Photodegradation of Raw Natural Rubber under Controlled Condition

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The photodegradation of various grades of raw rubber is studied using artificial solar energy produced from a 1 kW solar simulator. The rate of chain scission is a function of the purity of the rubber. The presence of chromophores accelerates the chain scission. The rubber can be efficiently degraded under solar source by the incorporation of an effective sensitiser system.

Polymers would degrade after prolonged exposure to sunlight or after irradiation with ultraviolet (UV) radiation. Though only 5% of the energy reaching the surface occupies the UV region from 300 nm to 400 nm it is enough to break a large variety of chemical bonds[1]. The presence of impurities capable of absorbing UV will accelerate the degradation process. Sensitising the polymer by incorporating additive will further enhance the degradation reaction. Nearly all the work so far reported on diene polymers has been technology in character.

Degradation of rubber under solar radiation involves many variables and it is time consuming. The condition chosen for artificial solar radiation will produce data peculiar to that condition, which simulates more closely the environment, found outdoor. The experiment generally attempts to reproduce the sunlight induced degradation process by an artificial light source. A 1 kW solar simulator (Applied Photophysics) was chosen as the emission spectrum *(Figure 1)* closely resembling the solar spectrum for air mass. Therefore, there

are advantages and disadvantages in the use of artificial solar source. However, solar simulation offers a relatively stable and controllable environment for the systematic study of photodegradation of rubber. Solar simulation will not replace natural exposure but a complimentary technique.

EXPERIMENTAL

Materials

The rubber used are commercially available latex grade SMR L, field grade SMR 20, skim rubber (rubber prepared from skim latex by centrifugation), deproteinised NR (DPNR) and synthetic polyisoprene *Natsyn 2200.* Tree laces were collected directly from the rubber tree barks, washed and dried in the oven at 80°C. Reagent grade chemicals were used in all experiments.

Methods

Preparation of sample. The chemical was first incorporated into the rubber on the two-

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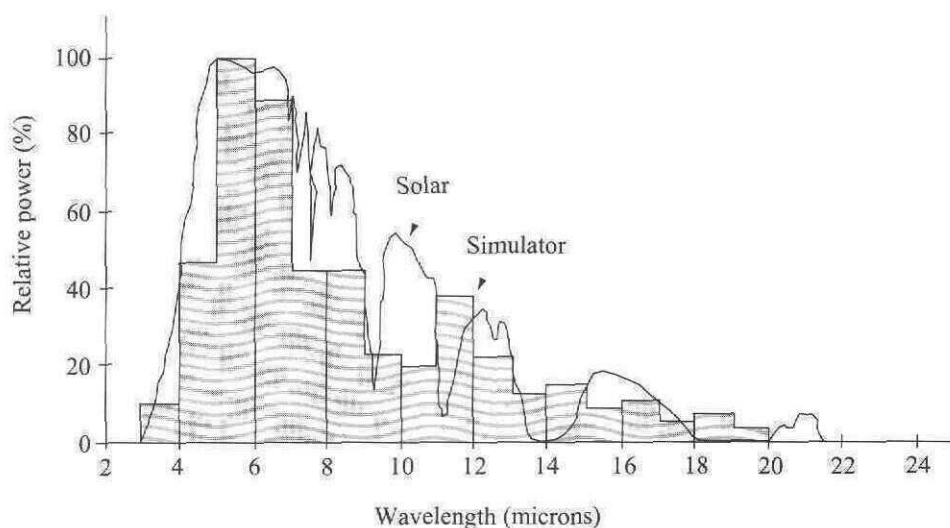[*] Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

Figure 1. Comparison of 1 kW solar simulator spectrum with air mass 2 solar simulator (Reproducible from instruction manual, Applied Photophysics Limited, London)

roll mill. All the addition was done under identical condition with identical number of passes. In the case of raw, unfilled, the rubber was masticated for similar number of passes. Thin sheet of rubber of about 2.5 mm thickness was obtained.

Photodegradation. The sheet rubber was cut into a strip of 1 cm × 60 cm. Six strips of rubber were then mounted onto the surface of a drum which rotates at 1 revolution per minute so as to compensate for spatial fluctuations in radiation. The rubber was then exposed to the solar simulator *(Figure 2)*. The solar simulator was switched on half an hour before the experiment started. The surface of the rubber was intermittently changed every hour. At a determined time of exposure, one of the strips was taken out and kept into a plastic bag purged with nitrogen. To ensure uniformity and the life of the high-pressure 1 kW metal halide discharge lamp, regular measurement

of the beam radiated was taken at regular interval. The measurement was taken by using UVX digital radiometer (UVP Incorporation, USA). *Table 1* shows the average value of the radiations at different wavelength.

