BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 12, pp. 2485 2489, 1995

0032-3861/95/\$10.00+0.00

Transmission electron microscopy methods for the determination of void content in polyimide thin film nanofoams

C. J. G. Plummer* **and J. G. Hilborn**
Laboratoire de Polymères, Ecole Polytechnique Fédérale de Lausanne, CH-1015, Switzerland

and J. L. Hedrick
IBM Research Division, Almaden Research Centre, 650 Harry Road, San Jose, CA 95120-6099, USA
(Received 9 November 1994)

Transmission electron microscopy (TEM) has been used to determine the porosity of polymer nanofoams produced by thermal decomposition of the thermally labile component of different copolymers. The results are compared with those obtainable by i.r. spectroscopy and density gradient methods, showing quantitative agreement for small pore sizes. TEM permits much higher spatial resolution than i.r. spectroscopy and is better suited to structures which scatter strongly at i.r. wavelengths.

(Keywords: TEM; nanofoams; void content)

Introduction

Multilayer technology for multichip modules is currently one of the most rapidly growing areas in microelectronics packaging, and cost-performance pressures are increasing the demand for better performance and higher density substrate technologies[1,2]. Polyimides and other high performance polymers are of great potential for such applications, owing to their ease of processing, low dielectric constants and exceptional thermal, thermo-oxidative and dimensional stability[3], but there remains a strong incentive to reduce their dielectric constants still further. Closed-cell foams with pore sizes of a few nanometres (hence 'nanofoams') are a means of doing so without compromising thermal stability and barrier properties (air has a dielectric constant of 1 so that, given that the best heterogeneous available polymeric films have dielectric constants of around 2.1, even modest void contents can lead to significant reductions). This is nevertheless only one example of the potential applications of nanofoams.

With such applications in mind, a new method has been developed for the synthesis of polyimide nanofoams using block and graft copolymers, in which the major component is an aromatic polyimide and the minor component is a thermally labile polymer, such as poly(propylene oxide) (PPO), poly(methyl methacrylate) (PMMA) or poly(α-methylstyrene) (PMS)[4-7]. The phase separation in such polymers depends on the block lengths and chain architecture, but typically occurs on length scales of the order of tens of nanometres. On heating, the labile phase decomposes to leave voids whose size and distribution will depend on the initial microstructure, and also on the synthesis and processing route (thermal or chemical imidization, crosslinking, matrix architecture), and the extent of matrix plasticization by the decomposition products. These latter can cause extensive blowing or coalescence[6]. However, whilst the resulting foam morphologies may vary considerably, it is the void volume fraction which is of paramount importance for the dielectric constant, and consequently a rapid, practical means is required of measuring this quantity in thin films.

Sorption techniques and small-angle X-ray scattering (SAXS) can provide detailed information on void contents and size distributions[8,9], but require specialized equipment and careful instrument calibration. Density measurements in a density gradient column may not be appropriate to open pore structures owing to penetration of the flotation fluid, giving inaccurate results. They also suffer from the need to detach the film from its substrate (glass or silica), which may distort the original void structure. Sanchez *et al.*[10] have therefore proposed two methods based on i.r. spectroscopy and assuming simple mixing rules to govern the measured quantities: (i) the absorption of a foamed film at a selected wavelength is compared with that of a homogeneous film of the same material and thickness; (ii) the refractive index is estimated from the interference fringes in the absorption spectrum and compared with that of a homogeneous film. This has the advantage of being an *in situ* technique and requires no assumptions about the void distribution or morphology. However, it is likely to be limited to foams containing pores or other structural features whose sizes are well below the wavelength of the i.r. absorption bands, because of possible scattering effects. In what follows we therefore advance complementary ways of obtaining void volume fractions from transmission electron microscopy (TEM). Evidently these entail microtoming all but the thinnest of films, with the attendant problems of microtome beam damage and relaxation of the original film structure. On the other hand, TEM offers high resolution and the possibility of characterizing very thin films.

---

[*] To whom correspondence should be addressed

Experimental

The foams investigated here were based on PMS/polyimide graft copolymers[6] and on PPO/polyimide triblock copolymers[7]. In each case, the imide component was derived from pyromellitic dianhydride with 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA/PMDA), as shown in *Figure 1*. The 3FDA/PMDA polyimide has a glass transition temperature (T_g) of 440°C and a decomposition temperature of 500°C, allowing decomposition of the labile coblocks well below the matrix T_g.

