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Dynamic mechanical properties of binary and ternary blends based on PVDF

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Summary

A universally accepted criterion when assessing blend compatibility is the existence of a single glass transition temperature, which changes as a function of blend composition. Differential scanning calorimetry and dynamic mechanical strain spectra are powerful tools in the study of polymer relaxation in the glass transition zone. In this research both techniques are employed to determine the glass transition temperatures of a series of polymer blends based on polyvinylidene fluoride. In the light of the data obtained further thought is given to the discrepancies between the results obtained with one and the other method, as well as to the compatibility of the experimental blends.

Introduction

Ever since Kwei (1) in 1969 discovered polyvinylidene fluoride (PVDF) and its excellent pyro-piezoelectric properties, the interest aroused by this polymer has been steadily growing. At present and due to the fact that the preparation of polymeric blends has proved to be the alternative to chemical synthesis, whenever new and advanced polymeric materials become available (2,3), efforts are made in pursuance of pyro-piezoelectric materials by blending polyvinylidene fluoride with other polymers (4-6). In this work polymer blends with a high polyvinylidene fluoride content (above 50%) to ensure the pyro-piezoelectric nature of the resulting material, were synthesized. The thermal and dynamic mechanical properties of the different blends were studied to the end of determining blend compatibility in the light of the changes undergone by the respective glass transition temperatures. As is well known, one of the most important requirements for these materials is component compatibility, which is known to be a potent conditioning factor of the physical properties achieved in the end product.
These systems were studied with the aim of achieving materials with good pyro-piezoelectric properties, suited for application in the field of sensors or robotics, whose excellent technological performance would gain headway over their ceramic competitors (7).

Experimental

Materials

All the polymers studied were commercial products and were used as received: The polyviylidene fluoride (PVDF) was Solef 6010, supplied by Solvay (M_w/M_n=4.5); the polyvinyl acetate (PVA) was Mowilith 50, a Hoechst product (M_w=260000) and the polymethyl methacrylate (PMMA) was supplied by Repsol, S.A.

Blending

Blends were prepared in a Brabender Plasticorder using a thermoplastic mixing-chamber type W60 preheated at 180 °C; rotor speed was set at 60 rpm and ten minutes of mixing were enough to get uniform dispersion of the components.

Methods

The calorimetric measurements were carried out on a Mettler TA-4000 differential scanning calorimeter at a heating rate of 10 °C/min. Before recording DSC-thermograms, samples were quenched at low temperature from the melt. The midpoint of the slope change of the heat capacity plot was taken as the glass transition temperature. The DSC-thermograms for every samples were carried out three times. The T_g data which appears in Table 1 is the average value.

The dynamic mechanical properties were analyzed with a DMTA Polymer Laboratory. Frecuencies chosen were: 3, 10 and 30 Hz and the temperature range was between -150 and +150 °C.

Results and discussion

In Table 1 the compositions of the different samples are compiled, as well as the values of the glass transition temperature obtained through differential scanning calorimetry (DSC). In all cases, i.e. both for binary and for ternary blends, a single glass transition temperature appears, which varies according to blend composition in such a way that it moves towards higher temperatures as a function of increasing presence of high Tg components in the blend. This is indicative of the fact that the experimental blends show compatible behaviours, in terms of the generally accepted criterion that component compatibility implies the existence of a single glass transition temperature.

Table 1.- Composition of different blends and glass transition temperature obtained by DSC experiments.

SAMPLE	Composition, wt-% PVDF/PVA/PMMA	GLASS TRANSITION TEMPERATURE (°C) $T_{g,blend}$
PVDF	100/0/0	-28.6
PVA	0/100/0	41.9
PMMA	0/0/100	120.5
FA82	80/20/0	4.1
FA64	60/40/0	21.0
FM82	80/0/20	-2.3
FM64	60/0/40	13.5
FAM811	80/10/10	-2.8
FAM631	60/30/10	20.2
FAM622	60/20/20	23.4
FAM532	50/30/20	25.2

Dynamic mechanical measurements generally provide more information about a material than other tests over a wide temperature and frequency range, because they are

