Polymer Communication

Thermal and radiation behaviour of HNBR and CSPE blends

M. Giurginca[a], T. Zaharescu[b],*

[a]CERELAST Bucharest, 181 Sos. Oltenitei, Bucharest 79628, Romania
[b]R&D Institute for Electrical Engineering, 313 Splaiul Unirii, Bucharest 74204, Romania

Abstract

The changes in crosslinking, chlorine or sulphur content and unsaturation were determined for three concentrations of hydrogenated acrylonitrile–butadiene rubber (HNBR)/chlorosulfonated polyethylene (CSPE) blends (25:75, 50:50 and 75:25 wt%), and for their individual components. Thermal degradation was carried out over the temperature range from 150 up to 190°C; radiation exposure was performed at three irradiation doses: 100, 200 and 300 kGy. Mechanistic aspects of thermal and radiation ageing are pointed out. It was found that the high activation energy required during the thermal degradation of the studied polymer systems is a consequence of the interaction of mixed components. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the search on material behaviour required for various applications, the processability of two or more polymer mixtures has attracted much interest [1–3]. A major feature of two polymer mixtures is the dependence of the resulting properties on various characteristics of components: structure, blending ratio, morphology, purity and stabilisation along with the prevalent conditions. The performances of mixtures depend also on the interaction that appears upon polymer compatibilisation. However, blend stability determines the success during both production and end-use.

Polymer blends offer combinations with certain physical properties, processing characteristics, durability and cost. The modification in the behaviour of polymer systems has been the subject of many relevant studies [4–12]. Homogenous mixtures consisting of various elastomers and/or plastomers represent largely required materials for industrial usage where oil products or corrosion agents are present [13].

It is generally accepted that hydrogenated nitrile butadiene rubber (HNBR) displays excellent durability in petroleum product environment under thermal degradation. In spite of its convenient resistance in various hydrocarbons at moderate or high temperatures, the mixtures containing HNBR and other different elastomers and/or plastomers have gained less applications in rubber products manufacture than nitrile rubber [14–16].

In a previous study [17] specific responses of HNBR blended with elastomers (nitrile rubber and cloroprene rubber) or plastomers (polyvinyl chloride or chlorinated polyethylene) to the action of thermal degradation were investigated.

The main goal of this paper is the thermal assessment of binary mixtures consisting of HNBR and CSPE because these materials satisfy the operation standards being successfully used in chemical industry or nuclear power plants.

It is of interest to investigate the changes in sol fraction simultaneously with the determination of sulphur and chlorine contents. Thus, in the kinetic depiction of structural modifications occurring in HNBR/CSPE blends during oxidative degradation, spectral data were used. They were also the basis of the mechanical approach of thermal and radiation ageing.

2. Experimental

2.1. Specimens

Three blends containing hydrogenated acrylonitrile–butadiene rubber and chlorosulfonated polyethylene (25:75, 50:50 and 75:25% w/w) were prepared on a roller-mill. CSPE, Carom CSM type (Romania) contained 33.6% chlorine, 1.3% sulphur and 1.4% molar unsaturation.

* Corresponding author. Tel.: + 40-1-322-2813; fax: + 40-1-321-3769.
E-mail address: traian@gw-chimie.math.unibuc.ro (T. Zaharescu).

Table 1
IR bands used for degradation assessment

IR band	Atom group
3350	Associated OH
2240	CN
1735	C=O
1610	C=C
1460	δCH_2 (internal standard)
1370	SO$_2$Cl
1150	

Table 2
Kinetic characteristics of thermal oxidation of HNBR/CSPE blends

Sample	Rate constant at 170°C (min^{-1})	Activation energy (kJ/mol)
HNBR	0.0023	162
CSPE	0.0028	167
HNBR/CSPE = 25:75	0.0022	179
HNBR/CSPE = 25:75	0.0018	192
HNBR/CSPE = 25:75	0.0012	206

HNBR, Therban 1907 (Bayer, Germany), showed 38.5% acrylonitrile and 0.3% molar unsaturation. The blending process was carried out by milling at 50°C.

For spectroscopic measurements 1% chloroform solutions were used in order to obtain cast films on KBr windows.

2.2. Degradation

Thermal ageing of specimens was performed in an automatically controlled oven (WSU-3, Germany) over the temperature range 150–190°C for 3000 min.

