

THERMAL AND FT-IR ANALYSIS OF POLYMER BLENDS BASED ON FUNCTIONALIZED POLYOLEFINS

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ABSTRACT

Blends of poly(vinylchloride) and polystyrene with ethylene-propylene copolymers containing 4 and 10 wt% of ester groups in the side chains (introduced by functionalization with peroxides and diethylmaleate) were examined by DSC and FT-IR spectroscopy. The results point to the occurrence of miscibility phenomena between the polymer components depending on the functionalization degree of the copolymer, the thermal history and the preparation conditions.

INTRODUCTION

Study of the structure-properties relationships of polymer blends is attracting a great deal of interest in academic and industrial circles. Owing to the poor miscibility of their components, polymer blends usually form heterogeneous systems whose ultimate properties can be greatly influenced by phase separation phenomena. However, polymer compatibility in blends can be increased through the introduction of polar groups on the macromolecular backbone to such an extent as to leave the properties of the original materials substantially unchanged [1, 2].

In the case of polyolefins, it has been reported that polypropylene or ethylene-propylene copolymers functionalized with ester groups derived from diethylmaleate (DEM), when mixed with poly(vinylchloride) (PVC), display a

shift of the carbonyl stretching band towards lower frequencies. This has been interpreted as evidence of intermolecular interaction between the two polymers [3].

The presence of such phenomena can have considerable effects on the glass transition behaviour of the system, as shown for several compatible blends [4]. Cases of limited miscibility may result in two separate transitions which fall between those of pure components, indicating the presence of one component-rich phase.

In this context, thermal and spectroscopic measurements were performed on blends of PVC or atactic polystyrene (PS) mixed with ethylene-propylene copolymers functionalized with diethylmaleate (FEPR) in order to show the effects of the degree of functionalization, the composition and the thermal history on molecular interaction between the components and the degree of dispersion of the phases present.

EXPERIMENTAL

The ethylene-propylene copolymer (Montepolimeri Ferrara, 76 mol % of propylene) was functionalized with DEM in the presence of dicumylperoxide at 473 K, according to a previous procedure [2]. Two degrees of functionalization, i.e. 4% and 10% grafted DEM units by weight (FEPR 4 and FEPR 10), were examined. Commercial PVC and PS samples were employed without further purification.

PVC/FEPR and PS/FEPR blends, with FEPR contents ranging from 0 to 50 wt%, were prepared by casting from 3% w/v THF solutions onto KBr windows. The solvent was removed by vacuum desiccation at 363 K for 24 hours. Mechanical mixtures of PVC and FEPR were prepared by vigorously shaking fixed amounts of polymer powders in a homogenizer at 93 K.

The thermal behaviour of blends was analyzed with a Perkin-Elmer DSC-2 apparatus operating under nitrogen flow. Film specimens (9+11 mg) were first scanned into DSC at a heating rate of 10 K min⁻¹, from 310 to 453 K (run I), held at 453 K for 5 minutes, cooled to the starting temperature at a nominal rate of 320 K min⁻¹ and again heated through the glass transition region (run II). Glass transition temperatures (T_g) of PVC or of PS in the blends were determined both at the onset and the midpoint of the transition, using a range of 8.5 mJ s⁻¹ full scale. DSC temperatures were calibrated with standard materials (azobenzene, benzyl, indium). The repeatability of the T_g measurement was checked on several samples with the same composition and was within ± 2 K.

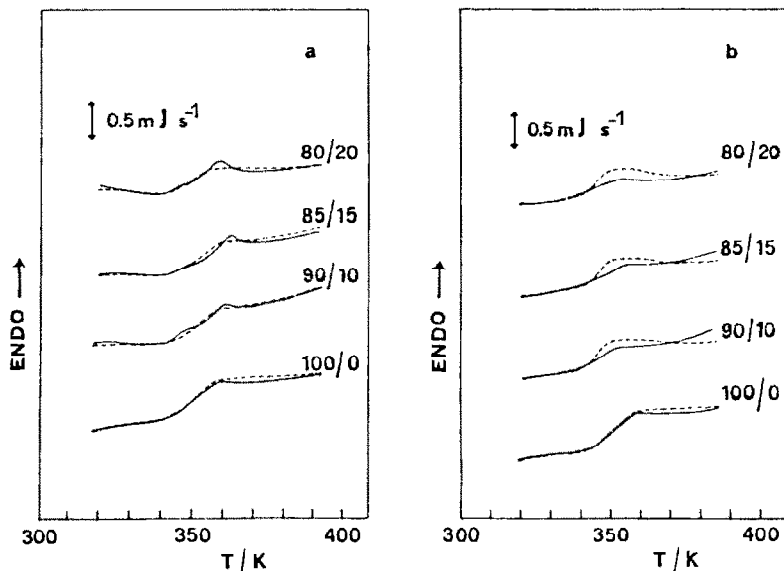


Fig. 1. DSC thermograms of PVC/FEPR 4 (a) and PVC/FEPR 10 (b) blends at various compositions (w/w%). (—): run I; (---): run II (heating rate: 10 K min⁻¹).

