Table 2a $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N = 10$

	$\langle P_2(\cos\theta)\rangle$		$\langle P_4(\cos\theta)\rangle$		
λ	Equation (19)	Numerical calculation	Equation (19)	Numerical calculation	*FEF*
3.5	0.339	0.335	0.185	0.183	0.099
4.0	0.422	0.417	0.287	0.281	0.213
4.5	0.486	0.481	0.366	0.358	0.301
5.0	0.537	0.534	0.429	0.423	0.371
7.5	0.692	0.688	0.620	0.611	0.581
10.0	0.769	0.766	0.715	0.707	0.685
15.0	0.846	0.844	0.810	0.804	0.790
20.0	0.884	0.883	0.857	0.853	0.842

Table 2b $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N = 50$

	$\langle P_2(\cos\theta)\rangle$		$\langle P_4(\cos\theta)\rangle$		
λ	Equation (19)	Numerical calculation	Equation (19)	Numerical calculation	*FEF*
8.0	0.354	0.355	0.203	0.206	0.116
10.0	0.483	0.483	0.362	0.363	0.293
15.0	0.655	0.655	0.575	0.575	0.529
20.0	0.741	0.742	0.681	0.681	0.647
25.0	0.793	0.793	0.745	0.744	0.717
30.0	0.828	0.827	0.787	0.787	0.764

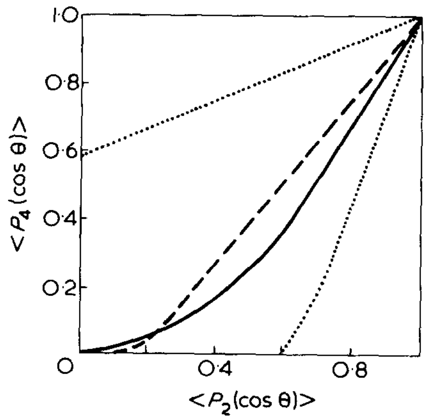

Figure 1 $\langle P_4(\cos\theta)\rangle$ as a function of $\langle P_2(\cos\theta)\rangle$. · · · · · · · , Upper and lower bounds on $\langle P_4(\cos\theta)\rangle$ for a given value of $\langle P_2(\cos\theta)\rangle$; ———, pseudo-affine rigid rod rotation theory; – – – –, modified rubber theory, present work

DISCUSSION

Despite the simplicity of the basic rubber model employed and the assumptions made to extend it to draw ratios $>\lambda_c$, the values predicted for both $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ have been shown to be in reasonably good agreement with experimental determinations of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for poly(ethylene terephthalate) drawn at 80°C, provided that the value of N is chosen appropriately, and a simple method of determining N has been given[6].

If samples drawn under similar conditions to a wide range of draw ratios are not available, it is possible to form some idea of whether the present model for the production of orientation is applicable by comparing the relationship between the values of $\langle P_4(\cos\theta)\rangle$ and $\langle P_2(\cos\theta)\rangle$ observed with that predicted by the present model and with that predicted by the other model frequently used in discussing the development of orientation, the pseudo-affine rigid rod rotation model[7]. *Figure 1* shows the mathematical limits on $\langle P_4(\cos\theta)\rangle$ for a given $\langle P_2(\cos\theta)\rangle$, together with the relationship between these quantities predicted on the basis of the pseudo-affine model and on the basis of equations (9), (18) and (19). Equations (9) and (18) have been used in the limit N, $\lambda \to \infty$ with $x = \lambda^2/N$ finite, but evaluation for finite N as low as 5 by the numerical method shows differences in the predicted $\langle P_4(\cos\theta)\rangle$ only of order 10^{-3}, and these occur only for $\langle P_2(\cos\theta)\rangle$ less than about 0.2.

ACKNOWLEDGEMENTS

We would like to thank Professor Ward for useful discussions and the SRC for providing a studentship for one of us (J. H. N.).