Exposure to γ-radiation was performed in air inside a GAMMACELL (USA) machinery provided with a ^{137}Cs source. Three total doses (100, 200 and 300 kGy) were applied; the dose rate was 0.54 kGy/h. Total doses and the dose rate were chemically determined by Fricke dosimetry measurements.

2.3. Measurements

Thermal and radiation degradation processes were monitored by IR spectral data [18] in order to assess the structural modifications. Perkin–Elmer 577 spectrophotometer (USA) has allowed to monitor the progress in the absorbency values of the stretching bands listed in Table 1. Thermally degraded specimens were analysed after casting of polymer
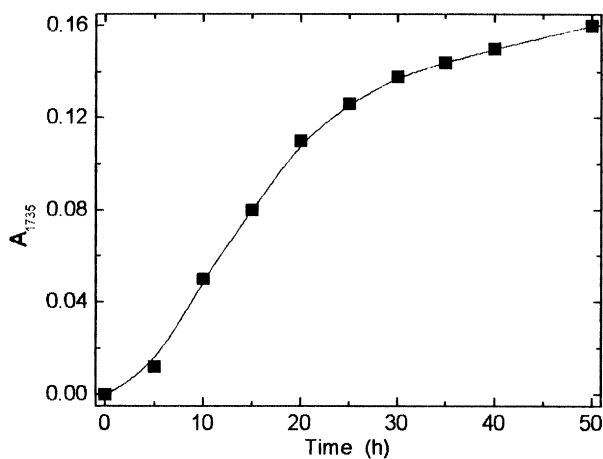

Fig. 1. Changes in the absorbency measured at 1735 cm^{-1} for HNBR/CSPE (50:50) samples at 170°C.

material on KBr windows; radiochemically processed samples were characterised using the soluble fraction after solvent removal on KBr windows.

The spectral study was completed by other measurements:

- gel formation was determined by sample dissolution in 1% methyl ethyl ketone [19] as the percentage of mass loss from initial mass;
- chlorine and sulphur contents were determined in the presence of oxygen by the Schöning technique [20];
- removed free hydrochloric acid was calculated by the subtraction of the remaining amount of chlorine from the total chlorine;
- unsaturation content was evaluated either from spectral data or from chemical methods using mercury acetate titration [21]; and
- chemical crosslinking levels were assessed by sol/gel measurements using the expression $[X] = 10^3 \rho/2M_c$, where $[X]$ represents the number of new intermolecular links, ρ the density of the processed sample and M_c the average numerical molecular weight [22].

3. Results and discussion

3.1. Thermal degradation

IR spectra have proved that during thermal degradation of HNBR/CSPE specimens two simultaneous processes occur: an increase in the content of oxygenated products suggested by the development in the absorbencies at 3350 and 1735 cm^{-1} and decreases in the absorbencies at 1370 and 1150 cm^{-1} ascribed to –SO$_2$Cl and –Cl, respectively, caused by their removal from the macromolecular backbone. Similar to the thermal behaviour of HNBR, CSPE and their blended systems show a low intensity band at 3350 cm^{-1}. This aspect was attributed to the thermal decomposition of hydroperoxydes at the testing temperatures [23] and also to their association by inter- and intra-molecular hydrogen bridges.

Structural changes that took place during thermal oxidation were confirmed by the evaluation of the C=O accumulation (Fig. 1) and by the estimation of changes in the unsaturation index, A_{1610}/A_{1460} (Table 1). From the time dependencies of A_{1735} the kinetic parameters of oxidation
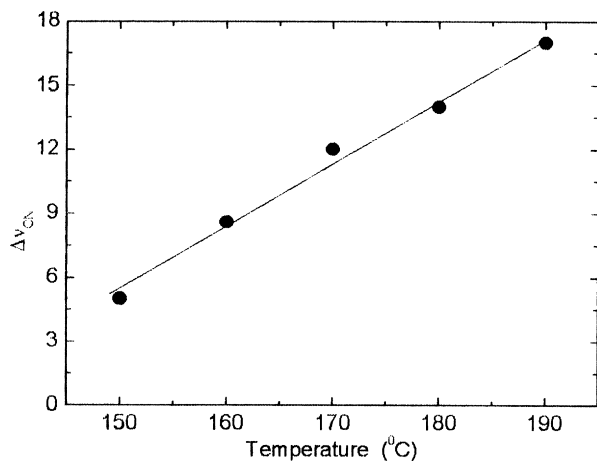
Table 3
Values of unsaturation degree and unsaturation index obtained for thermally degraded HNBR/CSPE blends

