

# Influence of Chemical Modification on Tribological Properties of Elastomers

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## SYNOPSIS

Physical properties of surface modified synthetic elastomers were studied to understand the factors that reduce friction and provide advantages in practical use. Bromination, iodination, sulfonation, and chlorination were investigated. The coefficient of friction  $\mu$  was measured using a modified version of the pin-on-disc apparatus. The surface energy, morphology, mechanical properties, and extent of chemical modification were also measured. An increased stiffness and microroughness were found to correlate with changes in the coefficient of friction. Sulfonation (100% H<sub>2</sub>SO<sub>4</sub>) was found to be the most effective and universally acceptable method of chemical treatment from a tribological point of view. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Surface treatment of polymers is an ideal way to improve their tribological properties, especially in the dry state. Modifications can lead to changes in the surface energy, decrease in tack, or increase in the chemical resistance of the elastomer. Modification can be performed in two different ways, chemical or physical processing. Chemical modification is the more reliable and simple method, enabling the treatment to be carried out satisfactorily on an industrial scale,<sup>1-11</sup> although recently there have been some promising physical methods reported.<sup>12,13</sup> Chemical modification of rubber vulcanizates allows change of the surface properties avoiding lost of elasticity and other characteristic features of the material, and broadens the number of technical applications available for rubber products. It provides a simple and effective means of allowing a rubber article, for example, gloves or windshield wiper blades, to slip more freely. A thin modified layer (up to tens of microns) arising from the surface treatment may also be a protection against chemical

attack, for example, from oils, salt water, or atmospheric aging, or may produce a smooth surface finish. Despite widespread industrial application of these methods there is a lack of a systematic investigation of the phenomena. In this article we examine the influence of different chemical treatments applied to rubber vulcanizates of typical synthetic elastomers on their tribological properties. The study covers physical, chemical, and structural effects arising from chemical processes.

## EXPERIMENTAL

### Materials

Peroxide vulcanizates of a range of polar and non-polar synthetic elastomers were studied: cis-1,4-polyisoprene, IR (Cariflex IR 305), manufactured by Shell; cis-1,4-polybutadiene, BR (Nipol BR 1221); and acrylonitrile-butadiene copolymer, NBR (Nipol N 41), manufactured by Nippon Zeon Co.; styrene-butadiene copolymer, SBR (Ker 1502), manufactured by Z. Chem. Oswiecim; ethylene-propylene-diene terpolymer, EPDM (Dutral TER 054/E), and ethylene-propylene copolymer, EPM (Dutral CO 054), produced by DSM. The samples were vulcanized using dicumyl peroxide, DCP (92 wt % of pu-

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**Table I** Composition of Rubber Mixes and Degree of Crosslinking of Their Vulcanizates

Material	IR	BR	SBR	NBR	EPDM	EPM
DCP (phr)	1.14	0.06	0.17	1.14	1.28	1.85
Degree of crosslinking $\nu$ (mol/cm <sup>3</sup> ) $\times 10^{-5}$	7.7	8.5	7.1	7.7	8.0	7.8

Degree of crosslinking was calculated from the values of equilibrium swelling in toluene, according to Flory and Rehner.<sup>19</sup>

riety), supplied by Merck-Schuhardt. Rubber master batches were prepared by mixing in a David Bridge laboratory two-roll mill for 15 min at  $313 \pm 2$  K. Because the surface energy of rubber vulcanizates was recently shown to depend on the density of crosslinks,<sup>14</sup> the amount of curing agent was individually adjusted to obtain a similar degree of crosslinking in the samples studied (Table I). To remove the products of degradation of the DCP during the vulcanization process, the samples were extracted with acetone or in the case of NBR with ethanol, using a Soxhlet apparatus for 72 h in the dark. Prior to chemical modification the samples were dried in vacuum at 333 K until constant weight was achieved. The rubber samples were prepared by pressing in a steel mold. Optimal conditions of vulcanization were determined with an Oscillating Disc Rheometer (WG02, Metalchem) according to ISO 3417 operated at 433 K for 30 min.

### Modification

Extracted rubber vulcanizates were modified using a dipping technique in which the chemicals used were always in excess, allowing concentration changes during the process to be ignored. Modifications were carried out under ambient conditions and the compositions of the solutions and method of preparation are in Table II.<sup>15-18</sup> The dipping time was generally less than 1 min; longer treatment times influence the surface morphology, causing shrinkage of the top layer and crack formation that

adversely affects the tribological properties of the rubber vulcanizates. Only in the case of iodination was the process carried out for a longer time, up to 30 min. The sample was then removed from the bath, washed with a stream of distilled water, and finally dried in a vacuum chamber at 333 K until constant weight was obtained.

### Techniques

#### Equilibrium Swelling

The density of crosslinking,  $\nu$  was calculated from the results of equilibrium swelling (48 h, 298 K) in toluene. The Flory-Rehner equation<sup>19</sup> was used

$$\nu = \frac{1}{V_1^0} \frac{V_2 + \chi V_2^2 + \ln(1 - V_2)}{V_2^{1/3} - \frac{V_2}{2}} \quad (1)$$

where  $V_1^0$  is the molar volume of the solvent (106.85 cm<sup>3</sup>/mol),  $\chi$  is the solubility parameter;

$$V_2 = \frac{V_p}{V_p + V_s} = \frac{1}{1 + \frac{V_s}{V_p}} = \frac{1}{1 + \frac{Q\rho_p}{\rho_s}} \quad (2)$$

where  $V_s$  and  $V_p$  are the volume of the solvent and polymer respectively,  $\rho_s$  and  $\rho_p$  the density of solvent and polymer, and  $Q$  the equilibrium swelling for the polymer;

**Table II** Composition of Modifying Solutions

No.	Modification	Description
1	Chlorination	Solution of Cl <sub>2</sub> in CCl <sub>4</sub> (12 wt %) <sup>15</sup>
2	Bromination	"Bromine water" (20 cm <sup>3</sup> bromine/400 cm <sup>3</sup> distilled water) <sup>16</sup>
3	Iodination	"Lugol's solution" (1 pt. I <sub>2</sub> /2 pt. KI/97 pt. distilled water) <sup>17</sup>
4	Sulfonation	"100% solution of SO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> " (mixture of fuming with concentrated sulfuric acid) <sup>18</sup>

