

Structure and Mechanical Properties of Nitrile Rubbers Modified with Iodine

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ABSTRACT: Nitrile rubbers, both common and hydrogenated, revealed some kind of ordering, as detected by WAXS. Strain-induced crystallization is responsible for the enhanced degree of crystallinity for HNBR. In the case of NBR, another mechanism has been proposed, namely specific interactions between carbon-carbon double bonds from butadiene and cyano groups from acrylonitrile monomer units, leading to an EDA complex formation. Iodination reduces the degree of crystallinity of both materials; however, their stiffness increases as the result of modification, probably due to dipole-dipole interactions or hindering effects accompanying introduction of "large" iodine atoms into the macromolecular structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 501–512, 1998

Key words: structure; crystallinity; iodination; NBR; HNBR

INTRODUCTION

Rubber goods very often have to be modified to improve their performance under certain exploitation conditions. Iodination carried out by dipping of the material in Lugol's solution¹ for a period of time of about 15–30 min showed to be very effective only when applied to nitrile rubber.² The modification significantly lowers the coefficient of friction of the material. Due to the treatment value of μ , this decreases by 30 even up to 60% for high and low loaded samples, respectively. Iodination produces a surface of higher energy, which results in increased adhesion. However, in the case of elastomers, the most important role in lowering friction is subscribed to the hysteretical component.³ The stiffening effect, accompanying the modification, dramatically reduces hysteresis loss during friction, finally leading to improved

tribological performance of the rubber. The sub-surface region plays a very important role as being responsible for accommodation of stresses and cooperation between a hard surface skin and an elastic bulk. It should exhibit a gradient nature, gradually changing its mechanical properties from the surface towards the bulk. Mechanical properties of polymers depend on their supermolecular structure. In this study the relationship between structure and mechanical properties of nitrile rubbers subjected to iodine treatment is investigated.

EXPERIMENTAL

Materials

The butadiene-acrylonitrile copolymer (NBR), Nipol N-31 (Nippon Zeon Co., Japan) and hydrogenated nitrile rubber (HNBR), Therban 1707 (Bayer AG, Germany), of the similar nitrile content of about 33 wt %, were the subject of these investigations. Samples were peroxide cured in a

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Table I Composition of the Rubber Mixes

No.	Component	Content [phr]	
		Mixture I	Mixture II
1.	Nipol N-31 (NBR) ^a	100.0	—
2.	Therban 1707 (HNBR) ^b	—	100
3.	Dicumyl peroxide (DCP) ^c	1.1	2.1

^a Butadiene–acrylonitrile copolymer (Nippon Zeon Co., Japan): 33 wt % of AN.

^b Hydrogenated butadiene–acrylonitrile copolymer (Bayer AG, Germany): 33.5(1 wt % of AN, residual double bonds content max. 1.0%).

^c Crosslinking agent, 92% of purity (Marck-Shuchardt, Germany).

Vulcanization parameters: 160°C/30 min (ISO 3417).

steel mould, under conditions (temperature/time) determined rheometrically according to ISO 3417, by means of an electrically heated press. An oscillating-disc rheometer, WG-02 (Met-alchem, Poland) was used for determination of vulcanization parameters. The amount of a curing agent, dicumyl peroxide (DCP), was established experimentally, to obtain the same degree of crosslinking, $\nu = 8.0 \pm 0.5 \times 10^{-5}$ mol/cm³, as calculated from the values of equilibrium swelling in ethanol.⁴ In this way the influence of the network density on mechanical properties of the vulcanizates was eliminated. The compositions of the materials studied are given in Table I.

Modification

Vulcanized samples of 1-mm thick were subjected to iodination by immersion in excess of Lugol's solution¹ (1 part of iodine, 2 parts of KJ, and 97 parts of distilled water), for a period of 15 min. After dipping, samples were washed extensively with distilled water and then dried in a vacuum chamber (at 50°C) up to the constant weight.

INSTRUMENTATION

Mechanical Properties

Mechanical properties in extension were studied with a mechanical testing machine, Zwick 1435 (Zwick GmbH, Germany), according to ISO 37. Dumbell specimens were used.

Structure

Fourier Transformed Nuclear Magnetic Resonance (FT-NMR)

Materials were characterized by ¹H-NMR. Spectra were recorded with a 250 MHz Bruker NMR

spectrometer. 5 to 10% solutions of the copolymers in CDCl₃ were investigated. Resonances observed were assigned according to Lindsay et al.⁵ and Singha et al.,⁶ and were attributed as follows: $\delta = 5.3$ – 5.6 ppm—olefinic protons of 1,4-butadiene units (*BD*), mainly of a *trans* configuration, $\delta = 4.9$ – 5.2 ppm—olefinic protons of 1,2-butadiene units, $\delta = 2.5$ – 2.6 ppm—methine protons of acrylonitrile units (*AN*), $\delta = 2.0$ – 2.3 ppm—methylene protons of 1,4-butadiene units, mainly of a *trans* configuration, $\delta = 1.6$ – 1.7 ppm—meth-

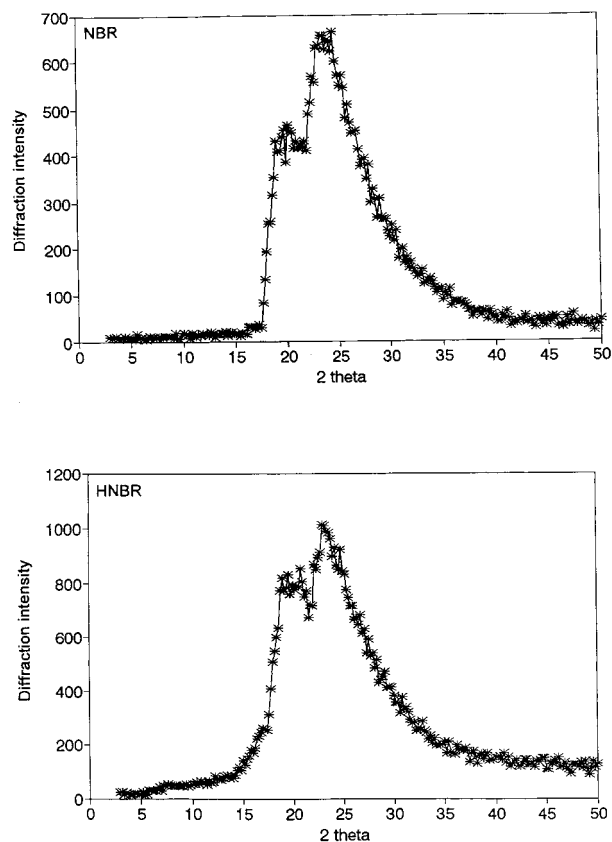


Figure 1 WAXS patterns of the vulcanizates.

