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Complexation between poly(hydroxyether of bisphenol-A) and three tertiary amide polymers

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The complexation behaviour between poly(hydroxyether of bisphenol-A) (phenoxy) and three isomeric tertiary amide polymers, namely poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), poly(*N*,*N*-dimethylacrylamide) (PDMA) and poly(2-ethyl-2-oxazoline) (PEOx), has been studied. Phenoxy forms interpolymer complexes with PMVAc and PDMA from tetrahydrofuran solutions over the entire feed composition range. However, complexation does not occur between phenoxy and PEOx from THF solutions, indicating a weaker intermolecular association in the phenoxy/PEOx blends than those in the phenoxy/PMVAc and phenoxy/PDMA blends. When using *N*,*N*-dimethylformamide as the solvent, only miscible blends are formed between phenoxy and all three tertiary amide polymers. Infra-red spectroscopic studies provide evidence of intermolecular hydrogen bonding between the hydroxyl groups in phenoxy and the carbonyl groups in tertiary amide polymers. The frequency shifts for the phenoxy hydroxyl group hydrogen bonded to the three tertiary amide polymers decrease in the order of PMVAc → PDMA → PEOx. Copyright © 1996 Elsevier Science Ltd.

(Keywords: interpolymer complexes; phenoxy; tertiary amide polymers)

INTRODUCTION

Interpolymer complexation behaviour has received increasing attention in recent years. Among the previously reported hydrogen bonding type polymer complex systems, one component polymer usually contains strong proton-donating groups in its polymer chains, such as carboxyl and phenolic hydroxyl groups. Poly(acrylic acid) (PAA)/poly(*N*-vinylpyrrolidone) (PVP)[1], poly(methacrylic acid) (PMAA)/PVP[1,2], PAA/poly(vinyl methyl ether) (PVME)[3], PAA/poly(2-ethyl-2-oxazoline) (PEOx)[4,5], poly(*p*-vinylphenol) (PVPh)/poly(*N*,*N*-dimethylacrylamide) (PDMA)[6], PVPh/PEOx[6], and phenol-formaldehyde resin/PDMA[7] are representatives of this type of interpolymer complexes.

Recently, we found that poly(styrene-*co*-allyl alcohol) (SAA) containing 4.5 and 6.5 wt% aliphatic hydroxyl groups can form interpolymer complexes with three tertiary amide polymers[8,9] at certain feed compositions, from methyl ethyl ketone (MEK) and from tetrahydrofuran (THF) solutions. It is envisaged that other aliphatic hydroxyl-containing polymers may also form interpolymer complexes with these tertiary amide polymers. In this paper, we report the complexation behaviour of poly(hydroxyether of bisphenol-A) (phenoxy) with three isomeric tertiary amide polymers, namely poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), PDMA and PEOx.

EXPERIMENTAL

Materials

Phenoxy was obtained from Scientific Polymer Products, Inc. PMVAc and PDMA were prepared in our laboratory as described previously[8,9]. PEOx was provided by the Dow Chemical Company. The molecular weights and glass transition temperatures of the polymers are listed in *Table 1*.

Preparation of interpolymer complexes and blends

Interpolymer complexes between phenoxy and PMVAc, PDMA or PEOx were obtained through mixing solutions containing 0.10 g of polymer per 10 ml of solvent. The precipitates, which formed upon mixing, were separated from the solutions by centrifugation and washed with the solvent. Supernatant liquids were allowed to evaporate to obtain the residual blends. For those systems which did not form interpolymer complexes, the solutions were allowed to evaporate slowly, at ambient temperature for THF solutions, and on a hot plate at 90–120°C for *N*,*N*-dimethylformamide (DMF) solutions. The complexes and blends were then dried *in vacuo* at 90°C for at least two weeks; they were stored in a desiccator to prevent the absorption of moisture. The nitrogen contents of the polymer complexes and the residual blends were determined by elemental analysis, using a Perkin–Elmer 2400 elemental analyser.