Several different 3FDA/PMDA/PMS graft copolymers were prepared in the fully imidized form, and also in the poly(amic alkyl ester) precursor form (*meta* and *para* isomers) following reference 7. The PMS block length was 18 000 g mol^{-1} and the PMS content was either 15 or 25 wt%, as assessed gravimetrically from the weight retention after decomposition of the thermally labile block. 3FDA/PMDA/PPO triblock copolymers were prepared according to reference 8, with various PPO block lengths and compositions.

Films of 10 to 25 μm in thickness were obtained by spin-coating solutions in *N*-methyl-2-pyrrolidone (NMP) at 2000 rev min^{-1} on 2.54 cm diameter Si wafers, or by doctor-blading. In the case of the poly(amic alkyl ester)/PMS films, thermal imidization was accomplished by heating to 265°C at 5 K min^{-1} and maintaining them at 265°C for 1.5 h in a nitrogen atmosphere. For foam formation, both the thermally and the chemically imidized 3FDA/PMDA/PMS films were heated to 325°C and held at this temperature for 2 h to effect the decomposition of the α-methylstyrene coblock. For the 3FDA/PMDA/PPO films, decomposition of the PPO was carried out at 300°C for 1 h.

The films were prepared for TEM using the Reichert-Jung Ultracut E ultramicrotome. Samples were mounted in epoxy resin and thin sections were taken parallel and perpendicular to the plane of the films at room temperature. Observations were carried out using the Phillips 300 TEM at an accelerating voltage of 100 kV and at various objective aperture sizes. *In situ* heat treatments made use of the TEM hot stage, and an effort was made to minimize beam damage by using a small spot size (so as to irradiate only a very small part of the specimen during observation). Software for the analysis of the TEM images was written using the National Instruments Labview™ programming language, incorporating Graftek Image Concept V.i™ image handling subroutines.

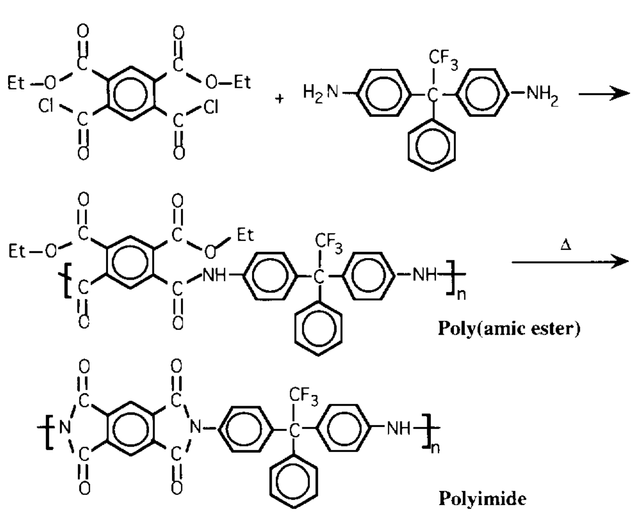

Figure 1 Synthesis and processing of the 3FDA/PMDA polyimide

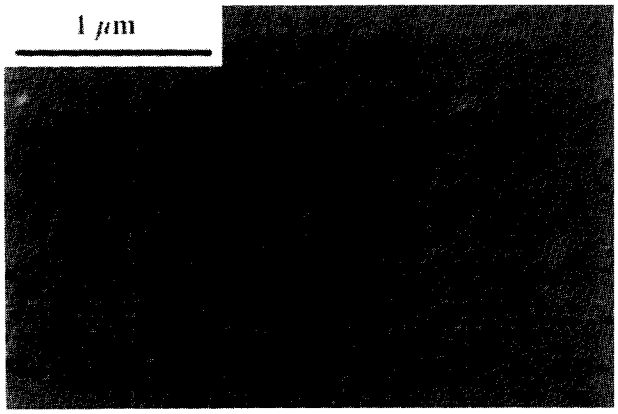

Figure 2 Digitized TEM negative of a heat-treated *meta* polyimide, 15 wt% PMS film

Results and discussion

Stereoscopic analysis. *Figure 2* is the structure of a 90 nm thick section taken perpendicular to the plane of a relatively thick foamed film of about 20 μm in thickness, showing approximately circular holes with diameters of 20–100 nm. Similar microstructures were seen in sections taken parallel to the plane of the films, which suggests that the holes corresponded to sections through non-overlapping spherical voids. If this is the case, then simple stereological techniques developed for the analysis of particle-filled polymers[11] may be used to estimate the void size distribution and volume fraction from the TEM images.

