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Compatibility of Ethylene–Vinyl Acetate Copolymers with Chlorinated Polyethylenes. 1. Compatibility and Its Variation with Temperature

David J. Walsh,* Julia S. Higgins, and Shamsedin Rostami

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, England. *Received April 26, 1982*

ABSTRACT: Blends of ethylene–vinyl acetate copolymers with various chlorinated polyethylenes were made by solvent casting from THF. Dynamic mechanical and DTA measurements showed them to be compatible at room temperature. Dynamic mechanical, optical and electron microscopy, and light scattering turbidity measurements showed them to phase separate at higher temperatures. The phase diagrams for the various mixtures were determined. Blends of those polymers with a higher concentration of chlorine or acetate functional groups show a higher phase separation temperature and are hence more compatible.

Introduction

At one time the compatibility or miscibility of two polymers was considered a rarity, but many compatible pairs of polymers have been discovered over the past 10 or 20 years. One of the most comprehensive lists of these appears in a recent book by Olabisi, Robeson, and Shaw.[1] Compatibility of two polymers is not expected to occur because the combinatorial entropy of mixing ΔS_m is very small, as predicted by[2]

$$\Delta S_m = -k(n_1 \ln \phi_1 + n_2 \ln \phi_2)$$

where ϕ_1 and ϕ_2 are the volume fractions of the two components and n_1 and n_2 are the number of molecules of the two components.

A very small unfavorable heat of mixing is therefore sufficient to cause incompatibility. However, in many real systems the heat of mixing can be favorable. This is often accompanied by a variable heat of mixing and/or an unfavorable entropy of mixing arising from a noncombinatorial contribution. This can result in phase separation at higher temperatures.

The favorable heat of mixing has often been attributed to a specific interaction between the two polymers such as a hydrogen bond. One example of this is poly(vinyl chloride) with polycaprolactone, where a shift in the infrared carbonyl adsorption has been observed.[3] PVC has also been observed to be compatible with many other carbonyl-containing polymers.[4,5] Both ethylene–vinyl acetate copolymers and various polyacrylates are used commercially as modifiers for PVC.[6]

PVC is not, however, a very convenient polymer to study because it has a complex semicrystalline and particulate structure that is not fully understood. In many ways chlorinated polyethylene is preferable. The crystallinity of polyethylene disappears at above ~25% chlorine content. Varying the chlorine content varies the interactions and hence the compatibility and phase separation temperatures. Also at lower chlorine content the polymers have a lower glass transition temperature, are more mobile, and hence more easily achieve equilibrium conditions.

In this paper we report on the compatibility of chlorinated polyethylene (CPE) with ethylene–vinyl acetate copolymers (EVA). We describe the phase diagrams obtained and the way that they vary with the composition of the two polymers.

Experimental Section

Table I
Properties of Chlorinated Polyethylenes

sample	% (w/w) Cl	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
H40	35.41	2.06×10^4	1.88×10^5	9.15
H48	44.05	2.39×10^4	1.82×10^5	7.63
CPE3	52.65	2.29×10^4	1.20×10^5	5.22

Table II
Properties of Ethylene–Vinyl Acetate Copolymers

sample	% C	% H	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
EVA40	74.46	11.55	3.37×10^4	1.3×10^5	3.86
EVA45	73.46	11.49	3.77×10^4	2.56×10^5	5.16

Materials. Two commercial chlorinated polyethylenes were used: Hypalon 40 and Hypalon 48 (kindly supplied by Du Pont, U.K., Ltd.). These polymers also contain a small number of SO_2Cl groups. Another CPE was prepared, in order to give a different chlorine content, from a commercial high-density polyethylene (nominal $\bar{M}_n = 1 \times 10^4$). This was dissolved in chlorobenzene (AR) at 130 °C to give a 5% (w/v) solution. It was photochlorinated by using irradiation from a 60-W tungsten lamp. The chlorine was bubbled through the solution, which was kept under a nitrogen blanket. The desired degree of chlorination could be obtained by adjusting the conditions. The reaction product was cooled and precipitated into a 10-fold excess of AR methanol, washed with methanol, and dried for 14 days at 50 °C in a vacuum oven. The degree of chlorination was determined by elemental analysis, and the molecular weights were obtained by gel permeation chromatography in tetrahydrofuran relative to polystyrene standards. The properties of all the CPEs used are given in Table I.

