

# Thermal Analysis of Poly(vinylidene fluoride) (PVDF) in Composites with Polypyrrole (PPy)

SUNITA PAWDE\* and NARENDRA BHAT

Physics Division, Department of Chemical Technology, University of Bombay, Matunga, Bombay-400 019, India

## SYNOPSIS

The melting behavior and dynamic mechanical properties of poly(vinylidene fluoride) (PVDF) in composites with polypyrrole (PPy) have been investigated using DSC/DTA and a Rheovibron viscoelastometer. Composites with varying percentages of PPy (5–50%) were synthesized using a solution-casting method with  $\text{FeCl}_3$  as the oxidant. It was observed that the melting point of PVDF increased as the percent of PPy was increased. A plot of  $\tan \delta$  vs. temperature showed the shift of the  $\alpha$  relaxation peak to higher temperature. These results, together with our earlier studies on the basis of XRD and IR, indicate molecular interaction, an antiplasticization effect of PPy, and partial phase transformation of PVDF to phase I ( $\beta$  form). © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The ferroelectric properties of poly(vinylidene fluoride) (PVDF) have been extensively studied.<sup>1,2</sup> It is well known that PVDF exists in at least four different crystalline forms. The most common form is phase II ( $\alpha$ ), which can be converted to polar phase I ( $\beta$ ) through various processes.<sup>3</sup> The piezoelectric property is governed mainly by the crystalline form, the degree of crystallinity, and molecular conformation. These can be altered by modifying PVDF by blending it with other polymers,<sup>4</sup> under high pressure,<sup>5</sup> or by  $\gamma$  or electron-beam radiation.<sup>6–8</sup> Conversion of phase II to phase I by poling at high electric fields or subjecting it to corona discharge leads to partial or complete conversion depending on field, temperature, etc.<sup>9</sup> Efforts are, therefore, being made to use radiation or high pressure followed by stretching to bring about a higher degree of conversion. Copolymerization with trifluoroethylene has also been attempted to give better piezoelectric properties and electromechanical coupling.<sup>10</sup>

In the present investigation, an attempt was made to form a composite with polypyrrole (PPy) so as to reduce the piezoresistance and bring about crystallization in the polar form without requiring ad-

ditional mechanical transformation. These composites have been characterized using DSC/DTA and thermomechanical analysis, the results of which are given in detail in this article. Characterization of the PVDF/PPy composites using other techniques such as wide-angle X-ray diffraction, small-angle X-ray scattering, IR spectroscopy, and electrical conduction behavior have already been reported elsewhere.<sup>11,12</sup>

## EXPERIMENTAL

Pure PVDF was obtained in the form of granules (Solvay). Pyrrole was obtained from Aldrich Chemicals and was distilled under vacuum before use.

PVDF granules were dissolved in DMF (2% wt/vol) at 70°C, to which a known percentage of pyrrole was added with  $\text{FeCl}_3$  as an oxidant. Thin films approximately 10 microns thick were cast on a glass plate at 70°C. These films were stripped off after complete evaporation of the solvent. The composite films of PVDF having 5, 10, 20, and 50% wt of PPy were prepared.

The samples were analyzed using a Stanton Redcraft STA DTA/TGA analyzer. The heating rate was maintained at 5°C/min. Some samples were also analyzed using a Perkin-Elmer differential scanning calorimeter (DSC 7).

\* To whom correspondence should be addressed.

The dynamic mechanical behavior of the films was investigated using a Rheovibron DDV II (Toyo Baldwin) analyzer. The sample of 2 cm length was fixed in two jaws and stressed at a frequency of 110 Hz. The scans were carried out for  $\tan \delta$  and  $\epsilon^*$  up to a temperature of 130°C.

