

Miscibility of chlorinated atactic polypropylene with ethylene–vinyl acetate copolymer and with poly(methyl methacrylate)

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Fourier-transform infra-red (FTi.r.) spectroscopy, differential scanning calorimetry, dynamic mechanical property measurements and phase-contrast microscopy have been employed to investigate two polymer blends from the points of view of component specific interactions, molecular motion and morphology. It was observed that chlorinated atactic polypropylene (CAPP) is well miscible with ethylene–vinyl acetate (EVA) copolymer but poorly miscible with poly(methyl methacrylate) (PMMA). Thermal scanning of FTi.r. spectra suggested that CAPP/EVA blends exhibit lower critical solution temperatures. We believe that the strong interactions between CAPP and EVA are due to hydrogen bonding rather than to dipole–dipole interactions. The reason for the weak interactions and poor miscibility of CAPP with PMMA was discussed.

(Keywords: polymer blends; miscibility; interaction; chlorinated polypropylene; ethylene–vinyl acetate copolymer; poly(methyl methacrylate))

INTRODUCTION

The study of polymer blends has undergone rapid development in recent years and is one of the more advanced domains in modern polymer science. Component miscibility or compatibility is extremely important for polymer mixtures since various physical properties of polymer blends, such as optical, dielectric and mechanical properties, are closely related to the miscibility of their components. To design a new polymer blend, miscibility needs to be considered in advance.

Chlorine-containing polymers, owing to the great polarity of the –Cl group, have been chosen to modify some polar polymers. In this respect, poly(vinyl chloride) (PVC), chlorinated polyethylene (CPE) and chlorinated poly(vinyl chloride) (CPVC) have been widely studied^{1,2}, and a number of miscible polymer blends have been found.

The chlorinated atactic polypropylene (CAPP) used in this work was obtained via solution chlorination of atactic polypropylene (APP)³. Compared with CPE and PVC, CAPP is easy to chlorinate since it is soluble in many organic solvents because of its amorphousness. Systematic studies on the chlorination of APP, and on the characterization of the structure and properties of the chlorinated products, were reported elsewhere³. In this paper we present the specific interactions and miscibility of CAPP, with an ethylene–vinyl acetate (EVA) copolymer and with poly(methyl methacrylate) (PMMA).

EXPERIMENTAL

Polymers

CAPP is a laboratory product obtained by chlorinating atactic polypropylene (kindly supplied by Beijing Xiangyang Chemical Plant) in carbon tetrachloride at 40°C, which contains 52.8% chlorine by weight. The chemical structure of CAPP was characterized via i.r. and ¹³C n.m.r.³.

EVA copolymer is an industrial product purchased from Beijing Organic Chemical Factory. The vinyl acetate content calculated from the results of C, H and O elemental analyses is 44.3 wt%. The ¹³C n.m.r. characterization (based on the treatment of Wu⁴) is shown in Table 1, indicating that it is a random copolymer.

PMMA was synthesized using radical polymerization in bulk with azobisisobutyronitrile (AIBN) as initiator according to the procedure described by McGaffery⁵. Its stereotacticity calculated from ¹³C n.m.r. spectra is given in Table 2.

Gel permeation chromatography

The number-average molecular weights and molecular-weight distributions of the polymers were measured on a Waters Associates 244 gel permeation chromatograph in tetrahydrofuran (THF). The apparent weight- and number-average molecular weights and dispersity indices are listed in Table 3.

Preparation of blends

Blends were prepared by slowly casting film from THF

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Table 1 Monomer sequence distribution in EVA copolymer (from methine carbon resonance)^a

| EVE | EVV | VVV |
|-----|-----|-----|
| 55% | 30% | 15% |

^aE, ethylene; V, vinyl acetate**Table 2** Microtacticity of PMMA (from methyl ¹³C resonance)

| mm | mr | rr |
|------|-------|-------|
| 6.1% | 36.9% | 57.0% |

Table 3 Results of g.p.c. measurements^a

| Polymer | \bar{M}_w | \bar{M}_n | DI |
|---------|-------------|-------------|------|
| CAPP | 31 100 | 9 100 | 3.43 |
| PMMA | 438 000 | 134 400 | 3.26 |
| EVA | 241 000 | 31 600 | 7.63 |

^a \bar{M}_w and \bar{M}_n relative to PS standards

solutions. The polymers were dissolved in 2% (w/v) in THF, and then the solutions were blended in various proportions. After thorough stirring, the mixed solution was poured on to a glass plate or NaCl window and solvent allowed to evaporate at room temperature. The films were dried and kept under vacuum for at least 72 h before further tests.