Two commercial ethylene–vinyl acetate copolymers were used, Evotane 40 (ICI, Ltd., with a nominal 40% (w/w) vinyl acetate content and hence designated EVA40) and Levapren 45N (Bayer, with a nominal 45% (w/w) vinyl acetate content and hence designated EVA45). The molecular weights were determined by GPC as described previously, and carbon and hydrogen contents were determined by elemental analysis. The properties are shown in Table II.

Since both of these types of polymers are based on polyethylene, one must consider the possibility of residual crystallinity. In our previous experience, solution chlorination of polyethylene to 35% (w/w) or more chlorine destroys all crystallinity at room temperature, and 40% (w/w) or more vinyl acetate in EVA also removes crystallinity. The particular polymers we used were checked by X-ray diffraction, using both Guinier and Philips cameras, and no crystallinity was observed. We are therefore essentially dealing with amorphous polymers in this work.

Preparation of Blends. Blends were prepared by casting from a common solvent. The polymers in various proportions were dissolved to a total of 2% (w/v) in THF (AR). The solutions were poured into a petri dish, and the solvent was allowed to evaporate to produce clear films. The petri dish was previously treated with a 2% solution of 1,1,1-trimethylchlorosilane in 1,1,1-trichloroethane to ease removal of the film. The film was kept under vacuum at 10^{-1} mmHg for at least 1 week before further tests. Attempts to cast films from other common solvents, toluene, cyclohexanone, and dioxane, produced cloudy samples over some

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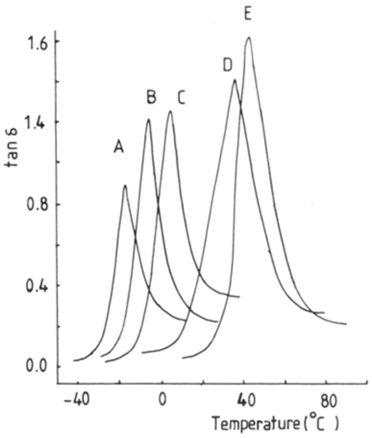

Figure 1. Plots of tan δ against temperature for mixtures of EVA45 and CPE3: (A) pure EVA45; (B) 20% (w/w) CPE3; (C) 50% CPE3; (D) 80% CPE3; (E) pure CPE3.

compositions, showing how some solvents can induce incompatibility.

Residual THF was checked for by infrared spectroscopy. No peaks due to THF were observable, though this was not a very sensitive test due to the lack of convenient strong peaks. We also observed the weight loss of the sample under the conditions of drying using a microbalance and found no further loss in weight after 1 week.

Dynamic Mechanical Measurements. These were carried out on a Rheovibron (Model DDV-11, Toyo Measuring Instrument Co. Ltd.). A strip of the sample was subjected to an imposed oscillatory frequency of 11 Hz. The temperature was scanned at 1 °C/min and a plot of tan δ against temperature obtained. A maximum in tan δ was taken as a measure of T_g. Peaks close to those of the pure components indicate little mixing whereas one peak at an intermediate temperature indicates a single mixed phase.

Differential Thermal Analysis. Measurements were made with a Du Pont 990 thermal analyzer. Sample sizes of 20 mg were used, with a sensitivity of 0.2 mcal/s. The samples were cooled to −100 °C and then scanned with a heating rate of 5 °C/min.

Optical and Electron Microscopy. The phase separation process was observed by using both optical and electron microscopy. The optical observations were carried out with a Zeiss Epinal interference microscope using the shearing mode. Samples were heated to a series of temperatures for up to 5 h. The samples were then examined in the microscope. The onset of phase separation was clearly visible.

The same procedure was used to prepare samples for electron microscopy. Specimens about 900 Å thick were cut with an ultramicrotome (LKB) equipped with a liquid-nitrogen-cooled cold chamber. A JEM 100B transmission electron microscope was used.

