

## Thermo-oxidative degradation of some polymer couples containing HNBR

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### Summary

In this paper thermal behavior of some HNBR blends with CPE, PVC, CR and NBR at three temperatures, 150, 170 and 190°C is presented. Changes in characteristic IR bands, gel fraction, and chlorine content were assessed. Some mechanistic differences between the studied systems, regarding the involvement the depletion of chlorine and modification in gel content, were pointed out. Cyclization of nitrile structure was also observed by means of 2240 cm<sup>-1</sup> band ascribed to >C=NH. Kinetic considerations are presented.

### Introduction

Polymer blends are of large application in rubber manufacturing area, because they exhibit high performances required under severe service circumstances: performances and durability. The thermal ageing as well as the action of various petroleum derivatives on NBR (acrylonitrile rubber) and XNBR (crosslinked acrylonitrile rubber) have been reported [1-6].

HNBR (hydrogenated acrylonitrile rubber) received special attention because of remarkable stability in hydrocarbons, and higher resistance at elevated temperatures. The information on thermal stability of hydrogenated acrylonitrile rubber and polyvinyl chloride have been reported [1, 2].

This work presents thermal oxidative ageing over the temperature range 150-190°C for several polymer systems consisting of HNBR blended with CPE (chlorinated polyethylene), PVC (polyvinyl chloride), CR (polychloroprene) and NBR (acrylonitrile butadiene rubber). IR spectroscopy was used as the main testing procedure. Details on gel and chlorine content complete the kinetic presentation on thermal behavior of studied systems.

### Experimental

#### *Materials and sampling*

Five blends consisting of couples, each of two components: hydrogenated

acrylonitrile-butadiene rubber (HNBR), polyvinylchloride (PVC), chlorinated polyethylene (CPE), polychloroprene (CR), and acrylonitrile butadiene rubber (NBR) were prepared at 70°C on roller mill. The main characteristics of the components are presented in table 1.

**Table 1.** Raw materials under investigation

Code	Sort/Provider	Characteristics
HNBR	<i>Therban 1907</i>	AcN* = 38.5%
	Bayer, Germany	unsaturation = 0.3 %
PVC	<i>PVC 70</i>	Kw** = 68 - 70
	Chimcomplex Borzesti, Romania	
CPE	<i>CPE 38</i>	Cl = 38 %
	Chimcomplex Borzesti, Romania	
CR	<i>Neopren WRT</i>	1,4- <i>trans</i> = 87 %
	Du Pont, USA	1,4- <i>cis</i> = 11 %
NBR	<i>Carom NBR 3865</i>	AcN* = 38 %
	Carom SA, Romania	

\* content of acrylonitrile; \*\*K werte

Certain blend formulations of were selected in order to preserve predominantly the main features of HNBR.

### Ageing

Thermal degradation of samples was performed in an air-circulating oven (Caloris, Romania), under isothermal conditions, at three temperatures: 150, 170, and 190°C. Thermal processing was managed for 24 h, but on the first 4 h significant changes in thermal degradation could be noted.

### Measurements

Thermal degradation was monitored by IR spectral records carried out on Perkin Elmer 577 (USA) that provide information on structural modifications and development in new oxygenated product concentrations.

Along with spectral data, other determinations were performed:

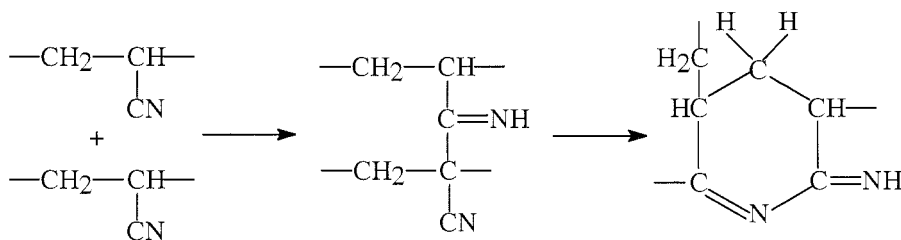
- *gel formation* determined by dissolution of polymer specimens in methylethylketone or benzene [8],
- *chlorine content* investigated by Schöniger technique in the presence of oxygen [9].

