

# Influence of Iodination on Tribological Properties of Acrylonitrile–Butadiene Rubber

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Received 24 June 1996; accepted 2 October 1996

**ABSTRACT:** Surface modification of acrylonitrile-butadiene copolymer (NBR) vulcanizates by treatment with an iodine solution results in a significant decrease in the coefficient of friction. The effect of modification is attributed to formation of a thin surface layer, incorporating iodine species, which has a higher modulus than the bulk material. The surface layer also has an increased roughness which, combined with the increased local stiffness, causes the reduction in friction. These factors overcome an observed increase in the surface energy after modification, which would act to increase the friction. NBR subjected to iodination kept its bulk elasticity, which plays an important part in the mechanism of deformation of the elastomer under conditions of friction, and ensures that the modified NBR retains its properties in engineering applications. The durability of the surface modification is attributed to interactions between iodine and nitrile groups from the acrylonitrile monomer units. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1927–1936, 1997

**Key words:** rubber; gradient polymers; surface modification; tribology

## INTRODUCTION

The use of rubbers as engineering materials in a dynamic contact environment is limited because of their poor tribological properties, especially when lubrication of the friction pair is not possible or should be avoided. The former situation occurs during the beginning of motion of the machine, when unstable dynamic conditions make creation of the lubricating film difficult. The latter case, when lubrication is not allowed, arises because of health protection regulations or ecological reasons. The advantages of systems that do not require lubrication are considerable savings be-

cause of simplification of mechanical construction, prolonged exploitation and cheaper maintenance of the machine, and ecological acceptability.

To meet the engineering requirements for rubbers in dynamic contact situations, the material has to be modified. It is essential for the modification to preserve the elastic properties of the rubber, which are required for the proper performance of the component. Treatment producing surface modification and leaving the bulk intact, and retaining its elastic properties, seems to be one of the best solutions for the problem. This article reports the effect on the tribological properties of acrylonitrile-butadiene (NBR) rubber of modification of the surface by treatment with an iodine solution. The surface structure of the modified rubber is also investigated by x-ray photoelectron spectroscopy and atomic force microscopy.

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Contract grant sponsor: Polish Committee for Scientific Research (KBN).

Contract grant number: PB1283/T08/95/08.

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**Table I Composition and Vulcanization Parameters of the Materials Studied**

Material	NBR	HNBR	BR
DCP [phr]	1.2	2.1	0.1
Degree of crosslinking, <sup>2,3</sup> $\nu$ [mol/cm <sup>3</sup> ] $\times 10^{-5}$	7.8	8.0	8.5

Parameters of vulcanization: 433 K/30 min (ISO 3417).

NBR—acrylonitrile-butadiene copolymer (Nipol N41, Nippon Zeon Co., Japan) 29 wt % of acrylonitrile,  $\approx 10\%$  of butadiene monomer units of 1,2 configuration. HNBR—hydrogenated acrylonitrile-butadiene copolymer (Therban 1706, Bayer AG, Germany),  $<0.9\%$  of double bonds, 32.5 wt% of acrylonitrile. BR—*cis*-1,4-polybutadiene (Nipol BR 1221, Shell Int., UK),  $\approx 96.5\%$  of *cis*-1,4 structure.

## EXPERIMENTAL

### Materials

Peroxide vulcanizates of acrylonitrile-butadiene copolymer (NBR), Nipol N41 (Nippon Zeon Co., Japan), hydrogenated acrylonitrile-butadiene copolymer (HNBR), Therban 1706 (Bayer AG, Germany), and *cis*-1,4-polybutadiene (BR), Nipol BR1221 (Shell Int., UK) were the subject of the investigation. Dicumyl peroxide (DCP, 92 wt % of purity), supplied by Merck-Schuhardt (Germany) was used as a curing agent. The rubber composition and parameters of vulcanization are given in Table I.

Rubber master batches were prepared by mixing in a David Bridge (UK) laboratory two-roll mill for 15 min at  $313 \pm 2$  K. Samples were cured in a steel mold, using an electrically heated press, under optimal conditions (time/temperature) determined rheometrically, according to ISO 3417. An oscillating disc rheometer, WG 02 (Met-alchem, Poland) was used.

Prior to modification the vulcanizates were extracted in methanol, during 48 h in the dark, using a Soxhlet apparatus. The extraction was carried out mainly to purify the rubber from decomposition products of DCP as well as antidegradants and stabilizers present in commercial polymers.

### Modification

Extracted samples were dried in a vacuum chamber at 60°C and then immersed in Lugol's solution<sup>1</sup> (1 pt. I<sub>2</sub>/2 pt. KI/97 pt. distilled water) for the controlled period of time, from 1 to 30 min, at ambient conditions. Immediately after the immer-

sion, the surface of the material was extensively washed with distilled water to stop the iodination. Finally, modified samples were dried again in a vacuum chamber at 60°C, to constant weight.

