

Effect of tacticity on the transition behaviour of poly(methyl methacrylate)/poly(vinyl chloride) blends. Thermally stimulated depolarization study

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The transition behaviour of blends of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) isotactic (i-PMMA) and syndiotactic (s-PMMA) was determined in the temperature range -150°C to $+130^{\circ}\text{C}$ by the thermally stimulated depolarization currents method (TSDC). The evolution of the current spectra was analysed as a function of blend composition. From the variation of properties of the peaks (presence or not of two T_g peaks, shifting or not of their positions, existence or not of interfacial components, regular or complex variation of the peak amplitudes...), it was concluded that i-PMMA and PVC form an incompatible system over the entire concentration range while in s-PMMA/PVC blends, some compatibility probably exists but only for concentrations in s-PMMA not higher than 10 wt%. By referring to literature data, this value is much smaller than the compatibility range found from d.s.c. and mechanical measurements but is close to that determined from optical and electronic spectroscopy methods. These results emphasize the important role played by the type of method used to find out compatibility of a given polymer pair and show that the TSDC technique may be particularly useful for studying the interfacial phenomena associated with phase separation owing to its exceptional ability for easily detecting Maxwell-Wagner-Sillars polarization generated by the trapping of charge carriers at phase boundaries.

Keywords Transition behaviour; depolarization; tacticity; blend; poly(methyl methacrylate); poly(vinyl chloride); thermal stimulation

INTRODUCTION

The usual result of mixing in the solid state two chemically different polymers is a two-phase polyblend, the transitional behaviour of which can be in principle described by a more or less strict superposition of the spectra of the two pure homopolymers according to the more or less important amount of molecular mixing taking place at the phase boundaries¹. There is some evidence, however, that miscibility may be achieved for certain systems, at least in limited ranges of composition and (or) temperature, which involves that, as in random copolymers, specific transitions may appear at temperatures located between those observed in each pure component. Typical examples of such compatible systems are poly(methyl methacrylate)/(poly(vinylidene fluoride))², poly(ethyl methacrylate)/poly(vinylidene fluoride)^{2,3}, polystyrene/poly(vinyl methylether)⁴ and poly(vinyl chloride)/poly(ϵ -caprolactone)⁵.

Starting from thermodynamic considerations, i.e. assuming that two polymers characterized by similar values of the solubility parameter δ have more chance to be compatible, Schurer *et al.*⁶ have recently investigated the miscibility properties of tactic poly(methyl methacrylate) (PMMA: $\delta=9.5$) and poly(vinyl chloride) (PVC: $\delta=9.6$) and concluded from differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.) that the pair syndiotactic s-PMMA/PVC forms a compatible system up to a composition corresponding with a monomer unit ratio of about 1:1 (60 wt % s-

PMMA) while phase separation occurs for higher s-PMMA contents as well as over the entire composition range of isotactic i-PMMA/PVC blends. It is the purpose of the present paper to report complementary data concerning the compatibility of these polymer pairs by using the method of thermally stimulated depolarization currents (TSDC). This method, which consists of measuring with a definite heating scheme, the currents generated by the release of a polarized state in a solid dielectric, was revealed as a particularly useful tool for characterizing the nature of phase separation because it allows not only the following of any modification of the relaxation properties but also the easy detection of Maxwell-Wagner-Sillars effects (MWS) due to trapping of charge carriers at phase boundaries⁷⁻⁹.

EXPERIMENTAL

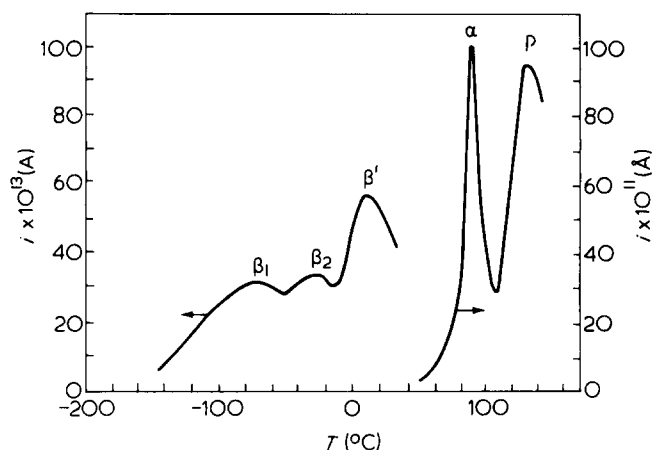
Materials

Poly(vinyl chloride) was a commodity of Solvay (RD-258). Before mixing it with PMMA 0.7 wt % of a stabilizer composed of 75 wt % di-n octyltin and 25 wt % epoxydated soya oil (Mark SS M9/68 Arguc Chemical) was incorporated in order to avoid thermal degradation. The polymers i- and s-PMMA were prepared according to the methods described by Goode *et al.*¹⁰ and Abe *et al.*¹¹, respectively. The molecular weights were determined by gel permeation chromatography with a Waters 200 chromatograph, the tacticities were measured by n.m.r. in 7.5% solution in *o*-dichlorobenzene at 150°C with a Cameca 250 spectrometer and the glass transition

