JOURNAL OF MATERIALS SCIENCE 19 (1984) 1510–1516

The effect of cross-linking on fracto-emission from elastomers

J. T. DICKINSON, L. C. JENSEN, A. JAHAN-LATIBARI
Department of Physics, Washington State University, Pullman, Washington 99164-2814, USA

During the fracture of elastomers in vacuum, one frequently observes the emission of particles such as electrons, ions, neutral molecules, and photons, which we call fracto-emission. We report here measurements of electron emission and positive ion emission accompanying and following the fracture of polybutadiene (BR) and a styrene–butadiene copolymer (SBR), where the degree of cross-linking has been altered either by varying the concentration of the cross-linking agent or by exposure of the material to ultraviolet or γ-ray radiation. Our results show that over the range of cross-link densities studied, both electron and positive ion emission increase with increasing cross-link density.

1. Introduction

Crack propagation through an insulating material or at an interface produces regions of high electronic and chemical activity on the freshly created surfaces. This activity causes the emission of particles, i.e. electrons, ions and neutral species, as well as photons, from the surfaces both during and after crack propagation; we call this emission fracto-emission (FE) (photon emission during deformation and/or crack propagation is often called triboluminescence). The work presented in this paper will focus on electron emission (EE) and positive ion emission (PIE) induced by the fracture of elastomers in a vacuum.

Although a considerable portion of our work has concentrated on the fracture of filled elastomers [1–7], where interfacial failure yields extremely high emission rates, we have also investigated a number of unfilled materials. A summary of electron emission (EE) and positive ion emission (PIE) data, as presented in Table I, shows that these elastomers produce EE and PIE with a wide range of intensities and durations (decay times) of the emission following fracture. None of the unfilled materials show intensities that match the filled materials. The intense emission accompanying interfacial failure has been attributed [8] to the strong separation of charge that occurs due to contact charging between dissimilar materials.

In unfilled systems we suspect that the same mechanism could be responsible, but with weaker degrees of charge separation and reduced discharge, and thus less EE and PIE. However, the role of mechanical deformation and the scission of bonds in an unfilled polymer which would produce this charge separation is not clearly understood.

The conceptual model we have presented [8] for the fracture-induced particle emission in cases where strong charge separation occurs can be summarized as follows:

1. the fracture event yields charge separation (usually patchy) producing an electric field, E, in the crack;
2. desorption of volatiles and/or fracture products raises the pressure, P, in the crack tip;
3. a gas discharge (dictated by P, E, and a distance d which characterizes the crack width) occurs, producing radio wave emission (RE) and photon emission (phE). Electron and ion bombardment of the crack walls occurs during this discharge;
4. bombardment of the fracture surfaces creates exo-emission, usually understood in inorganic crystals in terms of electron–hole production

0022–2461/84 $03.00 + .12

TABLE I Survey of elastomers investigated for EE and PIE

Material	Approximate decay times of fracto-emission	Ions detected/ cm crack wall
Electrons		
Neoprene	< 1 sec	10^2
Vitron	< 1 sec	10^3
Buna N	< 1 sec	10^2
Natural rubber	< 1 sec	10^3
Natural rubber (abraded)	Minutes	10^7
Silicone rubber	< 1 sec, minutes	10^5
Solithane	< 0.2 sec	10^4
Vinyl rubber (filled)	< 1 sec, minutes	10^4
Polybutadiene	0.04 sec, minutes	10^3
Polybutadiene (filled)	< 1 sec, minutes	10^7
Nylon-66	< 1 sec	10^4
Isoprene	< 1 sec	10^6
Amber rubber	< 1 sec	10^4
BAMO	< 1 sec	10^4
Positive ions		
Buna N	< 1 sec, minutes	10^3
Natural rubber	< 1 sec	10^4
Natural rubber (abraded)	Minutes	10^7
Silicone rubber	< 1 sec, minutes	10^3
Solithane	< 0.1 sec	10^6
Vinal rubber (filled)	< 1 sec, minutes	10^5
Polybutadiene	< 0.4 sec, minutes	10^5
Polybutadiene (filled)	< 0.2 sec, minutes	10^6
SBR – filled	< 1 sec	10^6

raising electrons into traps near the conduction band, which then undergo thermally stimulated migration until recombination with a hole occurs. This recombination can yield an emitted electron (thermally stimulated electron emission (TSEE) [9, 10]), say by an Auger process [10], or a photon (thermally stimulated luminescence (TSL) [9]);

