

Surface Modification Processing of Synthetic Rubbers by Ultraviolet Irradiation and Sputter Ion Etching Treatment

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ABSTRACT: The mechanism by which surface modification of two kinds of synthetic rubbers (ethylene-propylene and chloroprene) was brought about by ultraviolet (UV) irradiation and sputter ion etching treatments was studied from a physicochemical point of view. The most remarkable effect of this irradiation treatment was the rapid increase in adhesion properties and the simultaneous decrease in self-stickiness. This nonsticking effect was particularly important for the rapid production of articles from thin rubber sheets. The surface modification mechanism was studied by use of SEM, ESCA, FTIR, and related interfacial analytical procedures. It was shown that surface roughening with a quite thin layer of surface oxidation ($\sim 0.5 \mu\text{m}$ in depth) is a key factor for the development of nonsticking properties. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1625–1633, 1997

Key words: surface modification; ethylene-propylene and chloroprene rubbers; UV irradiation; sputter ion etching; antisticking effect

INTRODUCTION

Recently, small and thin rubber products have been widely used in such fields as electronics, automobiles, and related industries. In the production of these rubber products, tackiness is a very important property. When a small piece is cut out of a thin rubber sheet (about $\frac{1}{2}$ mm in thickness), the sticking of each piece must be prevented. Some kind of surface modifying agent such as talc (an antitack agent) or sodium disulfate (a strong reduction agent) is generally used. These reagents, however, give rise to various complicated

problems: difficulty in the removal of the modifier, unexpected deterioration in a later production process, contamination of the environment, and the like. If antistickiness can be attained without the use of these reagents, the manufacturing of small pieces from a thin rubber sheet will be greatly improved.^{1–4}

This article describes the effective production of such small pieces of thin rubber by use of ultraviolet (UV) or sputter ion etching treatment (see Fig. 1). Because surface modification can be attained by the method described here, rapid production of thin rubber articles has become possible without any of the disadvantages stated above. The improvement in the adhesion properties of the irradiated products and the surface modification mechanism will be described.

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- UV irradiation
- Ion etching

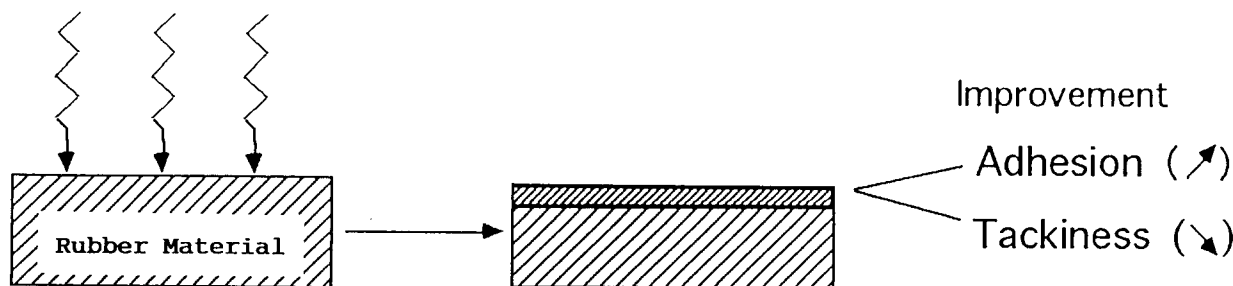


Figure 1 Schematic representation of the improvement of the adhesion properties of rubbers by irradiation methods.

EXPERIMENTAL

Materials

Two kinds of commercial grade rubbers (ethylene-propylene, EP, and chloroprene, CR), manufactured by Tohoku Rubber Company, Ltd., were used. All the samples were vulcanized for 30 min by heat pressing and were supplied in the form of a thin rubber sheet (about $\frac{1}{2}$ mm in thickness). The characterization is given in Table I.

Irradiation Procedures

UV irradiation was performed with a low pressure mercury lamp (nonexothermic type, 30 W, EL-J-60, Eikosha Co. Ltd., Osaka) and a UV-curing lamp (1000 W, UB 011-5, Eye Graphics Co. Ltd.) under the following conditions: atmosphere, air; distance between the sample and the UV source, 40 mm in the former and 150 mm in the latter. Sputter ion etching was carried out by use of an ordinary ion etching assembly (IB-2 type, Eiko

Engineering, Co. Ltd.). The etching conditions were as follows: atmosphere, under reduced pressure (0.1 torr); ion current, 5 mA; distance between the sample and electrode, 30 mm.