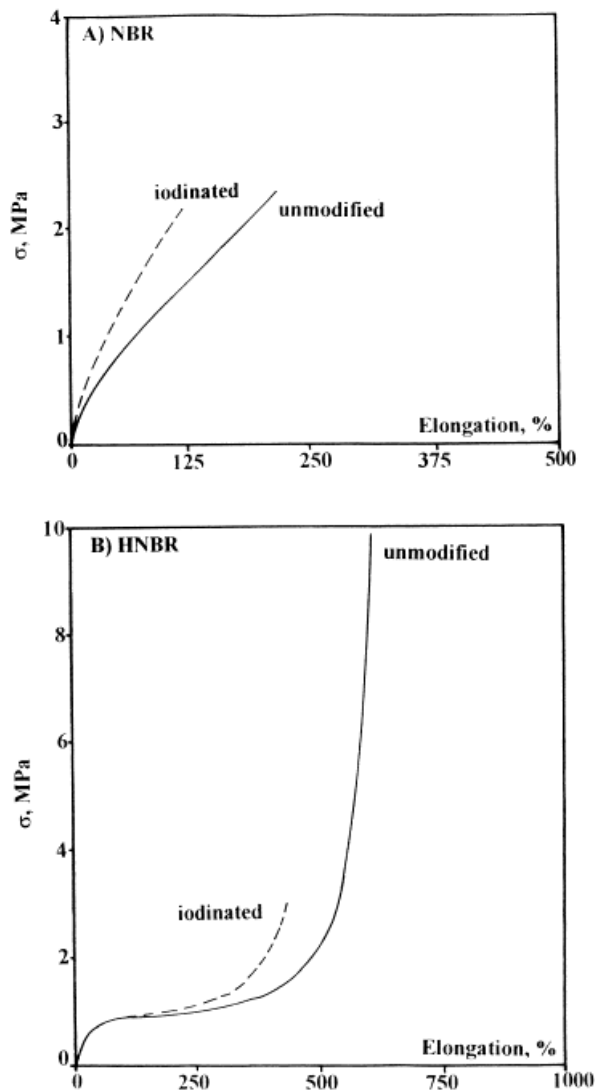


Figure 2 Tensile stress (TS) curves of the vulcanizates.

ylene protons of acrylonitrile units, $\delta = 1.2\text{--}1.4$ ppm—methylene protons of ethylene sequences (prominent in a HNBR spectrum), $\delta = 0.8\text{--}0.9$

ppm—methyl protons of ethyl groups attached to butadiene or acrylonitrile units (coming from a catalyst system used).

Fourier Transformed Infrared Spectroscopy (FTIR)

Structure of the materials subjected to specified elongations was also studied with a Bio-Rad 175C FTIR spectrophotometer. Thin films of $50 \pm 10\text{-}\mu\text{m}$ thick were scanned over the wavelength range of 500 to 4000 cm^{-1} under the following experimental conditions: 64 scans/accuracy of 2 cm^{-1} . Assignments for the polymers were as follows⁶: 2240 cm^{-1} , (—CN); 970 cm^{-1} , (olefinic C—H bending of *trans*-elements); 920 cm^{-1} , (olefinic C—H bending of 1,2 content); 755 cm^{-1} , (olefinic C—H bending of *cis*-elements); and 732 cm^{-1} , (rocking of saturated $\text{—CH}_2\text{—}$ units).

Dynamic Mechanical Thermal Analysis (DMTA)

Relaxation spectra of the materials were obtained with a PL-DMTA III (Polymer Laboratories Ltd., UK) instrument. A "two point" bending mode configuration was applied. Samples in the form of 1 mm-thick sheets were subjected to imposed oscillatory deformations of frequency $f = 1\text{ Hz}$ and amplitude $A = 0.2\text{ mm}$. A temperature range of -80 to 100°C was scanned at 1 deg/min heating rate. Storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) were plotted against temperature. A maximum in $\tan \delta$ curve was taken as a measure of T_g .

Crystallinity

Wide-Angle X-Ray Spectroscopy (WAXS)

The chain orientations at specified elongations were examined quantitatively by wide-angle X-ray spectroscopy (WAXS). Investigations were carried out in the scattering angle range of $5\text{--}40^\circ$ with a

Table II Mechanical Properties of the Vulcanizates

No.	Mechanical Properties ^a	Material			
		NBR	NBR mod.	HNBR	HNBR mod.
1.	σ_{100} [MPa]	1.2	1.9	0.9	1.0
2.	σ_{200} [MPa]	2.0	—	1.0	1.1
3.	σ_{300} [MPa]	—	—	1.1	1.3
4.	TS [MPa]	2.5	2.2	9.4	2.6
5.	ϵ_B [%]	248	107	594	402

^a σ_{100} , σ_{200} , and σ_{300} —moduli in extension (indices denote the degree of elongation). TS—tensile strength, ϵ_B —elongation at break.

