

## ***Reaction of Moist Ozone with Natural Rubber: A Study by Attenuated Total Reflectance Spectroscopy***

A.H. ENG<sup>\*,\*\*\*</sup>, S. KODAMA<sup>\*\*</sup>, K. NAGATA<sup>\*\*</sup> AND H. KAWASAKI<sup>\*\*\*</sup>

*Surface treatment of prevulcanised latex film with ozone water leads to the formation of ester, aldehyde, and ketone groups as indicated by a FTIR-ATR study. In the presence of proteins, the carbonyl oxide zwitterion intermediate reacts with the amino groups of the protein to produce rubber-bonded proteins on the surface. Reaction of moist ozone gas with dry rubber film produces more ozonides than with wet rubber gel and leads to the formation of visible cracks on the rubber surface. In the case of ozone-treated wet rubber gel, the tensile strength of the film remains high, indicating no significant ozone penetration. The reaction of ozone with natural rubber in the wet gel state may be used to chemically modify the surface of natural rubber products without sacrificing the excellent physical properties of the rubber*

Ozone attack on natural rubber was first recognised as being important in the early 1950s due to ozone cracking problems<sup>1</sup>. In the early stages of the reaction, ozone attack on natural rubber double bonds occurs very rapidly at the exposed surfaces. If stress is applied to the rubber sample during ozonisation, degradation at regions of high strain, e.g. surface defects, creates a retractive force, causing the underlying rubber chains to become exposed to the surface and therefore ozone attack on the exposed rubber continues. Eventually, this leads to the formation of the characteristic ozone cracks.

Gilbert reported that the nature of ozone cracking is very much dependent on the environment of the reaction<sup>2</sup>. In dry ozone, the

cracks were found to develop simultaneously on the rubber surface at the initial stage of the reaction and then grow at a uniform rate. The net result is the formation of distinctive visible cracks on the surfaces. In moist ozone, however, the crack's nuclei were reported to be continuously created by localised attack between micelle aggregates. The density of these cracks was much higher than that of dry ozone, resulting the formation of fine scale erosion on the surface with low ozone penetration into the interior part of the rubber sample. These differences, observed by Gilbert using optical microscopy, were speculated to be due to the modification of the ozone/rubber reaction by the water vapour. However, no direct evidence was given in the study. In this work, the chemical

---

\* Rubber Research Institute of Malaysia, P O. Box 10150, 50908 Kuala Lumpur, Malaysia

\*\* Industrial Technology Center of Okayama, 5301, Haga, Okayama 701-1296 Japan

\*\*\* Nihonshokusei Okayama Research Laboratory, 5325-2, Haga, Okayama 701-1296, Japan

# Corresponding author

modification of prevulcanised latex film surface by moist ozone was investigated by the FTIR-ATR (Attenuated Total Reflectance) spectroscopy technique to provide more detailed information on the chemical structure of the treated rubber surfaces.

#### EXPERIMENTAL

The natural rubber latex used was commercial prevulcanised latex. Deproteinised natural rubber (DPNR) latex with total nitrogen content 0.02% (w/w rubber), was supplied by Sumitomo Rubber Co., Japan. Natural rubber films were obtained by the coagulant-dipped method using a glass test tube as former and calcium nitrate as coagulant. The wet rubber gel was leached in water bath at 60°C for 1 min and dried in oven at 100°C for 30 min. The dry film was further leached in water bath for 1 min before drying at 100°C for 15 min. All ozone treatments of the rubber films were carried out on the formers, *i.e.* unstripped. The sample which was leached at wet gel state but not in dry films, *i.e.* no leaching was carried out after drying, was referred to as unleached sample.

Ozone water of low ozone concentration was generated by a Ohnit Ozone Generator. The wet rubber gel and dry rubber film were submerged into the ozone water for a specific period of time and dried as described above. Unvulcanised DPNR film was obtained by drying the wet rubber gel after leaching at room temperature to minimise the degradation of the rubber. The dried rubber film was then leached and extracted with acetone for 16 h at room temperature to remove the antioxidant and dried in the air before treating it with ozone water.

Control samples were obtained by dipping the rubber films into water bath set at the same temperature for the same period of time as the ozone water-treated samples.

Extractable protein content of the rubber films was determined using the reported method<sup>3</sup> except that the extraction time was extended to 24 h due to poor wetting properties of the film's surface. The rubber films were cut and peeled off from the former and placed directly in containers for extraction without applying lubricating powder to avoid interference. Lubricating powder, which is normally applied on the rubber film's surface to prevent the rubber surfaces from sticking to each other, is polar material which can improve the wetting properties of rubber film.

Moist ozone gas was obtained by pumping the ozone gas into a S-shape glass tube with a glass filter fitted open-end submerged into 200 ml distilled water contained in a three-litre reaction flask. The dry rubber film or wet rubber gel on a test tube former was then placed above the water surface, where ozone gas was surfacing out from the water, for a specific period of time.

FTIR-ATR measurements of the rubber films were carried out using a Perkin-Elmer FTIR 2000 spectrometer with a trapezoidal germanium crystal placed at 45° angle of the radiation beam.