Digitized TEM images were converted into binary form using a suitable threshold. The equivalent disc radius r was calculated for each hole in a given image from $2/\pi a^{1/2}$, where a is the hole area. For each image, $\langle r\rangle$, $\langle r^2\rangle$ and the total area fraction of holes, v_a, were calculated. From images of films of different thicknesses one can estimate the various moments of the distribution of R, the radius of the assumed spherical voids, and the void volume fraction, v, using

$$\langle r\rangle=\frac{\pi\langle R^2\rangle+2t\langle R\rangle}{4\langle R\rangle+2t}$$

$$\langle r^2\rangle=\frac{4\langle R^3\rangle+3t\langle R^2\rangle}{6\langle R\rangle+3t}$$

$$v_a=\frac{4\langle R^3\rangle+3t\langle R^2\rangle}{4\langle R^3\rangle}v \tag{1}$$

where t is the film thickness[11]. In the region of film illustrated in *Figure 2* (near to the centre of the cross-section), $\langle R\rangle$ was about 40 nm, with $\langle R^2\rangle$ and $\langle R^3\rangle$ equal to 3.4×10^3 nm^2 and 2×10^5 nm^3, respectively, and v_a was 20% in the 90 nm thick section shown. Thus v obtained by this method and for this part of the film was 9.3% (somewhat less than initial volume fraction of α-methylstyrene). For the sake of comparison, for a monomodal distribution of spheres of constant radius R, v has been shown to be[12]:

$$v_a = \frac{4R + 3t}{4R} v$$

(which is the limiting case of equation (1) when $\langle R^n \rangle \rightarrow R^n$). If we take $R = \langle R \rangle = 40\,\text{nm}$, we have for $v_a = 20\%$ and $t = 900\,\text{Å}$ that $v = 7.5\%$. Of course the pore size distribution here was not monomodal, and was indeed quite broad, with $\langle R^2 \rangle - \langle R \rangle^2$ of the order of $\langle R \rangle$ itself.

Optical densitometry of TEM plates. The approach described in the previous section is time-consuming, requiring microtomed slices of several known thicknesses, and depends on the pores being well separated, spherical, and having well defined edges (although the analysis can easily be adapted to other well defined morphologies). To cope with morphologies where the pore geometry is complex, with connectivity and overlap, we adapted the technique developed concurrently by Lauterwasser and Kramer[13] and Brown[14] for obtaining the volume fraction of voids in crazes in amorphous polymer thin films (crazes effectively being open-cell nanofoams). The theoretical background detailed in the cited references provides a firm basis for the assumption that the transmitted intensity of the electron beam, I_i, decays exponentially, with a decay constant proportional to the mass per unit area, m_i, of the specimen, so that:

$$I_i = I_h \exp(-\xi m_i) \tag{2}$$

where I_h is intensity in the absence of a sample (or that transmitted by a hole, hence the subscript h) and ξ is a materials constant. The transmitted intensity will change if we change m_i by (i) varying the sample thickness at constant density or (ii) by introducing voids into the sample at constant thickness (the two situations have been shown to be equivalent for crazed amorphous polymers[13,14]). In the case of a voided sample, the void content is:

$$v_i = 1 - \frac{m_i}{m_f}$$

where m_f is the mass per unit area of an unvoided film, so that from equation (2):

$$v_i = 1 - \frac{\ln(I_i/I_h)}{\ln(I_f/I_h)} \tag{3}$$

v_i may be determined directly from measurements of the transmitted beam intensity[14], or else indirectly by densitometry of a TEM photographic (negative) plate[13], which is the method we used here. Densitometry of TEM plates is based on the assumption of a linear relationship between the contribution to the optical density of the plate from the electrons and the total beam dose locally, which can only be justified where the plate is far from saturation (i.e. when the plate is underexposed): when this condition is fulfilled, results consistent with other techniques are obtained.