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Table 1 Characteristics of polymers

Polymer		M_n	M_w	T_g (°C)
Poly(hydroxyether of bisphenol-A)	(Phenoxy)	20300	30800	95
Poly(*N*-methyl-*N*-vinylacetamide)	(PMVAc)	3300	3700	136
Poly(*N*,*N*-dimethylacryamide)	(PDMA)	12000	19600	118
Poly(2-ethyl-2-oxazoline)	(PEOx)	38500	61500	56

Glass transition temperature (T_g*) measurements*

A Perkin-Elmer DSC-4 differential scanning calorimeter was used to measure the glass transition temperatures (T_g) of all samples. As tertiary amide polymers are highly hygroscopic, all the samples were preheated to 150°C and held at that temperature for 15 min to ensure complete removal of any moisture and residual solvent. The scanning rate was 20°C min^{-1} and T_g was taken as the initial onset of the change of slope in the differential scanning calorimetry (d.s.c.) curve. All the reported T_g values are taken as the average from several runs.

Fourier transform infra-red (FTi.r.) characterization

Infra-red (i.r.) spectra were recorded on a Perkin-Elmer 1725X *FT*i.r. spectrophotometer; 64 scans were signal-averaged at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell, equipped with an automatic temperature controller, which was mounted in the spectrophotometer. The sample chamber was purged with N_2. Samples for *FT*i.r. analyses were prepared by casting the DMF solutions onto KBr discs and then drying *in vacuo* at 90°C for at least two days.

Viscosity measurements

The viscosities of various polymer mixtures in DMF were measured using an Ostwald viscometer at 25°C. Measurements were conducted as a function of composition, with the polymer concentration kept constant at 0.010 g ml^{-1}.

RESULTS AND DISCUSSION

Complexation behaviour of phenoxy with tertiary amide polymers

Similar to poly(styrene-*co*-allyl alcohol) (SAA)[8,9], phenoxy can form interpolymer complexes with PMVAc and PDMA. Data on the yields and compositions of the polymer complexes and the corresponding residual blends, as well as their glass transition temperatures (T_g), are listed in *Tables 2* and *3*.

For the phenoxy/PMVAc system, complexation occurred in THF solutions at the entire feed composition range. The yields of complexes increased from 14.7 to 87.3 wt% with increasing PMVAc contents in the feed. The compositions of the complexes are rich in PMVAc, ranging from 70.4 to 95.5 mol% of PMVAc. The glass transition temperatures of these complexes are within a narrow range of 136–143°C and are higher than those of the component polymers, indicating a strong favourable intermolecular interaction between the two polymers.

Similar to the phenoxy/PMVAc system, phenoxy formed complexes with PDMA from THF solutions at the entire feed composition range. The yields of complexes increased from 2.5 to 46.5 wt% with increasing PDMA content in the feed and were clearly lower than those of the corresponding phenoxy/PMVAc complexes. The results indicate that the intermolecular interaction between phenoxy and PDMA is weaker than that between phenoxy and PMVAc. The compositions of the complexes, which depend on the feed composition, vary from 67.3 to 91.8 mol% of PDMA. The complexes also have T_g values higher than either of the component polymers.

Due to the strong ability of DMF in forming hydrogen bonds with proton donors, PMVAc and PDMA did not form interpolymer complexes with phenoxy through mixing their DMF solutions. The T_g *versus* composition curves (*Figures 1* and *2*) of both phenoxy/PMVAc and phenoxy/PDMA blends, cast from DMF solutions, are 'S'-shaped in form, which can be fitted by the Kwei

Table 2 Experimental data of phenoxy/PMVAc system

Feed composition PMVAc content		Polymer complexes			Residual blends		
(wt%)	(mol%)	Yield (wt%)	PMVAc content (mol%)	T_g (°C)	Yield (wt%)	PMVAc content (mol%)	T_g (°C)
10	24.2	14.7	70.4	136	85.3	16.5	95
25	48.9	24.0	71.4	137	76.0	40.4	97
50	74.2	71.2	80.3	137	28.8	56.7	99
75	89.6	85.9	86.2	140	14.1	93.9	113
90	96.3	87.3	95.5	143	12.7	99.2	118

