The evaluation of polymers for electron resists by mass loss measurements

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A technique for the evaluation of electron resists by 'in situ' mass loss measurements is described. The electron–specimen interaction is related to the chemical changes that occur during exposure of the resist to the electron beam. These chemical changes can be analysed using a TEM and, by measuring the change in transmitted beam intensity with exposure, some information on the number of independent processes can be obtained. From mass loss measurements, we can determine the sensitivity of the resist in cases where chain scission is the dominant mechanism and relate the formation of the residue to changes in contrast. The optimum exposure for development of PMMA can be related to the maximum number of isolated double bonds as measured by X-ray analysis of osmium tetroxide stained material. The technique of mass loss measurement can be applied to polymer blends and used to study the effect of additives on the beam damage properties. It is a quick, relatively simple and reliable technique giving quantitative data for the evaluation of electron resists.

(Keywords: electron beam interaction; mass loss; resists; poly(methyl methacrylate); polymer blends)

INTRODUCTION

With the increasing need for higher resolution in microcircuits the current technology is reaching its theoretical limits. U.v. radiation can be used to produce line resolutions of up to 2000 nm but the potential of electron resists is far greater. The practical limitations of electron resists lie in the loss of resolution due to electron scattering, development procedures and the sensitivity of the resist. In order to improve the resist, it is important to understand the nature of the chemical changes resulting from the exposure of the specimen to the electron beam.

A method suitable for the evaluation of these chemical changes in irradiated polymers is infra-red spectroscopy. This is, however, slow and in most cases not quantitative. On the other hand, during irradiation, all polymers are losing mass which can be measured accurately, quickly and relatively easily using a TEM and therefore it would be useful to utilize this technique for beam damage measurement. In many polymers, the mass loss can be related to chain scission. It has previously been observed that the changes occurring during beam damage do not follow a single exponential function and that they are slower at higher exposures. This can be explained by the slower degradation of a more stable structure[1] formed as a result of irradiation of the original material and it has been shown to a good approximation that the relative change in signal can be described by an equation[2]:

$$m/m_0 = (1 - A)e^{-K_1 D} + A e^{-K_2 D} \qquad (1)$$

where m_0 is the initial mass, D the exposure, K_1 the rate of decay of the original structure and A is the proportion of the more stable structure formed during irradiation, decaying at rate K_2.

By the evaluation of these material constants, it is possible to investigate the electron–specimen interaction of individual polymers and also to assess the effect of mixtures of polymers on the beam damage properties, specifically the mass loss of PMMA/POM and PVC/POM blends. In this work, we attempt to assess the application of mass loss studies for the evaluation of electron resists and in particular, the feasibility of resists with maximum mass loss, thus minimizing the need for development.

EXPERIMENTAL

Specimens were prepared using PMMA (Diakon ICI) M_w 120 000, POM M_w 142 000 and PVC (Corvic ICI) M_w 140 000 by casting onto glass, 0.5 wt% solutions using DMF as the solvent. Due to the low solubility of POM in DMF, it was necessary to increase the temperature of the solvent. The optimum temperature was found to be 165°C, this being the best compromise between solubility and oxidation. This compared with 50°C, which was used for the PVC and PMMA solutions. When the polymers are fully dissolved, the two components can be blended and cast onto a glass slide. For the given concentation, thin films of approximately 3000 Å thickness were produced. These were placed in a vacuum oven for 24 h at 50°C to remove the residual solvent. The specimens were then stripped from the glass slide in distilled water, mounted onto copper grids and finally covered with a 100 Å layer of carbon to reduce charging effects.

A technique has been developed for the 'in situ' measurement of mass loss using a Hitachi 700H TEM/STEM 200 keV instrument which has been substantially modified for accurate dosimetry. The modifications include a beam shutter and Faraday cages at three different levels, i.e. above the specimen, at the specimen level and at the screen level, the latter being used to measure the transmitted beam intensity. The transmitted beam intensity is dependent on the number of electrons

scattered outside the objective lens aperture. The smaller the aperture, the higher is the sensitivity to the changes in specimen thickness.

