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Electron beam damage of some chlorine containing polymers and PVC blends

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The electron beam damage of PVC, PVDC, chlorinated PE, chlorosulphonated PE (Hypalon) and chloroendic acid polyester has been studied by chlorine loss and mass loss measurements. The mass loss decay curves have been recalculated for true mass loss and correlated with the X-ray measurements of chlorine loss. It is shown that the major mechanism of degradation in these polymers is dehydrochlorination. The rate of dehydrochlorination is dependent on the chemical structure of the polymer, and in particular on the availability of hydrogen for HCl formation. However, in case of chloroendic acid polyester, more complicated volatile chlorinated compounds are also formed. The dehydrochlorination rate and mass loss of miscible PVC blends, namely PVC with organotin stabilizer, PMMA, PCL and SAN have been studied. The rate of chlorine loss from PVC was found to be unchanged for all blends except for PMMA and PCL, where it slightly increased due to the chemical reaction between the molecular fragments of both polymers. The differences between the thermal degradation and electron beam damage are also discussed.

1. Introduction

An understanding of the electron beam damage behaviour of polymers in the electron microscope is primarily important for imaging and analysis. There have been several attempts made to minimize the effect of electron beam irradiation by cooling the specimen to liquid helium temperatures [1], or by using chemical fixation [2]. The former is, however, experimentally very difficult and expensive and for synthetic polymers it provides only marginal improvement. The latter can be used only for polymers containing isolated double bonds. It has been shown previously [3, 4] that the isolated double bonds can be formed by partial irradiation, thus providing a very useful technique for enhancement and preservation of contrast in amorphous polymers. However, the only practical way to obtain the desired information from crystalline polymers is, in most cases, the elimination of any excessive irradiation of the specimen and the most efficient utilization of electrons.

The second, and perhaps the most important aspect of electron beam damage studies is that it can provide more information on the chemical structure of the polymer. Each polymer degrades in a characteristic way, which can be measured, for example, by loss of elements, using an X-ray signal [5] or EELS [6] and by mass loss, using the transmitted beam intensity [7]. The general behaviour of synthetic polymers during high energy irradiation has been outlined some time ago [8], but detailed mechanisms of degradation due to electron beam irradiation have been studied for very few polymers. Naturally, more emphasis has been placed on thermal and UV degradation, and only some recent reviews [9, 10] throw more light on the general problem.

The degradation process starts by a localized transfer of energy from a passing electron to the electron structure of an atom in the polymer chain, thus creating an excited state. This excitation can be rapidly quenched by a primary bond scission. The probability of this scission depends on the number of possible routes for the energy dissipation and, therefore, on the chemical structure of the polymer. For example, Partridge [11] has observed that the ratio of C–H to C–C bond scissions is about 14 and he has concluded that a considerably higher transfer of the excitation energy is possible along the C–C bonds in the polymer backbone than from the C–H bond to the main polymer chain. With polar side-groups this ratio can be different, but it is not clear how much and also which factors are the most important. The role of free radicals during irradiation at room temperature is also not clear as their activity and mobility is much lower than at elevated temperatures during thermal degradation. It can, therefore, be expected, that the free radical mechanisms can only be applied to the electron beam damage in the sense of localized chemical changes. It follows that the loss of mass or elements from the irradiated specimen is critically dependent on a given initial chemical structure.

The intention of this work is to compare the electron beam degradation of chlorine containing polymers in which the chlorine atoms have a different

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TABLE I

Polymer	Trade name	Supplier	Weight (% Cl)
PVC	Pevikon S 656	Kema Nobel	57
PVDC	Saran 925	Dow Chem.	70
Cl-PE	CPE 4213	Dow Chem.	42
Cl-S-PE	Hypalon 20	DuPont	30
chloroendic-acid polyester		ASEA-Plast	20
PMMA	Diakon MO 900	ICI	0
PCL	PCL 700	Union Carbide	0
SAN	Luran 368	BASF	0

chemical environment. The advantage of using chlorine is that it is the most common heavier element in polymers and X-ray energy dispersive analysis can, therefore, be utilized to a required degree of reliability. The data from mass and elemental loss measurements on different polymers are compared and an attempt is made to understand the structural differences for high and low electron beam sensitivity.

2. Experimental procedure

2.1. Specimen preparation

Commercial grade polymers have been used as received, i.e. without purification or additives. They are listed in Table I, together with the manufacturer and the chlorine content. Specimens 100 to 200 nm thick were cut from the polymers at room temperature using an ultramicrotome (LKB Ultratome V). Hypalon specimens were prepared by solvent casting onto a water surface. Some PVC and PVDC specimens were also solvent cast for comparison of these two techniques. All polymer blends were processed by using a Brabender Plasticorder. The specimens were mounted on copper or nylon grids and coated on one side with 5 to 20 nm of carbon, in order to reduce charging and shrinkage of the specimen during irradiation in the electron microscope.