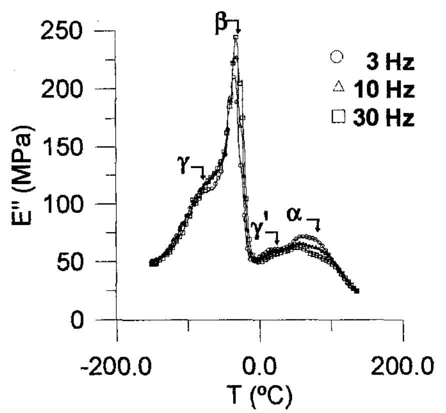

Fig. 1.- E" versus temperature for PVDF

especially responsive to the chemical and physical structure of polymers. These tests measure material response to sinusoidal or other periodical stresses. Since stress and strain are generally not in phase, two quantities can be determined, a modulus and a phase angle or damping term. The phase lag is a consequence of non-instantaneous material response. A certain time interval is necessary for molecule ordering, generally known as strain or relaxation time. Relaxation refers to a certain temperature range, in which there occurs a notable drop in the dynamic modulus, which directly relates to motion on the molecular plane (8-11). The dynamic modulus is one of the most basic of all mechanical properties, and its importance in any structural application is well known.

Damping tends to be the most sensitive indicator of all kinds of molecular motions occurring in a material, even in the solid state. The motions are of great practical importance in determining transitions, relaxation processes, structural heterogeneities and the morphology of multiphase systems, such as crystalline polymers, polymer blends and filled or composite materials. For these reasons the absolute damping value, as well as the temperature and the frequency at which the damping peak appears have a considerable bearing on the mechanical behaviour of polymers.

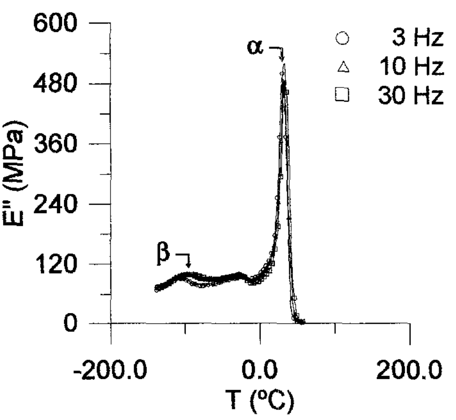

Fig. 2.- E" versus temperature for PVA

The dynamic mechanical relaxation spectrum of PVDF, which has been widely studied (12-17), presents up to four different relaxations. Fig.1 compiles loss modulus variation as a function of temperature for the three experimental frequencies for one of the PVDF samples. γ relaxation (-70°C) is attributed to restricted motion in the amorphous phase, actually to rotational chain movements in the amorphous phase (18);β relaxation (-40°C) corresponds to glass transition and hence to Brownian micromotion in the backbone in the amorphous zones (18,19); γ' relaxation (+50°C) appears in the amorphous phases and is attributed to folding movements (18). Finally, α relaxation (+100°C) has given rise to discrepancies and polemics in the literature, as to the decisive triggering factors. Some authors (20,21) explain it in terms of motion in the amorphous phase, and many others (22,23) have demonstrated that it is the crystalline phase which is liable to produce it. It

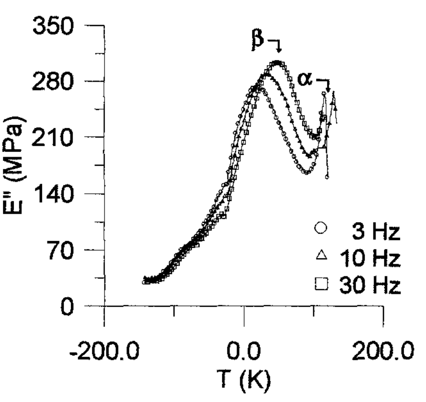

Fig. 3.- E" versus temperature for PMMA

has been related to molecular motion which alters the direction of the dipole, parallel, but not perpendicular to the chain axis.

