Miscibility of PVA/EVA systems by viscometry

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ABSTRACT

Viscometric data were applied to characterize the miscibility of poly(vinyl chloride) (PVC)/poly(ethylene-co-vinyl acetate) (EVA) mixtures using six samples of EVAs with different vinyl acetate content in the copolymer. Relative viscosity vs composition plots showed the imiscibility of PVC/EVA 31 and PVC/EVA 41 blends. The variation of the reduced viscosity, η_{sp}/C, with the concentration, C, has been studied for 50:50 by weight blends of PVC/EVA 45, PVC/EVA 45A, PVC/EVA 50 and PVC/EVA 70 in tetrahydrofuran at 25 °C.The presence of a sharp crossover and a consequent reduction of slope in η_{sp}/C vs C plots showed that these systems are miscible for a concentration range which corresponds to the regime of dilute solution.

INTRODUCTION

Viscometry has been introduced as a method to evaluate the miscibility of polymer mixtures because the macromolecules of both species may exist as a molecular dispersion with mutual atractions or repulsions which can influence the viscosity measurements. This influence can be explained as a result of the predominance of the polymer-polymer interactions over the polymer-solvent interactions. Detailed studies reported that plots of relative viscosity, η_r, *versus* blend composition show a deviation from linearity according to the degree of compatibility of polymer blends using a variety of systems, e.g., polystyrene (PS)/poly(methyl methacrylate (PMMA), PS/poly(vinyl chloride) (PVC), PVC/acrylonitrile-butadiene-styrene terpolymer (ABS), polystyrene (PS)/polybutadiene (PB), polyisoprene (PI)/polybutadiene (PB), and suggested a relationship between the hydrodynamical dimensions of different species and the presence of defined phases in the system. Plots for compatible systems are linear, whereas for incompatible systems plots are of S-type, indicating two phase formation with reversal of phases at intermediate compositions [1 - 5].

In systems composed from 50:50 by weight mixture of two polymers solutions, a hydrodynamic crossover was observed in the plot of reduced viscosity (η_{sp}/C) *versus* concentration (C). This crossover at which there is a change of slope of the straight line obtained using this plot has been attributed to the lack of compatibility between the polymers [1, 2, 4]. The proposed theories defined two critical concentrations according the de Gennes criteria _ a critical concentration, C^*, which is the limit between the regime of dilute and semi-dilute solutions and a critical concentration, C^{**}, ($C^{**}<C^*$) corresponding to the incipient overlap of spherical coils. Below C^*, a regime of dilute concentration prevails and the coils are mostly separated from each other; above C^*, the coils overlap and the individuality of the macromolecules disappears [1, 2, 6]. At a concentration higher than C^{**}, the macromolecular chains maintain their identities, but their hydrodynamic volumes will be smaller and the values of the reduced viscosity, η_{sp}/C, of the solution will be reduced indicating imiscibility between the two polymers.

In this work viscometric data were applied to characterize the miscibility of poly(vinyl chloride) (PVC)/ethylene-vinyl acetate copolymer (EVA) mixtures using EVAs with different vinyl acetate grades in the copolymer structure.

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EXPERIMENTAL

The poly(vinyl chloride) used in this work was a commercial product of Companhia Petroquímica Camaçari (CPC), with a density of 1.390 gcm^{-3}. Six ethylene--vinyl acetate copolymers were obtained from commercial sources and are listed in Table 1 along with pertinent characterizing information. Molecular weight distribution (MWD) of all samples was determined by size exclusion chromatography, SEC (Toyo Soda, model HLC 803A), operating with 10^3, 10^4, 10^5 Å µStyragel columns, at 25°C, with tetrahydrofuran (THF) as solvent, and using 0.05% polymer solution; the flow rate was maintained at 1ml/min. and polystyrene standards were used for calibration purposes. Glass transition temperature, Tg, was measured by differential scanning calorimetry conducted using a Perkin Elmer, model DSC-2 apparatus calibrated with indium (T_m=429.86K; ΔH_f=6.8 cal/g). The vinyl acetate (VA) content of EVAs samples were obtained by thermogravimetric analysis carried out on a Perkin Elmer, model TGA-7 thermobalance calibrated with alumel (T_c=163°C), nickel (T_c=354°C) and perkalloy (T_c=596°C) standards.