2.2. Measurement of chlorine loss and mass loss

A Jeol 200 B electron microscope, operated at 200 keV, was used for most of this work. The chlorine loss was measured using a Kevex 10 mm^2 Si–Li detector and Kevex 7000 μX multichannel analyser. The number of Cl–K line counts, accumulated in a 150 eV window, was digitally recorded every second and plotted after the experiment on a chart recorder as gross count rates against time. The effect of the background on the residual chlorine count after a long exposure (1000 C m^{-2} or more) was evaluated from a spectrum and recorded after the experiment.

The mass loss was measured by monitoring the change in the scattering power of the specimen with irradiation time. A small objective aperture (20 μm) was used to obtain maximum contrast. Unfortunately, the back scattering from the aperture and the resulting increased background level made a simultaneous recording of the X-ray signal difficult. Thus independent experiments for the elemental loss and for the mass loss had to be carried out. The electrons, scattered within the aperture, were collected by a small diameter Faraday cage situated above the fluorescent screen. Low magnification was used (projective lens switched off) in order to collect all the electrons within the Faraday cage. The electron current from the cage was monitored by Keithley 602 electrometer, connected to a chart recorder.

2.3. Correction of the data

The scattering power of a specimen changes with irradiation, especially when the proportion of light and heavy elements is altered by loss of some elements. For this reason a correction factor must be applied to the measured data in order to obtain the true mass loss or elemental loss.

The mass loss is measured by changes in the intensity of the primary beam I_0, which can be described [12] by Beer's law as

$$I = I_0 \, e^{-x/x_t} \tag{1}$$

where x is the mass thickness of the specimen, $x = \varrho t$, ϱ being the density and t the specimen thickness. The constant x_t is dependent on the atomic weight A and the total scattering cross-section σ

$$x_t = A/N_A\sigma \tag{2}$$

where N_A is Avogadro's number. After normalization to the initial parameters of the specimen (index 1), the relative change in mass thickness ϱt or in mass m (as the irradiated area remains constant) will be

$$\varrho t/\varrho_1 t_1 = m/m_1 = [\ln (I/I_0)/\ln (I_1/I_0)](\sigma_1 A/\sigma A_1) \tag{3}$$

This indicates that the measured intensities must be multiplied by a factor which takes into account the changes of average atomic weight and the scattering cross-section.

It has been shown by Reimer and Gilde [13] that for thin specimens (single scattering) the scattering cross-section σ is related to the atomic number Z

$$\sigma = CZ^a \tag{4}$$

where C is a constant. The exponent a is dependent on the contrast conditions (objective aperture and accelerating voltage) and also on the type of scattering mechanism.

The correction factor, f, for the mass loss measurements can therefore be calculated as

$$f = (Z_1/Z)^a (A/A_1) \tag{5}$$

The value of this exponent is between 1 and 3, but the best fit to the measured data was obtained for the exponent between 1.2 and 1.3, and the value of 1.25 has, therefore, been used. It must be noted, that this correction is very small (about 5% maximum) and can in most cases be omitted.

For specimens coated with a carbon layer, the change in intensity must be taken into account. Equation 3 has to be modified as follows

$$m/m_1 = [\ln (I/I_0)/\ln (I_1/I_0)] \times f(1 + m_C/m_1) - m_C/m_1 \tag{6}$$

where the index C refers to carbon. When the mass thickness of the coating layer and/or of the specimen

