

THE COMPATIBILITY OF BLENDS OF POLY(VINYL CHLORIDE) OR CHLORINATED POLY(VINYL CHLORIDE) WITH POLY(METHYL METHACRYLATE)

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ABSTRACT

IR spectral shifts of carbonyl vibrational absorption for ethyl acetate, which acts analogically as the structural unit of poly(methyl methacrylate), in cyclohexane, chloroform, chlorinated paraffins, poly(vinyl chloride) and chlorinated poly(vinyl chloride) were measured. The results suggest that there are specific interactions between the carbonyl groups and the chlorinated hydrocarbons which could be responsible for the apparent compatibility of poly(vinyl chloride) — poly(methyl methacrylate) and chlorinated poly(vinyl chloride) — poly(methyl methacrylate) blends. Additionally, the effects of the preparation mode of blend films on phase separation and observed compatibility are discussed.

From the viewpoint of thermodynamics, the compatibility of polymer blends principally depends on the enthalpy of mixing ΔH_m of the two polymer components. In the course of investigating the compatibility of chlorinated polyethylene(PE) with poly(methyl methacrylate) (PMMA), Walsh and his co-workers^[1] calorimetrically measured the heats of mixing ΔH_m of their model compounds, i.e. oligomeric PMMA with chlorinated octadecanes(COD). They reached a conclusion that there are two kinds of interactions between them, the first is the dispersion interaction and the other is regarded as specific interaction. As a consequence of some experimental observations, Fowkes^[2] proposed that the enthalpy of mixing may be expressed as a sum of two terms

$$\Delta H_m = \Delta H_m^d + \Delta H_m^{ab}$$

where the positive ΔH_m^d is the contribution of dispersion force and ΔH_m^{ab} is the contribution of the broad sensed acid–base interaction which is negative in magnitude. In reality, the physical meaning of the so-called acid–base interaction and that of the specific interaction are identical.

It is very difficult to carry out direct calorimetric determination of ΔH_m for polyblends. Even if the heat of mixing between oligomeric analogues is negative, it is not sufficient to predict the compatibility of the polymers for their molecular weights and other structural aspects are different from those of the model compounds^[3]. Recently, the shifts of infrared vibrational absorption frequency of some functional groups due to changing of environment are regarded as results of interactions between those groups and the media^[4–5]. Some authors even established quantitative relations between ΔH_m^{ab} and the shifts^[6]. Generally, spectroscopic measurements are more convenient to carry out for polymers than calorimetric ones. Therefore, it is very interesting to investigate whether it is possible to predict the compatibility of polymers from the infrared absorption frequency shifts. For this purpose, the compatibility of poly(vinyl chloride) (PVC)—

poly(methyl methacrylate) (PMMA) or chlorinated poly(vinyl chloride) (CPVC)—PMMA was studied in the present work. The reason for choosing CPVC as one of the object of study is that CPVC is similar to PVC in chemical structure but not in rigidity and conformation, and no detailed experimental data about CPVC—PMMA system are reported in the literature.

Three chlorinated paraffin samples with different chlorine content and chloroform were selected first as model compounds of PVC and CPVC and then a small amount of ethyl acetate (EtAc) used as analog of the structural unit of PMMA was dissolved in these chlorine containing compounds. The FT-IR spectra of carbonyl stretching vibration of EtAc in these solutions were determined and the results are shown in Fig.1. It can be seen from the picture that the absorption peaks shifted evidently with changing of the medium. If the carbonyl stretching frequency of EtAc dissolved in neutral solvent cyclohexane was taken as the reference state the experimentally measured IR frequency shifts $\Delta\nu_{c=O}$ are listed in Table 1, in which the $\nu_{c=O}$ and $\Delta\nu_{c=O}$ values of the trace EtAc absorbed by PVC and CPVC films cast from solutions are also listed. It can be seen that the IR frequency shifts $\Delta\nu_{c=O}$ increase regularly with increasing chlorine content of the medium. The IR frequency shifts of EtAc in PVC and CPVC films also follow the tendency of variation of $\Delta\nu_{c=O}$ in chlorine containing model compounds. The variation of $\Delta\nu_{c=O}$ with chlorine content is in parallel to the results reported by Walsh et al.^[11] that the heats of mixing increase regularly with increasing chlorine content of COD for oligomeric PMMA—COD mixtures. Since the IR shift values of EtAc in PVC and CPVC are rather large, comparable in magnitude to that of EtAc in chloroform, it could be judged that the contributions of ΔH_m^{ab} to the total heat of mixing are similar and probably possessing relatively large negative values for both cases. On the other hand, chloroform is a good solvent for PMMA. Therefore, we reached a decision that both PVC—PMMA and CPVC—PMMA blends are likely to be compatible.