Cloud Point Determination by Scattered Light. Phase boundaries were determined by measuring light scattered from the samples using a specially designed light scattering turbidimeter.[7] The films were supported in a sample holder located in a thermostatically controlled aluminum block. Light from a tungsten lamp was focused onto the sample, and the light scattered at 45° was measured by a photodiode. The temperature of the block could be altered at a controlled rate and a plot of scattered light against temperature was obtained. Results were corrected for changes in sensitivity of the diode with temperature. Abrupt increases in scattered light were considered as evidence of a cloud point. The samples could also be held at a preset temperature and the increase in scattering observed as a function of time. The temperature at which a gradual increase in scattering occurred could be obtained and this gives a much more reliable measure of the cloud point.

Results and Discussion

The dynamic mechanical results for mixtures of CPE3 with EVA45 are shown in Figure 1. They clearly show intermediate glass transitions, indicating compatibility. Other mixtures gave similar results but less clearly for mixtures of polymers with similar glass transitions.

The phase separation process was also followed by dynamic mechanical measurements. Samples of the film were heated for 5 h at a series of temperatures. The samples were then quenched in liquid nitrogen and scanned as before. Phase separation was indicated when the single peak began to split into two component peaks. An example of this is shown in Figure 2. The results found were generally in agreement with those found by other methods.

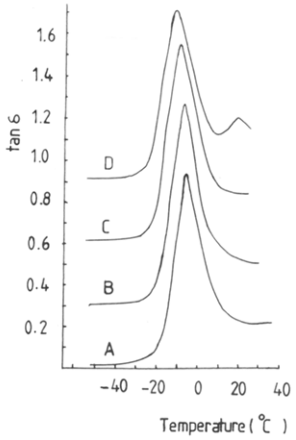

Figure 2. Plots of tan δ against temperature for a 35:65 mixture of H48 and EVA40 taken (A) as formed , (B) after heating at 42 °C (tan δ = +0.3), (C) after heating at 62 °C (tan δ = +0.6), and (D) after heating at 82 °C (tan δ = +0.9).

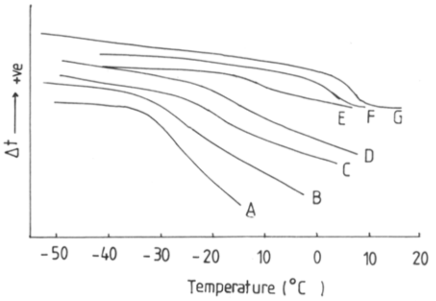

Figure 3. Plots of Δt against temperature from DTA for blends of EVA40 and H48: (A) pure EVA40; (B) 10% H48; (C) 35% H48; (D) 50% H48; (E) 70% H48; (F) 90% H48; (G) pure H48.

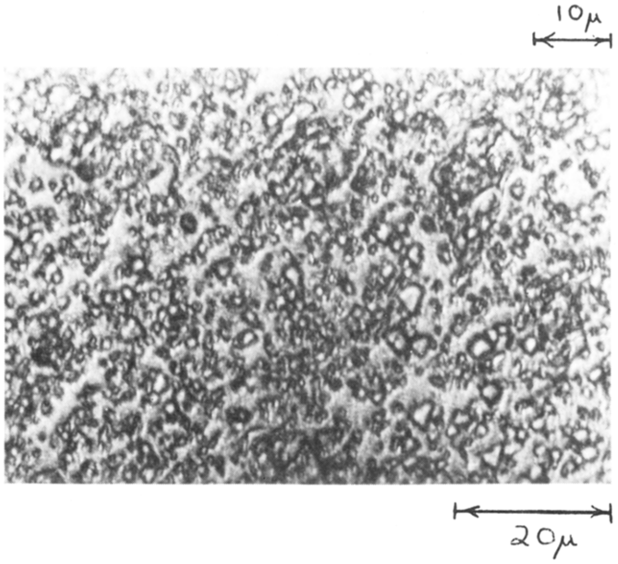

Figure 4. Picture from Zeiss Epinal microscope of an 80:20 CPE3–EVA40 blend heated at 90 °C for 3 h and then cooled quickly to room temperature.