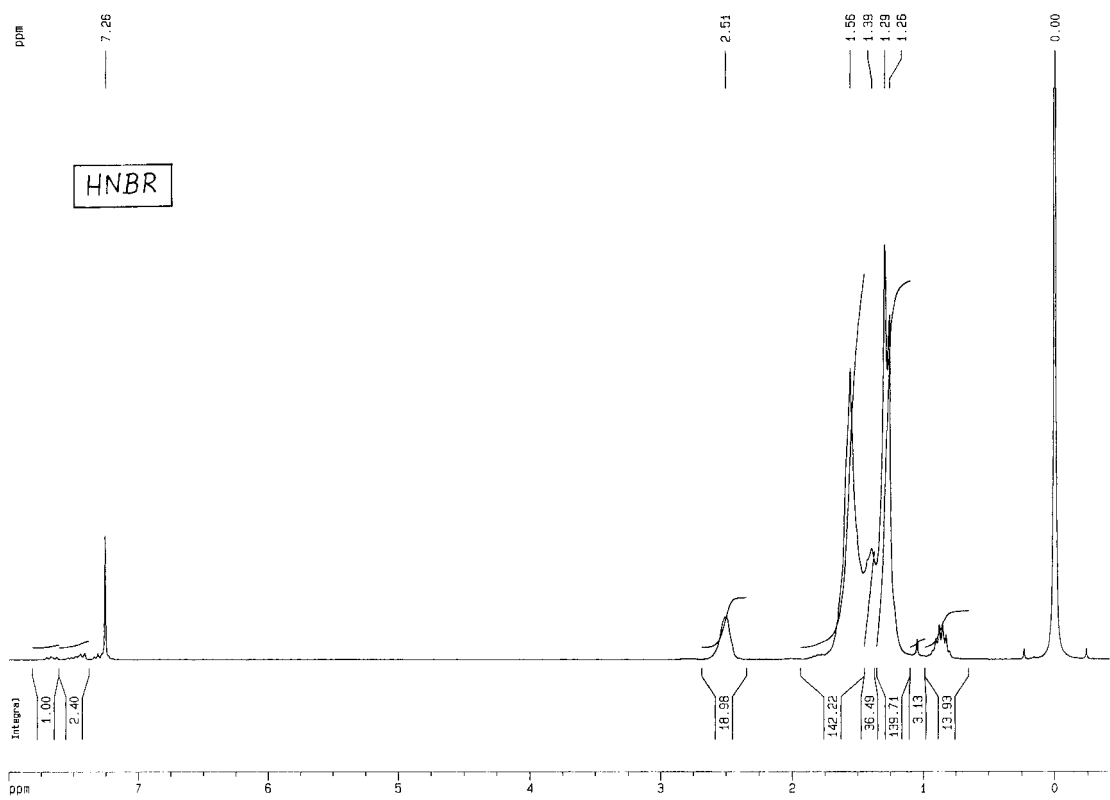
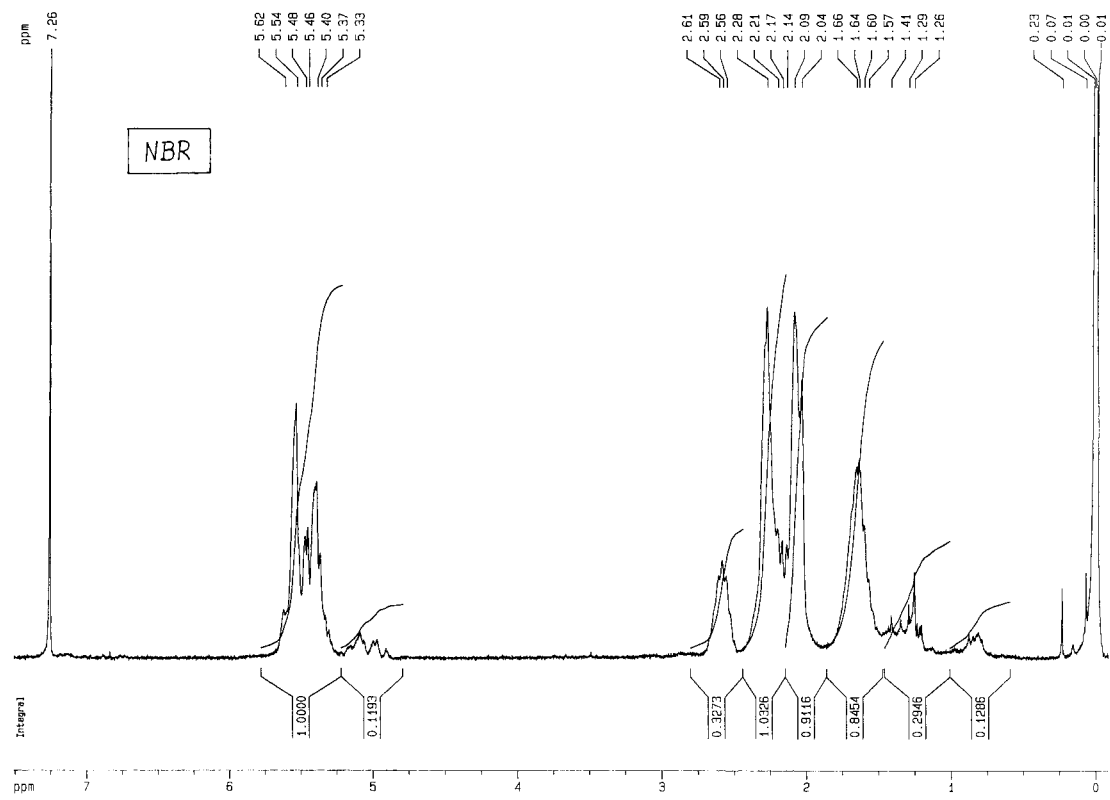


Figure 3 ^1H -NMR spectra of the polymers studied: (A) NBR, (B) HNBR.

Table III Structure of the Vulcanizates (FTIR)

No.	Material	Bands Absorbance				
		—CN	—CH=CH— 1,4 <i>trans</i>	—CH=CH ₂ 1,2	—CH=CH— 1,4 <i>cis</i>	—(CH ₂) _n —
1.	NBR	0.35	1.27	0.45	0.10	0.10
	Abs. Ratio	3.50	12.70	4.50	1.00	1.00
2.	NBR iodinated	0.73	1.68	0.98	0.26	0.26
	Abs. Ratio	2.81	6.46	3.77	1.00	1.00
3.	HNBR	0.40	0.00	0.00	0.00	0.26
	Abs. Ratio	1.54	—	—	—	1.00
4.	HNBR iodinated	0.23	0.00	0.00	0.00	0.15
	Abs. Ratio	1.53	—	—	—	1.00

step of 0.1°. Each diffraction curve was corrected for polarization, Lorentz factor, and incoherent scattering. Each measured profile was deconvoluted into individual crystalline peaks and an amorphous halo, following the procedure described by Hindeleh and Johnson.⁷ Fitting was realized using the method proposed by Rosenbrock.⁸ According to the method, an experimental X-ray diffraction pattern is approximated by the theoretical function:

$$Y_c = \sum_{i=1}^k Q_i + B \quad (1)$$

where k is the number of crystalline peaks.

Q_i is expressed either as a Gaussian or a Cauchy function, or as a combination of both.