Table 1 The carbonyl vibrational IR spectrum frequencies of EtAc in various chlorine containing media

Medium	Chlorine content (w%)	$\nu_{c=O}(\text{cm}^{-1})$	$\Delta\nu_{c=O}(\text{cm}^{-1})$
Cyclohexane	0	1748	
Chlorinated Paraffin-A	35	1740	-8
Chlorinated Paraffin-B	44	1738	-10
Chlorinated Paraffin-C	52	1736	-12
Chloroform	89	1732	-16
PVC	57	1734	-14
CPVC	67	1733	-15

For the compatibility of PVC—PMMA blends, a number of papers^[7-10] have appeared in literature since 1960's, but the results and conclusions reached are contradictory. In the present work, blend films of PVC—PMMA or CPVC—PMMA with various compositions were prepared by casting from 1% DMF solutions of the mixture, the dynamic mechanical and the light transmittance

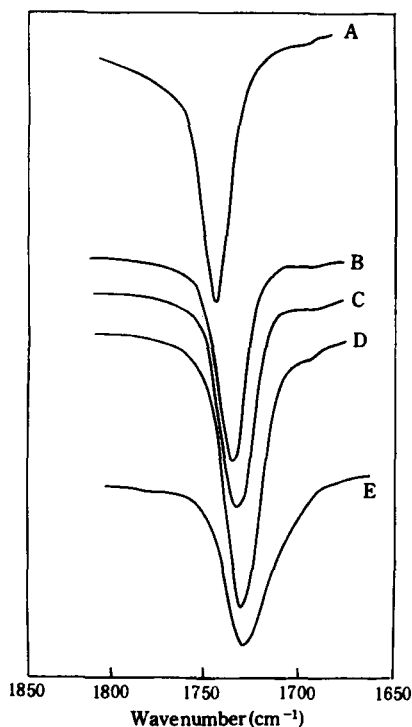


Fig.1 FT—IR spectra of EtAc in the neighborhood of 1750cm^{-1} in (A) cyclohexane, (B) chlorinated paraffin-A, (C) chlorinated paraffin-B, (D) chlorinated paraffin-C, (E) chloroform

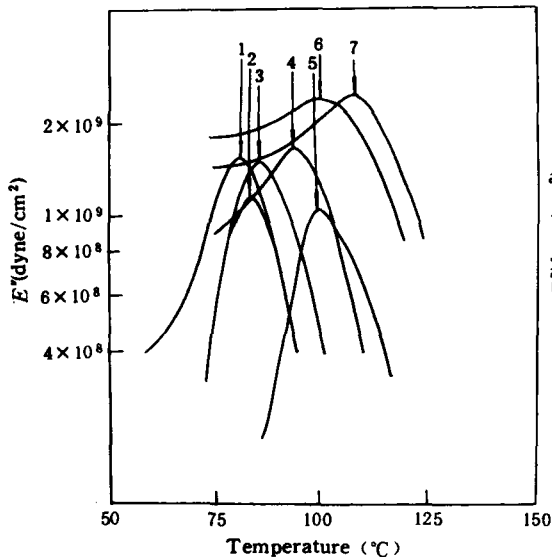


Fig.2 The plot of loss modulus E'' at 11HZ versus temperature for PVC—PMMA blends; weight fraction of PMMA: (1) 0.00, (2) 0.09, (3) 0.22, (4) 0.50, (5) 0.79, (6) 0.92, (7) 1.00