5. a portion of the electron emission strikes adjacent patches of positive charge yielding PIE via an electron stimulated desorption (ESD) mechanism [12]. Some of these positive ions are neutralized as they leave the surface, yielding the excited neutral component of FE that we have observed.

For crystalline materials that are known to be piezoelectric, e.g. SiO_2, PZT, and sucrose, we were not surprized to detect the simultaneous emission of electrons (EE), photons (phE), and radiowaves (RE) during fracture – clear evidence for the occurrence of a gaseous discharge in the crack tip during fracture. We were also able to induce the EE by prebombardment with energetic electrons in unfilled, unfractured BR. This and other evidence supports the above model for materials exhibiting strong charge separation during fracture.

Unfilled elastomers could produce separated charges, most likely patchy, during fracture and yield the same effects at lower intensities due to weaker discharges occurring in the crack tip. For patches of both signs and of small dimensions, postfracture probing of surface charge may yield nearly neutral results, making the charge separation difficult to detect. Nonetheless, we have recently detected both RE and phE during fracture of unfilled polybutadiene, supporting the idea that a discharge indeed occurs.

Presumably, the degree of charge separation should indeed be sensitive to the mechanical properties of the elastomers, namely that more rigid networks of cross-links would result in higher local stresses prior to fracture (inducing more charge separation) as well as the breaking of a larger number of principal bonds during fracture which may also contribute to charge separation. Thus in a more highly cross-linked material we might expect greater surface charging which in turn would cause a more intense discharge and result in more intense emission.

In this paper, we explore for the first time the possible influence of cross-link density on EE and PIE intensities during the following fracture of elastomers, where variations in cross-link densities were made by changing the concentrations of the cross-linking agent and by exposure of the elastomers to ultraviolet and γ-radiation.

2. Experimental procedure

The materials used in this study were polybutadiene (BR) and a copolymer of styrene–butadiene (SBR). Most of the samples used in this experiment were provided by The University of Akron, Institute of Polymer Science. The BR samples consisted of Diene 35 NFA (Firestone Tire and Rubber Co) mixed with dicumyl peroxide from 0 to 0.075 wt %.

The sample designations and the corresponding peroxide concentrations are as follows: BR-0, 0.000%; BR-1, 0.025%; BR-2, 0.050%; BR-3, 0.075%; SBR-1, 0.1%; SBR-2, 0.2%.

The SBR was made in the ratio of 25/75

styrene–butadiene (SBR 1502 Firestone Tire and Rubber Co) with 0.1% dicumyl peroxide resulting in a very weak cross-linking and with 0.2% dicumyl peroxide showing increased cross-linking. Cross-linking was carried out by heating each mixture for 2 h at 150° C. For BR-0, the Diene 35 NFA was simply pressed and heated at 100° C for 1 min, which produced a very weakly cross-linked material.

As an additional means of varying the cross-link density, BR and SBR samples were exposed to ultraviolet and γ-radiation. The ultraviolet source was a laboratory mercury lamp rich in 250 nm light. Although ultraviolet intensities were not measured, all exposures were done at constant distance (20 cm) for 24 h. The γ-radiation was from a calibrated 3000 c ^{60}Co source and exposure were again for 24 h. The cross-link density was determined by swelling measurements in benzene using a technique described by Mullins and Mason [13].

