

Structural Changes in Rubber During Milling

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SYNOPSIS

Processing operations such as milling, change the chemical structure of rubber. Infrared (IR) spectroscopy and electron spectroscopy for chemical analysis (ESCA) have been used to detect the formation of functional groups during the milling of natural rubber (NR), epoxidised natural rubber (ENR), styrene butadiene rubber (SBR), neoprene (CR), and acrylic rubber (AR). The concentration of carbonyl (>CO) groups as detected by IR spectroscopy increases with the time of milling for all the rubbers. The concentration of hydroxyl groups (—OH) in NR and ENR also increases during milling. ESCA spectra of the rubbers before and after milling reveal that the peaks are broader for milled rubber, and that the concentration of oxygen is also greater. In the case of ENR, however, the concentration of epoxide rings decreases and that of furan rings increases with the time of milling.

INTRODUCTION

The milling of rubber is an important operation for achieving suitable viscoelastic properties for further processing. During milling, rubber molecules are broken down. The chemical changes which occur are functions of temperature, rate of shear, shear stress, and viscosity of the rubber. Watson et al.^{1,2} and Bristow³ have studied the mechanochemical behaviour of natural rubber and concluded that free radicals are generated by the breakage of polymer chain and subsequently react in different ways depending on the conditions. Most of the work⁴⁻⁷ on these lines has been concentrated on natural rubber whose processing behavior changes significantly during mastication and milling. The mill breakdown behavior of ENR has been reported by Amu et al.⁸ and its oxidative aging has been investigated by Gelling.⁹ Extensive studies on the degradation of natural rubber vulcanizates have been reported by earlier workers.¹⁰⁻¹³ Shelton¹⁴ has studied the aging properties of NR and a few synthetic rubbers by spectroscopic techniques while Lin¹⁵ has reported oxidative degradation of NR, guayule, and polyisoprene by ESCA.

An exhaustive literature search shows that there is little work along these lines for synthetic rubbers, but it is expected that free radicals will be generated during milling. These radicals may react in a complicated way, resulting in changes in the viscoelastic properties of the rubbers. It is also important to note that breakage of polymer chains during milling may accelerate in the presence of the metallic surface of the roll. In essence, the structure of the milled rubber, and consequently its properties, may not be the same as those of the original material.

The present study is aimed at elucidating the structural changes of rubbers during milling using IR and ESCA techniques. Natural rubber (NR), epoxidised natural rubber (50 mol %, epoxy content), acrylic rubbers (AR-101, AR-201), neoprene rubber, and styrene butadiene rubber have been selected. These rubbers have been milled for different times in a laboratory size two-roll mill over a temperature range of 45 to 100°C.

EXPERIMENTAL

Natural rubber (ISNR-5, supplied by Rubber Board, Kottayam India), styrene butadiene rubber (1502, supplied by Synthetic and Chemicals Ltd., Bareilly), neoprene rubber (Butachlor MC-31, procured

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from Distugil, France), epoxidized natural rubber (50 mol % epoxy content, procured from Rubber Research Institute of Malaysia, Malaysia), and acrylic rubbers (AR-101 and AR-201, supplied by Japan Synthetic Rubber Co. Ltd., Japan) were used.

Mastication of rubbers was carried out on a laboratory size two-roll mill (15 cm × 33 cm) at different temperatures (45–100°C) and milling times. For all the cases the friction ratio of the rolls was kept constant at $f = 1.2$, except for natural rubber (NR) where the experiments were performed at $f = 1.2$ and $f = 2.0$.

IR Spectroscopic Study

The masticated rubber samples were immediately dissolved in spectroscopic grade chloroform and dried overnight with anhydrous sodium sulfate. Few drops of this solution were spread on potassium bromide plate and dried under vacuum for casting film. The film was analyzed by a Perkin-Elmer IR spectrophotometer (model 843). The absorbance ratios of different functional groups were calculated by the ASTM method (ASTM D 3677, Part 2).