Fourier-transform infra-red spectroscopy

Infra-red spectra were obtained on a Bruker IFS 113V FTi.r. spectrometer. A minimum of 100 scans at a resolution of 1 cm^{-1} (partly 0.5 and 2 cm^{-1}) were signal-averaged. A heating rate of about 1°C min^{-1} was used in the dynamic experiments.

Differential scanning calorimetry

Measurements were made with a Perkin-Elmer DSC-2C differential scanning calorimeter. Sample sizes of about 10 mg were used. The samples were rapidly heated first to 20°C above their T_g , then quenched to a lower temperature, and finally scanned with a heating rate of $10^\circ\text{C min}^{-1}$.

Dynamic mechanical measurements

These were carried out on a torsional braid analyser made in the Institute of Chemistry, Beijing. The temperature was scanned at 2°C min^{-1} and a plot of $\tan \delta$ against temperature obtained.

Phase-contrast microscopy

The morphology of blends was observed under a Carl Zeiss Jena microscope using the phase-contrast mode at room temperature.

RESULTS AND DISCUSSION

Component interactions

Completely miscible polymer mixtures can be considered as polymer/polymer solutions. According to solution thermodynamics, the essential condition for

miscibility is a negative free enthalpy of mixing, i.e.:

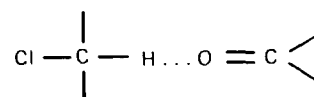
$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

For polymer mixtures, the entropy of mixing ΔS_m is very small owing to their large degrees of polymerization. In a first approximation, one can set $\Delta S_m = 0$ and it is then seen that the sign of ΔG_m is given by the sign of the enthalpy of mixing ΔH_m . Negative values of ΔH_m or certain specific interactions are therefore required in order to have miscibility.

Equation-of-state theory¹ gives a more detailed critical miscibility condition for two polymers. The theory also indicates that the essential condition for miscibility is $X < 0$, where X is an interaction parameter. Strong interaction between components is necessary for compatibility.

Intermolecular interactions mainly include van der Waals forces and hydrogen bonding. Van der Waals interactions are relatively weak, usually in the range of a few tenths of a kilocalorie, while hydrogen bonding is of the order of a few kilocalories⁷.

In chlorinated polypropylene, because of the greater electronegativity of the $-\text{Cl}$ group, the α -hydrogen atoms can easily approach other donor groups to form hydrogen bonds. On the other hand, both PMMA and EVA contain electron-donor carbonyl groups, and hence it is expected that the following H bond will be formed in their blends:



The i.r. spectrum mirrors bond vibrations of molecules. A band wavenumber correlates to the bond energy, etc., as follows⁸:

$$\nu = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{1/2}$$

where k is the force constant of the bond, μ the reduced mass and c the speed of light. Intermolecular interactions can affect the force constant k , and therefore bring about the band positions.

Taking the carbonyl group in EVA or PMMA as an example, because of the weakening of the original bond energy (k is decreased) its stretching vibration band will shift to a lower frequency as it forms H bonds or associations with other groups. Thus, the existence of H bonds in a system can be determined in the light of variations of i.r. spectra.

Coleman and coworkers² have studied quite a number of polymer blends using FTi.r. and confirmed that the position of the carbonyl stretching vibration does shift noticeably while the mixture is miscible, but does not for immiscible mixtures.

CAPP/PMMA mixtures. Since there is a desirable carbonyl group, PMMA was chosen to blend with CAPP. The original purpose was to find miscible mixtures. Unfortunately, the i.r. spectra did not give satisfactory evidence for miscibility. As illustrated in Figure 1 (curves A), variation of the blend compositions did not cause obvious shifts of the carbonyl stretching vibration.