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Table 1 Characteristics of polymers used

Code	Triads i-h-s	$\bar{M}_w \times 10^{-3}$	T_g ($^{\circ}\text{C}$)
i-PMMA	93-4-3	157	44
s-PMMA	5-7-88	203	105
PVC	-	85	73

Figure 1 TSDC spectrum of PVC (Polarizing Field $E_p = 10 \text{ kV cm}^{-1}$)

temperatures T_g were obtained by extrapolation at a zero heating rate from d.s.c. measurements carried out between 5°C and $50^{\circ}\text{C min}^{-1}$ with a Du Pont instrument (TA 990). The data are listed in Table 1.

Blends of PMMA and PVC were prepared according to two methods used by Schurer *et al.*⁶ i.e. either by reprecipitation from 3 wt % mixed PMMA-PVC solutions in DMF in an excess of 10:1 water-methanol mixture or by mechanically mixing the molten bulk polymers from previously finely dispersed powders obtained by lyophilization. The method of preparing films directly by evaporation of mixed PMMA-PVC solutions was found inapplicable with our specimens.

Sample preparation

Samples for TSDC measurements were obtained in the form of flat uniform discs, 70 mm in diameter and 0.5 mm thick, by compression moulding at 160°C with a pressure of 700 kg cm^{-2} . They were provided with two measuring electrodes and a guard ring either by evaporating aluminium under vacuum or by painting with colloidal silver and then were vacuum-oven dried over phosphorus pentoxide at 125°C for at least a week for relaxation of possible stresses which are known to sometimes affect the TSDC results⁸.

TSDC measurements

The experimental device used for recording the thermally stimulated currents has been described in a previous paper¹². The thermal cycles of polarization and depolarization consist essentially of the following steps: (1) heating to a temperature T_p higher than the upper T_g of the blend investigated; (2) application of a d.c. electric field $E_p = (0.5 - 60 \text{ kV cm}^{-1})$ for a time $t_p (= 10 - 60 \text{ min})$; (3) rapid cooling ($-b = 15^{\circ}\text{C min}^{-1}$) in the field to a temperature $T_0 \ll T_p$; (4) cutting off the external field and linear heating of the short-circuited samples at a rate $b (= 5^{\circ}\text{C min}^{-1})$.

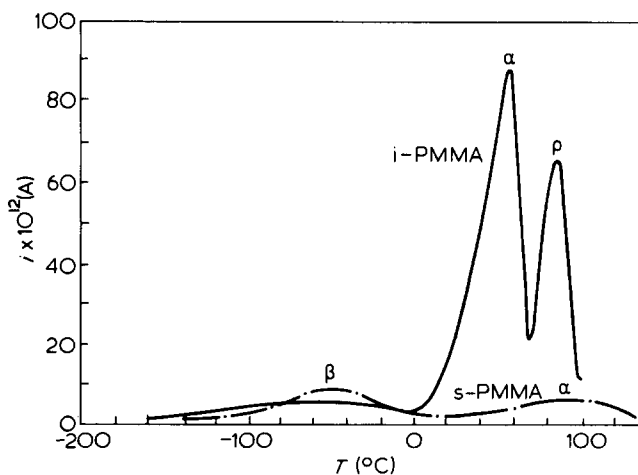
RESULTS AND DISCUSSION

Transition behaviour of pure polymers

Poly(vinyl chloride). Figure 1 shows the TSDC spectrum of PVC polarized at 140°C in a d.c. field of strength $E_p = 10 \text{ kV cm}^{-1}$. It is characterized by five partly overlapping peaks which will be designated by β_1 , β_2 , β' , α and ρ in order of increasing temperatures. The β_1 and β_2 peaks correspond well to the β unresolved broad loss peak observed from mechanical and dielectric measurements and can thus be ascribed to the so-called β relaxation (local chain movement of the crankshaft type¹³), the complex nature of which has been assumed by some authors¹⁴. The β' peak does not appear in pure PVC and therefore may be attributed to some relaxation process involving the stabilizer used.