TABLE 1. RADIATION INTENSITY OF SOLAR SIMULATOR

Wavelength (nm)	Intensity (μW/cm^2)
254	120 ± 10
310	300 ± 30
365	550 ± 50

Characterisation

Molecular weight. The number average and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$, respectively) were determined using high-

— 1 kW Solar simulator
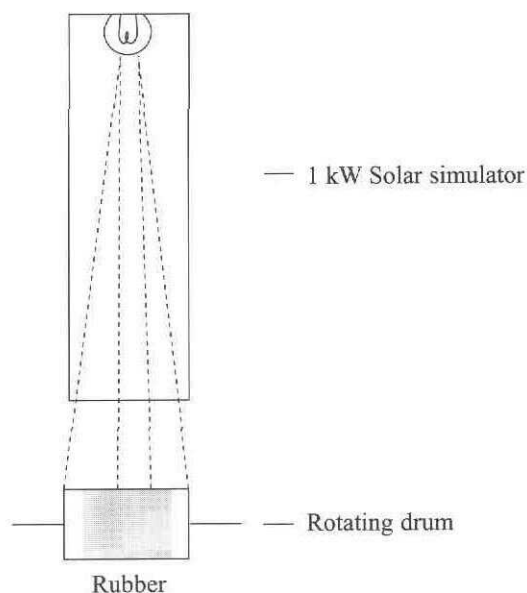
— Rotating drum

Rubber

Figure 2. Arrangement of the experimental set-up.

pressure liquid chromatography (Waters system). The system consisted of Waters 510 pump, column oven and Waters RI 410 refractometer. Spectroscopy grade tetrahydro-furan was used as solvent and Waters Styragel $10^6, 10^6, 10^5$ and 10^4 Å columns were used. The column temperature was set at 40°C and the flow rate of tetrahydrofuran was 0.8 ml/min. Synthetic polyisoprene with unimodal molecular weight distribution ($\overline{M}_w / \overline{M}_n = 1 - 1.2$) supplied from Polymer Laboratories, U.K. were used as the calibration standard.