## RESULTS AND DISCUSSION

### Characterization

Various films casted were characterized using IR spectroscopy, X-ray diffraction, and microscopy. The X-ray diffractogram for pure PVDF showed major reflection peaks corresponding to the  $\alpha$  phase.<sup>13</sup> The IR spectrum showed a typical absorption band at 530  $\text{cm}^{-1}$ , which is typical for the  $\alpha$  phase.<sup>14</sup> The electron microscopic observation of the sample showed large spherulites (20–30 microns) typical of the  $\alpha$  phase. The composite films of PVDF, containing PPy in different percentages, were also analyzed using these techniques. The X-ray diffractograms of (PVDF + PPy) composites showed a shift of the reflection peak due to (110) from  $2\theta = 20^\circ$  to  $20.8^\circ$ .<sup>15</sup> Similarly, the IR absorption spectra of the composites showed increase in the intensity of the absorption band at 510  $\text{cm}^{-1}$ , which is characteristic of the  $\beta$  phase. The microscopic evidence also showed a decrease in the spherulite size and transformation to the  $\beta$  phase. The percentage crystallinity as well as the crystallite size decreased. Additional absorption bands in the IR spectra corresponding to PPy are evident. All these changes suggest interaction at the molecular level and partial transformation to the  $\beta$  phase.

### Thermal Analysis

The thermal behavior of polymers is interesting as their structure and crystallization is very sensitive to temperature. The melting behavior and the related properties of PVDF have been reported by several workers.<sup>2,4</sup>

The melting behavior of PVDF is complicated as it exists in different polymorphs and the interconversion can occur during heating. The melting and crystallization temperatures ( $T_m$  and  $T_c$ ) reported in literature vary by a large amount even in the same phase of the sample or from one type of resin to another.<sup>12,16,17</sup> The highest melting point for the PVDF control reported is 200°C and the lowest is 160°C. The melting points of different phases, namely, phases II, I, III, and IV (i.e.,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ), have been found to be different. In the present

investigation, we tried to determine  $T_m$  and  $T_c$  for pure PVDF and its composites with pyrrole (PVDF/PPy). An illustrative DSC scan is shown in Figure 1. It may be seen from the figure that an endothermic peak corresponding to the melting of pure PVDF (phase II) appears at 163.9°C. When PVDF was doped with 5% PPy, the melting temperature increased to 178.5°C. When the percentage of pyrrole was further increased to 10%, the  $T_m$  decreased slightly. It was observed that in the other composites when the PPy content was increased further the value of  $T_m$  somewhat decreased. However,  $T_m$  for all the composites were higher than that for pure PVDF. These changes are shown in Figure 1 and Table I.

In the DSC scan, an exothermic peak was also noted in the region of 55°C, which varies nearly the same way as does the  $T_m$  for all the samples. It was also interesting to note that the heat capacities decreased as the percentage of pyrrole in the composites increased except in the case of the 5% PPy sample (Table I).

The recording of the DSC scan during cooling enabled us to observe the crystallization temperature,  $T_c$ , the values of which are given in Table I. It may be noted that  $T_c$  varies from 139.7°C for the control to 144.8°C for 50% PPy. During the cooling cycle also, an exothermic peak was observed that increased progressively with the doping level. These results show that the incorporation of PPy in the PVDF matrix makes the composites thermally more stable. The increase in the  $T_m$  can be either due to the higher percentage of crystallinity or due to the change of phase from II to I or due to cross-linking of pyrrole chains with PVDF.

Our wide-angle X-ray diffraction studies indicate that there is a partial conversion of phase II to phase I. Studies on the melting behavior<sup>2</sup> of each phase indicate that the  $T_m$  for phase I is higher.

### Dynamic Mechanical Analysis

The relaxation phenomena in PVDF have been investigated by various workers using different techniques such as dielectric measurement,<sup>18</sup> NMR,<sup>19</sup> and dynamic mechanical analysis.<sup>20</sup> Dynamic mechanical analysis from  $-160$  to  $150^\circ\text{C}$  have been reported for PVDF, which indicates three transition peaks designated as  $\alpha$ ,  $\beta$ , and  $\gamma$  at temperatures of 100,  $-40$ , and  $-70^\circ\text{C}$ .<sup>21,22</sup> Kakutani<sup>23</sup> indicated a further relaxation at peak  $\beta'$  at about  $50^\circ\text{C}$ . These peaks arise due to the various processes as follows:  $\alpha$  at  $100^\circ\text{C}$  is due to molecular motions in crystalline regions;  $\beta$  at  $-40^\circ\text{C}$  is due to micro-Brownian motion

