EFFECT OF MICROCRYSTALLINITY ON THE MECHANICAL PERFORMANCE OF POLYCARBONATE

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ABSTRACT

Samples of polycarbonate before and after remelting and isothermal solidification treatment were characterized by wide-angle and small-angle X-ray scattering, microhardness and stretching calorimetry techniques. Both PC samples could be regarded as structurally identical (X-ray-amorphous) ; however, the isothermally solidified sample exhibited higher microhardness and Young's modulus as well as lower linear expansion coefficient and greatly reduced breaking strain. These results are attributed to the overlap of a network of ultramicrocrystals on the original entanglement network in the reference (untreated) PC sample.

KEY WORDS : polycarbonate, X-ray scattering, microhardness, thermoelastic performance, microcrystallinity

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INTRODUCTION

A unique feature of the crystallization process in flexible-chain polymers is the nucleation and subsequent growth of folded-chain crystals (lamellae). The height of a critical crystallization nucleus is usually orders of magnitude smaller as compared to the total chain length, offering a possibility for a single chain molecule to traverse several lamellae. For this reason, the apparently solid polymers in the temperature interval below their melting points are "semi-crystalline" ; i.e., a substantial portion of material $(1 - X)$ (X being the degree of crystallinity) remains in a disordered, non-crystalline state at the interstitial regions between lamellae.

It is a common practice to assume (e.g. /1, 2/) that the mechanical performance of semi-crystalline polymers can be varied in a fairly broad interval by changing the crystallinity X . It turns out, however, that even the apparently X-ray amorphous samples of a given polymer (e.g., nylon 6 /3/, poly(ethylene terephthalate), PET /4/, synthetic rubbers /5/, etc.) may exhibit significantly different behavior depending on their thermal history. Regions of local, small-scale interchain order (ultramicrocrystals) of a size beyond the limits of resolution of existing X-ray techniques are believed to be responsible for this effect /3-5/. The purpose of the present note is to provide further experimental evidence for the effect of microcrystallinity on the mechanical properties of X-ray-amorphous samples of polycarbonate.

EXPERIMENTAL

Materials

Thin films of the commercial polycarbonate (Macrofol®, Bayer, thickness 250 μm) were used as a reference sample (hereafter referred to as PC-r). The isothermally solidified sample (PC-s) was prepared according to the following scheme: the initial PC-r was melted at 245 $^{\circ}\text{C}$ for 10 min, cooled to 190 $^{\circ}\text{C}$ and subsequently stored at this temperature for 180 min, and finally cooled to ambient temperature at a cooling rate of ~ 10 deg/min (this regime was claimed [6, 7] to favor the formation of interfacial transcrystalline layers in carbon fiber/PC composites). Specimens of the size 0.25x4.0x50.0 mm were cut from these films for subsequent structural, thermal and mechanical characterization.

Techniques

Wide-angle X-ray scattering (WAXS) patterns in the range of scattering angles (2θ) 5-40 deg were taken with a DRON-2,0 diffractometer (copper K_{α} radiation with nickel filter was used). The WAXS patterns were recorded in the step-by-step scanning regime using a scintillation counter and digital conversion. The scattering curves for all samples were normalized by thickness and X-ray absorption [8, 9].

Small-angle X-ray scattering (SAXS) data were obtained with the Kratky camera (KRM-type diffractometer). The primary beam intensity was controlled with a monitoring channel in the scattering angles range from 3' to 5 deg (2θ). Copper K_{α} radiation and nickel filtering of the primary beam were used. Recording of the scattering radiation with a scintillation counter

and digital conversion was performed using the step-by-step scanning regime. The geometrical parameters of the X-ray beam in the specimen plane and the detector position were chosen so as to satisfy the conditions of an "infinite" slit collimation (30 mm for the length of the homogeneous portion of X-ray beam and 290 mm for the specimen-detector distance). Thus, it was possible to determine the absolute scattering intensity of samples by calibrating the instrument with a standard Kratky sample of Lupolen [8, 9].