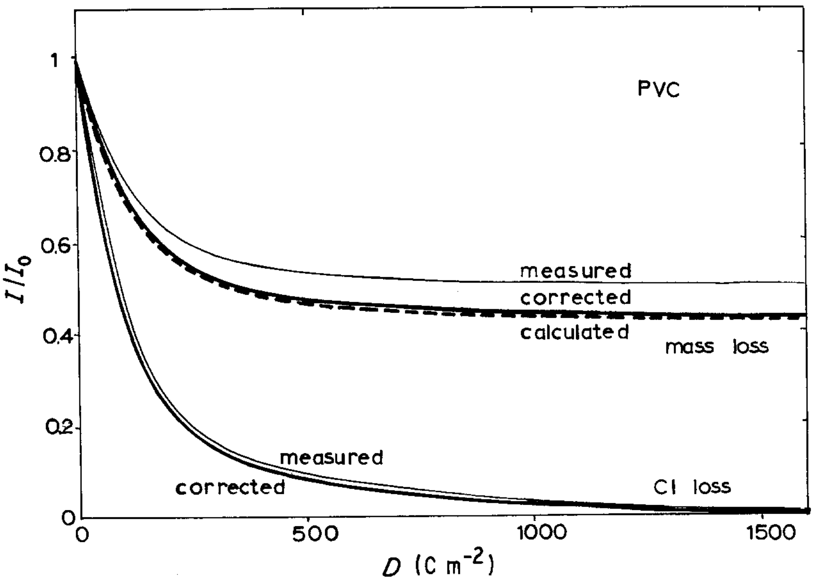

Figure 1 PVC chlorine loss and mass loss with irradiation. The measured data are corrected for changes in average atomic mass and compared with mass loss calculated from chlorine loss.

is not known it must be measured, for example by measuring the intensity I_C, transmitted through a carbon layer of the same thickness as the coating layer on the specimen. The relative mass thickness can then be calculated

$$m_C/m_l = [\ln (I_c/I_0)/\ln (I_l/I_0)](\sigma_l A_c/\sigma_c A_l) \qquad (7)$$

This correction is large for relatively thick carbon coating layers and must not be neglected.

A similar equation to Equation 3 can be derived for the X-ray measurement of changes in concentration of a particular element. The number of X-ray K-line counts n_K from an element i is related to its concentration c_i [12] by

$$n_K = (I_0/e)c_i(N_A/A)\sigma_K \varrho B \qquad (8)$$

where e is the charge of an electron and B is a constant for a particular element and geometry of the experiment, including collection angle and detector efficiency. The relative change in concentration can thus be written as

$$c_i/c_{i1} = (n_K/n_{K1})(\sigma_{K1} A \varrho_1/\sigma_K A_1 \varrho) \qquad (9)$$

It follows from Equations 3 and 9 that both the mass loss and the X-ray data must be multiplied by a correction factor, to take into account the chemical changes of the material during irradiation. Unfortunately it is very difficult to evaluate these factors accurately as the changes in density and scattering cross-section of organic molecules cannot be calculated with any reasonable accuracy. It might however be useful to estimate, at least approximately, the significance of this correction. The changes in density of irradiated PVC were previously evaluated [5, 14] by measuring the shrinkage and mass loss of isolated particles. It was concluded that the density remains constant to a good approximation.

The X-ray data are affected by the decrease of stopping power and fluorescence yield and by the increase of chlorine signal absorption with progressive loss of HCl. This can be verified by using a quantitative analysis. A computer program (Link RTS-2/FLS) was used on PVC specimens coated with a thin layer of lead (Pb-L line reference peak) [15] and the results confirmed that the relative change of X-ray counts is very similar to the relative change in concentration. Further verification has been obtained from FTIR spectroscopy (are under the C–Cl stretching peaks) [16], which again showed only a small deviation from the X-ray measurements.

A sensitive method for checking that the corrections are within the experimental error is to calculate the total mass loss from the known elemental loss as follows

$$R = m/m_l = (M_{WA} + M_{WB}R_B)/(M_{WA} + M_{WB}) \qquad (10)$$

where R is the total mass fraction at a given exposure, R_B is the fraction of residue of volatiles, M_{WA} molecular weight of non-volatiles (of a monomer unit) and M_{WB} molecular weight of volatiles. For PVC and other chlorinated polymers the volatiles are known to be HCl and the residue R_B can be calculated from chlorine loss X-ray decay curves. The corrections are shown in Fig. 1 for PVC as an example.

3. Results and discussion

3.1. Chlorinated polymers

The chlorine decay curves of PVC and PVDC have been discussed previously [4, 5, 14]. The higher residue of chlorine in PVDC has been interpreted by a higher probability of chlorine atoms being trapped on polyene structures, resulting in a more difficult dehydrochlorination. The different chemical environment will thus influence the degradation mechanism and it would be interesting to compare the dehyrochlorination and the mass loss of several different chlorinated polymers. Fig. 2 shows the chlorine decay curves of five different polymers and Fig. 3 the corresponding mass loss curves. There are substantial differences between the polymers and it would be interesting to find out to which extent the chlorine and mass losses are related to the chemical structure.

