BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 26, pp. 5065–5067, 1995

0032-3861/95 $10.00+0.00

The glass transition temperature of 6/6.9 random copolyamides

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The glass transition temperatures (T_g) of a 6/6.9 random copolyamide series have been investigated as a function of copolymer composition. The analysis was carried out using the technique of differential scanning calorimetry, and the degree of crystallinity was determined by wide angle X-ray diffraction. It was found that conventional models for determining T_g values do not fit the copolymers of this study. An appropriate description is achieved by considering a model that accounts for molecular interactions. Both hydrogen bond content and degree of crystallinity lead to the observed deviation in T_g from the values predicted by conventional models.

(Keywords: glass transition temperature; copolyamides; random copolymers)

The glass transition temperature (T_g) of a polymer is determined by factors such as chain structure and conformation, intermolecular interactions, the efficiency of molecular packing in the amorphous state and by the degree of crystallinity. The T_g of polyamides is specifically known to be greatly affected by hydrogen bonding. Miyake[1] and Trifan and Terenzi[2] have concluded that at room temperature most of the amide groups in polyamides are hydrogen bonded, irrespective of the number of CH_2 groups in the chain. As the amide group density increases, the hydrogen bond concentration is higher and the segmental mobility becomes more restricted, resulting in a higher T_g[3].

An amorphous single phase of two components (miscible homopolymers or random copolymers) is characterized by a single glass transition temperature, usually located in between those of the respective individual homopolymers (T_{g_1} and T_{g_2}). Random copolymerization, compared to homopolymerization, affects both intermolecular and intramolecular interactions, resulting in a copolymer that may have lower or higher T_g than its respective homopolymers[4].

Several theories have considered the relationship between the T_g of a random copolymer and the T_gs of the respective homopolymers, and a number of equations have been proposed, describing such relationships. The common theories are based on the free volume concept, and are expressed in terms of the thermal expansion coefficients of a polymer in the liquid (α_l) and in the glassy (α_g) state. For example, Gordon and Taylor[5] have suggested the following:

$$T_g = (w_1 T_{g_1} + K w_2 T_{g_2})/(w_1 + K w_2) \qquad (1)$$

$$T_{g_2} > T_{g_1}$$

where $K = (\alpha_{l,2} - \alpha_{g,2})/(\alpha_{l,1} - \alpha_{g,1}) = \Delta\alpha_2/\Delta\alpha_1$; T_g, T_{g_1} and T_{g_2} are the glass transition temperatures of the copolymer and the two respective homopolymers; and w_1 and w_2 are the weight fractions of the monomers in the copolymer.

When $K = T_{g_1}/T_{g_2}$ the Fox equation, for a random copolymer, is obtained[6]:

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2} \qquad (2)$$

These equations have successfully described the behaviour of conventional random copolymers provided that $T_{g_1} < T_g < T_{g_2}$, otherwise more elaborate equations are needed to describe the experimental observations. Moreover, this theory does not take into account intermolecular interactions, which may also depend on the sequence distribution of monomer units in the copolymer.

A single phase copolymer can be considered as a miscible blend of like (AA, BB) and unlike (AB) dyads, and these three components can be described by the two homopolymers and the alternating copolymer, respectively. Consistently, the copolymer glass transition behaves like that of a random solution of the three dyadic components[7].

By assuming additivity of the T_gs and equal reactivities of the comonomers, Dimarzio and Gibbs[8] have suggested the following relationship:

$$T_g = T_{g_1} F^2 + T_{g_2}(1 - F)^2 + 2F(1 - F)T_{g_{12}} \qquad (3)$$

where F is the molar fraction of monomer 1 in the copolymer and $T_{g_{12}}$ is the glass transition temperature of the respective alternating copolymer.

The Couchman equation[7] is obtained by assuming additivity of 'configurational' entropies as follows:

$$\begin{aligned} \ln T_g = {} & [r_1 F^2 \Delta C_{p_1} \ln T_{g_1} + r_2(1 - F)^2 \Delta C_{p_2} \ln T_{g_2} \\ & + 2F(1 - F)\Delta C_{p_{12}} \ln T_{g_{12}}]/[r_1 F^2 \Delta C_{p_1} \\ & + r_2(1 - F)^2 \Delta C_{p_2} + 2F(1 - F)\Delta C_{p_{12}}] \qquad (4) \end{aligned}$$

where r_1 and r_2 are the copolymerization reactivity ratios of the two monomers, and $\Delta C_{p_{ij}}$ is the contribution of

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the *ij* dyad to the heat capacity jump at the corresponding $T_{g_{ij}}$.

