

Melt Processing of Composites of PVDF and Carbon Black Modified with Conducting Polymers

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ABSTRACT: Conductive composites from poly(vinylidene fluoride) (PVDF) and a novel thermally stable conductive additive made via *in situ* deposition of polyaniline or polypyrrole on carbon black particles were produced by a melting process. Electrical conductivity in the order of 10^{-2} S/cm could be achieved with low contents of the conductive filler. Thermogravimetric analysis (TGA) showed that there is no appreciable degradation of the composites at temperatures as high as 300°C. Moreover, the addition of the conducting polymer-modified carbon black additive is advantageous to the melt processing of the composites, reducing

the melt viscosity in comparison to the addition of pure carbon black. Composites containing the β -phase of PVDF could be obtained via quenching from the melt, as indicated by X-Ray diffraction analysis. The type and amount of the additive and the quenching rate influence the formation of β -phase in the PVDF composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 553–557, 2004

Key words: additives; composites; crystallization; melt processing

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has been studied for a wide range of technological applications. As far as its crystalline structure is concerned, PVDF can exhibit four crystalline phases, the so called α , β , γ , and δ phases, among which the β -phase is of special interest due to its exceptional pyro and piezoelectric properties.^{1,2} Crystallization of PVDF in the β -form directly from the melt is not usual. Rather, PVDF- β is usually obtained by mechanical deformation from the α -phase or by casting a PVDF solution at temperatures $\sim 70^\circ\text{C}$. Most of the applications reported lie in the use of neat PVDF or VDF-copolymers as ultrathin films and membranes.^{3,4} The use of PVDF as a matrix for conductive composites has also been previously reported.^{5,6} To improve electrical conductivity to polymer systems, several works have been done using carbon black (CB)⁷ or intrinsically conducting polymers (ICPs)^{5,6,8,9} as conductive fillers in conventional polymers. However, the addition of particulate fillers such as CB in a polymer matrix can cause an excessive increase in the viscosity,¹⁰ hindering the melt processing of these materials. In this aspect, the use of a new class of conductive additives for plastics made via *in situ* deposi-

tion of ICPs on carbon black¹¹ (Eeonomer[®]) could improve electrical conductivity on rubbery and thermoplastic systems without a huge increase on viscosity, and consequently facilitate the melt processing of these materials.¹² In this work we show that a further advantage of the use of Eeonomer[®] lies in the fact that they are more thermally stable than other conducting composites or blends, allowing processing at high temperatures. In addition, X-ray diffraction analysis showed that composites containing the β -phase of PVDF could be obtained directly by quenching from the melt.

EXPERIMENTAL

Conductive compounds (Eeonomer[®]) were produced by Eeonix Co. (Pinole, CA) via *in situ* polymerization of polyaniline (PANI) or polypyrrole (PPY) onto CB particles. Table I shows the features of additives used in this work. The Eeonomer[®] KPO contains no ICP in its formulation (nonmodified CB). PVDF (Forafilon 4000 HD) was purchased from ELF-Atochem (France) and used as received.

The conductive PVDF/Eeonomer[®] composites were produced as follows: After drying at 125°C for 1 h, the additive was hot processed with PVDF in a high temperature Haake mixer at 180°C for 10 min and 80 rpm. After processing, the composites were pressed in the form of films at 200°C under pressure of 180 Kg/cm².

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TABLE I
Eeonomer® Type and Respective Content of Intrinsically Conducting Polymer (ICP) and Surface Area

Eeonomer®	ICP/ICP content (wt %)	Surface area (m ² /g)
KPO	—	1400
KP01	PANI/1	1200
KP05	PANI/5	800
KP10	PANI/10	700
KP15	PANI/15	600
KP20	PANI/20	570
KP40	PANI/40	400
KPY20	PPY/20	390

The latter allowed fabrication of good quality thin composite films with thickness varying from 150 to 200 μm .