B is a background function, which can be expressed as the polynomial:

$$B = a + bx + cx^2 + dx^3 \quad (2)$$

where x is the scattering angle 2θ .

$$Q_i = f_i \cdot A_i \cdot \exp \left\{ - \ln 2 \left[\frac{2(x - P_i)}{W_i} \right]^2 \right\} + \frac{(1 - f_i) \cdot A_i}{1 + [2(x - P_i)/W_i]^2} \quad (3)$$

Each peak is represented by four parameters: peak height A_i , peak width at a half height W_i , peak angular position P_i , and the profile function parameter f_i ; $f_i = 0$ for a Cauchy function, $f_i = 1$ for a Gaussian function, and can be any fraction for combined functions. If necessary, other functions could be used in a place of Q_i and B . All

the parameters are found by minimization of the function:

$$S = \sum_{i=1}^n (Y_{ci} - Y_{ei})^2 \quad (4)$$

where Y_{ci} and Y_{ei} are the calculated and experimental X-ray scattering intensities respectively, n is the number of intensity data. The minimization procedure is completed at a value of S given by:

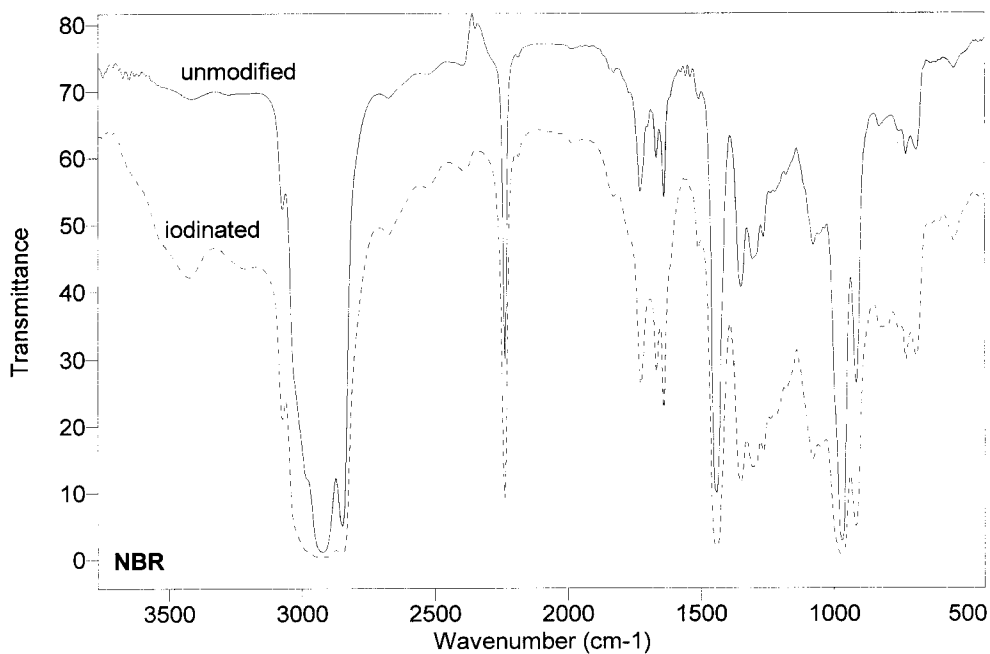
$$S = r^2 \cdot \sum_{i=1}^n (Y_{ei})^2 \quad (5)$$

where r is the relative experimental error.

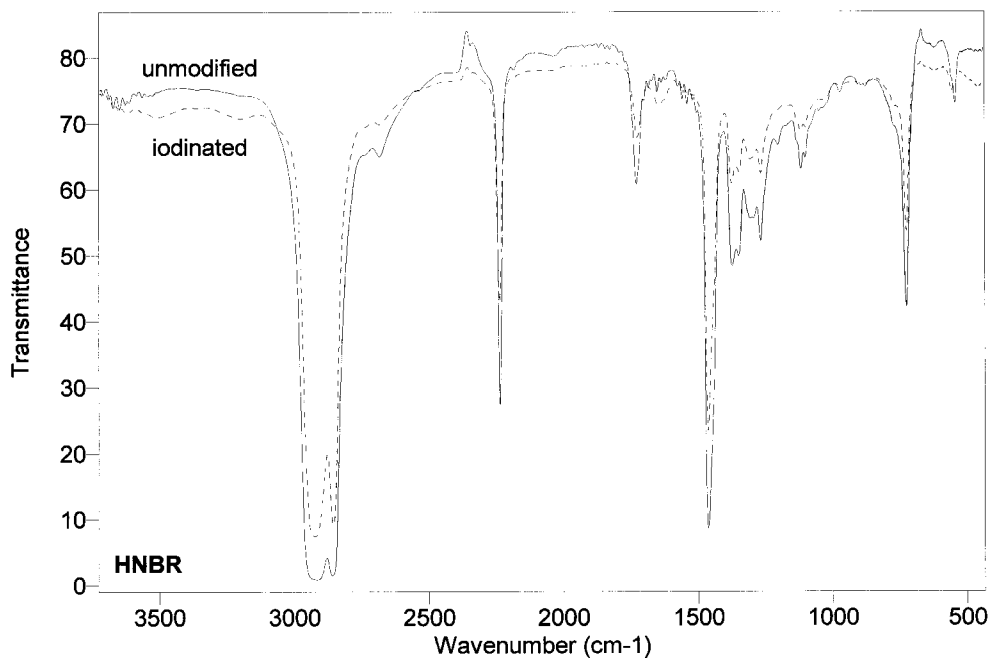
The degree of crystallinity was calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-rays scattering curve. Relative intensities were measured at two characteristic diffraction angles $2\theta = 19^\circ$ and $2\theta = 23^\circ$ (Fig. 1). They were calculated as the intensities of stretched specimens divided by those of unstretched ones, and illustrated in the way described elsewhere.⁹

Differential Scanning Calorimetry (DSC)

Heats of fusion were determined with a Perkin-Elmer DSC 7 differential scanning calorimeter, calibrated for temperature and enthalpy using indium standard. Samples of about 9–10 mg were frame-cut from sheets of constant thickness to avoid possible influence of the sample geometry on the shape of a DSC peak. Experiments were carried out under heating and cooling, over the temperature range of -100 to 50°C at a scanning rate of $10^\circ/\text{min}$. Glass transition temperature, T_g was taken as the temperature corresponding to 50% of the transition. Crystallization and melting



(a)



(b)

Figure 4 Effect of iodination on the polymers (FTIR): (A) NBR, (B) HNBR.

temperatures, T_c and T_m , respectively, were taken from the adequate curve extrema.

