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Miscibility of some phenoxy/polymethacrylate blends

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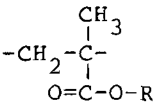
Summary

It has been reported that phenoxy is miscible with poly(methyl methacrylate), poly(tetrahydrofurfuryl methacrylate) and poly(tetrahydropyranyl-2-methyl methacrylate). However, we have found that phenoxy is immiscible with poly(ethyl methacrylate), poly(n-propyl methacrylate), poly(n-butyl methacrylate), poly(methylthiomethyl methacrylate), poly(methoxymethyl methacrylate) and poly(methoxycarbonylmethyl methacrylate). The miscibility behavior of various phenoxy/polymethacrylate blends cannot be satisfactorily explained by a non-hydrogen-bonded solubility parameter approach.

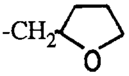
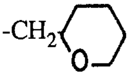
Introduction

Poly(hydroxyether of bisphenol-A) (phenoxy) is readily miscible with a large variety of polymers including polyesters (1-4), polyethers (5,6), poly(N-vinyl-2-pyrrolidone) (7) and polyethersulfone (8). Fourier-transform infrared (FTIR) spectroscopic studies have shown the existence of hydrogen-bonding interactions between hydroxyl groups of phenoxy and carbonyl groups or ether oxygen atoms of the other polymers (4,5).

We have earlier reported that phenoxy is miscible with poly(tetrahydrofurfuryl methacrylate) (PTHFMA) (9) and poly(tetrahydropyranyl-2-methyl methacrylate) (PTHPMA) (10), and the blends show lower critical solution temperature (LCST) behavior. It is believed that the presence of ether oxygen atoms in the pendant tetrahydrofuran and tetrahydropyran rings promotes miscibility. On the other hand, we have also found that poly(acetonyl methacrylate) (PACMA), a polymethacrylate containing additional carbonyl groups in the pendant groups, is immiscible with phenoxy (10). Several recent papers (11-13) report that phenoxy is miscible with poly(methyl methacrylate) (PMMA) and the blends show LCST behavior (11). It is desirable to extend the study to blends of phenoxy with other polymethacrylates in order to better understand the effects of the nature of the pendant groups of polymethacrylates on their miscibility behavior. In this communication, we report the miscibility of phenoxy with poly(ethyl methacrylate) (PEMA), poly(n-propyl methacrylate) (PnPMA), poly(n-butyl methacrylate) (PnBMA), poly(methoxymethyl methacrylate) (PMOMA), poly(methylthiomethyl methacrylate) (PMTMA) and poly(methoxycarbonylmethyl methacrylate) (PMCMA).



$$-CH_2-\underset{O=C-O-R}{\overset{CH_3}{C}}-$$

R = $-CH_2CH_3$	(PEMA; T_g = 65°C)
$-CH_2CH_2CH_3$	(PnPMA; T_g = 45°C)
$-CH_2CH_2CH_2CH_3$	(PnBMA; T_g = 20°C)
$-CH_2OCH_3$	(PMOMA; T_g = 56°C)
$-CH_2SCH_3$	(PMTMA; T_g = 53°C)
$-CH_2COCH_3$	(PACMA; T_g = 55°C)
$-CH_2COOCH_3$	(PMCMA; T_g = 55°C)
	(PTHFMA; T_g = 57°C)
	(PTHPMA; T_g = 62°C)

Experimental

Materials

Monomeric MCMA was prepared following the procedures by Evans and co-workers (14). PMCMA was prepared by solution polymerization in 2-butanone at 65°C for 6 hours, initiated by 0.25 wt% of azobisisobutyronitrile. The number- and weight-average molecular weights of PMCMA are 36,000 and 62,000 respectively. PMOMA and PMTMA were prepared in this laboratory as described previously (15-17). The following commercial polymers were used in this study: phenoxy (Scientific Polymer Products, M_w = 28,000), PEMA (Du Pont Elvacite 2042, M_w = 310,000), PnPMA (Scientific Polymer Products, M_w = 175,000), and PnBMA (Du Pont Elvacite 2044, M_w = 288,000).

Preparation of blends

Binary blends of phenoxy with various polymethacrylates in weight ratios of 1:3, 1:1 and 3:1 were prepared by solution casting from tetrahydrofuran (THF). Solvent was allowed to evaporate slowly at room temperature. The blends were then dried in vacuo at 90°C for one week.