The measured curves of increasing transmitted beam intensity against exposure were analysed using a computer and a curve fitting program to speed up the evaluation of the material constants K_1, K_2, and A in equation (1). In order to cancel the effect of the mass thickness variation, it is necessary to normalize the data and therefore the initial intensity I_1 at $t = 0$ must be accurately evaluated. This has been determined using the first initial data points, extrapolated on a log intensity/ exposure plot. The subsequent data points were then calculated using the following equation:

$$\text{Normalized mass } m/m_0 = \frac{\log I/I_0}{\log I_1/I_0} \qquad (2)$$

where I is the transmitted beam intensity at time t, I_0 is the transmitted beam current with only the carbon film present. Equation (2) does not include corrections for changes in density, average atomic weight or scattering cross section. It has been shown for PVC[3] that the density is not changing significantly with irradiation. Changes in scattering cross section with composition are difficult to take into account but, however, these corrections are small and will not greatly affect the relative evaluation of mass loss. It was also necessary to take into account in the analysis, the effect of contamination at high exposures. This was achieved by measuring the change in transmitted beam intensity with only the carbon film present as a function of exposure to the electron beam. Using this technique, it was possible to determine accurately the mass loss characteristics from areas less than $40\,\mu m$ in diameter, i.e. a total initial volume of approximately $400\,\mu m^3$.

ELECTRON BEAM DAMAGE

PMMA is one of the most important positive resist materials (first developed by Hatzakis[4]) and although there have been numerous improvements over this material using copolymers (such as MMA + methacrylic acid or methacryloyl) it is still of great interest to understand how the material acts as a positive resist. In *Figure 1*, the measured relative mass loss curves for POM and PMMA are plotted against log D and are compared with a single exponential curve. The fastest decay can only be obtained with a single exponential curve. The higher the residue A, and greater the difference between K_1 and K_2, the longer it takes to reduce the mass of the polymer. For PMMA, it can be seen from *Figure 1* that the initial slope is less than that for POM (which pertains to a pure exponential decay), therefore, even at low exposures, the residue A decaying at a rate of K_2 is affecting K_1. Consequently, the solubility of PMMA measured as a function of exposure will be lower than that for a material exhibiting pure chain scission due to the formation of a less soluble residue. This is equivalent to a change of *contrast* in polymer resists, contrast being calculated from $(\log(D_c/D_0))^{-1}$, where D_c for a positive resist is the extrapolated exposure for complete development and D_0 is the sensitivity[5]. The value of K_1 is related to the *sensitivity*, which, as shown above, is also affected by the residue level A. From the chemistry view point, the single exponential case can only occur if the
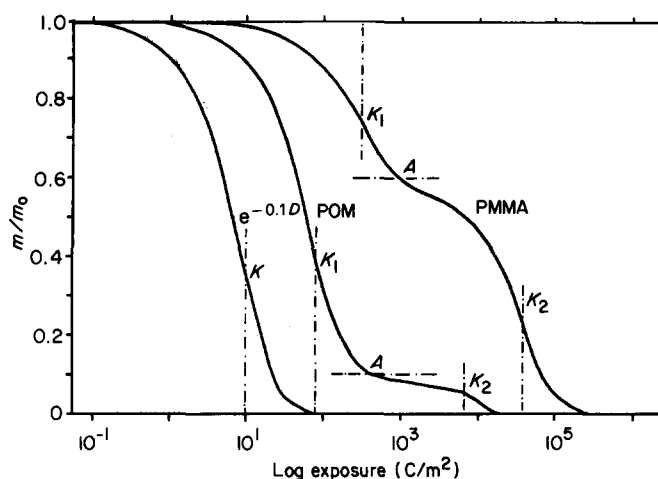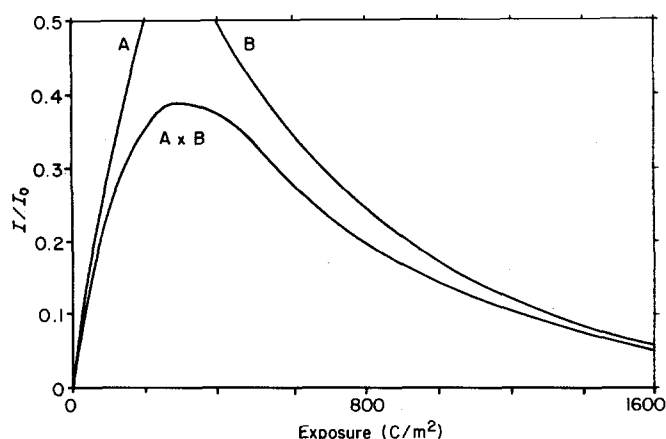

Figure 1 Mass loss curves for PMMA and POM as a function of log exposure

structure is not changing with irradiation. This will occur for example in a very simple molecule with volatile products being formed upon irradiation and where chain scission is the only mechanism. This is very unlikely, but some materials like POM are approaching this behaviour.