Conductivity measurements were carried out with the standard four point probe technique.¹³ Differential scanning calorimetry (DSC) analyses were performed in a Du Pont-2910 machine at a temperature ranging from 25°C up to 350°C at 10°C/min in N₂ atmosphere. The thermogravimetric analyses were taken in a Netzsch-TG 209 machine at temperatures from 25 to 800°C under dynamic argon flow. X-ray diffraction patterns were carried out in a Rigaku RU-200 B diffractometer, 2θ varying between 5 and 50°.

RESULTS AND DISCUSSION

Composite processing and thermal properties analysis

Figure 1 shows torque \times time curves obtained during the processing of the PVDF/Eeonomer® composites in the HAAKE rheometer. All curves correspond to composites containing 20 wt % of the additive. Higher

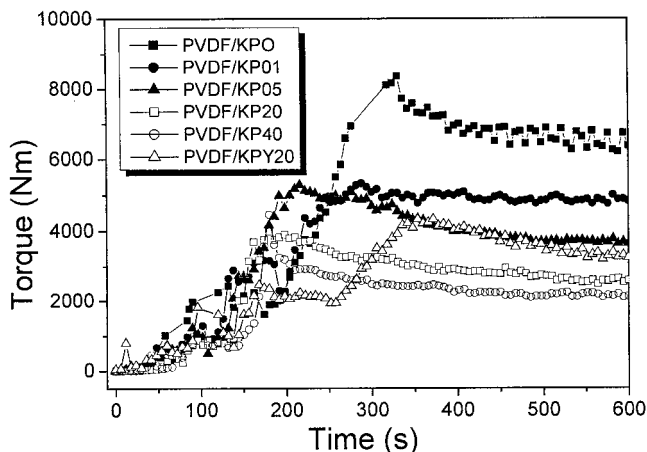


Figure 1 Torque curves for composites of PVDF with Eeonomer® containing different amount of PANI (KP) or PPY (KPY). All the composites contain 20 wt % of the additive.

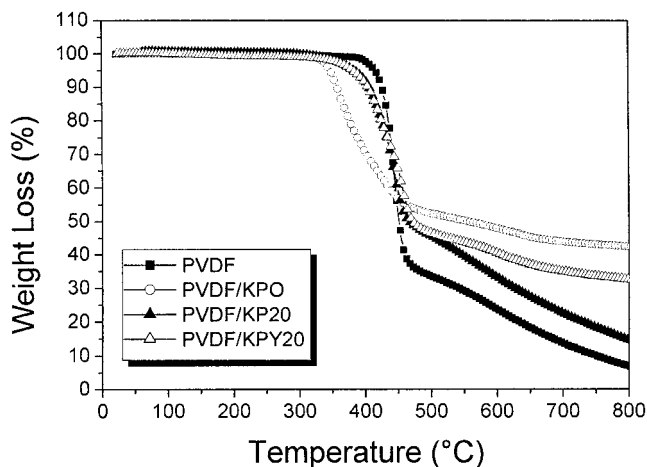


Figure 2 Thermogravimetric curves of the composites of PVDF with additives containing PANI (KP20), PPY (KPY20), or only carbon black (KPO), under argon at a scan rate of 10°C/min. All the composites contain 20 wt % of the additive.

values of torque are observed for PVDF/KPO composites. Lower torque values are found for the composites using PANI- or PPY-based additives. Besides, it can be seen that the higher the PANI content in the additive, the lower the torque values. The use of the additive containing PANI or PPY is advantageous compared to pure CB-based additive (KPO) due to the lower melt viscosity presented by such composites. This fact is related to the presence of PANI or PPY on the CB particles, which reduces the surface area of the filler. The smaller the surface area of the filler, the smaller the interactions with the polymer matrix and as a consequence, the smaller is the melt viscosity.

