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Effect of sepiolite on glass transition temperature and melting behaviour of semicrystalline polymer blends

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SUMMARY

Thermal analysis of blends poly(vinylidene fluoride) (PVF_2) with poly(methyl methacrylate) (PMMA) or polystyrene (PS) filled with sepiolite was carried out to examine the effects of the filler on properties such as melting behaviour and glass transition temperature. For the compatible PVF_2/PMMA system, the presence of the filler did not cause any substantial changes in the thermal behaviour of the blend. In the non-compatible PVF_2/PS system, some compatibilizaton is achieved in the blend, indicated by PVF_2 melting point depression as well as by a shift of the glass transition of the homopolymers in the blend.

INTRODUCTION

Among the different methods proposed to compatibilize non-compatible polymeric systems (1,2) one is of special interest: i.e. compatibilization by means of fillers, a method likely to have originated from the preferential adsorption of one of the polymeric components on the surface of the solid. The ocurrence of this phenomenon depends on several factors, such as the filler pore volume and distribution, wettability, and particularly any specific polymer-filler interaction. There has been reports of non-compatible systems made compatible by means of a filler (3,4) and others which do not behave in this way (5).

Among the criteria most commonly applied in compatibility studies of polymeric blends, use has been made of any variation in the glass transition temperature of the blend, as well as in the melting point when one of the components is crystallizable. A compatible semicrystalline system would theoretically yield a single glass transition, intermediate between those of the pure components, and a lower melting point than that of the pure semicrystalline component. From this depression, it is possible to calculate thermodynamic polymer-polymer interaction parameters χ_{23}. In contrast, an incompatible system would present two glass transitions, each of which would correspond separately to one of the components, as well as an unaltered melting point, independent of the composition of the blend (2). In this work the changes in the melting temperature are studied, as well as those affecting glass transition, resulting from the incorporation of sepiolite in two polymeric systems: One, was poly(vinylidene fluoride)/poly(methyl methacrylate) (PVF_2/PMMA), widely described as a compatible system (6-8); an incompatible system of PVF_2 with polystyrene (PS) was also examined. The technique used was differential scanning calorimetry. The results were assessed according to general models which describe the behaviour of compatible polymeric blends, such as the Fox (9) and Gordon-Taylor (10) models.

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EXPERIMENTAL

Materials

PVF_2 was Kynar 760 (Penwalt Corporation); PMMA was supplied by Repsol S.A.; PS was a BASF product (PS 143E) and the sepiolite (Pansil) was supplied by Tolsa S.A. in a micronised form. Sepiolite is a hydrated magnesium silicate; its characteristics have been described (11).

Blending

Blends were prepared in a Brabender Plasticorder using a thermoplastic mixing chamber type W60 preheated to 473 K. Rotor speed was set at 60 rpm; 10 minutes of mixing were enough to generate a steady-state torque response, indicating uniform dispersion of the components.

Method

Thermal behaviour was followed using a Mettler TA3000 differential scanning calorimeter. The samples were melted at 493 K for 10 minutes and then rapidly quenched using liquid N_2. The thermograms were then recorded at a heating rate of 10 K/min. Phase morphologies were followed by using optical and scanning electron microscopy. Thin films (5-10 μm) were observed in a transmission polarizing microscope (Jenaval), provided with a Mettler FP2 hot stage. Surfaces obtained from samples broken under uniaxial tension were studied using a JEOL (JSM-T330A) scanning electron microscope.

RESULTS

Melting behaviour

Table 1 shows the melting points and the crystallinities for PVF_2 in PVF_2/PMMA blends for filler-free systems as well as for blends containing sepiolite at 5, 10 and 20% by weight. It can be inmediately deduced that sepiolite does not significantly modify the melting point of PVF_2, although, for the highest filler level, a slight decrease of melting point can be observed. Filled samples showed higher crystallinities than the filler-free polymer. The thermograms (Fig 1) have shoulders, more evident for the filled samples. This feature also observed in polypropylene-sepiolite composites (12), is explained in terms of the morphological changes at the polymer-filler interface as a result of the generation of mesophases. In the case of blends, either filled or not, a depression of the melting point is observed, as expected because of the compatible nature of this system. The sepiolite affects the PVF_2 melting point in the blend, but the magnitude of the effect cannot be related to the filler concentration.