The α peak appears close to the glass transition temperature as determined by d.s.c. and may thus be related to micro-Brownian motions of chain segments. On account of its high amplitude and the high conductivity level of PVC at this temperature, however, it is likely that the current observed results not only from the rotation of the C-Cl dipolar entities but also to some extent from migration of ionic charge carriers previously trapped in the vicinity of the chain. This problem of the complex nature of the TSDC α relaxation has been encountered in several polymers^{15,16} but has not yet received satisfactory explanation. The ρ peak does not correspond to any known intrinsic transition. As shown by the marked influence exercised on its properties by doping, water sorption or thermal history¹⁶, it may be correlated to a space charge polarization.

Isotactic and syndiotactic poly(methyl methacrylate). The TSDC spectra of i- and s-PMMA are represented in Figure 2. In the low temperature region, they are characterized by a broad β peak similar to that observed in conventional atactic PMMA^{15,17}. In this last polymer, the comparison of the TSDC peak with the dielectric and mechanical β relaxation peaks has been investigated by several authors and the equivalence of the molecular mechanisms involved seems now well established^{15,17,18}. The corresponding transition is generally thought to arise from the hindered rotation of the ester side group around the C-C bond¹³. The fact that the tacticity has no significant influence on the peak position and that the amplitude is higher for the syndiotactic form are in accordance with the dielectric results of Mikhailov *et*

Figure 2 TSDC spectra of i- and s-PMMA ($E_p = 10 \text{ kV cm}^{-1}$)

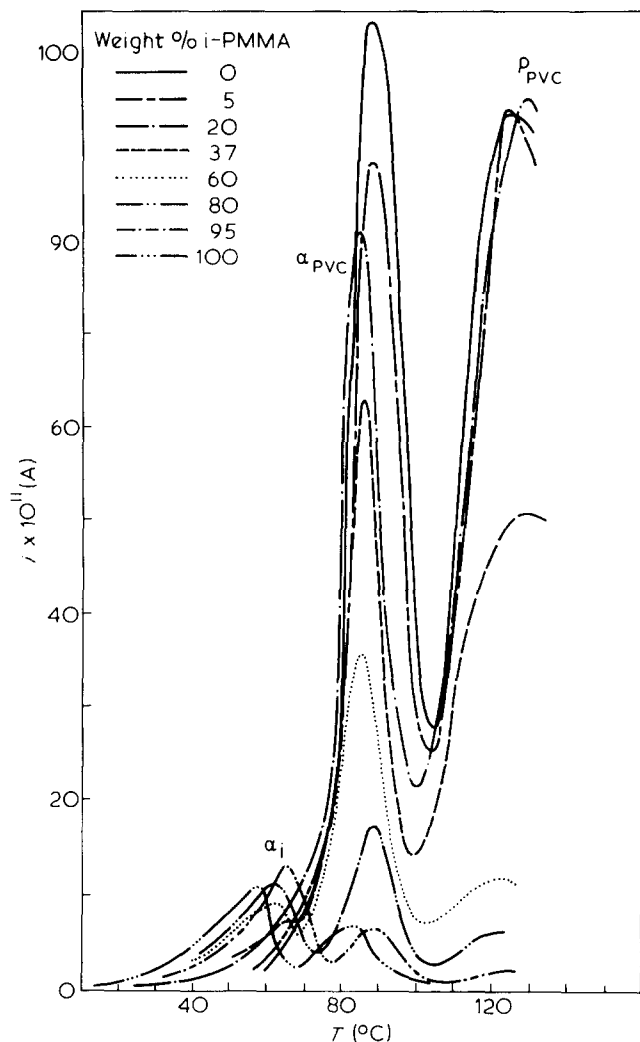


Figure 3 Comparison of TSDC spectra of i-PMMA, PVC and i-PMMA/PVC blends in the glass transition range ($E_p = 10 \text{ kV cm}^{-1}$)

al.¹⁹. It must be noted, however, that the activation energies determined from TSDC measurements by the initial rise method (9 and 12 kcal mol⁻¹ for i- and s-PMMA, respectively) are much lower than the dielectric values (respectively, 21 and 24 kcal mol⁻¹¹⁹). The origin of this discrepancy, also observed in a number of other polymers^{15,20}, is still obscure.

The α peaks are characterized by maximum temperatures close to the T_g 's determined from d.s.c. measurements and may thus be mainly ascribed to main-chain relaxations of the α type. From the large difference in magnitude observed for the two tactic polymers, it is clear that the chain backbone mobility is considerably enhanced by the isotactic configuration, which is in agreement with dielectric and mechanical results^{13,19}.

