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Chlorine loss and mass loss from polyvinylchloride and polyvinylidenchloride under the electron beam

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The loss of chlorine during the irradiation of PVC and PVDC in the electron microscope has been measured by the decay of the X-ray chlorine $K\alpha$ signal. A number of factors affecting the measured beam damage curves have been considered and the experimental errors reduced to ± 10%. The results show that the chlorine decay curves can be best described by the sum of two exponentials, corresponding to the two different chlorine decay processes, these being: the dehydrochlorination of the polymer molecules and the dehydrochlorination of the polyene structure formed by the beam damage. The higher initial chlorine content of PVDC compared to PVC will result in a larger amount of chlorine atoms reacting with the polyene structure, which is more stable in the electron beam than the undamaged polymer. The chlorine loss, measured by X-ray analysis, has been compared to the mass loss, measured by energy loss analysis, and also with the volume changes of isolated spherical PVC particles. It has been concluded that the mass loss is almost entirely due to chlorine loss and that the residual structure has a density similar to the undamaged PVC.

1. Introduction

The reliability of data gained from the electron/specimen interaction can be influenced by the beam damage, especially in the case of organic materials. For this reason a great deal of research into beam damage mechanisms, particularly of biological materials, has been done in the last two decades (for a review see, for example, Isaacson [1]).

The beam damage can be most easily assessed, for non-crystalline materials, by the loss of mass or the loss of elements. It has been shown for synthetic polymers that the different mass losses of two polymer phases and the subsequent changes of contrast in the transmission electron microscope can be used for the study of the composition of polymer blends [2–4].

For quantitative information, however, more detailed knowledge of the mass loss mechanism is needed. One of the first attempts to obtain quantitative data on the mass loss of synthetic polymers was reported by Bahr *et al.* [5], who found that the mass loss of a thin PVC film was about 55% of the initial mass after an exposure of $100\,\mathrm{C\,m^{-2}}$. They reported, that the residue was mainly carbon black and they noted a considerable shrinkage of the specimen. Reimer [6] measured the mass loss by contrast changes of thin PVC specimens at 60 keV, and also by weighing 5 μm thick specimens after irradiation. The contrast changes showed little temperature dependence, but the mass loss of the thick specimens was clearly dependent on temperature. Specimens at 40° C showed a slower rate of mass loss and had a higher chlorine content in the residue than those irradiated at 120° C. He suggested that the amount of chlorine remaining in the structure could be dependent on the reaction of chlorine with carbon–carbon double bonds.

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The effect of temperature, carbon coating and contamination were considered as an explanation for the large mass losses at extreme electron beam current densities, when the specimen was heated up by the electron beam [2]. The localized heating of the specimen by the electron beam was calculated by Isaacson [1] and by Talmon and Thomas [7]. They confirmed that the temperature of the specimen raised significantly only for very high exposure rates. Egerton [8, 9] studied the loss of carbon, nitrogen and oxygen at low temperatures (liquid nitrogen) and showed that the loss of molecular fragments decreases with the temperature of irradiation.

Several attempts have been made to find an equation which can describe the mass loss mechanism. Dubochet [10] measured the carbon loss of labelled carbon atoms from T4-bacteriophage and *E. coli* bacteria by autoradiography. He concluded that the carbon loss is dependent on the electron dose by the equation, $m = m_0 \exp(-0.51 D/D^{0.73})$, where m is the mass, m_0 the initial mass and D exposure in $\mathrm{C\,cm^{-2}}$. He could not fit his data to a single exponential function or even to an exponential with an offset. Egerton [9] has suggested that a sum of two exponentials can best describe the data from energy loss measurements, that is: $N/N_0 = e^{-k_1 D} + e^{-k_2 D}$, where N/N_0 is the normalized signal from the elemental peak, k_1 and k_2 are constants. Delgado and Hutchinson [11] measured the chlorine loss from thin PVC films at voltages of 10 to 30 keV, using a scanning electron microscope with an X-ray energy dispersive analyser. They found that the best fit for the chlorine decay curve can be obtained with the exponential function: $C = C_0 \exp(-E/\tau) + C_r$, where C is the predicted counts, E is the exposure in $\mathrm{C\,cm^{-2}}$ and C_0, τ and C_r are constants. Isaacson in his review paper [1], has also used an exponential function with an offset to explain the data from the literature, but he pointed out the poor correlation of the reported experimental values. In our recent work [12] an attempt has been made to identify and eliminate the experimental errors. It has been shown that the initial part of the decay curves of four different polymers can be fitted to an equation: $I/I_0 = (1 - A)\exp(-kD) + A$, where I/I_0 is the relative X-ray elemental peak intensity, D is the exposure, A and k are constants.