**Table III Amount of Modifying Element Added**

Modifying Element Added (wt %)	Modification/Time				
	5 s	30 s	60 s	15 min	30 min
<b>IR</b>					
Chlorination	0.83	2.85	3.77	—	—
Bromination	4.98	30.12	35.04	—	—
Iodination	—	—	0.51	0.98	1.23
Sulfonation	0.16	0.39	0.48	—	—
<b>BR</b>					
Chlorination	0.74	7.50	10.11	—	—
Bromination	2.70	20.02	24.92	—	—
Iodination	—	—	0.96	1.12	1.34
Sulfonation	0.26	1.36	1.62	—	—
<b>SBR</b>					
Chlorination	0.39	4.75	7.50	—	—
Bromination	2.43	14.89	18.24	—	—
Iodination	—	—	0.76	1.09	1.41
Sulfonation	0.19	0.80	1.07	—	—
<b>NBR</b>					
Chlorination	0.37	2.53	3.72	—	—
Bromination	3.62	10.95	13.06	—	—
Iodination	—	—	10.59	13.54	14.67
Sulfonation	1.26	3.34	3.83	—	—
<b>EPDM</b>					
Chlorination	0.34	1.90	2.10	—	—
Bromination	2.07	5.11	6.18	—	—
Iodination	—	—	0.00	0.02	0.03
Sulfonation	0.04	0.09	0.10	—	—
<b>EPM</b>					
Chlorination	0.00	0.30	0.39	—	—
Bromination	0.00	1.32	1.78	—	—
Iodination	—	—	0.00	0.00	0.00
Sulfonation	0.00	0.08	0.11	—	—

**Table IV XPS Analysis of Modified SBR Vulcanizates**

Material	S (wt %)	O/S Atomic Ratio	S (2p) Shift (eV)	C (1s) FWHM (eV)
IR	1.6	9.7	4.5	2.2
BR	10.3	3.6	4.6	3.5
SBR	6.0	4.1	4.5	2.8
NBR	10.6	3.7	4.5	3.5
EPDM	2.1	3.2	4.5	2.2
EPM	2.0	6.9	4.3	2.5

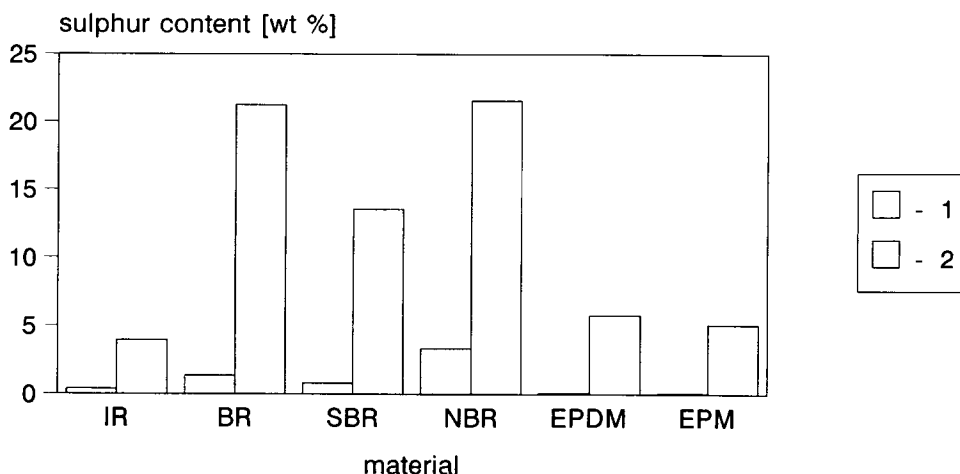
S (2p) core level shifts are relative to the binding energy, 165.0 eV, of elemental sulfur.<sup>24</sup> FWHM, full width half maximum.

$$Q = \frac{m_{SW} - m_D}{m_D} \quad (3)$$

where  $m_{SW}$  and  $m_D$  are the masses of swollen and dried sample, respectively. The degree of crosslinking of the samples was adjusted to  $\nu = 7.8 \pm 0.7 \times 10^{-5} \text{ mol/cm}^3$ .

### Scanning Electron Microscopy (SEM)

Original and modified samples were analysed using a Philips SEM 500 instrument. Cross sections, as well as surface morphology, were examined. The samples were gold coated to remove charging.



**Figure 1** Comparison between results of XPS and chemical microanalysis for sulfonated rubber vulcanizates. 1: chemical microanalysis; 2: XPS; time of modification,  $t = 30$  s.

### Polarized-Light Microscopy

Cross sections of rubber vulcanizates, before and after chemical modification, were compared using a biological microscope BIOLAR 40 (Pzo), equipped with a polarized-light attachment IP-3. Differences in the refractive indices resulting from chemical modification appeared as regions of different colors. Despite the gradient nature of the chemical treatment, assessment of the depth of modification was possible by this method.

### Fourier Transform Infrared (FTIR) Spectroscopy

Smoothed rubber films,  $50 \pm 10 \mu\text{m}$  thick, were studied, and for these films chlorination and bromination caused modification in the whole sample, confirmed by polarized-light microscopy on cross sections of the vulcanizates. The effect of iodination and sulfonation seemed to be limited to the "top" surface. The IR spectra were obtained with a Shimadzu FTIR instrument over a wavelength range of  $600\text{--}3000 \text{ cm}^{-1}$ , using 128 scans to achieve a resolution of  $2 \text{ cm}^{-1}$ .

### Chemical Microanalysis

Samples cut from the films were analyzed for chlorine, bromine, iodine, and sulfur.

### Surface Microroughness

The surface topography of the modified samples was characterized by an arithmetic average roughness parameter ( $R_a$ ) value, determined with a mechanical microprofilograph DEKTAK IIA (R.P.I. Metrolog

Division). The minimum load of 5 mg was applied to the "Sub-micron stylus" (no. 139308,  $5.0 \mu\text{m}$  radius) and the rubber surface was covered with a surfactant to prevent a "slip-stick" operation during measurement. The  $R_a$  parameter was calculated over a distance of 10 mm. The mechanical contact measurements proved to be relevant to most of our samples, which had a modified surface "skin" stiff enough to avoid any elastic interference during collection of the data. In fact no discontinuity in the surface profile resulting from stylus "jump" was observed. The  $R_a$  parameter of unmodified rubbers was taken from the surface of the steel mold used for vulcanization.

### Contact Angle Measurements

The sessile drop method was utilized for contact angle measurements. A wide range of liquids differing in polarity were used under ambient conditions. Contact angles were measured at different time intervals and the values were extrapolated to time  $\tau = 0$ . The value of the maximum contact angle was determined with an accuracy of  $\pm 2^\circ$ . The equipment used and methodology applied to determine the surface energy and its components have been described in detail elsewhere.<sup>20,21</sup> Following the results of recent investigations,<sup>14,22,23</sup> the polar interaction parameter between polymer surface and liquid was calculated from the geometric mean equation.