The composition-dependent values of T_g for many random copolymer series exhibit both negative and positive deviations from Fox's predictions (equation (2)). Lower than 'Fox-predicted' values of $T_{g_{ij}}$ may be attributed to a decrease in chain stiffness of the alternating copolymer relative to that of a 1:1 composition random copolymer, that exhibits a Fox-predicted $T_{g_{ij}}$ value. The reverse behaviour will be the case for higher than Fox-predicted values of $T_{g_{12}}$ (ref. 9). Another case of deviation from the Fox-predicted $T_{g_{ij}}$ values is when two comonomers differ in size and shape. As a result, the efficiency of the molecular packing in the alternating copolymer is lower than that of the corresponding random copolymer that exhibits a Fox-predicted $T_{g_{ij}}$ value, and thus copolymers containing high amounts of the two monomers will exhibit a T_g value lower than those of the respective homopolymers. In such systems, T_g as a function of composition goes through a minimum. Systems exhibiting such behaviour include copolymers of the monomer pairs methyl methacrylate/acrylonitrile, styrene/methyl methacrylate and acrylonitrile/acrylamide[4].

The decrease in T_g discussed above is a more common result of random copolymerization, because repulsion between unlike monomer units is much more common than attraction. However, there are a few exceptional systems in which the molecules of the random copolymer pack together more efficiently than those of the respective homopolymers, and as a result the T_g of the copolymer is higher than expected[4]. An example of a system that exhibits this behaviour is the copolymer of ethyl acrylate and vinylidene chloride[7].

In the present study, the T_g of a 6/6.9 random copolyamide series (obtained by copolymerization of azelaic acid, hexamethylene diamine and ω-aminocaproic acid; provided by EMS Laboratories, Switzerland) was investigated as a function of copolymer composition. In addition to their commercial interest, this series enables the study of the T_g behaviour of copolymers based on strongly interacting monomers.

Glass transition temperatures of the 6/6.9 copolyamide series were determined by thermal analysis using a Mettler TC 10 A Differential Scanning Calorimeter. Indium was used to calibrate the instrument. The measurements were carried out on samples of 10 mg under N_2 atmosphere. The samples were heated from -20 to 250°C (above their melting temperatures), cooled to -20°C and reheated, all at a rate of $10°\mathrm{C\,min}^{-1}$. The second heating run was used to determine the glass transition temperatures. The hydrogen bond content was determined by Fourier transform infra-red (*FT*i.r.) spectroscopy and the degree of crystallinity was determined by wide-angle X-ray diffraction. The degree of crystallinity of polyamide 6 was also determined by differential scanning calorimetry (d.s.c.) and was found to agree with the X-ray value: 40.4 and 41.4%, respectively.

Although the T_g values of polyamides 6 and 6.9 are quite close, the curve of polymer T_g *versus* comonomer 6.9 content has a distinct U-shape, hence the T_g of all copolymers studied is lower than that of either homopolymers, as shown in *Figure 1*. Copolyamides rich in caprolactam exhibit higher T_g values than copolyamides rich in the 6.9 comonomer, owing to the higher amide group density in the former, which enables the formation of a higher hydrogen bond concentration. The minimum T_g value is obtained for the composition of approximately equal amounts of comonomers. A similar behaviour has been reported for 6/12 (refs 10, 11) and 8/12 (ref. 3) random copolyamides. It was suggested that the T_g variation with composition was due to the irregularity of the amide group distribution along the copolymer chain, leading to a change in hydrogen bond content. However, a model describing this phenomenon has not yet been offered.

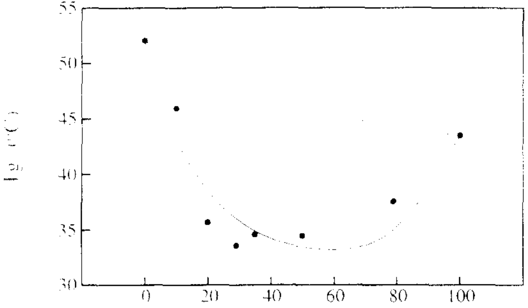

Figure 1 Glass transition temperature of 6/6.9 random copolyamides *versus* comonomer 6.9 content: ●, empirical values; , Couchman equation; , Fox equation