## INSTRUMENTATION

### Equilibrium Swelling

Samples of 30–50 mg weight were first extracted in acetone at ambient temperature for 48 h to eliminate impurities, then dried in vacuum at 60°C until constant weight ( $m_d$ ), which was attained usually after 12 h. The dried samples were swollen in excess toluene for 18 h at ambient temperature. The sample was then removed. Solvent retained at the surface was absorbed with filter paper, and the sample was immediately weighed ( $m_s$ ). Equilibrium swelling,  $Q_r$ , of the material was calculated as

$$Q_r = \frac{m_d - m_s}{m_s}$$

The crosslink density,  $\nu$  was calculated from the results of equilibrium swelling using the Flory–Rehner equation.<sup>2,3</sup> The percentage by volume of the polymer in a swollen sample,  $V_r$ , was calculated from

$$V_r = \frac{1}{1 + Q_r \cdot \frac{d_r}{d_s}}$$

where  $d_r$  and  $d_s$  denote the densities of the rubber and solvent, respectively. The degree of crosslinking of samples was adjusted to the value of  $\nu = 8.0 \pm 0.5 \times 10^{-5}$  mol/cm.<sup>3</sup> The influence of the crosslink density on the surface properties of rubber vulcanizates was noted in our previous work.<sup>4</sup>

### Equilibrium Modulus

Network structure parameters of the samples were obtained from equilibrium moduli in extension, determined cathetometrically at ambient temperature. Strips  $4 \times 20$  mm were cut from the thin rubber film ( $50 \pm 10$   $\mu$ m thick). Experiments were carried out in the range of relative deformation not exceeding  $\lambda = 2$ , obtaining at least six experimental points. Deformation at equilibrium was measured ca. 30 min after loading. The elas-

ticity constants,  $C_1$  and  $C_2$ , from the Mooney–Rivlin equation<sup>5,6</sup>

$$\frac{F}{A_0} = 2(C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}),$$

where  $F$  is the load in Newtons and  $A_0$  is the initial cross section in  $\text{m}^2$ , were determined graphically from a plot of  $\lambda^{-1}$  vs.  $F/2A_0(\lambda - \lambda^{-2})$ . The data were fitted to a straight line with a linear correlation coefficient of at least 0.95. The elasticity constants were calculated by averaging the results from six samples.

### Chemical Microanalysis

Samples of area of  $1 \text{ cm}^2$ , cut from the thin films, were analyzed for iodine content.

### Surface Topography

The surface topography of the samples was characterized by atomic force microscopy (Burleigh Co., USA, ARIS-3300). The area scanned was  $5 \times 5 \mu\text{m}$ . The cantilever had a spring constant of ca.  $0.05 \text{ Nm}^{-1}$  and surfaces were imaged at a constant force, ca.  $8.4 \text{ nN}$ .

### Contact Angle

The surface energy,  $\gamma_s$  of the samples and its components: dispersive,  $\gamma_s^d$  and polar  $\gamma_s^p$ , were determined by means of contact angle measurements using the experimental procedure, utilizing a wide range of liquids of different polarity, proposed by Kuczynski.<sup>7</sup> Small drops of liquids ( $\approx 2 \mu\text{L}$ ) were placed on the clean, flat, solid surface very gently, using a Hamilton syringe. The value of the contact angle was calculated each time as an average of six measurements and the accuracy of the contact angle data was  $\pm 2^\circ$ . Experiments were carried out under ambient conditions. The polar component of the surface energy was calculated from the value of the polar interaction parameter,  $I_{sl}^p$ . Following Owens<sup>8</sup> and Kaelble,<sup>9</sup>  $I_{sl}^p$  was considered as a geometric mean of polar components of the solid and the liquid.

### Infrared Spectroscopy (FT-IR)

The materials studied were cryogenically powdered, modified, and then mixed with KBr, pressed into discs, and analyzed with a Mattson

**Table II Degree of Iodination Determined by Chemical Microanalysis**

Material	Iodine Content [wt %]		
	Time		
	1 min	15 min	30 min
NBR	1.06	13.54	14.67
HNBR	1.92	11.45	13.95
BR	0.96	1.12	1.34

5000 (Unicam Analytical Systems, UK) FTIR spectrometer. Measurements were taken over a wavelength range  $400\text{--}4000 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$ .

### X-Ray Photoelectron Spectroscopy (XPS)

The x-ray source was operated at  $110\text{--}130 \text{ W}$  and generated  $\text{Mg K}\alpha$  photons ( $1253.6 \text{ eV}$ ). A  $100 \text{ mm}$  concentric hemispheric analyzer (Vacuum Science Workshop) was operated in the fixed analyzer transmission mode, with a  $50 \text{ eV}$  pass energy. The electron take off angle was normal to the surface. The relative atomic concentration of elements present on the surface was calculated using Wagner's sensitivity factors,<sup>10</sup> modified for our instrument. XPS spectra were deconvoluted using the method of Evans.<sup>11</sup> Shape parameters of the peaks: C (1s), O (1s), N (1s) and I (3d), were taken from known compounds. Spectra were corrected for charging by assigning the principal C1s signal a binding energy,  $E_B = 284.6 \text{ eV}$ .

### Tribological Investigations

Experiments were carried out with the "ring-on-disc" apparatus described earlier.<sup>12</sup> Basically it is a "pin-on-disc" machine, modified for testing elastic materials. Kinetic coefficients of friction were investigated at  $293 \pm 15 \text{ K}$ , over the sliding speed range,  $0.05\text{--}1.0 \text{ m/s}$  and normal pressure,  $5\text{--}200 \text{ kPa}$ . No lubricants were added.