### X-Ray Photoelectron Spectroscopy (XPS)

The X-ray source (Vacuum Science Workshop) was operated at 110–130 W and generated Al  $K\alpha$  photons

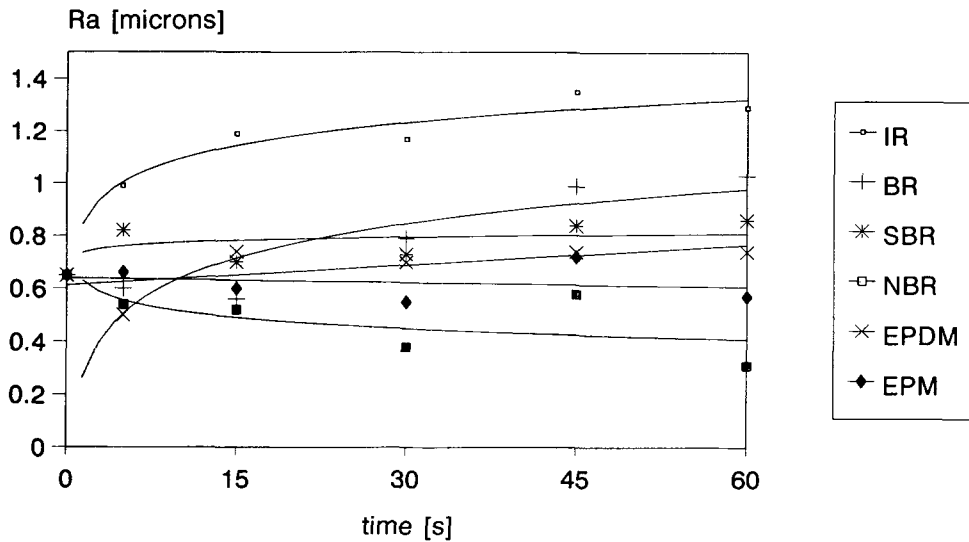


Figure 2 Surface topography of brominated rubber vulcanizates.

(1486.6 eV). A 100-mm concentric hemispheric analyzer (CHA) was operated in the fixed analyzer transmission (FAT) mode with a 50-eV pass energy and the electron takeoff angle was normal to the surface. Relative atomic concentrations of elements present on the surface were calculated using Wagner's sensitivity factors,<sup>24</sup> modified for our instrument.

**Mechanical Investigations**

Mechanical properties of the samples were obtained from equilibrium moduli measurements carried out cathetometrically. Strips were cut from the thin

rubber film ( $50 \pm 10 \mu\text{m}$  thick). The elasticity constants  $C_1$  and  $C_2$  were calculated from the simplified Mooney-Rivlin equation.<sup>25,26</sup>

$$\sigma = 2(C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \quad (4)$$

where  $\sigma$  is the stress and  $\lambda$  is the relative deformation of the sample.

**Tribological Investigations**

Experiments were carried out with a "ring-on-disc" apparatus described earlier.<sup>27,28</sup> This equipment is based on the "pin-on-disc" machine

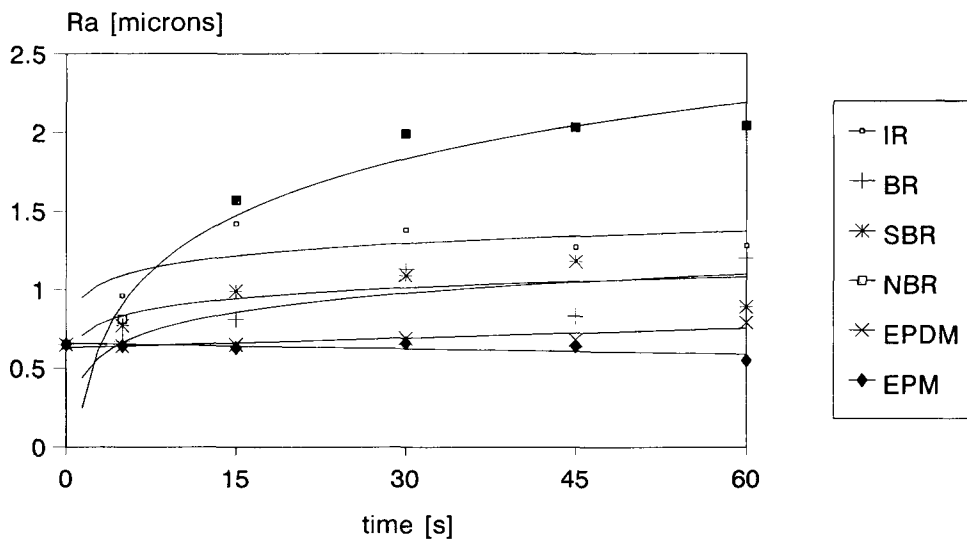
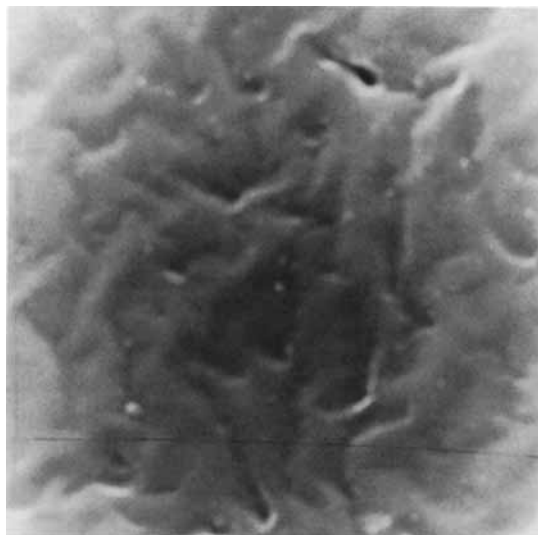
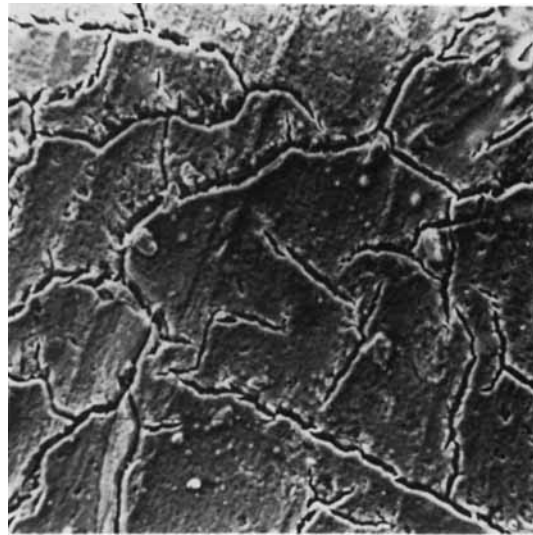


Figure 3 Surface topography of sulfonated rubber vulcanizates.