Changing casting solvent (butanone and chloroform

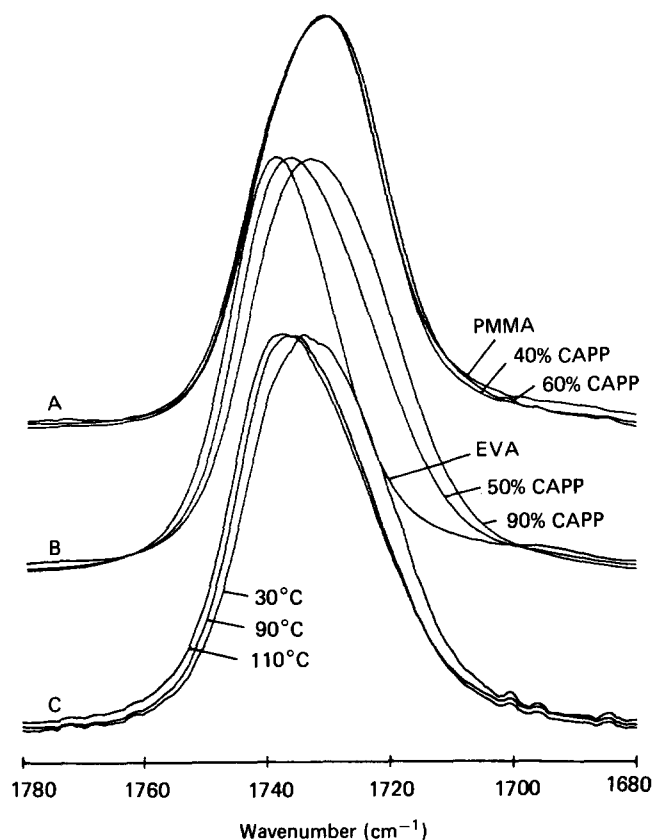


Figure 1 FTIR spectra in the carbonyl stretching vibration region: (A) PMMA/CAPP mixtures at room temperature; (B) EVA/CAPP mixtures at room temperature; (C) EVA/CAPP blend (20:80 w/w) at different temperatures

Table 4 Variations of band positions of carbonyl stretching with composition in EVA/CAPP blends

| | | | | | |
|-----------------------------------|--------|--------|--------|--------|--------|
| EVA (wt%) | 100 | 90 | 80 | 70 | 60 |
| Peak position (cm ⁻¹) | 1738.5 | 1738.3 | 1738.0 | 1737.8 | 1737.5 |
| EVA (wt%) | 50 | 40 | 30 | 20 | 10 |
| Peak position (cm ⁻¹) | 1736.3 | 1735.8 | 1734.9 | 1733.0 | 1732.0 |

instead of THF) did not give any indications for strong interactions and miscibility in the FTIR spectra.

CAPP/EVA mixtures. The IR spectra showed strong specific interactions between CAPP and EVA copolymer. The carbonyl stretching frequency shifted noticeably in blends with variation of the blend composition, as shown in Figure 1 (curves B). With increase of the content of CAPP, the band positions shifted gradually; the maximum shift is about 7 cm⁻¹ (see Table 4), which implies that there must be strong component interactions in these mixtures.

Temperature has significant effects on the band positions, too. The carbonyl stretching peak shifted gradually to higher wavenumbers (see Figure 1 (curves C)) on increasing the temperature, which indicated that the interactions in the blends were becoming weaker. According to Coleman's explanation², this results from phase separation of the mixtures.

Figure 2 gives a plot of the band positions of 20 EVA:80 CAPP mixture with temperature. The band positions of the blend shift to higher wavenumbers at higher tempera-

ture, approaching that of pure EVA (also shown), which implies that the H bond originally formed has been broken and two separated phases formed. Therefore, this polyblend system must exhibit a lower critical solution temperature (LCST) in its phase diagram.

The temperature dependence can be well understood in the light of molecular thermal motion. When the temperature rises, the H bond originally formed between CAPP and EVA would naturally be dissociated owing to increased thermal motion, and the carbonyl stretching restored at higher wavenumbers. This may be the main reason why most polymer mixtures have phase diagrams with an LCST feature.