In this work the electron beam degradation of PVC and PVDC is studied further, especially for high exposures, in order to reveal and better understand the chemical and structural changes resulting from the electron irradiation.

2. Experimental procedure

2.1. Specimen preparation

The PVC and PVDC polymers of a commerical grade were solvent cast from 1% tetrahydrofurane solution onto a water surface. No stabilizers or additives were used. The PVDC was a copolymer (SARAN 925) of approximately 85% PVDC and 15% PVC. Thin films, mounted on a copper grid, were coated on both sides with a thin layer of carbon (less than 10 nm thick). The thickness of the polymer films was estimated to be of the order of 200 nm. Some comparative studies were made on small isolated particles. These were manually selected from the suspension powder under the light microscope and placed on a carbon film supported by a copper grid. The particles were nearly spherical in shape and 10 to 20 μm in diameter.

2.2. X-ray energy dispersive analysis

The chlorine decay curves were determined by using two different systems. The first system was a Jeol 200B electron microscope with STEM and X-ray facilities. A Kevex 10 mm^2 Si/Li detector was connected to a Kevex 7000 μX multichannel analyser. The number of chlorine counts in a selected number of channels (a window), accumulated for a fixed period (usually 1 sec) was recorded digitally and printed out or plotted using an X–Y pen recorder as count rates against real time. The second system was a Hitachi 700H electron microscope with STEM and X-ray facilities. A Kevex 30 mm^2 Si/Li detector with 68° take off angle was connected to a Link 680 analyser with a Harwell 2010 pulse processor. The number of counts in a selected window (usually 240 eV) accumulated for 1 sec periods was plotted directly from the rate meter using a time $-Y$ recorder.

The measured decay curves have been recalculated (normalized) so that the initial signal is 1, i.e. 100%, and therefore the influence of parameters such as sensitivity of the measuring system, specimen thickness and thickness variations has been cancelled. On the other hand, there are many factors, which can severely distort the measured decay curves and they have to be carefully eliminated.

The exposure is perhaps the most important parameter which must be correctly evaluated. This involves an accurate measurement of the irradiated area measured directly on the fluorescent screen. For the second system, used mainly in the STEM mode, the area was measured on the CRT display screen, using reduced area scan. The magnification was calibrated several times during the experiments and the irradiated area measured on the electron micrographs and also directly on the specimen, using a light microscope. The electron beam current was measured with a Faraday cage placed just above the fluorescent screen of the Jeol 200B microscope and in a special specimen holder with the entry aperture at the same level as the specimen for the Hitachi 700H microscope. A Keithly 417 picoammeter was used to monitor the beam current before and after each experiment.

The specimen itself is often a major source of errors. The electrical charge which builds up during irradiation can deflect the beam to a new area. Alternatively the specimen can be moved, stretched and thinned down by the electrostatic forces, as we have observed when an area near the grid bar has been irradiated. Most polymer specimens also shrink as a result of the beam damage process and new material is drawn into the area under the electron beam. Coating of the specimen from both sides with a carbon layer of about 5 nm thick, eliminated charging and also reduced shrinkage to less than 10%. The effect of a constant layer-thickness on the decay curves has not been systematically investigated in this work, but seems to be small. On the other hand contamination, which builds up with the exposure, can significantly affect the measured curves and had to be kept at a minimum level. The signal at high exposures can also be affected by accidental pre-irradiation, as this will, after normalization, increase the relative signal at high exposures. New undamaged areas on the specimen have therefore to be carefully and systematically selected.

The linearity of the measuring system has also been evaluated and it has been concluded, that the only serious source of non-linearity is the dead time of the pulse counting system, particularly for the second system with the high take-off angle. To overcome this problem the beam current was selected as 10^{-9} A or less, and the accelerating voltage as 100 keV. The dead time was monitored for all the measurements, and because the changes from the beginning to the end of irradiation were only a few per cent, corrections were unnecessary. The decay curves might also be affected by the background signal, especially at high exposures. This has been measured as 4 count $\sec^{-1}$ on an empty copper grid and 1 count $\sec^{-1}$ when the specimen stage has been withdrawn, and this cannot therefore affect the measured decay curves significantly.