The ρ peak appearing at 85°C in i-PMMA shows properties typical of ionic processes¹⁶ and, like in PVC, probably corresponds to a space charge polarization. The occurrence of such a ρ peak at temperatures higher than the glass transition temperature seems to be a general phenomenon in polymers^{7,8,15} and the more likely explanation for its apparent absence in s-PMMA is that it is merged with the α peak.

Transition behaviour of i-PMMA/PVC blends

In agreement with the results of Schurer *et al.*⁶, two T_g 's close to that of the pure polymers were clearly found from

d.s.c. measurements over a large composition range (20–70 wt % i-PMMA), showing that two well-defined phases are present. This is also probably true in the extreme composition ranges because the observed single values of T_g remain practically composition-independent.

TSDC measurements in the α - ρ region. The TSDC spectra for blend compositions varying from 5 to 95 wt % i-PMMA are plotted in Figure 3, together with the spectra of the two pure homopolymers. They are generally composed of three peaks, which are labelled, in order of increasing temperatures, α_i (maximum temperature $T_M = 58^\circ\text{--}66^\circ\text{C}$), α_{PVC} ($T_M = 88^\circ\text{--}90^\circ\text{C}$) and ρ_{PVC} ($T_M = 123^\circ\text{--}131^\circ\text{C}$).

The α_i peak, which is only well individualized for blends containing more than 30 wt % i-PMMA, clearly corresponds to the glass transition of the PMMA phase. However, the evolution of its properties as a function of composition seems to indicate that another mechanism is also participating. As a matter of fact, its amplitude passes a maximum value before falling off to the value of pure i-PMMA (Figure 4), which cannot be explained on the basis of a simple additivity of properties, and its maximum temperature, although not very sensitive to the blend composition, is always significantly higher (5°–8°C) than that characterizing the pure polymer. Since this shifting is not observed by d.s.c., it must be related to a mechanism specific to the TSDC method, i.e. most probably interfacial polarization of the MWS type. This is confirmed by the fact that the activation energy is a function of the blend composition, varying from about 40 kcal mol⁻¹ for i-PMMA to 50 kcal mol⁻¹ for a 60/40 i-PMMA/PVC blend, which could not occur for an α relaxation taking place only inside a pure phase.

However, the behaviour of the α_{PVC} peak is close to that predicted for an intrinsic relaxation: its location, nearly independent of the blend composition, is close to that of pure PVC and its amplitude is a regularly, nearly linear function of the PVC concentration (Figure 5). This probably involves the charge carriers previously accumulated at the phase boundaries have been

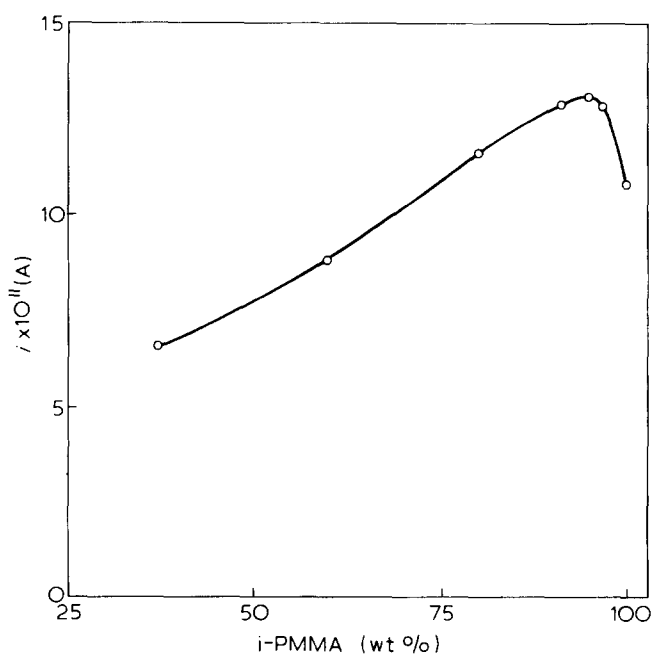


Figure 4 Effect of the blend composition on the maximum amplitude of the α_i TSDC peak for i-PMMA/PVC blends