Table 3 Experimental data of phenoxy/PDMA system

Feed composition PDMA content		Polymer complexes			Residual blends		
(wt%)	(mol%)	Yield (wt%)	PDMA content (mol%)	T_g (°C)	Yield (wt%)	PDMA content (mol%)	T_g (°C)
10	24.2	2.5	67.3	[a]	97.5	22.5	95
25	48.9	8.6	78.2	120	91.4	45.2	96
50	74.2	39.4	80.6	121	60.6	66.9	103
75	89.6	45.7	85.0	121	54.3	93.5	110
90	96.3	46.5	91.8	122	53.5	94.3	118

[a] Amount of complexes insufficient to make measurement

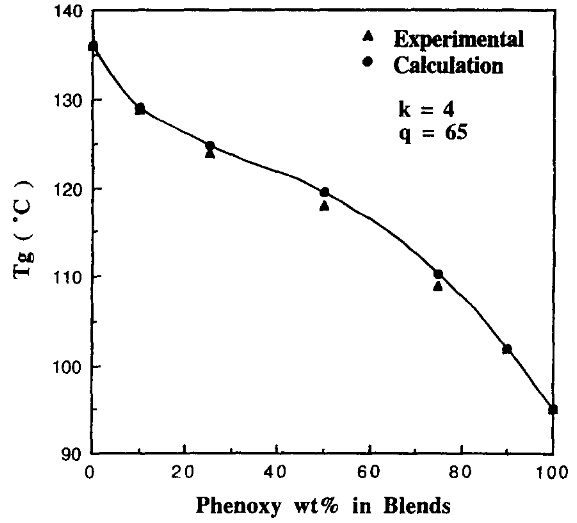

Figure 1 T_g *versus* composition curve of phenoxy/PMVAc miscible blends cast from DMF solutions

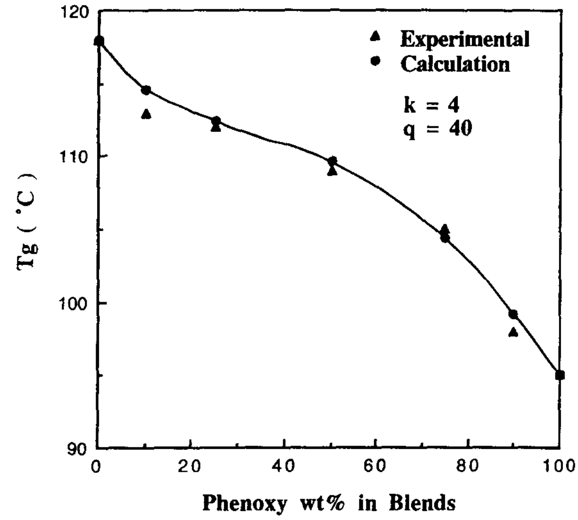

Figure 2 T_g *versus* composition curve of phenoxy/PDMA miscible blends cast from DMF solutions

equation[10,11]:

$$T_g(\text{blend}) = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) + qw_1w_2$$

where k and q are fitting constants, and have values of 4 and 65, and 4 and 40 for the phenoxy/PMVAc and phenoxy/PDMA systems, respectively.

Unlike the phenoxy/PMVAc and phenoxy/PDMA systems, complexation between phenoxy and PEOx did not occur upon mixing their THF or DMF solutions. Keskkula and Paul[12] have reported that THF-cast phenoxy/PEOx blends are miscible. This phenomenon shows that the intermolecular interactions between phenoxy and PEOx are weaker than those between phenoxy and PMVAc or PDMA. As shown in *Figure 3*, the T_g *versus* composition curve for the THF-cast blends can be fitted with the Kwei equation using k and q values of 5 and 70, respectively, but the corresponding curve for the DMF-cast blends is close to the composition average line.

