loss observed at 968 K was 96.21%. On the DTG curves the major peak is observed at 712 K, which corresponds to the scission of NBR chains left after acrylonitrile and butadiene. A small second peak corresponding to the degradation of polyethylene is observed at 883 K. The two-stage degradation of NBR was already reported by Morell et al. [28]. The gas chromatography and mass spectrum analysis of the acrylonitrile butadiene rubber pyrolysis products [26, 28] shows that a number of low-molecular-weight compounds, like butadiene and acrylonitrile are produced during the thermal fragmentation of NBR (as in Scheme 2). The degradation behavior of the elastomer based on two network precursors (rubbers) is marginally different from that of the individual rubber components. It has been reported that the thermal stability of one type of polymer can be improved by the

Table 4 The temperatures of selected mass losses (0.5; 10; 30%) for crosslinked rubbers (NBR, CSM) and its blend (NBR/CSM)

	Elastomer		
	NBR	CSM	NBR/CSM
Temperature of peaks at DTG curves (K)	712	556	621
	833	697	720
Mass loss at peaks (%)	50.63	23.25	25.33
	83.33	51.58	56.33
Total mass loss (%)	96.21	73.77	74.22
Temperatures for selected mass loss			
$T_{0.5\%}$ (K)	630	550	561
$T_{10\%}$ (K)	677	557	596
$T_{30\%}$ (K)	699	574	625
T_{end} (K)	968	1035	1036

incorporation of a second polymer. In the case of CSM/NBR rubber blends, the degradation starts at a higher temperature than that for CSM rubber vulcanizates. It has been reported that improved stability can be achieved by the incorporation of a second type of rubber macromolecules [27, 28]. The initial and final decomposition temperature and the mass loss at different temperatures of the blend are given in Table 4. The DTG curves for rubber blend shows two-stage degradation. One corresponds to CSM degradation and the other corresponds to NBR degradation. Table 4 presents the DTG peak values of NBR/CSM blend. The peaks are observed at 621 K and 720 K. It was found that if the NBR rubber is added to CSM, the peak (at 553 K) shifts to a higher temperature (621 K). The degradation products of the blends contain the products of decomposition of both network precursors (rubbers). The amount varies according to the composition.

Table 4 shows the temperature at which 0.5, 10 and 35% degradation of elastomers based on NBR, CSM and NBR/CSM take place. The degradation of CSM takes place at a lower temperature than that of NBR. In the case of rubber blend vulcanizates the mass losses (0.5%, 10% and 30%) take place at higher temperatures than that for elastomers based on CSM rubber. It is obvious that the addition of second network precursor (NBR rubber) increases the thermal stability. At 1036 K the amount of residue increases. However, elastomer based on pure NBR shows a slight decrease in the amount of residue at the same temperature.

Activation energy of degradation

The activation energy for the degradation of the rubbers and rubber blend are determined [29, 30] using the Arrhenius equation:

Table 5 The density ρ_p , the cross-linking density (ν), molecular mass of network chains between crosslink's (M_c), activation energy of degradation (E_a) according the Arrhenius equation and glass transitions (T_g) estimated by DSC for crosslinked rubbers (NBR, CSM) and its blend

	Elastomer		
	NBR	CSM	NBR/CSM
Density, ρ_p (gcm^{-3})	1.04	1.07	1.09
Crosslinking density, ν	301	342	505
M_c (gmol^{-1})	3820	2411	905
E_a (kJmol^{-1})	421	297	358
Glass transition, T_g (K)	253	235	251

$$\text{Log } w = \text{log } A + \frac{E}{RT} \quad (5)$$

where w is the residue weight at a particular temperature, A is the preexponential factor, E is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. Plots of $\log w$ versus $1/T$ are constructed and the value of the activation energy can be calculated from the slope. The activation energy values for NBR, CSM and NBR/CSM blends are given in Table 5.