#### RESULTS AND DISCUSSION

##### FTIR Spectra of Natural Rubbers

Figures 1(a) and 1(b) show the FTIR-ATR spectra of wet gel leached (referred to as unleached) and both wet gel and dry film-leached (referred to as leached) prevulcanised latex

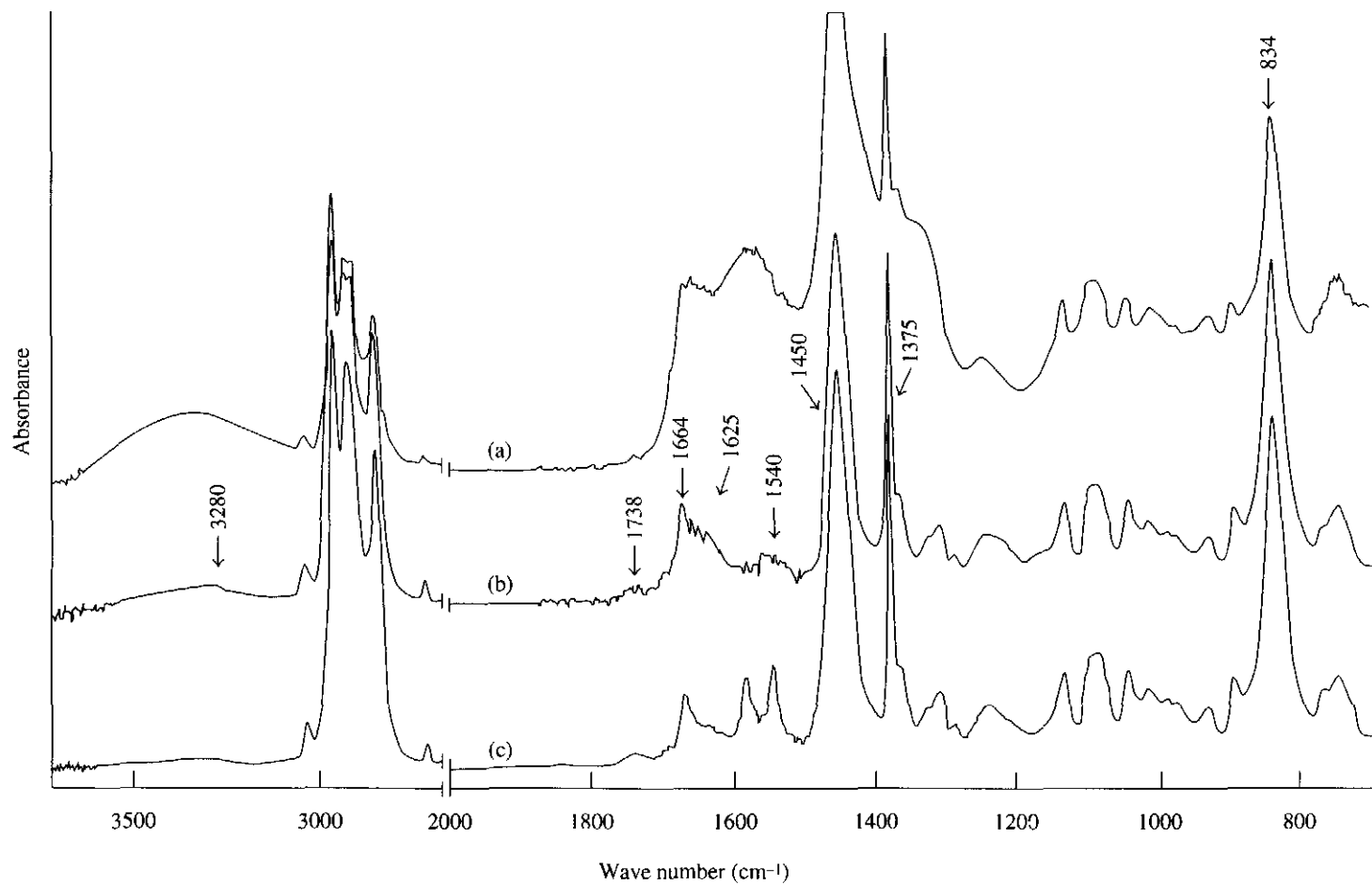


Figure 1. FTIR-ATR spectra of natural rubbers (a) outer surface of unleached rubber (b) outer surface of leached rubber, and (c) inner surface of wet gel unleached rubber.