FT*i.r. characterization*

Carbonyl region. *Figure 4* shows the i.r. spectra in the carbonyl stretching region, recorded at 150°C, of phenoxy, PMVAc, and a phenoxy/PMVAc blend containing 25 wt% PMVAc cast from DMF solutions. PMVAc (see curve A) has a strong absorption band centred at 1643 cm^{-1} for free carbonyl. Phenoxy (see curve B) has two bands at 1606 cm^{-1} and 1581 cm^{-1} which are assigned to the vibration of the aromatic ring in its polymer chain. A new band appearing at 1629 cm^{-1} in the spectra of the phenoxy/PMVAc blend (see curves C and D) can be reasonably considered as the contribution of the carbonyl groups in PMVAc which are bonded with the hydroxyl groups in phenoxy through hydrogen bonding. As shown in *Figure 5*, an increase in phenoxy content in the blends leads to an increase in the relative intensity of hydrogen bonded carbonyl band at 1629 cm^{-1} as compared with the free carbonyl peak, indicating

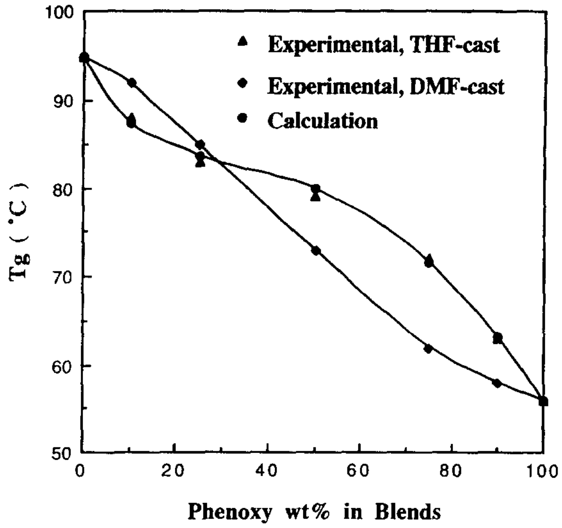

Figure 3 T_g *versus* composition curves of phenoxy/PEOx miscible blends cast from DMF and THF solutions

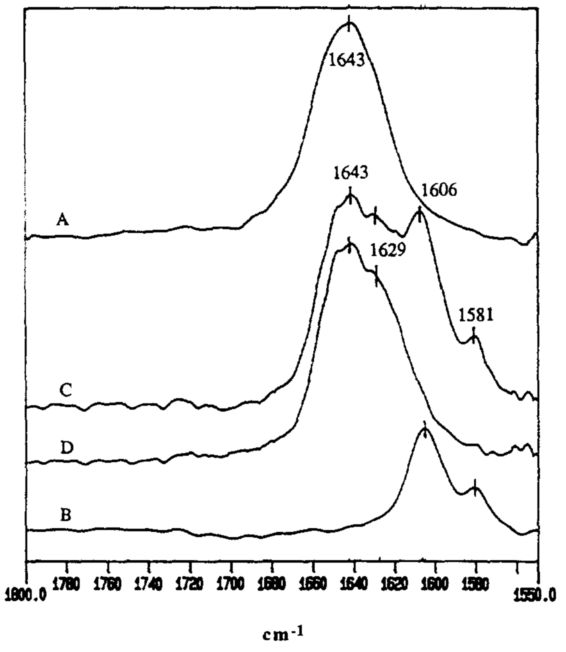

Figure 4 FT*i.r.* spectra, recorded at 150°C, of the carbonyl region, cast from DMF solutions: (A) PMVAc; (B) phenoxy; (C) phenoxy/PMVAc blend containing 25 wt% PMVAc; (D) spectrum obtained by subtracting the absorption of phenoxy in this region from spectrum C