ESCA Studies

For ESCA experiments, the rubbers, both milled for 15 min and unmilled, were dissolved in a solvent. The film made by evaporating the solvent was dried for 48 hrs under vacuum. A small portion of the film was placed in the high vacuum chamber of the instrument. The instrument used was ESCALAB MKII, made by V. G. Scientific Limited, U. K. The following conditions were maintained during the analysis. Radiation at 12 kV and 10 μ A output was employed; pass energies of the electron analyzer were set at 20 eV for a wide spectrum from 0 to 1250 eV and at 25 eV for an expanded spectrum. The analysis chamber was kept at constant vacuum (10^{-9} torr) during the experiment. Wide spectra were used mainly for identification of surface elements¹⁶ and the expanded spectra for peak area integration and peak line-shape analysis.

RESULTS AND DISCUSSION

IR Spectroscopy Studies

Epoxidized Natural Rubber and Natural Rubber

Figure 1 shows a plot of the absorbance ratio of carbonyl (>CO) and hydroxyl (-OH) groups to the methyl groups (-CH_3 at 1370 cm^{-1}) of epoxidized natural rubber versus time of milling. The rubber

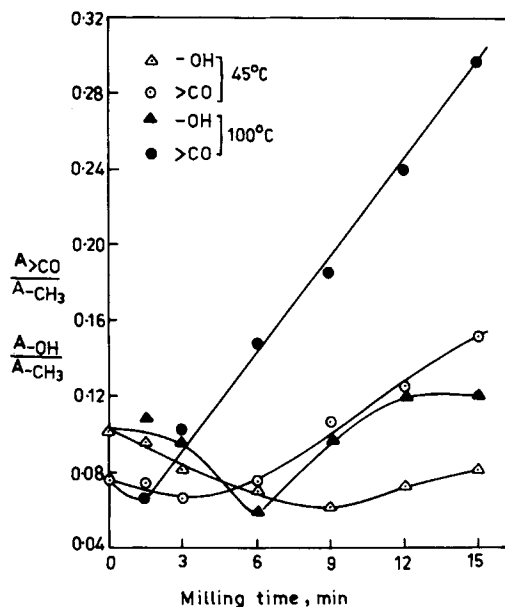
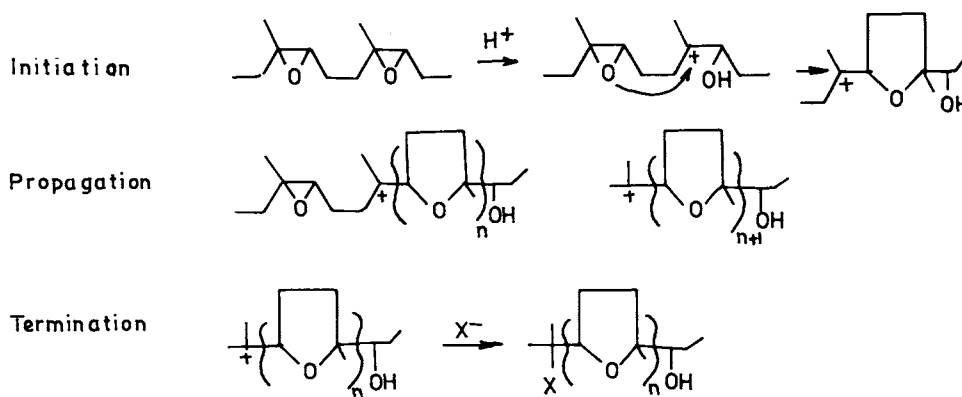


Figure 1 Plot of concentrations of carbonyl and hydroxyl groups of epoxidized natural rubber versus time of milling.

has been milled at 45° and 100°C. At both the temperatures, changes in the concentration of >CO and -OH groups are observed. ENR milled at 45°C shows a decrease in >CO concentration up to 3 min. of milling. An increase in the concentration of -OH function is noted after 9 min. Shelton¹⁴ has observed an increase in -OH concentration of polybutadiene rubber with the time of aging.