Morphology

The phase structures of the two polymer blends were examined under a phase-contrast microscope. CAPP/PMMA mixtures had obvious phase separation in most composition ratios, except for the two extremes (see Figure 3). For the CAPP/EVA system, no separated phases or domains were observed (Figure 4). These results confirm that the latter blend really has better miscibility than the former one.

Molecular motions

Glass transition temperatures (T_g) characterize segmental motions of polymers. For an immiscible multiphase system, every phase should possess its own T_g ; a homogeneous mixture, however, should have only one T_g . Therefore, the observation of a single T_g in a polymer blend is usually taken as ample proof for miscibility of that polymer mixture⁹.

In this work, however, the experimental results showed that the above principle has limitations. In the d.s.c. study of CAPP/PMMA mixtures, it was found that the blends showed a single T_g over the entire composition range in spite of being multiphase (see Figure 5). The reason may

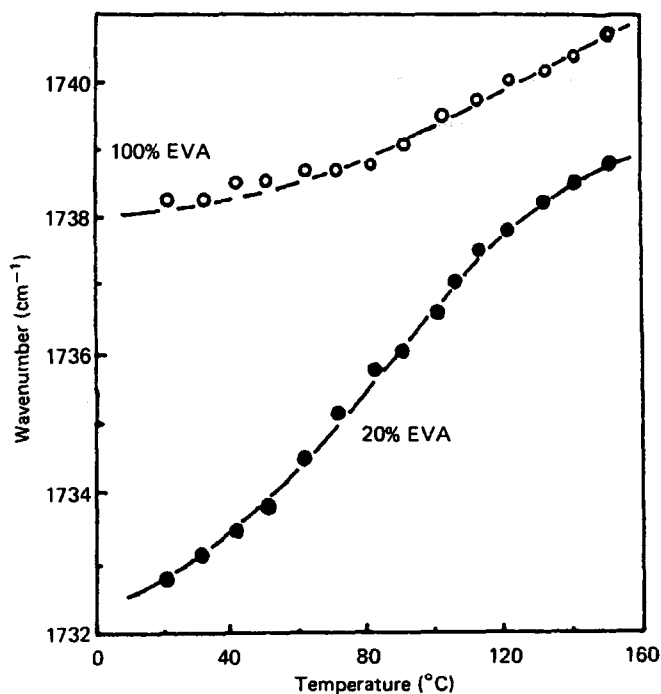


Figure 2 Plots of carbonyl stretching vibration positions versus temperature for pure EVA and 20:80 (w/w) EVA/CAPP blend