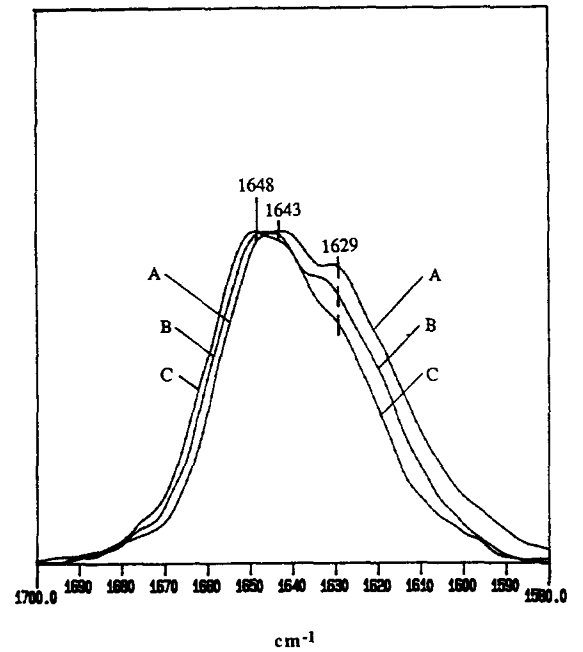

Figure 5 *FT*i.r. spectra, recorded at 150°C, of the carbonyl region (after subtracting phenoxy absorption) of phenoxy/PMVAc blends, cast from DMF solutions: (A) 25; (B) 50; (C) 75 wt% of PMVAc

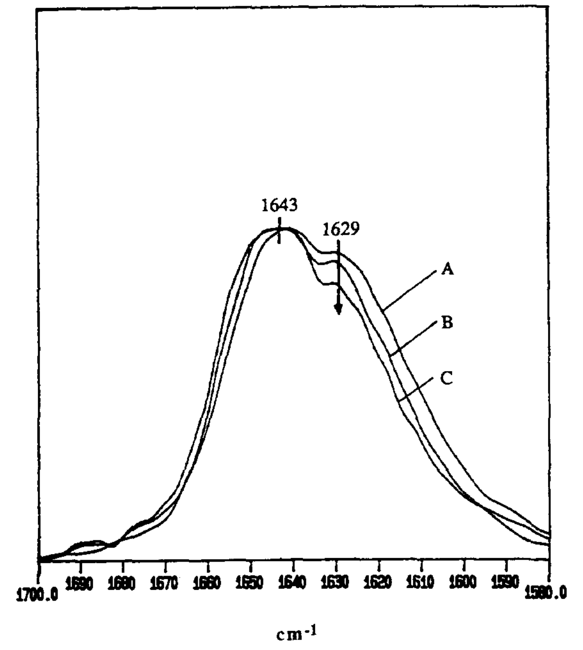

Figure 6 *FT*i.r. spectra of the carbonyl region (after subtracting phenoxy absorption) of the phenoxy/PMVAc blend containing 25 wt% of PMVAc, cast from DMF solutions, recorded at: (A) 120°C; (B) 150°C; (C) 180°C

that more carbonyl groups are involved in hydrogen bonding with the hydroxyl groups when the phenoxy concentration in the blends is increased. *Figure 6* shows the effect of temperature on the carbonyl band of the phenoxy/PMVAc blend containing 25 wt% of PMVAc (after subtracting the phenoxy absorption). The intensity of the peak at 1629 cm^{-1} decreases as the temperature is raised from 120 to 180°C, confirming that the peak at 1629 cm^{-1} is indeed due to the contribution of hydrogen bonded carbonyl groups.