Infrared spectra were obtained with a Perkin-Elmer 1750 FT-IR spectrometer. Each spectrum was recorded at a resolution of 2 cm⁻¹ for a total of 20 scans.

RESULTS AND DISCUSSION

DSC thermograms of PVC/FEPR 4 and PVC/FEPR 10 blends from solution are reported in Figs. 1a and 1b respectively. In Table 1 the values of the glass transition temperatures ($T_{g,onset}$, T_g) are collected for the various examined blends.

The T_g of the original PVC samples (about 357 K) is largely in agreement with the literature data [5], while for the cast polymer a value of 350 K was obtained. It has been inferred [6,7] that the T_g of PVC may be affected by the presence of residual solvent and by annealing processes. However, PVC films from solution were annealed at various temperatures above T_g for different times and then analyzed by DSC. In all cases, a sharp glass transition was recorded at about 350 K without endothermic peaks at lower temperatures, as a consequence of relaxation phenomena after cooling [7].

On run I, blends of PVC with FEPR 4 showed a glass transition at temperatu-

TABLE 1

Values of the glass transition temperatures (K), $T_{g,onset}$ and T_g , measured by DSC for PVC/FEPR and PS/FEPR at various compositions.

Blend composition (w/w%)	$T_{g,onset}$ run I	T_g run I	$T_{g,onset}$ run II	T_g run II
PVC/FEPR 4				
100/0	342	350	345	351
90/10	340	344 ^a	344	351
85/15	340	344 ^a	345	352
80/20	339	342 ^a	343	350
PVC/FEPR 10				
100/0	342	350	345	351
90/10	337	344	341	345
85/15	338	346	342	345
80/20	334	343	340	344
PS/FEPR 4				
100/0	369	373	371	374
90/10	366	371	368	372
80/20	335	338	347	353
65/35	332	336	340	345
55/45	338	341	349	355

^a Values of the first DSC transition (see text).

res lower than the T_g of PVC, followed by a second transition around 350 K. On run II, only one glass transition was observed for all compositions at about the same T_g as pure PVC.

The T_g values of these blends are plotted as a function of FEPR 4 content in Fig. 2. Usually no variations in T_g values on run II were noted on varying the cooling conditions of the blends in DSC.

On both runs, blends of PVC with FEPR 10 showed a glass transition temperature lower than that of pure PVC (Fig. 3). The drop observed in the case of the PVC/FEPR 10 80/20 blend was about 7 K. A similar shift has also been reported for blends of PVC with an ethylene-vinyl acetate copolymer (EVA) in the composition range 0+25 wt% of EVA [8].

Mechanical mixtures of PVC and FEPR 10 were also examined to compare

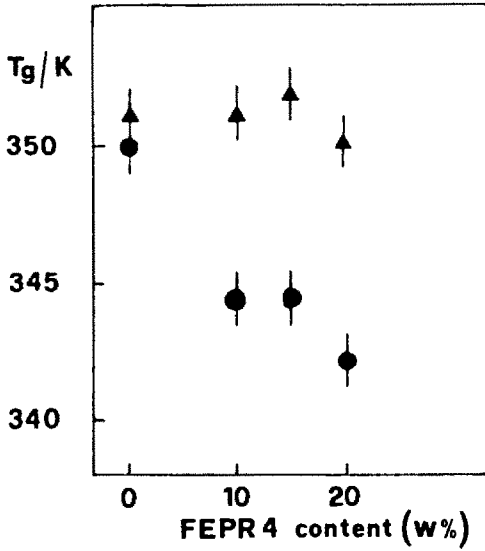


Fig. 2. Glass transition temperature, T_g , of PVC/FEPR 4 blends as a function of FEPR 4 content: (●) run I; (▲) run II.

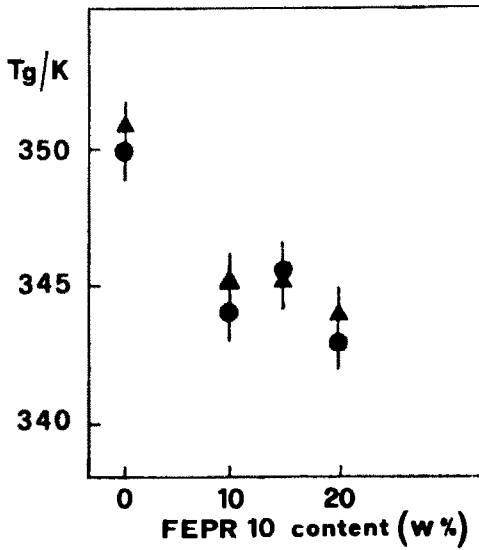


Fig. 3. Glass transition temperature, T_g , of PVC/FEPR 10 blends as a function of FEPR 10 content: (●) run I; (▲) run II.