The experiments were performed in vacuum at a pressure of 1×10^{-5} Pa. The vacuum system was equipped with a stress–strain device. The samples were supported in the pulling (tension) mechanism in clamps with an initial separation of 6 mm. The cross-section of these samples was 2 mm x 4.5 mm. The top edge of each sample was notched in the centre so that the crack propagated in the vicinity of the detector. Samples were all elongated at a rate of 10% sec^{-1}. The detectors used for charged particles were Channeltron Electron Multipliers (CEM) which produce a fast (10 nsec) pulse per incident particle with approximately 90% absolute detection efficiency for electrons and nearly 100% efficiency for positive ions with a gain of 10^6 to 10^8 electrons/incident particle. The detector was positioned about 2 cm away from the sample. The front of the CEM was biased with +300 or −2500 V to attract electrons or positive ions, respectively. Background noise counts ranged from 1 to 10 count sec^{-1}. Standard nuclear physics data acquisition techniques, using a micro-computer based multichannel analyser, were employed to acquire and store the emission data.

3. Results

The results of EE and PIE measurements from the fracture of BR with various concentrations of dicumyl peroxide are shown plotted on a log scale in Figs. 1 and 2. A comparison of both EE and PIE from different samples indicates the influence of the cross-linking agent and therefore cross-link

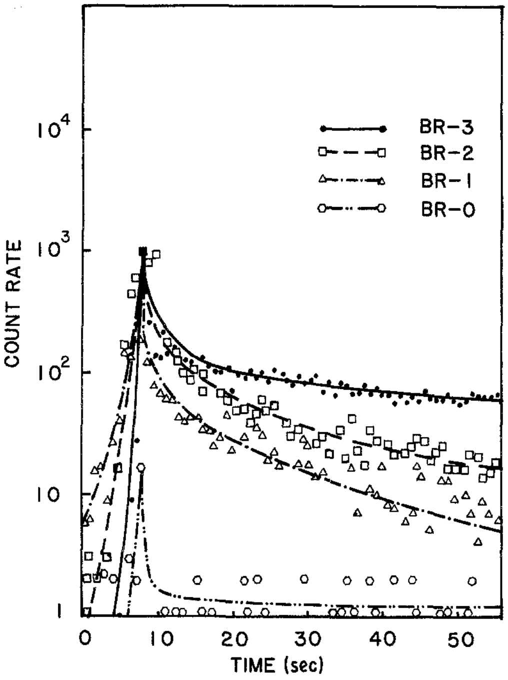

Figure 1 Electron emission plotted against time for polybutadiene cross-linked with varying concentrations of dicumyl peroxide.

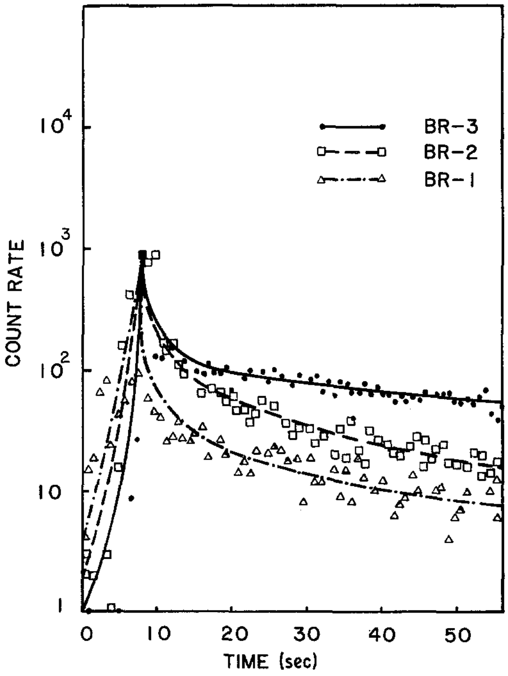

Figure 2 Positive ion emission plotted against time for polybutadiene cross-linked with varying concentrations of dicumyl peroxide.