Sample	Chemical unsaturation grade (%)				Spectral unsaturation level, $[X] \times 10^5$			
	Initial	After 4 h heating at			Initial	After 4 h heating at		
	(25°C)	160°C	170°C	185°C	(25°C)	160°C	170°C	185°C
HNBR/CSPE = 25:75	0.75	0.81	0.98	1.25	0.045	0.15	0.25	0.30
HNBR/CSPE = 50:50	0.72	0.78	0.92	1.23	0.050	0.13	0.23	0.27
HNBR/CSPE = 75:25	0.73	0.74	0.89	1.19	0.052	0.10	0.19	0.23

were obtained taking into account that degradation is a first order process (pseudomonomolecular reaction) [24]. In Table 2 the values of reaction constants and activation energy obtained for HNBR, CSPE and their three blends are listed. It can be noticed that the increase in HNBR content of the blends causes the growth in the ageing activation energy. A reliable explanation of this behaviour can be the increase in oxidation resistance brought about by the raising concentration of hydrogenated acrylonitrile butadiene rubber.

In Table 3 the changes in unsaturation assessed by two different procedures (chemical method and IR spectroscopy) are presented. The content of double bonds is augmenting as the amount of HNBR decreases at higher temperatures.

Under thermal degradation HNBR, CSPE and three of their mixtures change the chlorine and sulphur contents as is shown in Table 4. The consumption of organic functions contained in the initial materials was proved by the decreasing absorbencies at 1370 and 1150 cm^{-1}. Concomitant with the depletion of chlorosulphide and acrylonitrile units, new intermolecular links are created even during milling. Increased gel fraction and crosslinking levels were confirmed by two different methods (Table 5) to prove the similarity between the growths of gel content and intermolecular links.

A significant shift of 2240 cm^{-1} towards lower frequencies was pointed out (Fig. 2). It was caused by various reactions involving C–NH and the reaction of the new unit C=NH by a similar mechanism revealed during thermal treatment of polyacrylonitrile [25]. The oxidation of C=NH units generated imide structures [26] according to the reaction:

During thermal oxidation of chlorosulfonated polyethylene, partial remove of –SO$_2$Cl and –Cl takes place [27].

This process can be carried out by other reactions that generate oxygenated structures:

The elimination of chloride and chlorosulphonyl from both mixed polymers can bring about the recombination of radical intermediates, and new crosslinked structures are formed. This type of configuration was previously mentioned for blends containing HNBR and PVC [15,28].

These reactions can be explained by the thermal degradation mechanism of HNBR/CSPE blends, when several simultaneous paths are followed. Higher HNBR content rises the gel amount and crosslinking level as well. At the

Table 4
Sulphur and chlorine contents for aged HNBR/CSPE blends

Sample	Chloride content (%)				Sulphur content (%)			
	Initial	After 4 h heating at			Initial	After 4 h heating at		
	(25°C)	160°C	170°C	185°C	(25°C)	160°C	170°C	185°C
HNBR/CSPE = 25:75	27.0	24.0	22.2	21.4	0.92	0.91	0.89	0.87
HNBR/CSPE = 50:50	18.2	15.8	14.6	13.8	0.62	0.60	0.58	0.55
HNBR/CSPE = 75:25	9.1	8.3	7.4	6.9	0.33	0.32	0.30	0.24

Fig. 2. The shift of ν_{CN} band vs. measuring temperature.

same time, this component diminishes the unsaturation in the processed polymers systems where it is added. It was earlier reported [29] that the involvement of strong electron acceptor (cyan group) stimulates inter- and intra-molecular interactions. By this route other new structures would be formed:
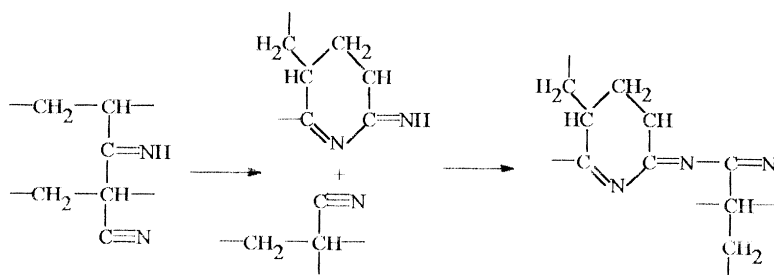
The described sequence of reactions takes place at moderate temperatures, even during the thermomechanical processing.