Measurements of Nonsticking Properties

A T-shaped (180°) peeling tester (Toyo Baldwin Co. Ltd.) was used. The two rubber sheets were pressed under preparation conditions (applied pressure, 300 gf/cm²; press time, 24 h; temperature, 20°C) and thereafter tested (distance of check, 20 mm; crosshead speed, 200 min/min).

Scanning Electron Microscopy (SEM)

A Hitachi scanning electron microscope (S-415 type) was used under the following conditions: accelerating voltage, 25 kV; atmosphere, vacuum; bright field image; magnification, 5000–15,000.

Table I Characterization of Samples

Notation	Type	Form	Composition	Color
EP	Copolymer	Thin sheet	Additives ^a	Black
CR	Homopolymer	Thin sheet	Additives ^b	Black

^a The commercial grade of ingredients are compounded, such as carbon black, rubricant, and the like. Total weight percent of the additives was about 70.

^b A similar type of ingredients are compounded including carbon black, naphthene oil, and the like. The weight percent of the additives was about 47.

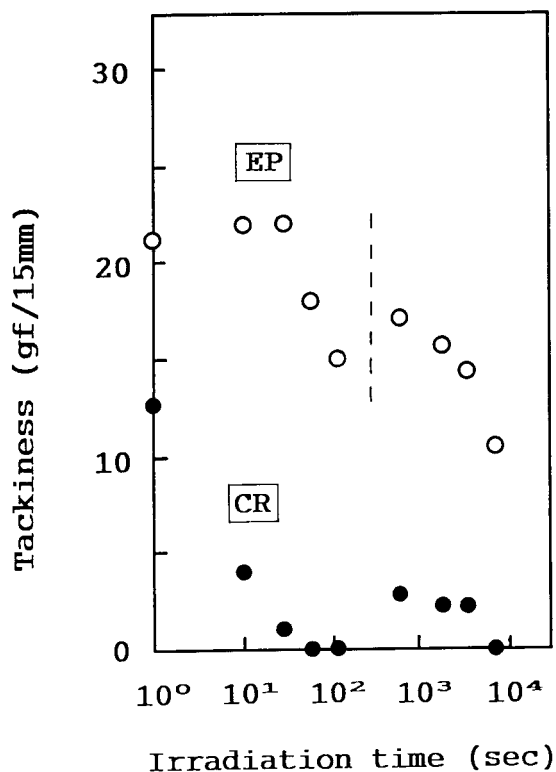


Figure 2 Changes in tackiness of thin rubber sheet due to UV irradiation. The broken line indicates the difference of the UV irradiation lamp. A stronger UV source caused a more rapid decrease in tackiness.

ESCA Measurements

A Shimadzu ESCA (type 1000) was used. Excitation X-ray irradiation was Mg K α line (1253.6 eV). A wide scanning spectrum was obtained under the following conditions: acceleration voltage, 10 kV; current, 10 mA; step, 0.2 eV;

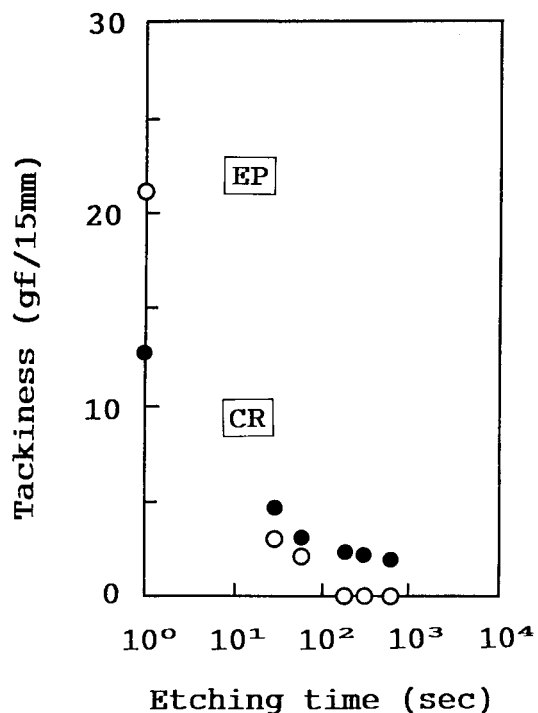


Figure 3 Changes in tackiness of a thin rubber sheet due to sputter ion etching treatment.

sampling time, 400 ms; scanning range, 0–1000 eV; a narrow scanning spectrum was obtained under the conditions: 10 kV; 30 mA, 0.05 eV; 1000 ms.