At higher temperature (100°C) the trend is similar to that observed at lower temperature (45°C). Here, the >CO concentration initially decreases with milling time (up to 1.5 min) and then sharply increases. The -OH concentration also follows a similar trend but the minimum is observed at 6 min. However, in both the cases the minima are shifted towards lower times at higher temperatures. For times past the minima, the concentration of >CO groups is higher when the milling temperature is higher.

The concentration of the epoxide group in ENR is found to change during milling. As shown in Figure 2 the epoxide concentration also decreased with milling time. However, the furan ring concentration in the rubber increases with milling time. This phenomenon may be explained by the mechanism proposed by Perera et al.¹⁷



Scheme 1

For comparison with ENR, similar studies have been carried out also on NR. Both carbonyl and hydroxyl groups are found to be present initially and their concentrations change during milling (Fig. 3).

There is a similar trend in the change of >CO concentration during milling at different temperatures (45 and 100°C) and friction ratios (1.2 and 2.0). The >CO concentration initially decreases with milling time (up to 1.5 min) and then a slight increase is observed until the concentration reaches a constant value.

When milling is performed at 45°C, the -OH concentration decreases with milling time (up to 1.5 min), then increases until 6 min of milling time and ultimately decreases. The maximum in the case of NR milled at 100°C is shifted to 1.5 min, after which the concentration of -OH decreases and becomes

constant. The shifting of maxima towards a shorter time may be due to an increased rate of chain scission, and other processes which take place during milling, at higher temperatures. It is observed that for NR milled at a high friction ratio, the -OH concentration increases and reaches an equilibrium value after 3 min of milling. The formation of -OH groups during the degradation of NR has also been observed by other workers.^{14,15} The difference in the >CO concentration of ENR for the rubbers milled at high and low temperatures is quite large after the minima, whereas in the case of NR this difference is marginal. The changes in -OH concentration of NR at low and high temperatures is irregular, unlike the case with ENR.

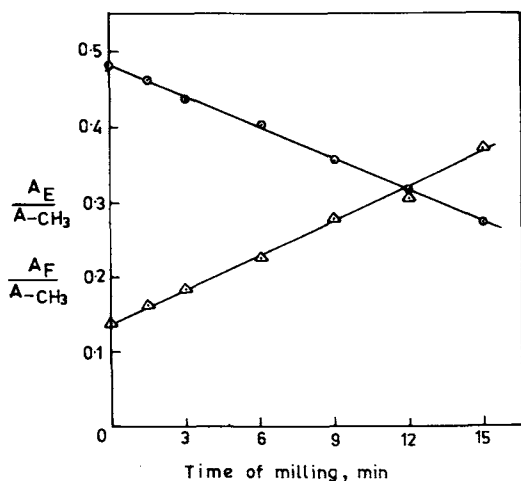


Figure 2 Change in concentrations of (Δ) furan ring and (\circ) epoxide ring of epoxidized natural rubber with time of milling.

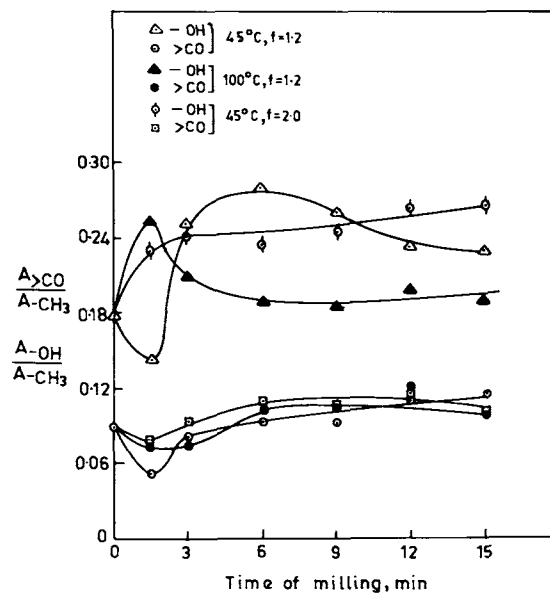


Figure 3 Variation of concentration of carbonyl and hydroxyl groups of natural rubber with the time of milling.