Thermogravimetric analyses (Fig. 2) showed that the composites are thermally stable with no detectable weight loss up to 300°C, which greatly increases the viability of melt processing. In addition, it is important to note that the thermodegradation occurs as a two-step process for both neat PVDF and composites. The first step usually corresponds to the fluoridic acid (HF) evaporation, leading to the formation of $\text{CH}=\text{CF}-\text{CH}=\text{CF}$ conjugations along the chains. In the second step, weight loss is probably due to chain scission. PVDF/KP20 and PVDF/KPY20 composites presented higher thermal stability than PVDF/KPO. PVDF/KPO composites start losing mass at $\sim 340^\circ\text{C}$, whereas PVDF/KP20 and PVDF/KPY20 start at $\sim 380^\circ\text{C}$. This fact is related to the presence of PANI or PPY in the additive formulation. It is well known that in inert atmosphere the thermal degradation of PVDF results in HF in addition to dimeric and oligomeric species.¹⁴ Apparently the PANI and PPY present in the additive seem to make the degradation kinetics slower upon absorbing the HF during the degradation process.

The electrical conductivity of the composites containing 20 wt % of additive was estimated at $\sim 10^{-2}$

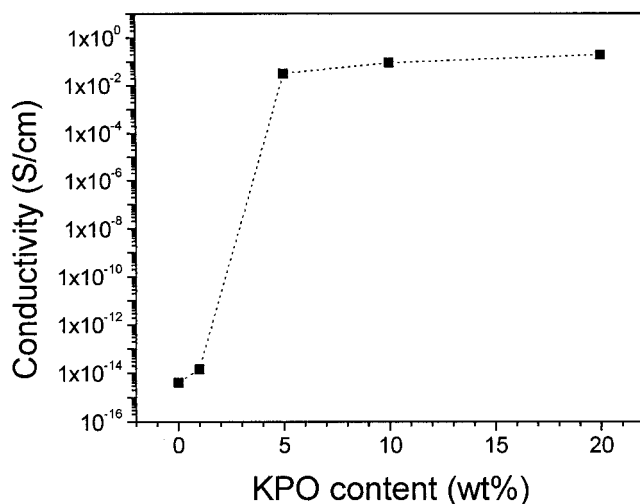


Figure 3 Electrical conductivity as a function of KPO amount for PVDF composites. A percolation point between 1 and 5 wt % of Eeonomer[®] is clearly visualized.

S/cm for the three different kinds of fillers (KPO, KP20, and KPY20). The percolation threshold, which is related to the amount of filler added to the polymeric matrix needed to promote the jump on the conductivity, was found to be between 1 and 5 wt % for all composites, as shown in Figure 3 for composites with PVDF containing different amounts of the additive KPO. The conductivity values jump from 10^{-13} S/cm to 10^{-2} S/cm for composites containing 1 and 5 wt %, respectively. After the percolation threshold, any additional amount of the filler does not cause any considerable change in the conductivity.

The similar values of percolation threshold found for all composites may be associated with the fact that when conductive CB particles are incorporated into a semicrystalline polymeric matrix, the conductive filler is preferentially located at the amorphous phase.¹⁵ This makes the percolation threshold depend mostly on the degree of crystallinity of the polymeric matrix, and not on the physical properties of the particle coverage (in this case, PANI or PPY).

The thermal stability of the conductivity was probed as a function of time and temperature. Figure 4 shows the normalized conductivity of the composites during exposure to high temperature at room atmosphere. As can be seen, the conductivity stays practically stable even after 170 h of treatment at 150°C in air. The thermal stability of the conductivity is desired in terms of hot processing of conductive composites. Reports in the literature¹⁶ show that PVDF/Poly(*o*-methoxyaniline) (POMA) blends presented a decrease of 4 orders of magnitude in the normalized conductivity after 170 h of thermal treatment under the same experimental conditions as described above.