Blends of PVC with the various EVAs were prepared in solution using tetrahydrofuran (Merck) or methyl ethyl ketone (MEK) (Merck) as solvents, at appropriate concentrations of PVC and EVA to obtain 9:1, 7:3, 5:5, 3:7, and 1:9 by weight PVC:EVA ratio. The viscosity measurements were carried out using an Ostwald-type 75 and two Ubbelohde-type 1 and 1C viscometers, in a bath at 25°C. All procedures were run with at least duplicate samples.

TABLE 1 - Characterization of polymers used in this study

Polymer	% VA Nominal	Calc.	Density (gcm^{-3})	Tg (°C)	$\bar{M}w$	$\bar{M}n$	$\bar{M}w/\bar{M}n$
PVC	----	----	1.390	86	152000	101000	1.5
EVA 31	31	32	0.949	-39	72000	23000	3.1
EVA 41	41	43	0.967	-40	65000	29000	2.2
EVA 45	45	45	0.975	-36	95000	29000	3.2
EVA 45A	45	46	----	-38	72000	34000	2.2
EVA 50	50	52	0.990	-37	157000	38000	4.2
EVA 70	70	70	1.055	-23	176000	54000	3.3

RESULTS AND DISCUSSION

Figure 1 shows relative viscosity (η_r) - composition plots of mixtures obtained by blending PVC with six different types of EVA. It can be seen that the plots of PVC/EVA 31 and EVA 41 are of S-type indicating two phase formation with inversion of phases at intermediate compositions (50-60% PVC). The plot of mixtures prepared with EVA 45 is linear between 0 and 70% PVC. At PVC concentrations greater than 70%, the data show a slight change of slope of the curve which is an indication of semi-miscibility. The lines given from blends of PVC with EVA 45A, EVA 50 and EVA 70 are linear and a single straight line satisfies the sets of data. These blends can be considered miscible.
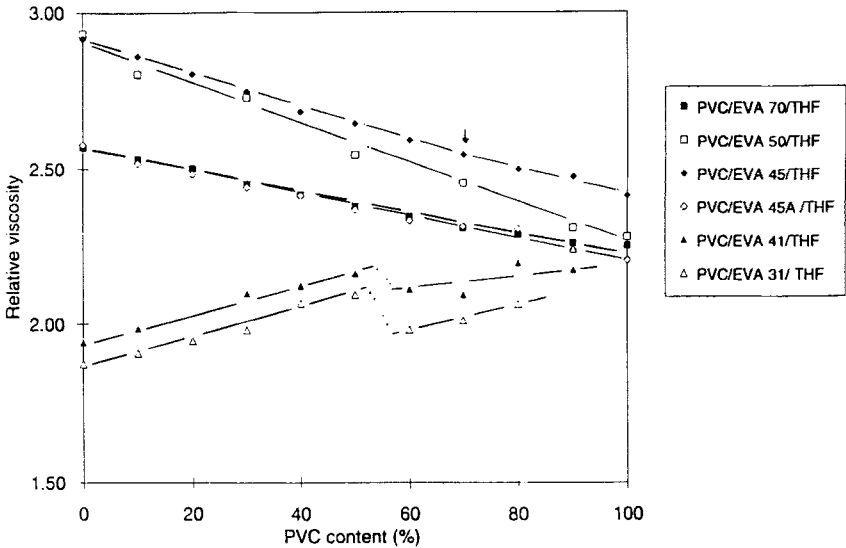
Figure 1. Relative viscosity-composition plots for PVC/EVA blends, at 25 °C, from 1% w/v THF solutions.