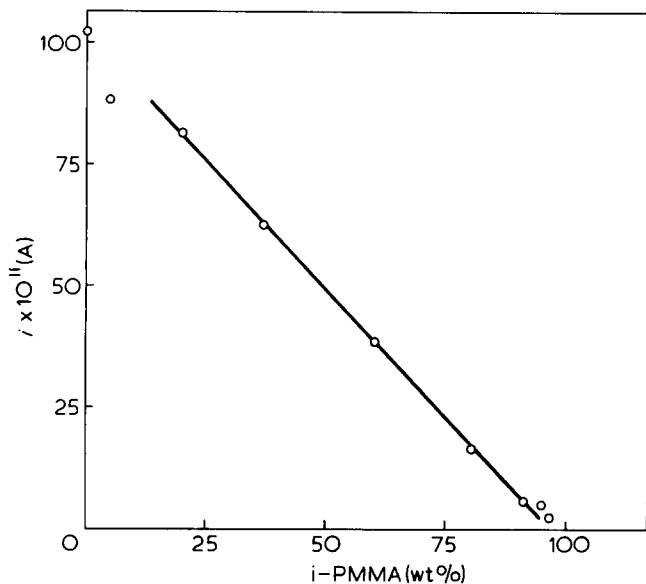


Figure 5 Effect of the blend composition on the maximum amplitude of the α_{PVC} TSDC peak for i-PMMA/PVC blends

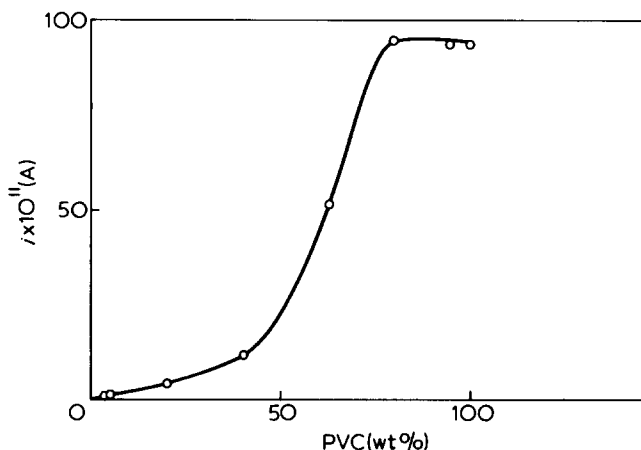


Figure 6 Effect of the blend composition on the maximum amplitude of the ρ_{PVC} TSDC peak for i-PMMA/PVC blends

detrapped by the molecular motions occurring during the glass transition of the i-PMMA phase and thus do not interfere with the true α_{PVC} relaxation.

The properties of the ρ_{PVC} peak are those expected from a mechanism involving a space charge polarization, i.e. migration of charge carriers over macroscopic distances in the more conductive PVC phase. As shown in Figure 6, its maximum amplitude is very weak up to about 40 wt % PVC (i.e. in a range of concentration corresponding to a dispersed PVC phase), after which it steadily increases up to 70 wt % (continuous PVC phase) and then remains fairly constant with composition. The truly ionic origin of this peak is confirmed by its complex field dependence (Figure 7): the peak amplitude reaches a maximum for a field of approximately 40 kV cm^{-1} (saturation effect) and then slowly decreases (probable interference with charge injection phenomena).

All the preceding experimental facts conclusively show that mixing i-PMMA and PVC has little influence on the intrinsic properties of each polymer in its glass transition range and involves the formation of an interfacial polarization at the phase boundaries. These conclusions are consistent with the existence of a well-defined two-phase structure over the whole composition range and

thus confirms that this polymer pair forms an incompatible system.

TSDC measurements in the β region. The TSDC spectra corresponding to the temperature range -150° to 0°C are represented in Figure 8. On account of the close superposition of the various β relaxations in this region (β_1 and β_2 relaxations of PVC and β relaxation of i-PMMA), the variation of amplitude of the resultant peaks as a function of blend composition is particularly complex. However, the blend composition does not markedly affect the maximal temperatures (the small shifts observed could be interpreted by the absolute and relative variations in the amplitudes of the overlapping peaks) nor the activation energies of the β (i-PMMA) and the β_1 (PVC) processes determined by the initial rise method after classical cleaning procedures (about $9\text{--}10 \text{ kcal mol}^{-1}$).

Due to the local nature of the relaxations involved in this temperature range, these results can be hardly interpreted in terms of compatibility. They only suggest that the characteristic parameters of the β processes are not much influenced by the blend composition, i.e. that the dipolar environment in the pure polymer and in the blends are locally not much different.