Styrene Butadiene Rubber

The absorbance ratio of carbonyl group (>CO) to methylene ($-\text{CH}_2-$) versus time of milling is shown in Figure 4. Two types of >CO are observed—one at 1731 cm^{-1} and another at 1703 cm^{-1} . The first peak corresponds to a stretching frequency of normal >CO and the second one due to the stretching of >CO which is in conjugation with delocalized π electrons¹⁸ of the benzene ring. Generation of these two types of >CO may be due to the presence of styrene and butadiene units in the copolymer. At 45°C the concentrations of both types of carbonyl groups decrease with milling time (up to 6 min) with a subsequent increase. This change is larger in the case of normal >CO than in the conjugated >CO . At higher temperature the trend is similar up to 9 min for normal >CO and 12 min for the conjugated >CO . After these both the groups show a decreasing tendency. It is also observed that normal >CO concentration attains a minimum value at 3 min when the rubber is milled at 100°C ,

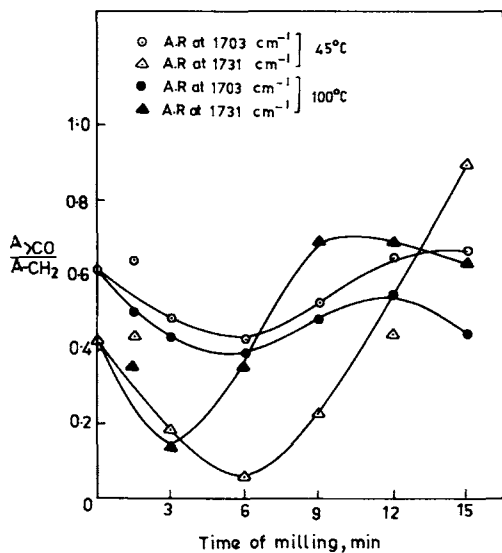


Figure 4 Plot of concentrations of carbonyl groups (at 1703 and 1731 cm^{-1}) of styrene butadiene rubber versus time of milling.

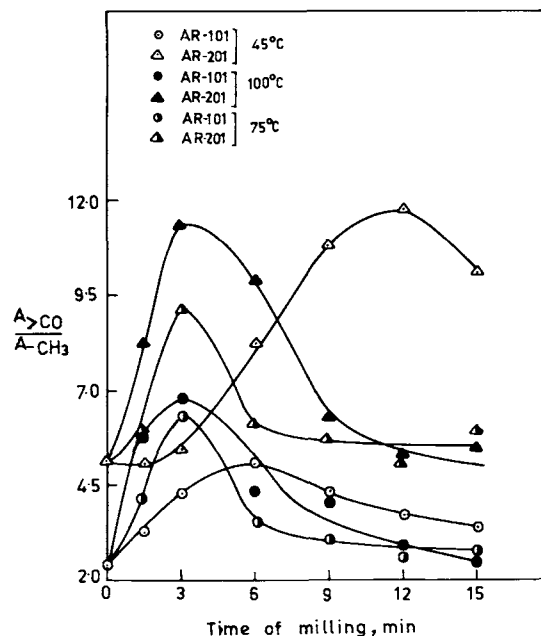


Figure 5 Plot of concentration of carbonyl group of acrylic rubbers (AR-101 and AR-201) as a function of milling time.

whereas the rubber milled at 45°C reaches the minimum at 6 min.

Acrylic Rubber

Acrylic rubber, which is a copolymer of ethyl or butyl acrylate and ethylidene norbornene (ENB) also shows a change in the concentration of carbonyl groups (>CO) during milling (Fig. 5). Two grades of acrylic rubber, JSR-AR 101 ($T_g = -22^\circ\text{C}$) and JSR-AR 201 ($T_g = -41^\circ\text{C}$) have been used. The concentration of >CO for rubber milled at 45°C increases with the milling time up to 6 min. for AR-101, and up to 12 min. for AR-201. There is a decrease afterwards.

