JOURNAL OF MATERIALS SCIENCE 26 (1991) 2579–2582

Mechanical study of poly(vinylidene fluoride)–poly(methyl methacrylate) amorphous blends

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Amorphous films of poly(vinylidene fluoride)–poly(methyl methacrylate) were prepared by initial precipitation from a solvent and rapid solidification at ≈ 15 °C from the molten state. The PVDF/PMMA compositions studied were 25/75, 45/55, 50/50, 55/45, 60/40 and 75/25. X-ray scattering analysis suggests that mixture of the two components throughout the composition range studied occurs at a molecular level. The parallel decrease of the microhardness, which obeys a simple expression: $H_{\text{blend}} = H_{\text{PMMA}}(1 - \phi)$ (ϕ being the PVDF concentration) and the glass transition temperature, T_g, following the predictions of Gordon and Taylor, reveals that the depression of microhardness is caused by the shift of T_g towards lower temperatures. It is pointed out that the effect of PVDF molecules is to act as a softening agent within the PMMA component.

1. Introduction

Microhardness (MH) has emerged in recent years as a technique capable of detecting structural and morphological changes in semicrystalline polymers [1–4]. The unoriented crystalline polymer can be considered as a composite system consisting of stacks of hard crystalline lamellae with a microhardness value, H_c, separated by compliant amorphous layers with a value H_a. Specifically, MH is an increasing function of both lamellar thickness, l, and crystallinity. In the case of flexible polymers well above T_g, where H_a is negligible, MH has been shown to be an increasing function of macroscopic density [3]. In this case the yield behaviour under the indenter has been described in terms of two preferential deformation modes: (a) crystal destruction for large crystallinities and (b) compression and displacement of chain segments against the local restraints of internal rotation of the predominant non-crystalline domains for low crystallinities [1]. Although a large amount of MH data has been collected for crystalline polymers, we have recently shown that MH can also furnish valuable structural information in the case of amorphous polymers [5]. For example, MH can detect with great precision the glass transition temperature, T_g, for non-crystalline polymers [5]. Molecular rearrangements taking place above and below T_g, such as physical ageing and thermal expansion, can also be followed by this technique. In amorphous polymers at temperatures below T_g, MH mainly depends upon temperature according to an exponential decrease of the type

$$H = H_0 \exp[-\beta(T - T_0)] \qquad (1)$$

where β is the so-called coefficient of thermal softening. Values of β between 1 and $20 \times 10^{-3}\ \text{K}^{-1}$ have been found for various amorphous polymers [5]. In the case of blends of two semicrystalline components such as polypropylene (PP) and polyethylene (PE) at temperatures lying near T_g, for the first component and $H_a \neq 0$, the hardness of the blend can be grossly described in terms of an additive model system [6]. Here, however, the coexistence of the different phases (for instance PP and PE) inhibits the crystallization capability of one phase and affects the annealing behaviour of the other phase, leading to deviations of the MH of the blends from the additivity law throughout the composition range.

The purpose of the present study is to supplement our earlier microhardness studies to the investigation of amorphous quenched blends of poly(vinylidene fluoride) (PVDF) and poly(methyl methacrylate) (PMMA) with reference to the MH additivity of the two components, in the light of the microstructural ("cluster size") and thermal (glass transition temperature) changes occurring. For this purpose fully homogeneous amorphous PVDF–PMMA blends were prepared. As is well known, these two polymers are compatible at high temperature [7]. It will be shown that although PVDF presents a T_g value well below room temperature and PMMA a T_g above room temperature, the T_g of the resulting amorphous blend lies always above room temperature according to the equation of Gordon and Taylor [8], a fact which has relevant implications for the yielding behaviour of the material.

2. Experimental procedure

Commercial samples of PVDF from Atochem and an atactic PMMA sample [9] were used in this study.

