Shifts in glass transition temperatures of synthetic polymers filled with microcrystalline cellulose

Alf de Ruvo and Elisabeth Alfthan
Swedish Forest Products Research Laboratory, Physics Department, Box 5604, S-114 86 Stockholm, Sweden

(Received 30 January 1978)

Measurement of shift in glass transition temperature for polystyrene and poly(vinyl acetate) filled with microcrystalline cellulose has been carried out. A simple derivation to calculate the zone of interaction is suggested. The results indicate that the zone of interaction is of the same dimension as the particle. It is suggested that the shift of T_g is induced by thermal stresses and caused by the difference in thermal expansivity and elastic modulus between synthetic amorphous polymers and cellulose. It does not seem plausible that pure interfacial phenomena should have a much smaller range in the synthetic polymer matrix.

INTRODUCTION

This investigation reports a series of measurements of shifts in the glass transition temperatures of synthetic polymers filled with microcrystalline cellulose. Dilatometry is used to detect the location of the transition temperatures of the synthetic polymer.

Previous work on similar systems has suggested that the shift of glass transition may be related to the intensity of the interaction in the interphase[1]. In general the observed shift increases to a limiting value as a function of the vol % of filler. This indicates that the intensity of the interaction ranges over a certain zone in the polymer matrix in which the molecular mobility is different from that present in the bulk phase.

di Benedetto[2] has suggested that the interaction in the interphase changes T in an analogous way to an increase in molecular weight. This author further suggests a simple derivation of the critical zone of influence. The derivation is based on the assumption that the vol % corresponding to maximum shift in T_g represents a value where all the polymer is influence by the interaction in the interphase. In these cases, the zone of interaction has been calculated to be of the order of 20–200 Å.

In the literature it is also advocated that the cause of the shift in the glass transition is due to adsorption phenomena in the interphase. Thus Yim and St Pierre[3,4] have found a linear relationship between the enthalpy of adsorption and the shift in T_g. Moreover, in several papers by Lipatov[5,6] it is argued that the packing density of the polymer is disturbed by the two phase situation. For a heterogeneous polymer system Lipatov also claims that in the interphase the segments may interdiffuse and form a quasihomogeneous blend which constitutes the adhesive interaction. These claims are reminiscent of the adsorption theory and diffusion theory. However, they have in common a disregard of the influence of the stress field in the vicinity of the interphase. This is created either during processing or due to the difference in expansion coefficients between the components.

EXPERIMENTAL

Materials

Polystyrene (PS, M_w = 110 000) was kindly provided by Dr B. Rånby, Polymer Depratment, Royal Institute of Technology. Poly(vinyl acetate) (PVAC, M_w = 45 000) was a commercial sample obtained from Merck. Molecular weight was estimated by means of gel permeation chromatography (g.p.c.).

Cellulose was obtained as a powder claimed to be microcrystalline (Sigma Chemical Company). The commercial name is Sigmacell, type 38. Also a sample with smaller dimensions was used named Sigmacell, type 19.

The specific surface area of the microcrystalline cellulose was determined by means of a commercial instrument (Micromentics, model 2100). Krypton gas was used as an adsorbant and the specific surface area was calculated by means of a simplified BET equation[7].

Manufacture of samples

It was necessary to prepare samples as pellets in order to be able to use a specially designed dilatometer. The synthetic polymers were dissolved in chloroform in a 5% by wt solution. Thereafter a suitable amount of cellulose powder was carefully dispersed by means of a Waring blender for 30 min. The solvent was evaporated at room temperature and then stored under vacuum (0.01 MPa) for 5 days at at 50°C. The mixture of cellulose and synthetic polymers was obtained as a thick film which was refined to a powder by means of a laboratory grinder.

This powder was compounded into a pellet in a press conventionally used for making KBr pellets for i.r. measurements. The samples were pressed at 400 MPa and contained around 1200 g/m^2.

Dilatometric measurement

In the determination of T_g a dilatometer previously described by Martin-Löf[8] was used. Essentially, changes in basis

0032–3861/78/1908–0872$01.00

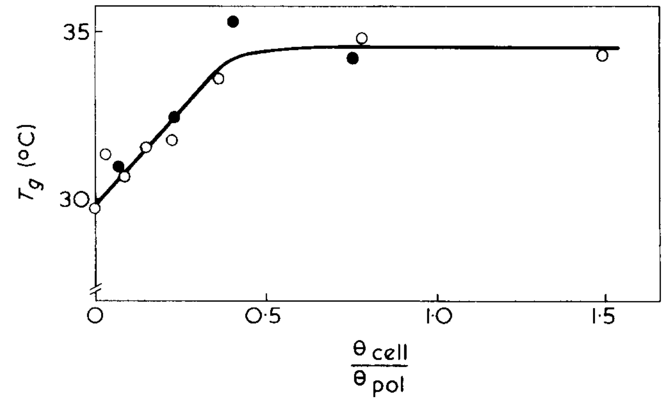

Figure 1 Shift in glass transition temperature for PVAC *versus* the ratio of volume fractions of PVAC and cellulose. ●, Sigmacell 19; ○, sigmacell 38

weight of the sample were measured *versus* temperature by means of β rays. It may be shown that the change in the intensity of the transmitted β rays *versus* temperature is proportional to the thermal expansivity. Proper corrections must be made, however, for the change in the absorption of the gas volume surrounding the sample.