FTIR Measurements

A Nicolet FTIR spectrometer (type 5DXB) was used. The thin surface of the irradiated rubber was investigated by the attenuated total reflect-

Table II Improvement of Adhesion Properties of Rubbers by Two Irradiation Methods

Sample	Properties	Treatments		
		Virgin	UV ^a	Supper Ion ^b
EP	Adhesion	240	955	1241
	Stickiness	21	14	0
CR	Adhesion	330	851	577
	Stickiness	13	2	0

The value of adhesion intensity is the averaged value of three or four measurements. Unit: gf/15 mm.

^a UV irradiation time was 1 h.

^b Ion etching time was 10 min.

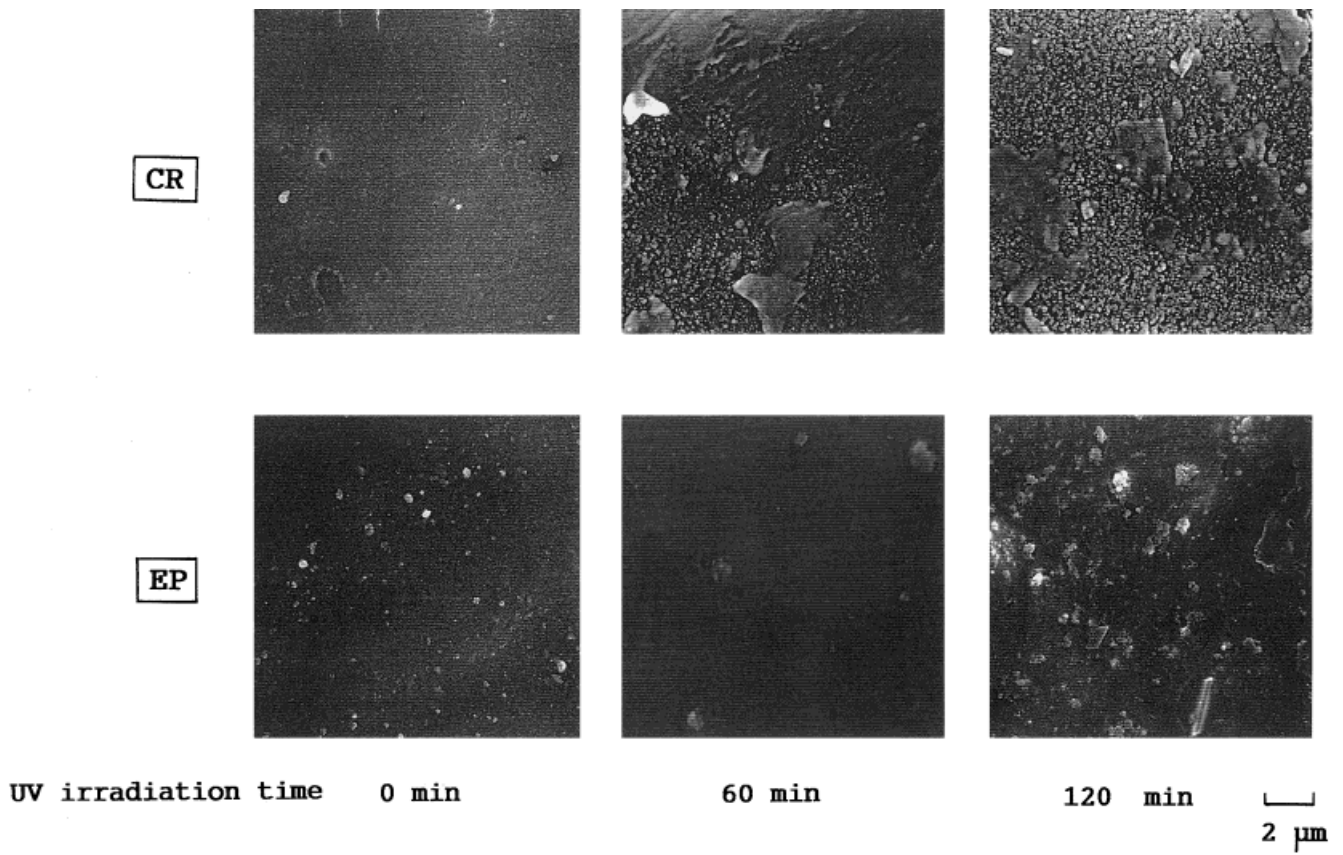


Figure 4 Observation of the UV irradiated rubber surface by a SEM photograph.