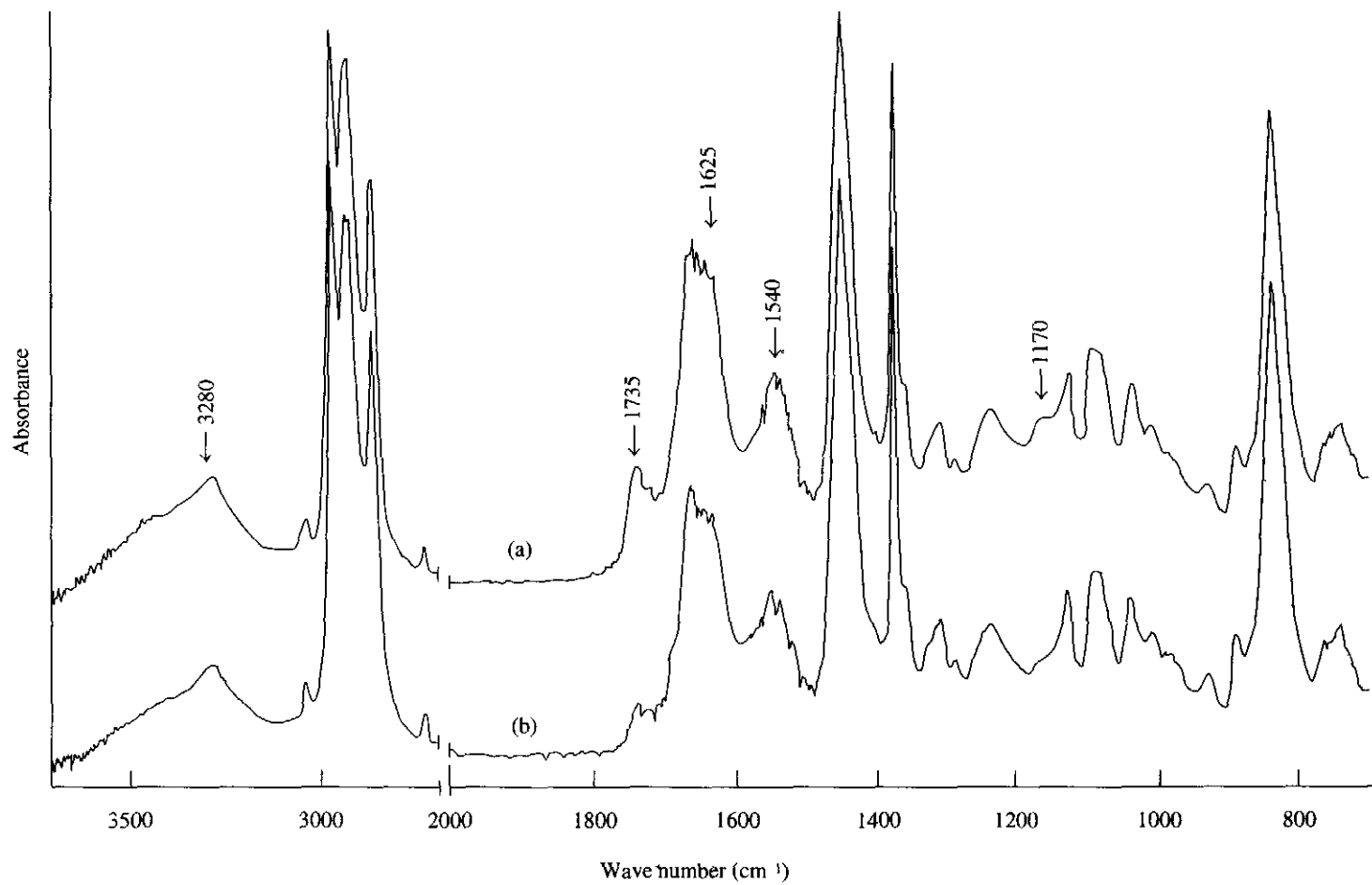
films, respectively. The major bands of *cis*-1,4 polyisoprene in the rubber are  $2850\text{ cm}^{-1}$  –  $3000\text{ cm}^{-1}$  C-H stretching,  $1664\text{ cm}^{-1}$  C=C stretching,  $1450\text{ cm}^{-1}$   $\text{CH}_2$  deformation,  $1375\text{ cm}^{-1}$  methyl C-H deformation, and  $834\text{ cm}^{-1}$  =C-H out of plane. The bands at  $3280\text{ cm}^{-1}$ ,  $1625\text{ cm}^{-1}$ , and  $1540\text{ cm}^{-1}$  in the spectrum of leached rubber film are due to N-H stretching, C=O of amide (amide I), and N-H bending of amide (amide II) groups in rubber proteins, respectively. In the case of unleached film, the intensities of these bands are stronger than those of leached film, indicating the presence of more rubber proteins on the surface of this sample. This is due to the migration of water-soluble proteins in the latex film from inner part of the rubber to the surface during drying<sup>3</sup>. The inner surface of the film, i.e. the former-contacting surface, therefore contains relatively low proteins as shown in Figure 1(c). The two bands in the region of  $1500\text{ cm}^{-1}$ – $1600\text{ cm}^{-1}$  in the spectrum are due to the residual coagulant, i.e. nitrate group of calcium nitrate. The band at  $1738\text{ cm}^{-1}$  is due to naturally occurring fatty ester groups of the rubber.