RESULTS AND DISCUSSION

Hydrogenation of nitrile rubber (NBR) yields a polymer of specific properties, which in principle

could be obtained by terpolymerization of ethene, 1-butene, and acrylonitrile. Contrary to statistically distributed 1,4-butadiene *cis*, *trans*, and 1,2 units, ethene sequences are chemically more resistant and able to crystallize.¹⁰ The characteristic induction period plateau, preceding the tremendous increase of tensile strength (*TS*) at an

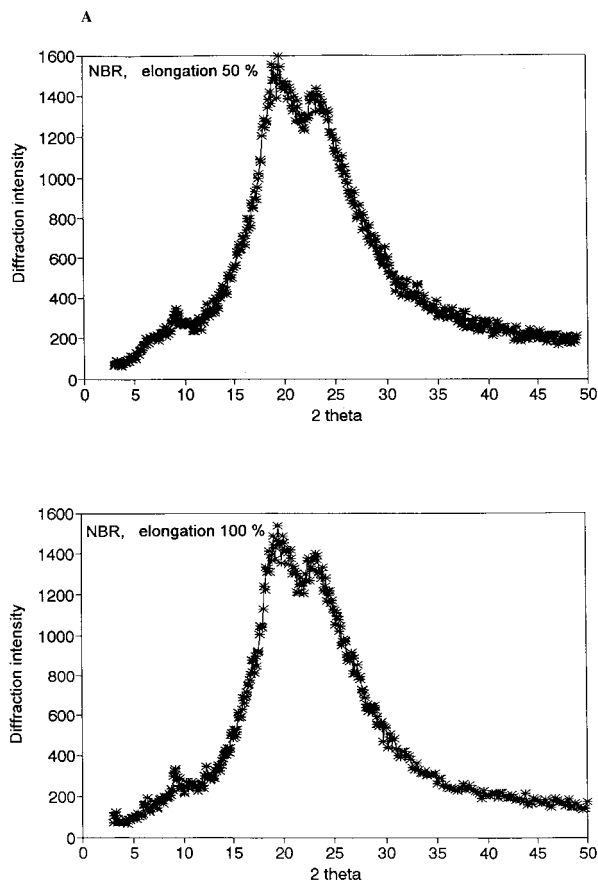


Figure 5 WAXS spectra of elongated samples: (A) NBR, (B) HNBR.

elongation of about 500%, is clearly visible in Figure 2. It results in better mechanical properties of HNBR in comparison to NBR (Table II). Contrary to mechanical experiments, X-ray diffraction does not differentiate between the crystalline phase being induced by elongation in HNBR and some kind of ordering in the case of NBR.

Structure of the Vulcanizates

Rather surprisingly, the materials exhibit a small degree of ordering, even before elongation, as suggested by WAXS (Fig. 1). However, $^1\text{H-NMR}$ spectra of the copolymers (Fig. 3) do not contain resonances that could be subscribed either to butadiene (*BD*) or acrylonitrile (*AN*)-rich sequences of more than four units. There is also no evidence of butadiene⁵ or acrylonitrile triads.^{11,12} Only methylene proton resonance, associated with *BD-BD* dyads, is observed near 2.10 ppm, as evident in the NBR spectrum. Some saturation of butadiene backbone at 1.2–1.4 ppm is also visible. Taking into consideration the free radical polymerization

of the materials, and in its consequence atacticity of the copolymers, the results of NMR analysis suggest their random structure. In the case of NBR, additionally to the 1,4 1,2 isomer form, at about 5 ppm was detected. Moreover the 1,4 structure can be of *trans*, as well as of *cis* (in minority, as suggested by a small absorption at 755 cm^{-1} in the FTIR spectra; Table III and Fig. 4) configuration. All these do not facilitate the formation of an ordered structure of the NBR studied. In the light of FTIR transmission data (Fig. 4), neither of the materials studied produce crystallinity due

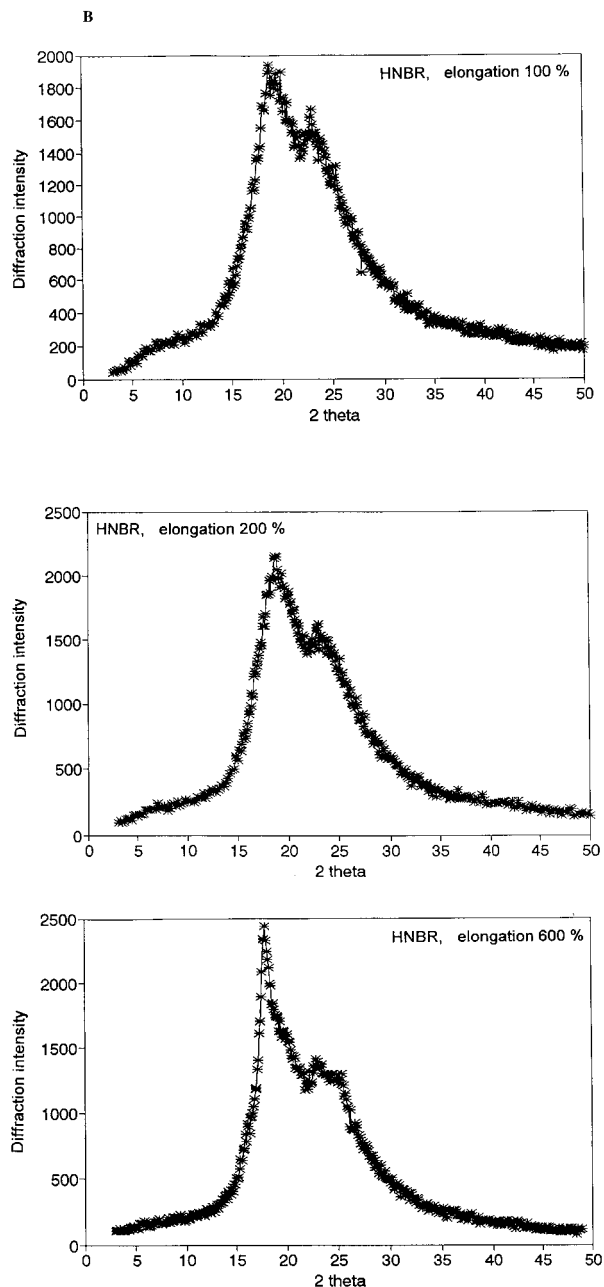


Figure 5 (Continued)

Table IV Degree of Crystallinity of the Vulcanizates (WAXS)

No.	Material	Elongation (%)	Crystallinity (vol. %)	Length of the Crystalline Area [Å] ^a			
				DI ₁₉	DI ₂₃		
1.	NBR	0	28.6	37.6	16.9		
		50	34.9	38.0	14.4		
		100	36.9	39.2	14.0		
2.	NBR iodinated	0	32.5	39.6	17.2		
		3.	HNBR	0	29.3	26.7	18.7
				100	48.0	30.4	16.2
4.	HNBR iodinated	0	31.4	27.6	15.4		
		100	36.3	35.5	18.5		
		200	34.4	34.2	16.5		

^a Calculated in the direction perpendicular to the scattering surfaces, I₁₉ and I₂₃ adequately.

