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Miscible blends of poly(tetrahydrofurfuryl methacrylate) with two hydroxyl-containing polymers

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Summary

Poly(tetrahydrofurfuryl methacrylate) (PTHFMA) was found to be miscible with poly(hydroxy ether of bisphenol A) (phenoxy) as shown by the existence of a single glass transition temperature in each blend. PTHFMA/phenoxy blends containing 50% or less of PTHFMA showed reversible lower critical solution temperatures. PTHFMA was judged to be miscible with poly(styrene-co-allyl alcohol) based on the optical clarity of the blends.

Introduction

The miscibility of homologous polymethacrylates with other polymers such as poly(vinyl chloride) (PVC) (1,2), poly(styrene-co-acrylonitrile) (SAN) (3) and poly(α-methyl styrene-co-acrylonitrile) (MSAN) (4) has been studied. The lower members of the polymethacrylates are readily miscible with these polymers but the higher members are not. We have recently reported that poly(tetrahydrofurfuryl methacrylate) (PTHFMA), a polymethacrylate with a large pendant group, is miscible with PVC, SAN and MSAN (5). The miscibility of PTHFMA with poly(hydroxy ether of bisphenol A) (phenoxy) and poly(styrene-co-allyl alcohol) (PSAA) is reported in this communication.

Experimental

The following polymers were used in this study: PTHFMA (Scientific Polymer Products, Inc., $[\eta]$ = 0.31 dl/g in toluene at 30°C), phenoxy (Union Carbide PKHH, M_w = 80,000) and PSAA (Scientific Polymer Products, Inc., hydroxyl content 5.4-6.0%, M_w = 1,600).

Blends were prepared by solution casting from tetrahydrofuran. Solvent was allowed to evaporate slowly at room temperature. The blends were then dried in a vacuum oven at 110°C for 48 hours.

Glass transition temperatures (T_g) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. The initial onset of the change of slope in the heat capacity plot was taken as T_g.

All the miscible blends were examined for the existence of lower critical solution temperatures (LCST). The sample was sandwiched between two microscopic cover glasses and then heated in a Fisher-Johns melting apparatus. The optical appearance of the sample was observed with a magnifying glass attached to the apparatus. A transparent sample which turned cloudy upon heating indicated the existence of LCST. The temperature at which the sample first showed cloudiness was recorded as the cloud point.

Results and discussion

All the PTHFMA/phenoxy blends were transparent. Each blend showed a single composition-dependent T_g as shown in Fig. 1. Thus PTHFMA is miscible with phenoxy over the entire composition range. The T_g's of the blends can be described by the Gordon-Taylor equation (6)

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

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, polymer 1 and polymer 2, respectively; w_1 and w_2 are the weight fractions of polymer 1 and polymer 2 in the blend; and k is a parameter. The curve in Fig. 1 is drawn using the Gordon-Taylor equation with a k value of 0.25.

PTHFMA/phenoxy blends containing 50% or less of PTHFMA turned cloudy when heated to 260-280°C, showing the existence of LCST. The cloud points are 260, 265 and 275°C for blends containing 10, 25 and 50% of PTHFMA, respectively. The phase separation induced by heating is reversed on cooling. Many miscible polymer blends show LCST behavior (7-9), and in most cases the phase separation is not reversible because of the low mobilities of the polymer chains. Other miscible blends which show

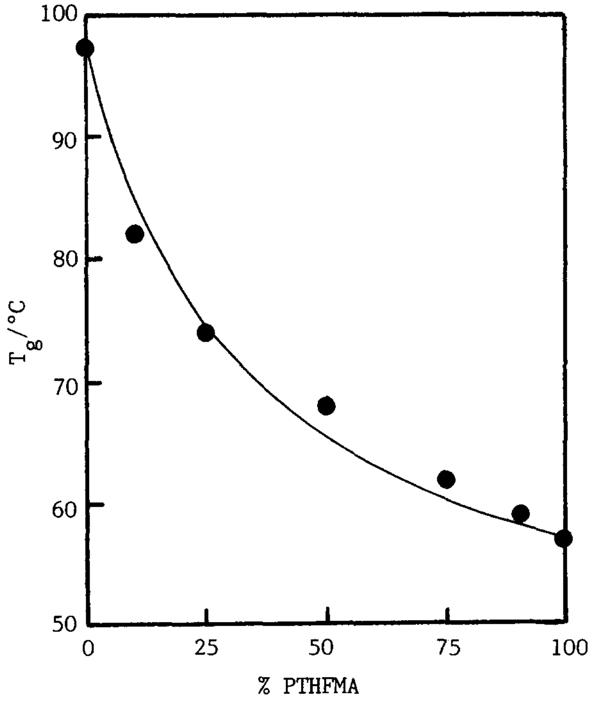

Fig. 1.
T_g-composition curve of PTHFMA/phenoxy blends.
●: experimental T_g

reversible LCST behavior include blends of phenoxy with poly(2,2-dimethyl-1,3-propylene succinate) and poly(2,2-dimethyl-1,3-propylene adipate) (10). Phase separation was not observed for PTHFMA/phenoxy blends containing 75 and 90% of PTHFMA up to 300°C, the upper temperature limit of the apparatus. However, all the PTHFMA/phenoxy blends began to show discoloration at 270-280°C caused by degradation of the polymers.