2.3. Electron energy loss spectroscopy

The spectrometer, based on the the usual 90° magnetic prism with a variable slit and resolution of about 3 eV, was attached to the Jeol 200B electron microscope and interfaced with the Kevex system.

The irradiated area was measured in the same way as for the chlorine decay curves, but the diameter of the beam had to be smaller (less than 1 μm) for the reason of focusing the beam in the spectrometer. The diameter of the beam was measured by scanning over a sharp edge and measuring the intensity change at a calibrated magnification on the CRT display screen.

The mass–thickness measurements were carried out using the intensity from the zero peak, recorded with an energy slit of 10 to 12 eV. The intensity was recalculated using Beer's law to obtain a relative mass–thickness: $I = I_0 \exp K(\rho h)$, where I is the intensity of the zero loss peak, ρ is the density and h is the thickness of the specimen. I_0 is the intensity value before irradiation and K is a parameter describing the sensitivity of the recording system.

3. Results and discussion

Fig. 1 shows a representative curve of the chlorine loss from a PVC and PVDC specimen. The curve is normalized with respect to the initial count rate and is plotted against the exposure. An estimated error of ± 10% confirms the experimental scatter, at least in the first and central parts of the decay curve. An average curve has been obtained from a large number of runs, using the two different systems, different specimens and different conditions. An attempt will now be made to interpret this curve and to find its physical meaning.

On the assumption that the main decomposition reaction in the irradiated PVC specimen is radiation limited dehydrochlorination, resulting in a polyene structure, the decay curve would follow the single exponential function:

$$I/I_0 = e^{-k_1 D} \tag{1}$$

It has been shown previously [11, 12], that a better fit is given by the exponential function with an

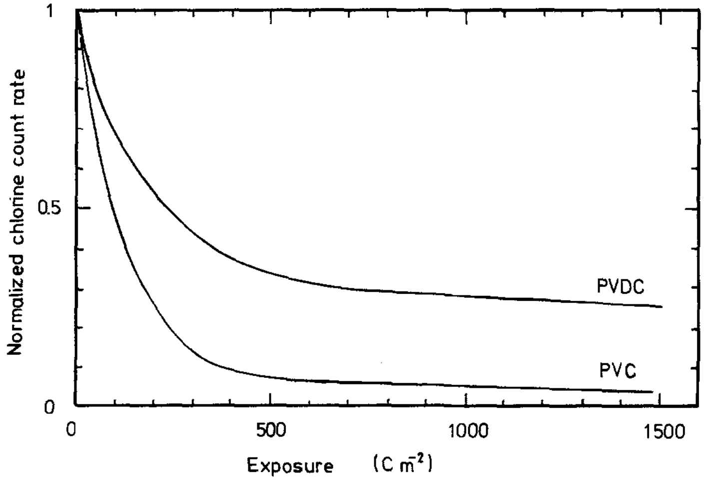

Figure 1 Normalized chlorine count rate against exposure at 200 keV CTEM, with exposure rate 3.9 A m^{-2} of solvent cast PVC and PVDC specimens.

offset, suggesting that some chlorine is left in a very stable form:

$$I/I_0 = (1-A)e^{-k_1D} + A \tag{2}$$

This equation, however, would not fit the experimental data for higher exposures. It is very unlikely that the experimental data are incorrect. The beginning of the decay curve can be affected by a number of parameters, as discussed above, but the end of the decay curve cannot be easily resolved because of the low signal-to-noise ratio. To increase the signal, the current density was increased by one order after the exposure of 1000 C m^{-2}. A new decay curve, similar in shape but decreasing much more slowly than the curve for the unirradiated area, has been obtained. This confirmed that the chlorine content in the sample was continuously decreasing, assuming, of course, that there is no strong dose-rate dependence. The chlorine loss was about 90 to 95% at the highest exposures used (up to 20 000 C m^{-2}). A sum of two exponentials can explain the experimental data very well:

$$I/I_0 = (1-A)e^{-k_1D} + Ae^{-k_2D} \tag{3}$$

This equation indicates, that there are two processes of dehydrochlorination: fast and slow (the constant k_2 being more than one order smaller than k_1).

