

The compatibility of poly(methyl methacrylate) and chlorinated polyethylene

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(Received 3 November 1981)

The compatibility of poly(methyl methacrylate) with chlorinated polyethylene was studied using differential thermal analysis and dynamic mechanical measurements. For around 50% chlorination of polyethylene they were found to be compatible and show an *LCST*, but not at 27% chlorination as had previously been thought. The previous results were explained as due to a matching of refractive indices over some temperatures. The compatibility was explained by the heat of mixing which becomes favourable at chlorination levels above approximately 46%.

Keywords Analysis; mechanical measurements; differential thermal analysis; compatibility; poly(methyl methacrylate); chlorinated polyethylene

Introduction

The area of polymer compatibility has received a lot of attention in recent years. A recent book by Olabisi, Robeson, and Shaw¹ describes the background and progress made.

Because of the very small combinatorial entropy of mixing, polymers are normally not compatible unless the polymers are very similar chemically or there is a specific interaction between them. An example of the first is poly(vinyl chloride) (PVC) with chlorinated polyethylene (CPE)². An example of the second is the many polymers found to be compatible with PVC such as polyacrylates and polymethacrylates³ where some hydrogen bonding is postulated to exist between the polymers. Hydrogen bonding might also be expected between CPE and polymethacrylates. In this communication we report studies of chlorinated polyethylene poly(methyl methacrylate) (PMMA) mixtures.

Whereas low molecular weight polymers are generally more compatible at higher temperatures, high molecular weight polymers are usually more compatible at lower temperatures, often exhibiting a lower critical solution temperature (*LCST*). An *LCST* can only arise if the heat of mixing is favourable (negative) and the entropy of mixing unfavourable (negative), or if the heat of mixing varies strongly with temperature.

In a recent letter⁴ we suggested that CPE with around 27% w/w chlorine showed the greatest compatibility with PMMA. We now know this to be incorrect, and the phase boundaries reported for that mixture arise because the refractive indices of the two polymers are similar and vary in different ways with temperature. We have since found greater compatibility at around 50% w/w chlorine. In this paper we give details of this system along with measured thermodynamic parameters for CPE/PMMA blends derived from studies of low molecular weight homologues.

Experimental

Poly(methyl methacrylate) of intrinsic viscosity 1.4 (Polysciences) was used as a high molecular weight sample. It was purified by dissolving in acetone and precipitating into distilled water. The polymer was filtered off and dried in a vacuum oven at 1 mm Hg and 50°C for one week. The molecular weight was determined by g.p.c.

and is given in *Table 1*.

Lower molecular weight poly(methyl methacrylate) polymers were prepared by solution polymerization⁵. By adjusting the ratio of monomer to solvent (chain transfer agent) different molecular weights were obtained.

Into an autoclave were placed methyl methacrylate (commercial redistilled), isopropanol (A.R.) and di-t-butyl peroxide (6×10^{-3} mol/mol isopropanol). The ratios of monomer to solvent are given in *Table 1*. The mixture was degassed and kept at 130°C for 5 h. The lowest molecular weight polymer product was evaporated to dryness, redissolved in isopropanol, filtered, and evaporated again to dryness. The higher polymers were solids and were reprecipitated into distilled water. All the samples were dried in a vacuum oven at 1 mm Hg and 50°C for at least two weeks.

Chlorinated polyethylene was prepared by photochlorination. The polyethylene was a commercial high density material with a nominal \bar{M}_n of 1×10^4 . Polyethylene (10 g) was dissolved in chlorobenzene (200 ml A.R.). The photo-reaction was initiated by irradiation from a 60 watt tungsten lamp. Chlorine was bubbled through the mixture at 25 cc min⁻¹. Controlling the time of reaction produced different degrees of chlorination. The samples were precipitated into a ten times excess of methanol and then dried in a vacuum oven at 1 mm Hg and 50°C for two weeks. Octadecane was chlorinated by an analogous process using 25 ml of octadecane. The product was extracted by evaporation to dryness and dried as above. Two commercial chlorinated paraffins

Table 1 Data for PMMA samples

Sample	Mols MMA/mol isopropanol	\bar{M}_w^*	\bar{M}_n^*
PMMA 1.4 (Polysciences)	—	72 800	29 000
PMMA 16	0.479	42 100	10 400
PMMA 17	0.072	12 200	3470
PMMA 1	0.029	—	502
PMMA 23	0.029	—	434

* All molecular weights were determined by g.p.c. in THF relative to polystyrene standards except the two very low molecular weights which were measured by v.p.o. at 37 ± 0.1°C using butan-2-one as a solvent

Cereclor 45 and Cereclor 52 (ICI) were also used. They were first dried in a vacuum oven at 1 mm Hg and 50°C for two weeks.