The structure of chlorinated polyethylene was investigated by Keller and Mugge, using ^{1}H and ^{13}C NMR [17]. According to their results the Cl-PE should be regarded as a copolymer of PVC and PE. In addition no vinylidene groups were found by NMR for

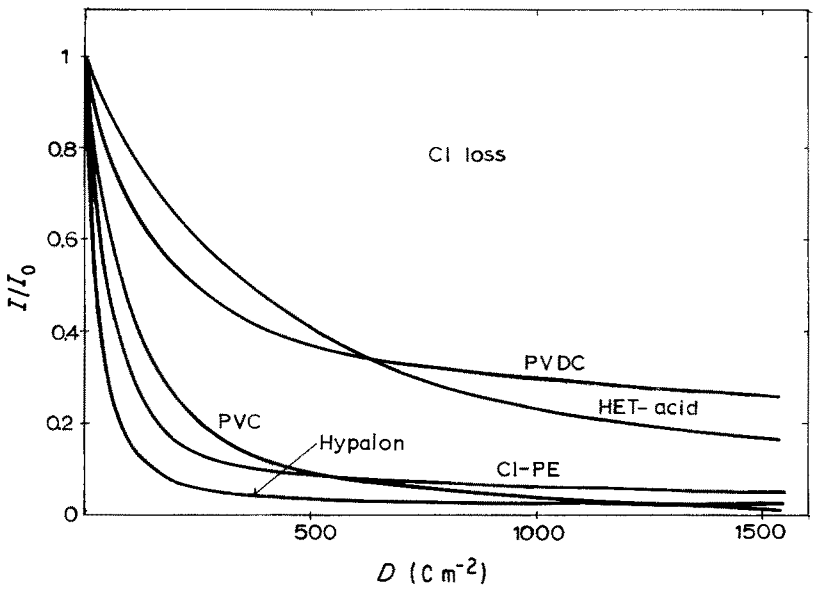

Figure 2 Chlorine loss curves for PVC, PVDC, Hypalon, Cl-PE and HET-acid show different behaviour on irradiation.

chlorine contents below 58%. Thermal degradation studies of Cl-PE by Oswald and Kubu [18] showed a maximum dehydrochlorination rate for chlorine content of 58%, which corresponds to pure PVC. The increased stability at a higher chlorine content than 58% was attributed to the presence of more stable vinylidene groups. The structure of our Cl-PE with 42% of chlorine can, therefore, be regarded as a random copolymer of PVC and PE. The electron beam degradation (Figs 2 and 3) shows similar characteristics to PVC, but the rate of chlorine loss is slightly higher. It can be suggested that the presence of PE chains increases the availability of hydrogen atoms, so that volatile HCl can be formed more easily.

Similar behaviour to Cl-PE is observed (Figs 2 and 3) for chlorosulphonated PE (Hypalon). It contains about 30% of chlorine by weight and about 1.5% sulphur. This means that there is only one chlorosulphone group per 85 carbon atoms and most of the chlorine is in the PVC type structure. The dehyrochlorination rate is however higher than for PVC and there is a constant chlorine residue at about 3% chlorine (this low level is difficult to measure accurately). It has been found in our earlier work [14] that the sulphur content is unchanged even after a long exposure. This indicates that the sulphur in chlorosulphone groups does not form a volatile compound. As the chlorine residue remains at the level approximately corresponding to chlorosulphone groups, it can be suggested that these groups are very beam resistant. All the chlorine lost from Hypalon is therefore lost from the vinyl groups. The dehydrochlorination rate is however faster than from Cl-PE. It is very difficult to understand why apparently the same PVC structures degrade at different rates. One possible explanation for the difference between Cl-PE and Hypalon is that they are made by chlorination of HDPE and LDPE respectively. The polymer branching in LDPE will increase the probability of formation of tertiary chlorines, which are well known to be weak points for thermal degradation. The tertiary chlorine can also make weak points for the electron beam degradation, but as will be seen later, the electron beam damage is not so selective. An alternative explanation could be that polymers prepared by a different route will have a different chain length available for unzipping reactions, as pointed out previously [16]. The total mass loss from Hypalon is about 20%,