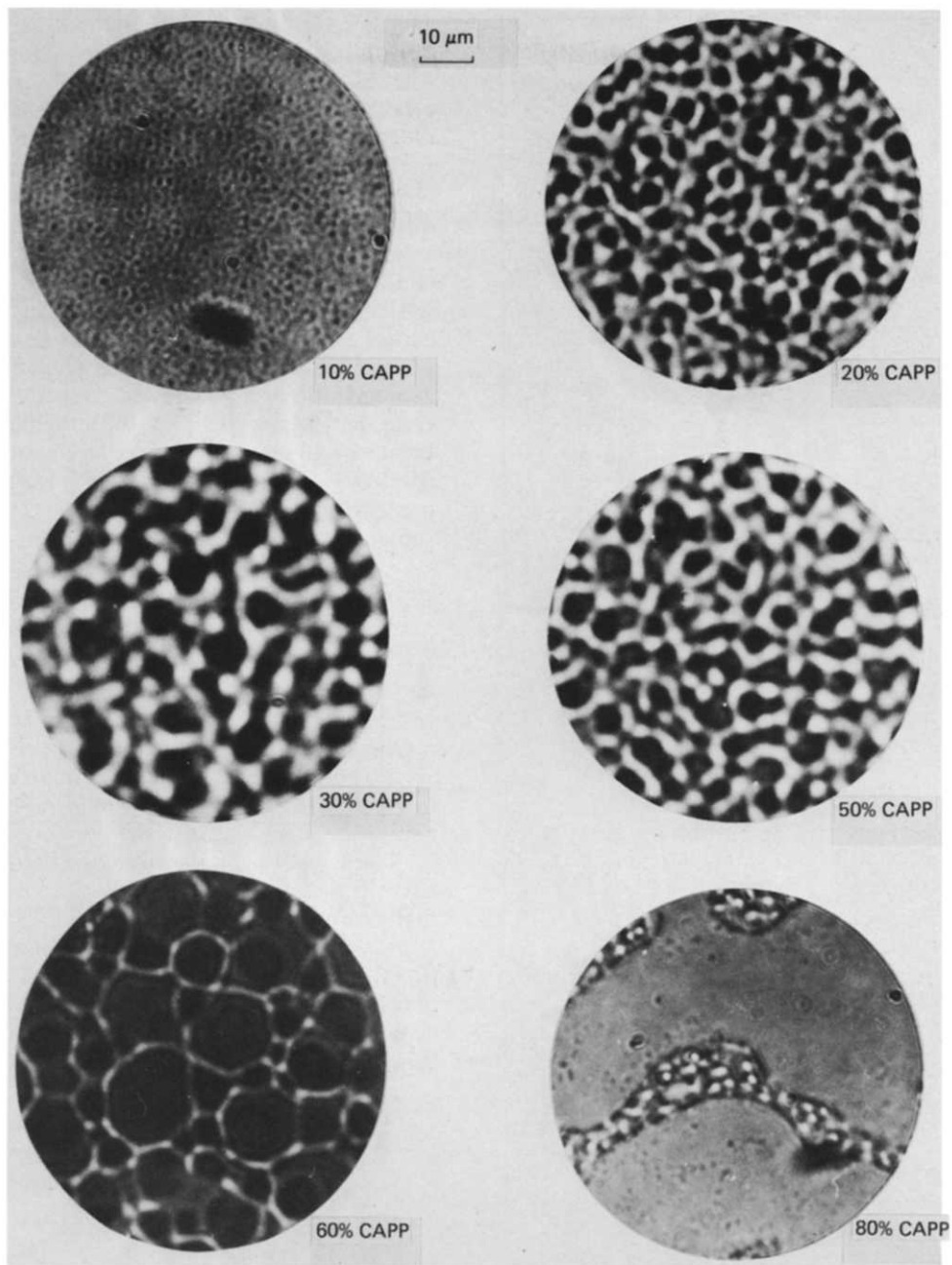


Figure 3 Phase-contrast microphotographs of PMMA/CAPP blends at room temperature

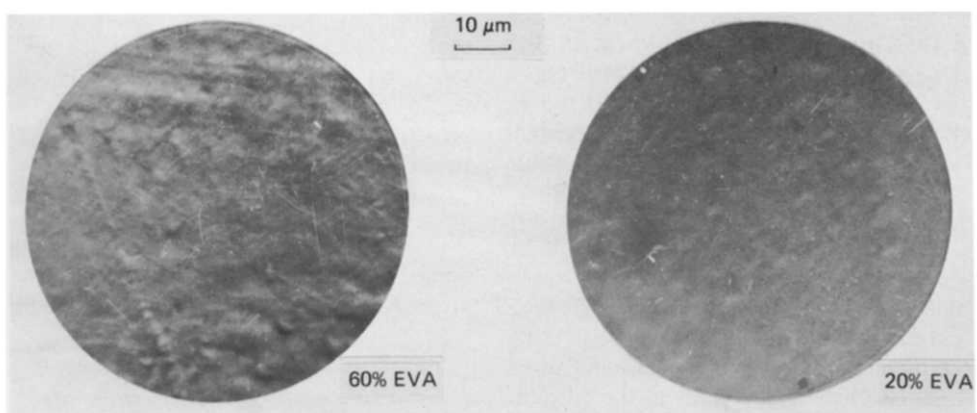


Figure 4 Phase-contrast microphotographs of EVA/CAPP blends at room temperature

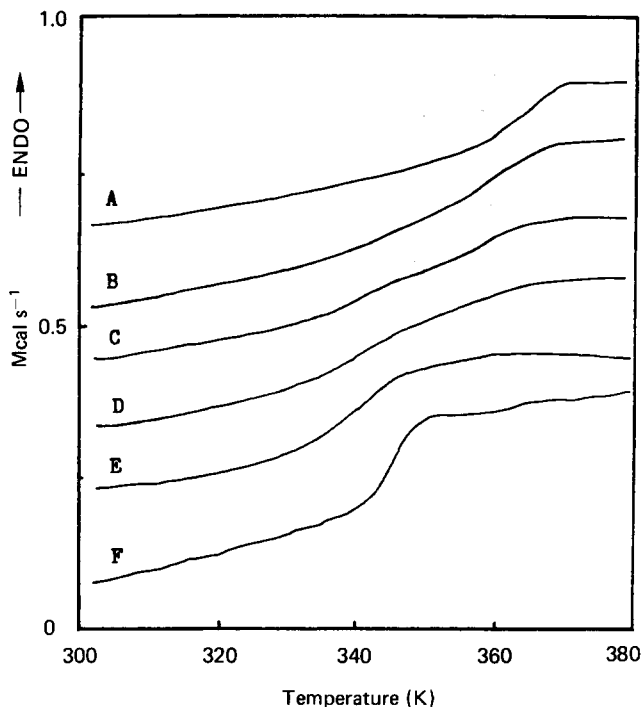


Figure 5 D.s.c. traces of PMMA/CAPP blends: (A) PMMA, (B) 20% CAPP, (C) 40% CAPP, (D) 60% CAPP, (E) 80% CAPP and (F) pure CAPP

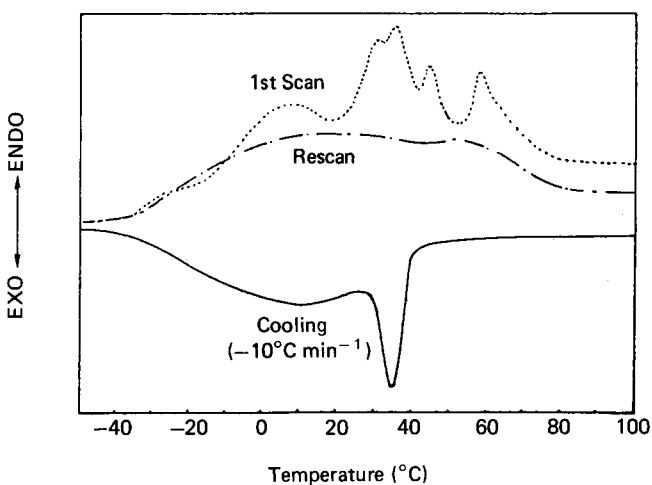


Figure 6 D.s.c. thermograms of a 90:10 (w/w) EVA/CAPP blend under different scanning conditions

be attributed to the small difference of the two components' T_g values (PMMA, 90.2°C; CAPP, 71.7°C).

In the d.s.c. thermograms of CAPP/EVA mixtures, an 'abnormal' phenomenon was observed: endothermic peaks while heating up and exothermic peaks while cooling down, respectively, occurred near the glass transition temperature (see Figure 6). This is more obvious for the blends with greater content of EVA copolymer.

Having analysed the X-ray diffraction (Figure 7) of the pure EVA copolymer, it was considered that these heating effects were caused by melting and crystallization of small polyethylene (PE) crystals (corresponding to the diffracting peaks) in the EVA copolymer.

Since the heating effect of crystallization interfered with the determination of the glass transition temperatures,

we chose a torsional braid analyser to measure the dynamic mechanical loss spectra of CAPP/EVA blends. The results showed that the transition positions shifted gradually to higher temperatures with increase of the CAPP content (Figure 8). Although the transitions seem to be more complicated with the interference of PE crystal melting, it is still evident that this system is really well miscible.

Like CPE/EVA mixtures¹⁰, the degree of chlorination of CAPP has a considerable effect on the miscibility of CAPP/EVA blends. CAPP with lower chlorine content causes a smaller shift of the carbonyl stretching vibration of EVA, and phase separation (LCST) of these blends is always observed at lower temperatures¹¹. This indicates that, for a given EVA, the miscibility in CAPP/EVA blends becomes poorer with decrease of chlorine content of CAPP. The dependence of miscibility on chlorine content of CAPP/EVA mixtures will be described in a separate article.