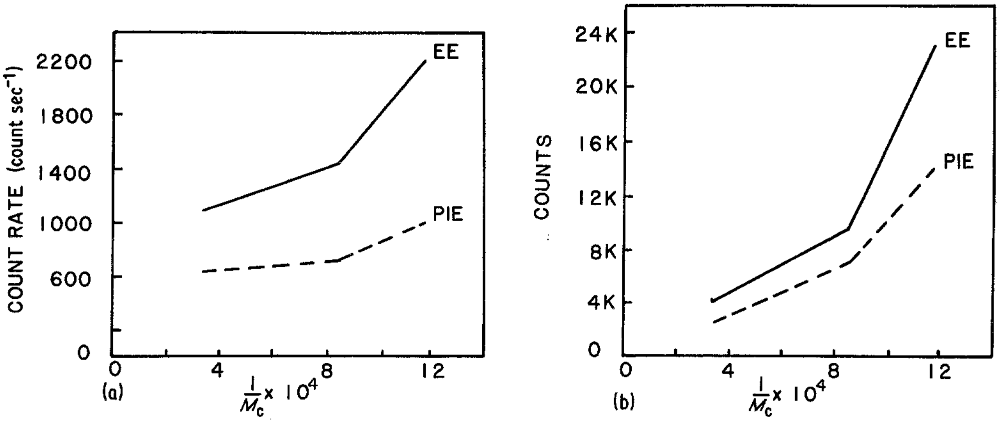

Figure 3 EE and PIE plotted against $1/M_c$, where M_c is the number average molecular weight between cross-links, and where $1/M_c$ is proportional to cross-link density.

density (CLD) on the emission. Both EE and PIE increase with the addition of more dicumyl peroxide. The data for EE measurements from the 0% dicumyl peroxide BR (BR-0) are also included in Fig. 1. We could not see any PIE from BR-0 samples, and the EE was relatively low. Variations in emission from sample to sample of BR-1 were quite high, about 50%. More consistency was observed for samples of BR-2 and BR-3, with variatons of about 20%.

Fig. 3 shows the dependence of EE and PIE at fracture, i.e. the peak count rate, and the total emission (for euqal time intervals of 400 sec) on $1/M_c$ where M_c is the number average molecular weight between cross-links of BR. The CLD is proportional to $1/M_c$. It is clear from these curves that for this substance, increasing CLD yields noticeably more EE and PIE at fracture, which is particularly evident in the total emission curves. It should be noted that in these samples the CLD was not varied over a very large range.

The change in fracture behaviour with increased CLD for notched samples strained at constant strain rate is evident in the observed rise in EE or PIE, which from previous measurements indicates the rate of crack growth and time required to fracture [2]. The curves shown in Figs. 4a and b have been shifted and normalized so that the peak emission rates coincide for BR-1 and BR-3 for four different samples. One can easily see the effect of increased CLD on the fracture; BR-3 is fracturing considerably faster. Qualitatively, this can be understood from the fact that as stress is applied to a rubber sample, the shorter chains reach a breaking point before the longer chains. At higher CLD, network chains become shorter and less extendible and hence prone to rupture before appreciable reorientation of the network