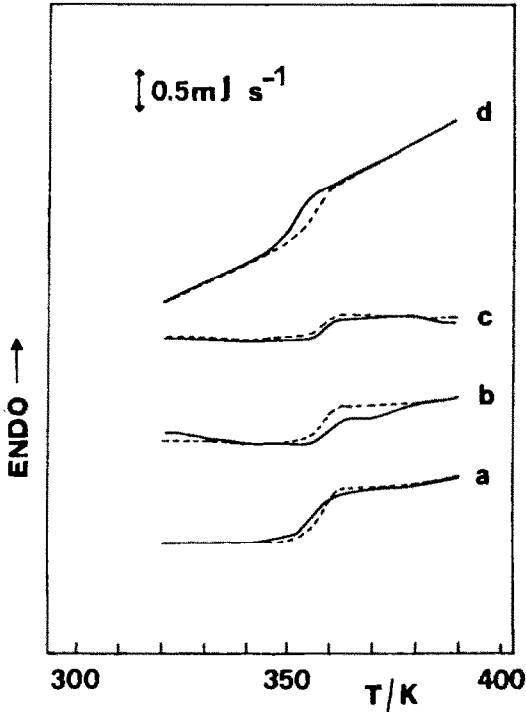


Fig. 4. DSC thermograms of PVC powder (a); and PVC/FEPR 10 85/15 mechanical mixture as prepared (b); after annealing at 363 K for 1 h (c); and after melt pressing at 423 K. (—) : run I; (---) : run II (heating rate: 10 K min⁻¹).

their thermal behaviour with that of the blends obtained from solution. Their glass transition behaviour appears to be independent of the composition and practically coincident with that of pure PVC powder. DSC thermograms of a sample containing 15 wt% of FEPR 10 are shown in Fig. 4. Nevertheless, it must be pointed out that a film of the same mixture (obtained by melt pressing at 423 K) displayed a T_g about 6 K lower than that of pure PVC (Fig. 4d).

The thermal behaviour of PS-with-FEPR 4 blends proved to be markedly affected by the composition. On increasing the copolymer concentration, a larger variation of T_g in the blends was observed with respect to that of PVC/FEPR systems. Shown in Fig. 5 are DSC traces of PS/FEPR 4 blends at various compositions. The values of T_g for these blends are reported in Table 1. For samples with concentrations of FEPR 4 higher than 10 wt%, a decrease of T_g of about 30 K with respect to that of pure PS was found on run I. It is worth noting that the T_g values of these blends on run II were higher than those recorded on run I. Such a trend may be related to conformational rearrange-

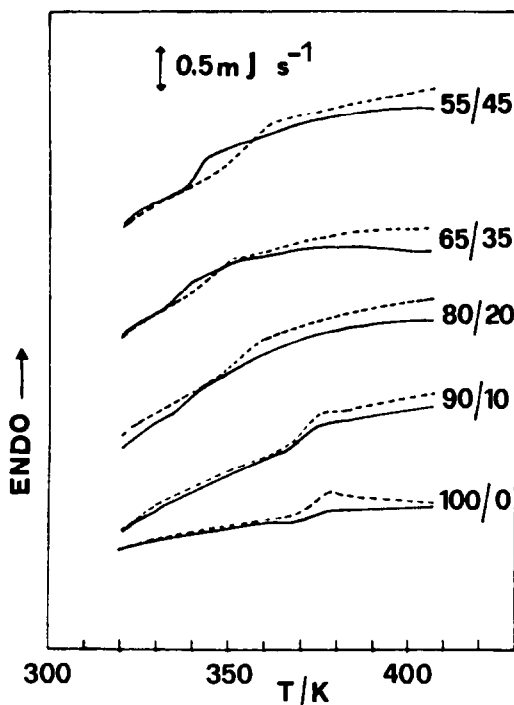


Fig. 5. DSC thermograms of PS/FEPR 4 blends at various compositions (w/w%). (—): run I; (---): run II. (heating rate: 10 K min⁻¹).

ments of the polymer chains as a result of the thermal treatments. Further investigations are now being performed on the glass transition behaviour of PS/FEPR blends as a function of thermal treatments.