## RESULTS AND DISCUSSION

### Degree of Modification

In Table II, the susceptibility of different materials, butadiene rubber (BR), hydrogenated acrylonitrile-butadiene rubber (HNBR), and acrylonitrile-

**Table III Influence of Iodination on the Network Structure Parameters (Elasticity Constants) of the Rubber Vulcanizates**

Network Parameter	Chemical Treatment		
	Unmodified	Iodination, 1 min	Iodination, 15 min
<b>NBR</b>			
$C_1$ [N/m <sup>2</sup> ] $\times 10^{-4}$	16.7	24.8	64.8
$C_2$ [N/m <sup>2</sup> ] $\times 10^{-4}$	4.5	4.6	26.2
$\nu$ [mol/cm <sup>3</sup> ] $\times 10^{-5}$ <sup>a</sup>	8.1	12.1	31.7
<sup>b</sup>	7.8		
<b>HNBR</b>			
$C_1$ [N/m <sup>2</sup> ] $\times 10^{-4}$	14.7	41.6	146.8
$C_2$ [N/m <sup>2</sup> ] $\times 10^{-4}$	5.9	10.0	53.9
$\nu$ [mol/cm <sup>3</sup> ] $\times 10^{-5}$ <sup>a</sup>	7.2	20.4	71.9
<sup>b</sup>	8.0		
<b>BR</b>			
$C_1$ [N/m <sup>2</sup> ] $\times 10^{-4}$	17.5	18.4	25.9
$C_2$ [N/m <sup>2</sup> ] $\times 10^{-4}$	8.9	10.3	8.2
$\nu$ [mol/cm <sup>3</sup> ] $\times 10^{-5}$ <sup>a</sup>	8.5	9.0	12.6
<sup>b</sup>	8.0		

Thickness of the sample  $50 \pm 10 \mu\text{m}$ .

<sup>a</sup> Calculated from the Mooney–Rivlin equation.<sup>5,6</sup>  $C_1$ ,  $C_2$ -elasticity constants.<sup>5,6</sup>

<sup>b</sup> Calculated from the equilibrium swelling measurements.<sup>2,3</sup>

trile–butadiene rubber (NBR) to iodination, are compared. Chemical microanalysis shows that BR reacts with iodine to a far lesser extent than the acrylonitrile copolymers. The hydrogenated copolymer, HNBR, reacts to a similar extent to the unhydrogenated material, suggesting that the nitrile group is the main site of interaction with the halogen.

The extent of modification depends on the time of treatment. The higher degree of iodination at a short time of treatment,  $\tau = 1$  min., observed for HNBR in comparison to NBR, is probably connected with EDA complex formation between nitrile groups and butadiene monomer units, described in our previous work.<sup>13</sup> The diffusion-controlled kinetics of iodination leads to a material with a gradient structure, which is confirmed by microscopy. Despite a significant difference in refractive indices between the modified and unmodified material, it is difficult to determine the depth of modification with a polarized-light microscope, but SEM observations gave values of  $\approx 1 \mu\text{m}$ .

### Network Structure

The calculated values of elasticity constants, Table III may only be used qualitatively, because they are sensitive to skin effects (depth of modifi-

cation compared to sample thickness) and cracking. However, they reflect changes in the network structure of the top layer of the sample.

Iodination of NBR and HNBR vulcanizates makes the surface of the samples significantly stiffer, whereas in the case of BR the effect is much less pronounced. After a long time of treatment, only a small amount of iodine has been incorporated in the top layer of the BR sample. At the same time an oxidative process, confirmed by changes in the IR spectrum of the sample, and accompanied simultaneously by crosslinking and degradation of the BR elastomer macromolecules<sup>14</sup> would explain the moderate changes in tribological properties of the material. Extracted BR is very susceptible to ageing.

The high efficiency of modification in the case of the copolymers may be the result of (a) free rotation of the chain fragments being restricted by the association of big iodine atoms with the nitrile groups; (b) structural modification from cyclization of adjacent nitrile groups (of small probability taking into consideration the random structure of the copolymer), or (c) intermolecular interactions of the modified polar macromolecules, ionic cluster formation, etc.

A loss of mobility arising from the incorporation of relatively large amounts of iodine into the

structure will produce a stiffening of the material that would account for the large increase in  $C_2$  observed after the longer treatments.

The higher values of the elasticity constants for modified HNBR compared to modified NBR are not caused by differences in iodine contents, which are in fact similar, but may relate to the distribution of iodine: part of the iodine will interact with the olefinic bonds in the latter. It should be noted that the olefinic bonds in the copolymer have a greater proportion of 1,2 butadiene compared to the mainly 1,4 butadiene structure of BR, and the former is more reactive.<sup>15</sup>

The very high values of  $C_1$  and  $C_2$  obtained in the case of NBR and HNBR subjected to the modification for 15 min are probably the result of an increase of the energy of cohesion density. Dipole-dipole interactions of iodine containing fragments and formation of multiplets or even ion clusters,<sup>16</sup> due to interactions between groups containing quaternary nitrogen, are likely to be responsible for the unexpected values of the elasticity constants. Such ionic clusters of reported dimensions 1–10 nm,<sup>17</sup> produced by multiplet aggregation,

**Table IV Influence of Iodination on the Surface Topography of NBR**

NBR Sample	Surface Topography [nm]			
	Z-avg.	Z-rms.	Z-var.	Z-peak
Unmodified	5.66	2.50	1.96	11.30
Iodinated, 15 min	13.49	6.44	5.24	26.90

Surface topography parameters were calculated according to the following equations:

$$Z_{avg} = \frac{1}{N} \sum_{i=1}^n Z_i \quad Z_{rms} = \frac{1}{N} \sum_{i=1}^n \sqrt{(Z_i - Z_{avg})^2}$$

$$Z_{var} = \frac{1}{N} \sum_{i=1}^n |Z_i - Z_{avg}| \quad Z_{peak} = Z_{max} - Z_{min}$$

can fulfill a role not only of multifunctional cross-links<sup>18</sup> but also of an active filler.