RESULTS AND DISCUSSION

Unfilled Rubber

The effect of exposure of various raw natural rubber (NR) grades to the solar simulator is illustrated by plotting the average number molecular weight ($\overline{M}_n$) against the exposure time. Generally, the exposure of raw rubber to the light source caused reduction in the molecular weight and the $\overline{M}_n$ decreased with time of exposure (*Figure 3*). The term Q = $[(\overline{M}_{n,o} / \overline{M}_{n,t}) - 1]$ is defined as equal to the average number of rubber bonds scission per original molecule. It measured only the net degradation effect without accounting side reaction such as chain branching and cross-linking occurrence as competitive processes [2]. In all the cases, as observed in *Figure 4*, the rubber degraded at higher rate after six hours of exposure. The upturn observed could indeed be due to a rapid increase in peroxide content after an induction period in which the overall peroxide content is low and relatively constant[1,3]. The observation agrees to Morand[4], which stated that a photophysical process initiated the light degradation and the radical produced after the electronic excitation will react with oxygen to initiate photoxidation. The photoxidation proceeds like thermoxidation at a faster rate and chain scissions are a linear function of the oxygen consumed[5]. Rapid scission was observed for skim and deproteinised rubber (DPNR) and is two-fold compared to SMR L and SMR 20. The differences are due to the presence of impurities, which are ketonic or peroxidic in nature capable of absorbing UV light at wave-length longer than 300 nm and initiating degradation of the polymer matrix[6]. Hydro-peroxide and carbonyl groups are recognised as chromophores, which initiate photodegrada-tion. It is generally accepted that of the two, hydroperoxide plays the more important role, certainly in the early stage of photoxidation. Chromophores are introduced in the rubber either as impurities or chemical residues during processing, or as oxidisation product due to prolonged exposure as in the case of tree laces or even as oxygen-substrate complexes[7]. The degradation can be accelerated
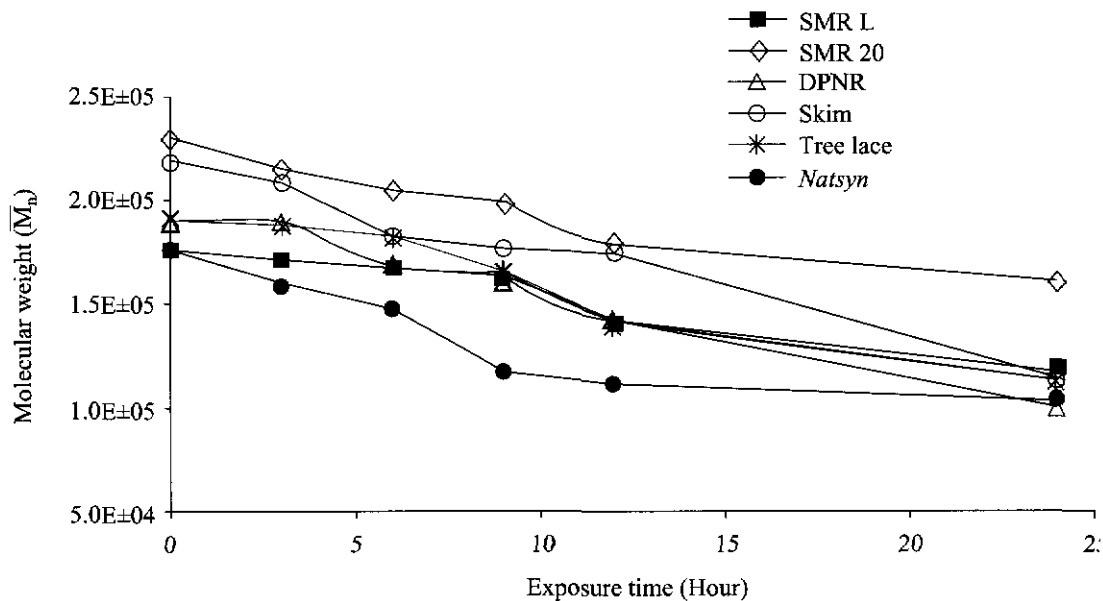
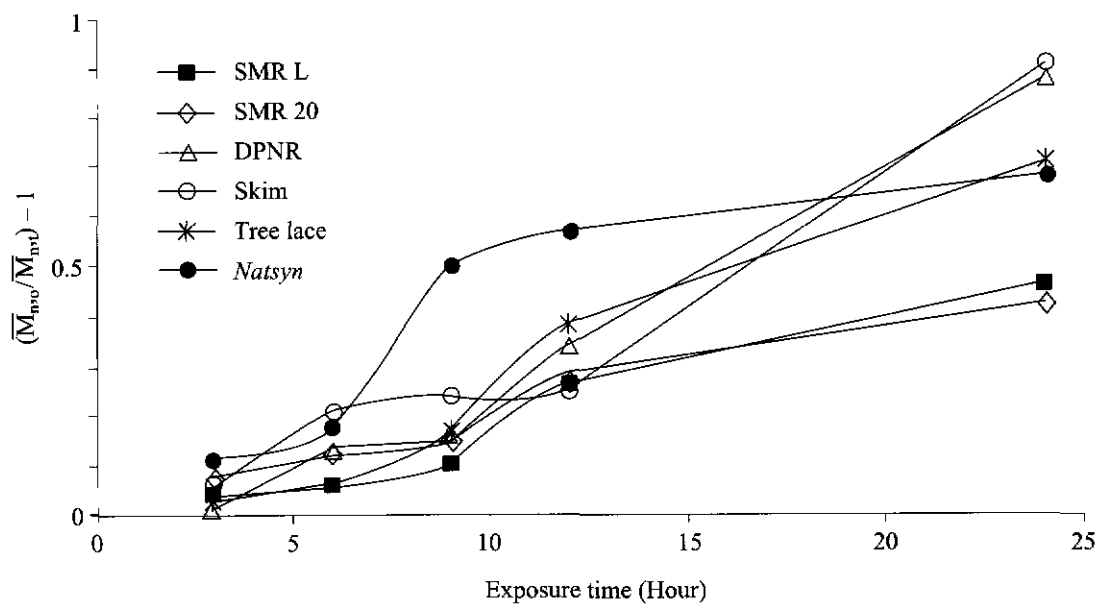*Figure 3. Effect of exposure of unfilled raw rubber on the molecular weight.*

Figure 4. Effect of exposure of unfilled raw rubber to the solar simulator on the chain scission.

or decelerated with impurities or additives[8]. A number of reagents[9] can react with carbonyl groups and inhibit its activity. The presence of such abnormal carbonyl group, lactone and epoxide in the rubber hydrocarbon have been claimed by other investigators[10-14]. Those abnormal products could also be due to the reaction of ozone with the unsaturated double bonds[15]. Diene rubbers are subject to attack by ozone even at low concentration found outdoor. The reaction of oxygen with ultra-violet light also yields ozone. Ozone is usually present in the atmosphere, the concentration ranges from 1 to 10 parts per hundred million under normal condition.