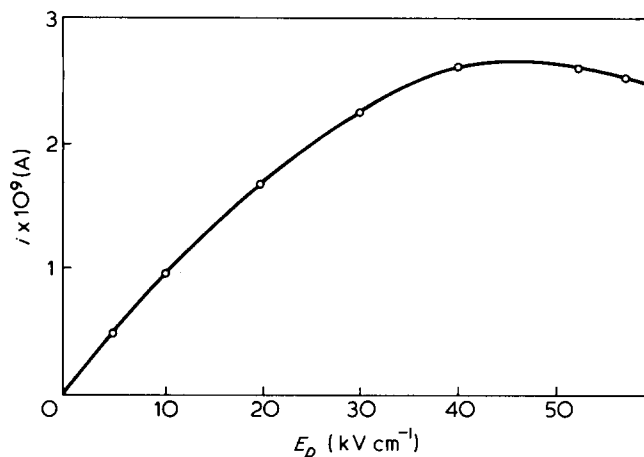


Figure 7 Field dependence of the maximum magnitude of the ρ_{PVC} peak for a 20/80 wt % i-PMMA/PVC blend

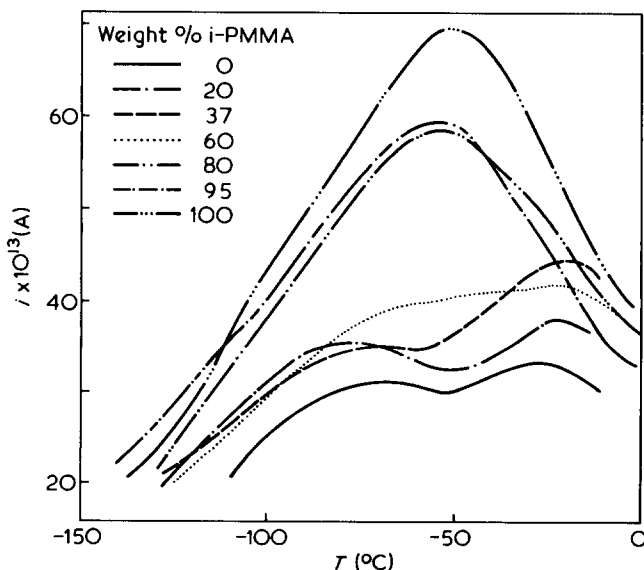


Figure 8 Comparison of TSDC spectra of i-PMMA, PVC and i-PMMA/PVC blends in the β relaxation region ($E_\rho = 10 \text{ kV cm}^{-1}$)

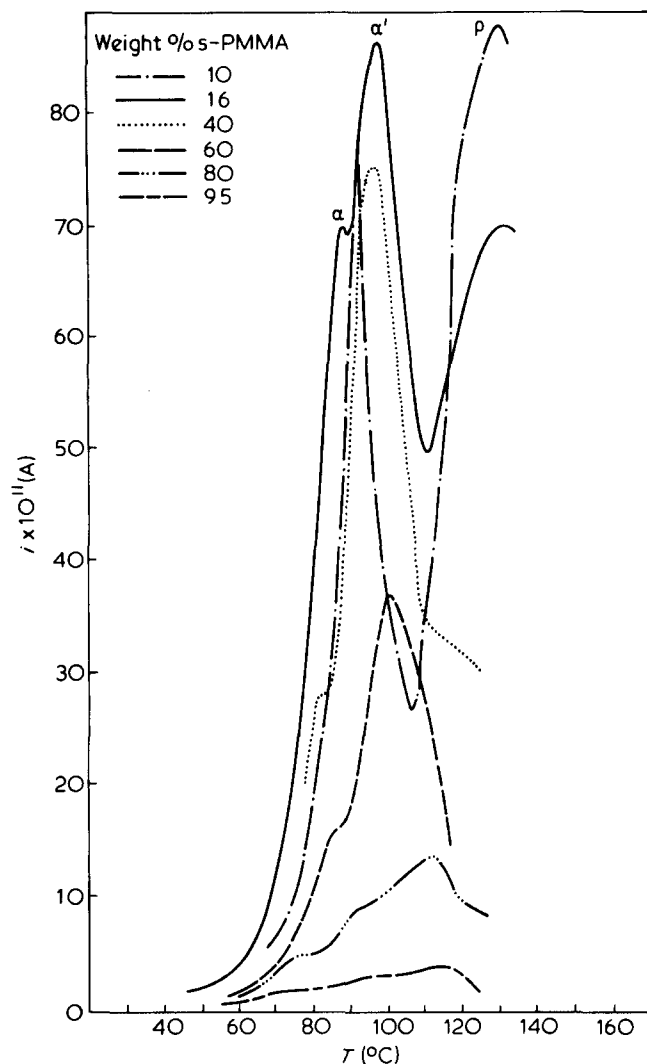


Figure 9 TSDC spectra of s-PMMA/PVC blends in the glass transition range ($E_p = 10 \text{ kV cm}^{-1}$)

Transition behaviour of s-PMMA/PVC blends

From d.s.c. measurements, a single T_g is found up to 60 wt % s-PMMA but, contrary to the results of Schurer *et al.*⁶, this value is only weakly dependent on the blend composition and remains close to the T_g of PVC, which does not allow us to formally conclude that s-PMMA and PVC form a compatible system in this range. At higher s-PMMA contents, a second T_g , also nearly composition-independent, appears near 105°C, i.e. the value of pure s-PMMA, unambiguously showing the existence of phase separation and thus incompatibility.