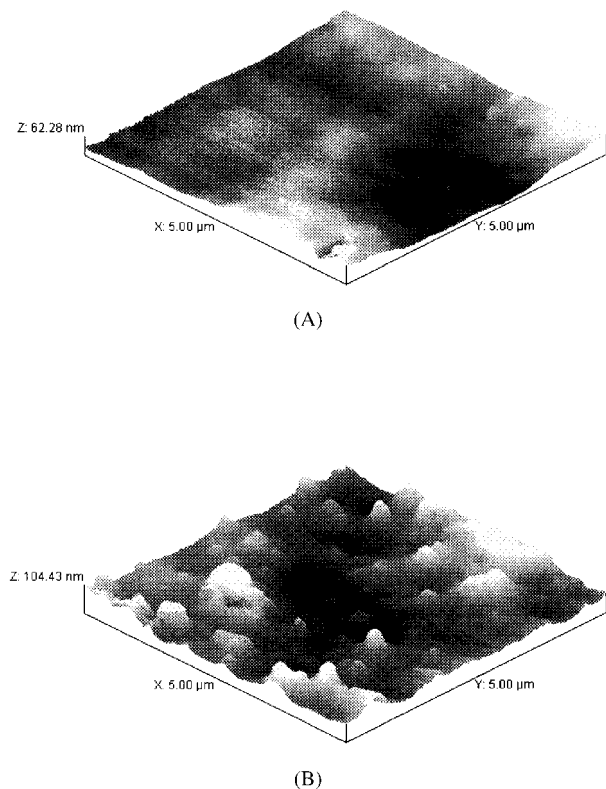
**Surface Topography**

The results of iodination of NBR are demonstrated in Figure 1, comparing the appearance of the polymer surface before and after the modification. The parameters of the surface geometry determined for unmodified sample are (on the nanoscale) appreciably different from the modified one (Table IV). Increase in the micro roughness after chemical treatment was also reported by Roberts and Brackley.<sup>19,20</sup> Optical microscopy of the iodinated thin films ( $50 \pm 10 \mu\text{m}$  of thickness) of NBR or HNBR, revealed small dark dots on the transparent background of the elastomer.

The rate of iodination process is fastest up to 15 min, then decreases asymptotically. Chemisorption of iodine on the elastomer surface leads to an initial darkening of the sample, which gradually lost its transparency. The effect was durable in the case of acrylonitrile copolymers, but less so for butadiene rubber. BR samples partly recovered their initial appearance because of halogen sublimation. IR spectra of modified samples showed that oxidation accompanying modification was significant in the case of BR, but was much less for NBR and HNBR.

**Surface Energy**

The surface energies of NBR and HNBR, calculated from contact angle measurements, change



**Figure 1** Influence of iodination on the surface appearance of NBR. (A) untreated; (B) after treatment (15 min).

**Table V Influence of Iodination on the Surface Energy of the Rubber Vulcanizates**

Component	Surface Energy, $\gamma_s$ [J/m <sup>2</sup> ] $\times 10^{-3}$		
	NBR	HNBR	BR
Without treatment			
$I_{sl}^{p,a}$	21.8	24.4	15.2
$\gamma_s^p$	2.3	2.9	1.1
$\gamma_s^d$	29.0	32.6	35.3
$\gamma_s$	31.3	35.5	36.4
Iodination, 15 min			
$I_{sl}^{p,a}$	23.2	30.7	15.2
$\gamma_s^p$	2.6	4.6	1.1
$\gamma_s^d$	33.5	35.6	35.3
$\gamma_s$	36.1	40.2	36.4

S—solid, L—liquid.

$I_{sl}^p$ —polar interaction parameter; <sup>a</sup> calculated from the geometric mean equation.<sup>6,7</sup>

$\gamma_s^p$ —polar component of the surface energy.

$\gamma_s^d$ —dispersive component of the surface energy.

$\gamma_s$ —total surface energy.

slightly after the surface treatment (Table V). No changes are observed in the case of BR. Iodination increases the dispersive component of the surface energy with both NBR and HNBR. The polar component increases slightly, although remains the minor fraction. Increase of the surface energy implies an increase in the reversible work of adhesion,<sup>21</sup> which would adversely affect the tribological properties. Though changes in surface roughness and chemical heterogeneity of the modified rubber surfaces affect the interpretation of contact angle data,<sup>22</sup> the conclusion remains that the improvement in the tribological properties on iodination does not arise from a decrease in the surface energy.