### Reaction of Natural Rubber Films with Ozone Water

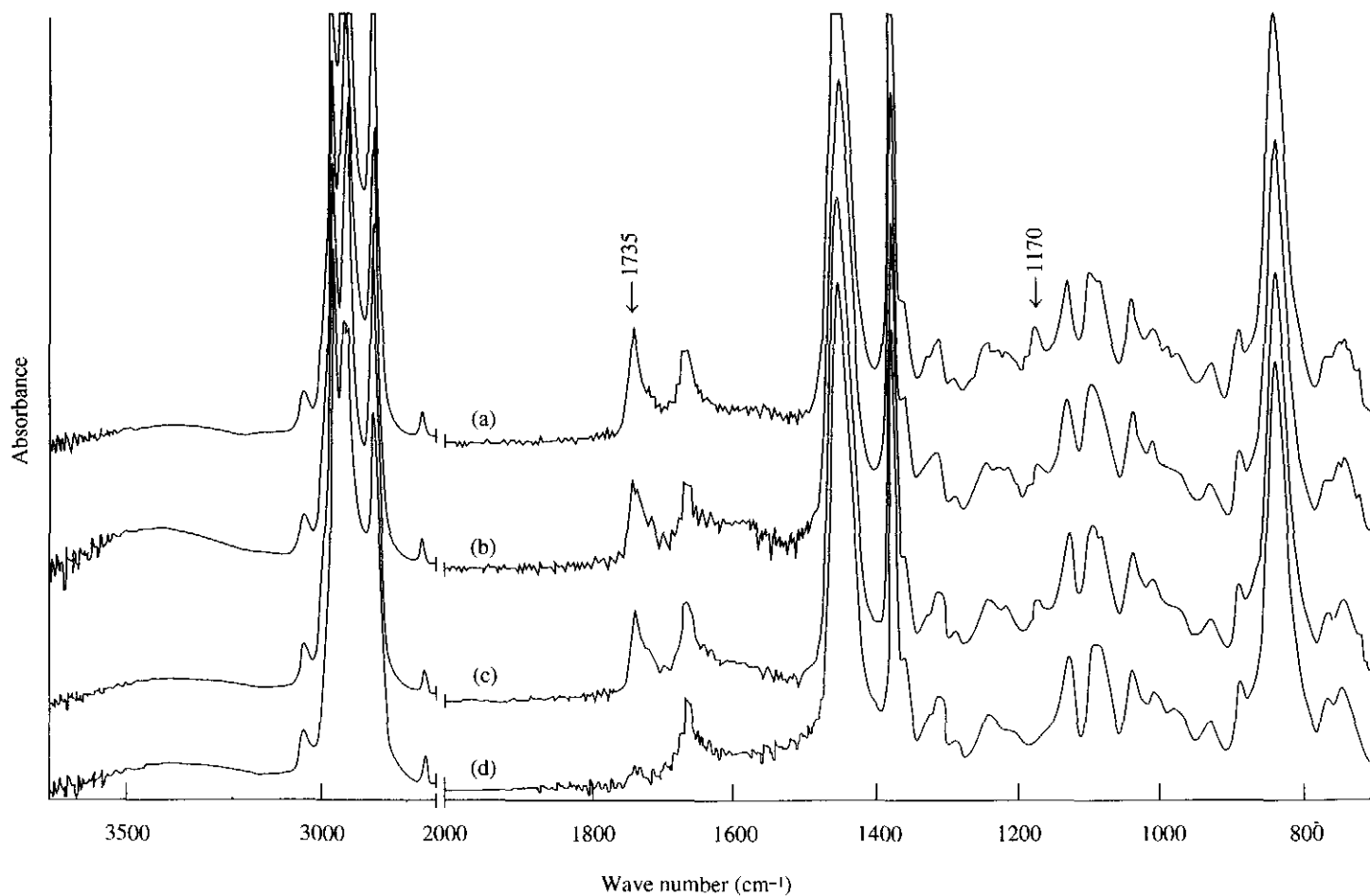
Initial attempt to modify the surface of prevulcanised natural rubber films by ozone was carried out by dipping both the dry rubber film and wet rubber gel into the ozone water containing 5 p.p.m. of ozone which was continuously being generated during the 2 hour treatment. The results are shown in Figure 2. Upon ozone treatment, the intensity of bands at  $3280\text{ cm}^{-1}$ ,  $1625\text{ cm}^{-1}$ , and  $1540\text{ cm}^{-1}$ , which are due to proteins, as described above, was found to increase for both dry film and wet gel samples

when compared to the corresponding bands in Figure 1(b). The relative intensity of these bands remained unchanged even after the treated films were further leached in water at  $60^\circ\text{C}$  for 3 min. In addition, in the case of dry rubber film, an increase in the intensity of the band at  $1735\text{ cm}^{-1}$ , which is due to ester groups, and formation of a new band at  $1170\text{ cm}^{-1}$  which is attributable to C-O in ether group, were also observed after the ozone treatment. These observations were less prominent in the case of wet gel sample. The relative intensities of these bands, i.e.  $1735\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$ , were also found to decrease when the ozone treatment time was reduced from 2 h to 1 h indicating that ozone treatment leads to the formation of ester groups.

In order to avoid interference of proteins in the interpretation of the spectrum of ozone-treated rubber, highly purified DPNR latex films were treated with the ozone under the same conditions as the above and the results are presented in Figure 3. In the absence of proteins, the ozone-treated films show stronger absorption bands at  $1735\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$ . Furthermore, the relative intensity of these bands was found to increase when the treatment time was extended from one hour to two hours as shown in Figures 3(c) and 3(a), respectively. The relative intensity of these bands remained unchanged even after acetone extraction, indicating that the ester groups are an integral part of the ozone-treated rubber surface. The absence of bands at  $3280\text{ cm}^{-1}$ ,  $1625\text{ cm}^{-1}$ , and  $1540\text{ cm}^{-1}$  in these samples after the ozone treatment clearly indicates that these bands, shown in Figure 2, are due to the rubber proteins and not derived from the degradation products of natural rubber. A closer examination of the carbonyl absorption region revealed the presence



*Figure 2 FTIR spectra of ozone-treated (5 p.p.m., 2 h) rubbers (a) outer surface of rubber treated in dry film state, and (b) outer surface of rubber treated in wet gel state.*

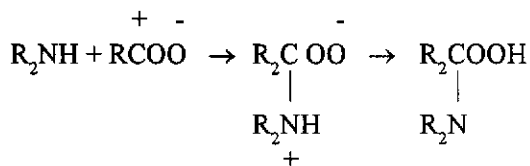


*Figure 3. FTIR spectra of DPNR (a) outer surface of rubber treated with ozone water for 2 h (b) outer surface of rubber treated with ozone water for 1 h followed by acetone extraction (c) outer surface of rubber treated with ozone water for 1 h, and (d) outer surface of untreated rubber.*

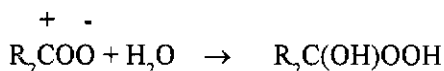
of bands at  $1716\text{ cm}^{-1}$  and  $1723\text{ cm}^{-1}$  which are probably due to ketone and aldehyde groups.

The mechanism for the reaction of ozone with natural rubber was originally proposed by Criegee<sup>4</sup> and it is summarised in *Figure 4*. Based on this proposal, the mechanism for the reaction of natural rubber hydrocarbon with ozone water in the absence of rubber proteins in the present study is suggested to involve the formation of molozone which subsequently decomposes to produce an aldehyde or ketone groups and carbonyl oxide zwitterions. The zwitterions can further undergo rearrangement reaction to form ester group as shown in *Scheme 1*.

