Notes to the Editor

Visual evidence of clustering of water in glassy polymers

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Publication of the paper by Pogany[1] on craze formation, whitening, and resultant anomalous diffusion of water in polystyrene and epoxy resins after immersion in water at elevated temperatures prompts the author to submit this Note describing some phenomena observed here during the development of a plastic carbonated beverage container.

The initial observation was that transparent bottles blow moulded from an acrylonitrile/methyl acrylate/butadiene copolymer (79/15/6%)[2], packed with a carbonated cola drink, and stored for two weeks at room temperature, became almost opaque after they had been emptied and allowed to dry out. Preliminary investigation showed that compression moulded films of the same material became opaque after immersion in warm water for a short period of time (1 h at 40°C) (*Figure 1*). Examination of dried bottle walls by optical microscopy revealed (*Figure 2*) the presence of numerous voids with diameters of the order of 1 μm in the walls of bottles which had been immersed in warm water for a short time (20 min at 60°C), whereas in the walls of bottles which had been held at 0% relative humidity (r.h.) since production (*Figure 3*) very few such voids could be seen. Further investigation by scanning electron microscopy of both free (inside) surfaces (*Figures 4* and *5*) and fracture surfaces (*Figures 6* and *7*) of dried bottle walls clearly showed that immersion in warm water for a short time (20 min at 60°C) greatly increased the mean size of voids throughout the wall structure. (*Figures 4* and *5* show voids covered by a thin skin which ballooned out as the void grew. In the upper right quadrant of *Figure 5* can be seen one such void whose ballooning skin apparently burst, revealing the void itself.) Thus, while voids existed even in the wall of a bottle which had been stored at 0% r.h. between its production and examination (*Figures 3, 5* and *7*), they are of a size (about 0.1 μm) which is relatively inefficient in scattering light. The bottle from which this sample was taken was quite transparent. Upon exposure to moisture, however, (*Figures 2, 4* and *6*) the voids increased to a size approximately equal to the wavelength of visible light (about 0.6 μm average), which is the size most efficient in scattering light[3]. The bottle wall from which this sample was taken was noticeably translucent. [Care must be taken in interpreting the optical micrographs (*Figures 2* and *3*) in this area, since firstly, 0.1 μm voids are too small

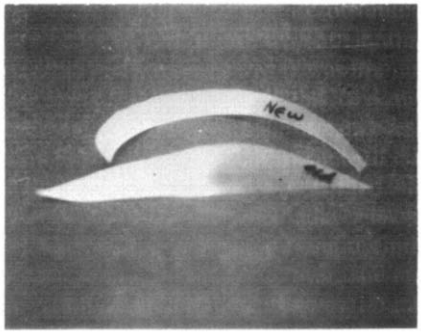

Figure 1 Compression moulded films of acrylonitrile copolymer which had been partly immersed in water for 1 h at 40°C. 'New' and 'old' refer to different lots of resin

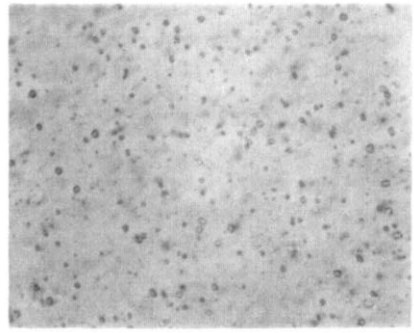

Figure 2 Optical photomicrograph (1000 X) of wall of blow-moulded bottle which had been immersed in water for 20 min at 60°C

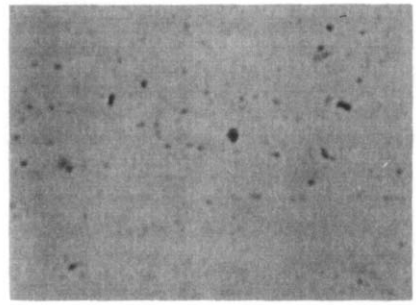

Figure 3 Optical photomicrograph (1000 X) of wall of blow-moulded bottle which had been kept at 0% r.h. for 1 week, between production and examination

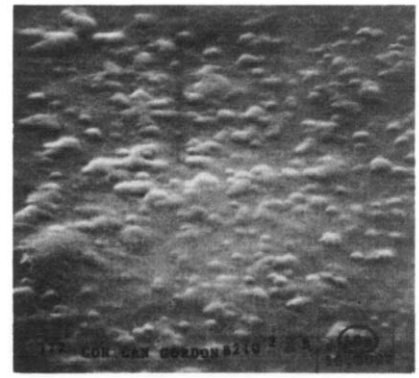

Figure 4 Scanning electron micrograph (10 000 X) of free (inside) surface of wate treated bottle of *Figure 2*

Figure 5 Scanning electron micrograph (10 000 X) of free (inside) surface of desiccated bottle of *Figure 3.*

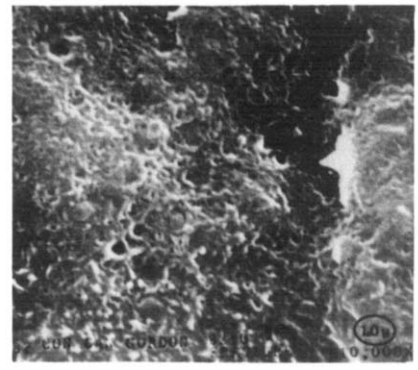

Figure 6 Scanning electorn micrograph (10 000 X) of fracture surface (cross-section) of water treated bottle of *Figure 2*

Figure 7 Scanning electron micrograph (10 000 X) of fracture surface (cross-section) of desiccated bottle of *Figure 3*

to be resolved optically; and secondly, in transparent media in the absence of objects in the plane of focus, out-of-focus objects from other planes assume unwarranted prominence. Scanning electron micrographs do not pose these problems, because of greater resolution of the instrument, and because only surfaces can be observed.]