As shown above, it is possible to obtain some information from mass loss curves on the number of independent mechanisms and their dependence on exposure. It is also possible to obtain further information on the chemical structure of the irradiated material by chemical analysis such as the use of staining techniques.

Of particular importance for the development of electron resists is the exposure at which chain scission reaches a maximum, thereafter, cross linking becoming the dominant mechanism. It has been shown previously[6] that isolated double bonds are formed in all polymers and that they are destroyed upon further irradiation by the formation of conjugated sequences or by crosslinking. These isolated double bonds can be revealed by staining with osmium tetroxide and their number related to osmium X-ray counts and also to density changes. For simple calculations[2] it was possible to obtain the probability of formation and destruction of these bonds. When applied to our present results for PMMA, we can evaluate the exposure for which the maximum chain scission occurs. This is illustrated in *Figure 2* where the curve A corresponds to the formation of isolated double bonds, or chain scission, and this must be related to mass loss. Therefore the curve A can be calculated as $A = 1 - e^{-K_1 D}$. The maximum in osmium staining intensity (and therefore the peak of the curve A × B) for PMMA is known to be 300 C/m^2 (ref. 6), whence it can be calculated that $n \simeq 0.5$ in the equation $A \times B = (1 - e^{-K_1 D})e^{-nK_1 D}$. This indicates that for PMMA, chain scission is twice as likely as crosslinking, which might be obvious from the consideration that two chains must undergo scission to form one crosslink. It is interesting to note that the maximum staining peak occurs for PMMA at an exposure $D = \ln(n/(n+1))/K_1 \simeq 1/K_1$ ($n = 0.5$) and this coincides with the exposure needed for maximum reduction in molecular weight.

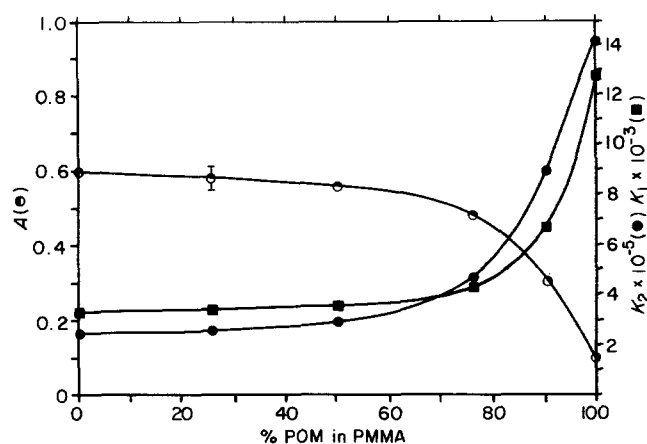In order to understand the meaning of the data it is important to be able to correlate the exposures used in our experiment (0.3 μm film and 200 keV) with a typical exposure used for an electron resist (1 μm film and