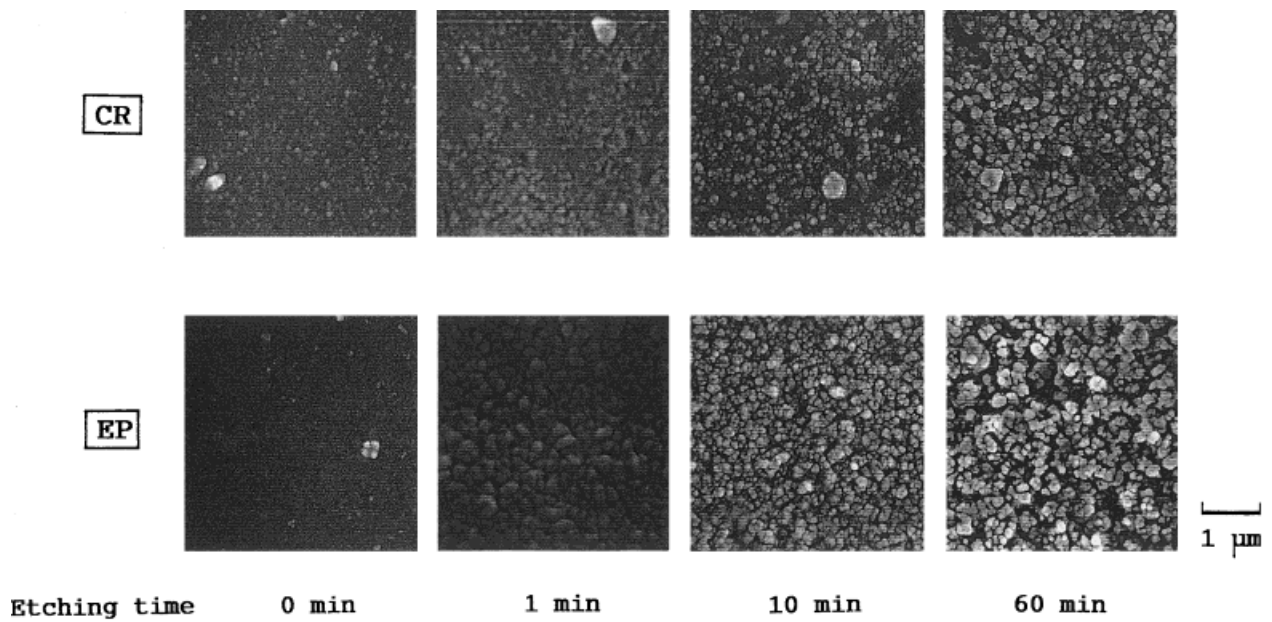


Figure 5 Observation of the ion etched rubber surface by a SEM photograph.

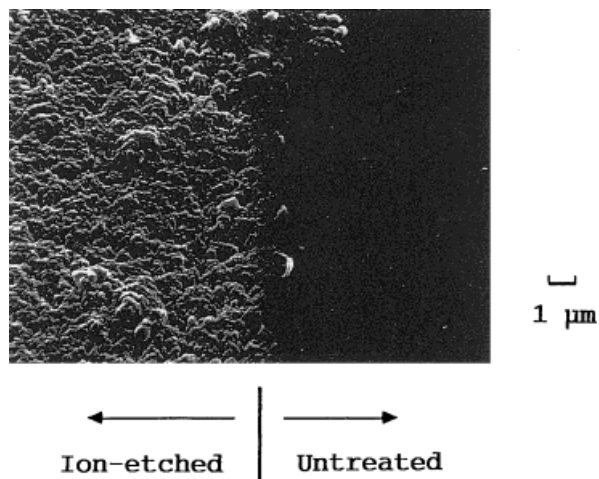


Figure 6 Observation of the interfacial region of an ion etched rubber surface.

tion (ATR) method: ATR crystal, KRS-5; incident beam angle, 60° ; resolution, 4 cm^{-1} .

Gloss Measurements

The gloss of irradiated specimens was measured with a Minolta GM-60 (Minolta, Co. Ltd.) under the following conditions: incident beam angle, 60° ; resolution, 0.1 gloss; precision, 1 gloss.