It is clear that these results do not fit the predictions of Fox (equation (2)), or Gordon–Taylor (equation (1)), namely that composition-dependent T_g values are always between the T_g values of the corresponding homopolymers. Therefore, in an attempt to describe the T_g values of the series currently under study, equations (3) and (4) were applied. The best fit was obtained using the Couchman model (equation (4)) with the following parameters: $T_{g_1} = 52°\mathrm{C}$ and $T_{g_2} = 43.5°\mathrm{C}$, corresponding to the measured T_g values (middle points) of polyamide 6 and polyamide 6.9, respectively; F = molar fraction of caprolactam; $\Delta C_{p_1} = 0.182\,\mathrm{J\,(g\,K)}^{-1}$ and $\Delta C_{p_2} = 0.224\,\mathrm{J\,(g\,K)}^{-1}$, the contribution of the amorphous phase of polyamide 6 and polyamide 6.9 to heat capacity jump at T_g, calculated according to the following relationship[12]:

$$\%\mathrm{CRYS} = 1 - \Delta C_p/\Delta C_{p_{\mathrm{amorph}}} \qquad (5)$$

where %CRYS is the degree of crystallinity, as measured by X-ray diffraction, and ΔC_p is the total heat capacity change at T_g (thermal analysis and X-ray diffraction were performed on the same samples). Equal reactivity ratios of the comonomers ($r_1 = r_2$) were assumed. By best curve fitting to the measured T_gs, based on equation (4), the thermal properties of the 6/6.9 alternating copolymer were calculated as: $T_{g_{12}} = 28°\mathrm{C}$, $\Delta C_{p_{12}} = 0.60\,\mathrm{J\,(g\,K)}^{-1}$. *Figure 1* shows measured and calculated T_g values according to both Fox and Couchman. While the Fox equation predicts only small deviations from linear additivity, the Couchman equation, as above, fits quite closely the measured results and is able to describe the deep minimum in the curve. A worse fit was obtained by applying equation (3), which resulted in $T_{g_{12}} = 16°\mathrm{C}$, a value which indeed seems to be too low.

Since the two 6 and 6.9 comonomers are similar in shape, it is unlikely that the efficiency of the copolymer's molecular packing is significantly reduced; it is more likely to be due to a decrease in the hydrogen bond content. The calculated $T_{g_{12}}$ of the alternating copolymer (28°C) is lower than the measured T_g (35°C) of the random copolyamide (same composition), indicating that the chain stiffness of the former is lower than that of the latter, again presumably due to less hydrogen bonding in the alternating copolymer.

*FT*i.r. spectroscopy shows[13] that the hydrogen bond content in the copolyamide 6/6.9 series decreases and the hydrogen bond strength increases as the comonomer content increases, probably owing to the increased irregularity of the amide group distribution along the polymer chain. A combination of thermal analysis and *FT*i.r. data indicates that the T_g increases with an increase in the hydrogen bond content, i.e. with an increase in segmental mobility restrictions. Another factor affecting the T_g is the presence of a crystalline phase (e.g. ref. 14). X-ray diffraction patterns confirm that the inclusion of either comonomer 6.9 into polyamide 6, or caprolactam into polyamide 6.9 reduces the degree of crystallinity. A combination of thermal analysis and X-ray diffraction data[13] indicates that the T_g increases with increasing degree of crystallinity. This may suggest that crystals restrict the segmental mobility in the adjacent amorphous phase and thus affect the T_g at a level increasing with an increase in the degree of crystallinity. Both hydrogen bond content and degree of crystallinity were found to correlate with the T_g of the copolyamides and since neither can be altered without affecting the other, their individual effects on T_g cannot be evaluated. It is suggested, however, that hydrogen bonding has the major influence on T_g because it restricts the segmental mobility within the entire amorphous phase, whereas crystals affect only those segments located in their proximity. The latter effect may only be significant in highly crystalline polymers, which is not the present case.

In conclusion, the conventional models for prediction of T_g values of random copolymers do not fit the 6/6.9 copolymers of this study. An appropriate description is achieved by considering a model that accounts for molecular interactions, which depend on the sequence distribution of the monomers in the copolymer. This Couchman model considers properties of the homopolyamides and their respective alternating copolyamide as well. Both hydrogen bond content and degree of crystallinity affect the T_g and lead to the observed deviation in T_g from the values predicted by conventional models.

Acknowledgement

Fruitful discussions with Professor V. Privalko, Academy of Sciences of Ukraine, are greatly appreciated.

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