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Prediction of glass transition temperatures: Binary blends and copolymers

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Abstract

Glass transition temperature T_g values characterize pure polymers, polymer blends, copolymers, as well as matrices in polymer-based composites. T_gs as function of composition reflect miscibility (or lack of it) and determine all properties. We present a new equation for the dependence of T_g on composition in blends as well as in copolymers. We compare results obtained from earlier equations (Fox, Gordon–Taylor, Kwei) and those from the new equation with experimental data.

Keywords: Polymer thermodynamics; Miscibility; Glass transition; Blends; Copolymers

1. Introduction and scope

There is no glass transition temperature T_g; there is a glass transition *region*. The change from the glassy state into a liquid or a rubbery state is gradual. T_g values are reported by analogy with the melting temperature T_m values — so as to represent a region by a single number. While T_m values do not depend on the direction of the change (freezing a liquid, melting a solid) or on the change rate, the location of the glass transition region depends on both factors. In his classical 1958 study of polyvinyl acetate (PVA) Kovacs [1] has shown how the T_g location varies with the cooling rate of the liquid.

Different experimental techniques lead to different T_g values, including: differential scanning calorimetry (DSC); thermomechanical analysis (TMA) which provides linear isobaric expansivity $\alpha_L = (\partial L/\partial T)_P/L$ where L is length of the specimen; dielectric analysis (DEA); and dynamic mechanical analysis (DMA) [2–9]. The differences are due to different time responses of motions of side- or main-chain polar groups; electrical, mechanical or thermal stimulation of the motion, etc. In DMA alone the results vary when one obtains a T_g value from the storage modulus E', or from the loss modulus E'', or from tan $\partial = E''/E'$.

While these complications exist, T_g values are useful indeed for a variety of purposes. Particularly needed are T_g values as a function of composition x for binary polymer blends; they tell us whether the blends are miscible, or compatible, or not miscible at all. This situation is illustrated in Fig. 1. Full miscibility is characterized by a single glass transition temperature for all the blends. In compatible systems we have two T_g values which depend on x. In immiscible polymers – not an infrequent case – T_g values for pure components do not change with composition. The miscibility (or lack of it) is decisive for all properties.

T_g reflects also many other features and properties of polymeric systems: helical twisting power in chiral nematic phases [10]; changes of T_g with residual stress [11]; effects of fillers [12]; nanoconfinement effects on segmental motions in polymer composites [13]; consequences of aging [14]. When we wish to achieve compatibility, then changes in T_g represent a measure of success of that operation. Curing conditions can be optimized [15] or a compatibilizing agent [16,17] evaluated. Still further, one often performs de-aging on purpose — thus

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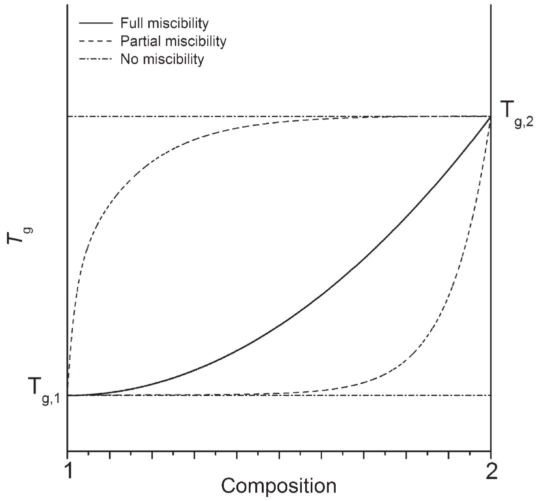

Fig. 1. A schematic representation of the dependence of T_g on composition in binary polymer blends: — fully miscible system; – – – compatible system; – · – · – immiscible system.

increasing T_g [18–20]; ironing of textile garments is an example.