Fig. 2 shows the behaviour of the loss modulus, as obtained from a poly vinyl acetate sample for the three frequencies under study. Our results are in full agreement those found by Schmieder and Wolf (24) as early as in 1953 in mechanical shear measurements at about 10 Hz. These authors observed three secondary peaks for PVA at -100, -30, and 30°C. The higher and lower temperature peaks correlate well with the dielectric results and are referred to as β and α, respectively. The β mechanism is generally thought to involve motions of the -OCOCH3 side-groups. The α relaxation can be treated in terms of the cooperative rotational motions within the backbone and coincides with the glass transition temperature. Our results absolutely confirm the findings of these authors, including the -30°C peak, which again seems less prominent and has no dielectric equivalent. It may conceivably be due to impurities.

Although for PMMA up to five different relaxations have been detected, in our research we observed but the two most relevant relaxations. In fact, at the higher frequency and under the experimental conditions stated, it proved to be impossible to record the relaxation corresponding to the higher temperature, as shown in Fig. 3. The α relaxation is related to glass transition and is indicative of a mechanism involving backbone motions.

Table 2.- T_g's values obtained by dynamic mechanical measurements at 3 Hz

	Composition, wt-%	**GLASS TRANSITION TEMPERATURE (°C)**		
SAMPLE	**PVDF/PVA/PMMA**	$T_{g,PVDF}$	$T_{g,PVA}$	$T_{g,PMMA}$
PVDF	100/0/0	-37.1	-	-
PVA	0/100/0	-	41.2	-
PMMA	0/0/100	-	-	115.7
FA82	80/20/0	-58.5	27.8	-
FA64	60/40/0	-79.6	31.3	-
FM82	80/0/20	-48.3	-	67.7
FM64	60/0/40	-81.1	-	84.7
FAM811	80/10/10	-52.3	25.3	55.7
FAM631	60/30/10	-78.9	31.4	76.2
FAM622	60/20/20	-76.4	31.3	70.1
FAM532	50/30/20	-85.9	34.6	65.6

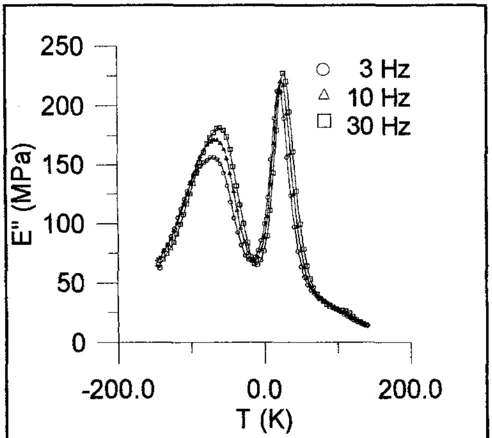

Fig. 4.- E" versus temperature for FA82

The β relaxation is generally assigned to the rotation of the -OCOCH3 side groups. The remaining relaxations observed by other authors are attributed to the rotation of methyl groups in the ester side-chain, the absobed water and the rotation of α-methyl groups (9).

For all, i.e. for the binary and ternary blends under study, the results obtained from dynamic mechanical analysis and compiled in Tables 2, 3 and 4 show that in all cases there appear the glass transition temperatures corresponding to each of the homopolymer constituents in the different blends. Figs. 4 and 5 show, as an example, the variation of E" versus temperature for FA82 and FAM622, respectively. In some polymer blends there is overlap between different contributions. In these cases, a non-linear curve fitting software has been used to asses the maxima positions and to discern between the different relaxations.

In all cases, as was to be expected, the glass transition temperature gradually shifts to higher temperature ranges, when increasing the frequency at which the tests are being conducted.

As regards the glass transition temperature of PVDF, both in the ternary and binary samples, significant Tg temperature drops take place, which become the more prominent the higher the amorphous polymer portion in the blend, or for balanced blends, when the amorphous polymer is PMMA.