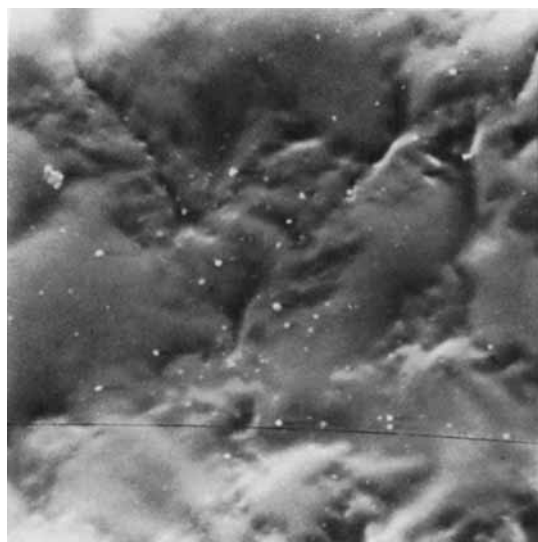
x 640

a) BR before treatment



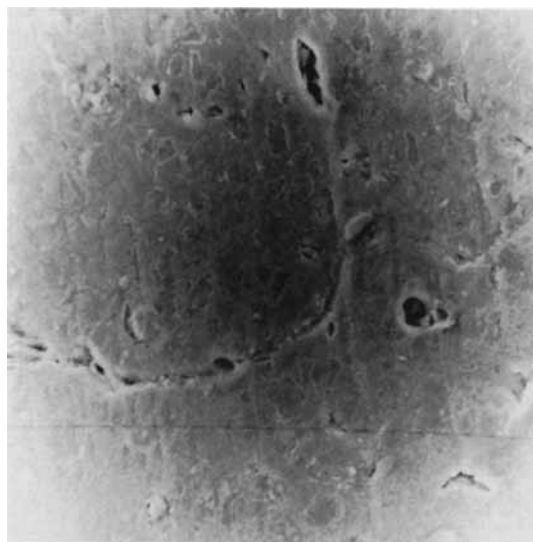
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b) BR after treatment



x 640

c) SBR before treatment



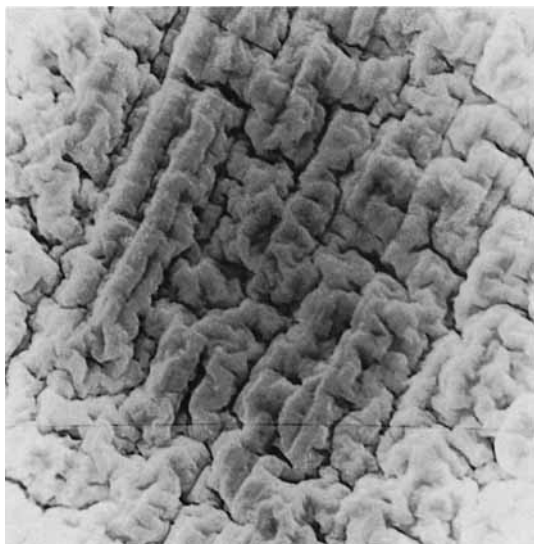
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d) SBR after treatment.

**Figure 4** SEM pictures showing the influence of bromination on the surface morphology of rubber vulcanizates: (a) BR before treatment; (b) BR after treatment; (c) SBR before treatment; (d) SBR after treatment.

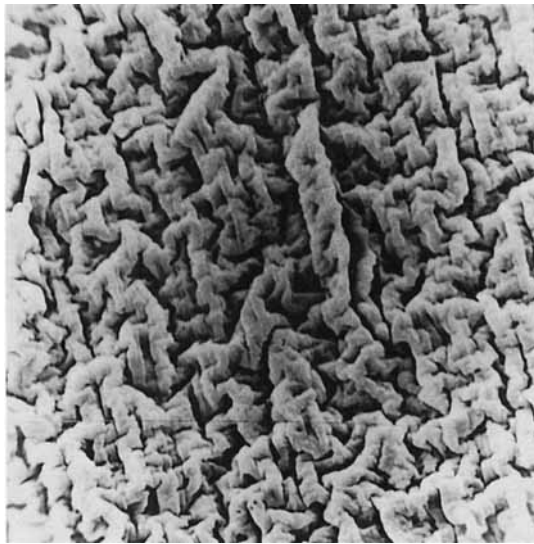
modified for testing elastic materials.<sup>27</sup> Kinetic coefficients of friction were investigated at  $293 \pm 15$  K without lubrication. The sliding speed ( $v$ )

or normal pressure ( $p$ ) were changed over a wide range;  $v = 0.05\text{--}1.0$  m/s, and  $p = 50\text{--}200$  kPa.



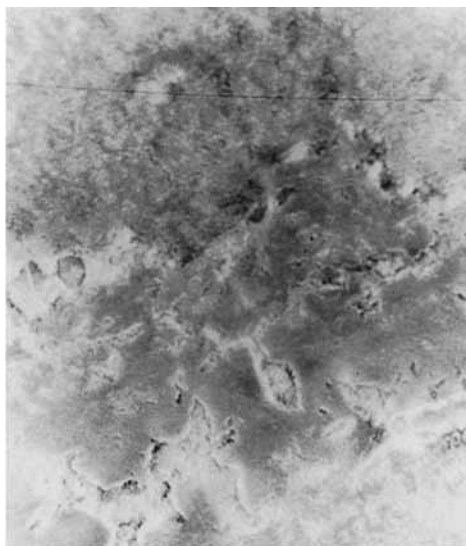
x 640

a) BR



x 640

b) SBR



x 640

c) IR.

**Figure 5** SEM pictures showing the surface of rubber vulcanizates after sulfonation treatment: (a) BR; (b) SBR; (c) IR.

**RESULTS AND DISCUSSION**

Chemical treatment produces a modified outer layer that has a different physical and chemical structure

from those of the original material. The depth of modification depends on the time of treatment and type of chemistry taking place.