Figure 2 Calculated curves for the formation and destruction of isolated double bonds for PMMA as a function of exposure
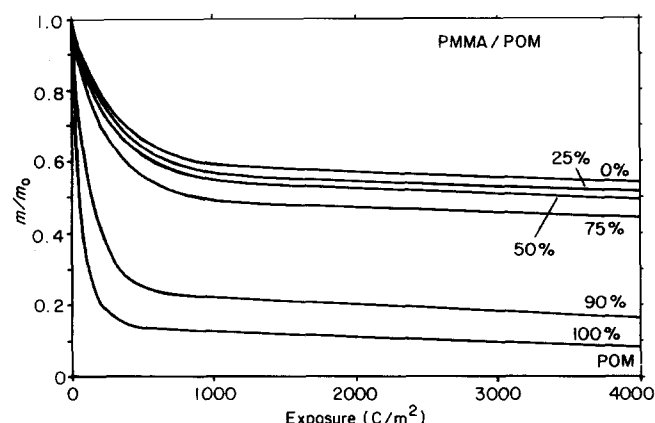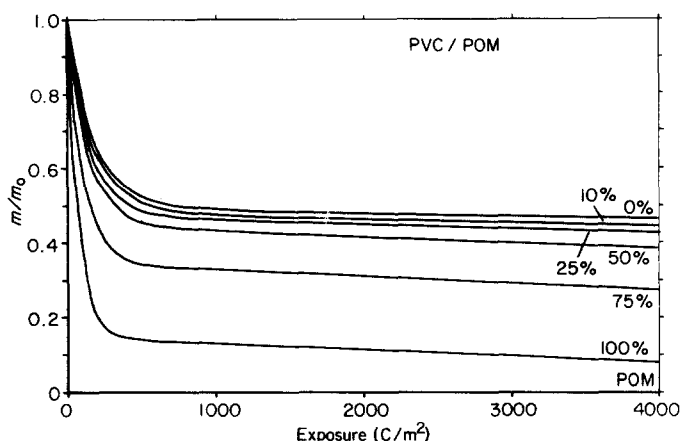

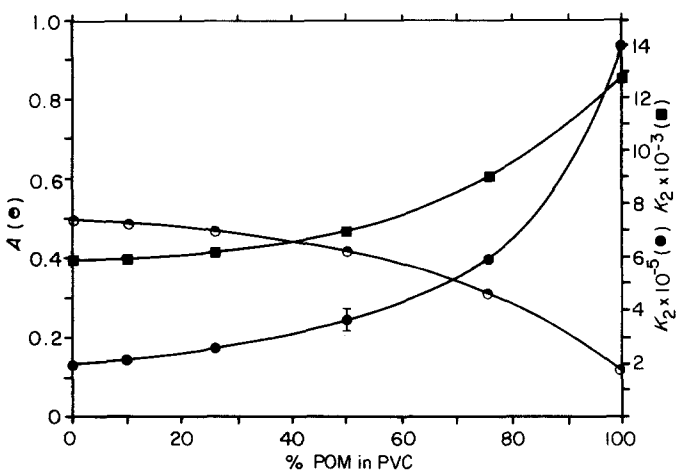**Figure 3** Mass loss curves for polymer blends of PMMA and POM

Figure 4 Change in the evaluated constants as a function of percent addition of POM to PMMA
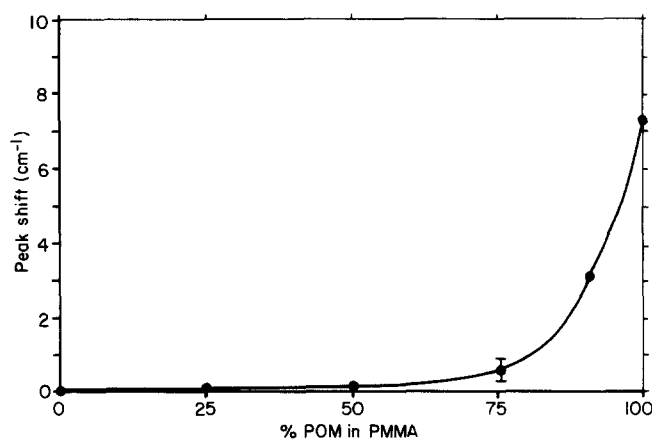
magnitude higher than those used for electron beam lithography to achieve similar energy dissipation and thus similar chemical changes. By using a multiplication factor of 80 for our exposure scale, the correlation with data for the sensitivity of PMMA can be achieved (i.e. 48 C/m^2 measured from *Figure 1* against 60 $\mu C/cm^2$ [7]). The exposure used for full development of PMMA as a resist then coincides with the $1/K_1$ value and therefore with the exposure needed to achieve the maximum level of isolated double bonds.