RESULTS AND DISCUSSION

Irradiation Effect on Adhesion Properties of Rubbers

Figure 2 shows the variation of adhesion properties of UV irradiated specimens. With regard to

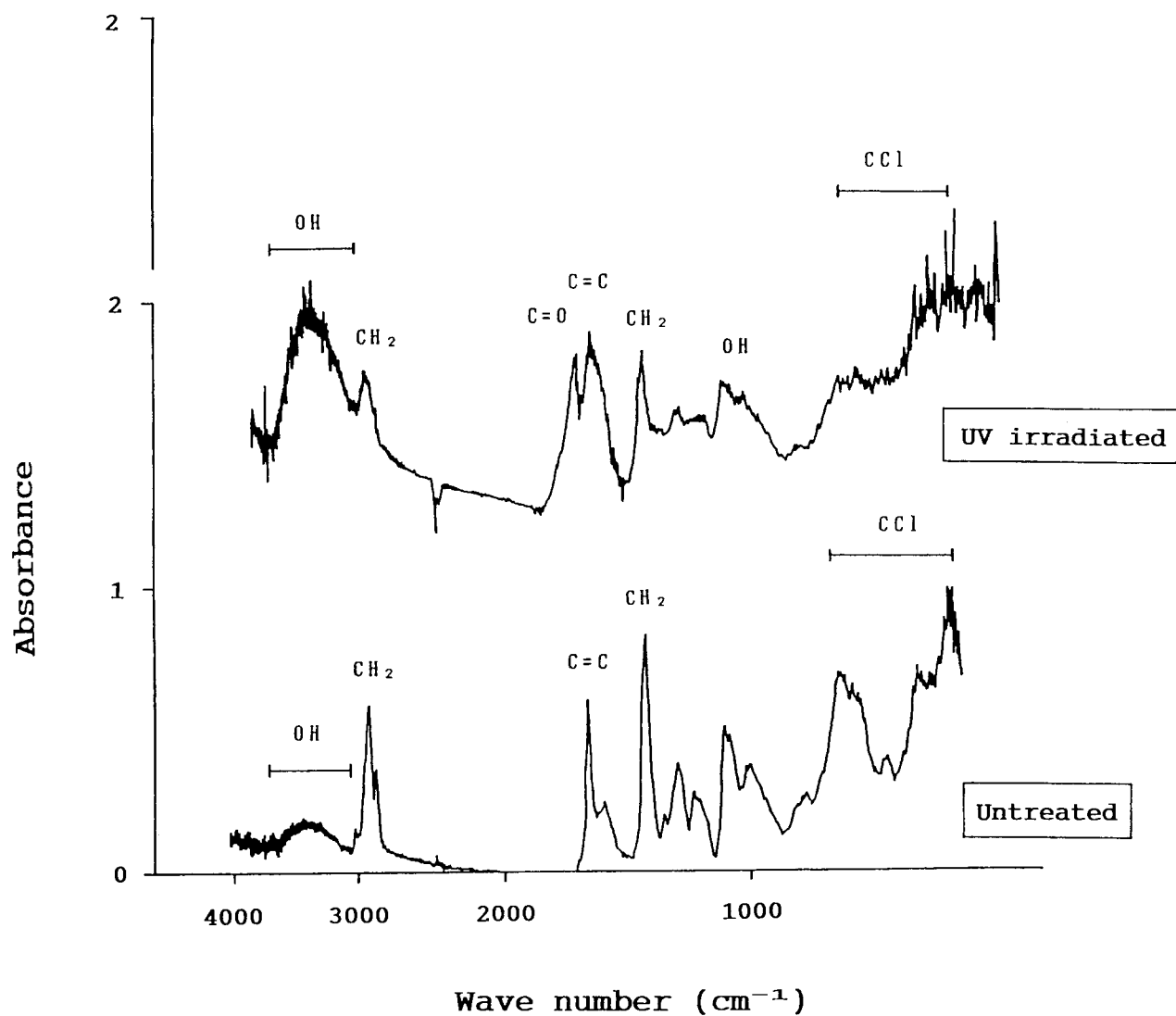


Figure 7 FTIR-ATR spectra of CR surface before and after UV irradiation. UV irradiation time, 2 h.

the tackiness of original samples, EP was more sticky than CR material. When UV irradiations were carried out in air, the tackiness decreased with the increase of UV irradiation time. The extent of its effect was dependent on the kind of rubber material and the irradiation conditions: the effect was more remarkable in CR than in EP rubber. It was very hard to diminish the tackiness of the EP rubber completely by the UV method under the given conditions. However, this disadvantage could be improved with the use of a more powerful UV irradiation source. As a matter of fact, tackiness decreased more rapidly with a stronger UV source.

In the case of sputter ion etching, the tackiness decreased an extreme amount within a quite short etching time (Fig. 3). The effect was equally drastic in both specimens. It is possible to say that the ion etching method is more powerful than the UV irradiation method with regard to this point. In the comparison of both methods, it is important to note that adhesion properties of irradiated samples such as adhesion intensity with epoxy resin increased remarkably in both cases (see Table II). Thus, these irradiation methods brought about a simultaneous increase of adhesion properties and drastic reduction in tackiness (self-adhesion).