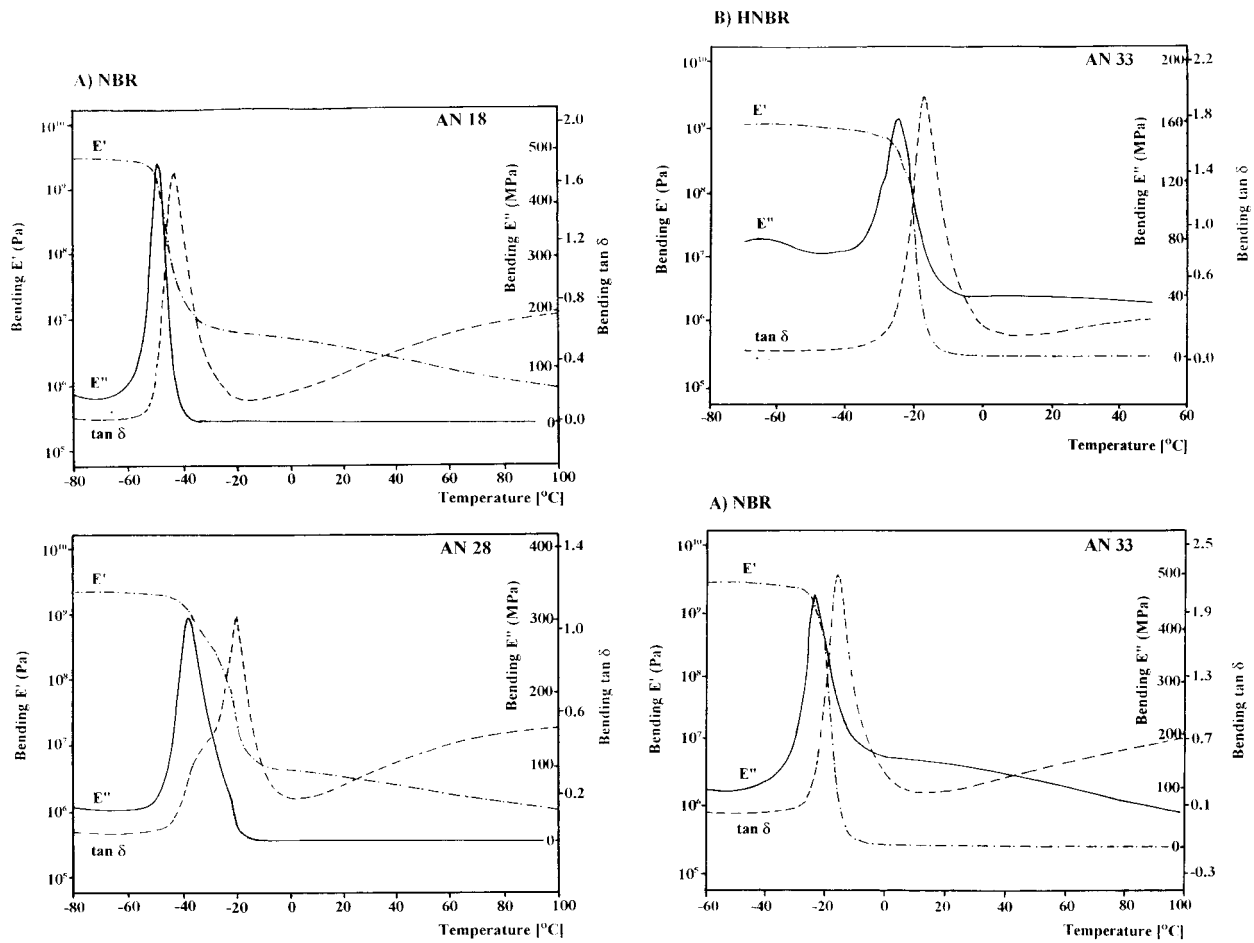


Figure 6 DMTA spectra of the polymers: (A) NBR, (B) HNBR.

