JOURNAL OF MATERIALS SCIENCE LETTERS 5 (1986) 1213–1215

Simultaneous residual stresses and crystallinity changes during ageing of polyoxymethylene

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Physical ageing of polymers is a well-known phenomenon reflected in structural, physical and mechanical property changes while the polymer gradually approaches its state of equilibrium [1]. Crystallizable thermoplastics exhibit upon ageing changes in properties the extent of which mainly depends on the polymer's thermal and mechanical history. Usually, physical ageing in crystallizable polymers has been related to structural changes such as volume relaxation and secondary crystallization. Coxon and White [2] have recently reported on another ageing effect related to partial relaxation of residual stresses in injection-moulded polypropylene. The stress levels were found to be markedly reduced upon ageing at a temperature as low as -40° C (below T_g). Furthermore, they have suggested that in semicrystalline polymers ageing may proceed even after annealing at elevated temperatures.

Polyoxymethylene (POM), an engineering semicrystalline thermoplasic, exhibits a relatively high degree of crystallinity. Its structure, morphology and mechanical behaviour are sensitive to mechanical and thermal history [3–5], which is especially pronounced in injection-moulded articles. In addition, POM is expected to exhibit post-moulding warpage, dimensional changes and even cracking, the extent of which strongly depends on moulding process parameters such as melt and mould temperature and injection rate and pressures. Hammer *et al.* [6] have found that unstable low levels of crystallinity produced by quenching of POM increase rapidly on exposure to room temperature which is high above the polymer T_g [7]. Moreover, quenching of a polymer from elevated temperature results in the build up of residual stresses (e.g. [8, 9]), the level of which depends on the initial and final temperatures, the crystallization and glass transition temperatures and the Biot number, which takes into account the specimens dimensions, thermal diffusivity and heat transfer coefficient. These residual stresses may be an additional source for the observed changes occurring on ageing of POM [3, 5].

The objective of the present work is to investigate simultaneously the room-temperature ageing effect on the residual stresses profile and the degree of crystallinity in a quenched POM.

Polyoxymethylene (Delrin 150, Dupont) granules were injection moulded to form 110 mm × 110 mm × 5 mm plates. The plates were first annealed at elevated temperature to relax all stresses and then slowly cooled to room temperature. Bars 10 mm × 110 mm in dimension were cut from the plates and were placed in an aluminium mould to avoid any distortions during the quenching experiments. The mould was constructed with six rectangular cavities, to accommodate the POM bars. Following the insertion of dry bars, the mould was tightly closed and then heated in an oven to 180° C ($> T_m$). Quenching was carried out by immersion of the mould into an ice–water bath. The residence time in both oven and bath was sufficient to attain a uniform desired temperature through the bars thickness. The quenched bars were demoulded and left to age at room temperature up to 150 days.

Residual stresses were measured by the "layer removal" method, described by Treuting and Read [10]. The experimental procedure was described elsewhere [9]. The same "layer removal" method was also utilized to measure the through-the-thickness degree of crystallinity gradient in the POM bars. Per cent crystallinity was determined using wide-angle X-ray diffraction in the reflection mode. To verify the applicability of this procedure the crystallinity gradient in annealed bars was determined. A constant level of $82 \pm 2\%$ crystallinity was obtained, which is satisfactorily within the accuracy limits of the X-ray degree of crystallinity determination.

Residual stress profiles (stress against distance from the specimen's centre) of POM specimens having an initial uniform temperature profile of 180° C and quenched to ice–water temperature followed by ageing at room temperature are depicted in Fig. 1. The quenching of a melt to a temperature below the crystallization temperature resulted in the build up of compressive stresses in the surface layers and tensile stresses in the inner layers, as predicted by the thermoelastic theory [11] and previously observed in amorphous (e.g. [9]) and semicrystalline polymers [2, 12]. However, the profiles include unbalanced compressive and tensile stresses. Upon ageing the surface compressive stresses first increase to rather high values, attaining a maximum value of about 50 MN m^{-2}, after 120 days at room temperature, followed by a large decline upon further annealing. Simultaneously, the tensile stresses at the centre increased with ageing; however, the changes measured are quite small, between 5 and 15 MN m^{-2}. It should be mentioned that all residual stresses were calculated, for practical reasons, on the basis of a uniform and constant elastic modulus, which is not the case in any quenched polymer [13], especially not in the presently studied system. Because the modulus value was taken as that of a quenched specimen the reported residual stresses (Fig. 1) are actually underestimated.

