polymer communications

High pressure crystallization of poly(ethylene oxide) and poly(methyl methacrylate) mixture

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(Received 28 April 1993; revised 10 June 1993)

Dynamic mechanical and thermal properties of the binary mixture of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) crystallized at 500 and 0.1 MPa were studied. The result shows that the separation of the PEO and PMMA molecules occurs at high pressure.

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); crystallization)

Introduction

It is known that poly(ethylene oxide) (PEO) is semi-miscible with poly(methyl methacrylate) (PMMA) at atmospheric pressure. Melting point depression of PEO occurs with increasing PMMA content in the mixture[1], and the glass transition temperature, T_g, of the sample changes continuously with the weight fraction between the two T_gs of the component polymers[2]. However, the melting and crystallization behaviour of PEO in the mixture with PMMA changes at elevated pressure[3]. X-ray diffraction and optical microscopic observation of the mixed sample crystallized at 500 and 0.1 MPa show that crystallization of PEO in the mixture is hindered by the PMMA molecule at 0.1 MPa, but under high pressure the effect of hindrance of PMMA on the crystallization of PEO is decreased. It is considered that this difference occurs due to the separation of the molecules of PEO and PMMA under high pressure. In this work, to confirm the occurrence of crystallization of PEO apart from PMMA under high pressure, d.s.c. and dynamic mechanical measurement of the binary mixture of PEO and PMMA crystallized at 0.1 and 500 MPa are performed.

Experimental

Samples of PEO, with a molecular weight of 5 000 000, and PMMA, with a molecular weight of 93 300, were purchased from Scientific Polymer Products, Inc. Pure PEO and the mixed powder of 0.4 g of PEO and PMMA with weight fraction of PEO, $W_{PEO} = 0.6$, were dissolved in 80 ml of 1,2-dichloroethane at room temperature in a laboratory dish and the solvent was evaporated at 25°C for 2 days. The film sample was completely dried in a vacuum oven. The blend film of about 0.01 mm in thickness was cut into a strip of 5 mm × 20 mm. The film was sandwiched with cut slide glass, wrapped with aluminium foil and covered by epoxy resin to avoid attack by pressure-transmitting silicone oil.

High pressure crystallization was performed at 500 MPa using high pressure differential thermal analysis apparatus described elsewhere[4]. After pressurizing the sample in the high pressure vessel, the temperature was increased at a rate of 6 K min^{-1}. The temperature of the sample was kept at about 20°C above the melting temperature of PEO at 500 MPa (about 110°C) for 10 min, and then cooled down to room temperature at a rate of about 5 K min^{-1}; the rate changed from about 7 K min^{-1} at high temperature to 3 K min^{-1} at around room temperature. The crystallization of the sample at 0.1 MPa was performed in the same pressure vessel filled with silicone oil.

The dynamic mechanical measurement was performed from −160 to 55°C using Rigaku TMA 8140C. D.s.c. was performed using Rigaku DSC 8130D. The film sample was cut and used in the d.s.c. measurement.

Results and discussion

In the dynamic mechanical measurement of the polymer–polymer binary mixture, the temperature change of the storage modulus, E', depends on the miscibility of the component polymers. If the polymer pairs are immiscible and their T_gs are different, the decrease of E' due to the T_g of each polymer appears independently. In contrast, if the polymer pairs are miscible, the decrease of E' occurs around the new T_g due to the amorphous phase composed of the amorphous chains of the component polymers.

Figure 1 shows the temperature change of E' of pure PEO and the binary mixture of PEO/PMMA with $W_{PEO} = 0.6$ crystallized at 0.1 and 500 MPa. The curve of E' of the pure PEO sample crystallized at 0.1 MPa shows a drastic decrease of E' due to its T_g at about −50°C, and E' gradually decreases to its melting temperature on further heating. Pure PEO and the binary mixture crystallized at 500 MPa show almost the same behaviour in the temperature change of E' at around −50°C. However, the curve of E' of the binary mixture crystallized at 0.1 MPa shows different behaviour in the decrease of E'. In this sample, E' decreases above about −50°C up to the melting temperature of PEO (about 70°C). This means that in the mixture crystallized at 0.1 MPa, the molecules of PEO and PMMA are mixed in the amorphous phase. In contrast, in the mixture crystallized at 500 MPa, the molecules of the two polymers are separated even in the amorphous phase.

Figure 2 shows the d.s.c. curve of melting of pure PEO and PEO/PMMA binary mixture with $W_{PEO} = 0.6$ crystallized at 0.1 and 500 MPa. The peak melting temperature of the endothermic peak of pure PEO is 69.7°C for both samples crystallized at 0.1 and 500 MPa.