The existence of molecular interactions between the polymer components in the blends from THF solutions has been demonstrated by FT-IR analysis.

Fig. 6a shows infrared spectra in the carbonyl stretching region of pure FEPR 4 and PVC/FEPR 4 blends containing 10 and 15 wt % of FEPR 4. Fig 6b reports the correspondent spectra relative to pure FEPR 10 and PVC/FEPR 10 blends. The shift towards lower frequencies and the larger width at half height in the case of PVC/FEPR 10 blends with respect to PVC/FEPR 4 ones may be attributed to the larger content of ester groups available for the interaction, involving mainly the carbonyl groups of the functionalized polymer and the methine hydrogen of PVC; this is in agreement with previous investigations on the poly(ϵ -caprolactone)/PVC system [9]. These results, which evidence major intermolecular interactions in the case of PVC/FEPR 10 blends, may explain the different trend (run II) of Figs. 2 and 3 if one hypothesizes a

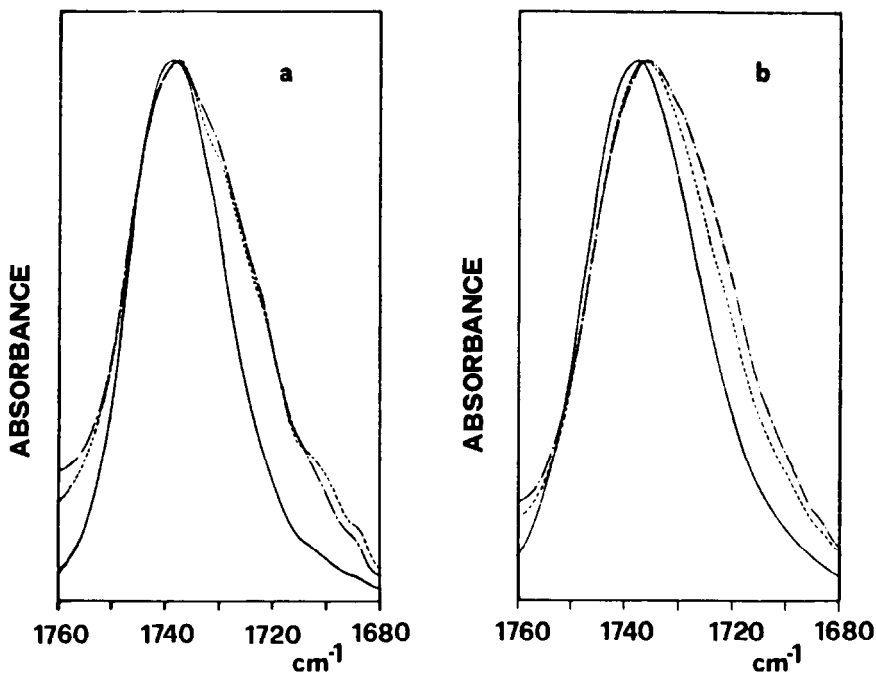


Fig. 6. IR spectra of the carbonyl stretching band of PVC/FEPR blends.

(a): (—) pure FEPR 4; (---) PVC/FEPR 4 85/15; (- · - · -) PVC/FEPR 4 90/10.

(b): (—) pure PVC/FEPR 10; (---) PVC/FEPR 10 85/15; (- · - · -) PVC/FEPR 10 90/10.

demixing of the PVC/FEPR 4 blend during heating, attributable to a minor number of interchain interaction points as a consequence of the lower degree of functionalization.

An analogous, though less evident, behaviour was observed in the PS/FEPR 4 spectra. The kind of intermolecular interactions in this case remains to be determined.

CONCLUDING REMARKS

The DSC analysis of PVC/FEPR and PS/FEPR blends indicates that their glass transition behaviour depends on the degree of functionalization of the polymer component, the thermal history and the preparation conditions. A decrease in the T_g of PVC or PS occurred consistently in blend samples from solution (run I), the greatest effect being noticed in the case of PS/FEPR 4 blends. IR data support the existence of interactions between the polymer chains. These results can be accounted for by the occurrence of partial

miscibility between the polymer components, as reported for some polymer blends [4].

The presence of a complex glass transition (run I) in PVC/FEPR 4 blends can be ascribed to the existence of different phases or domains in which the two polymers may be distributed, which is in agreement with FT-IR-microscope analysis [10]. On run II, no variations were observed in the T_g of PVC/FEPR 4 blends with respect to pure PVC, indicating that segregation between the polymer components probably occurs during heating, as observed in the case of PVC/EVA systems [11]. To account for this behaviour, it must be pointed out that the lower concentration of functional groups along the FEPR chains decreases the interactions with PVC chains, both for thermodynamic and structural reasons.

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