Improvement of desired properties of polymer-based materials (PBMs) can be achieved not only by blending but also by synthesis of copolymers. If polymers are partly crystalline, then not only T_g but also T_m values are pertinent [21]. A potentially quite useful category of PBMs are polymer liquid crystals (PLCs) [22–26] because of their strength higher than that of engineering polymers, low α_L values and also improved thermal stability at elevated temperatures. PLCs are multiphase systems, with a single copolymer forming at a given temperature several phases; location of phase transitions including T_gs is best accomplished by a combination of several experimental techniques [6,22].

We have decided to develop an analytical equation for T_g as a function of concentration. Thus, our objective is a single equation that can serve for blends as well as for copolymers.

2. Experimental

PEO (Sigma Chemical Co., USA) with a molecular weight of 4000 g mol^{-1} was used. The epoxy resin used was diglycidyl ether of bisphenol-A (DGEBA) with a degree of oligomerisation $n \approx 0.1$ and a number-average molecular mass of 360 g mol^{-1}. 4,4′-diaminodiphenylmethane (DDM, chemical grade, average M_n=198 g mol^{-1}) from Aldrich Chemical Inc. (USA) was the curing agent. Experiments were performed at the University of Athens as described earlier [27, 28].

Glass transition temperatures for poly(vinyl alcohol) (PVA) (M_w=1.95 · 10^{5}g mol^{-1}), linear poly(ethylene) (PE) (M_w=1.27 · 10^{5}g mol^{-1}) and a series of PVA/PE copolymers were taken from a publication by Funke and her colleagues [29] who used pressure–volume–temperature determinations for the purpose.

3. Extant equations

Given the importance of the problem, several attempts have already been made to create a $T_g(x)$ equation. The first of those that are currently in use is the Fox equation [30]; for a binary system 1+2 we have

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{1-x_1}{T_{g,2}}. \tag{1}$$

T_g pertains to the blend, $T_{g,i}$ to pure component i, and x_i is the mass (weight) fraction of component i. Clearly $x_2 = 1 - x_1$. Eq. (1) is symmetric with respect to the components and allows prediction from properties of pure components only.

Another equation in use is that of Gordon and Taylor (GT) [31]

$$T_g = \frac{x_1 T_{g,1} + k_{\mathrm{GT}}(1-x_1)T_{g,2}}{x_1 + k_{\mathrm{GT}}(1-x_1)}. \tag{2}$$

k_{GT} has to be evaluated from experimental data and represents unequal contributions of components to the blend.

There is also the equation of Kwei [32]:

$$T_g = \frac{x_1 T_{g,1} + k_{\mathrm{KW}}(1-x_1)T_{g,2}}{x_1 + k_{\mathrm{KW}}(1-x_1)} + q x_1(1-x_1) \tag{3}$$

with two parameters, k_{Kw} and q. The index 2 in Eqs. (2) and (3) refers to the higher T_g component.

4. Development of our equation

In the simplest imaginable case T_g is a linear function of composition. For real cases let us define the deviation from linearity:

$$\Delta T_g = T_g - T_g^{\mathrm{lin}} = T_g - \left[x_1 T_{g1} + (1-x_1)T_{g2}\right]. \tag{4}$$

Looking again at Fig. 1, consider another simple case: ΔT_g can be represented by a parabola: $\Delta T_g = x_1(1-x_1)a_0$ where a_0 is a parameter for a given system. ΔT_g will now have the highest value at $x_1 = x_2 = 0.5$. At that point we have $x_1 - x_2 = 2x_1 - 1 = 0$.

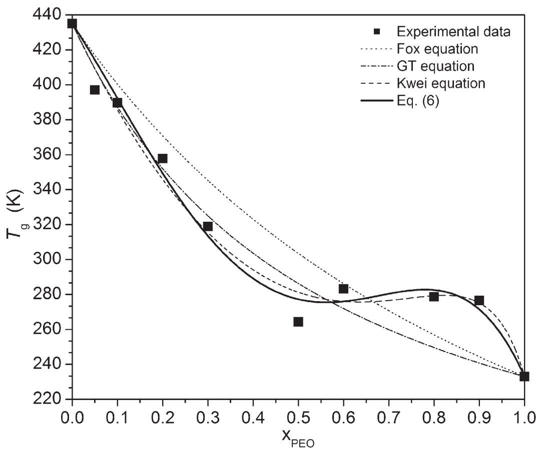

Fig. 2. Results for the binary PEO+ER blends as a function of composition. ■ experimental results; …… Fox equation; – – – Kwei equation (k_{Kw}=7.0, q=−514); – · – · – Gordon–Taylor equation (k_{GT}=0.36); — calculated from Eq. (6) (a_0=−227, a_1=284, a_2=316).