Table 3.- T_g's values obtained by dynamic mechanical measurements at 10 Hz

	Composition, wt-%	**GLASS TRANSITION TEMPERATURE (°C)**		
SAMPLE	**PVDF/PVA/PMMA**	$T_{g,PVDF}$	$T_{g,PVA}$	$T_{g,PMMA}$
PVDF	100/0/0	-34.4	-	-
PVA	0/100/0	-	44.1	-
PMMA	0/0/100	-	-	123.2
FA82	80/20/0	-54.7	31.6	-
FA64	60/40/0	-75.9	35.2	-
FM82	80/0/20	-44.3	-	69.7
FM64	60/0/40	-87.3	-	88.7
FAM811	80/10/10	-50.7	26.8	57.1
FAM631	60/30/10	-68.7	35.0	80.0
FAM622	60/20/20	-73.7	34.1	75.9
FAM532	50/30/20	-72.3	35.9	71.3

PVA and PMMA are observed to present identical glass transition behaviours. For binary blends downward shifts are observed for the Tg zone, as had occurred with PVDF. Yet in contrast to PVDF, Tg increases with increasing amorphous polymer content. Likewise in the ternary blends, the Tg's of either polymer present at lower temperatures, as compared to those of the unblended polymers pure and simple. The most significant downward shifts are achieved for the lowest PVA/PMMA ratios in the blends. At this stage it should also be pointed out that the blends containing both polymers, when prepared under the experimental conditions stated elsewhere (25), i.e. from melts, prove to be incompatible.

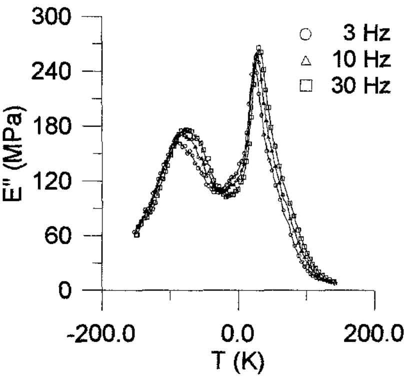

Fig 5.- E" versus temperature for FAM622

In summary, in all the experimental blends the respective glass transition relaxations of the component homopolymers can be observed, however at comparatively, in some instances considerably lower temperatures.

Table 4.- T_g's values obtained by dynamic mechanical measurements at 30 Hz

	Composition, wt-%	**GLASS TRANSITION TEMPERATURE (°C)**		
SAMPLE	**PVDF/PVA/PMMA**	$T_{g,PVDF}$	$T_{g,PVA}$	$T_{g,PMMA}$
PVDF	100/0/0	-33.0	-	-
PVA	0/100/0	-	47.1	-
PMMA	0/0/100	-	-	>130
FA82	80/20/0	-51.1	35.3	-
FA64	60/40/0	-78.9	38.8	-
FM82	80/0/20	-42.5	-	73.0
FM64	60/0/40	-96.1	-	94.2
FAM811	80/10/10	-47.5	28.8	59.1
FAM631	60/30/10	-65.0	40.0	85.9
FAM622	60/20/20	-68.7	35.4	80.0
FAM532	50/30/20	-72.3	40.1	88.6

Conclusions

In the light of these findings it is legitimate to conclude that a given compatible system may not be molecularly homogeneous under a particular set of conditions, and that individual molecules of each component may cluster in very small domains, i.e. microheterogeneities may appear. Furthermore, if different techniques are responsive over different ranges, one may be led to different conclusions concerning the compatibility of the blend, or see differences in Tg dependence on blend composition. For example, if the moleular process responsible for the jump in heat capacity observed by DSC involves longer range motions than the segmental Brownian micro-motions accountable for the dynamic mechanical peak, a particular blend may be judged compatible by DSC, but heterogeneous by dynamic mechanical measurements.

Hence the existence of a single glass transition temperature, as observed for the experimental blends by DSC on the one hand, and on the other hand the significant drops determined by means of dynamic mechanical measurements, which could be indicative of enhanced chain mobility arising from the decrease in molecular interactions, allow for the the conclusion the discrepancies encountered are due to the differences in test sensitivity, but that the blends themselves may be considered compatible.

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