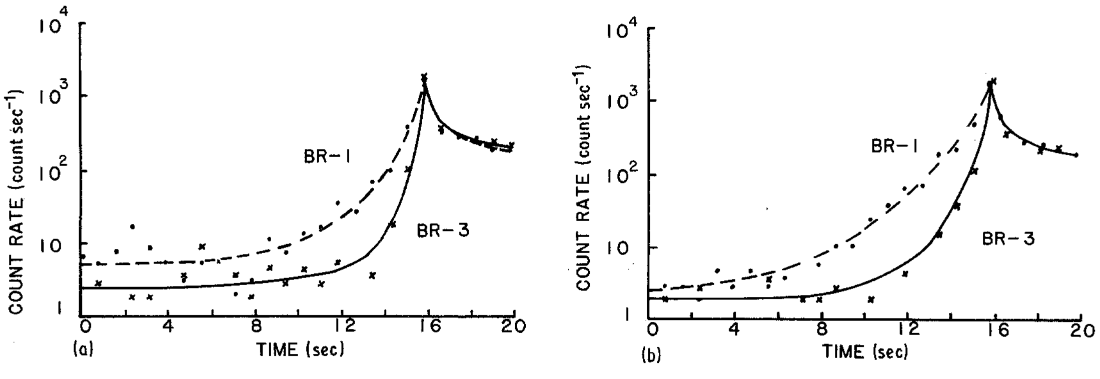

Figure 4 Plots of (a) EE against time, and (b) PIE against time for fracture of samples of BR with different cross-link densities, during fracture.

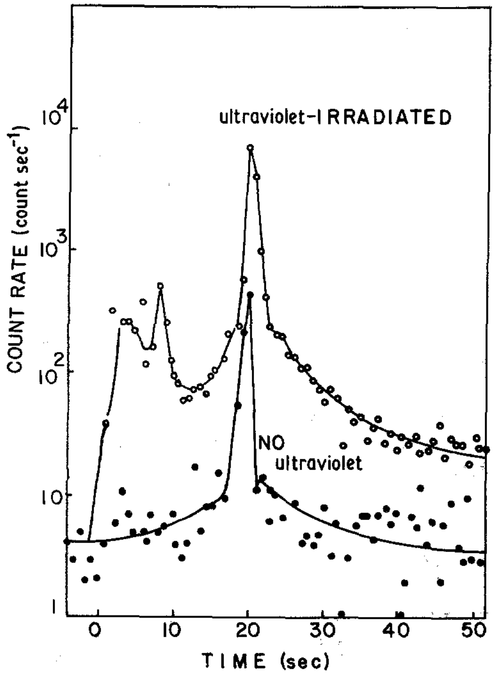

Figure 5 EE for BR-2 with and without exposure to γ-radiation.

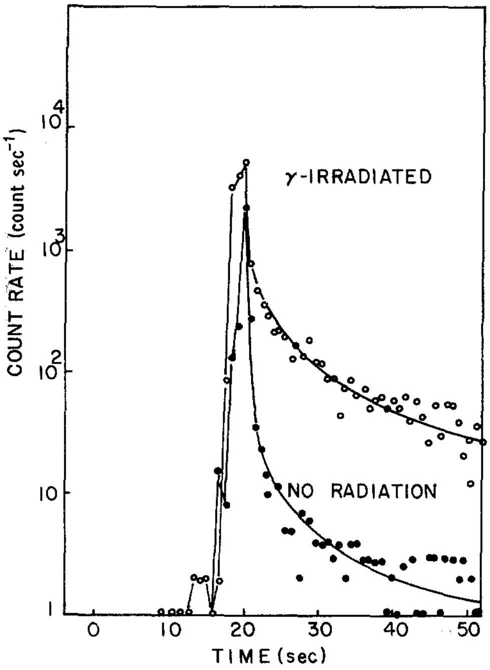

Figure 6 EE for SBR-1 with and without exposure to γ-radiation.

as a whole occurs. On the other hand, at a low CLD it has been proposed that plastic flow of the chains is high. Therefore at low CLD the plastic deformation high and thus it takes longer for the sample to break, while at high CLD the sample fractures in a more brittle manner.