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Cell cracking in open cell rigid polymeric foams

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(Received 19 December 1977; revised 16 May 1978)

INTRODUCTION

Water-soluble inorganic salts dispersed in polymers can be leached out by subjecting the polymer/salt particles to immersion in water. The leaching method was employed by Fossey and Smith[1] to produce polyethylene foams and by Gregorian[2] to prepare cross-linked microporous polyolefin films. Nielsen and Lee[3] studied the mechanical properties of polystyrene filled with ground rock salt and polystyrene foams produced by extracting the salt with water. A similar technique was used by Smith[4] to prepare polyurethane foams, and has also been applied to the manufacture of microcellular

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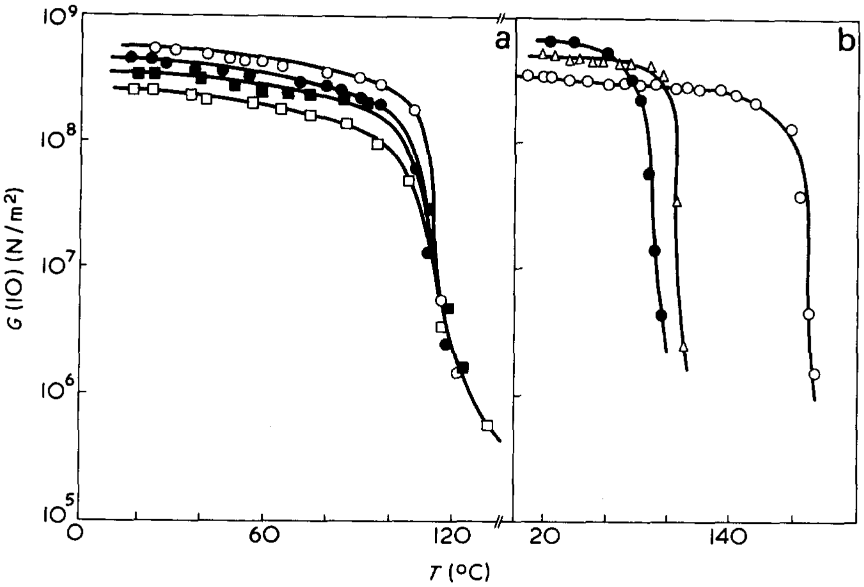

Figure 1 10 sec shear moduli determined by the Clash–Berg technique for: (a) PMMA forms (○, void fraction = 0.05; ●, void fraction = 0.11; ■, void fraction = 0.22; □, void fraction = 0.33); (b) ○, PS form; △, SAN foam; ○, PSF foam. All contained 0.21 void fraction

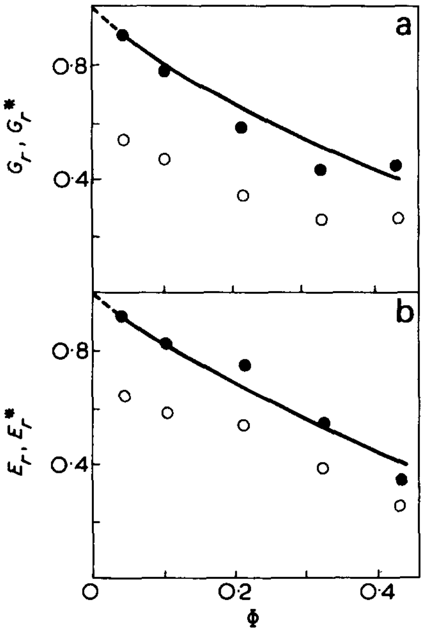

Figure 2 (a) Relative shear moduli of PMMA foams: ○, experimental values (G_m = 10^9 N/m^2); ●, corrected values based on G_m^* = 6.8 x 10^8 N/m^2. (b) Relative tensile moduli of PMMA foams: ○, experimental values (E_m = 31.2 x 10^8 N/m^2); ●, corrected values based on E_m^* = 22 x 10^8 N/m^2. Solid lines correspond to equation (1)

polyurethane sheet materials.[5] The role of the salt is to act as a temporary filler giving, upon its removal, a cellular polymer having interconnected cells. By proper selection of the temporary filler one can introduce cells of desired shape and size. The limitiations of this method according to Thomas[6] stem from its applicability to the production of only open cell flexible foams.