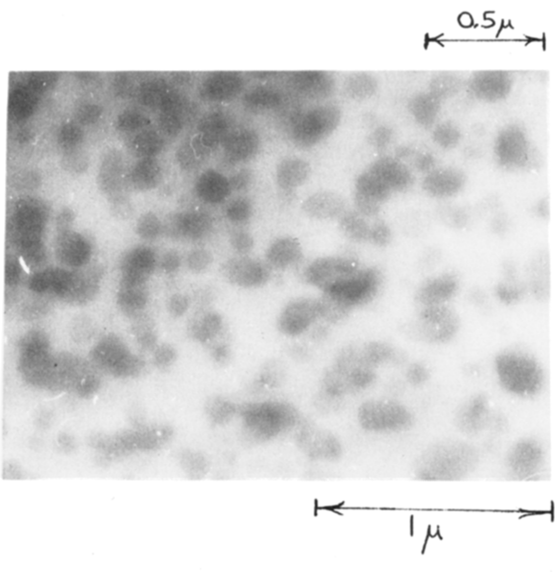

Figure 5. Electromicrograph of a 40:60 CPE3–EVA 40 blend heated at 90 °C overnight.

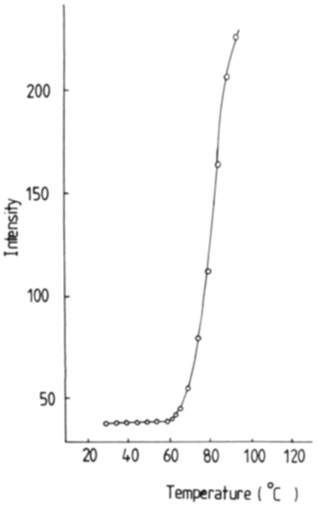

Figure 6. Plot of scattering intensity (arbitrary units) against temperature for a 65:35 H48–EVA40 blend.

The compatibility was confirmed by DTA. In Figure 3 we show the results for blends of H48 and EVA40. The position of the transition can be seen to change monotonically with the composition. Dielectric relaxation measurements gave corresponding results but they are less sensitive and are not presented here.

The phase separation could also be observed by phase contrast microscopy. At room temperature no structure was observable in the blends. After heating for 5 h at some temperature and quenching, phase separation was clearly visible. An example of the structure that developed after prolonged heating above the expected cloud point is shown in Figure 4. A similar experiment observing the phase separation by electron microscopy gave similar results. An example of the phase-separated structure observed is shown in Figure 5. In each case the temperatures of phase separation confirmed those found by other methods.

The cloud point curves for all the series of blends were finally determined by use of the light scattering machine as this was the most convenient method for obtaining the information. Because all our polymers are elastomers at the temperature of testing, we expect kinetic factors not to be very important. An example of the plots of scattering against temperature during a programmed heating run is shown in Figure 6. The point of phase separation where the scattering intensity increases can be identified within ±2 °C in the best cases and always within ±5 °C. The time dependency of the intensity can be illustrated, however, in this case by plotting the scattered intensity against time while holding the temperature at a given value after heating to that value at a controlled rate. The results are shown in Figure 7. One observes no increase at 54 °C and a marked increase at 66 °C with time. The phase separation appears to be slowly reversible. Samples slowly become clear again at lower temperatures over long times depending on how far the separation was allowed to develop. This was not, however, studied in any detail.

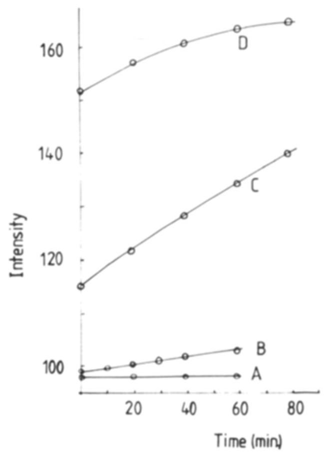

Figure 7. Plots of scattering intensity (arbitrary units) against time for a 65:35 H48–EVA40 blend heated at 0.2 °C/min to a set temperature and then held at (A) 54, (B) 66, (C) 76 °C, and (D) 83 °C.

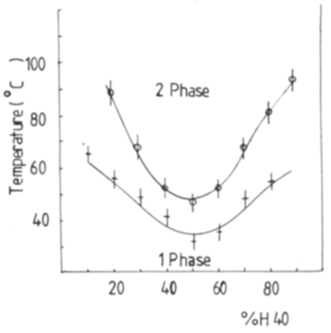

Figure 8. Phase diagrams for blends H40–EVA40 (+) and H40–EVA45 (O).