Filled Rubber

The exposure of raw natural rubber to the solar radiation as shown in *Figure 3* caused molecular weight reduction but at a low rate of chain scission. The rate of chain scission can be further improved by the addition of photosensitiser. Sensitised photodegrdation can be achieved either by mixing photoactive additives with the polymer or introduction of photoactive group permanently in polymer chain or synthesing polymers which have photoactive sequences in their main chain. We have done extensive screening and optimising the effect of addition of sensitiser in the NR on its degradation. A mixture of carbonyl sensitiser with metal carbonyl salt and a carboxylic acid has been identified and the degraded rubber produced was found to have low gel content (<5%) in toluene. The exposure of filled rubber with the mixture to the solar simulator enhanced the reduction in molecular weight (*Figure 5*). Similar trend in the reduction was observed as that in the unfilled rubber.
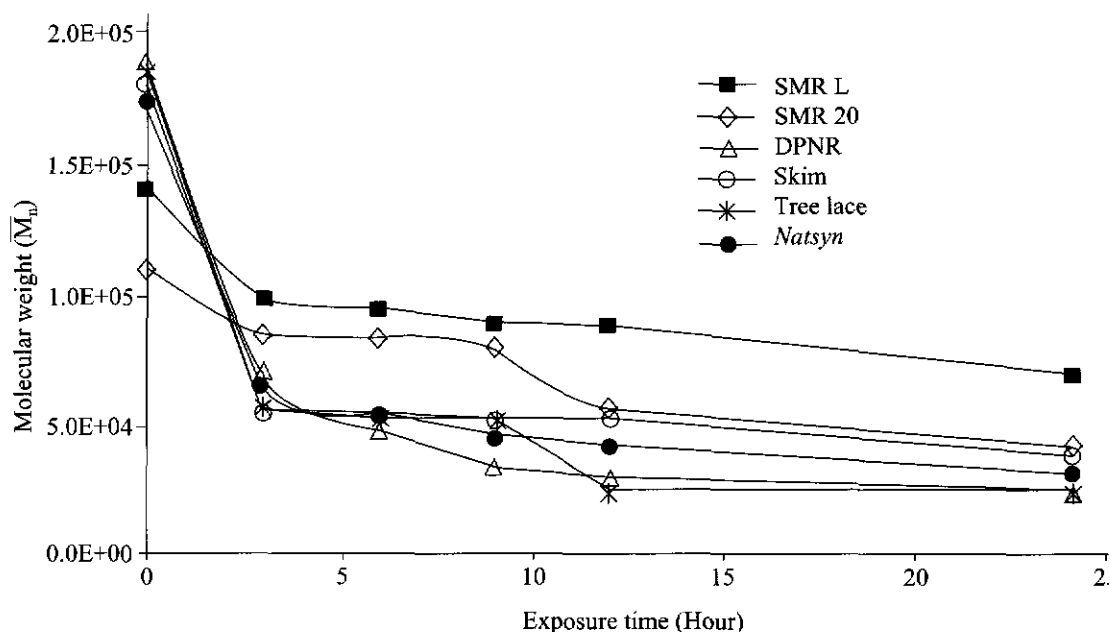

Figure 5. Effect of exposure of filled raw rubber to the solar simulator on the molecular weight.

The initial photophysical stage is further improved by the availability of radicals due to the electronic excitation of the mixtures, which produce synergistic effects. As shown in *Figure 7* and after 24 h of exposure, degraded rubber with $\overline{M}_n$ of about 25 000 are obtained for tree laces and DPNR, whereas the final $\overline{M}_n$ for degraded SMR 20, skim and *Natsyn 2200* are less than 40 000. The differences observed in the chain scission of the filled rubber (*Figure 6*) compared to the unfilled (*Figure 4*) can be attributed to the interaction of the impurities with the mixture which in turn deactivate or enhance the activity of the sentised mixture as photosensitiser. The initial structural constituent of the rubber is a major factor in determining the chain scission as illustrated by the result in *Figure 6*, particularly in the case of the SMR grade. In the processing of SMR, certain chemicals are added and reacted with the abnormal groups.