0032-3861/93/194166-02

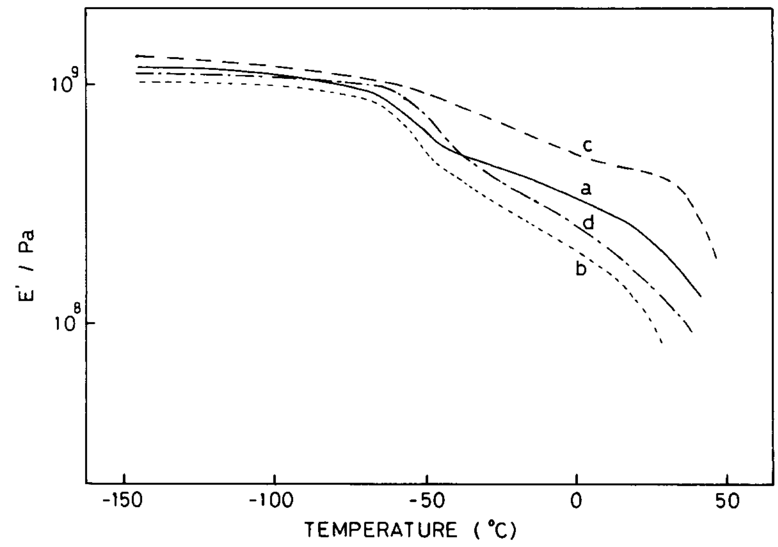

Figure 1 Temperature dependence of E' of pure PEO and the binary mixture of PEO and PMMA with $W_{PEO}=0.6$. a, Pure PEO crystallized at 0.1 MPa; b, pure PEO crystallized at 500 MPa; c, PEO and PMMA mixture crystallized at 0.1 MPa; d, PEO and PMMA mixture crystallized at 500 MPa

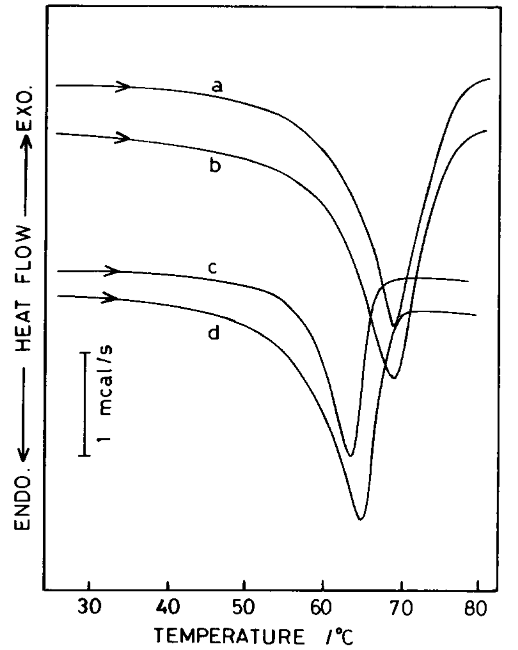

Figure 2 D.s.c. curves of melting of pure PEO and the binary mixture of PEO and PMMA crystallized at 0.1 and 500 MPa. The notation of the d.s.c. curves corresponds to that used in *Figure 1*

In the binary mixture, the peak temperature of melting of PEO crystallized at 0.1 MPa is 62.5°C and that of the sample crystallized at 500 MPa is 64.7°C. The melting temperature of PEO in the mixture crystallized at 500 MPa is about 2°C higher than that of the sample crystallized at 0.1 MPa. Furthermore, the heat of fusion of the sample crystallized at 500 MPa is larger than that of the sample crystallized at 0.1 MPa (13.1 mcal g^{-1} for 500 MPa crystallized sample and 12.4 mcal g^{-1} for 0.1 MPa crystallized sample). This effect may be reasonably interpreted as follows. At 500 MPa, the PEO and PMMA molecules are separated in the crystallization process and most of the PEO molecules crystallize apart from the PMMA molecules. On the contrary, at 0.1 MPa the crystallization of most of the PEO molecules is impeded by the PMMA molecules. Takahashi *et al.*[5] reported that the PMMA molecules were extracted from the region between PEO lamellae after a long time. It is considered that under high pressure the extraction of PEO molecules from the mixed region of PEO and PMMA molecules should occur. In conclusion, the mixing of PMMA and the application of pressure affect the melting and crystallization behaviour of PEO.

Experimental work is now in progress for samples with different weight fractions.

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