The properties of the polymers and oligomers are shown in Table 2. The degrees of chlorination were determined by elemental analysis. The densities of the chlorinated octadecanes was determined by use of a picnometer. The molecular weights were measured by g.p.c. relative to polystyrene standards or by vapour phase osmometry in the case of the oligomers. Glass transition temperatures were measured using a Rheovibron at 11 Hz, quoted values are the peak values of $\tan \delta$.

Preparation of blends. Samples of mixed polymers with various ratios of each polymer were prepared by coprecipitation. The polymers, in various proportions, were dissolved to a total of 5% (w/v) in THF (A.R.). The solutions were then poured with stirring into a 20 times excess of distilled water. The polymers were then dried in an oven for 72 h at 50°C. The samples were pressed at 140°C for 15 min to produce films 0.3 to 0.6 mm thick. Other films were cast from solutions in MEK (A.R.) in petri dishes. The rate of evaporation was controlled by partial covering. The films were generally opaque at room temperature, except for those with polymers having the highest degree of chlorination.

Light scattering. Phase boundaries were examined by measuring scattered light from the sample using a specially designed light scattering photometer⁶. The films were supported in a sample holder located in a thermostatically controlled aluminium block. Light from a tungsten lamp was focussed onto the sample and the intensity of light scattered at 45° was measured using a photodiode. The temperature of the block could be altered at a controlled rate and a plot of scattered light intensity against temperature was obtained. Results were corrected for changes in sensitivity of the diode with temperature (determined experimentally).

Dynamic mechanical measurements. Dynamic mechanical measurements were carried out on a Rheovibron (Model DDV-II, Toyo Measuring Instrument Co. Ltd.). A strip of the sample was subjected to an imposed oscillatory frequency of 11 Hz. A

temperature range from -60°C to 170°C was scanned at 1°C min⁻¹ heating rate and a plot of $\tan \delta$ against temperature obtained. A maximum in $\tan \delta$ was taken as a measure of T_g . Peaks close to those of the pure polymers indicate little mixing whereas one peak at some intermediate temperature indicates a single mixed phase.

Differential thermal analysis. Measurements were made on a DuPont 990 apparatus using a sample weight of around 10 mg. The temperature of phase separation could be determined by d.t.a. The sample was heated at 100°C min⁻¹ held at the upper temperature for 10 min and then quenched to -20°C. The sample was then scanned at a rate of 10°C min⁻¹. The upper temperature of fast heating was changed by 10°C intervals. Phase separation was shown by the first appearance of new transitions in the subsequent scan.

Refractive index. This was determined for the oligomers using an Abbe '60' refractometer (Bellingham and Stanley) using the sodium D line. The measurements were made at different temperatures with an accuracy of $\pm 0.2^\circ\text{C}$.

Heat of mixing. The heat of mixing of various oligomers was measured using a modified NBS batch type calorimeter⁶. The machine has an accuracy of ± 0.02 J/g as determined by an acid base reaction. However the viscosity of the oligomers made mixing difficult and we estimate an error of ± 0.1 J/g for our system. The machine was calibrated using a heating coil immersed in the particular systems under investigation.

Results and Discussion

Solution cast blends of PMMA with chlorinated polyethylenes having the highest degrees of chlorination, CPE 16 or CPE 17 (51.6 and 49.8% w/w respectively) were found to produce clear films. Solution cast blends with all other mixtures were opaque as were all moulded samples. This observation suggested compatibility for PMMA with CPE 16/17. This was confirmed by dynamic mechanical measurements on blends containing different ratios of the polymers. The result for one such system is shown in Figure 1; glass transitions between those of the two components were found.

The blends were found to become opaque on heating and so the process was followed using light scattering but this was found to give irreproducible results possibly due to diffusion control. We therefore used differential thermal analysis measurements, heating the samples to a series of temperatures for 10 minute periods and noting the temperature where the glass transitions started to separate towards the pure component values. The systems show lower critical solution temperatures at 100°-130°C. We also tried to find the effect of the molecular weight of the PMMA. Lower molecular weight samples had higher LCSTs. The resultant phase boundaries for CPE 16 and CPE 17 with various molecular weights of PMMA are shown in Figures 2 and 3. The errors in each point are $\pm 10^\circ\text{C}$, but the effect of molecular weight is nevertheless demonstrated within experimental error.