If the local beam-induced change in optical density of the plate is Φ_i, then[13]:

$$v_i = 1 - \frac{\ln(\Phi_i/\Phi_h)}{\ln(\Phi_f/\Phi_h)} \tag{4}$$

The local optical density of the TEM plate is $\Phi_{i+p} = \Phi_i + \Phi_p$, where Φ_p is the optical density of a developed, unexposed plate. Thus the transmitted intensity J_i of a light beam of incident intensity J_0 passing through the plate will be:

$$J_i = J_0 \exp[-(\Phi_i + \Phi_p)] \tag{5}$$

In our present set-up we used a television camera to digitize a TEM plate placed on a light table, giving a 256 grey-level image with $G_i \sim J_i^{\gamma}$, where G_i is the local grey-level and γ depends on the camera (it is usually about 0.4 for non-specialized equipment[15]). The non-linearity of the camera can be measured and corrected for using a suitable look-up table (LUT) during subsequent image analysis. However, where the exponential relationship between G_i and J_i holds:

$$\Phi_i + \Phi_p = -\ln\left(\frac{J_i}{J_0}\right) = -\frac{1}{\gamma}\ln\left(\frac{G_i}{G_0}\right)$$

and similarly

$$\Phi_i = \frac{1}{\gamma}\ln\left(\frac{G_p}{G_i}\right) \tag{6}$$

where G_p is the grey-level of an unexposed plate, and G_0 is the grey-level in the absence of the plate. Hence in terms of a grey-level image of a TEM plate, and regardless of γ:

$$v_i = 1 - \frac{\ln[\ln(G_p/G_i)/\ln(G_p/G_h)]}{\ln[\ln(G_p/G_f)/\ln(G_p/G_h)]} \tag{7}$$

(the subscripts f and h refer to parts of the image or images corresponding to the unvoided film and holes as previously).

For a voided film with a thickness of the order of, or very much less than, the void sizes and spacings, G_h and G_f can be estimated by selecting a suitable area of the image (if holes cannot be detected unambiguously, a second plate exposed without the specimen at the same condenser settings can be used). G_p can be taken from the unexposed regions at the edge of a given plate. The overall void content, v, of a film of uniform thickness may then be estimated by averaging v_i over the whole image. Since the number of pixels in a typical image is likely to be very much greater than the total number of grey-levels, this is done most efficiently by constructing an LUT giving a value of v_i calculated from equation (7) for all possible values of G_i, thus avoiding redundant floating-point operations. The software also allowed for selection of arbitrarily shaped subregions of the image and generation of a grey-level or false colour 'map' of the local void content: the grey-level in the original image is substituted by $v_i \times 255$, as shown in *Figure 3*, obtained from the image of *Figure 2*. v obtained from optical densitometry was $9 \pm 0.5\%$, which is in reasonable agreement with the value of 9.3% obtained by the stereographic method.

Comparison with other techniques. Results for the foams from different 3FDA/PMDA/PMS graft copolymers are given in *Table 1*. (Density column measurements proved difficult for these materials owing to the relatively high degree of interconnectivity of the voids, and have not been included in the table.) The results all showed roughly the same trend, with void content increasing with the initial content of PMS, and where well defined spherical voids existed in the samples, the TEM methods appeared consistent. The quantitative disagreement between the TEM results and those from i.r. may be accounted for in several ways. First, for void sizes in the micrometre range, caused by blowing of the softer thermally imidized matrices, there may be significant scattering at i.r. wavelengths, which makes the absorption technique less reliable. Second, at high void contents, microtome damage and void collapse during preparation may have an adverse effect on the TEM results. Finally, the i.r. technique will tend to give an average value of the void content for the whole film, whereas the TEM techniques involve a very much smaller sample volume. Thus, if there is an inhomogeneous distribution of void content, either through thickness or in the plane of the films, care must be taken when comparing results from the different methods. In such cases (and we believe inhomogeneity to be a major source of discrepancy in the results of *Table 1*), TEM should be considered a complementary technique to i.r. in that it allows characterization of the void content distributions, but is less suited to obtaining mean values for the void content.

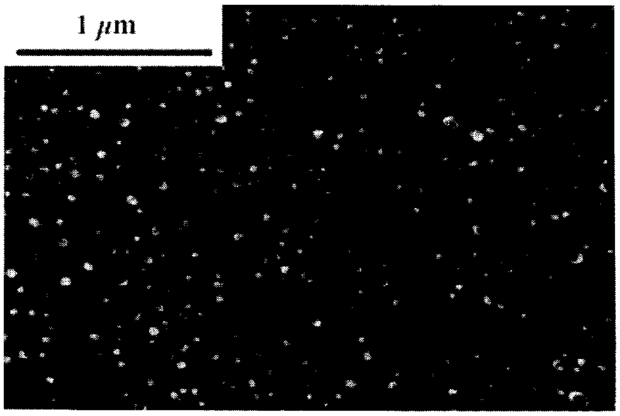

Figure 3 Distribution of v_i calculated from the image of *Figure 2* (the grey-level is given by $v_i \times 255$)