An attempt will now be made to explain the observed effect, i.e. that a certain portion of the total chlorine content is decreasing with irradiation at a slower rate than the rest of it. The first explanation is the transfer of new material into the irradiated zone due to specimen shrinkage. This would certainly increase the chlorine content; however, the shrinkage was less than 15% and the rate of shrinkage was coincident with the chlorine loss; in other words this shrinkage effect would influence mainly the beginning of the decay curve and, in addition, it will be minimized by normalization. The measurement of chlorine loss from isolated spheres has given decay curves identical with those measured on a thin film specimen.

The second possible explanation is a slow diffusion controlled evaporation of volatile, chlorine containing products of irradiation. If evaporation occurs slowly enough to be comparable to the duration of the experiment, the count rate should decrease during an interruption in the irradiation. The chlorine count rate was measured after interruptions of durations from a few seconds to 1 h. No decrease in the count rate was observed larger than the scatter of the experimental data. It can therefore be concluded that at least the first and central parts of the decay curve result from a radiation limited process. This conclusion is in agreement with the published results [9, 11, 13] for the room temperature irradiation.

The third explanation can be the presence of two different structures. It is unlikely that two different structures are present in the unirradiated PVC or PVDC materials and therefore it must be assumed that a different, more stable structure is formed by the electron beam damage process. The chemical changes are clearly visible when the irradiated specimen is examined under the light microscope. The beam damaged areas are brown and purple in colour, known to be associated with the polyene structure. This darkening cannot be caused by contamination; Fig. 2 shows the light micro-

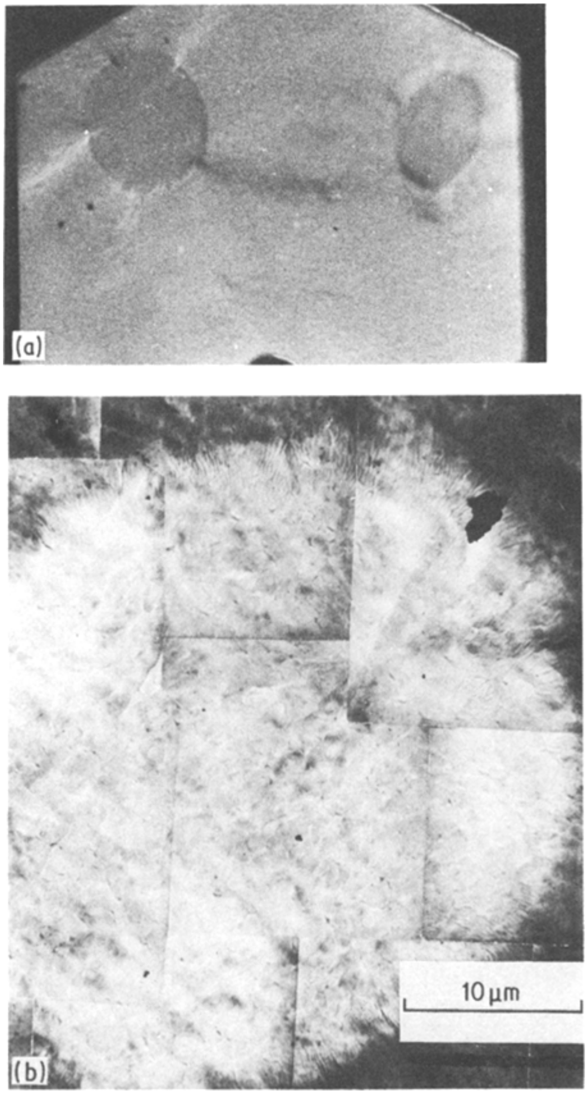

Figure 2 Micrographs of an irradiated area of a PVC specimen. (a) Optical micrograph; the irradiated area appears darker, but is thinner, as seen on (b). (b) Electron micrograph of the same area, the thickness was reduced by irradiation to about 50%.

graph and the electron micrograph of the same area. It is evident that the irradiated area has a lower mass–thickness, being more transparent to electrons, and the darkening effect in the light microscope is therefore due to the discolouration only. The formation of the polyene structure as a result of dehydrochlorination by thermal and radiation degradation has been reported previously (for example, [14]). There is a certain probability that some chlorine atoms will be found trapped on the polyene structure and because the polyene structure is more radiation resistant than the undamaged PVC or PVDC molecules, its presence might be responsible for the slow chlorine loss at high exposures.