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Blends of the two polymers were prepared in a wide composition range by dissolving the polymers in hot acetone and further precipitation with water. The precipitates were dried in a hot vacuum oven for a period longer than 24 h. Blend plates of 1 mm thickness were pressure-moulded at 190 °C and 150 bar and rapidly quenched to ≈ 15 °C under a pressure of 50 bar. To determine the T_g value of each blend, differential scanning calorimetry (DSC) was performed using a DSC IV Perkin-Elmer at a scanning rate of 40 °C $\min^{-1}$ and using indium as a calibration standard. Fig. 1a illustrates a typical DSC scan for the 50:50 blend, showing the bend in $\Delta H/\Delta T$ at which the glass transition takes place. X-ray diffractograms of the amorphous blends were taken using nickel-filtered Cu$K\alpha$ radiation in conjunction with a powder diffractometer with a discriminating unit. Fig. 1b shows, as an example, the scattering maximum obtained for the 50:50 blend. The average value, D, of the bundles of molecules ("cluster size") which is equivalent to the "crystallite size" concept for a semicrystalline polymer was obtained from X-ray line broadening data using Scherrer's formula $D = \lambda/\beta\cos\theta$, where λ is the wavelength of the radiation used, β is the integral breadth of the X-ray scattering halo in radians and θ is the Bragg angle under consideration. The density of each sample was independently measured by the flotation method using cyclohexane ($\rho = 0.7785\ \mathrm{g\,cm^{-3}}$) and carbon tetrachloride ($\rho = 1.5940\ \mathrm{g\,cm^{-3}}$) at 20 °C. The MH value was derived from the average value of the impression diagonals using a Vickers pyramidal diamond. Four different loads of 0.05, 0.1, 0.2 and 1 N and a loading cycle of 0.1 min were used. For further details see Baltá Calleja *et al.* [3].

3. Results and discussion

Fig. 2 shows the linear decrease of MH as a function of PVDF concentration (ϕ). The obtained value of MH = 213 MPa for the starting compression-moulded PMMA material is gradually depressed with the increasing values of ϕ according to the simple expression

$$H_{\mathrm{blend}} = H_{\mathrm{PMMA}}(1 - \phi) \qquad (2)$$

This means that the PVDF molecules do not offer any mechanical contribution to the yield behaviour of the blend. In fact, these flexible molecules are just apparently acting as a plasticizer within the blend. Hence, extrapolation of the MH in Fig. 2 for $\phi = 100\%$ ("purely amorphous" PVDF, $T_g \approx -40$ °C) tends to a value equal to zero, which is consistent with the data reported for the amorphous component (H_a) of semicrystalline polymers (PE) well above T_g [10]. In addition, the presence of one single X-ray halo (Fig. 1b), as well as one single T_g value (see Fig. 1a) for all the blends throughout the composition range investigated favours the view that these materials are composed of homogeneous mixtures of the two polymers at molecular level. The density, the spacing (d_a) derived from the maximum of the scattering halo and the cluster size D (coherently diffracting domain), derived from the integral width, are collected in Table I as a function of ϕ. These data clearly show that density increases and the frequently occurring interatomic distance d_a within this disordered molecular alloy concurrently decreases with ϕ. Additionally, the cluster size notably increases from 1.7 nm for pure PMMA up to 2.45 nm for $\phi = 0.75$. However, these coherently diffracting domains are sufficiently small to prevent

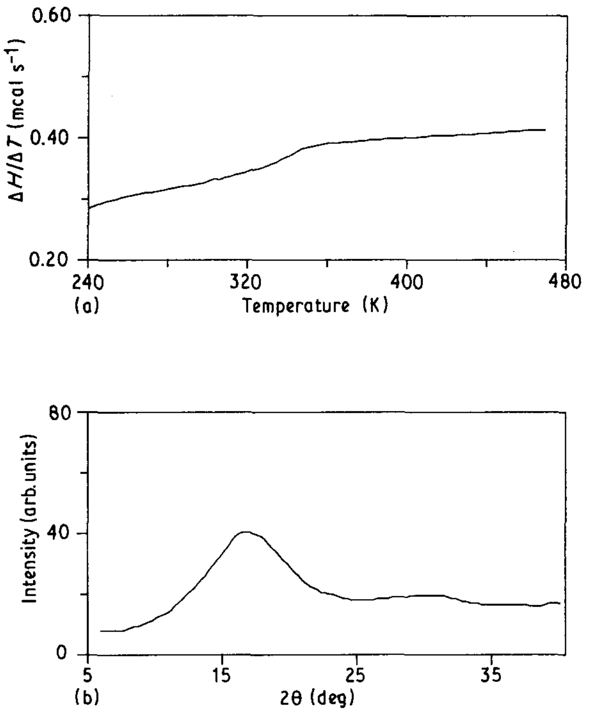

Figure 1 (a) Endothermic scan of the 50:50 PMMA–PVDF blend showing the appearance of one single glass transition temperature (1 cal = 4.19 J). (b) X-ray diffractogram of the same blend showing a single amorphous halo.