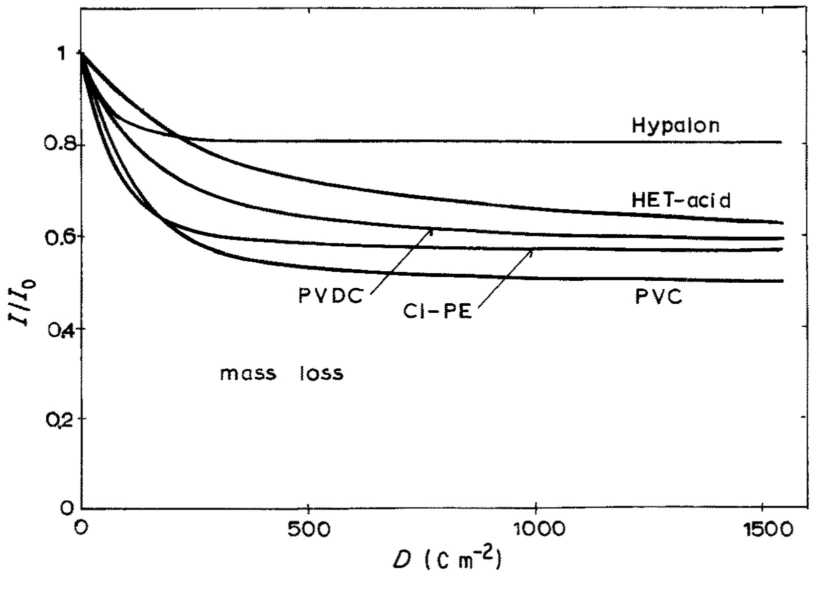

Figure 3 Mass loss curves for PVC, PVDC, Hypalon, Cl-PE and HET-acid. The mass loss is dependent on the chemical structure of the polymer.

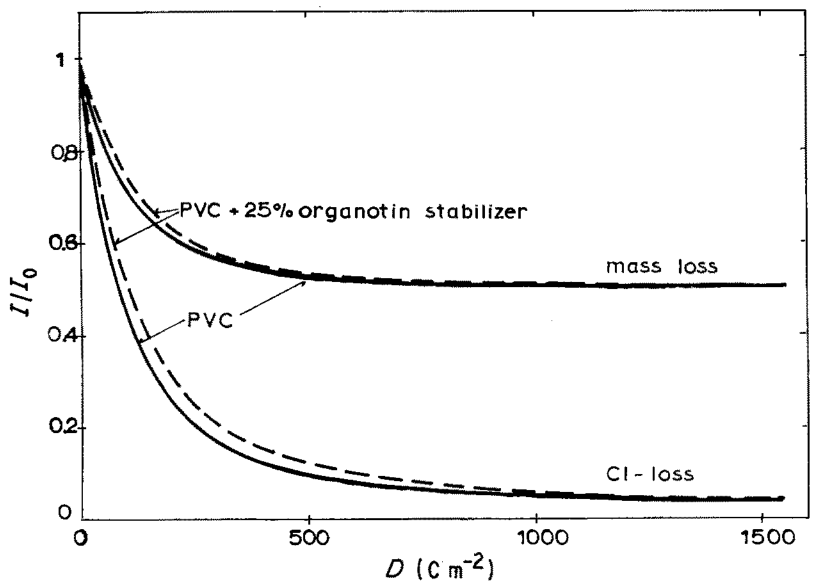

Figure 4 Chlorine loss and mass loss from pure and stabilized PVC.

which is less than would correspond to the total chlorine content, usually present in Hypalon. It is unlikely that 10% of the chlorine is retained in the structure undetected and the most likely explanation could be that the level of chlorination in the material used in this work is 10% lower than normally specified for Hypalon.

From the investigation of Hypalon it is apparent that chlorine in the chlorosulphone groups is much more resistant to the electron beam damage than in vinyl or vinylidene groups. The amount of chlorine in these groups is, however, very small and it is difficult to reach a definite conclusion. It might be, therefore, useful to compare the previous results with another polymer which is known to be more stable. The chloroendic acid polyester (or HET-acid) might be a suitable polymer. It has a very good thermal stability and is sometimes incorporated in polyester thermosets to improve heat and fire resistance. Specimens used in this work were prepared from uncrosslinked HET-acid, containing about 20% of chlorine by weight. The chemical structure of the chloroendic acid part of the molecule is shown in Table I. There are only two hydrogen atoms available for the formation of a volatile HCl and it has been expected that a chlorinated aromatic structure will be formed by electron beam degradation. The chlorine decay curves should thus show a rapid decrease to 66% of the chlorine level, followed by a slow dechlorination, comparable to other chlorinated aromatic compounds, e.g. chlorinated copper pthalocyanine. The measured chlorine decay and mass loss curves (Figs 2 and 3) however show that this is not the case. The dechlorination is slow, but faster than for pthalocyanine and the decay rate is not reduced at 66%. A possible explanation could be that the chlorine is not removed as HCl, but in the form of a volatile chlorinated hydrocarbon. The mass loss measurements confirm a significant loss of other elements, as the mass loss calculated from the chlorine loss gives higher values. It is not possible at present to identify this hydrocarbon, but it can be concluded that a relatively large volume of the molecule must be involved in the chemical reaction, following the electron excitation. It is not clear from the present work if the reactions are confined to the HET-acid molecular groups or if the other part of the polyester chain can also participate.