High activation energy means a high temperature sensitivity of the material. It can be seen that the rubber blends exhibited higher activation energy than the pure components indicating the better thermal stability achieved by blending. The C–C linkages formed during vulcanization, according FTIR spectra of rubber blend (spectrum 3, Fig. 1) are less flexible and have higher bond energy and higher thermal stability than pure components [31].

Differential scanning calorimetry (DSC)

From DSC curve quantitative information about the melting and phase transitions were obtained. DSC analysis can also be used as an effective tool for evaluating the compatibility in polymer blends. The melting and phase transitions of NBR, CSM and cross-linked NBR/CSM blend were analyzed by using DSC. DSC scans for the individual components of the blend, CSM and NBR, and NBR/CSM (50/50) blend were represented in Fig. 4 and Table 5. T_g of the individual components in the blend was found to be 253 and 283 K for NBR and CSM rubbers, respectively. In the NBR/CSM rubber blend two glass transition temperatures were detected (T_{g1} and T_{g2} at about 293 and 303 K), in good agreement with internal friction results reported by Vaaben et al. [32] studying similar cured blends. The existence of two T_g is one distinctive features related to the presence of partial immiscible blend. On the other hand, it is well known that the cross link distribution is not even in partially immiscible cured blend [33]. Therefore, the

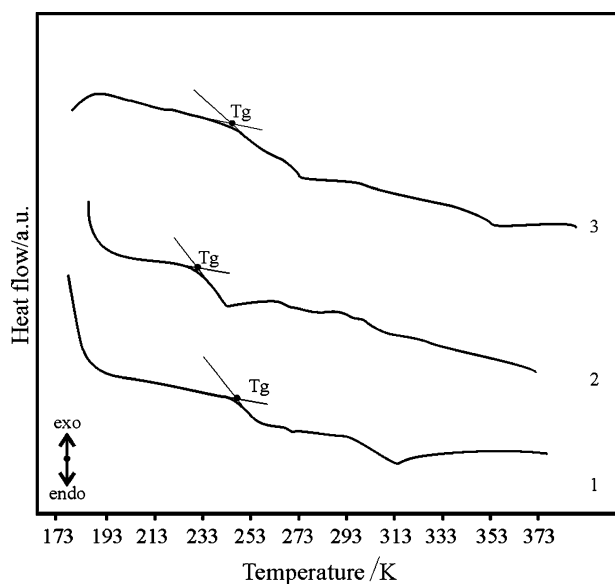


Fig. 4 DSC curves of crosslinked material based on pure rubbers: (1—NBR; 2—CSM) or its blend (3—NBR/CSM)

networks present in each phase of the blend should be different, according different curative distribution and cross links density in both phases. T_g of blend are shifted to 251 K due to the restriction on the segmental motion of the polymeric chain by the cross-linking and this was explained by Essawy et al. [34, 35]

Some calculated data for the “relative” crosslinking density of NBR, CSM and NBR/CSM rubber blend, ν , determined from swelling measurements are summarized in Table 5. There is an increase in cross linking density of the elastomer based on rubber blend, and the initial and final decomposition temperature are higher than decomposition temperatures of pure rubbers. The greater values of cross-link density of rubber blend might reduce the penetration of toluene into the polymer matrix during swelling process.

Conclusion

The thermal stability chlorosulphonated polyethylene (CSM) rubber, acrylonitrile rubber (NBR) and their blend (NBR/CSM) was studied. It was found that the initial degradation temperature of elastomer based on pure CSM is lower than of NBR elastomer. By adding NBR to CSM compounds, the degradation temperature of crosslinked materials increased. The degradation products of NBR contain butadiene and acrylonitrile and that of CSM contains a large number of products like ethylene, chloroethylene, sulphochloroethylene and so forth. However, blend shows a higher degradation temperature than CSM. As the NBR was added to the CSM rubber, the degradation