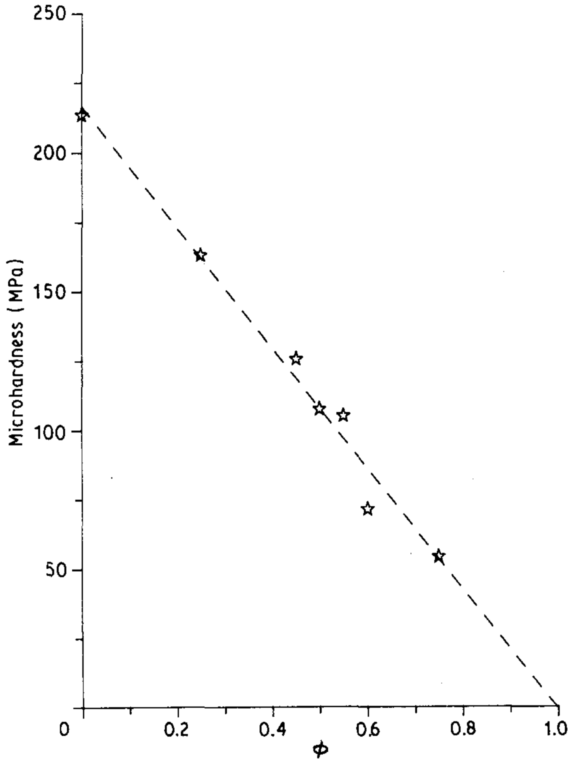

Figure 2 Plot of microhardness of PMMA–PVDF blends as a function of increasing content, ϕ, of the latter component.

the PVDF molecules from crystallizing within them, yielding, as a result, one single glass transition temperature. The average intermolecular packing within the blends improves with increasing amount of PVDF molecules, and the microstructure of the material shows better ordered microdomains with increasing ϕ, leading, consequently, to an increase of the macroscopic density values.

It is noteworthy that the parallel decrease of d_a and concurrent increase of ρ, and the resulting decrease of MH with ϕ is, at first sight, at variance with earlier results obtained with semicrystalline polymers [1–4, 11]. In the case of PE, for instance, molecular packing improvement [11] and density rise [3] always led to a MH increase. In order to explain the obtained MH decrease with ϕ for the PVDF–PMMA blends it is most illuminating to examine the variation of T_g with increasing ϕ. Fig. 3 shows the conspicuous decrease of T_g as a function of ϕ which fits very well with the predictions of Gordon and Taylor [8]:

$$T_g^B = \frac{T_{g1}\phi + kT_{g2}(1 - \phi)}{\phi + k(1 - \phi)} \qquad (3)$$

where T_{g1} and T_{g2} are the T_g values for PMMA and PVDF, respectively, and k is a constant equal to 1.70. The parallel decrease of MH and T_g (Figs 2 and 3) with ϕ immediately suggests that the depression of the former quantity is caused by the shift of T_g towards lower temperatures owing to the presence of the PVDF which acts as a softening agent. The T_g shift thus reduces the difference $\Delta T = T_g - T$ between the temperature of measurement T and the actual value of T_g of the blend, and MH consequently decreases according to Equation 1. Fig. 4 substantiates this contention by showing the linear correlation found between the MH depression $\Delta H = H_{\text{PMMA}} - H_{\text{PVDF}}$ and ΔT with increasing ϕ. In other words, the PVDF–PMMA blends behave as if they were single-phase homogeneous materials where the temperature of measurement is virtually increased with increasing ϕ.

TABLE I Macroscopic density ρ, mean interatomic distance d_a and "cluster size" D as function of PVDF concentration ϕ for PMMA–PVDF blends

ϕ	ρ(g cm^{-3})	d_a(nm)	D(nm)
0	1.1838	0.60	1.69
0.25	1.2766	0.54	1.87
0.45	1.3701	0.52	2.14
0.50	1.3901	0.53	2.23
0.55	1.4190	0.51	2.26
0.60	1.4437	0.51	2.30
0.75	1.5462	0.49	2.44
1.0	1.7400[a]	0.47	2.80

[a] Value taken from Lewis [12].