A change in the slope of a plot of the intensity of β rays *versus* temperature indicates the location of the T_g. The reproducibility of the measurements of T_g was ±1°C. The scanning rate was 5°C/h.

In order to make accurate and reproducible measurements it was necessary to minimize the effects of compounding by starting the measurements after annealing the sample by making 10 temperature cycles around T_g.

THEORETICAL CONSIDERATIONS

The interaction between a synthetic polymer matrix and filler may be described by the following expression due to Lipatov[5]:

$$T_g = T_{gs} + \Delta T_g \nu \tag{1}$$

where T_g is the measured value of glass transition temperature; T_{gs} is the glass transition temperature of synthetic polymer; ν is the volume fraction influenced by the surface and ΔT_g is the difference in T_g at $\nu = 1$. It may be assumed that the distance of interaction from the surface of the filler material is d.

The volume fraction of the polymer which is influenced by the surface is then:

$$\nu = \frac{\theta_c}{\theta_p}\hat{s}d\rho_c \tag{2}$$

where s is the specific surface (m²/kg); ρ_c is the density of filler (kg/m³); d is the range of the zone of interaction; θ_c is the volume fraction of filler; and θ_p is the volume fraction of synthetic polymers.

Inserting equation (2) in equation (1) yields the following expression:

$$T_g = T_{gs} + \frac{\theta_c}{\theta_p}\hat{s}d\rho_c\Delta T_g \tag{3}$$

Thus a straight line should be obtained when T_g is plotted *versus* the ratio of the volume fraction of the filler and the synthetic polymer. When $\nu = 1$ no further change in T_g occurs and all the matrix polymer is influenced by the interaction.

However, it may also be assumed that the shift in glass transition temperature, ΔT_g, is induced by the presence of a stress field surrounding the particles. For a hydrostatic pressure this may be expressed by the following general form:

$$\Delta T_g = \frac{\delta T_g}{\delta P}\Delta P \tag{4}$$

The range and the character of the stress field determines the contributions to the T_g (discussed in a separate paper).

RESULTS

Plots of the change in T_g *versus* the volume of cellulose and synthetic polymer according to equation (3) are given in *Figures 1* and *2*. The general form is as expected with an initial linear region which reaches a permanent level for the shift in T_g.

The curves may be evaluated with regard to the zone of interaction, d, by means of identifying the critical volume ratio where the linearity of T_g is interchanged to the constant level. Thus:

$$d\hat{s}\left(\frac{\theta_c}{\theta_p}\right)_{crit}\rho_c = 1 \tag{5}$$

where $\rho_c \approx 1.5 \times 10^3$ kg/m³.

The results are summarized in *Table 1*. It is seen that the zone of interaction is of the same order as the particle size.

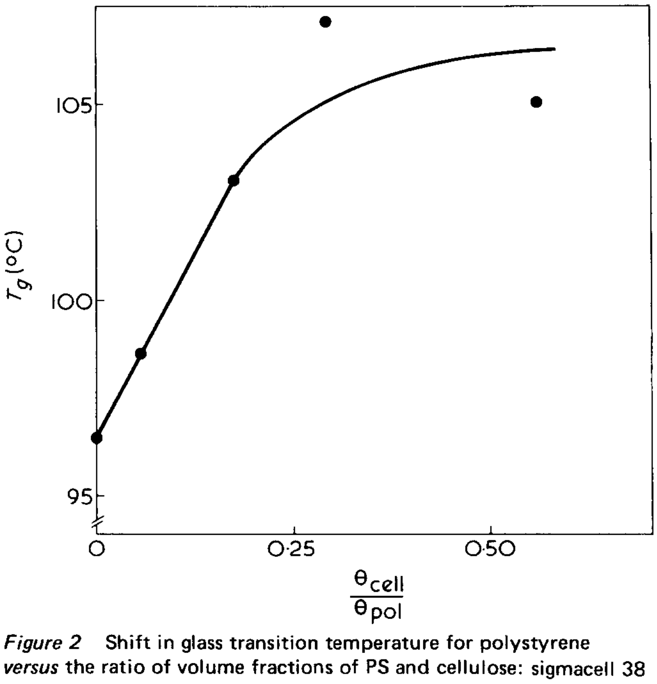

Figure 2 Shift in glass transition temperature for polystyrene *versus* the ratio of volume fractions of PS and cellulose: sigmacell 38