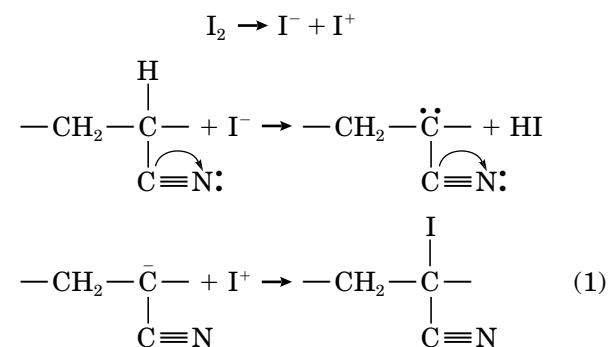
## Chemical Structure of the Surface

### Mechanism of Modification

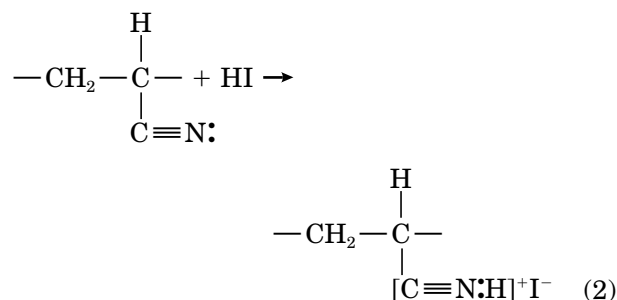
Iodination for modification of elastomers, contrary to chlorination or bromination, has not attracted much attention.<sup>23,24</sup> It is a complex process, involving substitution, addition, and probably specific interactions. FT-IR data indicate the small extent of the reactions taking place in BR, which is a consequence of the *cis*-1,4 structure of the elastomer. Unsaturation in the side chain, present in 1,2-polybutadiene, makes it more reactive.<sup>25</sup> It may be deduced that 1,2-butadiene

monomer units are mainly responsible for any iodine contained in the butadiene part of NBR.

An absorption peak, detected near 1710 cm<sup>-1</sup>, coming from the carbonyl group, indicates that oxidation processes accompany the modification. The main action of iodine is, however, connected with its interaction with acrylonitrile monomer units. The big iodine molecules are easily susceptible to polarization. The following ionic mechanism of reaction is postulated. The  $\alpha$ -hydrogen atoms of the acrylonitrile monomer units are activated by the nitrile group thereby becoming acidic, and are attacked by iodine.



The HI produced reacts, in turn, with a nitrile group to form a salt.



NMR studies of the NBR show that the amount of acrylonitrile diads and triads does not exceed 3%, i.e., NBR is a random copolymer. Cyclised nitrogen structures<sup>26</sup> are, therefore, unlikely and it is not necessary to consider further mechanisms of interaction of the iodine.

### XPS

Surface analysis performed on vulcanizates of the polar elastomers, polychloroprene rubber (CR), chlorosulfonated polyethylene (CSM), and nitrile rubber (NBR) subjected to iodination, revealed the characteristic I (3d) peak only in the case of

**Table VI Chemical Composition of the Surface of NBR Determined with XPS**

Element	$E_B$ [eV]	Atom %
C(C)	284.6	60
C(N)	286.0	10
C(-O)	286.2	12
C(=O)	287.6	1
O	532.6	11
N	399.5	5

NBR. CR and CSM were not prone to the modification as may be expected.

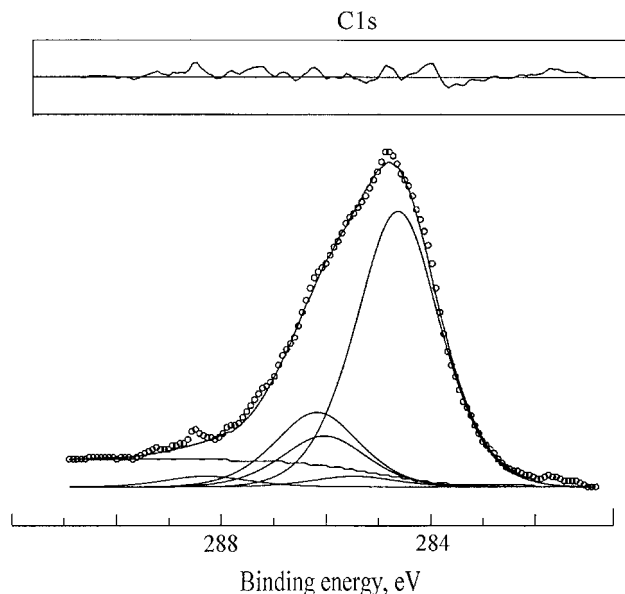
XPS analysis of the unmodified NBR sample (Table VI) showed a small silicone contamination, which survived washing with ethanol, but a significant amount of oxygen. The carbon signal (Fig. 2 and Table VI) is composed of unresolved contributions from carbon in several environments. Expected contributions<sup>10</sup> will occur at 284.6 eV ( $-C-C-$ ) and 286.0 eV ( $-C-C\equiv N$ , both carbons) from the nominal rubber composition, and 286.2 eV ( $-C-O-$ ) or 287.6 eV ( $-C=O$ ) from oxidized material. Deconvolution of the carbon envelope does not give a unique solution, but adding the constraints of the expected number of peaks and their approximate contributions as a starting point for the deconvolution gives results which can be examined for consistency with the other elements present. The deconvoluted carbon contributions are given in Table VI, where it may be seen that the atom ratio  $C(N)/N = 0.10/0.05 = 2.0 \pm 0.4$  with a conservative error of 10% per peak, cf. expected value of 2.0 [note C(N) includes both C shifted by N].