The effects of group X on the extent of the rearrangement reaction was studied by Young *et al*<sup>5</sup> in 1946. They reported that the rearrangement reaction occurs more readily when X is a good electron donor and therefore the extent of this reaction was found to be in the increasing order of  $X=p\text{-NO}_2\text{-C}_6\text{H}_4 < \text{C}_6\text{H}_5\text{O} < \text{HO} < \text{C}_2\text{H}_5\text{O} < (\text{C}_2\text{H}_5)_2\text{N}$ . In the case of natural rubber, the methyl group of the polyisoprene, having electron donating property, is expected to remain attached to the zwitterion. In the presence of water, the electron donating effect of oxygen atom in the water molecule probably assists the rearrangement reaction. These explain the formation of ester, aldehyde and ketone in the ozone-treated DPNR. For non-DPNR samples, the amount of ester group formed was found to be relatively small when compared to that of DPNR. This is probably because the carbonyl oxide zwitterion could react with the amino groups of proteins by a mechanism such as:

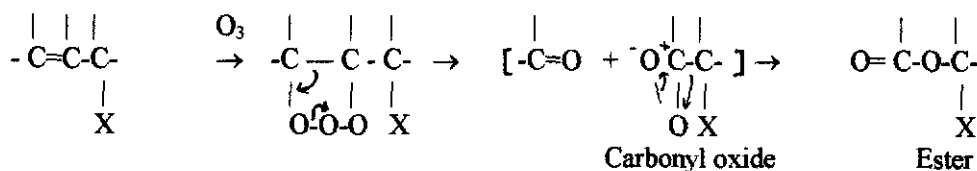


as proposed by Loan *et al*<sup>6</sup>. These would render the proteins insoluble in water and the formation of relatively less amount of ester groups. This is supported by the observation that the extractable protein in prevulcanised latex film decreased with prolonged ozone treatment as shown in *Table 1*. The decrease could also be due to better solubility of the degraded rubber proteins on the surface which were produced by ozone attack on the proteins. It should be noted that the expected similar reaction of the zwitterion with water molecule in the absence of proteins did not occur under the conditions employed such as:



The rearrangement reaction to form ester groups seems to be more favourable than the reaction with water under the conditions employed. In addition, the characteristic band at  $1123\text{ cm}^{-1}$  due to five-membered ring ozonide was not observed in both cases although the ozone attack on natural rubber under ambient conditions<sup>1</sup> is expected to produce ozonide (III), diperoxide, or polymeric peroxide (IV), aldehyde or ketone (II and VI) and ester (V) groups as shown in the reactions in *Figure 4*.

There were no cracks or other physical changes such as tensile strength and tackiness observed in any samples treated with the ozone water.



Scheme 1

### Reaction of Natural Rubber with Moist Ozone Gas

Although the use of ozone water to modify the surface of natural rubber described above is convenient, the low solubility of ozone in water under ambient conditions makes the process time-consuming. Therefore, the experiment on ozone treatment of wet rubber gel was carried out using moist ozone gas where a high concentration of ozone could be used. As mentioned above, ozone attack on strained dry natural rubber can lead to ozone cracking of the rubber. The rubber film on test tube used in the present study was found to be strained upon drying, i.e. extended by about 4% in length. The presence of stress is expected to influence the nature of ozone cracking of the rubber. However, the chemical aspect of the ozone attack on the rubber is expected to remain unchanged. The use of moist ozone could

prevent the wet rubber gel from drying up after which the rubber film becomes strained during the surface treatment. A dry rubber film was also treated with the ozone under the same conditions for comparison.

Figure 5(a) shows the FTIR-ATR spectrum of rubber film from wet rubber gel after treating it with moist ozone gas. The bands at 1735 cm<sup>-1</sup> and 1719 cm<sup>-1</sup> are due to ester and ketone or aldehyde groups, respectively, while the bands at 1207 cm<sup>-1</sup> and 1010 cm<sup>-1</sup> can be assigned to C-O-C of ester groups. The intensity of the latter bands was found to decrease upon acetone extraction for 16 h as shown in Figure 5(b), indicating that they are due to low molecular weight compounds. The band at 1115 cm<sup>-1</sup> is due to ozonide groups. When the film was boiled in distilled water for 5 min, the ozonides hydrolysed to form aldehyde and ketone. These changes are indicated in Figure 5(c). The bands

TABLE 1 EXTRACTABLE PROTEIN CONTENT OF PREVULCANISED LATEX FILMS

Treatment time (min)	0	1	3	5	10
EP in control sample (mg/g)	0.82	0.24	0.19	0.14	0.11
EP in ozone water sample (mg/g)	0.82	0.22	0.14	0.11	0.06