The effect of irradiation of elastomers on EE alone is shown in Figs. 5 to 8 for BR-2 and SBR-1, which were strained at the slower rate of 5% sec^{-1} (the changes in intensity and shape for BR-2 with and without ultraviolet irradiation were relatively small so they are not shown). Note that the irradiated materials have higher peak intensities and more emission after fracture, similar to the changes induced by variation in dicumyl peroxide content. Table II summarizes the measured emission totals and $1/M_c$ values for these materials

TABLE II Average total EE for samples of BR and SBR with and without exposure to radiation

Material	Average total EE	$1/M_c$
SBR-1	23000	0.00024
SBR-1 (ultraviolet-irradiated)	27000	0.00029
SBR-1 (γ-irradiated)	38000	0.00110
BR-2	35000	0.00100
BR-2 (ultraviolet-irradiated)	53000	0.00160
BR-2 (γ-irradiated)	84000	0.00500

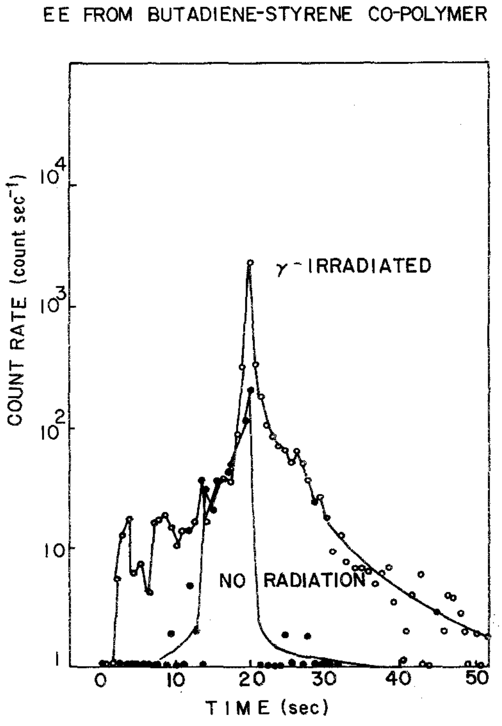

Figure 7 EE for SBR-1 with and without exposure to ultraviolet radiation.

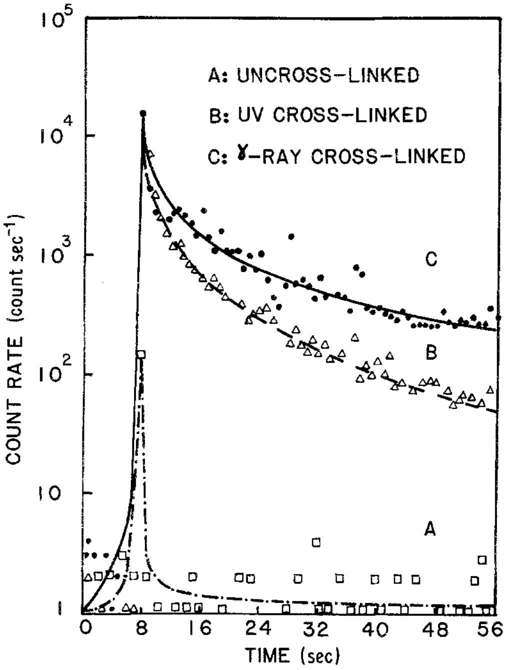

Figure 8 EE for BR-0 with and without exposure to ultraviolet and γ-radiation.

before and after irradiation. In these cases, the irradiated material shows the evidence of increased brittleness by yielding EE at earlier times, i.e. the crack started moving at a lower strain (see Figs. 5 to 7).

The most dramatic change in EE with irradiation is for the BR-0, which is shown in Fig. 8, yielding an increase in emission of up to 100 times. The cross-link densities of the irradiated BR-0 were not measured, but the exposed samples were considerably stronger, indicating an increased number of linkages over the weakly cross-linked BR-0.

4. Discussion

The results we have presented here clearly indicate that increasing CLD produces changes in the intensities and time dependence of the EE and PIE accompanying fracture of these elastomers.

The time-dependence effects observed are due to the influence of cross-linking on the time dependence of fracture at constant strain rates, namely the more brittle nature of crack motion with increasing CLD.