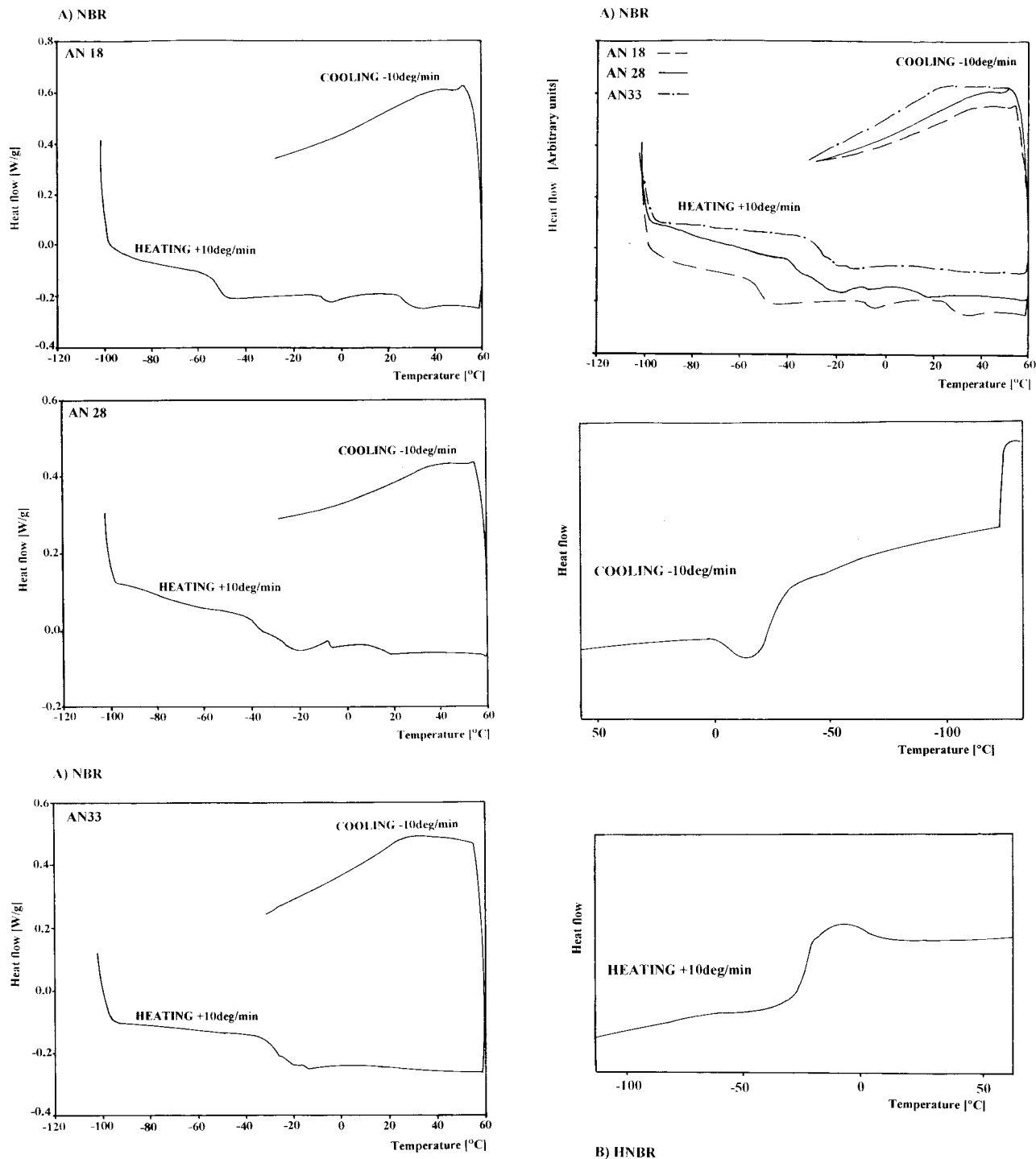


Figure 7 DSC spectra of the polymers: (A) NBR, (B) HNBR.

to elongation. Even in the spectra of HNBR there is no characteristic peak coming from the crystalline phase being formed. It could be the result of short ethylene chain fragments being involved in the process. They are likely to be visible by X-rays as an ordered phase; however, they are not long enough for IR to be detected as a crystalline phase.

WAXS spectra of elongated samples are demonstrated in Figure 5. Explanation of the data, given in Table IV, could probably lay in specific interactions between unsaturated butadiene and acrylonitrile monomer units of the rubber. Formation of EDA complexes between carbon-carbon double bonds and cyano groups was reported in the subject

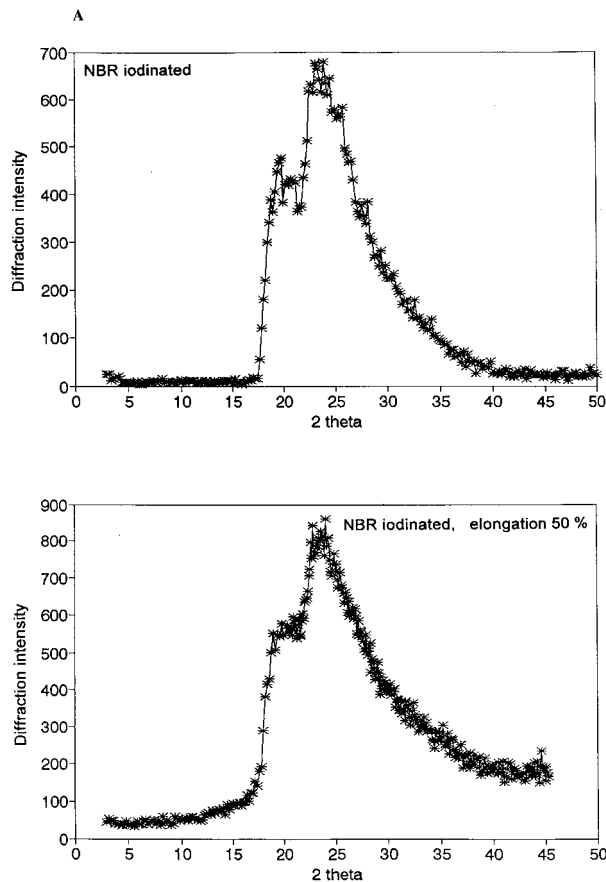
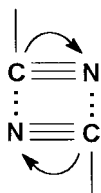


Figure 8 WAXS spectra of iodinated samples subjected to elongation: (A) NBR, (B) HNBR.

literature.¹³ Such interactions are likely to influence WAXS data, as X-ray diffraction monitors changes in electron clouds distribution. However, the same diffraction pattern visible in the spectra of “conventional” as well as hydrogenated copolymers (Fig. 1), makes the above interpretation impossible. As a matter of fact, it is very difficult to measure such crystallinity (paracrystallinity) accurately by a simple WAXS method. In our opinion, a small “crystalline” peak, visible over an amorphous halo in the WAXS spectra, is likely to be the result of strong dipole–dipole interactions between cyano groups.



DMTA spectra revealed only one relaxation transition for the both copolymers (Fig. 6). Two relaxations were reported in the literature^{14,15} for

NBR containing $20 < \text{AN} < 30$ wt %. There is up to now no HNBR available of AN content below 30 wt %. Multiphase structure cannot be the explanation of the unexpected ordering in the NBR studied, detected by X-ray diffraction. Also, DSC spectra (Fig. 7) do not confirm the WAXS data. “Crystallization ability” has been detected only for the saturated copolymer. Experimental results suggest different mechanisms to be involved in creation of the ordered structure in the polymers studied. FTIR data (Table III), as expected,