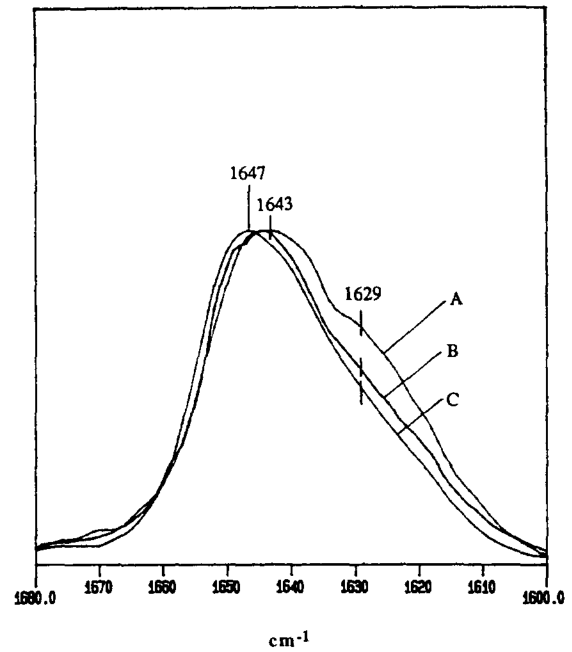

Figure 7 *FT*i.r. spectra, recorded at 140°C, of the carbonyl region (after subtracting phenoxy absorption) of phenoxy/PDMA blends, cast from DMF solutions: (A) 20; (B) 40; (C) 60 wt% of PDMA

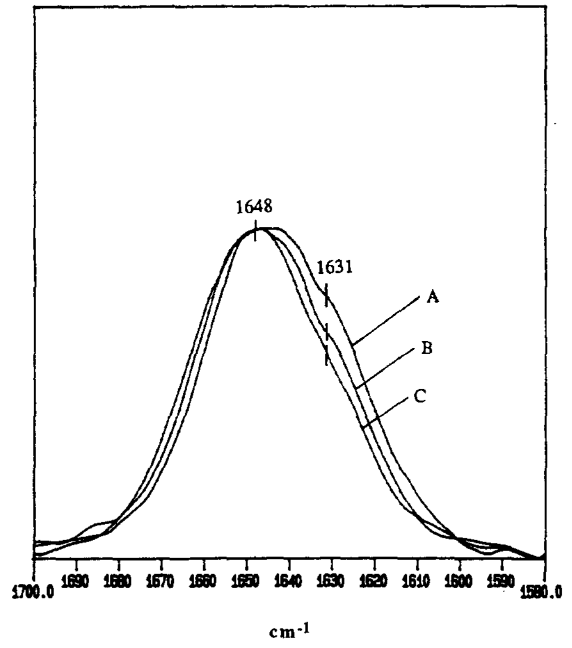

Figure 8 *FT*i.r. spectra, recorded at 140°C, of the carbonyl region (after subtracting phenoxy absorption) of phenoxy/PEOx blends, cast from DMF solutions: (A) 20; (B) 40; (C) 60 wt% of PEOx

Figures 7 and *8* depict the *FT*i.r. spectra in the carbonyl region, recorded at 140°C, of phenoxy/PDMA and phenoxy/PEOx blends (after subtracting the phenoxy absorption) cast from DMF solutions. The relative intensities of the shoulders at 1629 cm^{-1} and 1631 cm^{-1}, which correspond to the contributions of hydrogen bonded carbonyl groups of PDMA and PEOx, respectively, increase with increasing phenoxy content in the blends.

Hydroxyl region. The spectra of the hydroxyl stretching region can also provide valuable information on intermolecular hydrogen bonding between the component

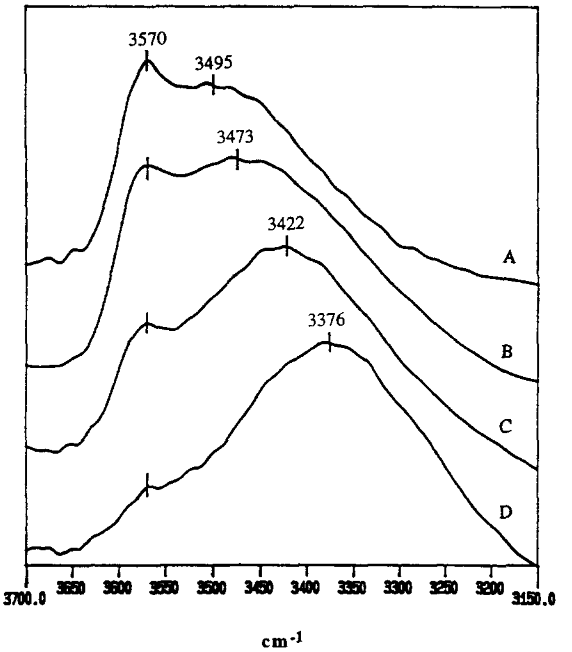

Figure 9 *FT*i.r. spectra, recorded at 140°C, of the hydroxyl region of phenoxy/PMVAc blends, cast from DMF solutions: (A) 0; (B) 10; (C) 25; (D) 50 wt% PMVAc