An explanation of the changes in intensity with CLD, which can be quite dramatic as shown in BR-0, demand a detailed understanding of the FE mechanisms in unfilled elastomers. We have implied in Section 1 that localized charge separation occurring during fracture may be playing a crucial role even in "homogeneous" polymers. In fact we have recently detected RE and phE during fracture of BR-2, indicating that a discharge is occurring. We suggest that this, in turn, leads to or at least enhances EE and PIE because of the bombardment of the fracture surfaces by charged particles created in the discharge. Why BR should exhibit the charge separation necessary to yield breakdown is not clear. A piezoelectric effect is one likely candidate for the initial cause of charge separation. Wada [14] states that most polymers can exhibit piezoelectricity due to the presence of certain impurities or embedded charges in the bulk material. In addition, the fracture process itself, i.e. the breaking of bounds, may lead to charge separation due to some asymmetry in the electron clouds associated with the molecules undergoing scission, i.e. a non-adiabatic process. At this point, however, we cannot really distinguish between these possible causes nor provide details of the charge separation process.

5. Conclusions

The relationship between CLD and fracto-emission intensity has been examined for unfilled BR and SBR. A clear increase in intensity with increasing CLD was observed. Previous results on systems exhibiting strong charge separation (including BR filled with glass beads) have indicated that particle bombardment during fracture is responsible for the resulting EE and PIE. The same mechanism may be involved in unfilled materials. This suggests that, on a local scale at least, charge separation is occurring in "homogeneous" elastomers. Although the cause of such charge separation in BR and SBR is not at this time fully understood, we have demonstrated that FE is sensitive to the microstructure and fracture-dependent properties of the material.

Acknowledgements

We wish to thank Dr A. N. Gent, University of Akron Institute of Polymer Science, for providing us with the samples of BR and SBR. We also thank E. E. Donaldson for helpful discussions. This work was supported by the Office of Naval Research, contract N0014-80-C-0213, and by a grant from the M. J. Murdock Charitable Trust.

References

1. J. T. DICKINSON, E. E. DONALDSON and M. K. PARK, *J. Mater. Sci.* **16** (1981) 2897.

2. J. T. DICKINSON and L. C. JENSEN, *J. Polymer Sci. Polymer Phys. Ed.* **20** (1982) 1925.
3. J. T. DICKINSON, M. K. PARK, E. E. DONALDSON and L. C. JENSEN, *J. Vac. Sci. Technol.* **20** (1982) 436.
4. J. T. DICKINSON, L. C. JENSEN and M. K. PARK, *Appl. Phys. Lett.* **41** (1982) 443.
5. *Idem, ibid.* **41** (1982) 827.
6. J. T. DICKINSON, in "Adhesive Chemistry – Developments and Trends", edited by L. H. Lee (Plenum, New York) to be published.
7. J. T. DICKINSON, L. C. JENSEN and A. JAHAN-LATIBARI, *J. Rubber Chem. Technol.* **56** (1983) 927.
8. *Idem*, *J. Vac. Sci. Technol.* to be published.
9. R. CHEN and Y. KIRSH, "Analysis of Thermally Stimulated Processes" (Pergamon Press, New York, 1981) pp. 48–52.
10. J. A. RAMSEY, Exo-emission, in "Progress in Surface and Membrane Science", Vol. 11 (Academic Press, New York, 1976) pp. 117–80.
11. H. D. HAGSTRUM, in "Inelastic Ion-Surface Collisions", edited by N. H. Tolk, J. C. Tully, W. Heil and C. W. White (academic Press, New York, 1977).
12. M. L. KNOTEK, Proceeding of the International Conference on X-Ray and Atomic Inner-Shell Physics "X-'82", *AIP Conf. Proc.* **94**, (1982) 772.
13. L. MULLINS and A. G. MASON, "The Chemistry and Physics of Rubber-like Substances", edited by L. Bateman (Wiley, New York, 1963) pp. 144–53.
14. Y. WADA, "Electronic Properties of Polymers", edited by J. Mort and G. Pfister (Wiley, New York, 1982) pp. 109–60.

Received 29 July
and accepted 12 September 1983