TSDC measurements in the α - ρ region. In Figure 9 some spectra obtained for blend compositions varying from 10 to 95 wt % s-PMMA are represented. According to the range of composition investigated, they are composed of two peaks α and ρ (up to 10 wt % s-PMMA) or three peaks α , α' and ρ (at higher s-PMMA concentrations). The most significant feature here is the progressive individualization of the α' peak for increasing s-PMMA concentrations (for the sake of clarity, the corresponding spectra are shown on a larger temperature scale in Figure 10). As a matter of fact, this peak cannot be ascribed to any transitional or ionic behaviour of s-PMMA since it is obvious from the large difference in amplitude characterizing the TSDC peaks of the constituent polymers (compare Figures 1 and 2) that most of the

currents observed in the blends result either from motions involving the C-Cl units of PVC or from charge carrier migration leading to space charge or MWS polarization. In addition, it can be seen (Figure 10) that passing from 10 to 16 wt % s-PMMA (i.e. decreasing the number of active C-Cl dipolar units) results in a marked increase of total polarization in the glass transition region ($\alpha + \alpha'$ peaks) and in a simultaneous decrease of the space charge polarization (ρ peak). This phenomenon is a particularly clear indication of the interfacial nature of the α' peak (MWS polarization) and thus shows that phase separation occurs to some extent for blend compositions higher than 10 wt % s-PMMA.

The variation of amplitude of this α' peak as a function of blend composition is complex (Figure 11), as may be expected from the fact that a MWS polarization is governed by competitive phenomena, i.e. successive increase and decrease of active interfaces when passing from a continuous PVC phase to a continuous s-PMMA phase, on one hand, and progressive decrease of the

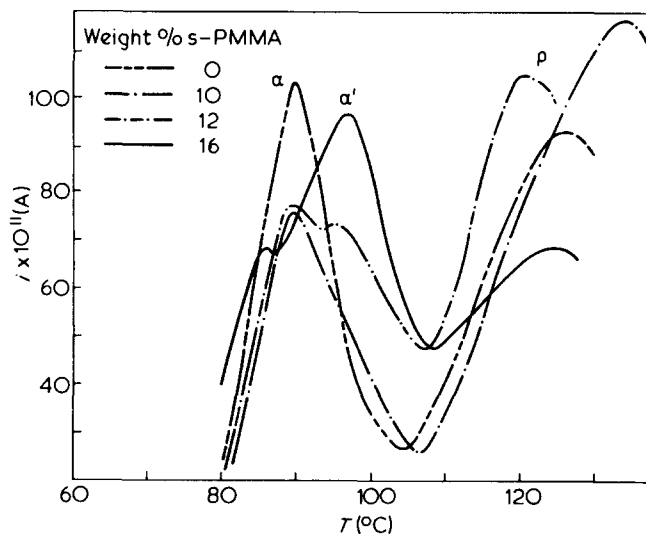


Figure 10 Comparison of TSDC spectra of PVC and s-PMMA/PVC blends (10–16 wt % s-PMMA) in the glass transition range ($E_p = 10 \text{ kV cm}^{-1}$)

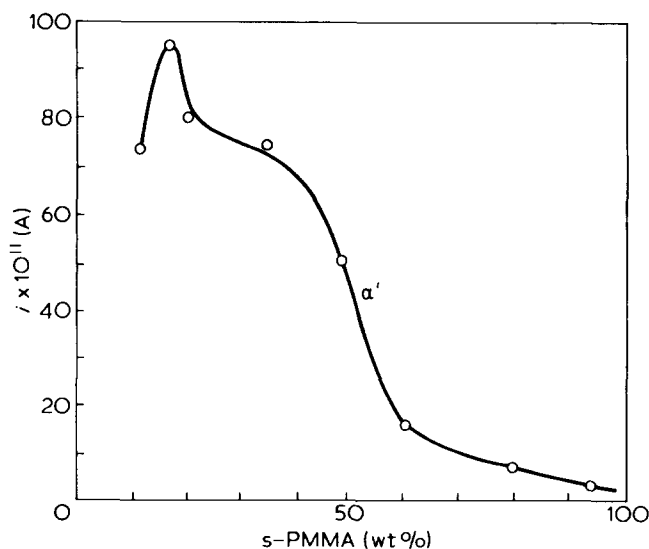


Figure 11 Effect of the blend composition on the maximum amplitude of the α' TSDC peak for s-PMMA/PVC blends