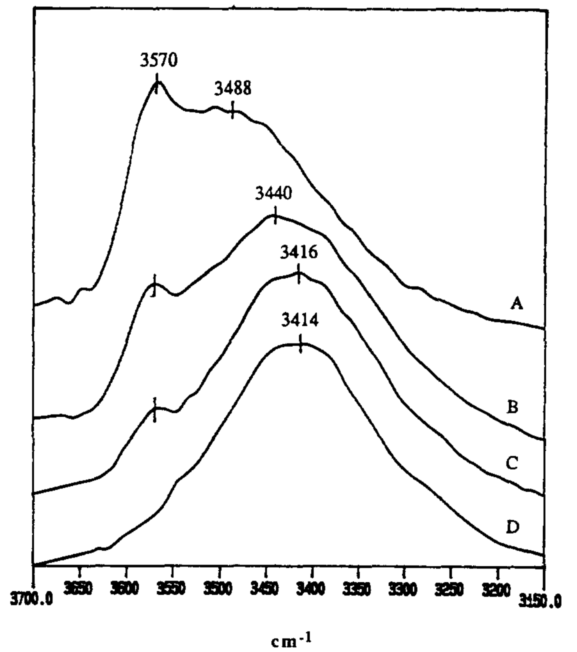

Figure 10 *FT*i.r. spectra, recorded at 140°C, of the hydroxyl region of phenoxy/PDMA blends, cast from DMF solutions: (A) 0; (B) 20; (C) 40; (D) 60 wt% PDMA

polymers in the blends. *Figure 9* illustrates the hydroxyl region, recorded at 140°C, of phenoxy/PMVAc blends cast from DMF solutions. Phenoxy has a band at 3570 cm^{-1} which is attributed to the free hydroxyl groups, and a broad band centred at 3495 cm^{-1}, representing a broad distribution of hydrogen bonded or self-associated hydroxyl groups (see curve A). With increasing PMVAc content in the blend, the intensity of the free hydroxyl band at 3570 cm^{-1} decreases, indicating that a great number of free hydroxyl groups are involved in the intermolecular association with the carbonyl groups. Furthermore, the centre of the broad hydrogen bonded band shifts gradually to lower frequencies when the PMVAc content in the blends increases. As the frequency difference between the free hydroxyl groups and the hydrogen bonded hydroxyl groups can be used as a measure of the average strength of the intermolecular interactions[13], the above observations reveal that the average strength of the hydrogen bond between the phenoxy hydroxyl group and the PMVAc carbonyl group ($\Delta\nu = 194\,\mathrm{cm}^{-1}$) is considerably higher than that of the self-associated hydroxyl groups in phenoxy ($\Delta\nu = 75\,\mathrm{cm}^{-1}$). In our previous report[8], we found that the frequency shift for the SAA hydroxyl group hydrogen bonded with the PMVAc carbonyl group ($\Delta\nu = 145\,\mathrm{cm}^{-1}$) is only slightly higher than that of the self-associated hydroxyl groups in SAA(4.5) ($\Delta\nu = 127\,\mathrm{cm}^{-1}$), and SAA(4.5) cannot form interpolymer complexes with PMVAc at the entire feed composition range from THF solutions. These results suggest that the hydrogen bonding interaction between phenoxy and PMVAc is stronger than that between SAA and PMVAc. As a result, phenoxy has a stronger ability to form complexes with PMVAc as compared with SAA.