A Leitz Tester equipped with a square-based diamond indenter was used for the room-temperature microhardness (H) measurements. The H values were calculated from the standard equation [10, 11] $H \text{ (MPa)} = kS$, where S is the slope of the straight-line plot of the residual projected indentation area $A \text{ (m}^2\text{)} = d^2$ vs. the contact load applied $P \text{ (N)}$, $d \text{ (m)}$ is the diagonal length of the impression, and $k = 1.854$ is the geometrical factor. In a loading cycle of 0.1 min the loads of 0.5, 1 and 1.5 N were used. For each point, at least 3-5 measurements were averaged. The correlation coefficients and the standard deviations for the linear A vs. P fits obtained were 0.998 and 1.16, respectively.

The mechanical work (W) and concomitant heat effects (Q) in the step-wise loading (stretching)/unloading (contraction) cycles were measured (with the estimated mean error below 2 %) at room temperature with the stretching calorimeter described in detail elsewhere (12-15). In a typical experimental run, each specimen was stretched at a constant velocity q^+ to a predetermined strain ε_i , stored at fixed ε_i to the full completion of mechanical and thermal relaxations, and thereafter allowed to contract at the same velocity q^- to zero force. The typical difference between fixed strains in two successive steps, $\varepsilon_{i+1} - \varepsilon_i$, varied from several digits in the fourth place to a few digits in the third place within the strain intervals below and above 0.02, respectively.

RESULTS AND DISCUSSION

Structure and microhardness

Fig. 1a illustrates the WAXS patterns for the reference and annealed samples. complete absence of sharp crystalline reflections on the WAXS curves (open circles in Fig. 1a) indicates that the PC-r is in a disordered (glassy) state. The diffuse maximum at $2\Theta \approx 17^\circ$ and the shoulder at $2\Theta \approx 25^\circ$ evidence a short-range order on the scale of 0.53 nm and 0.36 nm (presumably, inter- and intramolecular spacings, respectively). These data are very similar to those for an original (unannealed) sample of PC studied by Neki et al. /16/. The smooth decay of the SAXS curve for the PC-r sample (open circles in Fig. 1b) also points to the absence of large-scale structural heterogeneities.

Both WAXS and SAXS patterns of the PC-s (solid circles in Figs. 1a, 1b) are virtually indistinguishable from those of the PC-r ; hence, both samples can be regarded as structurally identical (X-ray-amorphous). However, as can be seen from Table 1, the microhardness of the PC-s sample is about 5 % higher ; this difference, albeit seemingly small, still is outside the error limits and suggests a somewhat better molecular packing. The experimental value $H = 124.9$ MPa for the PC-r is nearly the same as that for an amorphous (glassy) poly(ethylene terephthalate) /11/. Assuming that the microhardness of crystallized PC would be also similar to that for PET with a spherulitic morphology ($H_{sph} = 200-220$ MPa), it can be readily shown that the increased microhardness of the PC-s ($H = 130.8$ MPa) would be equivalent to a volume fraction of ordered morphological entities at the level of $\Phi = 0.06-0.08$.

Thermoelasticity

In the interval of small strains ($\varepsilon \leq 0.025$) the specific (per unit sample mass m) mechanical work (W/m) and specific heat effects (Q/m) for both PC-r and PC-s obeyed (cf. the representative plot in Fig. 2) the classical equations of the thermoelasticity of solids [17]

$$W/m = E\varepsilon^2 / 2\rho ; \quad (1a)$$

$$Q/m = E\alpha_L T\varepsilon / \rho \quad (1b)$$

where E is the Young's modulus, α_L is the linear expansion coefficient, and ρ is the density. As can be seen from Table 1, irreversible (non-elastic) effects for PC-r and PC-s set on at approximately the same yield strain ε^* (corresponding to a difference between W/m and Q/m in stretching and contraction cycles higher than 30 J/kg); however, the Young's modulus of PC-s is 15 % higher, and its linear expansion coefficient is about 10 % lower than those for PC-r, respectively. It can be thus concluded that PC-s is slightly stiffer than PC-r which is in a qualitative agreement with the microhardness data.

It seems appropriate to mention at this point that the data available (Table 1) are consistent with the expected [10] correlation between the microhardness, H , and the apparent yield stress, $\sigma^* = E\varepsilon^*$. The proportionality coefficient C in the relationship, $H = C\sigma^*$, is somewhat lower (2.4 and 2.0 for PC-r and PC-s, respectively) than the theoretical value ($C = 3$); however, this discrepancy, most probably, is related to the different loading regimes assumed (stretching and compression, respectively).