The results were also checked in several cases by doing a similar experiment to the above using dynamic mechanical analysis. Samples were heated to a series of temperatures and then quenched. They were then scanned on the Rheovibron in order to observe the transitions. The results confirmed those obtained by d.t.a.

Table 2 Data for chlorinated polyethylenes and octadecane

Sample	Degree of chlorination wt%	Density		M_w	M_n	M_w/M_n	T_g
		25°C	70°C				
COD 1	17.3	0.8976	0.8651				
COD 2	24.6	0.9511	0.9180				
COD 3	33.4	1.0531	1.0167				
COD 3A	34.9	1.0807	1.0457				
COD 4	43.2	1.1417	1.1054				
COD 5	52.9	1.2579	1.2169				
CPE 1	36.9	1.10×10^5	1.58×10^4	6.96			-10
CPE 2	27.4	1.08×10^5	1.52×10^4	7.11			-8
CPE 3	48.0	1.20×10^5	1.80×10^4	6.67			26
CPE 4	35.7	1.15×10^5	1.89×10^4	6.08			-10
CPE 16	51.6	1.98×10^5	2.53×10^4	7.83			39
CPE 17	49.8	1.82×10^5	2.08×10^4	8.78			32
Cereclor 45	45.7	—	395 (v.p.o.)	—			—
Cereclor 52	53.1	—	437 (v.p.o.)	—			—

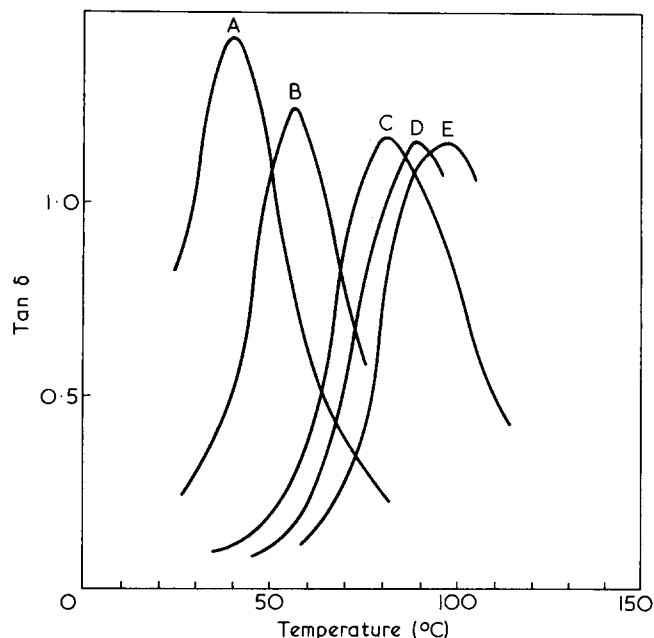


Figure 1 Dynamic mechanical results for blends of CPE 16 with PMMA 1.4; weight percent CPE, A = 0.900, B = 0.742, C = 0.522, D = 0.247, E = 0.100

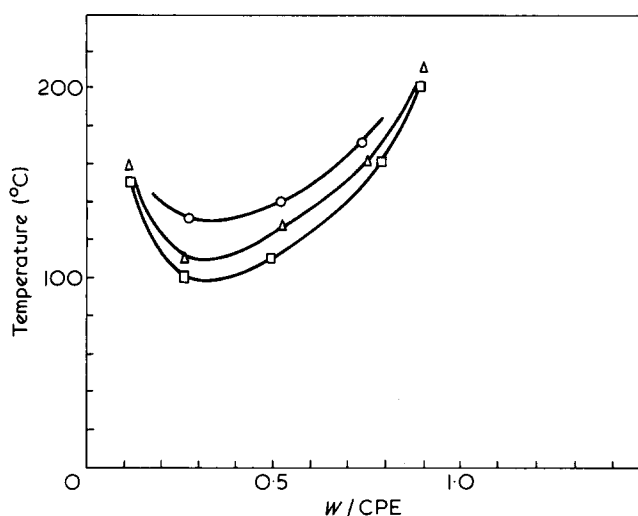


Figure 2 Phase diagram for blends of CPE 17 with PMMA of molecular weight; \circ - 12200 (PMMA 17), Δ - 42100 (PMMA 16), and \square - 72800 (PMMA 1.4)