temperature increased, indicating higher thermal stability of the blend. It is found that for CSM/NBR, the peak at DTG curves (at 556 K) shifts to a higher temperature (621 K). Glass transition determination by DSC method revealed that CSM/NBR blend is thermodynamically immiscible. This is concluded by the existence of two glass transitions, corresponding to pure CSM and NBR rubbers. Infrared studies confirmed that cross-linking takes place through allyl chloride and amide produced due to hydrolysis of $-C=N$ group. It was found that the initial degradation temperature of elastomer based on CSM rubber is lower than of NBR rubber. It is estimated that the mass loss of the crosslinked rubber blends at any temperature was between those of the crosslinked pure rubbers. The activation energies for the degradation of elastomer based on rubber blend were higher than for pure rubbers (calculated according the Arrhenius equation).

References

- Janowska G, Rybiński P, Jantas R. Effect of the modification of silica on thermal properties and flammability of cross-linked butadiene-acrylonitrile rubbers. *J Therm Anal Calorim.* 2007;2: 511–7.
- Janowska G, Rybiński P. Influence of carbon black on thermal properties and flammability of cross-linked elastomers. *J Therm Anal Calorim.* 2008;3:697–701.
- Khatua BB, Das CK. Effect of processability on the thermal stability of the blends based on polyurethane. Part II. *J Therm Anal Calorim.* 2000;63:565–76.
- Sulkowski WW, Mistarz S, Borecki T, Moczyński M, Danch A, Borek J, et al. Kinetic parameters from thermogravimetric study of used rubber granulates-polyurethane composites. *J Therm Anal Calorim.* 2006;84:91–7.
- Jin FL, Park SJ. Thermal stability of trifunctional epoxy resins modified with nanosized calcium carbonate. *Math Sci Eng A.* 2008;478:334–8.
- Sultan W, Busnel JP. Kinetic study of polyurethanes formation by using differential scanning calorimetry. *J Therm Anal Calorim.* 2006;83:355–9.
- Lizymol PP, Thomas S. Rheological behaviour of binary and ternary blends of poly(vinyl chloride) (PVC), poly (ethylene-co-vinyl acetate) (EVA) and poly (styrene-co-acrylonitrile) (SAN). *Eur Polym J.* 1997;33:1397–9.
- Cowie JMG, McEwen IJ, McIntyre R. Aging and degradation of polymer blends, chap. 14. Dordrecht: Academic Publisher; 2003. p. 976.
- Lin B, Yang L, Dai H, Hou Q, Zhang L. Thermal analysis of soybean oil based polyols. *J Therm Anal Calorim.* 2009;95: 977–83.
- Radhakrishnan CK, Sujith A, Unnikrishnan G. Thermal behaviour of styrene butadiene rubber/poly(ethylene-co-vinyl acetate) blends TG and DSC analysis. *J Therm Anal Calorim.* 2007;90: 191–9.
- Zaharescu T, Jipa S, Giurginca M, Podina C. Thermal and radiation behaviour of HNBR and CSPE blends. *Polymer.* 2000;49: 7583–7.
- Zaharescu T, Jipa S, Podina C. Thermal behaviour of ethylene-propylene elastomer. *Polym Test.* 1998;17:99–106.
- Lee YS, Lee WK, Cho SG, Kim I, Ha CS. Quantitative analysis of unknown compositions in ternary polymer blends: a model study on NR/SBR/BR system. *J Analyt Appl Pyrolysis.* 2007;78:85–94.
- Kole S, Chaki TK, Bhowmick Anil K, Tripathy DK. Effect of ageing on the dielectric behaviour of silicone-EPDM blends. *Polym Degrad Stab.* 2003;225:21–35.