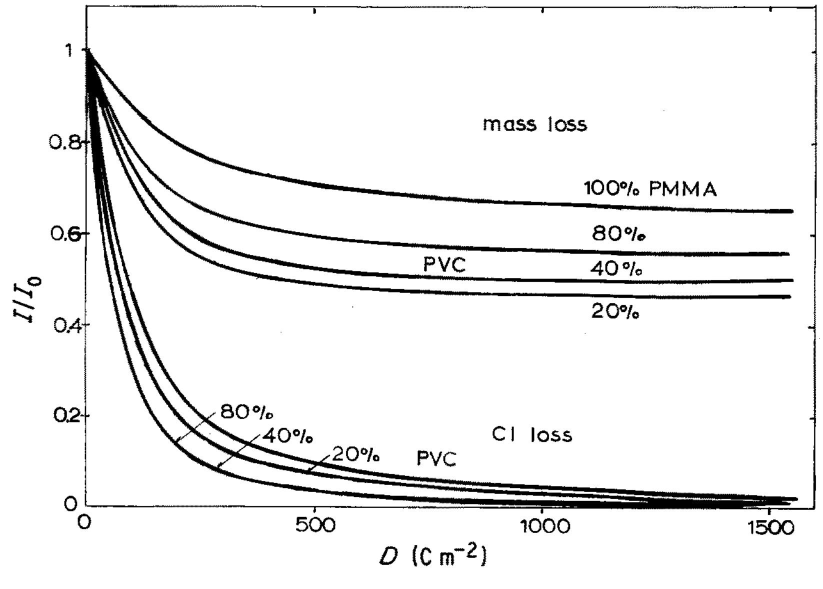

Figure 5 Mass loss and chlorine loss from PVC–PMMA blends.

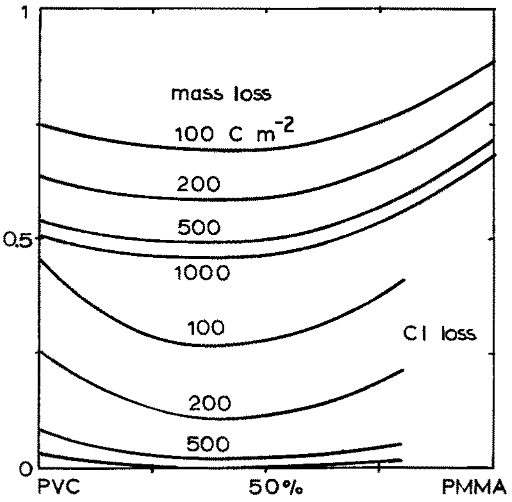

Figure 6 Mass loss and chlorine loss dependence on composition for PVC–PMMA blends at different exposures.

3.2. Blends with PVC

In order to establish the effect of the surrounding molecules on the dehydrochlorination of the PVC chain, blends of PVC with organotin stabilizer, PMMA, PCL, SAN and Hytrel have been studied. All these compounds form miscible blends with PVC, which means that the phases are very small and the contact area between the two types of molecules is very large.

The first obvious choice of a blend, which should show a clear decrease of dehydrochlorination is PVC with a stabilizer. The stabilizers usually work as HCl absorbers, reducing the autocatalytic effect of HCl on PVC. They also protect the PVC chain from dehydrochlorination, which is called true stabilization. The mechanism of true stabilization is not yet fully understood, but it has been proposed (as reviewed for example in [19] or [20]) that the stabilizer will react with free radicals, formed by loss of chlorine atoms. It is also possible [20], that the stabilizer will remove a weakly bonded chlorine (e.g. tertiary chlorine) before thermal dissociation occurs, thus preventing the initiation of unzipping reaction. From previous experiments [14] it has been observed, that when the specimen was coated on both sides with an organotin stabilizer, all HCl molecules evolved from the irradiated specimen reacted with the stabilizer. Consequently, no chlorine loss could be measured. However, when PVC was blended with 3% stabilizer, the rate of chlorine loss was identical to the unstabilized PVC. Even for 25% mixture the difference was insignificant (Fig. 4). This observation cannot be explained by a poor dispersion of the stabilizer, as the X-ray analysis of the tin content has shown. A possible explanation could be that the electrons initiate the dehydrochlorination (or introduce free radicals) randomly and not at weakly bonded chlorines as in the case of thermal degradation. The molecules of the stabilizer have a low mobility at room temperature and cannot respond quickly enough to prevent the formation and loss of HCl molecules.