Its well known that the solvent can influence the macromolecular dimensions and viscosity data. In discussing the viscosity of polymer solutions the constant k determined by the slope of the equation

$$\ln \eta_r = [\eta] \, C + k \, [\eta]^2 \, C^2$$

is positive for suspensions while is usually negative for polymer solutions [7 - 9]. For this reason, an evaluation of the solvent behaviour on polymer 1-solvent, polymer 2-solvent and polymer 1-polymer 2 interactions was carried out using methyl ethyl ketone (MEK) as solvent. In this experiment were used the polymers EVA 45 and EVA 70 which were soluble in MEK, and the results are presented in Figure 2.
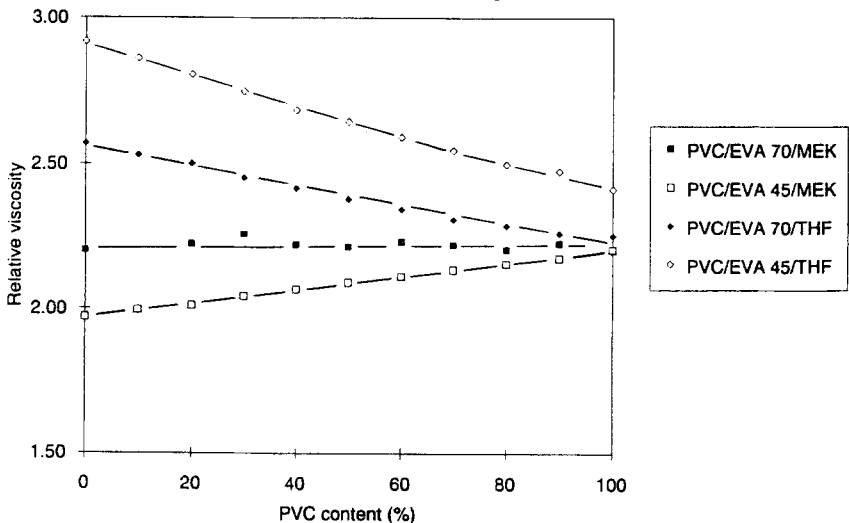

Figure 2. Relative viscosity-composition plots for PVC/EVA blends, at 25 °C, from 1% THF and MEK solutions.

For solutions obtained using THF as solvent, the data are similar to previous ob-servations which are drawn for comparison purposes. However, there is a change of the slope of the straight lines obtained using MEK as solvent. This means that in MEK the coils are not so extended as in THF which is a good solvent for PVC and EVA. Gillespie [7] pointed out that the constant k is a function of hydrodynamic volume and so can be associated to miscibility; this concept could be extended to relative viscosity-composition data.

Since the miscibility of polymer blends can be characterized using the variation of the reduced viscosity, η_{sp}/C, as a function of concentration, C, the determination of C* and C** was carried out for PVC/EVA/THF systems, using solutions with 50wt% of PVC and 50wt% of EVA. Figures 3 - 6 show the results obtained for EVA 45, EVA 45A, EVA 50 and EVA 70.
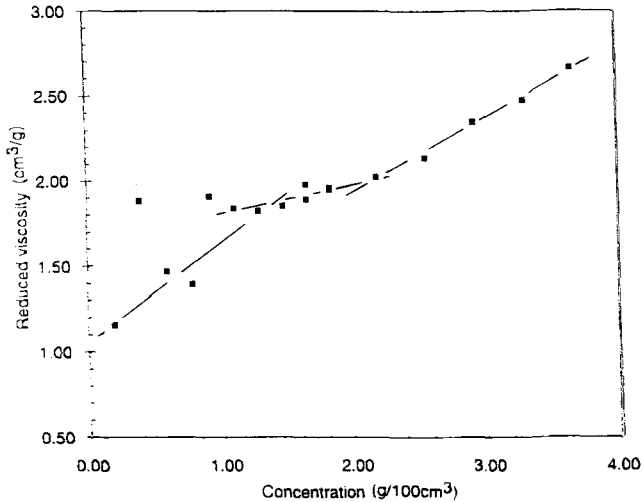