- Rybinski P, Janowska G, Antkiewicz W, Krauze S. Thermal stability and flammability of butadiene-acrylonitrile rubber cross-linked with iodoform. *J Therm Anal Calorim.* 2005;81:9–13.
- Cibulková Z, Polovková J, Lukeš V, Klein E. DSC and FTIR study of the gamma radiation effect on *cis*-1,4-polyisoprene. *J Therm Anal Calorim.* 2006;84:709–13.
- Gu A, Liang G. Synthesis, morphology, and viscoelastic properties of cyanate ester/polyhedral oligomeric silsesquioxane nanocomposites. *J Polym Sci A Polym Chem.* 2003;43:3887–98.
- Radhakrishnan CK, Sujith A, Unnikrishnan G. Dynamic mechanical properties of styrene butadiene rubber and poly (ethylene-co-vinyl acetate) blends. *J Therm Anal Calorim.* 2008;15:161–71.
- Varghese H, Bhagawan SS, Thomas S. Thermogravimetric analysis and thermal ageing of crosslinked nitrile rubber/poly(ethylene-co-vinyl acetate) blends. *J Therm Anal Calorim.* 2001;63:749–63.
- Marzocca AJ, Ghilarducci A, Salva H. About the activation energies of the main and secondary relaxations in cured styrene butadiene rubber. *J Appl Polym Sci.* 2009;113:2361–7.
- Kijima M, Fujiya D, Oda T, Ito M. Efficient thermal conversion of polyene-type conjugated polymers to nano-structured porous carbon materials. *J Therm Anal Calorim.* 2005;81:549–54.
- Prolongo SG, Prolongo G. Epoxy/poly(4-vinylphenol) blends crosslinked by imidazole initiation. *J Therm Anal Calorim.* 2007;87: 259–68.
- Ismail H, Yusof AMM. Blend of waste poly (vinylchloride) (PVCw)/acrylonitrile butadiene-rubber (NBR): the effect of maleic anhydride (MAH). *Polym Test.* 2004;23:675–83.
- Bhattacharjee S. PhD Thesis, Positron annihilation spectroscopy study of rubber-carbon black composites. Indian Institute of Technology, Kharagpur, 1992. p. 75.
- Agostini DLS, Constantino CJL, Job AE. Thermal degradation of both latex and latex cast films forming membranes. Combined TG/FTIR investigation. *J Therm Anal Calorim.* 2008;91:703–7.
- Markovska IG, Lyubchev LA. A Study on the thermal destruction of rice husk in air and nitrogen atmosphere. *J Therm Anal Calorim.* 2007;89:809–14.
- Salgueiro W, Barbosa S, Somoza A. Free volume in polypropylene matrix binary and ternary composites. *Rad Phys Chem.* 2006;18:204–7.
- Morrell PR, Patel M, Skinner AR. Accelerated thermal ageing studies on nitrile rubber O-rings. *Polym Test.* 2003;22:651–6.
- Graic N. Encyclopedia of polymer science and technology, vol. 4. New York: Wiley; 1967. p. 159.
- Gillen KT, Bernstein R, Celina M. Lifetime predictions of EPR materials using the wear-out approach. *Polym Degrad Stab.* 2006;91:3197–207.
- Nigam V, Setua DK, Mathur GN. Characterization of rubber epoxy blends by thermal analysis. *J Therm Anal Calorim.* 2001;64:521–7.
- Vaaben SR, Aguilar A, Avalos F, Ramos-de Valle LF. Carbon nanoparticles as effective nucleating agents for polypropylene. *J Therm Anal Calorim.* 2008;93:947–52.
- Wunderlich B. Quenching of polymer inside aluminum DSC pans: origin of an apparent artifact. *Therm Acta.* 2008;476:63–5.
- Essawy H, El-Nashar D. The use of montmorillonite as a reinforcing and compatibilizing filler for NBR/SBR rubber blend. *Polym Test.* 2004;23:803–7.
- Rao V, Johns J. Thermal behavior of chitosan/natural rubber latex blends TG and DSC analysis. *J Therm Anal Calorim.* 2008;92: 801–6.