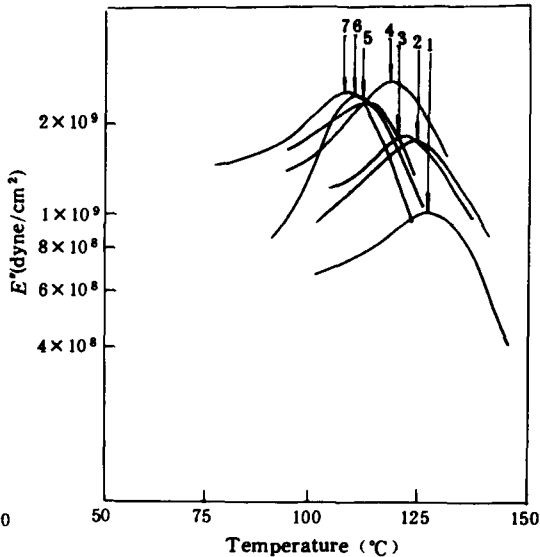


Fig.3 The plot of loss modulus E'' at 11HZ versus temperature for PVC—PMMA blends; weight fraction of PMMA: (1) 0.00, (2) 0.09, (3) 0.22, (4) 0.51, (5) 0.67, (6) 0.84, (7) 1.00

measurements for the resulting films were conducted to determine the compatibility. The variations of the loss modulus E'' with temperature for the film samples of homopolymers and blends of PVC—PMMA or CPVC—PMMA are shown in Fig.2 and 3 respectively. It can be seen from the pictures that the peak positions in the dynamic mechanical spectra shift regularly with the changing of composition of the blends and there is not any obvious indication for the presence of double peaks. If the temperature corresponding to the maxima of the peak is defined as the glass transition temperature T_g of the blends, then the results obtained are listed in Table 2 and could be satisfactorily represented by equation

$$\frac{1}{T_g} = \frac{W_1}{T_{g,1}} + \frac{W_2}{T_{g,2}}$$

where the subscripts 1 and 2 denote the two components and W denotes the corresponding weight fraction of the homopolymer in the blends. The variations of the light transmittance of the films with the compositions of the blends are shown in Fig.4. For PVC—PMMA blends, all the light transmittance values are higher than 90%, and regardless of the compositions. For CPVC—PMMA blends, since CPVC itself is light yellow colored, the values of transmittance are lower than those of corresponding PVC—PMMA blend films, but still higher than 80%. In the light of above experimental results and those generally accepted arguments^[11], we may conclude that both of the blends studied in the present work are compatible over the whole composition range.

Table 2 Glass transition temperature of blends

Sample	W_{PMMA}	$T_g(^{\circ}C)$
PVC—PMMA	0.00	79
	0.09	82
	0.22	85
	0.50	93
	0.79	98
	0.92	100
	1.00	105
	0.00	126
	0.09	122
CPVC—PMMA	0.22	119
	0.51	117
	0.67	111
	0.84	109
	1.00	105

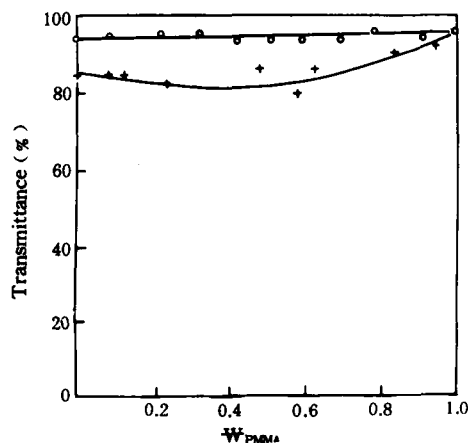


Fig.4 The variations of light transmittance of PVC—PMMA (○) and CPVC—PMMA (+) blend films at 550nm with the composition of the blend