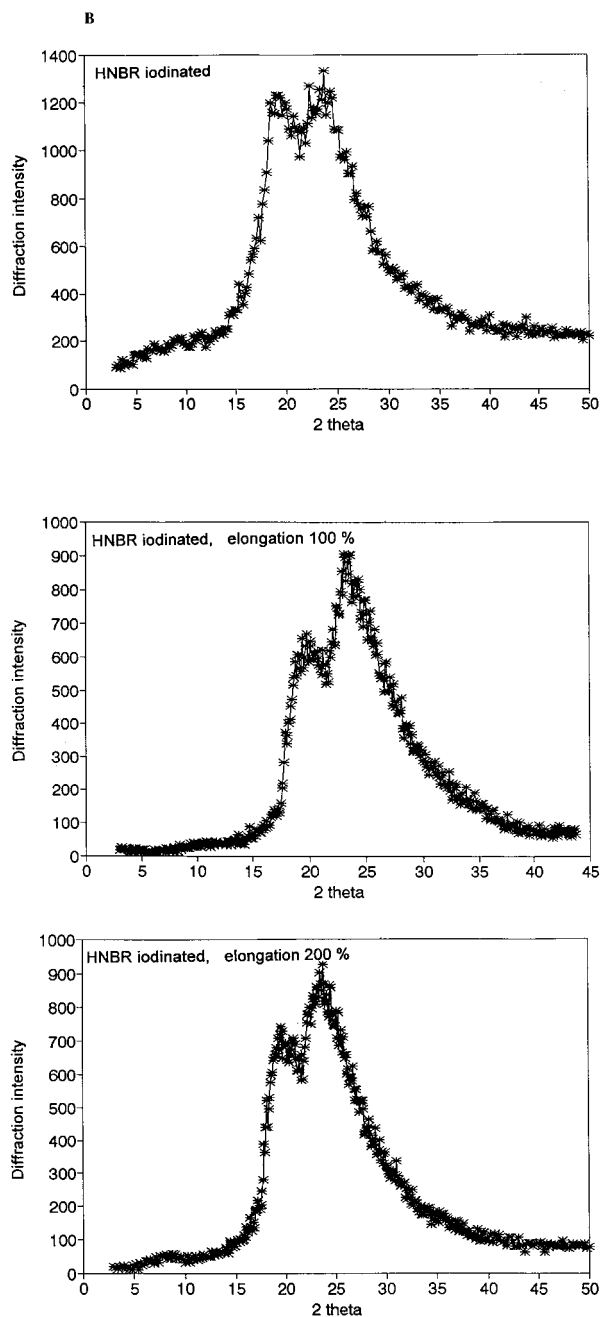


Figure 8 (Continued)

showed more complex mechanism of iodination for NBR. Calculated ratios of the band's absorbance undoubtedly point out unsaturated chain fragments to be involved in the modification, additionally complicating interpretation of the experimental results. Contrary to HNBR, in the case of NBR we can say only about a paracrystalline structure present in the material.

The Effect of Iodination

Some degree of oxidation accompanying the modification is visible due to iodine treatment. The effect is more pronounced in the case of unsaturated copolymer, where an additional band at 3400 cm^{-1} coming from —OH stretching vibrations is clearly visible (Fig. 4). Assignment of the bands, accompanying oxidation of butadiene-acrylonitrile copolymers, was performed according to Beachell and Spitsbergen.¹⁶ Due to iodine treatment the overall stiffening of both materials was observed.¹⁷ The effect, however, is more pronounced in the case of NBR, due to its unsaturation.¹⁸ The degree of crystallinity, determined by WAXS shows however the decrease of structure order as the result of modification (Fig. 8). The data are given in Table IV. A similar effect was reported earlier for nylon 6 undergoing iodination.¹⁹ The discrepancy might be the result of dipole-dipole interactions or hindering effects. "Large" iodine atoms introduced to the materials, on the one side lowers its structural order, but on the other side makes it stiffer, significantly reducing freedom of the chains' rotation.

Changes detected in the relative diffraction ratios I_{19} and I_{23} (calculated from the WAXS experiments, Fig. 8), due to the iodination, are illustrated as a function of extension in Figures 9 and 10. The ratio of the relative data I_{19}/I_{23} is similar

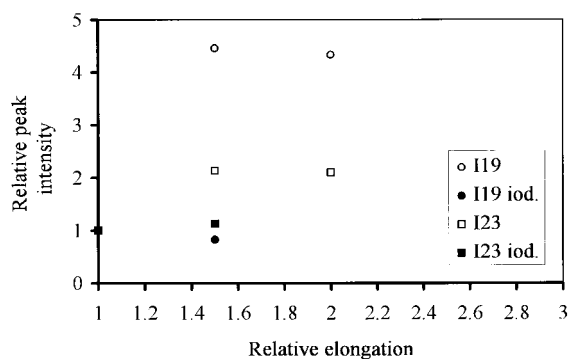


Figure 9 Influence of iodination on intensity of the relative diffractions for NBR, depicted in the function of sample elongation.

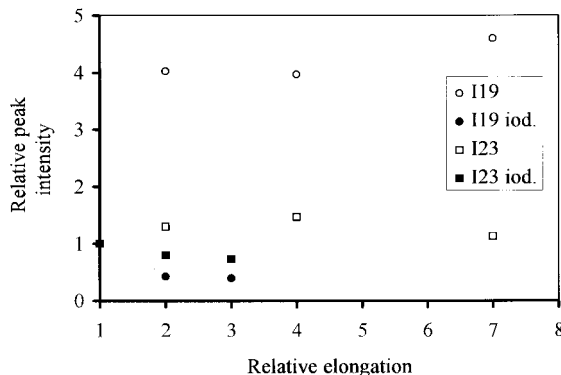


Figure 10 Influence of iodination on intensity of the relative diffractions for HNBR, depicted in the function of sample elongation.

for the elastomers studied; however, absolute values of both intensities are higher for NBR. Due to iodination, the ratio shows the same trend, but its value significantly decreases. Moreover, the relative diffractions decrease to values below 1, excluding I_{19} for NBR subjected to iodination, remaining practically at the same level. It means that the modification results in lowering of the characteristic diffractions intensities. The decrease, being different for I_{19} and I_{23} , suggests a new composition of the ordered (paracrystalline) phase, produced by the iodine treatment. A slight lowering of the degree of crystallinity is accompanied by undergoing simultaneously changes in its composition. It must be the result of specific location of iodine atoms in the material structure and its reaction with negatively charged nitrogen atoms from —CN groups.¹⁷ The modification, however, was not able to eliminate the strain-induced crystallization process, observed in the case of HNBR (Fig. 2). The results obtained, showing higher efficiency of iodination in the case of NBR, point out carbon-carbon double bonds to be the place of iodine attack as well.

CONCLUSIONS

(1) Iodination results in stiffening of NBR and HNBR vulcanizates. The effect is limited to the surface region and is the most probably connected with a presence of "large" iodine atoms in the structure of macromolecules. The modification results in lowering of the degree of crystallinity. (2) WAXS spectra of nitrile rubbers show two different ordered structures, increasing in volume with the increase of the degree of elongation, at diffraction angle $2\theta = 19^\circ$ and 23° . (3) The relative inten-

sities of diffractions at 19° and 23° vary with the degree of elongation and depend on the modification. (4) Ratio of the relative intensities of diffractions at 19° and 23° consistently follows the same tendency; however, the changes produced by iodination are slightly more pronounced in the case of HNBR.

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