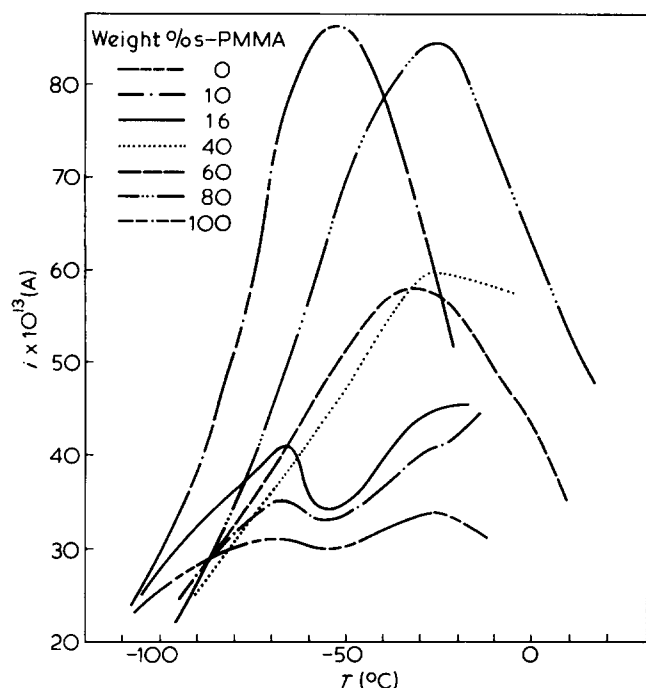


Figure 12 Comparison of TSDC spectra of s-PMMA, PVC and s-PMMA/PVC blends in the β relaxation region ($E_p = 10 \text{ kV cm}^{-1}$)

number of available ionic carriers for decreasing concentrations in PVC, on the other.

The evolution of the properties of the α peak (i.e. the TSDC peak corresponding to the glass transition as observed in d.s.c. experiments) is difficult to quantitatively follow since it only appears as a small shoulder of the α' peak in the greatest part of the composition range. It is apparent, however, that its position is only weakly dependent on the blend composition, which is in agreement with the d.s.c. results and confirms the existence of two phases.

TSDC measurements in the β -region. The low temperature TSDC spectra obtained in some s-PMMA/PVC blends are shown in Figure 12. For the same reasons as reported for i-PMMA/PVC blends (close overlapping of the different relaxations of the β type in this region), they are complex and most of the variations observed are difficult to explain on the basis of compatibility concepts. Their detailed analysis will be attempted in a future piece of work.

CONCLUSIONS

From our TSDC measurements carried out on a variety of blend compositions, there is considerable evidence that i-PMMA and PVC form an incompatible system over the whole concentration range and that, in s-PMMA/PVC blends, the compatibility range is limited to 10 wt % s-PMMA. These conclusions are mainly based on the evolution, in the glass transition region, of behavioural characteristics such as absence of significant shifting of the T_g peaks, existence of an interfacial component (MWS polarization) in the vicinity of the first T_g of the blend and variation of peak amplitudes as a function of blend composition. Clearly, if all these properties can be only explained by phase separation, they do not necessarily disprove the existence of a certain amount of molecular mixing at the interfacial level (diffuse interface at the phase boundaries).

As far as the i-PMMA/PVC pair is concerned, our results confirm the d.s.c. and mechanical data of Schurer *et al.*⁶ whereas, for the s-PMMA/PVC system, the maximum compatibility range found is much smaller than that obtained by these authors (60 wt % s-PMMA) and approximates better to the 5 wt % value observed by electron microscopy by Razinskaya *et al.*²¹ for blends of PVC and atactic PMMA (which is well known to be characterized by a fairly high degree (60%) of syndiotactic character)¹³. As already noted by Schurer *et al.*⁶, such discrepancies might possibly be explained by differences in molecular weight of the starting polymers or structure of the stabilizer used. In fact, the type of method adopted to find out compatibility and the temperature range in which the investigations are made also play a prevailing role and there are several examples in the literature of controversy around the degree of miscibility of a given polymer pair according to the d.s.c., optical, mechanical, dielectric or other measurements which are carried out⁶. It thus seems that combining these methods with a detailed study of the phase morphology of the blends is the only way to unambiguously resolve the problem of the applicability range of each of them. This will be attempted in a further paper.

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