EP Extractable protein

Conditions – Control. Dry film, water, 23°C

Ozone water. Dry film, 5 p.p.m. ozone, 23°C

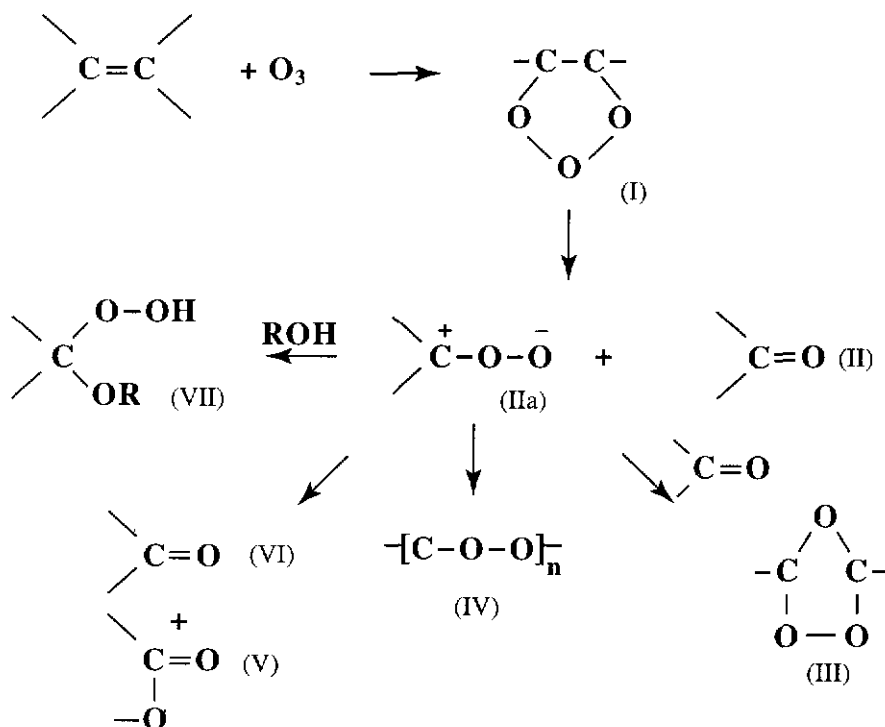


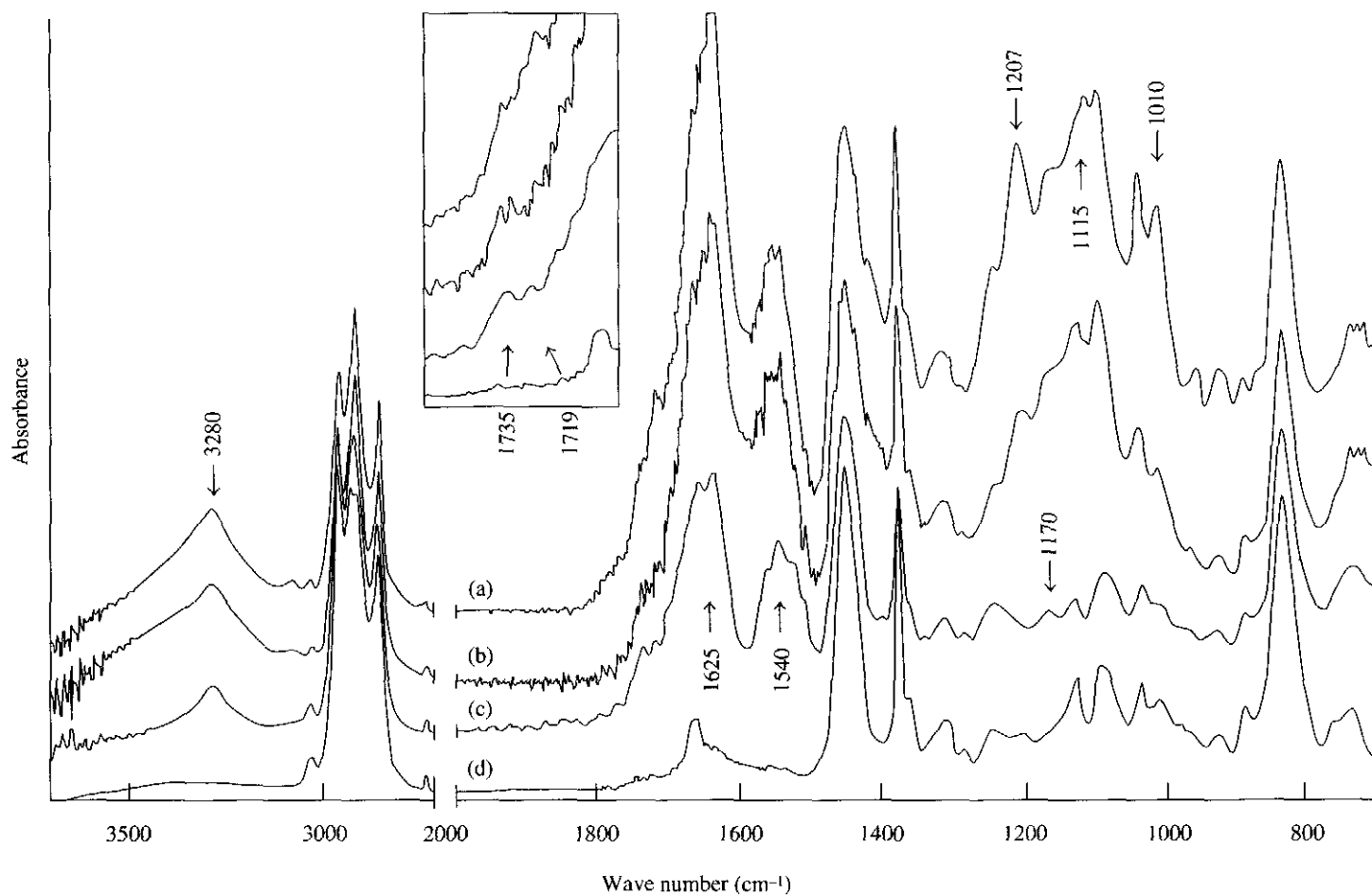
Figure 4 Mechanism for ozonolysis of natural rubber as proposed by Criegee<sup>4</sup>

due to proteins and ester groups were found to remain even after the extraction, indicating that they are bonded to the rubber molecule.