Phenoxy is miscible with many polyesters and poly(vinyl alkyl ether)s (10-15). Fourier-transform infrared (FTIR) spectroscopic studies have shown that there is hydrogen-bonding interaction between the hydroxyl group of phenoxy and the carbonyl group or the ether oxygen of other polymers (14,15). It is likely that the formation of miscible PTHFMA/phenoxy blends also involves hydrogen-bonding interaction between the hydroxyl group of phenoxy and the carbonyl group and ether oxygen in the tetrahydrofuran ring of PTHFMA.

PTHFMA/PSAA blends were transparent. However, the closeness of the T_g's of PTHFMA (57°C) and PSAA (56°C) precluded the use of T_g measurement to ascertain the miscibility of the blends. An immiscible blend can be transparent if the difference between the refractive indices of the two component polymers is smaller than 0.01 or the domain size is smaller than the wavelength of visible light. The refractive indices of PTHFMA and PSAA are estimated to be 1.504 and 1.580, respectively, by the Vogel method (16). The Vogel method provides a good estimation of the refractive index of a polymer. For example, the refractive index of polystyrene is estimated to be 1.590 as compared to the experimental value of 1.591 (16). The transparency of PTHFMA/PSAA blends is therefore not a result of matching refractive indices of the two polymers. All the blends remained transparent up to 260-270°C where they began to show discoloration. The optical clarity of PTHFMA/PSAA blends is taken as an indication of miscibility.

Similar to phenoxy, PSAA is miscible with many polyesters (17-19). FTIR studies have also shown the existence of hydrogen-bonding in PSAA/poly(ϵ-caprolactone) blends (19). Since PTHFMA is immiscible with poly(styrene) (5), the miscibility of PTHFMA/PSAA blends appears to indicate the importance of hydrogen-bonding interaction in achieving miscibility. However, as PSAA is a copolymer, the intramolecular interaction between styrene and allyl alcohol units in PSAA can also be an important factor as suggested by recent theories on the miscibility of homopolymer/copolymer blends (20-22).

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References

1. D.J. Walsh and J.G. McKeown, Polymer 21, 1330 (1980).
2. D.J. Walsh and J.G. McKeown, Polymer 21, 1335 (1980).
3. J.S. Chiou, D.R. Paul and J.W. Barlow, Polymer 23, 1543 (1982).
4. S.H. Goh, D.R. Paul and J.W. Barlow, Polym. Eng. Sci. 22, 34 (1982).
5. S.H. Goh and K.S. Siow, J. Appl. Polym. Sci., in press.
6. M. Gordon and J.S. Taylor, J. Appl. Chem. 2, 495 (1952).
7. R.E. Bernstein, C.A. Cruz, D.R. Paul and J.W. Barlow, Macromolecules 10, 681 (1977).

8. T. Nishi, J. Macromol. Sci.-Phys. B17, 517 (1980).
9. T. Hishi, CRC Critical Reviews in Solid State and Materials Science 12, 329 (1985).
10. J.E. Harris, S.H. Goh, D.R. Paul and J.W. Barlow, J. Appl. Polym. Sci. 27, 839 (1982).
11. G.L. Brode and J.V. Koleske, J. Macromol. Sci.-Chem. A6, 1109 (1972).
12. L.M. Robeson and A.B. Furtek, J. Appl. Polym. Sci. 23, 645 (1979).
13. L.M. Robeson, W.F. Hale and C.N. Merriam, Macromolecules 16, 1644 (1981).
14. M.M. Coleman and E.J. Moskala, Polymer 24, 251 (1983).
15. E.J. Moskala and M.M. Coleman, Polym. Commun. 24, 206 (1983).
16. D.W. Van Krevelen, "Properties of Polymers", 2nd edition, Elsevier, Amsterdam, Chap. 10 (1976).
17. R.S. Barnum, S.H. Goh, D.R. Paul and J.W. Barlow, J. Appl. Polym. Sci. 26, 3917 (1981).
18. E.M. Woo, J.W. Barlow and D.R. Paul, J. Appl. Polym. Sci. 29, 3837 (1984).
19. F. Cangelosi and M.T. Shaw, Polym. Prepr. 25(1), 258 (1984).
20. R.P. Kambour, J.T. Bendler and R.C. Bopp, Macromolecules 16, 753 (1983).
21. G. ten Brinke, F.E. Karasz and W.J. MacKnight, Macromolecules 16, 1827 (1983).
22. D.R. Paul and J.W. Barlow, Polymer 25, 487 (1984).

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