From the thermal degradation studies of PVC blends it is known [21] that the dehydrochlorination can be altered by the presence of other polymers, although to a lesser extent than by stabilizers. Fig. 5 shows the chlorine loss and mass loss for PVC–PMMA blends with exposure to the electron beam. A slight increase of the dehydrochlorination rate is apparent. This is more clearly illustrated in Fig. 6, where mass losses after a given exposure are plotted against composition of the blends. The deviation from a straight line shows clearly the enhanced mass loss. In order to explain this behaviour, it might be useful first to consider the thermal degradation. McNeil and Neil [21] found that the chain scission of PMMA in PVC blends was more rapid than in pure PMMA at the beginning of thermal decomposition, but the reverse was observed at final stages. This was explained by the chlorine radical attack on the PMMA chain, causing a monomerization at lower temperatures than would be expected for pure PMMA. The decreased monomerization at final stages of thermal decomposition was explained by the interaction of HCl with the ester groups of PMMA, resulting in the formation of a more stable anhydride. Different behaviour of PVC–PMMA blends was observed during the electron beam

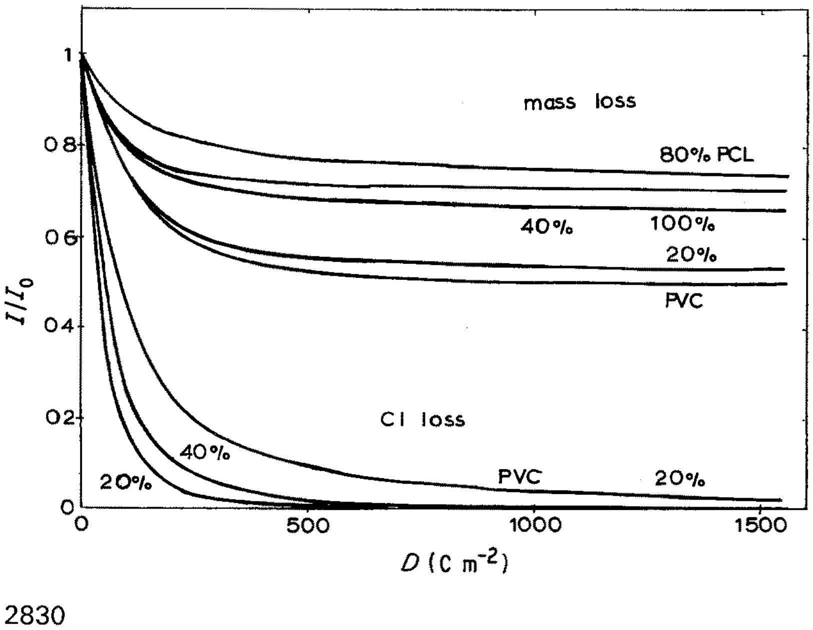

Figure 7 Mass loss and chlorine loss from PVC–PCL blends.

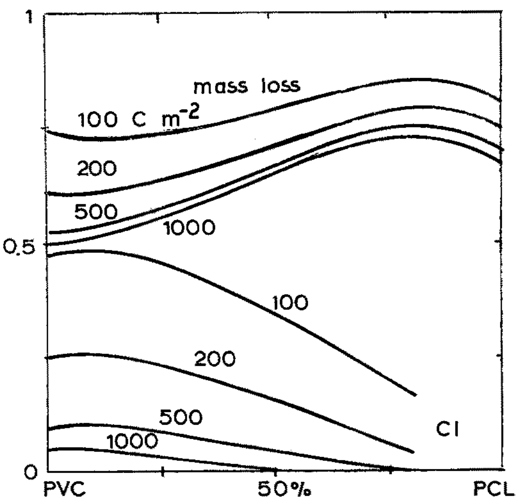

Figure 8 Mass loss and chlorine loss dependence on composition for PVC–PCL blends at different exposures.

irradiation, i.e. the rate of chlorine loss was increased. The mass loss calculated from the chlorine loss was nearly the same as the measured mass loss, indicating that the major contribution to the total mass loss is from PVC. The differences were too small for a quantitative evaluation of the mass loss from both polymers. The later stages of the electron beam degradation also differ from the thermal degradation, as the rate of chlorine loss in not reduced by the presence of PMMA. This can be explained by a faster removal of HCl from a thin specimen placed in a vacuum. Alternatively, room temperature may be insufficient for the reaction between HCl and the ester groups to occur. The PVC blends with PCL show an enhanced dehydrochlorination of PVC (Fig. 7). Similarly the mass loss dependence on composition (Fig. 8) shows an increase in the loss of mass from PVC, but a decrease of mass loss from PCL. As PCL has a limited solubility in PVC (about 30%, [22]), the mass loss data can be interpreted by the formation of two phases: PVC with 30% PCL and PCL with some PVC. It is uncertain as to whether PVC is soluble in PCL, but the mass loss data suggest a partial solubility at both ends of composition. If this is taken into account (and further work on the microstructural characterization is needed), the above behaviour can be explained in a similar way as for PMMA, i.e. enhanced decomposition of PVC by the presence of oxygen radicals, and retarded decomposition of PCL by anhydride formation.