3.2. Radiation behaviour

The IR spectral data drawn for γ-irradiated HNBR/CSPE mixtures display similar results as was obtained for thermally degraded systems when the ageing of specimens was carried out in air. Some discrepancies in the ν_{1735} and ν_{3350} bands ascribed to oxygenated products could be detected by exposure to γ-radiation; low IR band intensities and relative constant absorbencies over the whole dose range were displayed.

The outstanding modifications in IR spectra were found in the bands ascribed to δ SO$_2$ and δ Cl. The decrease in sulphur and chlorine contents during the exposure to γ-radiation (Table 6) can be correlated with slight increase in unsaturation. For irradiated samples this small growth of unsaturation was higher than the similar property determined for thermally processed specimens. The same behaviour was found for individually γ-irradiated CSPE [30]. This process is accompanied by the significant augmentation in gel content. An advanced crosslinking was also determined

Table 5
Changes in gel content and crosslinking level for thermally degraded HNBR/CSPE blends

Sample	Gel content (%)				Crosslinking level, $[X] \times 10^5$	
	After milling at 50°C	After 4 h heating at			After 4 h heating at 160°C	After 4 h heating at 185°C
		160°C	170°C	185°C		
HNBR/CSPE = = 25:75	34.4	70.0	73.5	82.8	3.45	7.2
HNBR/CSPE = 50:50	39.7	74.2	78.4	83.8	3.85	7.7
HNBR/CSPE = 75:25	69.7	85.0	88.2	91.6	4.00	8.2

Table 6
Values of unsaturation degree and unsaturation index obtained for irradiated HNBR/CSPE blends

Sample	Chemical unsaturation grade (%)			Chloride content (%)			Sulphur content (%)		
	100 kGy	200 kGy	300 kGy	100 kGy	200 kGy	300 kGy	100 kGy	200 kGy	300 kGy
HNBR/CSPE = 25:75	0.75	0.79	0.82	26.2	25.0	23.4	0.90	0.88	0.87
HNBR/CSPE = 50:50	0.73	0.75	0.78	17.4	15.0	13.1	0.59	0.56	0.55
HNBR/CSPE = 75:25	0.70	0.72	0.73	8.6	7.3	6.1	0.32	0.29	0.25

Table 7
Changes in gel content and crosslinking level for irradiated HNBR/CSPE blends

Sample	Gel content (%)			Crosslinking level, $[X] \times 10^5$		
	100 kGy	200 kGy	300 kGy	100 kGy	200 kGy	300 kGy
HNBR/CSPE = 25:75	82.4	83.6	89.2	3.3	5.4	8.5
HNBR/CSPE = 50:50	81.8	82.7	86.1	3.9	6.4	9.2
HNBR/CSPE = 75:25	80.0	81.0	84.3	4.8	7.2	11.0
HNBR 100	78.2	80.0	83.6	3.0	4.9	6.2

(Table 7). The contribution of HNBR to the increased gel content suggests a "self-crosslinking" during γ-exposure and this process occurs likely due to the thermal crosslinking.

4. Conclusion

The behaviour of HNBR/CSPE blends during thermal degradation and radiochemical processing emphasises some relevant aspects:

- Processes start on the chlorosulfone and chlorine sites by their removal, and consequently, hydrochloric acid is expelled.
- Material crosslinking is initiated by imine intermediates and/or by inter- and intra-molecular interactions. Direct result of HCl presence would be the hydrolysis of acrylonitrile.
- The activation energy involved in thermal degradation of HNBR/CSPE blends is higher than similar values displayed by the components. It suggests a higher chemical and radiation stability in comparison with individual polymers.
- Radiation exposure induces "self-crosslinking" and this treatment can be applied to the studied materials for the improvement of their lifetime.

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