The application of the "layer removal" method for

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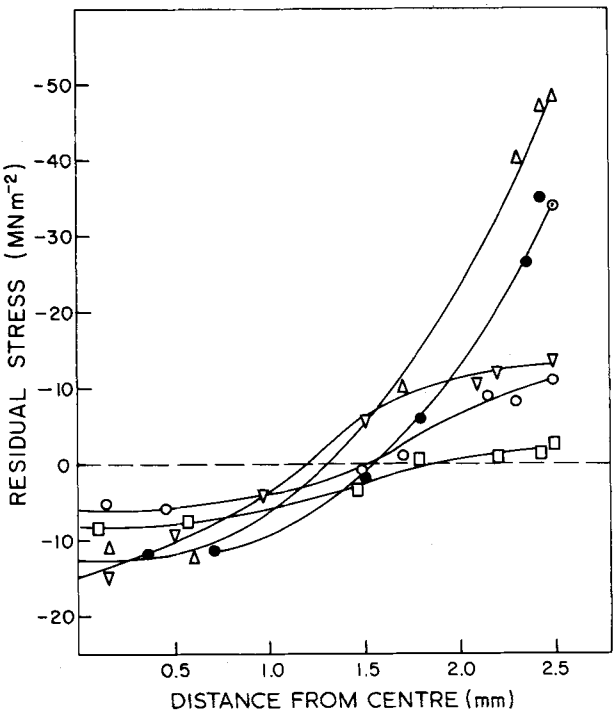

Figure 1 Residual stresses through the thickness distribution in POM quenched from 180 to 0° C and aged at room temperature for various lengths of time (days): (□) 30, (○) 60, (●) 90, (△) 120, (▽) 150.

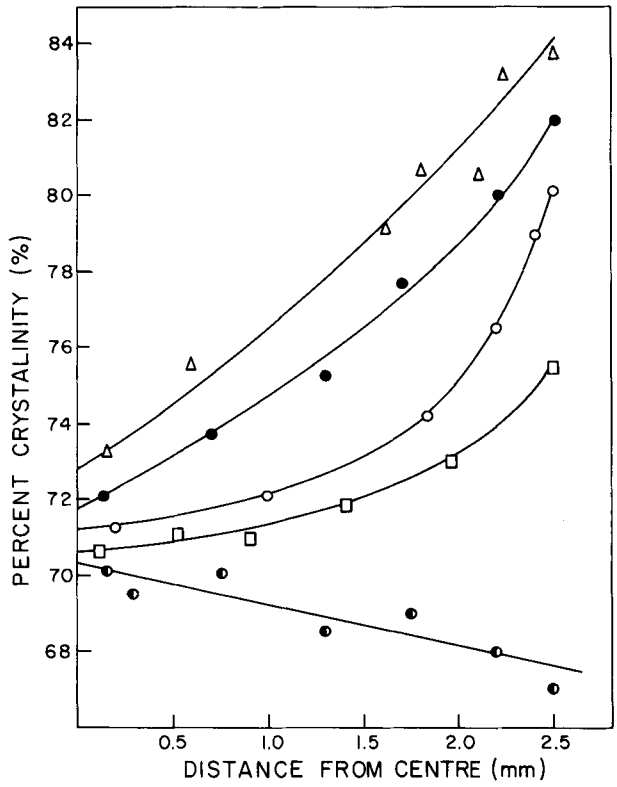

Figure 2 Degree of crystallinity through the thickness distribution in POM quenched from 180 to 0° C and aged at room temperature for various lengths of time (days): (◐) 0, (□) 30, (○), 60, (●) 90, (△) 120.

measuring the degree of crystallinity profile in POM plates was found to be a very powerful means of determining the crystallinity distribution. Crystallinity values reported in the literature are usually either average values obtained by such methods as calorimetry, density and transmission X-ray diffraction, or values characteristic of the surface, obtained for example by X-ray diffraction in the reflection mode.

As seen in Fig. 2, the initial crystallinity following quenching of POM specimen is highest at the centre and gradually decreases toward the surface. This expected profile stems from the low heat conduction of the polymer which results in lower cooling rates with increasing distance from the surface. Upon ageing, the degree of crystallinity increases throughout the material, but at a much higher rate at the surface layers than in the interior. In agreement with the literature [6], the unstable lower crystallinity in the surface layers increases to higher levels compared to the more stable interior layers. Consequently, the slope of the crystallinity profile changes from a negative to a positive one attaining its equilibrium value after ageing for 120 days at ambient temperature. The crystallinity after 150 days ageing was found to be very similar to the one obtained already after 120 days. The rather large changes observed in the POM crystallinity and its distribution are quite surprising, especially because of the relatively low ageing temperature at which they occur (150° C below T_m).

Because the midplane tensile stresses as well as the degree of crystallinity in this region do not change to a large extent during ageing whereas those at the surface layers are highly dependent on ageing, the latter are depicted in Fig. 3. The surface compressive stresses sharply incline on ageing up to 120 days, and upon further ageing decline to a rather low level. Simultaneously, the surface degree of crystallinity gradually increases and levels off after 120 days ageing. It is interesting that the observed relaxation of residual stresses occurs following completion of the crystallization process. Annealing at elevated temperatures is expected to expedite both the crystallization and the stress relaxation processes.