A similar trend is observed when milling is done at higher temperatures (75°C , 100°C). As observed in an earlier section, the maxima of the curves shifted towards the lower time scale of the plot with an increase in the temperature of milling. The maxima of AR-101 are observed at 6 min at 45°C and 3 min at both 75° and 100°C . The maxima for AR-201 are 12 min at 45°C and 3 min at both 75°C and 100°C . After reaching a maximum value, the decrease in >CO concentration is also faster at higher temperatures. These observations indicate that the

chain scission process becomes faster as the temperature increases. It is interesting to note that the maxima of the curves at 75° and 100°C occur at 3 min for both the rubbers.

Neoprene Rubber

The presence of carbonyl groups and changes in its concentration during milling are also observed in the case of neoprene (CR) rubber. A plot of the absorbance ratio of carbonyl group to methylene group versus time of milling is shown in Figure 6. When milling is done at 45°C, the carbonyl concentration increases after an initial decrease. At a higher milling temperature (100°C), the trend remains similar but the minimum concentration is observed at 1.5 min. This is due to the fact that the reaction is faster at 100°C. The trend in the change of >CO concentration is apparently similar to that for NR and ENR.

In order to ascertain the reasons for the initial decrease in the functional group concentrations in ENR, NR, SBR, and CR, the samples from three different positions of the bale or chips (surface, center, and in-between) have been taken and the spectra analyzed. It is observed that the concentration of the >CO function in the case of ENR, NR, SBR, and CR is greater at the surface, as expected, and that of the -OH group is greater at the centre. Hence, the decrease in >CO functionality in the initial stages of milling may be due to homogenization of the materials during this process. However, there is also material loss, i.e., evaporation of low

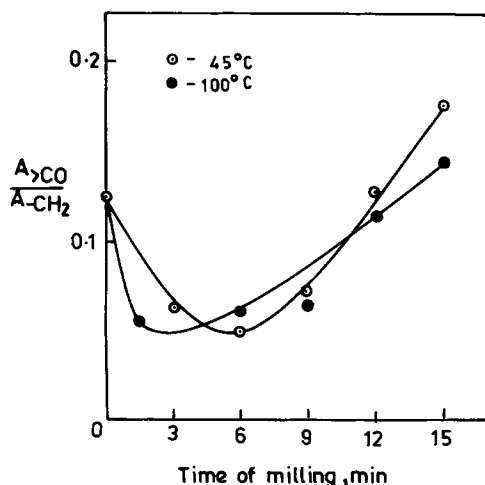


Figure 6 Concentration of carbonyl group of neoprene rubber as a function of milling time.

molecular weight polymer,¹⁵ as is evident from the C1s peaks of the ESCA spectrum.

ESCA Studies

The presence of carbon and oxygen in the rubbers have been carefully examined by XPS spectra. The expanded scans of each element have been recorded to study the peak profiles in detail. The integration of peak areas after correction with the elemental sensitivity factor¹⁹ produces the atomic concentration of the element. The energy scale calibration is made with respect to the C1s core peak, which is taken as 285.0 eV.

XPS spectra of all the rubbers before and after milling are shown in Figures 7-12 and the results are summarized in Table I. It is observed that C1s core peak for unmilled rubber occurs at 285 eV and O1s at 532 eV. For polar rubbers, there are shoulders and a multiplicity of C1s peaks due to the epoxide groups in ENR, the ester group in AR-101 and AR-

201, and the -C-C1 linkages in polychloroprene.