## Results and Discussion

During thermooxidation of elastomers and their couples, several modifications in IR spectra may be noticed. For all studied blends correlation between the accumulation of oxygen-bearing groups and the heating conditions, temperature and duration can be pointed out. In the case of NBR/CR samples, it was possible to detect a light change in the double bond (1,4-*trans*) content. Other modifications detected in studied systems are specific to each type of elastomer that was included in formulation. Structural

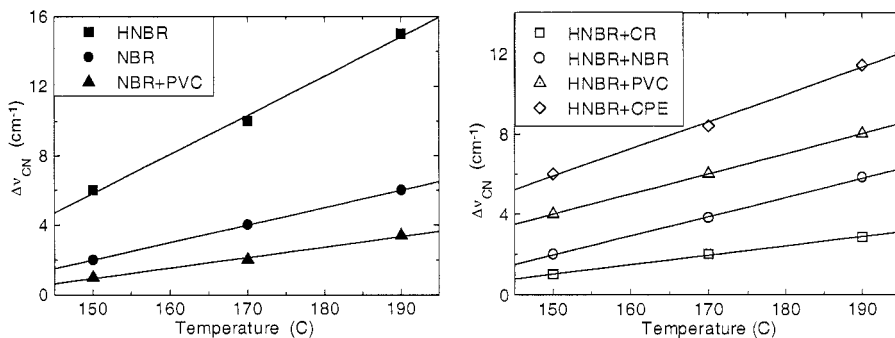
modifications occurred in NBR and HNBR (mono or dicomponent matrix) starting with changes in 3480 and 1725  $\text{cm}^{-1}$  bands were ascribed to the formation of some oxygenated groups such as dimeric OH, and C=O. At higher temperatures, the band at 3480  $\text{cm}^{-1}$  moves towards 3300  $\text{cm}^{-1}$  indicating a progress in molecular association involving OH groups and/or an enhancement in hydrogen bond strength. The creation of intra and interchain hydrogen bridges explains the stability of these materials. Simultaneous light decrease in the absorbance of bands at 960  $\text{cm}^{-1}$  (trans C=C unit), accompanied by the modification in the absorbance of 910  $\text{cm}^{-1}$  band (C=C groups) were observed in the acrylonitrile butadiene rubber [10].

The evolution of absorption band at 2240  $\text{cm}^{-1}$  characterizes the thermal process occurred in both elastomers. By increasing temperature, the shifting of this band towards lower frequencies proves that destruction process affects cyan units, as well, and the appearance of >C=NH structure would be the result of the following reaction reported for polyacrylonitrile [11]:



**Figure 1.** Cyclization on nitrile structures.

The shifting of  $\nu_{\text{CN}}$  band vs temperature for all studied polymer couples is presented in figure 2. Through the obtained  $\Delta\nu_{\text{CN}}$  values the higher one was found for HNBR/CPE blends, while the lowest figure was obtained for HNBR/CR.



**Figure 2.** Shifting of 2240  $\text{cm}^{-1}$  band.

The variation of  $\nu_{\text{CN}}$  vibration band may explain the cyclization, as an alternative way in mechanistic description of degradation process for HNBR polymeric couples. Thermal degradation of NBR alone or in the blend with PVC, starts with oxygen attack at  $\alpha$ -methylene group and /or at C=C bonds [12].

Spectroscopic investigation on the degradation of HNBR blends provides some main features:

*HNBR/PVC*

- appearance and increase in the content of oxygen-bearing groups at 3480 and 1725  $\text{cm}^{-1}$ ;
- diminishing in the concentration of C-Cl bonds, detected at three IR bands (695, 625 and 615  $\text{cm}^{-1}$ );
- lowering of  $\text{CH}_2$  and C-C structure amounts, pointed out at 1430-1260 and 1100-1000  $\text{cm}^{-1}$ , respectively;
- change in chlorine content, due to the removal of Cl function after C-Cl bond scission.

*HNBR/CPE*

- appearance and increase in the content of the oxygenated units R-CH=CH-COOH and R-COCl at 1800 and 1725  $\text{cm}^{-1}$ , respectively;
- diminution of chlorine content.

*HNBR/CPE*

- appearance and increase in the content of oxygen-bearing groups at 3480  $\text{cm}^{-1}$  (OH/OOH) and 1725  $\text{cm}^{-1}$  ( $\delta\text{C}=\text{O}$ );
- decrease in the optical density of bands assigned to  $\text{CH}_2$  and C-Cl at 1460  $\text{cm}^{-1}$  and inside the spectral domain of 750-500  $\text{cm}^{-1}$ ;
- modification in chlorine content and removing hydrochloric acid from macromolecule

The chlorine amounts initially contained in the chlorinated component of HNBR blends are reduced during their thermal degradation because of the thermal effect on macromolecules (table 2).