**Table V IR Analysis of Modified SBR Vulcanizates**

Group	(C=C) CH=CH <sub>2</sub>		(C—H) CH <sub>2</sub>		C=C <i>trans</i>		(C—H) CH=CH		(CH <sub>2</sub> ) CH <sub>2</sub> =CH	
	Wave No. (cm <sup>-1</sup> )	1640	1450	1450	1271	1271	967	967	918	918
Chlorination time (s)	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
0	1.5	1.5	4.6	4.6	2.9	2.9	8.1	8.1	4.6	4.6
5	0.7	0.5	1.4	1.1	1.2	0.8	2.7	1.9	2.4	1.6
30	0.4	0.3	1.3	1.0	0.6	0.5	2.4	1.8	1.2	0.9
60	0.3	0.3	1.1	0.9	0.5	0.4	2.0	1.7	1.1	0.9
Bromination time (s)	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
0	1.5	1.5	4.6	4.6	2.9	2.9	8.1	8.1	4.6	4.6
5	0.6	0.5	1.3	0.9	1.2	1.0	2.9	2.3	2.2	1.6
30	0.6	0.4	1.1	0.9	1.2	0.8	2.9	2.3	1.4	1.1
60	0.4	0.3	2.7	2.2	0.9	0.7	1.5	1.8	1.3	1.0
Iodination time (min)	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
0	1.5	1.5	4.5	4.5	2.9	2.9	8.1	8.1	4.6	4.6
1	0.5	0.4	1.3	0.9	1.0	0.7	2.9	2.0	2.1	1.4
15	0.4	0.3	1.6	1.1	0.5	0.4	2.5	1.8	1.1	0.8
30	0.4	0.3	1.4	1.1	0.5	0.3	2.3	1.7	1.1	0.8
Sulfonation time (s)	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>	<b>1</b>	<b>2</b>
0	1.5	1.5	4.6	4.6	2.9	2.9	8.1	8.1	4.6	4.6
5	0.6	0.5	1.3	1.0	1.2	1.0	2.9	2.0	1.7	1.4
30	0.6	0.5	1.2	1.0	1.2	1.0	—	0.8	1.6	1.3
60	0.5	0.5	1.1	1.0	1.2	0.9	—	—	1.6	1.3

1, in relation to styrene 760 cm<sup>-1</sup>. 2, in relation to styrene 699 cm<sup>-1</sup>.

### Degree of Modification

The diffusion control of the chemistry leads to a gradation of the structure in the modified layer confirmed by microscopic observations. Despite a significant difference in refractive indices between a modified surface and bulk material, it was difficult to assess the depth of modification with polarized-light microscopy. From SEM observations, values of 5–50 μm thickness were found. The largest values were obtained by bromination, the smallest ones by sulfonation or iodination. BR was, in general, the most prone to modification, and the effects were least pronounced for EPM or EPDM. The microanalysis data (Table III), are in accord with the expected reactivity of the polymers; however the small amount of sulfur is surprising in view of the significant changes observed in other properties.

XPS measurements were performed on the sample subjected to sulfonation and the characteristic S (2p) sulfur peak was observed at binding energy of 169.5 eV, which corresponds to —SO<sub>3</sub>H.<sup>29</sup> The expected S/O atomic ratio equal to ≈ 3 was not observed for all samples and a large excess of oxygen atoms reflected oxidation of the surface (Table IV).

Oxidation is observed in IR and EPM and to a lesser extent in BR, SBR, NBR, and is practically absent for EPDM vulcanizates. The C (1s) peak shape provides information on the sulfonation and oxidation. A shift of only 0.4 eV is produced by the —C—SO<sub>3</sub>H group<sup>24</sup> and the C (1s) peak becomes broadened after treatment because of contributions from both sulfonated and oxidized carbon. The full-width half-height (FWHM) data for the C (1s) signals (Table IV) are in a good agreement with the observed reactivity of the elastomers toward the modifying agents.

Calculated sulfur contents for the samples were compared with data obtained from microanalysis (Fig. 1) and indicate that chemical modification is limited to the top surface. These observations are consistent with the concept of a diffusion controlled process moderated by the effects of chemical modification.<sup>30,31</sup>

### Surface Morphology

Microroughness measurements, *R<sub>a</sub>*, show appreciable differences between different types of treat-



**Table VI Surface Energy of Modified Rubber Vulcanizates**

Component	Surface Energy (J/m <sup>2</sup> ) × 10 <sup>-3</sup>					
	IR	BR	SBR	NBR	EPDM	EPM
Without treatment						
$I_{SL}^p$	8.7	15.2	22.5	21.8	9.4	11.6
$\gamma_s^p$	0.4	1.1	2.5	2.3	0.4	0.7
$\gamma_s^d$	22.0	35.3	35.3	29.0	30.0	29.9
$\gamma_s$	22.4	36.4	36.4	31.3	30.4	30.6
Chlorination (30 s)						
$I_{SL}^p$	20.3	17.4	24.0	25.4	13.1	11.6
$\gamma_s^p$	2.0	1.5	2.8	3.2	0.8	0.7
$\gamma_s^d$	22.7	32.6	33.4	33.4	28.2	29.9
$\gamma_s$	24.7	34.1	36.2	36.6	29.0	30.6
Bromination (30 s)						
$I_{SL}^p$	16.0	15.2	23.0	24.0	10.9	11.6
$\gamma_s^p$	1.3	1.1	2.6	2.8	0.6	0.7
$\gamma_s^d$	22.7	35.3	33.7	29.9	29.0	29.9
$\gamma_s$	24.0	36.4	36.3	32.7	29.6	30.6
Iodination (15 min)						
$I_{SL}^p$	13.1	15.2	22.5	23.2	12.3	11.6
$\gamma_s^p$	0.8	1.1	2.5	2.6	0.7	0.7
$\gamma_s^d$	21.9	35.3	33.4	33.5	28.3	29.9
$\gamma_s$	22.7	36.4	35.9	36.1	29.0	30.6
Sulfonation (30 s)						
$I_{SL}^p$	20.3	30.5	26.1	27.6	16.0	11.6
$\gamma_s^p$	2.0	4.6	3.3	3.7	1.3	0.7
$\gamma_s^d$	34.4	39.1	38.1	33.4	30.7	29.9
$\gamma_s$	36.4	43.7	41.4	37.1	32.0	30.6

S, solid; L, liquid;  $I_{SL}^p$ , polar interaction parameter, calculated from the geometric mean equation<sup>14,22,23</sup>;  $\gamma_s^p$ , polar component of surface energy;  $\gamma_s^d$ , dispersive component of surface energy;  $\gamma_s$ , total surface energy.

ment; and only for EPM and EPDM, which are highly chemically resistant, are the changes in roughness barely visible. However, sulfonation did cause degradation of the surface, especially in the EPM where the sample became softened and tacky. The kinetics of modification are demonstrated with chosen examples of bromination and sulfonation (Figs. 2, 3). The processes occur rapidly at the beginning, the first 5–15 s, and reach a constant  $R_a$  value after about 30 s. Increases in the microroughness after chemical modification were reported by Roberts and Brackley.<sup>31,32</sup> The character of the surface topography depends strongly on the solution used. Chlorination and bromination were accompanied by oxidation processes resulting in microcracks appearing in the surface, especially for BR (Fig. 4).

Chemisorption of halogens on the elastomer surface led to darkening or an opaque appearance of

the sample. In the case of iodination the sample that darkened initially regained its lost transparency due to iodine sublimation. Oxidation during iodination was not significant.

Sulfonation was also accompanied by oxidation processes, but they were of minor importance, chemical etching taking place during the treatment and dominating the process (Fig. 5). Only in the case of IR vulcanizates was this characteristic topography pattern absent; instead small cracks were observed as a result of strong oxidation and bloomed or chemisorbed sulfur regions were visible (Fig. 5).