Estimation of Modification Mechanism at Rubber Surface by Spectroscopic Methods

The surface of the irradiated specimens was studied by SEM observation. The results are shown in Figures 4–6. The relatively flat surface of the original sample became roughened with the progress of the UV irradiation, and minute cracks were simultaneously formed (Fig. 4). In the case of ion etching (Fig. 5), minute nodules were also formed. It is particularly clearly indicated in Figure 6 that the surface roughening occurs only in a quite thin surface layer; its depth was estimated to be about 0.5 μm .

Figure 7 shows the FTIR spectra of the samples. The appearance of a broad band near the 3400 and 1700 cm^{-1} region suggests the formation of various oxygen containing functional groups such as carboxylic acid (COOH), ester (COO), and alcohol (OH) groups through an oxidation reaction.^{5–7}

The occurrence of an oxidation reaction is more clearly indicated by ESCA spectra in Figures 8 and 9. In Figure 8, the reduction of C_{1s} and the increase of the O_{1s} peak are obvious.^{8–10} Even in the comparison of the O_{1s} intensity of untreated and UV irradiated CR rubber in Figure 9 (top), the intensity of

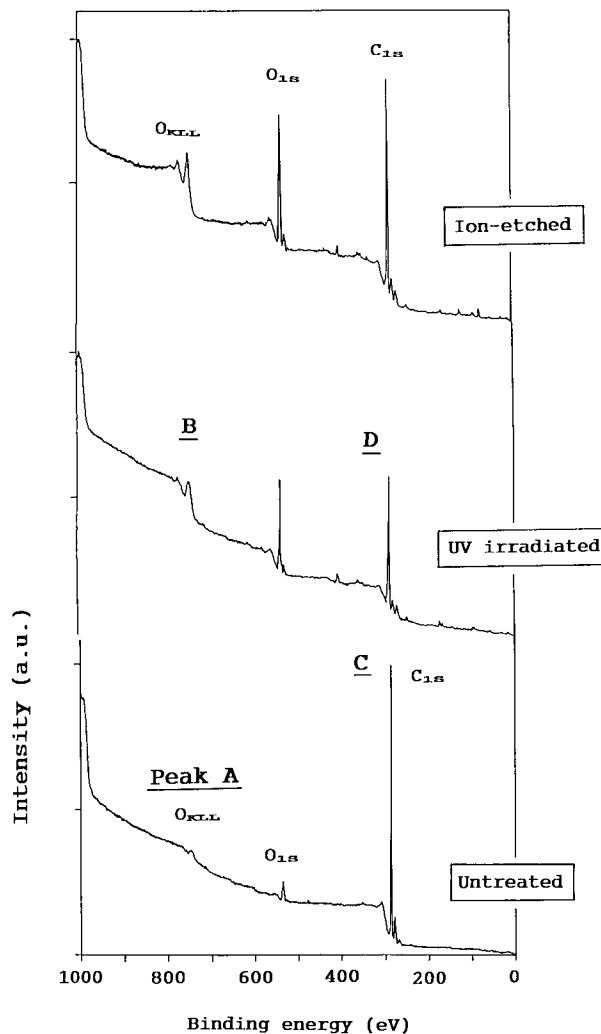


Figure 8 ESCA spectra of CR rubber (wide scanning).

the irradiated sample is greatly enhanced, in fact 10 times stronger, with a slight shift of the peak position (from 533.0 to 534.5 eV). In the comparison of the C_{1s} peak of untreated (left) and UV irradiated specimens (right), the peak of the former is between the CH_2 and CO groups, while the peak of the latter is between the CO and $\text{C}=\text{O}$ groups. Particularly the ESCA peak in the latter case shifted gradually from 287.4 to 286.1 eV and remained constant at this value. These results indicate that:

1. a small extent of oxidation had already occurred in the original rubber;
2. irradiation-induced oxidation occurs only at the thin outer surface of the rubber;