Narkis and Joseph[7] studied glassy polymeric foams produced by salt extraction showing that this method is suitable for the preparation of rigid as well as flexible foams. Essentially open cell foams having an irregular cracked cell structure were formed. These samples are studied further in the present work with reference to the effects of void content and temperature on their elastic properties.

EXPERIMENTAL

The foamed samples were prepared by mixing the polymer [commercial poly(methyl methacrylate), PMMA; polystyrene, PS; styrene–acrylonitrile copolymer, SAN; and polysulphone, PSF] with a given amount of salt particles (105–210 μm) on a two-roll mill for approximately 15 min at 180°C for the PMMA, PS and SAN samples, and at 250°C for the PSF samples. The resulting milled sheet was cut and moulded to a thickness of about 3.2 mm. Specimens cut from these sheets were soaked in water for periods of several months. All samples were initially immersed in water at 50°C for three months. The water temperature was then gradually increased to 80°C for an additional three months. Exceptionally, polysulphone samples were soaked in boiling water for another three months following the 50°C extraction.

Tests of tensile strength at room temperature were performed using an Instron universal tester at a crosshead speed of 2 mm/min. Torsional experiments were performed using a Clash–Berg torsional stiffness apparatus. The torsion angle was detected 10 sec after application of the torque, according to the test procedure of Tobolsky[8]. Porosity measurements were performed with an Aminco–Winslow mercury porosimeter.

RESULTS AND DISCUSSION

The open cell structure of the foam is likely to be obtained during the leaching cycle by an osmotic pressure great enough to burst the thin cell walls. In a previous publication[7] it has been shown that these glassy polymeric foams have a highly cracked structure formed during the extraction process, this being indicated by the ultimate tensile properties.

In *Figure 1a* Clash–Berg shear isochronal modulus–temperature curves (G vs T) for PMMA samples containing different void contents are shown.

From this plot, according to the 'Tobolsky method' the glass transition temperature (T_g) of a material can be calculated. T_g is defined, in this case, as the temperature corresponding to the following value of the modulus:

$$\log G(K) = \frac{\log G_1 + \log G_2}{2} \qquad (1)$$

where G_1 and G_2 are the values of the moduli corresponding to the glassy and the rubbery plateau, respectively, and K

Table 1 Comparison between the volumetric fraction of the salt content (ϕ_{salt}) and the volumetric fraction of mercury penetrated (ϕ_{mercury}) into a foamed specimen

	ϕ_{salt}	ϕ_{mercury}
PMMA	0.432	0.506
PMMA	0.22	0.31
PMMA	0.053	0.159

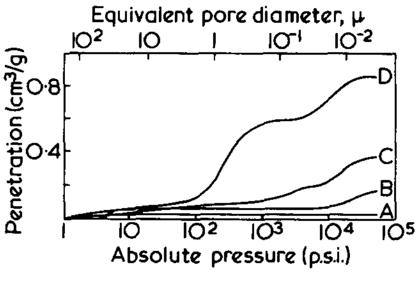

Figure 3 Porosity measurements: A, solid PMMA; B, PMMA foam, void fraction = 0.055; C, PMMA foam, void fraction = 0.223; D, PMMA foam, void fraction = 0.443

is a fixed time after starting the experiment. As suggested from Tobolsky we have measured the shear modulus after 10 sec, $G(10)$.