Figures 10 and *11* show the hydroxyl stretching region, recorded at 140°C, of phenoxy/PDMA and phenoxy/PEOx blends cast from DMF solutions. The two blend systems exhibit the same trend as in the phenoxy/PMVAc blends. The frequency shifts for the phenoxy hydroxyl group hydrogen bonded with tertiary amide polymers decrease in the order PMVAc → PDMA → PEOx. This trend is consistent with the ability of the three tertiary amide polymers to form complexes with phenoxy as mentioned earlier.

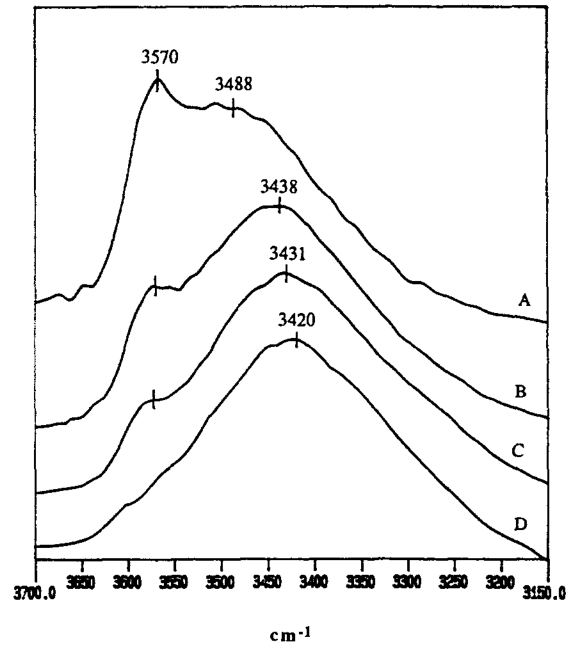

Figure 11 *FT*i.r. spectra, recorded at 140°C, of the hydroxyl region of phenoxy/PEOx blends, cast from DMF solutions: (A) 0; (B) 20; (C) 40; (D) 60 wt% PEOx

Viscosities of polymer solutions

The strong interpolymer interactions between phenoxy and the three tertiary amide polymers are also evidenced from the viscosities of the polymer mixtures in DMF. *Figure 12* shows the reduced viscosities of the three systems as a function of composition. In all three cases, the reduced viscosity is lower than that predicted

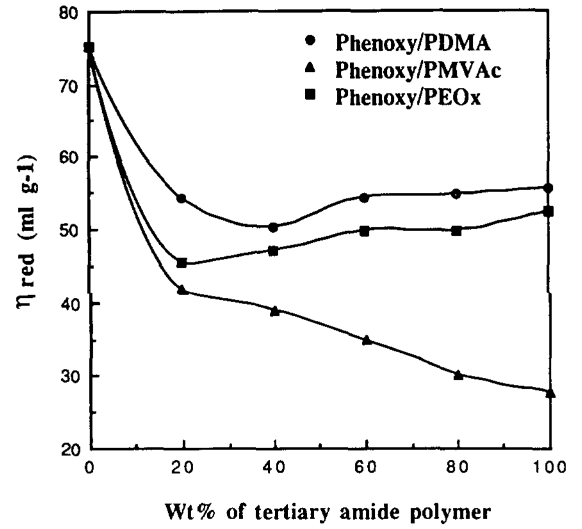

Figure 12 Viscosities of polymer mixtures in DMF: (●) phenoxy/PDMA; (▲) phenoxy/PMVAc; (■) phenoxy/PEOx

by the linear additivity rule, indicating the existence of strong interpolymer interactions. Similar behaviour has also been observed for other systems in which interpolymer complexation occurs[14,15].

CONCLUSION

Phenoxy forms interpolymer complexes with PMVAc and PDMA from THF solutions over the entire feed composition range, but not with PEOx. The abilities of the three isomeric polymers to form interpolymer complexes with phenoxy are in the order of PMVAc → PDMA → PEOx, the same as those of SAA/tertiary amide polymer systems reported previously[8,9].

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