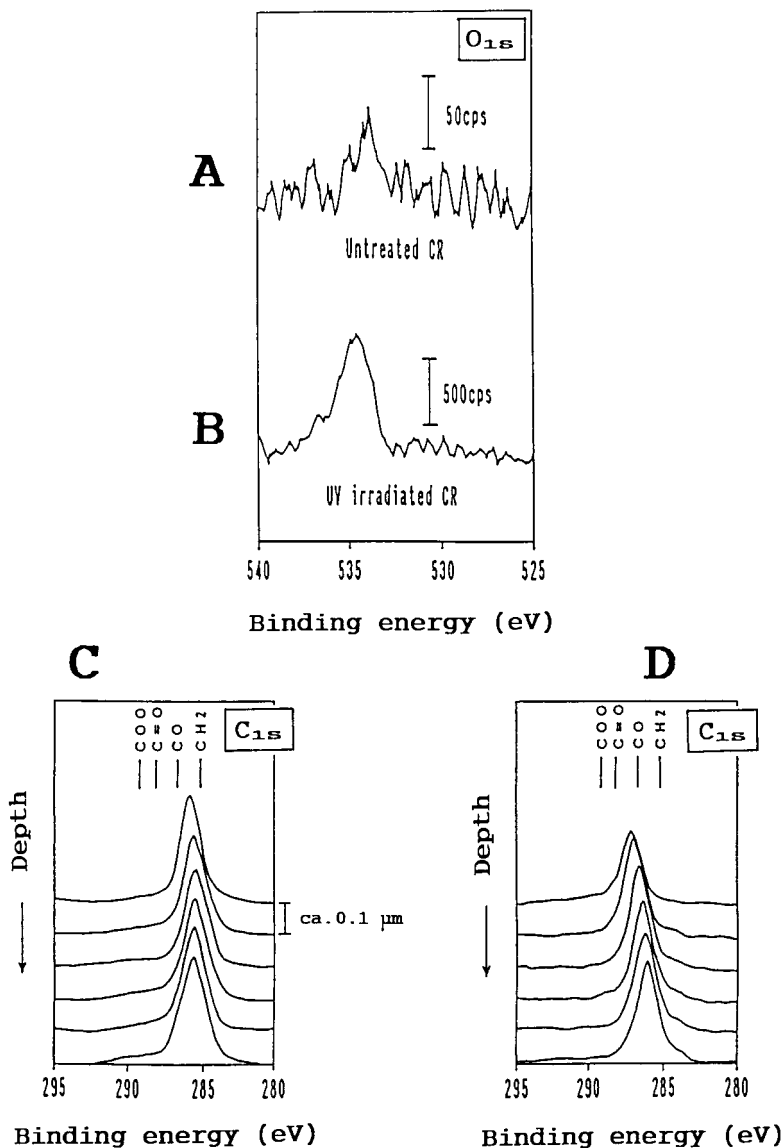


Figure 9 Expanded ESCA spectra (narrow scanning).

3. various types of oxygen containing functional groups, such as carbonyl, hydroxyl, and ester groups, are formed; and
4. from the depth analysis, the thickness of the oxidized thin surface layer was calculated to be about $0.5 \mu\text{m}$.

This value was in agreement with the one ($\sim 0.5 \mu\text{m}$) obtained through surface observation by SEM in Figure 6. Even in the results of the ion sputter etching treatment, similar results were obtained, although experimental data are not presented here.

Evaluation of Surface Modification by Gloss Tester

It is important to note that the changes in the surface layer of the rubbers could be detected by the naked eye. The luster of black rubber gradually diminished and finally became a dull shade of brown. The extent of its effect was evaluated by use of a gloss meter.

Figure 10 shows a change in the gloss of irradiated rubber samples measured by a gloss tester. All the experimental data fall on a single smooth curve. A difference due to the difference of irradiation sources was not observed. (A similar single smooth curve was also obtained in the CR material.) This figure directly indicates the extent of

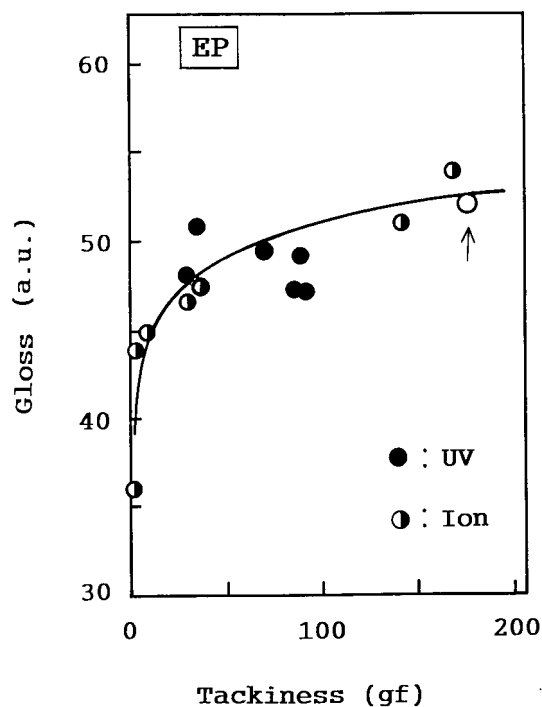


Figure 10 Relationship between gloss and tackiness of irradiated rubber sheet. The open circle indicates the value of unirradiated specimens (averaged value of several measurements).