The binding energy of the oxygen species corresponds to an alcohol or ether linkage and it is possible that the ether crosslinks, or alcohol species derived from the dicumyl peroxide are being observed. In which case, the high concentration of oxygen functionalities obtained from XPS suggests that there is segregation of peroxide to the surface, which results in a high concentration of crosslinks or formation of alcohols. Correcting the O concentration for siloxane and carbonyl oxygen gives  $O = 0.11 - 0.01 - 0.01 = 0.09$  atom % and  $C(-O)/O = 0.12/0.09 = 1.3$ , i.e., the atom ratio is consistent with C(-O) being alcohol + ether groups, with expected C(-O)/O ratios of 1.0 and 2.0, respectively.

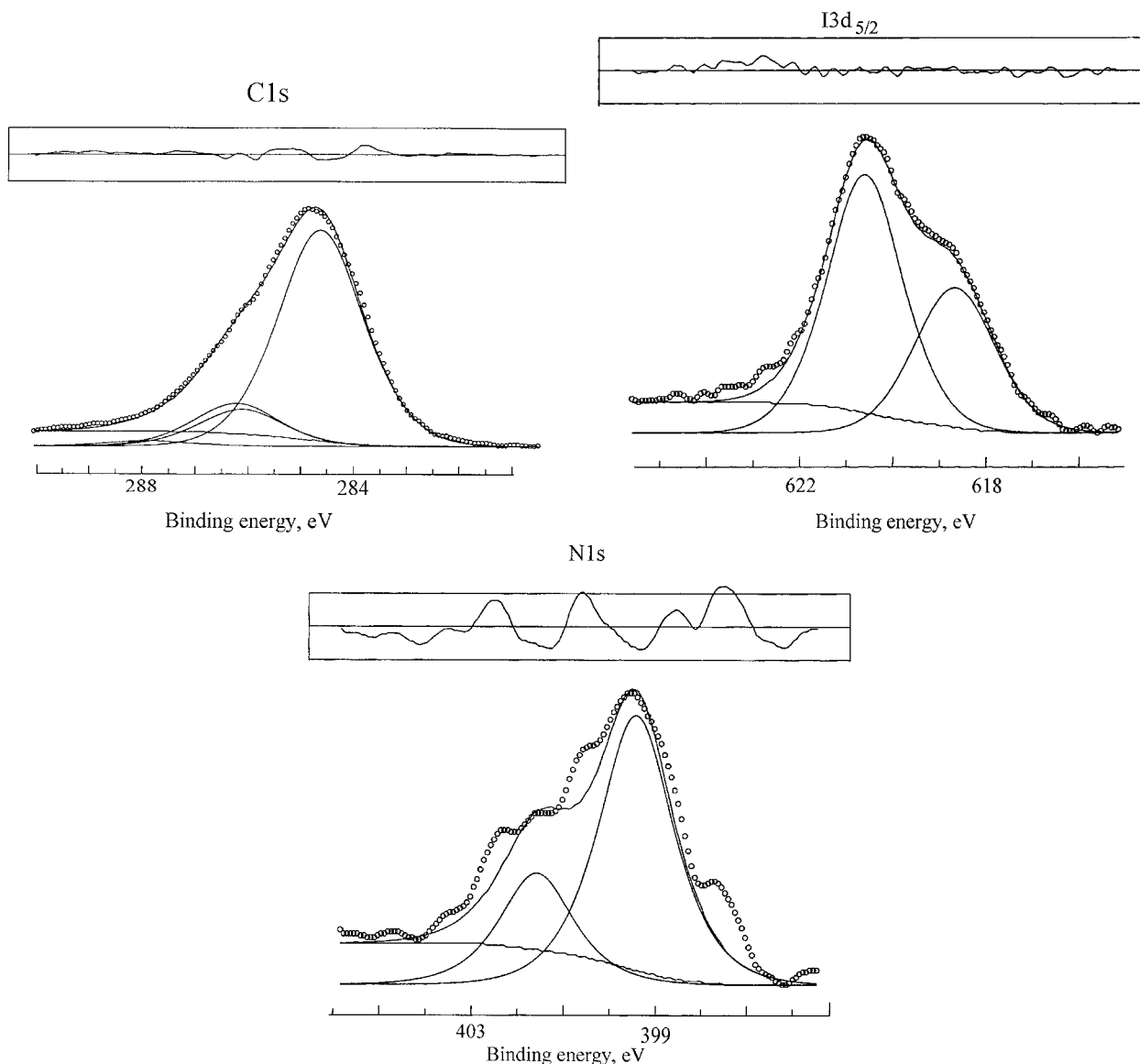
The single N1s signal at 399.5 eV is assigned to the nitrile nitrogen, and is the least ambiguous measure of the relative amount of acrylonitrile at

the surface, hence keeping in mind that theoretically  $C(N) = 2 \times N$ , the XPS atom ratio  $N/(N + C(C) + C(N))$  is  $0.05/(0.05 + 0.60 + 2 \times 0.05) = 0.07$ . The molecular weights of the comonomers are similar so the bulk monomer fraction of acrylonitrile is 0.29. The bulk atom fraction  $N/(N + C(C) + C(N))$  is, therefore,  $0.29/(0.29 + (0.29 + 4 \times 0.71) + 2 \times 0.29) = 0.07$ , in apparent agreement with the XPS result. However, the XPS calculation has neglected the oxygen functionalities, i.e., has assumed that they originate from impurities. If the oxygen functionalities are, as expected, part of the matrix they should be taken into account and the XPS value for the N : C atom ratio at the surface becomes  $N/(N + C(C) + C(N) + C(O)) = 0.05/(0.05 + 0.60 + 0.10 + 0.12) = 0.06$ , i.e., slightly less than the bulk value. The conclusion is that the acrylonitrile content of the surface of the unmodified NBR is the same or slightly less than that of the bulk material.