CONCLUSION

The exposure of raw NR to the artificial solar source causes degradation. The extent of degradation of the rubber is subjected to the purity and the production process. The presence of chromophores accelerates the chain scission. Sensitising the rubber increased the rate of chain scission tremendously. The efficiency of the sensitiser system is dependant on the purity of the starting material. The availability of an efficient sensitiser system will also provide an alternative method of degrading rubber and as a method of producing value-added materials from waste rubber.
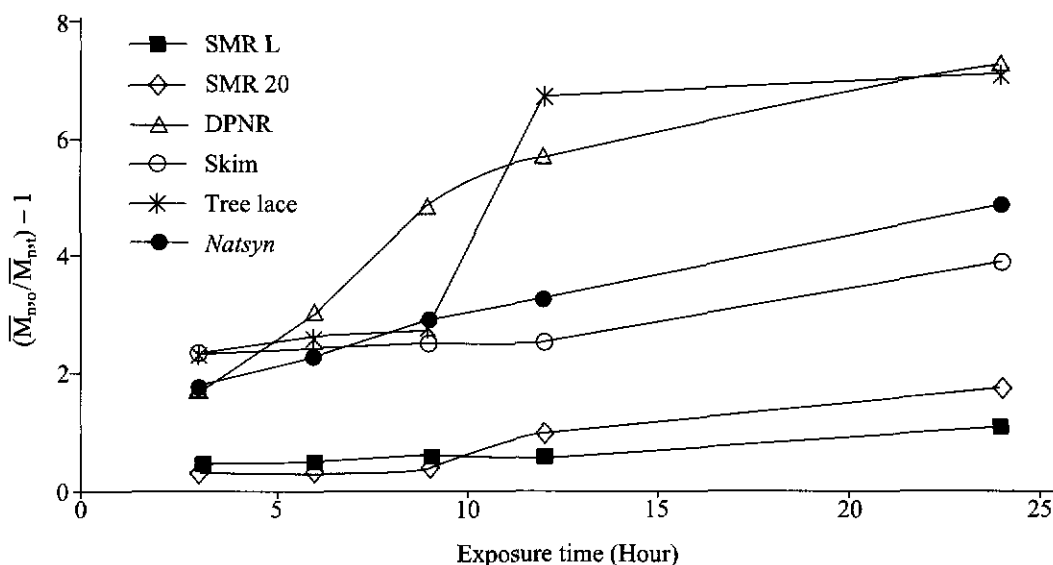
ACKNOWLEDGEMENT

Figure 6. Effect of exposure of filled raw rubber to the solar simulator on the chain scission.
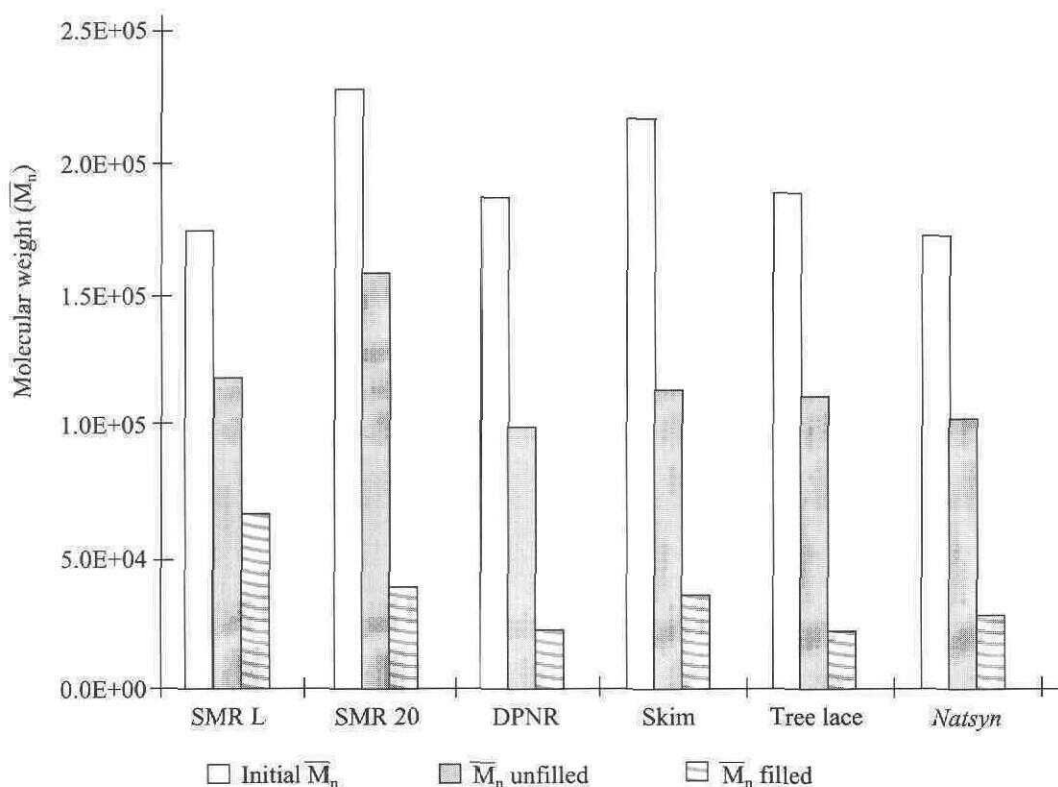
Figure 7. Molecular weight of rubbers after 24 hours exposure to the solar simulator.