Figure 3. Variation of the reduced viscosity of the 50:50 mixture of PVC:EVA 45 as a function of concentration at 25 °C. Solvent: THF.
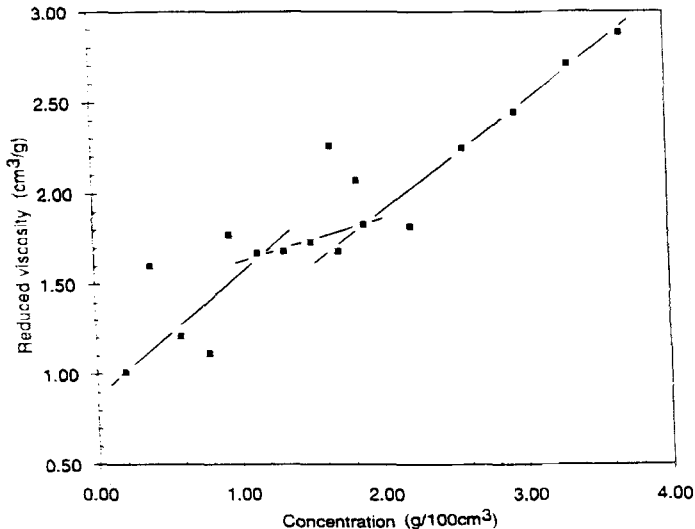

Figure 4. Variation of the reduced viscosity of the 50:50 mixture of PVC:EVA 45A as a function of concentration at 25 °C. Solvent: THF.
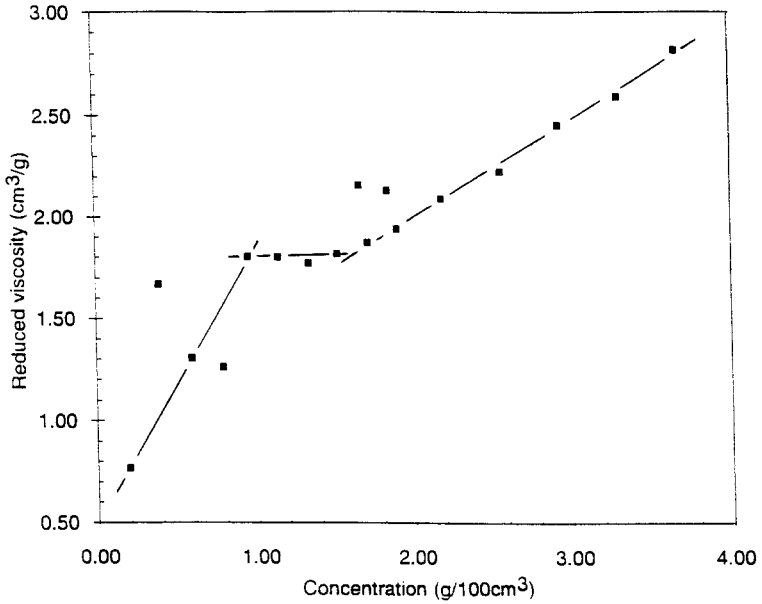
Figure 5. Variation of the reduced viscosity of the 50:50 mixture of PVC:EVA 50 as a function of concentration at 25 °C. Solvent: THF.
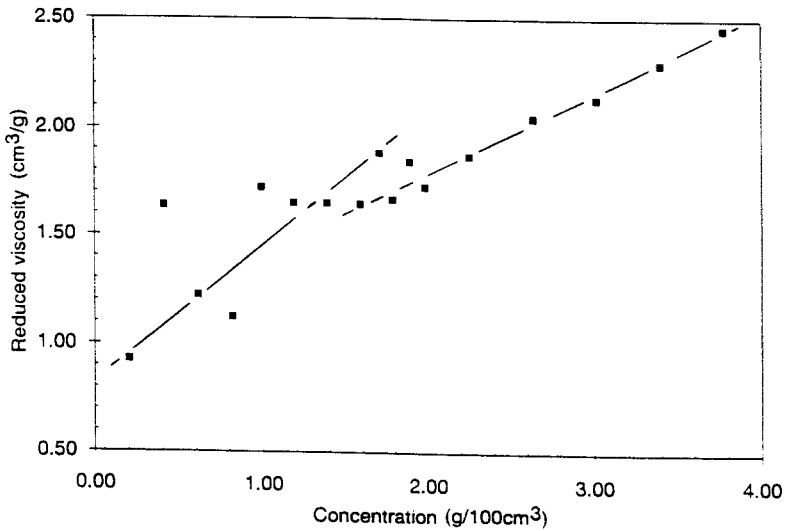