The XPS data for the iodine modified NBR are given in Figure 3 and Table VII. The silicone contamination and oxygen concentrations are similar to those of the unmodified material. Pronounced new features are the presence of iodine and the splitting of the N1s signal. Iodination can produce an organic iodide, or an iodide salt by reaction with a nitrile group, and the iodine  $3d_{5/2}$  signal shows two forms of iodine I1, BE 618.6 eV, and I2, BE 620.4 eV. Iodide ion has a BE of ca. 618.9 eV; thus, I1 is assigned to an  $I^-$  species. Organic



**Figure 2** X-ray photoelectron C1s spectrum of unmodified NBR.



**Figure 3** X-ray photoelectron spectra of iodinated NBR: C1s, I3d<sub>5/2</sub>, N1s (the poor statistics are the result of the weak N1s signal).

iodide would be ca. 1 eV higher in BE, and the value for I2 is consistent with  $\equiv\text{C}-\text{I}$ , though the  $\text{I}_3^-$  ion would also be a candidate.<sup>10</sup> Evidence for the former assignment may be obtained from consideration of the N1s signal. The two types of nitrogen<sup>11</sup> correspond to  $\equiv\text{N}$ , BE 399.3 eV relative concentration 0.04, and  $\equiv\text{N}-^+$ , BE 401.4 eV relative concentration 0.01, i.e., only a fraction of the nitrile groups are converted to quaternary species. The concentration of  $\text{I}^-$ , 0.01, matches that of the  $\equiv\text{N}-^+$ , 0.01. There is insufficient positive nitrogen to account for I2 being the  $\text{I}_3^-$  species; therefore, I2 is assigned to  $\equiv\text{C}-\text{I}$ .

Lastly, considering the C1s signal (Fig. 3), the envelope was deconvoluted using the same principles as for the unmodified NBR, with the addition of a contribution representing the C(I) at ca. 285.4 eV. The deconvolution data are given in Table VII and are examined for consistency as follows: the atom ratio  $\text{C}(\text{N})/\text{N} = 0.10/0.04 = 2.5 \pm 0.5$ , within the experimental error of the theoretical value 2.0: the atom % O corrected for siloxane and carbonyl is  $0.11 - 0.01 - 0.01 = 0.09$ , and therefore,  $\text{C}(-\text{O})/(\text{O}) = 0.14/0.09 = 1.6$ , again consistent with C(-O) being ethers plus alcohols.



**Table VII Atomic Ratio of the Elements Present on the Surface of Iodine Modified NBR**

Element	$E_B$ [eV]	Atom %
C(C)	284.6	54
C(I)	285.4	2
C(N)	286.0	10
C(—O)	286.2	14
C(=O)	287.6	2
O	532.3	11
N(C≡N)	399.3	3
N(N <sup>+</sup> )	401.4	1
I(I <sup>-</sup> )	618.6	1
I(C—I)	620.4	2

### Tribological Properties

The effect of iodination is apparent in the case of copolymers NBR and HNBR, significantly lowering the coefficient of friction, in contrast to BR for which  $\mu$  remains practically unchanged (Table VIII). The coefficient of friction for untreated elastomers,  $\mu$ , decreases with an increase of the normal load applied to the sample. An increase of  $\mu$  with increasing load for iodinated polymers, also reported in our previous article,<sup>27</sup> is ascribed to inadequate durability of the modified layer when exposed to extreme friction conditions. The influence of velocity on the coefficient of friction is negligible,  $\mu$  decreasing very slightly with increasing velocity (Table IX).

The tribological properties of a material are determined by adhesion at the sliding contact surfaces and the hysteresis properties of the elastomer, the latter influence arising from the polymer characteristics in the subsurface to bulk region. Changes in surface energy of the rubber should correlate with changes in the adhesional component of friction, and iodination of the copolymers

should lead to an increase of the adhesional component, considering the significant increase of the surface energy produced by the modification. The observed lowering of  $\mu$  after iodination is the result of the importance of the elastomeric properties combined with the changes in surface topography. The AFM data showed that the micro-roughness increased markedly after modification. Iodination also greatly increased the elasticity constants, and the increased micro roughness of the surface and its greater stiffness reduce the contact area and finally lead to lower values of the coefficient of friction.

### CONCLUSIONS

Iodination of butadiene–acrylonitrile copolymers is shown to be tribologically effective (lowering the coefficient of friction), for both NBR and HNBR. BR incorporates only negligible amounts of iodine and shows little effect. Electron microscopy of modified NBR and HNBR showed that iodination was confined to a thin surface layer. XPS measurements allowed covalently and ionically bonded iodine to be assessed, leading to the conclusion that iodine interacts with the majority of the nitrile groups at the surface to give the quaternary salt or substitution  $\alpha$  to the nitrile group, the latter species being predominant. Measurement of the modulus indicates an increased stiffness after modification, which arises from the presence of the big iodine atoms associated with the acrylonitrile comonomer.