The influence of type and amount of Eeonomer[®] on the melting temperature of the composites was ana-

lyzed by DSC measurements. Figure 5 depicts the melting temperature (T_m) as a function of KPY or CB KPO present in the composite. For both composites, a decrease in T_m is observed as a function of additive amount. It is known that the T_m is related to the lamellar thickness of the PVDF spherulites: spherulites comprising thicker lamellas tend to melt at temperatures higher than those comprising thinner lamellas. The experimental data from Figure 5 suggest that the addition of KPO and KPY interfere in the crystallization of PVDF from the melt in such a way that thinner lamellas are formed.

In addition to the decrease on the PVDF T_m , the presence of the Eeonomer[®] particles in the polymeric matrix promotes an actual reduction of the crystallinity of PVDF. Figure 6 shows the enthalpy calculated from the endothermic curves of PVDF as a function of KPO and KPY20 contents in the composite. The non-linearity of the curves indicates a strong tendency of the filler to hamper the crystallization of PVDF- α . It will be discussed later that such tendency can result in the formation of the β -phase PVDF from the melt when a high cooling rate is applied.

Influence of Eeonomer[®] on the crystallization of β - phase PVDF cooled from the melt

X-ray diffractograms from neat PVDF and composites containing Eeonomer[®] with different amount of PANI in its formulation are shown in Figure 7. All the composites contain 20 wt % of the additive. Diffraction peaks (2θ) characteristics of the α -phase at 17.5, 18.4, 20, and 26.5° can be observed for neat PVDF. As one can observe, the incorporation of the filler causes a

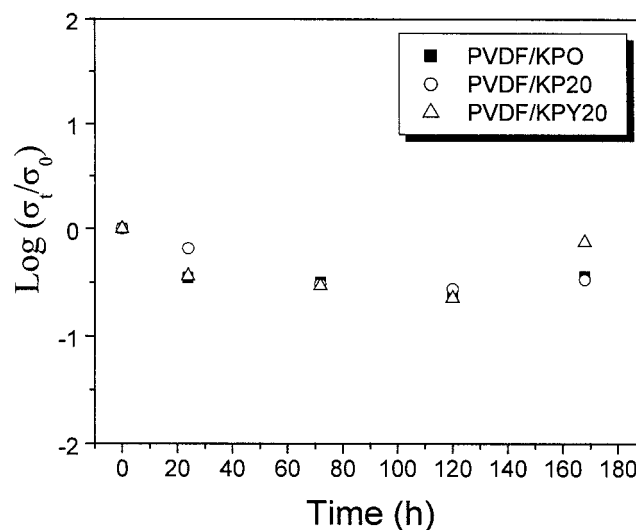


Figure 4 Electrical conductivity stability of composites of PVDF with additives containing PANI (KP20) or PPY (KPY20) or only carbon black (KPO), at 150°C in air. All the composites contain 20 wt % of the additive.