Table 1.- Melting point (K) and crystallinity measured for unfilled and sepiolite filled PVF_2/PMMA blends.

Blend composition	Sepiolite wt%							
PVF_2/PMMA	0		5		10		20	
wt%	T_m	x_c	T_m	x_c	T_m	x_c	T_m	x_c
100/0	444.9	47.5	444.1	50.3	444.3	50.9	442.6	49.9
90/10	444.1	44.8	442.6	46.3	442.1	45.2	442.6	44.3
70/30	438.6	46.4	438.6	43.1	438.0	48.5	438.0	46.1
50/50	431.1	19.9	430.8	19.9	429.8	18.6	431.2	13.8

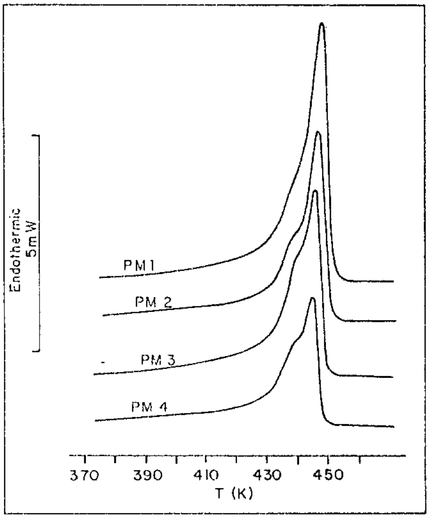

Figure 1.- DSC melting thermograms of sepiolite-filled PVF_2: PM1, unfilled; PM2, 5 wt% sepiolite; PM3, 10 wt% sepiolite and PM4, 20 wt% sepiolite.

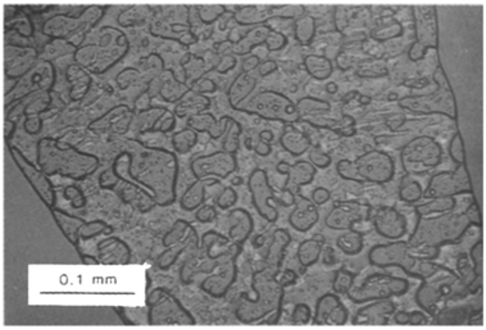

Figure 2.- Optical micrograph of a thin film of PVF_2/PS 50/50 blend at 473 K.

The system PVF_2/PS is non-compatible, as can be seen in Fig. 2 where the phases of the system can be clearly distinguishable, when observed by means of ligh transmission microscopy. The melting temperatute and crystallinity level for the various blends under study are shown in Table 2. It can be observed that PVF_2 crystallizes in blends of all compositions as distinct from the PVF_2/PMMA system where crystallization is inhibited for blends containing PMMA$>$50% by weight. Fig 3 show the PVF_2 melting point as a function of PS concentration in the blend, for filled as well as for unfilled systems, showing that for filler-free samples the melting point of the PVF_2 in the blend corresponds to that of the homopolymer, independent of the composition of the blend; whereas in the filled samples, the melting point is depressed, the effect being greater for higher sepiolite concentrations, especially for blends with PS concentration $>$ 50% by weight. This effect indicative of compatibilization of the system, as it does not occur for clearly non-compatible unfilled systems.