It is interesting to note (*Figures 4* and *5*) that there does not seem to be any great difference in the number of voids present before and after treatment, except where small voids, during growth, may have fused to form large elongated voids. Thus, the opacification seems to have resulted essentially entirely from the growth of pre-existing voids in the transparent bottle walls, with no evidence of the formation of new voids.

It was shown originally by Zimm and Lundberg[4], and since then by many others[5–12], that the diffusion of water in many polymers is not Fickian, but that the water molecules tend to be immobilized in clusters, rather than to diffuse individually through the polymer. In such systems, water–water interactions tend to be favoured over water–polymer interactions, and thus water molecules tend to cluster. Clustering could well be facilitated by the existence of voids such as those observed here; growth of the voids in the presence of moisture could then occur by accretion of more water molecules to the nascent clusters. In any case, it is clear that the voids are related to the presence of water, since opacification of the bottle wall occurred only after the bottle had been emptied of its aqueous contents and allowed to dry out.

This leaves the question of how the original voids were formed, a question which the observations described above were not intended to answer. It may be noted, however, that on being informed of the problem, the material supplier was able to modify its procedures in such a way as to essentially eliminate the whitening problem in bottles produced subsequently.

REFERENCES

1 Pogany, G. A. *Polymer* 1976, **17**, 690
2 Salame, M. *Preprints ORPL Div. Am. Chem. Soc. 164th Meeting New York* **9/72**, 113
3 Condon, E. U. 'Handbook of Physics', 2nd Edn. (Eds E. V. Condon and H. Odishaw), McGraw-Hill, New York, 1967, Ch 6, pp 6–128
4 Zimm, B. H. and Lundberg, J. L. *J. Phys. Chem.* 1956, **60**, 425
5 Barrer, R. M. and Barrie, J. A. *J. Polym. Sci.* 1958, **38**, 377
6 Yasuda, H. and Stannett, V. *J. Polym. Sci.* 1962, **57**, 907
7 Barrie, J. A. and Platt, B. *Polymer* 1963, **4**, 303
8 Stannett, V. and Williams, J. L. *J. Polym. Sci. (C)* 1966, **10**, 45
9 Wellons, J. D. and Stannett, V. *J. Polym. Sci. (A-1)* 1966, **4**, 593
10 Williams, J. L., Hopfenberg, H. B. and Stannett, V. *J. Macromol. Sci. (B)* 1969, **3**, 711
11 Orofino, T. A. Hopfenberg, H. B. and Stannett, V. *J. Macromol. Sci. (B)* 1969, **3**, 777
12 Starkweather, Jr, H. W. *Macromolecules* 1975, **8**, 476

Molecular weight of SAN copolymers: values of the constants for viscometric determination

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Determination of molecular weights of polymers by viscometry applying the formula $[\eta] = KM^{\alpha}$ offer an easy, quick and fairly accurate method.

K and α values for SAN polymers containing 24 wt % and 54 wt % of acrylonitrile (AN) using methyl ethyl ketone (MEK) as solvent are known in literature[1]. We have found that the reported K and α values ($K = 3.6 \times 10^{-4}$ and $\alpha = 0.62$) for SAN containing 24% AN are not applicable for SAN containing 27% AN which conforms to Type III of the ASTM specifications[2]. The values of K and α for SAN containing 27% AN were therefore determined and are reported here.

EXPERIMENTAL

SAN, prepared by suspension polymerization was first purified by dissolving in MEK followed by precipitation with excess methanol and drying *in vacuo* at 45°–50°C. This purified SAN was analysed and found to contain 27% AN; the weight-average molecular weight ($\bar{M}_w$), as determined by light scattering was found to be 230 000. The sample was then fractionated by precipitation using MEK (solvent) and methanol (non-solvent) at 30°C. The fractions were isolated by centrifuging (15 000 r.p.m.) and vacuum dried at 45°–50°C. Each fraction was separately dissolved in purified MEK to prepare a 0.6 to 0.7% solution and the viscosity determined at 30°C at different dilutions using an Ubbelohde

Table 1 Intrinsic viscosities and molecular weights of SAN fractions

Sample fraction	Fraction (wt %)	ACN content (wt %)	$[\eta]$	Average $\bar{M}_w$ by light scattering method
Unfractionated Sample		27.0	–	230 000
I	7.20	27.2	1.74	549 000
II	14.26	26.9	1.22	357 000
III	9.56	27.0	1.12	312 000
IV	21.54	26.95	0.84	208 000
V	20.05	26.5	0.724	166 000
VI	13.04	26.95	0.66	129 000
VII	14.35	27.5	0.437	80 000