The shallow depth of modification obtained was probably due to use of iodine solutions of moderate activity (Lugol's solution). Application of solvents to cause swelling of the rubber surface and further introduction of iodine molecules deeper in the ma-

**Table VIII Influence of Iodination on the Coefficient of Friction of the Rubber Vulcanizates: Influence of the Normal Pressure**

$p$ [kPa]	Coefficient of Friction, $\mu$					
	NBR	NBR iod.	HNBR	HNBR iod.	BR	BR iod.
40	1.6–2.0	0.5–0.6	1.1–1.3	0.4–0.5	1.7–1.8	1.5–1.6
90	1.7–1.8	0.5–0.6	1.1–1.2	0.5–0.6	1.2–1.4	1.3
140	1.4	0.5–0.6	1.1–1.2	0.5–0.7	1.1–1.2	1.2
180	1.1	0.7	1.0–1.2	0.6–0.7	0.9–1.0	1.0
220	1.0	0.7	0.9–1.0	0.6–0.7	0.9–1.0	0.9

Conditions of friction:  $v = 0.1$  m/s,  $p = 40$ – $220$  kPa,  $T = 293 \pm 15$  K, “dry” friction.

**Table IX Influence of Iodination on the Coefficient of Friction of the Rubber Vulcanizates: Influence of the Velocity**

$v$ [m/s]	Coefficient of Friction, $\mu$					
	NBR	NBR iod.	HNBR	HNBR iod.	BR	BR iod.
0.1	1.1	0.7	1.0–1.2	0.6–0.7	0.9–1.0	1.0
0.5	0.8–0.9	0.6	1.0	0.7–0.8	0.8–0.9	1.0
1.0	0.7–0.8	0.5	0.9–1.0	0.9	0.8	0.9

Conditions of friction:  $p = 180$  kPa,  $v = 0.1$ – $1.0$  m/s,  $T = 293 \pm 15$  K, “dry” friction.

terial is not advisable, however, because it would lead to formation of a thick modified layer, which would be unable to cooperate with the elastic bulk under dynamic conditions prevailing during friction. For the surface treatment of elastomer to be effective from the tribological point of view, it should produce a stiff, thin skin in the material. Changes of the surface energy, in the case of these elastomers, play a minor role in friction generated in dynamical processes.

Dariusz M. Bielinski thanks the Polish Committee for Scientific Research (KBN) for the financial support, Grant No PB 1283/T08/95/08, enabling the study. Scott O’Neill is grateful to EPSRC for funding.

## REFERENCES

1. *Polish Farmakopea*, 4th ed., Vol. 2, Polish Ministry of Health and Social Help, PWL, Warsaw, 1970, p. 636.
2. P. J. Flory, *J. Chem. Phys.*, **11**, 521 (1943).
3. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
4. M. Zaborski, J. Rucinski, and D. M. Bielinski, *Polimery*, **36**, 109 (1991).
5. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
6. R. S. Rivlin, *Philos. Trans. R. Soc. Lond.*, **A 240**, 459, 509; **A 241**, 379 (1948).
7. J. Kuczynski, *Polimery*, **35**, 219 (1990).
8. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13**, 1741 (1969).
9. D. H. Kaelble and K. C. Uy, *J. Adhesion*, **2**, 50 (1970).
10. D. Briggs and M. P. Seah, *Practical Surface Analysis*, 2nd ed., Vol. 1, J. Wiley & Sons, Chichester, UK, 1992.
11. S. Evans, *Surface Interface Anal.*, **17**, 85 (1991).
12. D. Bielinski, K. J. Janczak, T. Janczak, and L. Slusarski, *Polimery*, **10**, 380 (1991).
13. L. Slusarski and M. Zaborski, in *Polymer Blends*, Vol. 2, M. Kryszevski, A. Galeski, E. Martuscelli, Eds., Plenum Press, New York, 1984, p. 143.
14. A. V. Tobolski, I. B. Prettymann, and J. H. Dillon, *J. Appl. Phys.*, **15**, 324 (1944); W. Hofman, *Gummi u Asbest*, **20**, 602, 714 (1967).
15. J. Mirza, N. Schon, and J. Thormer, *Kautsch. Gummi Kunstst.*, **39**, 615 (1986).
16. L. Slusarski, M. Zaborski, and J. Kuczynski, in *Advances in Polymer Blends and Alloys Technology*, Vol. 4, K. Finlayson, Ed., Technomic Publishing Co., Inc., Lancaster, 1993, p. 62.
17. C. T. Meyer and M. Pineri, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 115 (1974); **13**, 1057 (1975); **16**, 569 (1978).
18. E. P. Otocka and F. R. Eirich, *J. Polym. Sci., Polym. Phys. Ed.*, **6**, 921 (1968); *ibid.*, **6**, 933 (1968).
19. A. D. Roberts and C. A. Brackley, *Rubber Chem. Technol.*, **63**, 722 (1990).
20. A. D. Roberts, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **50**, 321 (1992).
21. S. Wu, *J. Adhesion*, **5**, 39 (1973).
22. A. W. Neumann, *Adv. Colloid Interface Sci.*, **4**, 105 (1974).
23. I. A. Abu-Isa, *J. Appl. Polym. Sci.*, **15**, 2865 (1971).
24. R. Rajalingam and R. Krishan, *Acta Polym.*, **42**, 651 (1991).
25. B. A. Dogadkin, *Chemistry of Elastomers*, WNT, Warsaw, 1976.
26. J. M. G. Cowie, *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed., J. Wiley & Sons, Chichester, UK, 1994.
27. D. M. Bielinski, L. Slusarski, S. Affrossman, M. Hartshorne, and R. A. Pethrick, *J. Appl. Polym. Sci.*, **56**, 853 (1995).