The blends of PMMA with chlorinated polyethylene having a lower degree of chlorination, CPE 2 (27% w/w C1), were then further studied. These had previously been thought to show a compatibility gap between 65° and 90°C. We examined the effect of molecular weight on this phase diagram using light scattering but could find no effect even at very low molecular weight. This was not expected. Also it was difficult to understand how compatibility could occur at 27% chlorination and 52% chlorination but not between. The result at 27% chlorination had been checked by a dynamic mechanical experiment but spurious peaks can arise from secondary processes. We therefore checked the results using d.t.a. and two separate transitions were always found. This compares with the 52% chlorination blends where one intermediate transition was found which separated into two separate transitions when the samples were heat treated as

described earlier.

In order to explain the light scattering results observed for the lower chlorine content sample we measured the refractive indices of a series of oligomeric chlorinated polyethylenes and PMMAs as a function of temperature. The results are shown in Figure 4. It is apparent that around 27% chlorinated polyethylene the refractive index is very similar to PMMA. Also the refractive index varies with temperature to a different degree for CPE than for PMMA. It is most probable that the phase diagrams previously obtained are a completely unpredictable result of similar refractive index and different temperature coefficient and would not have been observed had we not happened to prepare samples with very close to 27% chlorination.

To understand the reasons for the compatibility we measured the heats of mixing for a series of chlorinated octadecanes for different compositions mixed with an oligomeric PMMA. The results are shown in Figure 5. One can see that the heat of mixing is unfavourable for chlorine contents up to 43% w/w but at 52.9% C1 the heat of mixing is favourable for compatibility. We also show

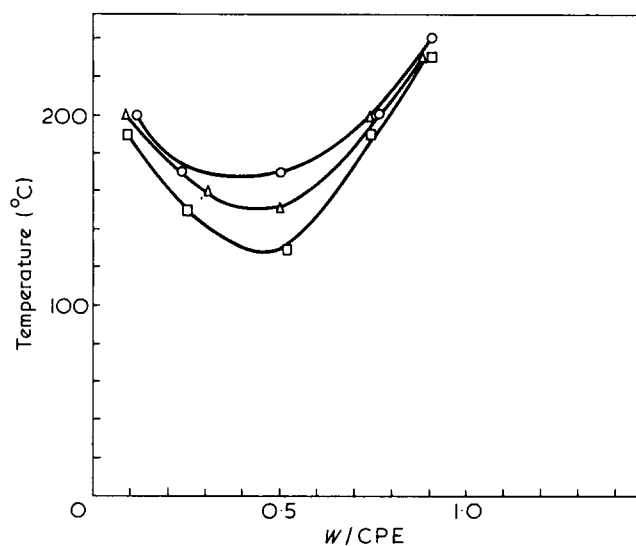


Figure 3 Phase diagram for blends of CPE 16 with PMMA, molecular weights as shown in Figure 2

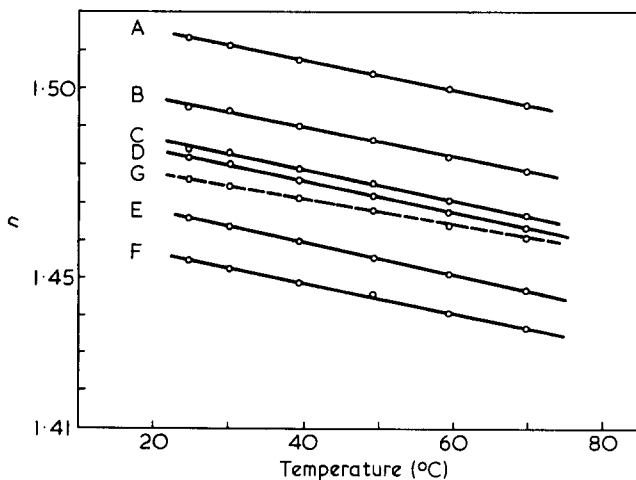


Figure 4 Plots of refractive index against temperature for chlorinated octadecanes, A = COD 5 (52.9% Cl), B = COD 4 (43.2% Cl), C = COD 3A (34.9% Cl), D = COD 3 (33.4% Cl), E = COD 2 (24.6% Cl), F = COD 1 (17.4% Cl), and oligomeric PMMA, G (broken line)