The effect of the polymer structure on the decay curves is illustrated by comparing PVC and PVDC. To emphasize the differences, the chlorine decay curves are plotted on a double logarithmic scale (Fig. 3). It is obvious that the major difference in the chlorine content is at high exposures. The higher initial chlorine content of PVDC, compared to PVC, will increase the probability of the chlorine atoms remaining on the more stable polyene structure thus resulting in a higher chlorine residue. This means that the constant A in Equation 3 should be larger for PVDC than for PVC, as found. The constants A, k_1 and k_2 in Equation 3 were calculated for the best fit to the measured chlorine decay curves, and average values of a large number of measurements are given in Table I.

The values of A correspond well to those

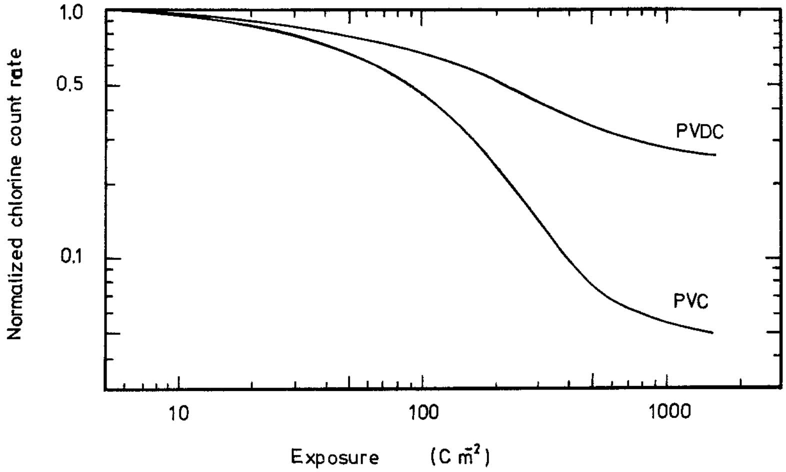

Figure 3 Normalized chlorine decay curves for PVC and PVDC plotted on a log/log scale at 200 keV CTEM, with exposure rate 3 A m^{-2}.

calculated for the best fit to the initial part of the curve, in our previous work [12]. The values of k_2 are also different for both polymers, suggesting that the structures formed by the irradiation of PVC and PVDC are not identical. This cannot be explained with our present knowledge of the irradiation processes and here further work is required.

The mass loss measurements can provide some additional information on the beam damage mechanism. It was possible, with the EELS spectrometer, to measure the changes in the intensity of the zero loss peak and thus to follow the decrease in the mass–thickness of the specimen during irradiation. Fig. 4 shows the mass loss against exposure graph for PVC and PVDC. It must be noted however, that the mass loss measurements could not be made at very high doses due to the contamination in the microscope. When the mass loss at high exposures is compared with the chlorine loss data, it becomes obvious that the total mass loss is mainly due to the chlorine loss for both polymers. For example, PVC will lose about 90% chlorine at 600 C m^{-2}. This will account for 50% of the total mass loss as observed, and therefore there is no measurable loss of carbon (Fig. 4).

The structure of the material is continuously changing during the beam damage and it might be interesting to find out to what extent the dehydrochlorinated carbon skeleton remains in the original configuration or to what extent it forms a new structure. The measurements of density and volume changes can be useful in this respect. Some irradiation experiments were carried out on small spherical PVC particles, 10 to 20 μm diameter, irradiated with an electron beam 42 μm diameter. (These experiments were also valuable as evidence that the material transfer into, or from the irradiated zone does not affect the chlorine decay curves obtained from thin films.) The dimensional changes were measured on the electron micrographs, taken at regular intervals, or directly on the STEM CRT display screen. The changes in the X-ray chlorine peak were recorded simultaneously. The results are shown in Fig. 5. The volume changes, calculated from the measured changes in diameter will give the same results as the volume changes, calculated from the chlorine loss data, only if a constant density is assumed. The mass–thickness changes are therefore thickness changes, resulting from volume shrinkage and not from surface etching. This means that the material shrinkage will compensate immediately for the loss of chlorine atoms and a continuous molecular re-structuring is an integral part of the beam damage process.