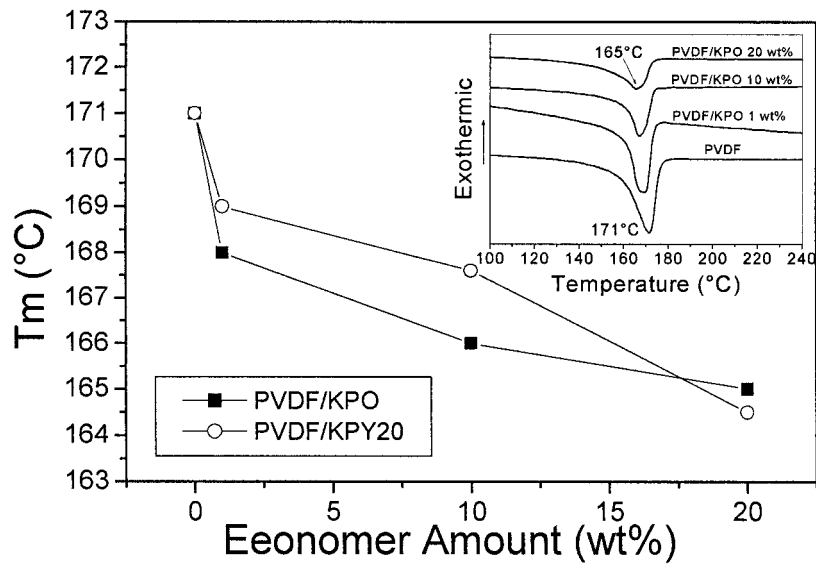


Figure 5 Composite T_m as a function of KPO and KPY20 amount. The inset shows the DSC curves for neat PVDF and for composites containing different amounts of KPO in its formulation.

reduction in the intensity of the α -phase characteristic peaks, especially for the peak at 26.5° . Also, this effect is more remarkable for Eeonomer[®] containing smaller quantities of PANI and consequently higher quantities of CB. In the extreme case of the PVDF/KPO composite, such effect is very clear. Moreover, the presence of a new peak at 21° in the PVDF/KPO composite suggests that some amount of the β -phase was formed in the composite, since diffractograms of the β -phase exhibit one peak at 21° .¹ To check if composites could be cooled from the melt directly in the β -phase, composites containing different amounts of KPO and subjected to different cooling rates were tested. One set of samples in the form of pressed films was melted at

220°C for 20 min and then allowed to cool at room temperature (25°C). A second set of samples was melted at 220°C for 20 min and then immediately immersed in ice bath at 0° , which provided a high cooling rate. The results are shown in Figures 8 and 9, respectively. As it can be observed in Figure 8, the β -phase is not formed for any additive content, for samples cooled at room temperature. For samples cooled in ice bath, however, the β -phase is formed for composites containing 20 wt % of KPO (Fig. 9). Reports in the literature¹⁷ state that β -phase crystallization from the melt was only possible for very thin samples (thickness $< 5 \mu\text{m}$) cooled at very high cool-

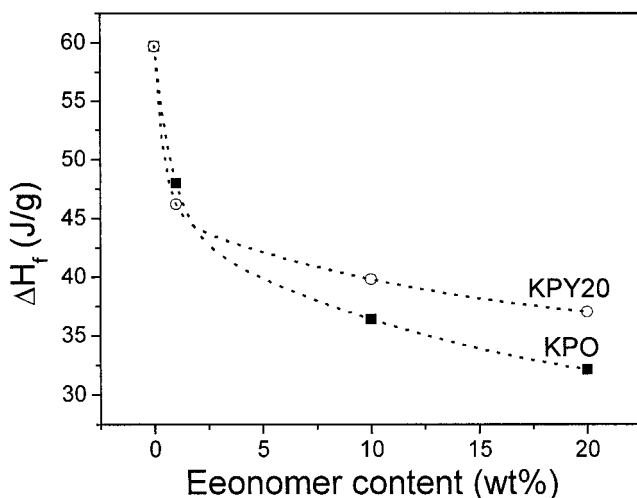


Figure 6 Enthalpy variation as a function of KPO and KPY20 contents in PVDF composites.

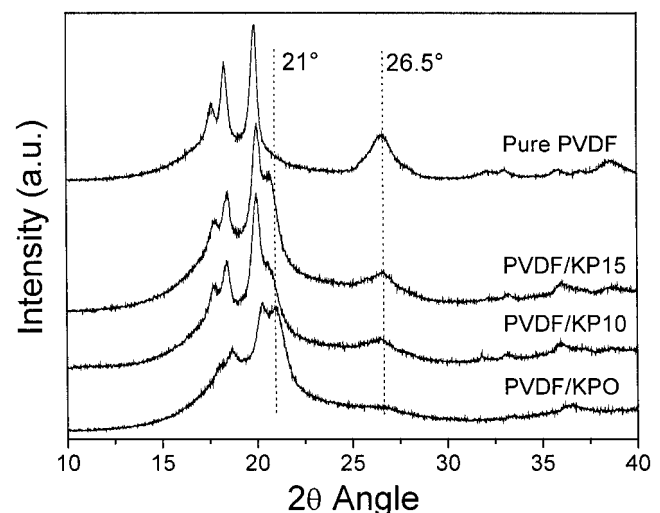


Figure 7 X-ray diffractograms for PVDF and for composites with additives containing different amounts of PANI. All the composites contain 20 wt % of the filler.