Although the peak width of the C1s peak does not alter during milling, broader O1s peaks with shoulders are observed for milled rubbers. For example, ENR shows a shoulder at 535.7 eV with peak width at half height for O1s peak (w_{O1s}) of 2.0 eV. w_{O1s} changes from 1.8 to 3.0 eV for NR, 1.8 to 2.2 eV for SBR, 1.4 to 2.6 eV for AR-101, 2.4 to 2.6 eV for AR-201, and 2.2 to 2.3 eV for CR. This broadening of the O1s peak is due to the formation of C-OH and C=O linkages in the rubbers. IR spectroscopic studies also reveal formation of these groups for the milled rubbers. The appearance of shoulders at higher binding energy than the core peaks indicate oxidation of the rubbers. The atomic percent of oxygen is also drastically increased during milling. As shown in Table I the initial concentration of oxygen is different for different rubbers and the change in the concentration is a function of the nature of the rubber. The increase of atomic percent of oxygen is as follows: 0.6% for ENR, 4.7% for NR, 2.5% for SBR, 5.8% for AR-101, 2.5% for AR-201, and 2.5% for CR.

Mechanism

The mechanism of degradation during milling may be summarized as follows²⁰:

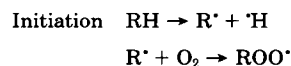
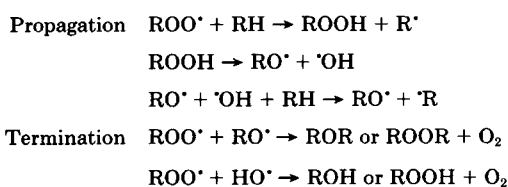


Table I Summary of the Results Obtained from ESCA

Rubber	Before Milling					After Milling				
	Peak Position eV		Peak Width at Half Height, eV		Atomic % of O ₂	Peak Position eV		Peak Width at half Height, eV		Atomic % of O ₂
	C1s	O1s	C1s	O1s		C1s	O1s	C1s	O1s	
ENR	285.0 288.3	532.0*	1.5	1.6	16.6	285.0 288.5	532.2* 535.7	1.5	2.0	17.2
NR	285.0	532.5*	1.8	1.8	11.3	285.0	532.5*	1.8	3.0	16.0
SBR	285.0	532.0*	1.6	1.8	3.5	285.0	532.3*	1.6	2.2	6.0
AR-101	285.0 289.4	532.2*	1.8	1.4	17.4	285.0 289.4	532.2*	1.8	2.6	23.2
AR-201	285.0 289.0	532.2*	1.6	2.4	24.2	285.0 289.0	532.2*	1.6	2.6	26.7
CR	285.0	532.3*	1.8	2.2	3.5	285.0*	532.3*	1.8	2.3	6.0

* Multiple peaks observed around this binding energy.



Thus, alcohol (ROH), carbonyl (ROR), carboxyl (ROOH), and ester functional groups are contained in the major oxidative degradation products. From this study the generation of >CO and —OH func-

tional groups during milling of both natural and synthetic rubbers can be confirmed.

Moreover, natural rubber contains traces of peroxides from internal sources,¹⁴ which may be responsible for the generation of free radicals and the initiation of the degradation process. ENR, as derived from NR, also contains peroxides and hence the above process is favored for it also. Synthetic rubbers may also initiate free radical reactions as shown above, but the rate obviously will depend on the structure of the molecule and surface energy. When the milling operation is performed at higher temperature, the above process is accelerated.

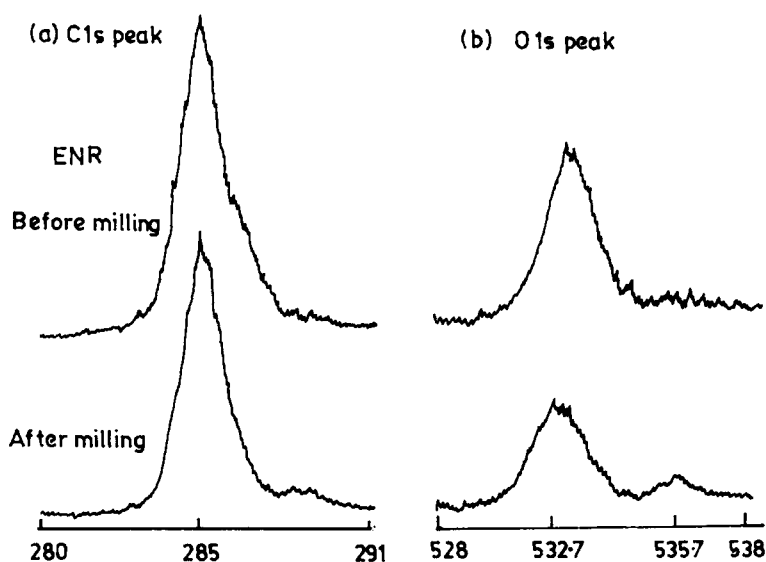


Figure 7 XPS spectra of epoxidized natural rubber (C1s and O1s core peaks).