The blends of PVC and SAN behave differently. The chlorine decay curves (Fig. 9) show very small deviation from pure PVC. The mass loss data (Fig. 10) are close to straight lines, showing a purely additive behaviour. There is, therefore, no interaction between the molecules or their fractions formed by electron beam degradation. This result again seems to differ from the thermal degradation. If it is assumed that PS behaves in a similar way as its copolymer SAN, the results obtained from PVC–PS blends can be utilized [23]. This shows a significantly reduced dehydrochlorination of PVC, for which the most probable explanation is the chlorine free radical attack on PS, causing chain scission and formation of less reactive radicals. The PS, therefore, acts partially as a stabilizer during the thermal degradation, but not during the electron beam irradiation, as discussed above for stabilized PVC.

4. Conclusions

The chlorine loss and mass loss measurements of pure homopolymers, their copolymers and blends, clearly show the differences between the electron beam and thermal degradations. The energy transfer from an electron to the polymer chain seems to be completely random. The thermal degradation on the other hand is likely to be initiated at chemically weak sites.

At room temperature the mobility of molecules and their fragments is much reduced, resulting in a different degradation route for the electron beam damage than at higher temperatures during the thermal degradation.

The results from the thermal behaviour of polymers cannot, therefore, be applied directly to the polymer behaviour in the electron microscope.

The mass loss measurements together with the elemental loss measurement can provide some

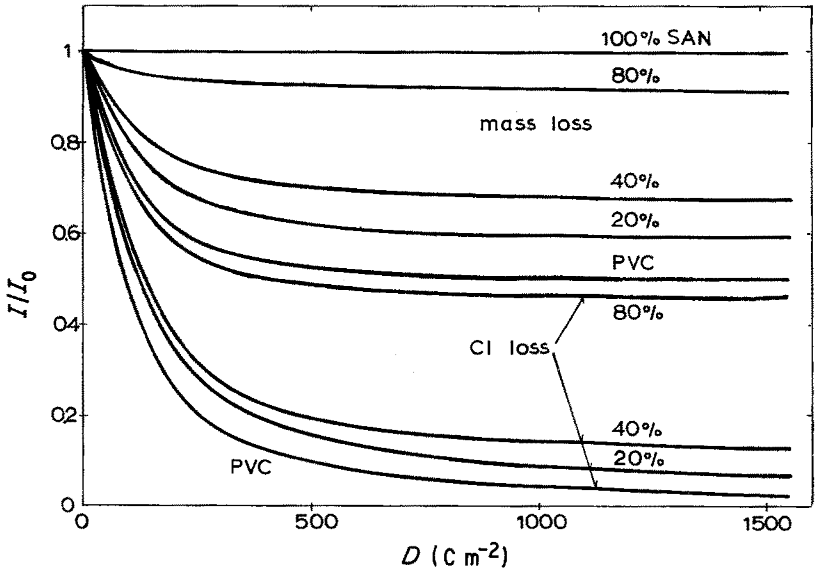

Figure 9 Mass loss and chlorine loss from PVC–SAN blends.

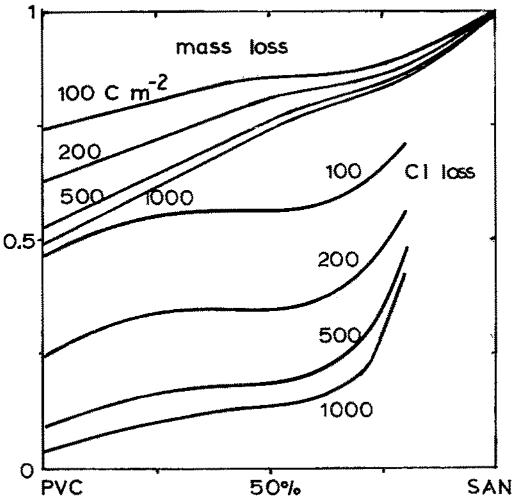

Figure 10 Mass loss and chlorine loss dependence on composition for PVC–SAN blends at different exposures.

additional information on the polymer structure, e.g. on the degree of chlorination or polymer miscibility.

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