There were no visible cracks found in the ozone-treated film. The film showed tensile strength of 22.3 MPa as compared to that of control sample of 24.5 MPa. These indicate that ozonolysis only took place on the rubber surface and that no significant penetration of ozone into the inner part of rubber occurred. This is confirmed by the spectrum in *Figure 5(d)*. The outer surface of the rubber was found to change from tacky to smooth and non-stick after the

ozone treatment. These changes, however, were non-permanent because the modified rubber layer on the surface does not adhere strongly to the underlying rubber film and therefore its resistance to physical friction is rather low. These results imply that ozone treatment of natural rubber in wet gel state may be used to introduce polar functional groups onto the surface without changing the tensile properties of the rubber film.

In the case of dry film rubber, as shown in *Figure 6(a)*, in addition to the band at  $3278\text{ cm}^{-1}$ , two rather sharp bands of similar intensity



*Figure 5 FTIR spectra of natural rubber treated with moist ozone gas (16,000 p p m ) in wet gel state  
 (a) outer surface of the sample treated for 1 h (b) outer surface of the sample treated for 1 h followed by acetone extraction  
 (c) outer surface of the sample treated for 1 h followed by boiling in water for 5 min, and (d) inner surface of the sample treated for 1 h*

appeared at  $3533\text{ cm}^{-1}$  and  $3410\text{ cm}^{-1}$  after the ozonolysis, probably due to primary amines derived from degraded rubber proteins. Although bands due to OH groups may also appear in this region, these groups normally show broad absorption bands. These two bands were not found in the case of treated wet rubber gel mentioned above. The bands due to ester and ketone or aldehyde groups were found to appear at  $1735\text{ cm}^{-1}$  and  $1718\text{ cm}^{-1}$ , respectively. The intensity of these bands is relatively weaker than that of those in the spectrum of the treated wet rubber gel. The most distinctive band in the spectrum, which centred at  $1123\text{ cm}^{-1}$ , is due to the ozonides. Upon acetone extraction, the intensity of these bands decreased significantly [Figure 6(b)] as in the case of treated wet rubber gel, indicating that chain scission of the rubber to form low molecular weight compounds had occurred. When the treated film was boiled in distilled water, a complete hydrolysis of the ozonides was observed as indicated in Figure 6(c). The bands due to amines were also found to disappear after the treatment. However, other functional groups remained on the surface of the rubber. The presence of a substantial amount of ozonides on the rubber surface after treating with the moist ozone indicates that this functional group does not easily hydrolyse even in the presence of moisture. The ozonides in the treated film were also found to remain intact even after the film was stored for one week under ambient conditions.

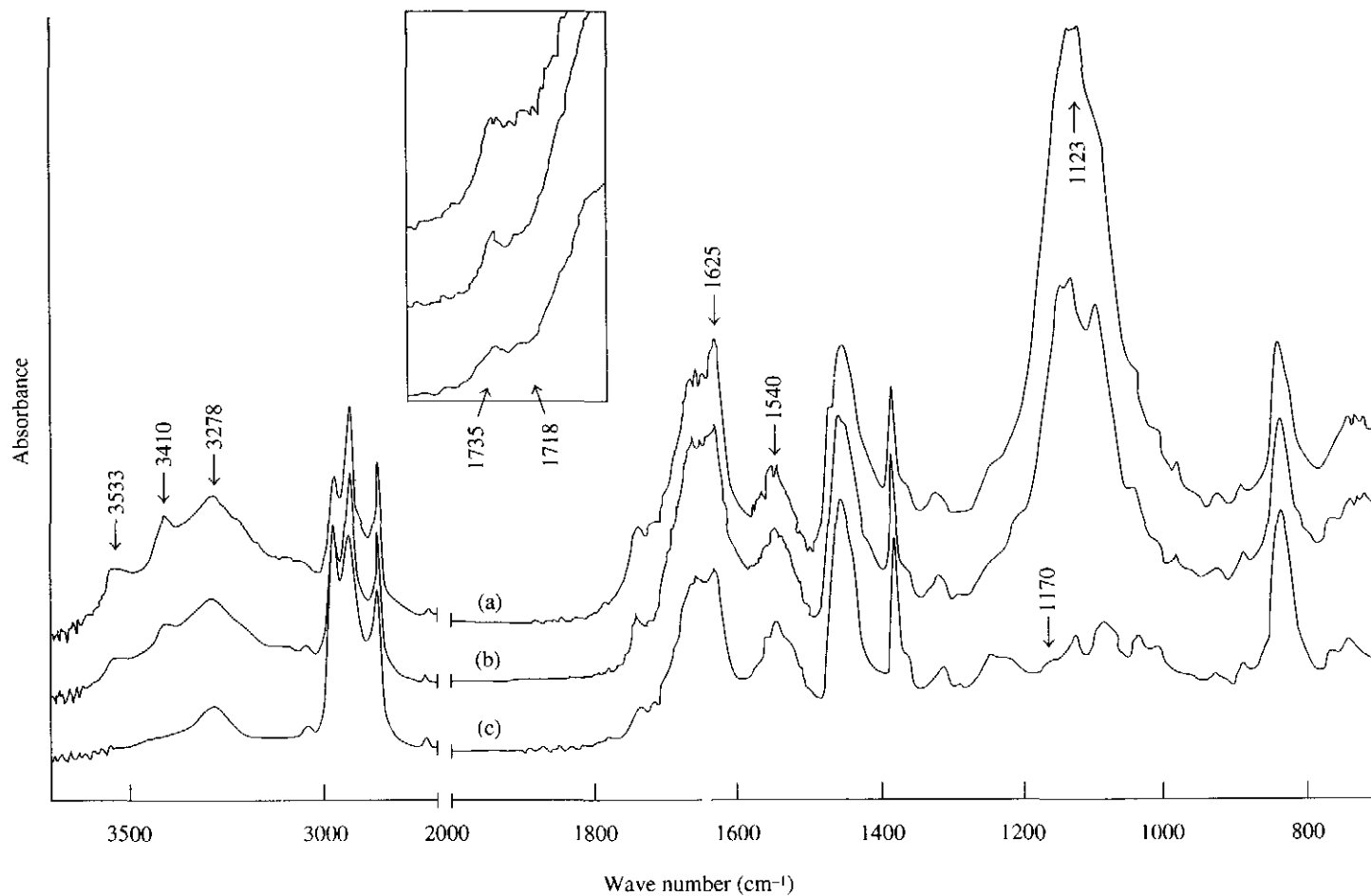
The ozone-treated dry rubber film showed serious visible cracks. The ozone was found to have completely penetrated into a rubber film of about 0.18 mm thickness and the rubber film broke into small fragments after the ozone treatment. Although the chemical structure of the treated surface is different from that of treated wet rubber gel, the tackiness of the