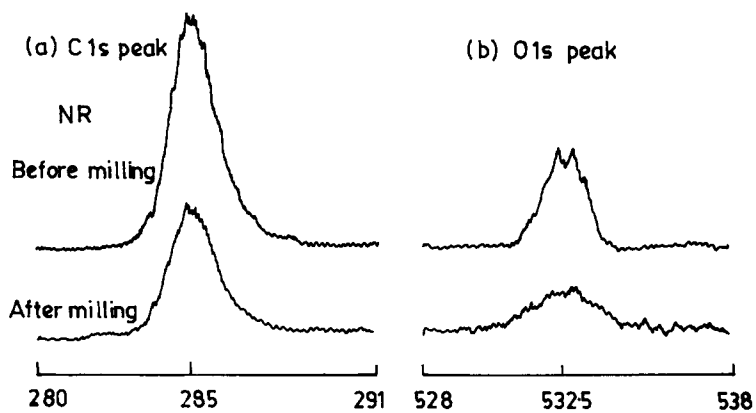


Figure 8 XPS spectra of natural rubber (C1s and O1s core peaks).

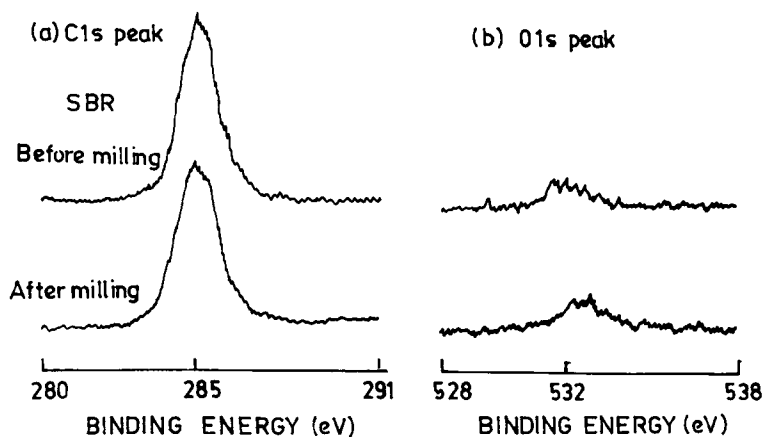


Figure 9 XPS spectra of styrene butadiene rubber (C1s and O1s core peaks).

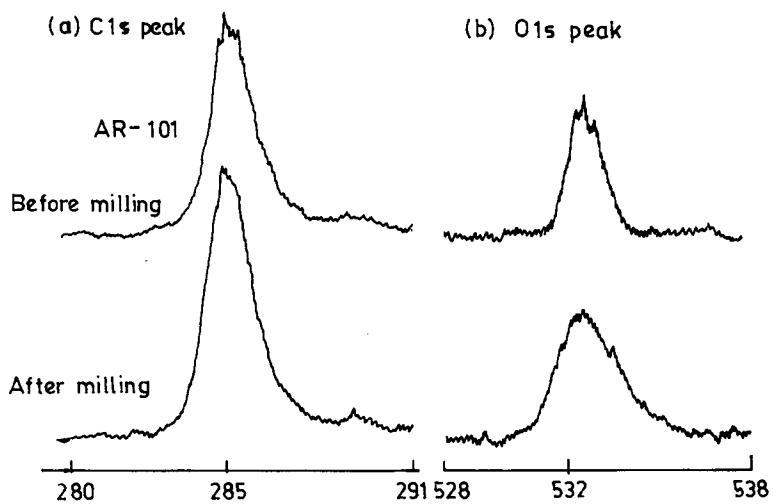


Figure 10 XPS spectra of acrylic rubber AR-101 (C1s and O1s core peaks).