$T_{g's}$ analysis

The results obtained from glass transition temperature analysis of the various systems, obtained from the shift of the baseline in the DSC thermograms are summarized in Tables 3 and 4. For the PVF_2/PMMA system, it was observed that for samples containing PMMA at concentration$\geqslant$50% there is one single transition (as shown in Table 3), whereas this transition characteristic of the homogeneous system was not detected for blends having PMMA concentrations below 50%, due to the resolution capacity of the technique employed. The T_g data for $\Phi_{PMMA} \geqslant 50\%$ fit the Gordon-Taylor equation (Eq.1) proposed for compatible blends and copolymers (10), in good agreement with reported results for this system (13):

$$(T_g^{PMMA} - T_g^{b})(1 - \Phi_{PVF2}) + k(T_g^{PVF2} - T_g^{b})\Phi_{PVF2} = 0$$

where k is $\alpha_{PVF2}/\alpha_{PMMA}$, α's being the difference between the thermal expansion coefficients below and above $T_{g's}$ of the homopolymers, and T_g^b is the glass transition temperature of the homogeneous

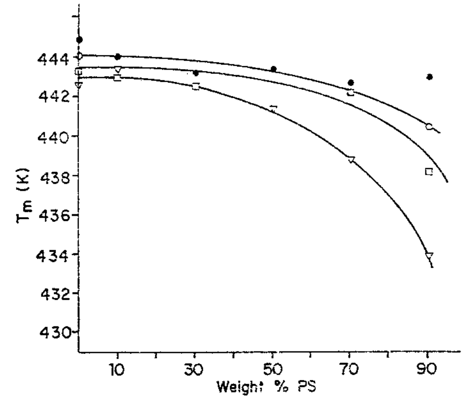

Figure 3.- Dependence of melting point T_m of PVF_2 crystals on weight percent of PS for filled and unfilled blends: ● unfilled, ○ 5 wt% sepiolite, □ 10 wt% sepiolite and ▽ 20 wt% sepiolite.

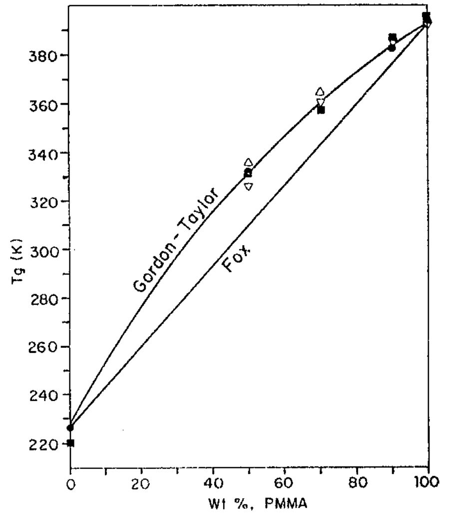

Figure 4.- Dependence of glass transition temperature of PVF_2/PMMA blends on the PMMA content: ● unfilled system, ▼ 5 wt% sepiolite, ■ 10 wt% sepiolite and △ 20 wt% sepiolite.

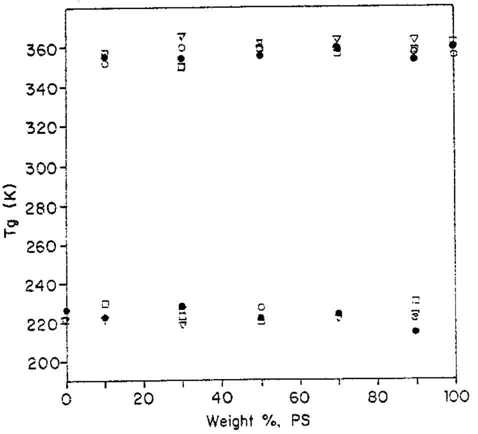

Figure 5.- Effect of blend composition on the T_g of PVF_2 and PS in the PVF_2/PS blends: ● unfilled system, ○ 5 wt% sepiolite, □ 10 wt% sepiolite and ▽ 20 wt% sepiolite.