Figure 6. Variation of the reduced viscosity of the 50:50 mixture of PVC:EVA 70 as a function of concentration at 25 °C. Solvent: THF.

It is evident the similarity between Figures 3-5. All present a S-type profile. There are two changes of the slope of the curve of η_{sp}/C vs C. For low concentrations of the mixture, the change in the slope which is sharp, means that the critical region C** is reached (~ 1%). The macromolecular coils begin to have the first contacts [2]. Since the molecules do not tend to overlap they shrink in size and their hydrodynamic volume decrease because of the appearance of imiscibility between PVC and EVA. In this concentration range, all mixtures obtained from the studied EVAs show a decrease of the slope of the straight line as compared to the slope of the dilute solution region. The decrease of the slope is therefore associated to the incompatibility which does exist in these systems. The second change in the slope, which can be seen in Figures 3 - 5, was attributed by Pierri and Dondos [2], to the transition from the regime of dilute to semi-dilute solution. These data show that this change is not abrupt and corresponds to the overlapping of the different polymer coils, i.e., the critical region C*.

Figure 6 shows the viscometric results obtained for PVC/EVA 70 blends. The points lie on two straight lines with a hydrodynamical crossover, and the slope in the higher concentration range is smaller than that for the dilute solutions.

As shown by Pierri and Dondos [2], the molecular weight can influence the viscometric results. They obtained a critical concentration on going from the regime of dilute solution to that of semi-dilute solution using a single polymer. The C* value for a high molecular weight polymer sample appears at a relatively lower concentration [2]. This effect was observed in the studied PVC/EVA systems. Table 2 present the values of C* and C** obtained for the different PVC/EVAs.

Table 2. Critical values C** and C* for PVC/EVA systems

Polymer blend	C**	C*	C*/C**	$\overline{M}w$
PVC/EVA 45	1.3	2.2	1.8	95000
PVC/EVA 45A	1.1	1.9	1.7	72000
PVC/EVA 50	1.0	1.6	1.6	157000
PVC/EVA 70	1.4	1.7	1.2	176000

These authors noticed that as the molecular weights become higher, the ratio C*/C** also becomes higher. From Table 2, it can be seen that values of C*/C** does not change significantly for mixtures from EVA 45, EVA 45A and EVA 50. However, the increase of the vinyl acetate content in EVA (EVA 70) cause an increase of the compatibility between PVC and EVA; there is an increase of the concentration C** at which the chains of PVC and EVA begin to repel each other.

These results explain the apparent miscibility shown in Figures 1 and 2. At the concentration of 1%, all systems were under the regime of dilute solutions.

CONCLUSION

PVC/EVA mixtures from EVAs with intermediate to high content of vinyl acetate (45 to 70%) may be considered miscible when the relative viscosity is plotted against the polymer composition. The plots the reduced viscosity of a 50:50 by weight mixture of these two polymers showed that these systems can be considered miscible under the regime of dilute solution. For the regime of semi-dilute solution this plot present a crossover which characterizes the imiscibility of PVC/EVA systems.

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