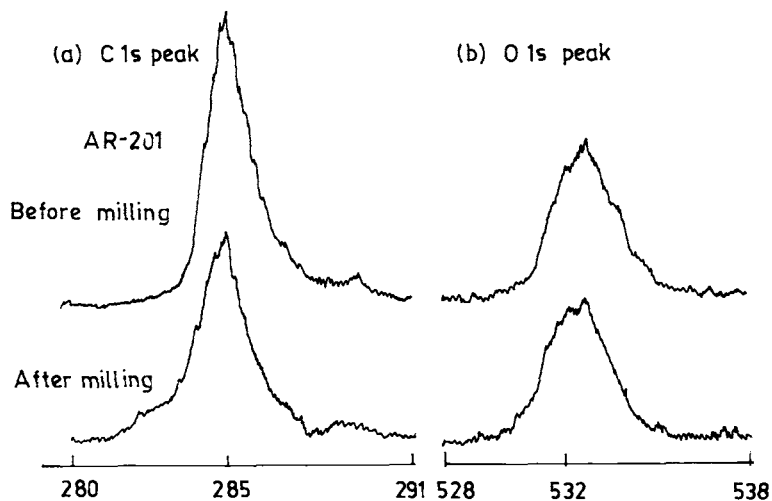


Figure 11 XPS spectra of acrylic rubber AR-201 (C1s and O1s core peaks).

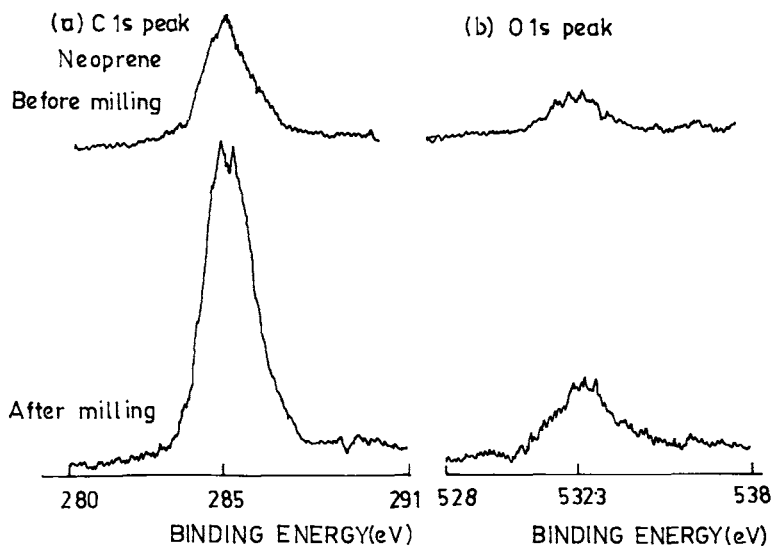


Figure 12 XPS spectra of neoprene rubber (C1s and O1s core peaks).

CONCLUSIONS

Structural changes of ENR, NR, SBR, AR, and neoprene rubbers during milling have been investigated by spectroscopic techniques.

IR spectroscopy shows that ENR and NR contain small amounts of >CO and —OH , the concentration of which changes during milling. It is observed that SBR and neoprene rubbers also contain >CO and its concentration first decreases and then starts increasing.

The acrylic rubbers show an increase in >CO concentration up to a certain time in the milling process and then a decrease. This is contrary to the observations made with SBR and neoprene rubbers.

The above changes in concentration of >CO and —OH accelerate when the temperature of milling is higher. The concentration of epoxide rings in ENR decreases whereas furan ring concentration increases with the time of milling.

ESCA studies also reveal changes similar to those of the IR spectroscopic study. In all cases the atomic percent of oxygen increases for milled rubbers.

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