### Chemical Structure of Surface

Chemical modification of polymers has been the subject of numerous studies<sup>33–36</sup> and is a very complex process involving substitution, addition, cy-

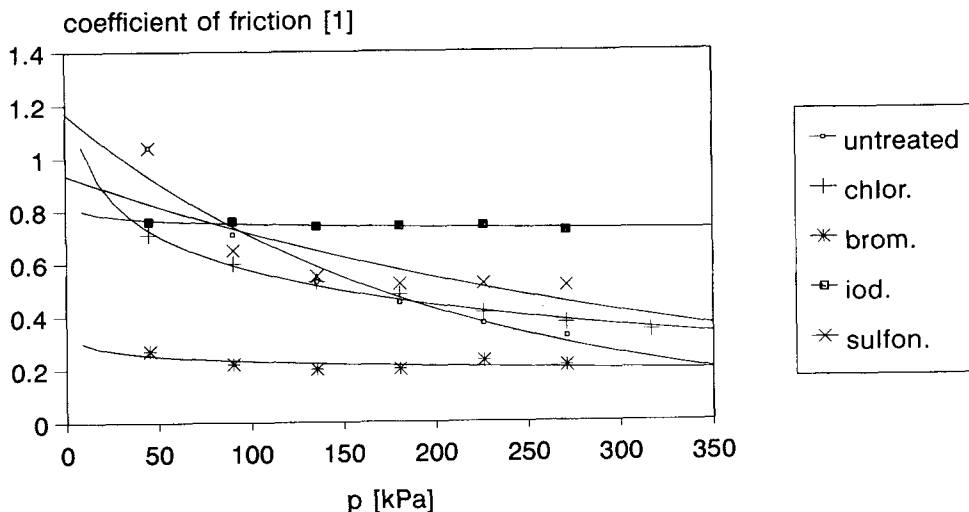
Table VII Mechanical ( $C_1$ ,  $C_2$ ) Analysis of Modified Rubber Vulcanizates

Network Parameter	Chemical Treatment								
	Untreated	Chlorination		Bromination		Iodination		Sulfonation	
		30 s	60 s	30 s	60 s	1 min	15 min	30 s	60 s
<b>IR</b>									
$C_1$	15.6	10.4	8.1	239	402	9.8	15.6	9.7	10.4
$C_2$	5.2	7.7	9.3	378	97	7.6	10.3	6.8	8.9
$\nu$	7.2	5.1	4.0	117	197	4.8	7.7	4.8	5.1
	7.7								
<b>BR</b>									
$C_1$	17.5	12.8	20.7	136	237	18.4	25.9	44.5	43.6
$C_2$	8.9	14.3	5.2	142	223	10.3	8.2	24.2	97
$\nu$	8.0	9.0	14.5	66.6	116	9.0	12.6	21.8	21.3
	8.5								
<b>SBR</b>									
$C_1$	14.5	25.8	15.4	62.0	352	12.1	21.2	22.4	26.5
$C_2$	19.0	7.5	6.9	327	234	9.72	18.4	16.1	12.0
$\nu$	7.2	12.7	7.6	30.4	173	6.0	10.5	11.0	13.1
	7.1								
<b>NBR</b>									
$C_1$	16.7	16.2	14.3	381	285	24.8	64.8	165	402
$C_2$	4.5	5.4	6.0	144	71.3	4.6	26.2	146	44.2
$\nu$	8.1	7.9	7.0	186	139	12.1	31.7	80.7	196
	7.7								
<b>EPDM</b>									
$C_1$	16.0	13.3	16.5	7.3	6.7	7.5	11.9	8.3	10.1
$C_2$	25.9	35.3	27.2	34.4	35.0	37.3	33.8	38.0	36.6
$\nu$	7.8	6.5	8.1	3.6	3.3	3.7	5.81	4.1	4.9
	8.0								
<b>EPM</b>									
$C_1$	15.9	—	23.7	—	24.3	—	24.5	—	25.2
$C_2$	27.9	—	11.6	—	7.8	—	29.5	—	25.2
$\nu$	8.0	—	11.6	—	11.9	—	6.3	—	6.1
	7.8								

Thickness of the sample,  $50 \pm 10 \mu\text{m}$ . All  $C_1$  and  $C_2$  in  $\text{N/m}^2 \times 10^{-4}$ . All  $\nu$  calculated from the equilibrium swelling measurements,<sup>19</sup> in  $\text{mol/cm}^3 \times 10^{-5}$ .

clization, *cis-trans* isomerization or additional crosslinking via carbocations.<sup>37</sup> FTIR data indicate a mechanism of double bond rupture and partial or complete replacement of hydrogen with halogen in methylene, or in the case of bromination or iodination also in the methyl groups.<sup>37,38</sup> Chlorination of IR leads to the appearance of a new absorbance at  $835 \text{ cm}^{-1}$ , ascribed to a pendant double bond.<sup>35</sup> Peaks corresponding to halogenation, C—Cl ( $770$  and  $525 \text{ cm}^{-1}$ ) were also observed. Spectra of sulfonated surfaces show absorption peaks at  $1170$ ,  $1040$ , and  $1010 \text{ cm}^{-1}$  arising from the S=O stretching vibrations in the  $\text{SO}_3\text{H}$  group. The peak at  $900 \text{ cm}^{-1}$  can be attributed to

cyclization<sup>10</sup> or moisture<sup>39</sup> associated with the sulfonation processes. An absorption near  $1710 \text{ cm}^{-1}$ , coming from the carbonyl group, indicates that oxidation processes accompany the modification. Its intensity is highest in the case of bromination, consistent with microanalysis data (Table V). The absorbance peaks at  $760$  and  $699 \text{ cm}^{-1}$  for phenyl ring vibrations were chosen as internal standards. The halogenation reaction proceeds through two steps: addition of halogen, resulting in the creation of macroradicals, which lead to degradation<sup>4</sup> or crosslinking<sup>37</sup> depending on the free radical concentration, and sulfonation, producing mainly cyclization.<sup>37</sup>