Figure 5 Mass loss curves for polymer blends of PVC and POM

Figure 6 Change in the evaluated constants as a function of percent addition of POM to PVC

25 keV). A 200 keV electron travelling through an organic material will lose about 0.35 keV per micrometre of travel. As the maximum thickness of our specimen is approximately 0.3 μm, we can say that less than 0.05 % of the energy has been absorbed. On the other hand, for a 1 μm thick electron resist on a substrate, approximately 4% of the 25 keV energy is absorbed. The remaining energy is absorbed by the substrate, with the exception of a few percent which is emitted back into the resist due to secondary electrons, back scattered electrons and X-rays. We can therefore say with confidence that the exposure in our experiment must be approximately two orders of

Figure 7 Shift in the carbonyl stretching band for PMMA with increasing concentration of POM
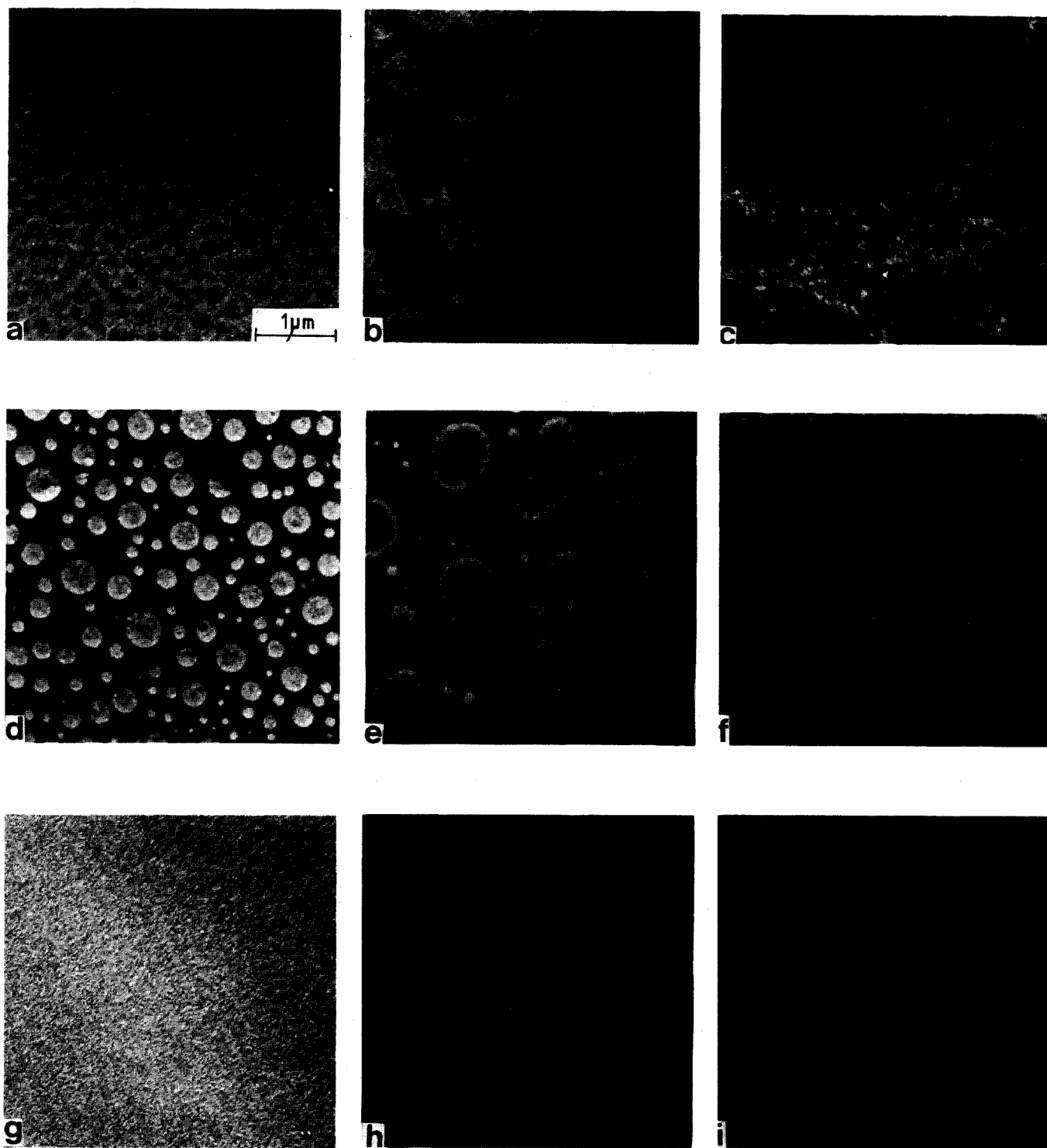
Figure 8 STEM electron micrograph of solvent cast polymers: (a) PMMA/25% POM; (b) PMMA/50% POM; (c) PMMA/75% POM; (d) PVC/25% POM; (e) PVC/50% POM; (f) PVC/75% POM; (g) pure PMMA; (h) pure POM; (i) pure PVC