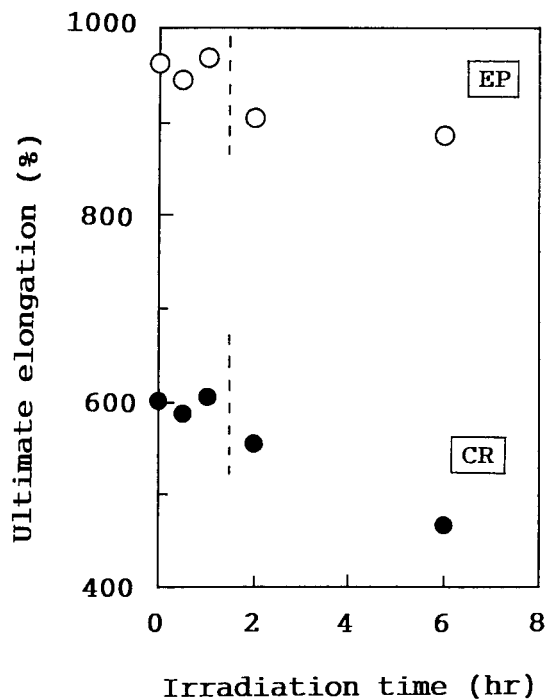


Figure 11 Changes in bulk mechanical properties of rubbers by UV irradiation. It must be noted that the actual surface modification is carried out in a quite short irradiation, as indicated by the dotted line.

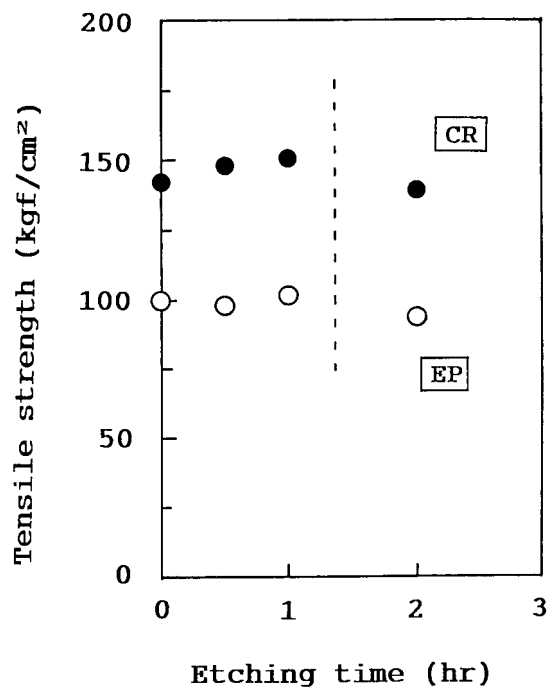


Figure 12 Changes in bulk mechanical properties of rubbers by ion etching.

modification in the rubber. In other words, this figure is, so to speak, a *kind of calibration curve*; one can evaluate to what extent the surface of the irradiated sample is modified, or to what extent irradiation should be carried out on the rubber, based on this curve.

Relatively small changes in the mechanical properties of irradiated specimens (Figs. 11 and 12) indicated reasonable results that modification occurred only at the surface and bulk properties remained largely unaffected, particularly in EP rubber.

This surface modification processing was employed industrially by Tohoku Rubber Co. Ltd. (Japan) and the production of thin rubber articles was greatly improved. It is worthwhile noting that this method together with the use of far-infrared irradiations is accompanied by no disadvantages in the production of specialized articles for electronic uses, as described above.

CONCLUSION

1. The surface modification of two kinds of industrial rubbers (EP and CR) was carried out by means of UV and sputter ion etching treatments. The adhesion properties to chemicals increased, whereas sticki-

- ness (self-adhesion) decreased. The relationship between the irradiation source and time and the resulting sticking properties were clarified.
2. The mechanism of the surface modification reaction was studied and discussed. SEM and ESCA observations revealed that the decrease in self-adhesion was caused by a combination of surface roughening and a surface oxidation reaction. The depth of the oxidized surface layer was about 0.5 μm .
 3. The application of these methods to an industrial manufacturing process was described. The simultaneous use of far-infrared irradiation with UV irradiation has brought about a remarkable improvement in efficiency in the production of small pieces of thin rubber articles in electronic device applications.

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