Erratum: Confinement-induced vitrification in polyethylene terephthalate [Phys. Rev. B **75**, 224201 (2007)]

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In recent papers, we proposed a theoretical model to describe relevant mechanisms that take place at the late stages of crystal growth in cold-crystallized poly(ethylene terephthalate) (PET).[1,2] In the course of crystallization, progressive confinement of the noncrystalline domains hinders segmental motion, eventually leading to structural arrest. From the point of view of thermodynamics, this process is connected with a gradual increase of the chemical potential in the amorphous phase.

We found that an initial chain orientation in the glass enhances the confinement effect of the crystals by

$$\overline{\Delta\mu} \equiv \delta\mu|_{\kappa=4} - \delta\mu|_{\kappa=1}, \tag{1}$$

where κ describes chain orientation in the amorphous state. A value of $\kappa=1$ is assumed for isotropic material, while $\kappa=4$ for the oriented one (the draw ratio of PET after cold drawing is ≈ 4). In our previous paper, we have estimated $\overline{\Delta\mu}$ from experimental data using the following equations [cf. Eqs. (12) and (20) of Ref. 1]:

$$|\Delta\mu| \simeq H_f \frac{T_m^0 - T}{T_m^0} \tag{2}$$

and

$$|\overline{\Delta\mu}| = |\Delta\mu|\left(1 - \frac{l_c}{l_{c0}}\right), \tag{3}$$

where H_f is the melting enthalpy, T_{m0} and T are the melting and crystallization temperatures, respectively, and l_c and l_{c0} are the lamellar thicknesses at the end of the crystallization process for $\kappa=4$ and $\kappa=1$, respectively.

On the other hand, based on statistical thermodynamic considerations, we arrived at an expression for $\overline{\Delta\mu}$ as a function of the density autocorrelation length $\xi|_{\kappa=1}$ in the amorphous domains, and of the statistical segment length, a [Eq. (17) in Ref. 1]. In the case of PET crystallized at 100 °C from the glassy state, a value of $\xi|_{\kappa=1}=1.3$ nm was obtained, using the experimental estimate of $\overline{\Delta\mu}$ derived from the above Eqs. (2) and (3) and assuming an a parameter of approximately one monomer length.

We have recently realized that two errors were introduced in the estimation of $\xi|_{\kappa=1}$. We first reported an erroneous value of the melting enthalpy of PET, the correct one being $H_f=25$ kJ/mol. In second place, a more appropriate value for the statistical segment length a seems to be $n \sim 3-4$ monomer lengths.[2,3] Furthermore, we have now introduced a factor of T/T_{m0} in Eq. (2), as it has been shown to better describe $\Delta\mu$.[4]

Taking into account the above three considerations, we now find (assuming $n=4$) the following values for $\xi|_{\kappa=1}$ and its ratio with the interlamellar thickness l_a within the semicrystalline stacks, $\Lambda \equiv \pi\xi/l_a$ [Eq. (18) in Ref. 1]:

1. $\xi|_{\kappa=1}=0.4$ nm.
2. $\Lambda \approx 0.3$ for the unoriented sample.

Preceding studies report $\xi|_{glass}=1.5$ nm for the characteristic length of cooperativity of PET at the glass transition temperature, T_g ($T_g \simeq 70$ °C) (see Ref. 12 in Ref. 1). Although the density autocorrelation length and the characteristic length of cooperativity are different physical quantities, it is reassuring that values of $\xi|_{\kappa=1}$ and $\xi|_{glass}$ are found to be close to each other. In addition, the finding that $\xi|_{\kappa=1} < \xi|_{glass}$ is consistent with two main issues:

1. The temperature at which $\xi|_{\kappa=1}$ is estimated (100 °C) is higher than T_g (70 °C);
2. The Gaussian chain model adopted in our calculations (see Ref. 1) describes a relaxed liquid, where the freezing of modes associated to the glass transition process is not envisaged.

In summary, the statistical mechanical approach developed still satisfactorily describes, after the above corrections, the confinement of the amorphous domains as a consequence of crystal growth. A number of simplifications have been adopted in our model; in spite of this, the $\xi|_{\kappa=1}$ value above reported for cold crystallized PET is found to be in good agreement with published data on the characteristic length of cooperativity of PET.

[1] F. J. Baltá Calleja, G. Di Marco, A. Flores, and M. Pieruccini, Phys. Rev. B **75**, 224201 (2007).

[2] M. Pieruccini, A. Flores, U. Nöchel, G. Di Marco, N. Stribeck, and F. J. Baltá Calleja, Eur. Phys. J. E **27**, 365 (2008).

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