4. Conclusions

In the present work an attempt has been made to

TABLE I

	A	k_1	k_2
PVC	0.10 ± 0.04	0.0080 ± 0.0015	0.000 50 ± 0.000 20
PVDC	0.40 ± 0.10	0.0060 ± 0.0010	0.000 30 ± 0.000 05

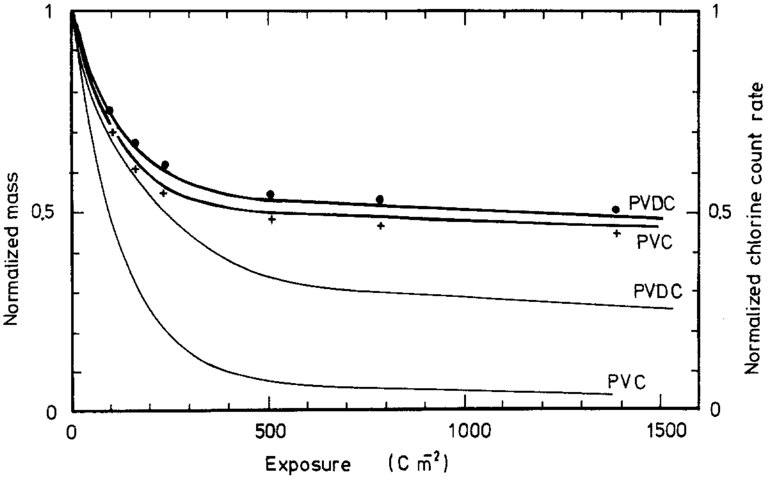

Figure 4 Residual mass curves for PVC (+) and PVDC (●) calculated from chlorine decay curves (thin lines) and EELS measurements of mass thickness (thick lines).

obtain quantitative data on the beam damage mechanisms of PVC and PVDC. The experimental errors were identified and to a large extent eliminated, so that it was possible to measure the chlorine decay curves with a reproducibility better than ± 10%. These curves were analysed and it was found that a function with two exponential terms would describe the beam damage process very well. The first term describes the dehydrochlorination of the original polymer structure. The second term, which is related to a much slower process, describes the dehydrochlorination of a structure formed by the beam damage and containing conjugated double bonds, i.e. polyenes. The amount of chlorine, which reacts with the polyene structure and which decays more slowly, is dependent on the original polymer structure and can explain why PVDC has a higher chlorine residue than PVC.

The measurements of mass–thickness using EELS were found to be less accurate than X-ray measurements, nevertheless they confirmed no detectable contribution of carbon loss to the total mass loss, i.e. the mass loss of PVC and PVDC is due to dehydrochlorination only. The measurements of volume changes of isolated PVC particles were compared with the chlorine loss and it was concluded that the density of the specimen remains unchanged during irradiation. All three methods of detection of radiation damage used in this work are sufficiently different for PVC and PVDC that they can be utilized for the identification of these polymers.

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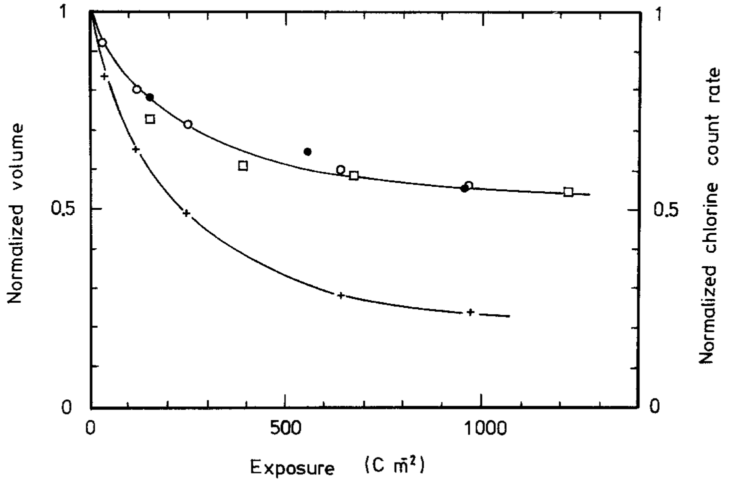

Figure 5 Comparison of volume changes of isolated PVC particles with data calculated from the chlorine decay curve. (●, □) measurements on particles, (+) measured chlorine decay, (○) volume calculated from chlorine decay.

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