Table 1

Polymer	$\left(\frac{\theta_c}{\theta_p}\right)_{crit}$	$\hat{s}$(m²/kg) × 10^{-3}	ΔT_g(K)	d(calc) (μm)
PS	0. 25	1.37	9.5	2.0
PVAC	0.40	1.37	5	1.3

Table 2 Modulus, E, volume expansion coefficient, α, and pressure dependence of glass transition temperature of polymers

Polymer[a]	E (Pa)	α_{glass} (K^{-1})	$\frac{\delta T_g}{\delta P}$ (Pa/K)
PVAC[a]	2×10^5	2.4×10^{-4}	2.1×10^{-3}
PS[a]	2×10^5	2.3×10^{-4}	3.1×10^{-3}
Cellulose[b,c]	3×10^7	$\sim 0.5 \times 10^{-4}$	–

[a] Ref 11; [b] ref 12; [c] ref 13

Pure interfacial phenomena such as adsorbed layers of molecules would rather be expected to yield a distance on the molecular scale. A change in particle size from 38 μm to 19 μm did not affect the determination of T_g within the limit of experimental accuracy.

It is notable that many previous authors have used filler material with a very high specific surface area. In these cases the zone of interaction is naturally limited to small distances by virtue of equation (3) which may make it difficult to distinguish between plausible mechanisms leading to the shift in T_g.

However, a shift in T_g due to the term $\delta T_g/\delta P$ must imply an extremely high level of stress. From the characteristic data of the polymers collected in *Table 2* it is possible to calculate the shift in T_g at various temperature differences.

It is notable that cellulose has a lower volume expansion coefficient and a higher modulus than the synthetic polymers. This is essential as it implies that a high level of thermal stresses may be established during temperature variations. In *Table 2* the properties of cellulose are given in the chain direction. Considering that the elastic modulus of cellulose is considerably larger than for the synthetic polymers an estimate of the thermal stress may be made by the following equation[9]:

$$\Delta P = E_{\text{pol}}(\alpha_{\text{pol}} - \alpha_{\text{cell}})\Delta T/1 + u \qquad (6)$$

where ΔP is the thermal stress (Pa); E is the modulus of the polymer (Pa); ΔT is the temperature difference (K) and u is Poisson's ratio (0.33 for a glassy polymer). By inserting the values given in *Table 2* in equations (4) and (6) it may be seen that the shifts in T_g *versus* the temperature difference for PS and PVAC may reach the same order as obtained in this study. Large shrinkage stresses may also develop when solvent is evaporated in the glass transition regime of the matrix polymer. These effects may qualitatively be described in the same manner as in equation (6).

From the given example it seems that the shift in T_g observed for both polymers may well be explained by the presence of thermal or shrinkage stresses.

CONCLUSION

The findings in this study indicate that the calculated zone of interaction between cellulose and synthetic polymers is surprisingly high. It is suggested that the relatively large difference in expansivities and high elastic properties of cellulose may constitute the physical conditions for the creation of thermal or shrinkage stresses large enough to raise the T_g. This may in general be the case for many composite polymer materials where cellulose is incorporated in amorphous matrices. The most common case would be wood fibres where cellulose, present as crystalline microfibrils, is embedded in amorphous wood polymers, predominantly lignin and hemicellulose.

REFERENCES

1 Landel, R. F. *Trans. Soc. Rheol.* 1958, **2**, 53
2 Droste, D. H. and di Benedetto A. T. *J. Appl. Polym. Sci.* 1969, **13**, 2149
3 Yim, A and St Pierre, L. E. *Polym. Lett.* 1960, **7**, 237
4 Yim, A., Chahal, R. S. and St Pierre, L. E. *J. Colloid Interface Sci.* 1973, **43**, 583
5 Lipatov, Yu. S. and Fabulgate, F. Y. *J. Appl. Polym. Sci.* 1972, **16**, 2131
6 Lipatov, Yu S., Babich, V. F. and Rosovizky, V. F. *J. Appl. Polym. Sci.* 1974, **18**, 1213
7 Micromeretics Instrument Corporation, Model 2100, Instruction Manual, Coulter Electronics
8 Martin-Löf, S. and Söremark, Ch. *J. Appl. Polym. Sci.* 1971, **15**, 1465
9 Nicolas, L. and Mashelkar, R. A. *J. Appl. Polym. Sci.* 1976, **20**, 561
10 Rigdal, M. and de Ruvo, A. *Int. J. Polym. Mater.* submitted for publication
11 Kaeble, D. M. 'Physical Chemistry of Adhesion', Wiley – Interscience
12 Mark, R. F. *J. Polym. Sci. (C)* 1971, **36**, 393
13 Kubat, J. *et al. Sven. Papperstidn.* 1969, **72**, 763