To investigate a possible solvent effect on miscibility, blends were also prepared by co-precipitation method. THF solutions of polymer mixtures were poured into excess methanol to obtain the blends. The blends were then dried in vacuo at 90°C for one week.

T_g measurements

The glass transition temperatures (T_gs) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20°C/min. The T_g value was taken as the initial onset of the change of slope in the DSC curve. Each sample was scanned several times to check the consistency of the T_g values.

Results and Discussion

Blends containing PEMA, PnPMA and PnBMA

All the blends cast from THF were cloudy, indicating the heterogeneous nature of the blends. DSC measurements showed the existence of two T_gs in each blend and the values were close to those of phenoxy and the polymethacrylate. DSC curves of various 1:1 blends are shown in Fig. 1. Similarly, blends prepared by co-precipitation method also showed two T_gs in each blend. Thus, phenoxy is immiscible with PEMA, PnPMA and PnBMA. The results show that phenoxy has a very narrow miscibility range with poly(n-alkyl methacrylate)s. Phenoxy is miscible with PMMA, but not with higher members of the poly(n-alkyl methacrylate)s. Coleman and co-workers (18) have recently predicted the miscibility of phenoxy with poly(n-alkyl methacrylate)s using parameters obtained from FTIR studies and non-hydrogen-bonded solubility parameters (δ_{nh}). They predicted that phenoxy was miscible with PMMA, but was immiscible with PEMA and other higher members of the poly(n-alkyl methacrylate)s. The present work confirms their prediction.

Blends containing PMOMA and PMTMA

PMOMA was included in this study in view of the miscibility of phenoxy with PTHFMA (9), PTHPMA (10) and some polyethers such as poly(ethylene oxide) (PEO) and poly(vinyl methyl ether) (PVME) (6). PMTMA was also studied in order to investigate the effect of the replacement of oxygen by sulfur on the miscibility behavior. We have earlier reported that PMMA is miscible with PMOMA but not with PMTMA (19).

THF-cast blends of phenoxy with PMOMA and PMTMA were also cloudy. The immiscibility of these blends was confirmed by T_g measurements which showed the existence of two T_gs in each blend. Typical DSC curves are shown in Fig. 1. Blends prepared by co-precipitation were also found to be immiscible.

Blends containing PMCMA

The miscibility of phenoxy/PMMA is a result of hydrogen-bonding interactions involving the hydroxyl groups of phenoxy and the carbonyl groups of PMMA (13). It is rather surprising to note that PACMA, which contains an additional carbonyl group in each polymer segment, is immiscible with phenoxy (10). This prompted us to study the miscibility of phenoxy with PMCMA. The pendant group of a PMCMA segment resembles that of a PMMA segment other than an intervening $-COOCH_2-$ group.

Interestingly, phenoxy is immiscible with PMCMA as shown by the opacity of the cast blends and the presence of two T_gs in each blend as shown in Fig. 1. Blends prepared by co-precipitation were also found to be immiscible from T_g measurements.

Miscibility behavior

Coleman and co-workers have used a δ_{nh} approach to explain the miscibility of polymer blends (20,21). The essence of their approach is that miscibility between two polymers is favored if their δ_{nh} values are closely matched and the intermolecular interactions are strong. For polymers able to interact with strong hydrogen-bonding