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

**Figure 6** Tribological properties of modified IR vulcanizates.

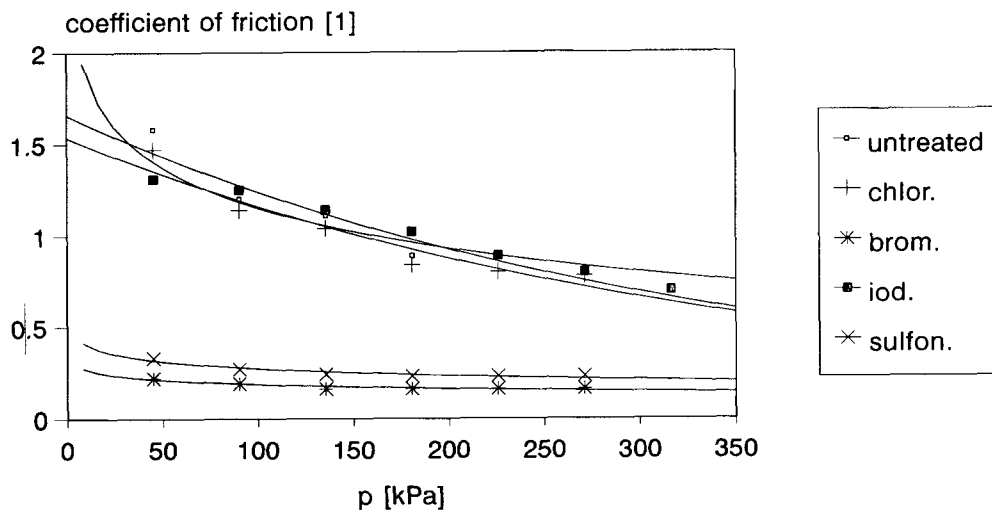
**Surface Energy**

The surface energy, calculated from contact angle measurements, changes slightly due to the surface treatment. Increase of the surface energy implies an increase in the reversible work of adhesion<sup>40</sup> and ultimately adversely affects the tribological properties. The surface energies of the vulcanizates were obtained before and after chemical treatment (Table VI). Measured  $R_a$  values were generally lower than  $1 \mu\text{m}$ , making the effect of surface topography on the contact angle values insignificant. Small differences between contact angles for the same liquid

have been observed, which may be partially the result of heterogeneity of the modified rubber surface.<sup>41</sup>

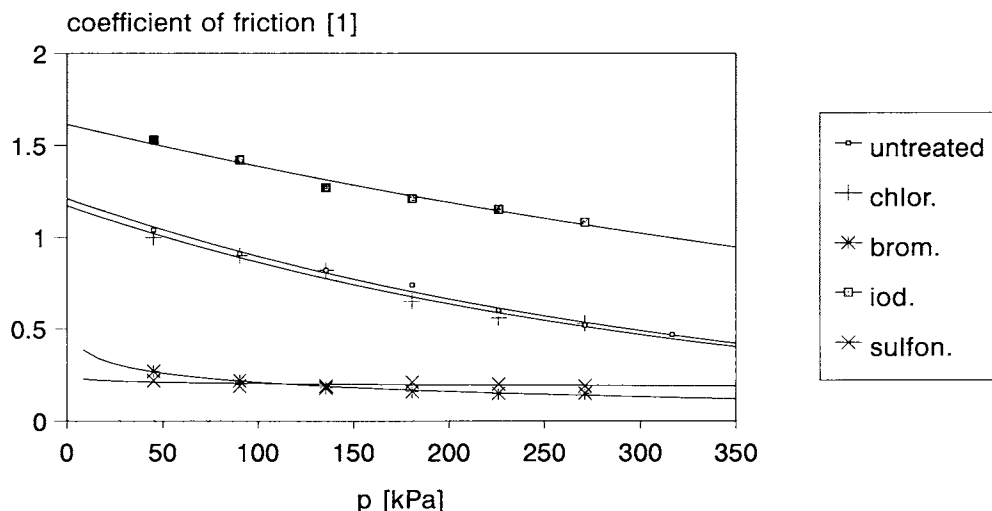
**Mechanical Properties**

Values of  $C_1$  and  $C_2$  (Table VII) may only be used qualitatively because they will be sensitive to skin effects and cracking, but they do reflect changes in the average hardness of the specimen. For polyolefin vulcanizates the treatments are not completely effective, producing only a limited extent of modification. Sulfonation, bromination, and in the case of



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

**Figure 7** Tribological properties of modified BR vulcanizates.



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

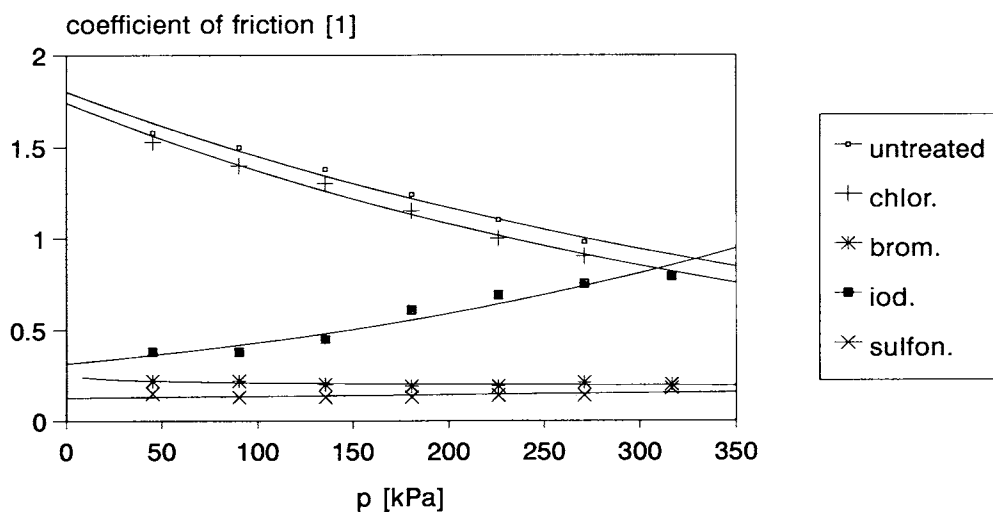
**Figure 8** Tribological properties of modified SBR vulcanizates.

NBR, iodination, make the sample stiffness increase significantly. Chlorination and iodination have a smaller effect. A decrease of stiffness,  $C_1$ , resulting from chemical degradation was observed for IR, EPDM, and EPM. The modulus given by  $6(C_1 + C_2)$  reflects an increase in the microhardness of most of the samples<sup>25,26</sup> (Table VII). The increase in  $C_2$  in the case of bromination indicates the formation of a highly packed surface layer. The decrease of  $C_2$  in the case of chlorination reflects degradation. The high efficiency of iodination in the case of NBR may be explained by structural modification, changing the conformation and improving the mechanical

properties. WAXS investigation of iodination of nylon 6 demonstrated similar effects.<sup>42</sup> X-ray diffraction data showed changes in the surface crystallinity conformation of the N—H groups from  $\alpha$  to  $\gamma$  structures.