From *Figure 1a* it can be seen that an increase in the void content results in lower values for the moduli, while the glass transition temperature is practically unchanged. A similar conclusion regarding the transition region is obtained by analysing *Figure 1b* which shows the modulus–temperature curves for PS, SAN and PSF foams all containing about 21% voids. Taking temperature readings (*Figure 1*) corresponding to a shear modulus value of 10^7 N/m^2 [8] the following results indicative of the glass transition temperatures are obtained: PMMA – 115°C; PS – 92°C; SAN – 105°C; PSF – 190°C. These values are in good agreement with values of T_g for such polymers in the literature[9].

In *Figure 2a* the relative values of the shear modulus G_r for PMMA foams are shown as open circles. The value of G_m for the virgin unfilled polymer is 10^9 N/m^2 and the Poisson ratio, ν_m, is taken as 0.3. In this Figure a line corresponding to the Kerner equation is also shown.

The specific Kerner equation for foams can be expressed as follows[10]:

$$\frac{E_m}{E_c} = \frac{G_m}{G_c} = 1 + \frac{15(1-\nu_m)}{7-5\nu_m}\,\frac{(1-\phi_m)}{\phi_m} \tag{2}$$

In this equation E_c, G_c and E_m, G_m are the elastic and shear moduli of the foamed material and of the unfoamed matrix respectively, ν_m is the Poisson ratio of the matrix, and ϕ_m is the volume fraction of polymer in the material.

It can be seen that all the experimental data lie appreciably below the theoretical prediction. In the previous work[7] a dramatic reduction in the tensile strength was also found in 5% void-containing PMMA foams compared with void-free solid PMMA. This effect was explained on the basis of a cracked structure which is formed during the long extraction step by large internal forces developed by the high osmotic pressures. A similar model is appropriate to describe the behaviour of the elastic modulus reported in *Figure 2*. Assuming that the present system is formed as a foamed–cracked structure in which the crack matrix has a shear modulus G_m^*, the corrected relative shear modulus G_r^* is given by G_c/G_m^*. G_m^* is calculated for the PMMA foam containing 5% voids as:

$$G_m^* = G_c\left[1 + \frac{15(1-\nu_m)}{7-5\nu_m}\,\frac{(1-\phi_m)}{\phi_m}\right] \tag{3}$$

giving a value of 5.8×10^8 N/m^2. Using this new value, apparently representing the elastic modulus of the cracked matrix, the values of G_r^* for the other experimental points can be calculated. These points are shown as filled circles (●) in *Figure 2a* and a line connecting them gives good correlation with the theoretical Kerner equation line. A similar approach has been used for the tensile elastic modulus of the same materials again giving good agreement with theoretical prediction. In this case the value of E_m is 31.2×10^8 N/m^2 and the corrected E_m^* is 22×10^8 N/m^2.

It is possible to conclude from the strength properties, as well as from the elastic properties, that foams produced by salt extraction can be modelled as composite systems comprising voids dispersed in a cracked matrix. Such a model is expected to behave like an open cell structure as suggested by several authors[1,6,7]. In order to verify such a model experimentally some preliminary experiments were undertaken using a mercury porosimeter. With this instrument the amount of mercury penetrating into a known sample as a function of an applied pressure can be measured. This technique also permits the calculation of the fraction of voids (ϕ) to which the mercury can penetrate, giving information on the degree of open cell structure. *Table 1* shows that the volumetric fraction of mercury penetrated into a foamed specimen is always larger than the original volumetric fraction of the salt content. This confirms that the proposed foamed/cracked structure is in agreement with the mechanical data, since the rather higher values found with the porosimeter can be attributed to the presence of cracks in addition to the voids vacated by the salt particles. Some typical integral porosity curves taken from the preliminary experiments are shown in *Figure 3*. The shape of these curves indicates the presence of a void distribution curve consisting of two different groups of cavities. These porosity curves can be also represented in a differential way (not shown here) giving two maxima which can probably be attributed to a structure containing large voids interconnected by cracks.

Additional microscopy and porosity studies are in progress to complete the understanding of these foamed/cracked structures.

ACKNOWLEDGEMENT

The authors with to thank Mr E. Joseph for preparing the foamed samples.

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