For the foams from the 3FDA/PMDA/PPO triblock copolymers, chemical imidization was used throughout, and the void sizes were correspondingly small (about 20 nm). The void structure was in fact very close to that of the original phase-separated morphology and hence relatively little spatial inhomogeneity was anticipated. The voids were not spherical, so that stereographic methods were inappropriate, but since the void sizes were in all cases very much less than i.r. wavelengths and there was little interconnectivity, both the i.r. and the density measurements were believed to be more reliable than in the case of the 3FDA/PMDA/PMS foams. As shown in *Table 2*, we did indeed find much improved agreement between the results of the various techniques.

Conclusions

TEM has been used to determine the porosity of polymer nanofoams produced by thermal decomposition of the thermally labile component of different graft copolymers. The results are compared with those obtainable by i.r. spectroscopy and density gradient methods, showing quantitative agreement for small pore sizes. Porosity measurements by stereography of TEM images of microtomed samples is limited to samples with relatively simple morphologies and is time-consuming. On the other hand, the same information can be obtained more efficiently and for a wider variety of structures by optical densitometry of the TEM negatives. This method thus offers a practical means of obtaining much higher spatial resolution than i.r. spectroscopy and is better suited to structures which scatter strongly at i.r. wavelengths. It may also provide an alternative

Table 1 Results for foams from different 3FDA/PMDA/PMS graft copolymers (block lengths all 18 000 g mol^{-1})

Imide form and imidization route	PMS content (wt%)	Approx. void size (nm)	Void content (%)		
			I.r.	TEM stereography	TEM densitometry
Meta, chemical	15	40	8	9	9
Meta, chemical	25	40	29	–	20
Meta, thermal	14	1200	22	10	11
Meta, thermal	23	1200^a	24	–	22
Para, thermal	27	1200	28	28	27

^{a}The microstructure here was highly interconnected and a void size was hard to define

Table 2 Results for foams from different *meta* 3FDA/PMDA/PPO triblock copolymers (all chemically imidized with void sizes of approximately 20 nm)

Block length (g mol^{-1})	PPO content (wt%)	Void content (%)		
		Density column	I.r.	TEM densitometry
2300	10	9	–	10
2300	23	16	–	18
5600	15	13	–	12
5600	24	18	–	19
3500	15	14	13	14
3500	25	18	20	19

means for the characterization of two-component phase-separated systems, given a knowledge of the electron scattering cross-sections of the different phases.

References

1 Carey, D. H. *IEEE Micro* 1993, **13**, 19
2 Garrou, P. *Proc. IEEE* 1992, **80**, 1942
3 Tummala, R. R. and Rymaszewski, E. J. 'Microelectronics Packaging Handbook', Nostrand Reinhold, New York, 1989
4 Charlier, Y., Hedrick, J. L., Russell, T. P., Swanson, S., Sanchez, M. and Jerome, R. *Polymer* submitted
5 Hedrick, J. L., Labadie, J. W., Russell, T. P. and Volksen, W. *Polymer* 1993, **34**, 22
6 Hedrick, J. L., DiPietro, R., Plummer, C. J. G., Hilborn, J. G. and Jérome, R. *Polymer* in press
7 Hedrick, J. L., Charlier, Y., DiPietro, R., Jayaraman, S. and McGrath, J. E. *J. Polym. Sci., Polym. Chem. Edn* in press
8 Russell, T. P. *Polym. Eng. Sci.* 1984, **24**, 345
9 Dullien, F. 'Porous Media: Fluid Transport and Pore Structure', Academic Press, New York, 1979
10 Sanchez, M. I., Hedrick, J. L. and Russell, T. P. *J. Polym. Sci., Polym. Phys. Edn* 1995, **33**, 253
11 Maestrini, C., Merlotti, M. and Vighi, M. *J. Mater. Sci.* 1992, **27**, 599
12 Underwood, E. E. 'Quantitative Stereology', Addison-Wesley, Reading, MA, 1970
13 Lauterwasser, B. D. and Kramer, E. J. *Phil. Mag.* 1979, **39A**, 469
14 Brown, H. R. *J. Mater. Sci.* 1979, **14**, 237
15 Jähne, B. 'Digital Image Processing', Springer Verlag, Berlin, 1993