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Miscibility of poly(methoxymethyl methacrylate) and poly(methylthiomethyl methacrylate) with poly(methyl methacrylate)

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Summary

Poly(n-propyl methacrylate) is known to be immiscible with poly(methyl methacrylate) (PMMA). However, we have found that poly(methoxymethyl methacrylate) is miscible with PMMA, indicating the importance of ether oxygen atoms in achieving miscibility. On the other hand, poly(methylthiomethyl methacrylate) is immiscible with PMMA.

Introduction

Polymers containing ether oxygen atoms in their main chains or side groups are miscible with some carbonyl- or hydroxyl-containing polymers. A well-known example is the poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA) blend system (1-10). Spectroscopic study indicates a van der Waals type interaction between planar PEO segments and PMMA (7). Poly(vinyl methyl ether) (PVME), a polymer containing ether oxygen atoms in its pendant side groups, is miscible with poly(hydroxy ether of bisphenol-A) and poly(vinyl phenol) (11-12). The miscibility of these blends arises from hydrogen-bonding interactions involving the hydroxyl groups and the ether oxygen atoms (11-12).

Poly(alkyl methacrylate)s are immiscible with each other (13). For example, PMMA is immiscible with poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PnPMA) and poly(n-butyl methacrylate) (PnBMA) (13). In a recent paper, we reported that by incorporating chlorine atoms into the pendant groups of PMMA, the resulting polymer poly(chloromethyl methacrylate) (PCMMA) is miscible with PMMA, PEMA and PnPMA (14). In this communication, we report the calorimetric study on the miscibility of poly(methoxymethyl methacrylate) (PMOMA) and poly(methylthiomethyl methacrylate) (PMTMA) with PMMA. It is of interest to study how the presence of oxygen or sulfur atoms in the pendant alkyl groups affects the miscibility behavior.

Experimental

PMMA with an M_w of 120,000 was obtained from Du Pont (Elvacite 2010). The monomers, methoxymethyl methacrylate and methylthiomethyl methacrylate, were prepared following the procedures reported by Ueda et al. (15,16). PMOMA was prepared by solution polymerization in 2-butanone at reflux temperature for 24 h using 0.25 wt% of azobisisobutyronitrile (AIBN) as initiator. PMTMA was prepared by solution polymerization in 2-butanone at reflux temperature for 6 h using 0.20 wt% of AIBN as initiator. The polymers were obtained by precipitation of the solutions in excess methanol. The M_n of PMOMA is 17,000 and the M_w of PMTMA is 48,000 as determined by intrinsic viscosity measurements using the appropriate Mark-Houwink equations (15,16).

Various blends were prepared by solution casting from tetrahydrofuran at room temperature. The films obtained after solvent evaporation were dried in vacuo at 90°C for at least 72 h.

A Perkin-Elmer DSC-4 differential scanning calorimeter was used to measure the glass transition temperatures (T_g) of various samples using a heating rate of 20°C/min. Each sample was scanned between 30° and 150°C for several times and the initial onset of the change of slope in the DSC curve was taken as T_g.

Results and Discussion

All the PMOMA/PMMA blends were transparent, a good indication that PMOMA might be miscible with PMMA. The miscibility of these blends was ascertained by T_g measurements. Each of the blends showed only one composition-dependent T_g as shown in Fig. 1. Thus PMOMA is miscible with PMMA. The T_g-composition curve of the miscible blend system can be described by the Gordon-Taylor equation

$$T_g \text{ (blend)} = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)$$

where T_{gi} and w_i are the T_g and weight fraction of polymer i in the blend respectively, and k is an adjustable parameter. The curve in Fig. 1. was drawn using a k value of 0.30.

Since PnPMA is immiscible with PMMA (13), the miscibility of PMOMA with PMMA clearly demonstrates the importance of ether oxygen atoms. Thus, the replacement of methylene groups in the pendant groups of PnPMA with ether oxygen atoms does affect the miscibility behavior.

In contrast, all the PMTMA/PMMA blends were translucent. DSC measurements revealed the presence of two glass transitions in each blend. The T_g values of the blends are summarized in Table 1. The lower T_g values correspond to that of PMTMA. The upper T_g values are significantly lower than that of PMMA. This indicates the presence of PMTMA in the PMMA-rich phase.

Nevertheless, the translucency and glass transition behavior show the two-phase nature of PMTMA/PMMA blends.

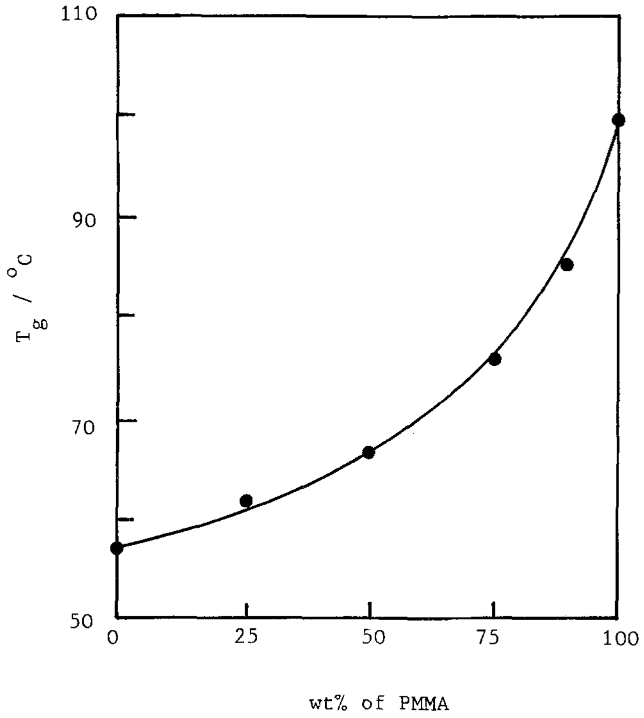

Fig. 1. T_g-composition curve of PMOMA/PMMA blends

Table 1. T_g values of PMTMA/PMMA blends

wt% of PMMA in blend	T_g
0	53
10	54, 95
25	54, 92
50	52, 86
60	54, 87
75	53, 84
90	54, 82
100	100

The results show that the replacement of ether oxygen atoms of PMOMA with sulfur atoms leads to immiscibility. A plausible explanation is that the larger size and the smaller electronegativity of sulfur as compared to oxygen reduces the interaction with the carbonyl group of PMMA and consequently results in the observed immiscibility.

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