REFERENCES

1. CICCHETI, O. (1970) Mechanism of Oxidative Photodegradative and of UV Stabilization of Polyolefins. *Adv. Polymer sci.*, **7**, 70–112.

2. KELLER, R. W., AND H.L. STEPHENS, (1983) Degradative Effects of Guayule Resins on Natural rubber. II. Kinetics studies. *Rubber Chem. Technol.*, **55**, 161–179.

3. ALLEN, N. S. (1986) Recent Advances in the Photoxidation and Stabilisation of Polymers. *Chem. Soc. Rev.*, **15**, 373–404.

4. MORAND, J. L. (1973) Oxidation of Photo-excited Elastomers. *Rubber Chem. Technol.*, **45(3)**, 481–495.

5. Mc KELLER, J. F. AND ALLEN, N. S. (1979) *Photochemistry of Man-made Polymers.* Chp. 2. London: Appl. Sci. Publisher.

6. RABEK, J. F. (1975) Photosensitised Degradation of Polymers. Ultraviolet Light Induced Reactions in Polymers. *ACS Symposium*, **Series 25**, 255–271.

7. BUGORKOVA, V. S., AGEYEVA, T. A. AND GALPERIN, V. M., (1991) Basic trends in the Creation of Photo- and Biodegradable Polymeric Materials. A survey. *Int. Polym. Sc. Technol.*, **18(11)**, T81–T89.

8. SHALABY, S. W. (1979) Radiative Degradation of Synthetic Polymers: Chemical, Physical, Environmental and Technology Considerations. *J. Poly. Sc. Maromol. Rev.*, **14**, 419–457.

9. SEKHAR, B. C. (1960) Abnormal Groups in Rubber and Microgel. *Proc. Rubber Technol. Conf., London*, 460.

10. GREG, E. C. JR. AND MACEY, J. H. (1973) The relationship of Properties of Synthetic Poly (isoprene) and Natural Rubber in the Factory. The Effect of Non-rubber Constituents of Natural Rubber. *Rubber Chem. Technol.*, **46(1)**, 47–69.

11. BURFIELD, D. R. (1974) Epoxy Groups Responsible for Crosslinking in Natural Rubber. *Nature, London*, **249**, 5452–5457.

12. HASMA, H. (1992) Proteins of Natural Rubber Latex Concentrate. *J. nat. Rubb. Res.*, **7(2)**, 102–112.

13. ENG, A. H., TANGPAKDEE, J., KAWAHARA, S. AND TANAKA, Y. (1997) Distribution and Origin of Abnormal Groups in Natural Rubber. *J. nat. Rubb. Res.*, **12(1)**, 11–20.

14. ENG, A. H., ESUKI, S., KAWAHARA, S., AND TANAKA, Y. (1994) Structural Characterisation of Natural Rubber. Role of Ester Groups. *J. Appl. Polym. Sci. Polym. Symp.*, **53**, 5–15.

15. DAVIS, A. AND DAVID SIMS (1984) *Weathering of Polymers*. Chp. 6, London: Applied Science Publisher.