ELECTRON BEAM DAMAGE OF POLYMER BLENDS

It can be seen from *Figure 1* that POM is decaying more quickly than PMMA and it might be interesting to investigate if a mixture of these two polymers will result in an increased rate of degradation. It is likely that oxygen radicals are formed during the irradiation of POM[8] and these might affect the chain scission of PMMA. The mass loss *versus* exposure of the polymers and their blends are plotted in *Figure 3*. From these curves, constants K_1, K_2, and A were calculated for the best fit with a computer

using equation (1). These constants are plotted in *Figure 4*. It can be seen that the changes are not purely additive and that the total mass loss is lower and slower than expected. This can only be interpreted as an interaction between the two polymers. A similar affect can be observed for the PVC/POM system (see *Figure 5*). However, here the interaction is much weaker, as the deviation from straight lines in *Figure 6* is not as large as for the PMMA/POM system. It is difficult, without further information on the chemical changes, to speculate on the mechanisms of degradation and the nature of the interaction. From our preliminary infra-red analysis

using *F Ti.r.*, it follows that one feature which indicates the presence of weak interaction, is the shift in the carbonyl stretching band at $1728.3\,\mathrm{cm}^{-1}$ for pure PMMA to $1731.4\,\mathrm{cm}^{-1}$ for 90% POM (*Figure 7*). This could be due to weak hydrogen–oxygen coupling, to which a similar analysis has been applied to the presence of PCL in PVC by Coleman and Zarian[9]. The peak at $1735.5\,\mathrm{cm}^{-1}$ for pure POM is due to end groups and is very weak in intensity. It is not possible at this stage to evaluate the effect of the addition of POM on the beam damage mechanisms of polymer blends, but these results indicate that the behaviour of polymer blends is not purely additive.

MICROSTRUCTURE OF POLYMER BLENDS

The degree of molecular chain interaction will affect the dispersion of phases in polymer blends[10]. Only for miscible systems can we expect a strong influence on the degradation characteristics. The presence of a microstructure is also important for the homogeneity of the resist material, as it can seriously affect the resolution. It was expected, from the strong influence blending has on the mass loss, that the phase dispersion would be good. However, the electron micrographs in *Figure 8* show phases up to 1 μm in diameter. For PMMA/POM blends, the mass thickness contrast between phases, and also the diffraction contrast in 75 and 100% POM specimens, is disappearing with irradiation. This can be expected for phases with different beam damage characteristics. The image contrast in PVC/POM however is increasing due to a slower mass loss from the PVC phase which has a higher mass thickness. Close examination reveals a very fine structure in the individual phases and this, together with the observed changes in mass loss, suggests partial miscibility of the investigated polymers. It was not possible in this work to evaluate the level of partial miscibility or the mass loss characteristics of the individual phases. The volume of material affected by the interaction is not known and for this reason it is not possible to say if only boundary regions, or large volumes are involved in the interaction.

CONCLUSIONS

The technique of '*in situ*' mass loss measurement provides valuable information on the chemical changes that occur during exposure of the material to the electron beam. It is a quick, relatively simple and reliable technique giving quantitative data for the evaluation of electron resists. From the mass loss curves, we can evaluate the sensitivity of the material and obtain some information on the number of independent processes occurring during irradiation. Materials like POM are approaching the behaviour of a single exponential decay where chain scission is the dominant mechanism, but the single exponential case can only occur if the structure does not change with irradiation. On the other hand, the irradiation of PMMA gives rise to a less soluble residue that affects the measurement of sensitivity and contrast and it has been shown that the optimum exposure for development of the resist is related to the maximum number of isolated double bonds as measured by osmium staining techniques.

Additives blended with the polymer can significantly change the properties of the electron resist and it has been shown that the use of mixtures of polymers is not purely additive, i.e. we have an interaction between the components of the blend. For electron resists, we require good dispersion which can only be achieved for low concentrations of the second phase. Poor dispersion can reduce the resolution significantly. It is proposed that this technique be developed further to allow smaller areas to be evaluated thus enabling interfaces between the polymer phases to be studied.

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