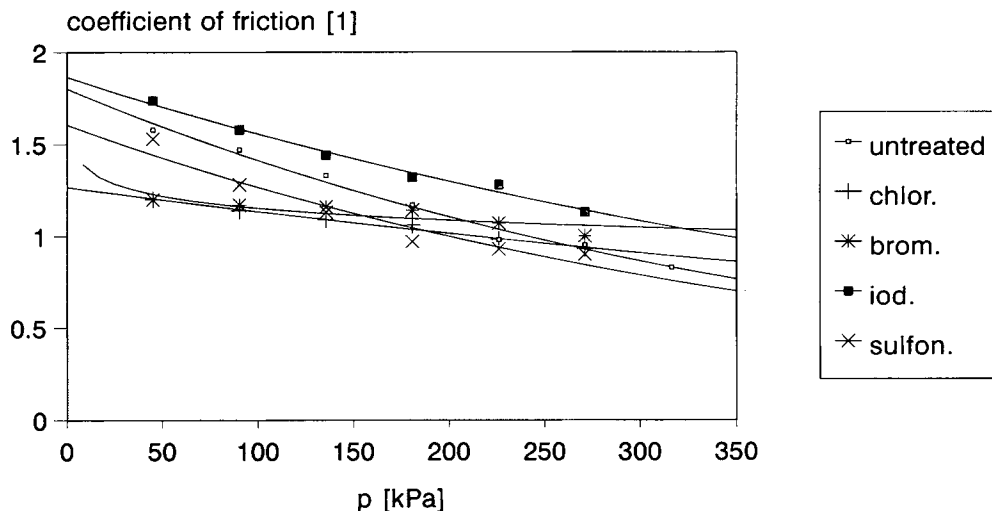
### Tribological Properties

The coefficient of friction  $\mu$  (Figs. 6–11) decreases with an increase of the normal load applied to the sample as a result of changes in the bulk stiffness, and more importantly, from an increase of the friction contact area in the case of chlorination or io-



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

**Figure 9** Tribological properties of modified NBR vulcanizates.



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

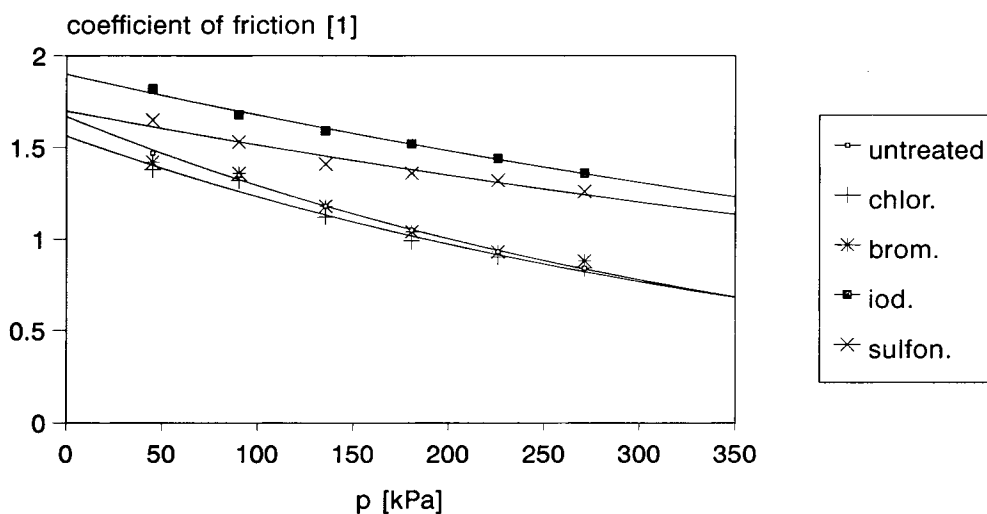
**Figure 10** Tribological properties of modified EPDM vulcanizates.

dination. For bromination or sulfonation, the surface layer is very hard, which explains the small effect of pressure on their coefficients of friction. The influence of velocity on the coefficient of friction was hardly noticeable, very slightly decreasing with increasing velocity. Only in the case of iodination of NBR was an increase of  $\mu$  observed, probably because of inadequate durability of the modified layer when exposed to extreme friction conditions.

The effects of surface energy on the tribological properties have been observed previously.<sup>39</sup> A similar tendency is observed in this study, but in this case the surface energies are much lower, probably be-

cause the chemical reactions were carried out without any activation (ambient conditions), over a short time, and with solutions of moderate reactivity. Chemical modification did result in a small increase of the adhesional component of friction. It should be noted that in industrial processing exposure times are generally longer.

Surface microroughness is an important factor that should be analyzed along with the stiffness. When the material is brittle, even if the surface is rough, it will be smoothed down during friction. There is no "cooperation" between a thick stiff surface layer and an elastic bulk in carrying the applied



friction conditions:  $v=0.08$  m/s,  $T=293-313$  K,  $p=0-350$  kPa, without lubrication

**Figure 11** Tribological properties of modified EPM vulcanizates.

load, especially in dynamic conditions. In "thick layer" modifications (brominated vulcanizates), surface microcracks, resulting from oxidation processes, favored wear of the material, and quite large amounts of debris were observed.

When the modified layer has a high mechanical modulus and is very thin, the composite is not so "fragile." The stiff surface shows some dynamic susceptibility that makes it more compatible with the bulk. An increased surface microroughness makes the contact area smaller that results in lower values of the coefficient of friction. A thin skin structure was obtained with sulfonation, the most effective chemical treatment from the tribological point of view. A similar mechanism of friction was observed for iodinated NBR vulcanizates. A significantly increased stiffness of the surface lowers the hysteretical component of friction, that finally causes a decrease of the coefficient of friction. The adhesional component of friction is of minor importance in these cases.

But what happens when the stiffness of the material decreases due to the chemical treatment? Such behavior was observed in the case of chlorinated or sulfonated IR, EPM, and EPDM. The answer depends on how much the surface energy has changed due to the modification. If the material is reactive as with IR, increased adhesion from sulfur aggregates present on the surface, dominate the friction phenomenon. The wear has a cohesion character and goes on intensively, large irregular debris being observed, leaving characteristic cohesion patterns on the surface.

In the case of the chemical resistant materials, EPDM or EPM, a tacky layer arises that is very quickly wiped away during friction exposing the unmodified bulk. In both of these cases modification is ineffective from the tribological point of view.

## CONCLUSIONS

Chemical treatment of elastomers leads to the generation of a surface layer and improved tribological properties. Each of the methods is effective for particular types of material: sulfonation for BR, SBR, and NBR; bromination for IR, BR, SBR, NBR, and EPDM; and iodination for NBR. The tribological results were interpreted taking into consideration adhesional and hysteretical components of friction. For sulfonation or iodination the modified layer was thin; in the case of bromination or chlorination the modification was deeper. For a surface treatment to

be effective and lead to lowering of the coefficient of friction, it should produce an increase of stiffness of the surface layer. Changes in the surface energy, causing an increase of adhesion were found to be too small to compete with the dominating hardening effect.

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