The most striking difference between PC-r and PC-s is, however, in their mechanical performance above ε^* . In contrast to the PC-s which failed at the breaking strain $\varepsilon_b = 0.048$

(Table 1), the reference PC-r could be stretched to more than an order-of-magnitude higher strains before its rupture at the breaking strain $\varepsilon_b = 0.530$ (cf. Fig. 2b and Table 1). In this respect, PC-r and PC-s are similar to the quenched (glassy) and annealed (semi-crystalline) samples of poly(ether-ether-ketone), respectively /14/, although the difference between the breaking strains for these two latter samples was not as dramatic.

It can be easily verified that the most salient features of the thermoelastic behavior of PC-r in the stretching regime (Fig. 2b) are very similar to those of the PC sample studied by Koenen et al. /18/. This behavior could be quantitatively explained /18/ assuming that the total strain energy density $W = W_e + W_g$ in the interval of elastic strains below ε^* is dominated by the solid-body elastic contribution $W_e = f(E, \varepsilon^*)$ (eq. (1a)). However, in the interval of inelastic strains above ε^* the contribution of the “forced” elasticity of the entanglement network, $W_g = G_g (\lambda^2 + 2/\lambda - 3)/2$, comes into play. Here G_g is the appropriate elasticity modulus, and $\lambda = \varepsilon + 1$ is the stretching ratio. Therefore, the mechanical failure of the PC-s shortly above ε^* , implies that the microcrystallinity, how low it might seem to be, is still sufficient to suppress the network contribution W_g .

In terms of the van der Waals model of rubber elasticity /19, 20/, the basic phenomenological parameters controlling the mechanical performance of a rubber sample in the stretching deformation mode are the limiting network strain accounting for a finite chain extensibility, $\lambda_m = (M_c/M_u)^{1/2}$, and the parameter of global interchain interaction, a : the smaller the λ_m and/or the higher the a , the stiffer is the network. (here M_c and M_u are the effective molar masses of the elastically active chain strands between the network junctions, and of the stretching invariant unit, respectively). Assuming that this model can be also applied to the forced elasticity phenomenon in the glassy PC considered here, one may suggest that the higher stiffness and poor extensibility of the PC-s are associated with the greatly reduced λ_m and/or increased a

brought about by the overlap of the network of ultramicrocrystals on the original entanglement network in the PC-r. The size of these ultramicrocrystals is believed to be well below 3-5 nm (which corresponds, roughly, to about 6-8 interlayer spacings) ; otherwise, crystalline reflections would have been observable on WAXS patterns /21, 22/. This interpretation is qualitatively consistent with the model calculations of the drawability limits of amorphous and semi-crystalline polymers /23/ which predict a drastic decrease of the breaking strain of an amorphous polymer resulting from the increase of the parameter of interchain interactions above a definite critical value.

CONCLUSIONS

The reference and isothermally solidified samples of PC can be regarded as structurally identical (X-ray-amorphous) ; however, the latter sample exhibits higher microhardness and Young's modulus values as well as lower linear expansivity and greatly reduced breaking strain. These results are tentatively attributed to the overlap of a network of ultramicrocrystals (of size below the resolution of X-ray techniques) on the original entanglement network in the reference PC sample.

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Table 1

Thermomechanical properties of PC-r and PC-s

	PC-r	PC-s
H / MPa	124.9	130.8
E / GPa	2.0	2.4
$\alpha_L \times 10^5 / \text{K}^{-1}$	5.8	5.3
ε^*	0.025	0.028
ε_b	0.530	0.048

Figure captions

Fig. 1. Wide-angle (a) and small-angle (b) X-ray scattering patterns for PC-r (opened circles) and PC-s (filled circles). To avoid overlap, the upper curves were displaced vertically by about 200 units.

Fig. 2. Specific mechanical work (circles) and specific heat effects (triangles) in stretching (filled symbols) and contraction (opened symbols) deformation regimes for PC-s (a) and PC-r (b).

Fig. 1

FIG. 1. Continued.

Fig. 2

Fig 2