ing rates, due to the low thermal conductivity of PVDF, which reduces the effective cooling rate within the sample. The formation of the β -phase in the PVDF/KPO composites with thickness from 150–200 μm is therefore quite interesting. We believe that the presence of Eeonomer[®] in conjunction with a high cooling rate can preclude the α -phase formation (which exhibits maximum crystallization rate at $\sim 140^\circ\text{C}$).¹⁸ Thus, the melted material is allowed to reach temperatures around 60 to 70°C , where the maximum in the crystallization rate for the β -phase occurs.

CONCLUSION

The melt processing of conductive polymeric composites represents an important issue in the technological application of these materials allowing manufacturing at industrial scale. Such composites can be obtained with thermoplastics filled with CB modified with conducting polymers. Besides the electrical conductivity, the use of these new thermally stable additives as conductive fillers takes advantage of the higher thermal stability and lower values of the melt viscosity compared to the composites containing only CB.

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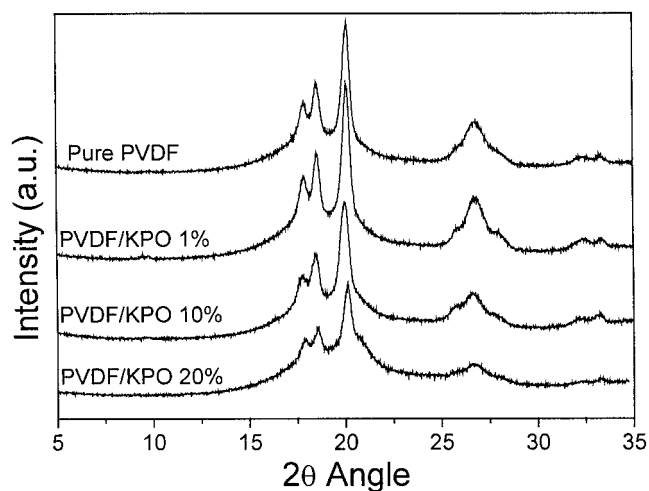


Figure 8 X-ray diffractograms for PVDF and PVDF/KPO composites at various concentrations cooled at room temperature.

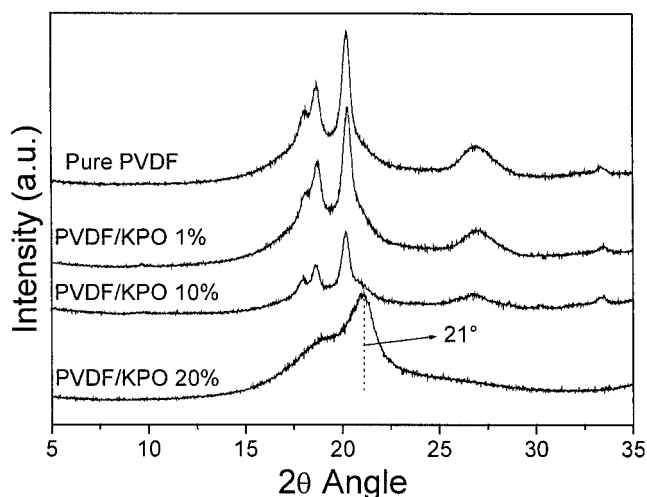


Figure 9 X-ray diffractograms for PVDF and PVDF/KPO composites at various concentrations cooled in an ice bath.

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