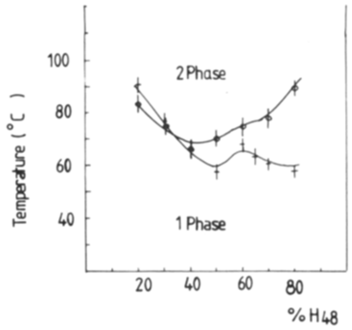

Figure 9. Phase diagrams for blends H48–EVA40 (+) and H48–EVA45 (O).

The phase diagrams for the six possible blends of two EVAs with three CPEs are shown in Figures 8–10. In each case for a given CPE, the EVA45 has a higher LCST and hence is more compatible. In each case for a given EVA,

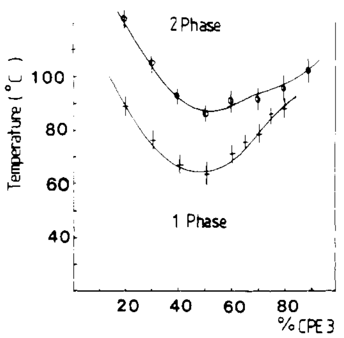

Figure 10. Phase diagrams for blends CPE3-EVA40 (+) and CPE3-EVA45 (O).

the CPE3 has a higher LCST than H48, which has a higher LCST than H40. Hence the CPE3 is more compatible than H48, which is more compatible than H40. For both sets of polymers this coincides with a higher concentration of interacting groups, resulting in a higher degree of compatibility as would be expected. In many cases the phase diagrams show indications of asymmetry or even bimodality. This is not an unusual phenomenon in polymer/polymer phase diagrams[8] and various explanations of it have been given.

Conclusions

Various chlorinated polyethylenes and ethylene-vinyl acetate copolymers have been found to be compatible at all compositions at room temperature. They all show evidence of an LCST, phase separating at temperatures between room temperature and 100 °C. The polymers with a higher concentration of functional groups, chlorine or acetate, respectively, show the higher LCST and are hence more compatible. This shows the importance of the specific interaction in causing compatibility and of the relative concentrations of interacting groups in determining the degree of compatibility and the temperatures of the phase separation boundaries. In a further paper we proceed to explore the detailed thermodynamics of the system.[9]

Registry No. EVA, 24937-78-8.

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Compatibility of Ethylene-Vinyl Acetate Copolymers with Chlorinated Polyethylenes. 2. Investigation of the Thermodynamic Parameters

David J. Walsh,* Julia S. Higgins, Shamsedin Rostami, and K. Weeraperuma

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, England. *Received April 26, 1982*

ABSTRACT: An investigation was made into the thermodynamic parameters of the compatible polymer system ethylene-vinyl acetate copolymer/chlorinated polyethylene. The heats of mixing of low molecular weight analogues were measured and found to be negative, favorable for mixing. The interaction parameter was measured by inverse gas chromatography and this was found to be negative, changing to positive at higher temperatures, consistent with the observed phase separation on heating. The effect of pressure on the phase boundary was also measured. The phase boundary moved to higher temperatures with increasing pressure, which predicts a densification on mixing. It was concluded that it would be necessary to invoke an unfavorable noncombinatorial entropy contribution to the free energy of mixing in order to accommodate the heat of mixing measurements with the observed phase separation on heating.

Introduction

The compatibility of polymers, as of any other materials, is determined by the free energy of mixing ΔG. A favorable free energy of mixing is a necessary but not sufficient requirement for compatibility, but if one can predict the free energy of mixing as a function of composition, then one can predict whether the two polymers are compatible under those conditions of temperature and pressure.

The theoretical problem is therefore to predict ΔG from known or measurable properties of the substances. Various theories have been developed to deal with this problem in the case of polymer solutions and mixtures. Most are basically Flory-Huggins, or lattice, models, which assume a lattice on which the polymer molecules can be arranged and therefore calculate an entropy of mixing. This combined with a heat of mixing, depending on an interaction function and some function of composition, gives ΔG. These models have been very successful in explaining many properties of polymer solutions but have some shortcomings, especially in that they do not take account of possible volume changes on mixing. Corresponding-state and equation-of-state models seek to overcome this. The parameters of pressure, temperature, and volume are expressed in a reduced form by dividing them by reduction parameters, and volume changes are allowed. The calculations are much more complicated, and a great deal of information (often not available) about the materials is required. In many circumstances despite all this effort

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