surface was also found to decrease in the similar manner and no oily surface was observed.

As mentioned above, the moist ozone (2 p.p.m.–50 p.p.m.) treatment of strained dry natural rubber was reported<sup>2</sup> to produce no visible cracks on the surface. This is not found to be the case in the present study where a high concentration (16 000 p.p.m.) ozone was used. Under these conditions, the moisture does not protect the strained dry rubber from complete ozone penetration. The discrepancy could be due to the difference in the concentration of the ozone used. It is interesting to note that ozonolyses of wet rubber gel and dry rubber film produced different chemical structure on the rubber surfaces. The proteins in the wet rubber gel are expected to be in hydrated form and therefore the ozone attacks were mainly on the hydrophobic natural rubber molecule as indicated in Figure 5. On the other hand, both rubber proteins and rubber molecule in the dry rubber film were exposed to ozone and therefore it is not surprising that the proteins were also attacked by ozone as indicated by the presence of primary amines. In the case of wet rubber gel, the major products are ester and ketone or aldehyde compounds, indicating that rearrangement of carbonyl oxide to form ester is favourable. This is similar to ozone water-treated rubber. For dry rubber film, however, recombination of the carbonyl oxide with the aldehyde group to form ozonide is more prominent.

## CONCLUSION

The reaction of ozone water with prevulcanised latex film produces aldehyde, ketone, and ester groups. In the presence of rubber proteins, the carbonyl oxide intermediate reacts with the



*Figure 6 FTIR spectra of natural rubber treated with moist ozone gas (16 000 p p m ) in dry film state  
(a) outer surface of the sample treated for 1 h (b) outer surface of the sample treated for 1 h followed by acetone extraction, and  
(c) outer surface of the sample treated for 1 h followed by boiling in water for 5 min*

amino group of these compounds and this leads to the formation of rubber-bonded proteins on the surface. In addition to these reaction products, ozonides are formed when wet rubber gel is treated with moist ozone gas. However, the reaction does not produce visible cracks on the rubber surface. On the other hand, treatment of strained dry rubber film with moist ozone leads to the formation of visible cracks and produces amines and large amount of ozonides on the rubber surface, indicating that both rubber proteins and rubber double bonds are attacked by the ozone. The ozonides in both cases become hydrolysed when boiled in water. Ozone treatment of natural rubber in wet gel state may be used to introduce polar functional groups onto the rubber surface without changing the tensile properties of the rubber.

#### ACKNOWLEDGEMENTS

The authors would like to thank Ohnit Co., Japan for the use of the Ohnit Ozone Generator, Sumitomo Rubber Co., Japan for supplying DPNR latex, the Director General of Industrial Technology Center of Okayama and Director General of Malaysian Rubber Board for their permission to publish this paper. The first author also wishes to thank Japan Science and Technology Corporation (JST) for the award of a STA (Science and Technology Agency) Fellowship.

*Date of receipt: February 1998*

*Date of acceptance: May 1998*

#### REFERENCES

1. LAYER, R.W. AND LATTIMER, R.P. (1990) Protection of Rubber Against Ozone *Rubb. Chem. Technol.*, **63**, 426–450
2. GILBERT, J.H. (1962) Degradation and Cracking of Elastomers by Ozone *Proc. 4th Rubb. Technol. Conf. London (Messenger, T.H., ed)*, 696–710.
3. YEANG, H.Y., SUNDERASAN, E. AND HAFSAH MOHD GHAZALY (1995) Latex Allergy Studies: Extraction of Natural Rubber Latex Proteins with Reference to Film Thickness, Latex D.R.C. and Protein Migration Behaviour *J. nat. Rubb. Res.*, **10**(1), 46–62.
4. BARNARD, D., CUNEEN, J.I., LINDLEY, P.B., PAYNE, A.R., PORTER, M., SCHALLAMACH, A., SOUTHORN, W.A., SWIFT, P. McL. AND THOMOS, A.G. (1970) Natural Rubber. *Encyclopedia of Polymer Science and Technology* (Mark, H.F. and Gaylord, N.G., eds.), **12**, 227–229 New York Interscience Publishers
5. YOUNG, W.G., McKINNIS, A.C., WEBB, I.D. AND ROBERTS, J.D. (1946) Allylic Rearrangements. XIX Studies of the Ozonization of Allylic Systems. *J. Am. Chem. Soc.*, **68**, 293–296.
6. LOAN, L.D., MURRAY, R.W. AND STORY, P.R. (1968) Ozone Attack and Antioxidant Action in Elastomers. *J. Inst. Rubb. Ind.*, **2**, 73–76.