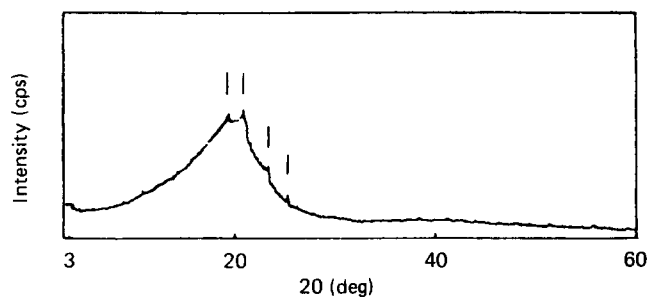


Figure 7 X-ray diffraction diagram of the pure EVA copolymer

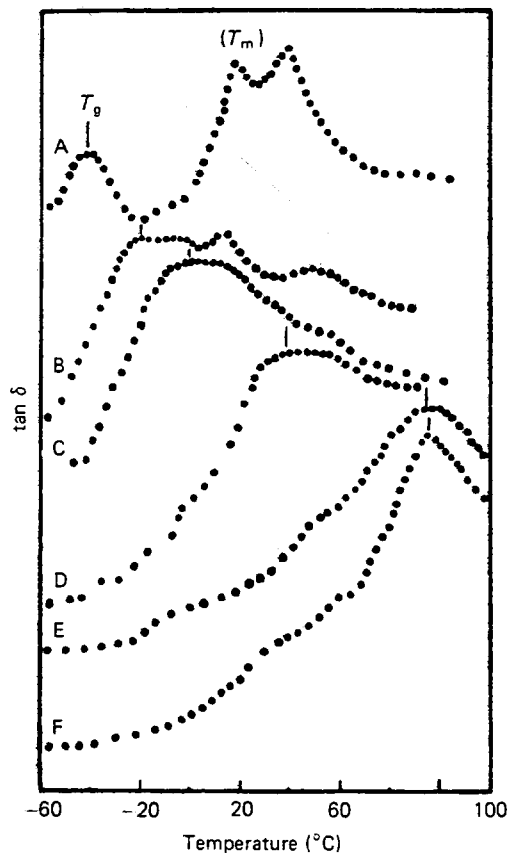


Figure 8 Plots of $\tan \delta$ against temperature of EVA/CAPP mixtures: (A) pure EVA, (B) 80:20 (w/w), (C) 60:40, (D) 40:60, (E) 20:80 and (F) pure CAPP

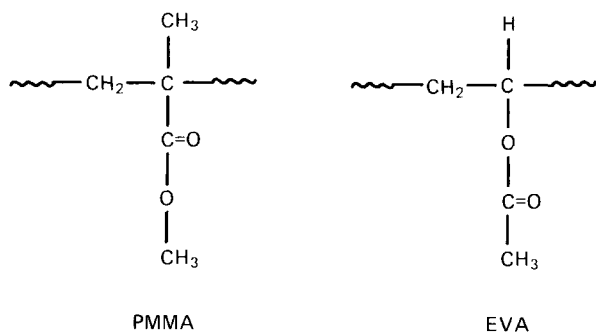
Discussion on nature of component interactions and structure effects on miscibility

Component interactions. The compatibility of chlorinated polypropylene (CPP) with polycaprolactone (PCL) was attributed by Prud'homme *et al.*¹² to dipole-dipole interactions in the form $>C=O \dots Cl-C$ instead of hydrogen-bonding interactions like $>C=O \dots H-C-Cl$. Their argument is based on the grounds that the chlorination of polypropylene is dominantly tertiary substitution, as reported in the literature, and therefore CPP does not have enough hydrogens to be able to form H bonds.

FTi.r. spectra in the present work (Figure 2) showed that the carbonyl stretching vibration of CAPP/EVA mixtures shifted appreciably, indicating that the component interactions are quite strong. The comparison¹⁰ of PCL in CCl_4 , $CHCl_3$ and CH_2Cl_2 showed that only $CHCl_3$ and CH_2Cl_2 , which contain protons, have the capability of shifting considerably the carbonyl stretching of PCL, while in the case of PCL in CCl_4 and THF, where only dipole-dipole interactions exist, no significant shifts in carbonyl stretching were observed. So it seems to us that the component interactions in CAPP/EVA are most probably a hydrogen-bonding interaction.