**Table 2.** Modification in chlorine content

Blends	Chlorine amount (%)			
	Initial	after heat treatment for 4h at		
		150 <sup>o</sup> C	170 <sup>o</sup> C	190 <sup>o</sup> C
HNBR+PVC	17.0	16.2	15.3	13.6
HNBR+CR	8.1	7.2	6.1	5.6
HNBR+CPE	7.1	6.4	5.4	4.8

Determination of gel content (table 3) confirms the fact that the structural modifications detected on IR spectra involve  $-\text{CN}$  units. This function presents large electron affinity, allowing the formation of cyclic structure together with  $>\text{CH}-$  groups that result in intermolecular and intramolecular bridging of macromolecular free radicals [13, 14].

At selected temperatures, the evolution of C=O group content warrants the assessment of some kinetic parameters in degradation process. The accumulation of carbonyl function, as a measure of the progress in oxidation state, follows a first order kinetics (pseudomonomolecular reactions) [15]. Details on kinetic characteristics (oxidation induction time and activation energy) are listed in table 4. The removal of chlorine

atoms from the second component of blends provides active structures that promote faster oxidation of hydrogenated acrylonitrile butadiene rubber. The most obvious example

**Table 3.** Change in gel content

Elastomers and couples	Gel content (%) after heat treatment for 4h at		
	150 <sup>0</sup> C	170 <sup>0</sup> C	190 <sup>0</sup> C
HNBR	3.6	4.8	17.2
NBR	40.0	52.8	78.0
CR	65.0	75.0	83.6
CPE	40.0	72.0	80.0
HNBR+NBR	11.2	20.1	35.4
HNBR+CR	16.2	21.3	32.5
HNBR+CPE	12.8	19.4	36.2
NBR+PVC	32.0	46.0	52.0

is the case of polyvinyl chloride. The oxidation induction time is the longest of studied polymer series. It indicates good thermal stability. On the contrary, the blend consisting of hydrogenated acrylonitrile butadiene rubber (HNBR) and polyvinyl chloride (PVC) shows the shortest induction period of this series. PVC suffers easily thermal dehydrochlorination [16]. Isolated double bonds and systems of conjugated double bonds are formed stepwise in degrading PVC [17]. PVC is a limit case when the concentration of unsaturation is high. The attack of oxygen leads easily to the peroxy radicals as the intermediates of propagation step of degradation. Similar behavior was pointed out in the case of acrylonitrile butadiene rubber/polyvinyl chloride where the oxidation characteristics do not differ essentially from HNBR/PVC thermal resistance. The other studied mixtures present intermediate thermal parameters due to their structural peculiarity.

**Table 4.** Induction periods and activation energies for thermal degradation of studied systems

Elastomers and couples	Induction time at 170 <sup>0</sup> C (h)	Activation energy (kJ/mol)
HNBR	4	218
NBR	1	155
CR	8	96
CPE	4	156
PVC	25	175
NBR+PVC	5	148
HNBR+NBR	5	205
HNBR+CR	8	126
HNBR+CPE	10	78
HNBR+PVC	3	106

The present results support the assertion that significant thermal stability of HNBR,

alone or in blends, is a result of high saturation of its macromolecular backbones. Another cause of the HNBR satisfactory behavior during thermal oxidation consists of the availability of cyan structure to the reorientation, offering light flexibility of saturate molecular chain as compared to NBR structure that contains double bonds which hinder relative movement of component fragments.

## Conclusions

The behavior of HNBR blends with NBR, PVC, CR and CPE, under thermal degradation conditions, emphasizes some relevant aspects:

- destruction begins, most probably, by dehydrohalogenation of chlorinated structures;
- during degradation processes oxygen-bearing groups (carbonyl/carboxyl type) appear; for polymer couples activation energies, corresponding to the formation of oxygenated functions, are lower in comparison with the energetic condition for the degradation of HNBR monosystem;
- decrease in the thermal stability of HNBR bonds would be assigned to dehydrohalogenation, accompanied by the formation of HCl, Cl<sub>2</sub> and -COCl;
- destruction of HNBR/NBR couple is dominated by the involvement of -C≡N units in the structuring processes, including creation of new intra- and intermolecular links;
- structuring of the studied polymer couples is lower relative to the behavior of individual components.

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