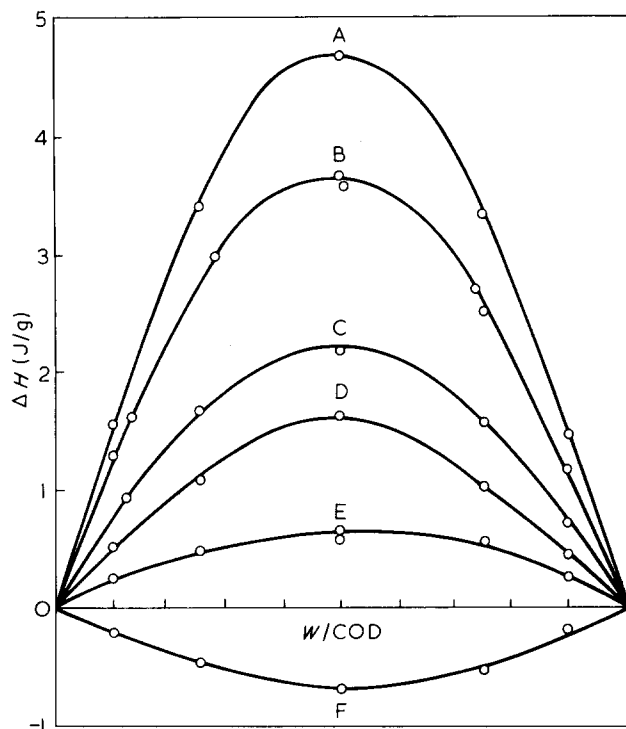


Figure 5 Heats of mixing for oligomeric PMMA (23) with chlorinated octadecanes plotted against weight fraction COD; A = COD 1 (17.4% Cl), B = COD 2 (24.6% Cl), C = COD 3 (33.7% Cl), D = COD 3A (34.9% Cl), E = COD 4 (43.2% Cl), F = COD 5 (52.9% Cl)

results for two chlorinated paraffins with PMMA at two temperatures in Figure 6. The Cereclor 52 shows a favourable heat of mixing and Cereclor 45 very close to zero. The asymmetric dependence on composition for Cereclor 45 cannot be explained by experimental error and may reflect some matching of the concentrations of the groups responsible for the specific interaction at higher weight percent cereclor balanced by an unfavourable dispersive interaction. The fact that the heat of mixing becomes negative around the region where the higher molecular weight polymers are compatible is expected because this term dominates the free energy of mixing for high polymers. The high positive values of the heat of mixing for mixtures containing materials with a low percentage of chlorine supports our conclusion that the corresponding polymers are not compatible with PMMA.

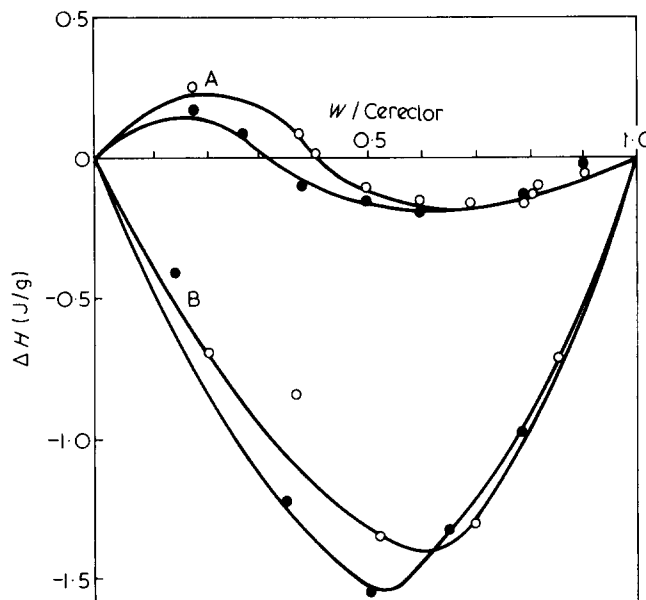


Figure 6 Heat of mixing for oligomeric PMMA (1) with A; Cereclor 45, and B Cereclor 52, plotted against weight fraction Cereclor, at two temperatures, \circ = 70°C, \bullet = 85°C

Conclusion

Chlorinated polyethylenes with 49.8 and 51.6% chlorine are compatible with poly(methyl methacrylate) if the samples are cast from MEK at room temperature and exhibit a lower critical solution temperature. At lower degrees of chlorination the polymers are not compatible at all compositions. The compatibility can be by the heat of mixing which becomes favourable for higher chlorine contents.

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