Microstructure characterization³ of CAPP by i.r. and ^{13}C n.m.r. revealed that, although the tertiary hydrogens in atactic polypropylene have higher activity to chlorination, there still exists a large proportion of $>CHCl$ and $-CH_2Cl$ groups in the molecular chains. Quantitative treatment of the ^{13}C n.m.r. spectrum showed that there are about 12.5 mol% $-CHCl-$ carbons and 11.4 mol% $-CH_2Cl$ carbons in this CAPP. Therefore, CAPP potentially has the ability to form H bonds.

Structure effects. The structural unit of PMMA is very similar to that of EVA as shown below:



The interactions and miscibilities of CAPP with PMMA and with EVA are, however, quite different. Some researchers have already found that PMMA is not well compatible with PVC and they attributed this either to the complex semicrystalline nature of PVC¹³ or to the stereoisomerism of PMMA^{14,15}. Since we found that both PVC² and CAPP (in this work) do have good miscibility and strong interactions with EVA, but not with PMMA, it seems to us that the above-mentioned attribution may not be sound. In addition, the PMMA we used is dominantly syndiotactic (see Table 2), which should be favourable for miscibility according to the

literature^{14,15}, but CAPP is still poorly miscible with it. Therefore, other origins for their poor compatibility should be explored.

Comparing the structures of PMMA and EVA, we note that the carbonyl group in EVA is linked to the main-chain carbon atom through an $-O-$ bridge and thus it is easier for it to approach another component to form associations. In PMMA, however, the carbonyl is directly connected to the carbon atom of the main chain and is hence less accessible to the protons of another component. This may be one of the main reasons for the poor miscibility of PMMA with CAPP.

CONCLUSIONS

Chlorinated atactic polypropylene (CAPP) has been found to be miscible with an ethylene-vinyl acetate (EVA) copolymer but not with poly(methyl methacrylate) (PMMA) at room temperature. The strong interaction between CAPP and EVA is responsible for their miscibility, and it is due to hydrogen bonding rather than dipole-dipole interactions. *FTi.r.* spectra suggest that CAPP/EVA blends have a lower critical solution temperature (*LCST*). We postulated that the weak interaction and poor miscibility of CAPP with PMMA is related to the mobility of the carbonyl group in PMMA.

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REFERENCES

- Solc, K. 'Polymer Compatibility and Incompatibility', MMI Press, London, 1981
- Coleman, M. M. and Painter, P. C. *Appl. Spectrosc. Rev.* 1984, **20** (3-4), 255
- Li, W., Shi, L. and Shen, D. 'Preprints of National Symposium on Polymers', Wuhan, China, 1987, pp. 640, 646
- Wu, T. K., Ovenall, D. W. and Reddy, G. S. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 90
- McGaffery, E. L. 'Laboratory Preparation for Macromolecular Chemistry', McGraw-Hill, New York, 1970
- Randall, J. C. 'Polymer Sequence Determination, Carbon-13 NMR Method', Academic Press, New York, 1977
- Pimentel, G. C. and McClellan, A. L. 'The Hydrogen Bond', W. H. Freeman, San Francisco, 1960
- Shen, D. 'Application of Infrared Spectroscopy to Polymer Research', Scientific Press, Beijing, 1982
- Olihi, O., Roberon, L. M. and Shaw, M. T. 'Polymer/Polymer Miscibility', Academic Press, New York, 1979
- Varnell, D. F., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Polym. Eng. Sci.* 1983, **23**, 658
- Li, W. Ph.D. Dissertation, Institute of Chemistry, Academia Sinica, 1988
- Allard, D. and Prud'homme, R. E. *J. Appl. Polym. Sci.* 1982, **27**, 559
- Walsh, D. J., Higgins, J. S. and Rostami, S. *Macromolecules* 1983, **16**, 388, 391
- Albert, B., Jerome, R. and Teyssie, P. *Macromolecules* 1985, **18**, 388
- Vanderschueren, J. and Janssens, A. *Polymer* 1982, **23**, 395