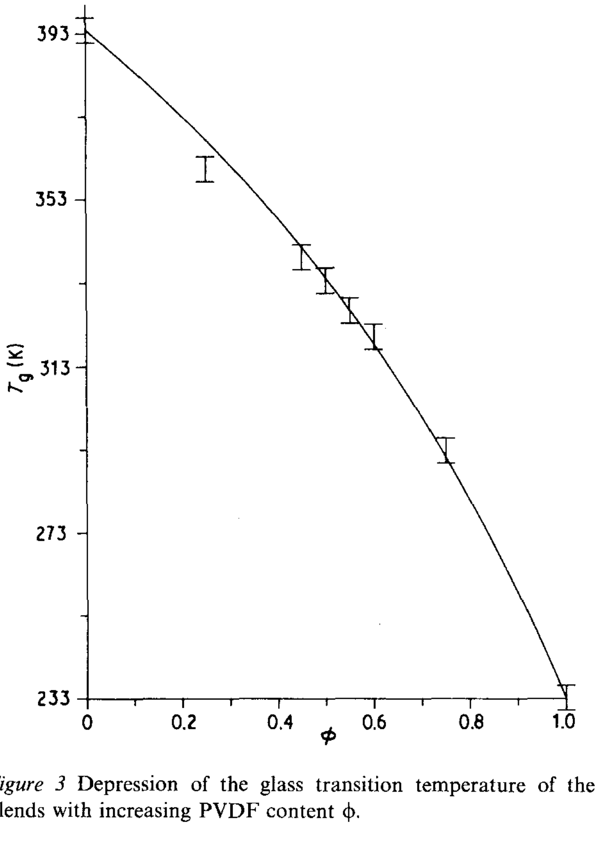

Figure 3 Depression of the glass transition temperature of the blends with increasing PVDF content ϕ.

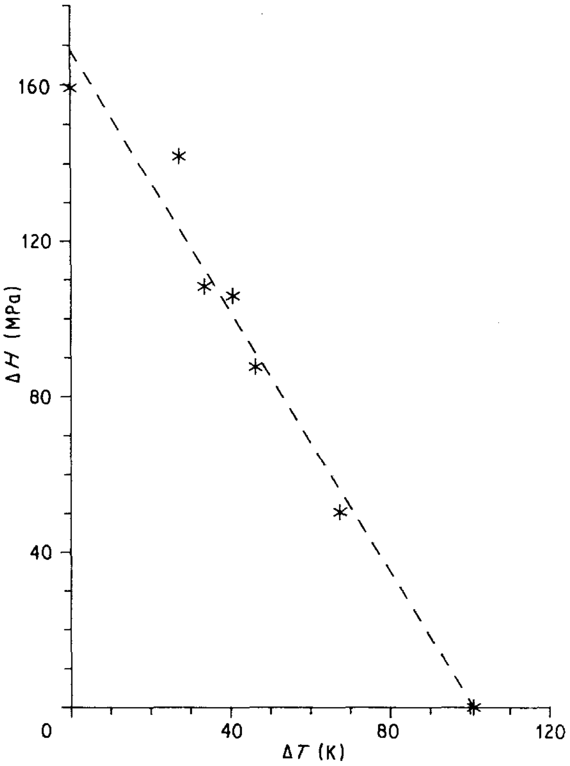

Figure 4 Hardness depression from the original H_{PMMA} value as a function of the T_g shift, $\Delta T = T_g - T$, with increasing content ϕ.

In conclusion, molecular packing, density and internal order play only a secondary role, in contrast to temperature, which is the dominant parameter in determining the yield behaviour (microhardness) of glassy homogeneous polymer blends below T_g. It is to be noted that the driving force for the MH depression of the blends is primarily due to the presence of flexible PVDF molecules which act as softening elements within the material.

Acknowledgement

This work was generously supported by CICYT (Spain) grant MAT88-0159.

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Received 7 December 1989
and accepted 14 August 1990