The conclusion reached for the compatibility of PVC—PMMA blends is in accordance with those obtained by Walsh^[7] and Kozłowski^[8] but is contrary to Schurer^[9] and Razinskaya^[10]. The discrepancy may probably be originated from the difference in the mode of blend film preparation. In Table 3, the film preparation method, the average molecular weight of the componental homopolymers and the conclusion reached about the compatibility by those authors are gathered together. It is shown that all the blend films prepared by slow evaporation of the solvent are compatible and those prepared by precipitation method are not. In the course of precipitation, the

Table 3 Methods for preparing PVC-PMMA blend films and the results of compatibility

Author	Method	$\bar{M}_v$		Compatibility
		PMMA	PVC	
Razinskaya (1972)	precipitation from THF solution	102,500	159,500	when W_{PMMA} in the range of 0.05—0.98, incompatible
Schurer (1975)	evaporation from DMF solution or precipitation from DMF solution	80,000	55,000	when W_{PMMA} higher than 0.60, incompatible
Walsh (1980)	evaporation from MEK solution	100,000*	35,000	compatible
Kozlowski (1984)	evaporation from DMF solution	90,000	102,000**	compatible
	evaporation from DMF	256,000	80,000	compatible
this work	evaporation from DMF	256,000	39,000 (CPVC)	compatible

* $\bar{M}_n$ ** $\bar{M}_w$

phase separation of the solution undoubtedly occurred first. The separated phases are different both in composition and molecular weight distribution of the componental homopolymers. Therefore, the observed incompatibility about the resulting film after removal of the solvent mixture is comprehensible since the segregated phase domains still exist.

EXPERIMENTAL

The poly(methyl methacrylate) sample ($[\eta]=160\text{ml/g}$) used was prepared by bulk polymerization according to general procedure. The poly(vinyl chloride) (type III, $[\eta]=117\text{ml/g}$), chlorinated poly(vinyl chloride) ($[\eta]=61\text{ml/g}$) and chlorinated paraffins used were supplied by Zhenjiang Resin factory, Anhui Institute of Chemical Technology, and Nanjing Fifteenth Plastic Factory, respectively.

The intrinsic viscosity of PMMA was determined in chloroform at 25°C, and the viscosity average molecular weight was calculated according to $[\eta]=9.6 \times 10^{-3} M^{0.78}$. The intrinsic viscosities of PVC and CPVC were determined in tetrahydrofuran, and using $[\eta]=3.63 \times 10^{-3} M^{0.92}$ to calculate the molecular weight. The chlorine contents of PVC and CPVC were determined by the method described in reference [12].

FT-IR spectra of EtAc in different media were recorded on a Nicolet 170SX instrument. 50 scans at a resolution of 2cm^{-1} were signal-averaged. The concentration of EtAc was 3% (w/w).

Blend films were prepared by casting from 1% dimethyl formamide solution of the polymer mixture. Solvent evaporation was performed at 80°C under reduced pressure (10mmHg) for 10 hours. The resulting films were dried at 120°C under vacuum until reaching constant weight.

Dynamic mechanical measurements were conducted by a Rheovibron DDV-II apparatus (TMI

Co.). The scanned temperature was from 50°C to 150°C, and the frequency was set at 11HZ.

The light transmittance of blend films was measured at a wavelength of 550nm with a 72 model spectrophotometer. The film thickness was controlled within $0.006 \pm 0.0005\text{cm}$.

Keywords:

Blends; Compatibility; Poly(vinyl chloride); Chlorinated poly(vinyl chloride); Poly(methyl methacrylate)

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