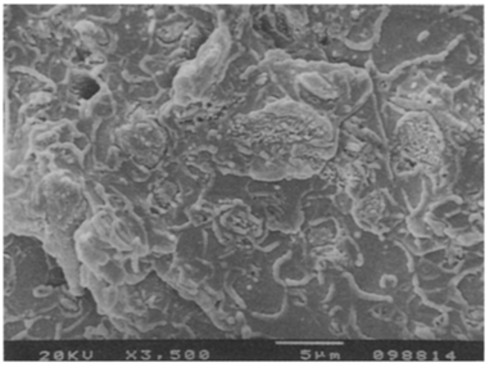

Figure 6.- SEM micrograph of the fractured surface for the PVF_2/Ps system (50/50) containing 20 wt% of sepiolite.

system (Fig. 4). Plots of $T_g^{\ b}$ vs $(T_g^{\ PMMA} - T_g^{\ b})\ (1 - \Phi_{PVF2})$ are linear, giving k = 0.57 from the slope and 221 K for $T_g^{\ PVF2}$, in reasonable agreement with the experimental value of 227 K.

For the PVF_2/PS system, the behaviour conforms in general terms to that expected for a non-compatible system, i.e. there are two independent transitions, easily attributable to the two components of the blend (Fig. 5), transitions which are slightly displaced (5-8 degrees) relative to the

Table 2.- Melting point (K) and crystallinity measured for unfilled and sepiolite filled PVF_2/PS blends.

Blend composition	Sepiolite wt%							
PVF_2/PS	0		5		10		20	
wt%	T_m	x_c	T_m	x_c	T_m	x_c	T_m	x_c
100/0	444.9	47.5	444.1	50.3	444.3	50.9	442.6	49.9
90/10	444.0	48.5	444.0	48.8	443.0	50.7	443.4	44.7
70/30	443.2	45.5	442.6	48.8	442.5	44.1	442.6	42.8
50/50	443.3	45.1	443.5	50.2	443.4	53.0	441.4	41.1
30/70	442.7	49.4	442.1	46.6	442.2	41.3	438.8	44.5
10/90	443.0	47.3	440.5	48.9	438.2	54.6	433.9	36.7

Table 3.- Glass transition temperature (T_g) (K) of unfilled and sepiolite filled PVF_2/PMMA blends.

Blend composition	T_g(K)			
PVF_2/PMMA	Sepiolite wt%			
wt%	0	5	10	20
100/0	227	222	222	222
50/50	333	326	331	336
30/70	358	361	358	365
10/90	383	385	386	386
0/100	393	392	396	395

unblended components, when the polymer ratio or the filler concentration in the blend is changed. This fact, cannot be taken as conclusive evidence of total compatibilization of the blend, but it shows partial compatibility.

Table 4.- Glass transition temperature (T_g) (K) of PVF_2 and PS for the different unfilled and sepiolite filled PVF_2/PS blends.

Blend composition	Sepiolite wt%							
PVF_2/PS	0		5		10		20	
wt%	$T_{g,1}$	$T_{g,2}$	$T_{g,1}$	$T_{g,2}$	$T_{g,1}$	$T_{g,2}$	$T_{g,1}$	$T_{g,2}$
100/0	227	-	222	-	222	-	222	-
90/10	223	355	223	353	230	357	222	-
70/30	228	354	226	360	223	351	219	366
50/50	222	356	227	358	221	359	222	362
30/70	224	359	222	360	223	357	221	364
10/90	215	354	222	357	230	359	223	363
0/100	-	360	-	356	-	362	-	361

Subscripts 1 and two refers to PVF_2 and PS respectively

A a general conclusion, it can be stated that the presence of sepiolite in the concentration range studied (up to 20% by weight) does not substantially modify either the compatibility or the thermal behaviour of the PVF_2/PMMA system, whereas the results obtained for the PVF_2/PS system suggest partial compatibilization of the system under certain conditions (high filler contents), as demonstrated by the SEM micrographs obtained (Fig 6).

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