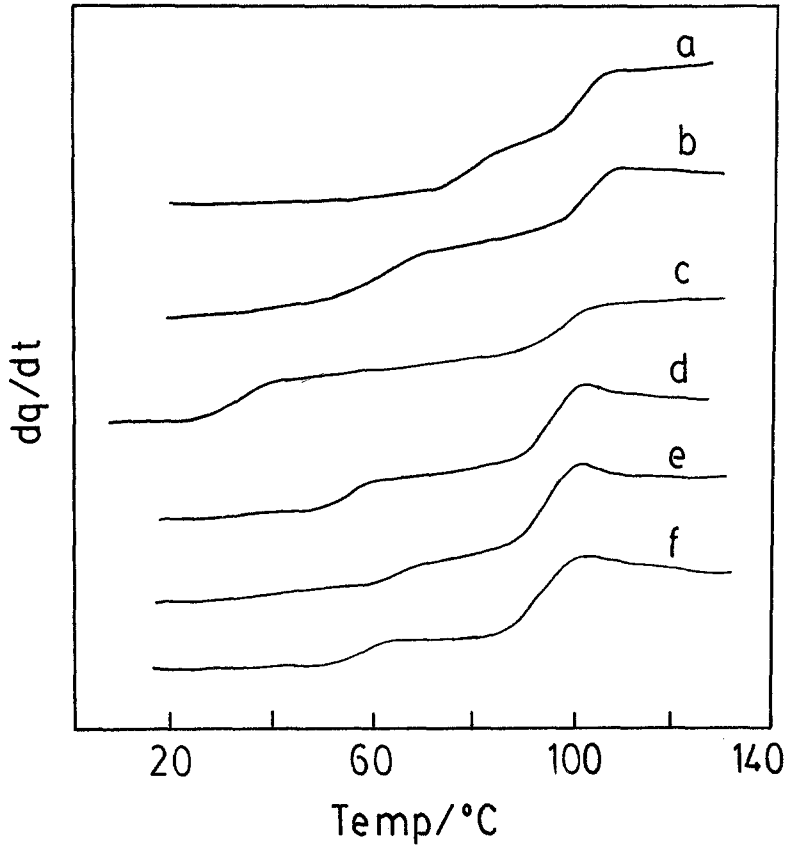


Fig. 1. DSC curves of THF-cast 1:1 phenoxy/polymethacrylate blends.
(a) PEMA, (b) PnPMA, (c) PnBMA, (d) PMOMA, (e) PMTMA and (f) PMCMA

interactions, a mismatch in δ_{nh} values as large as 2.5-3.0 (cal/cm^3)$^{1/2}$ [5.1-6.1 (J/cm^3)$^{1/2}$] can be tolerated. The δ_{nh} values for phenoxy, PMMA, PEMA, PnPMA and PnBMA are 20.9, 18.4, 18.2, 17.9, 17.8 (J/cm^3)$^{1/2}$, respectively (20,21). The difference in δ_{nh} values between phenoxy and poly(n-alkyl methacrylate) increases from PMMA to PnBMA. Thus, the misciblity between phenoxy and higher members of the poly(n-alkyl methacrylate)s is not favored.

From the group molar attraction constants (F) and group molar volumes (V) provided by Coleman and co-workers, the δ_{nh} values for PMOMA was found to be 19.1 (J/cm^3)$^{1/2}$. For PMTMA, the F and V values for sulfur are not available from Coleman's work. In this case, we use Small's F value of 460 (J/cm^3)$^{1/2}$/mol (22) and Fedor's V value of 12.0 cm^3/mol (22) for sulfur to obtain a δ_{nh} value of 20.3 (J/cm^3)$^{1/2}$ for PMTMA.

The immiscibility of phenoxy with PMOMA is rather surprising. Each PMOMA segment contains two sites, carbonyl group and ether oxygen, capable of interacting with phenoxy. Yet, PMOMA is immiscible with phenoxy. In terms of the δ_{nh} approach, the immiscibility of phenoxy/PMOMA blends is also unexpected. The δ_{nh} values for PEO and PVME are 19.3 and 17.3 $(J/cm^3)^{1/2}$, respectively, and these two polymers are miscible with phenoxy. PMOMA, with a δ_{nh} value of 19.1 $(J/cm^3)^{1/2}$, should be very likely to be miscible with phenoxy, but it is not. The δ_{nh} value of PMTMA is even more closely matched to that of phenoxy, but the blends are also immiscible.

Similarly, the immiscibility of phenoxy with PMCMA (δ_{nh} = 20.3 $(J/cm^3)^{1/2}$) cannot be accounted for by the δ_{nh} approach. Cowie and Elexpuru (23) have recently reported that while poly(n-alkyl methacrylate)s are miscible with poly(α-methylstyrene-co-acrylonitrile) (αMSAN), several poly(dialkyl itaconate)s are immiscible with αMSAN. Each poly(dialkyl itaconate) segment also contains two -COO- groups. It is also interesting to note that PACMA has a δ_{nh} value (21.2 $(J/cm^3)^{1/2}$)) very closely matched to that of phenoxy, and yet it is immiscible with phenoxy (10). However, Coleman (24) has pointed out that the solubility parameter approach does not consider polymers such as PACMA and PMCMA where there are two different interacting sites in each segment.

In summary, phenoxy is miscible with a limited number of polymethacrylates. The immiscibility of some blends found in this work cannot be satisfactorily explained by the non-hydrogen-bonded solubility parameter approach.

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