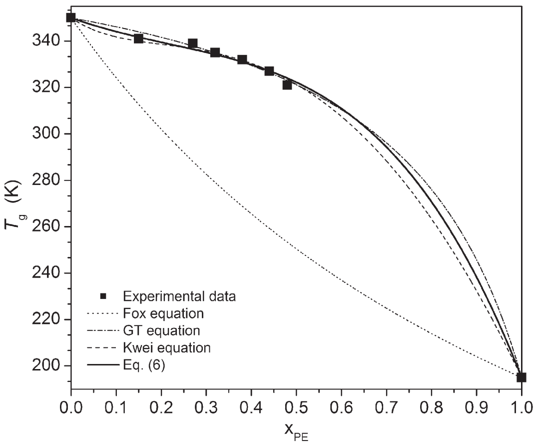

Fig. 3. Results for the PVA/PE copolymers as a function of composition. Symbols as in Fig. 2: ■ experimental results; ...... Fox equation; – – – Kwei equation (k_{Kw}=0.32, q=356); – · – · – Gordon–Taylor equation (k_{GT}=4.38); — calculated from Eq. (6) (a_0=199, a_1=126, a_2=13.2).

For systems of any complexity, we define a cubic polynomial centered around $2x_1-1=0$:

$$\Delta T_g = x_1(1-x_1)\left[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2 + a_3(2x_1-1)^3\right]. \tag{5}$$

From Eqs. (4) and (5) we have

$$T_g = x_1 T_{g1} + (1-x_1)T_{g2} + x_1(1-x_1) \times \left[a_0 + a_1(2x_1-1) + a_2(2x_1-1)^2 + a_3(2x_1-1)^3\right]. \tag{6}$$

5. Calculations and confrontation with experiment

We have tested the equations first against data for blends of PEO with aromatic amine-cured DGEBA (the epoxy resin, ER) since the ΔT_g values in the PEO+ER system are large and their dependence on composition is s-shaped. This is the case irrespective of the molecular weight of the linear polyetheric modifier [26]. Two techniques have been used to obtain the $T_g(x)$ dependence for PEO+ER blends: the dielectric-related technique of thermally stimulated current (TSC) [33] and DSC. Here we discuss only the DSC results, but similar conclusions arise from the dielectric data. Parameters have been obtained by a least-square minimization. Fig. 2 shows that good results were obtained by using three terms in Eq. (6). At $x_{PEO}=0.5$ where the largest deviation from linearity is observed, Eq. (6) agrees with the experiment somewhat better than the Kwei curve. Undoubtedly, an even better agreement of Eq. (6) with the experimental data could have been obtained by inclusion of the a_3 term.

Results for the PEO+ER system are displayed in Fig. 3. Here the curves obtained from different equations nearly coincide. Again, we have used the first three terms in Eq. (6). Here a_2 is smaller by a whole order of magnitude than in the preceding case; we are dealing with a *simpler system*. The results obtained from the Fox Eq. (1) stand apart, but we recall that these are predicted from data for pure components.

The present results seem sufficient for demonstration of utility of our new equation. In “very well behaving” miscible systems the Fox Eq. (1) might be sufficient. With increasing system complexity, the one-parameter Gordon–Taylor equation, the two-parameter Kwei equation, and finally our new equation can be used. Our equation alone provides a measure of the system complexity. In simple parabolic systems only one-parameter a_0 is sufficient. The number of a_i parameters needed to represent the experimental data characterizes how complicated the system is — for polymer blends as well as for copolymers.

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