In the system studied here, two major processes occur simultaneously upon ageing. On the one hand, room temperature "annealing" of the ice–water quenched POM provides a path to an overall system of lower free enthalpy. This is the result of secondary crystallization processes which include further crystallization of amorphous macromolecules (or portion of molecules) as well as crystal perfection including the decrease in defect concentration, crystal stress relief and changes in crystal size. These processes are especially encouraged in systems that because of quenching involve poorly crystallized macromolecules which are exposed to temperatures above T_g [14]. As a result of the relative low ageing temperature, the rate of the secondary crystallization is rather low compared to that observed at elevated temperatures [6]. In addition, the occurrence of this secondary crystallization process at low temperatures results in the build up of internal stresses. As seen in Fig. 3, higher stresses were measured in regions of greater crystallinity. These stresses probably act in turn as an additional driving force for further cyrstallization. The build up of internal stresses during crystallization at relatively low temperatures of the quenched POM may stem from the many strained entangled tie molecules obtained

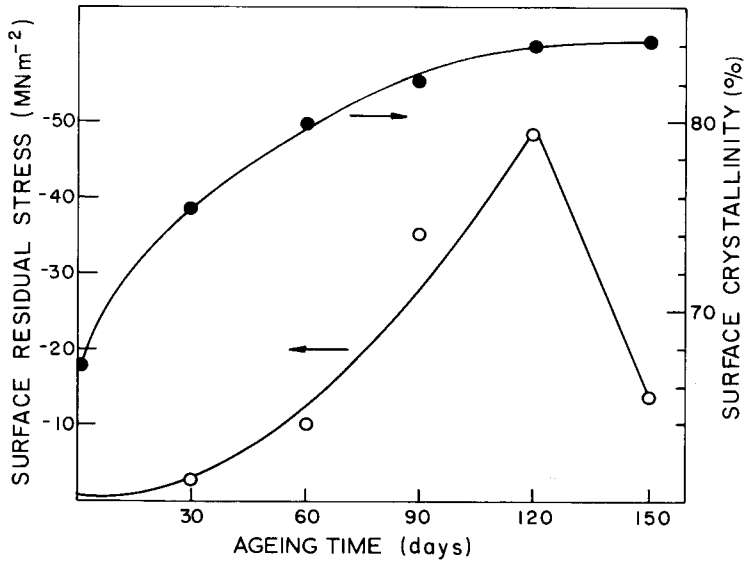

Figure 3 The effect of room-temperature ageing on the surface residual stresses and degree of crystallinity in a quenched (180 → 0° C) POM.

during quenching, the mobility of which is largely retarded by the crystals they are "pinned" in. On the other hand, ageing above T_g is expected to relax internal stresses, as recently reported for polypropylene [2]. Consequently, the residual stresses depicted in Fig. 1 are the resultant of the two opposing processes. In fact, once significant crystallization ceases (after ageing for 120 days) the residual stresses markedly decline.

In conclusion, the effects of ageing above T_g in semicrystalline polymers, such as the POM studied here, are due to the composite nature of the material. The ageing kinetics are influenced by such parameters as the ageing temperature, the stability of the crystalline structure, the structure of the amorphous phase and its unique interaction with the crystalline phase. The ageing process is a self-retarding one depending on the distance from the equilibrium state of the material. From a practical point of view, controlled ageing at elevated temperature should prevent the occurrence of adverse phenomena such as warpage, dimensional instability and premature failure.

Acknowledgement

The authors acknowledge the technical assistance of Mrs S. Ben-Arie.

References

1. L. C. E. STRUIK, "Physical Aging in Amorphous Polymers and Other Materials" (Elsevier, Amsterdam, 1978).
2. L. D. COXON and J. R. WHITE, *Polym. Engng Sci.* **20** (1980) 230.
3. E. S. CLARK, *SPE J.* **23** (1967) 46.
4. *Idem, Polymer Symp.* **20** (1973) 325.
5. J. BOWMAN, *J. Mater. Sci.* **16** (1981) 1151.
6. C. F. HAMMER, T. A. KOCH and J. F. WHITNEY, *J. Appl. Polym. Sci.* **1** (1959) 169.
7. W. H. LINTON and H. H. GOODMAN, *ibid.* **1** (1959) 179.
8. L. C. E. STRUIK, *Polym. Engng Sci.* **18** (1978) 799.
9. A. SIEGMANN, A. BUCHMAN and S. KENIG, *ibid.* **22** (1982) 40.
10. R. G. TREUTING and W. T. READ Jr, *J. Appl. Phys.* **22** (1951) 130.
11. B. A. BALEY and J. H. WEINER, "Theory of Thermal Stresses" (Wiley, New York, 1960).
12. D. P. RUSSEL and P. W. R. BEAUMONT, *J. Mater. Sci.* **15** (1980) 208.
13. A. SIEGMANN, A. BUCHMAN and S. KENIG, *Polym. Engng Sci.* **21** (1981) 997.
14. B. WUNDERLICH, "Macromolecular Physics", Vol. 2 (Academic, New York, 1976) p. 168.

Received 27 May
and accepted 5 June 1986