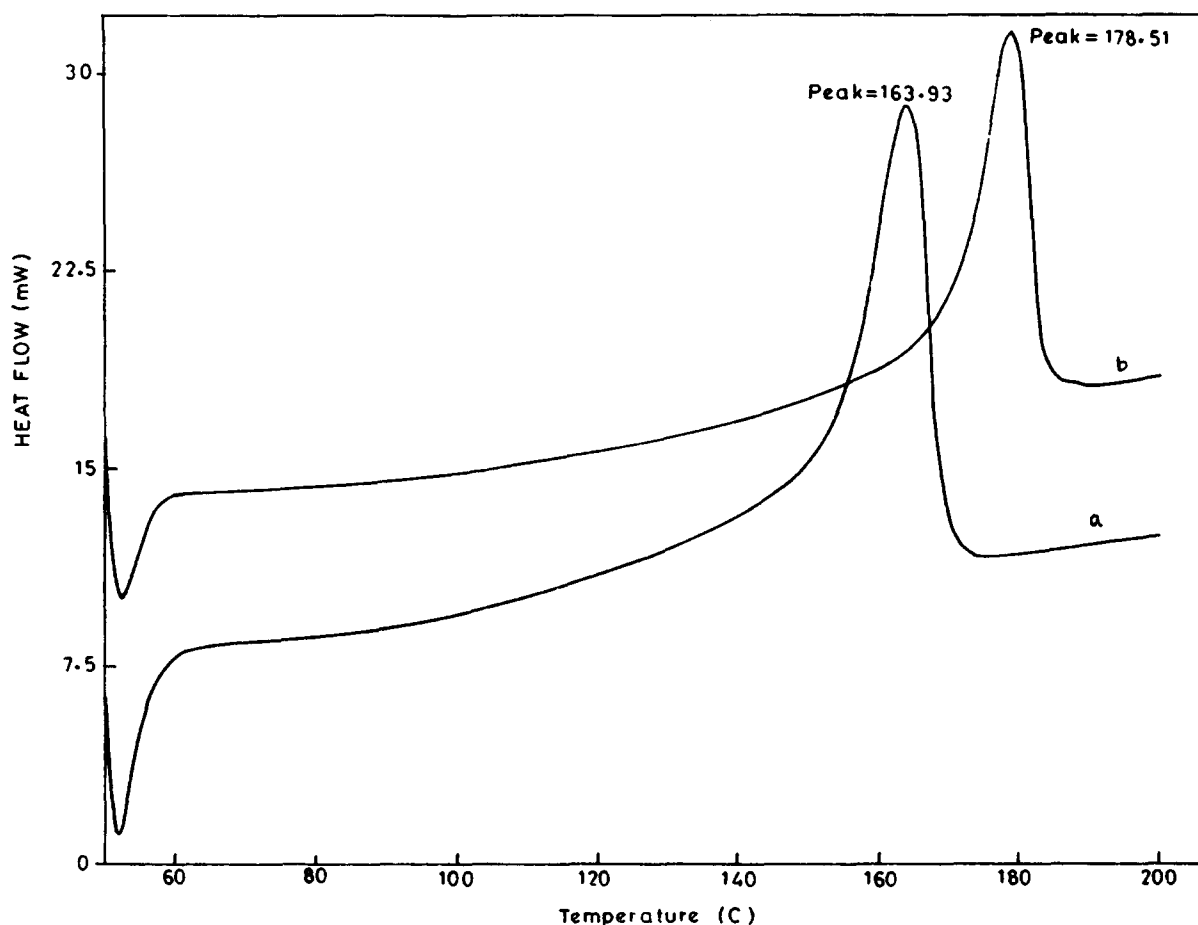


Figure 1 DSC scan of (a) pure PVDF and (b) its composite with PPy.

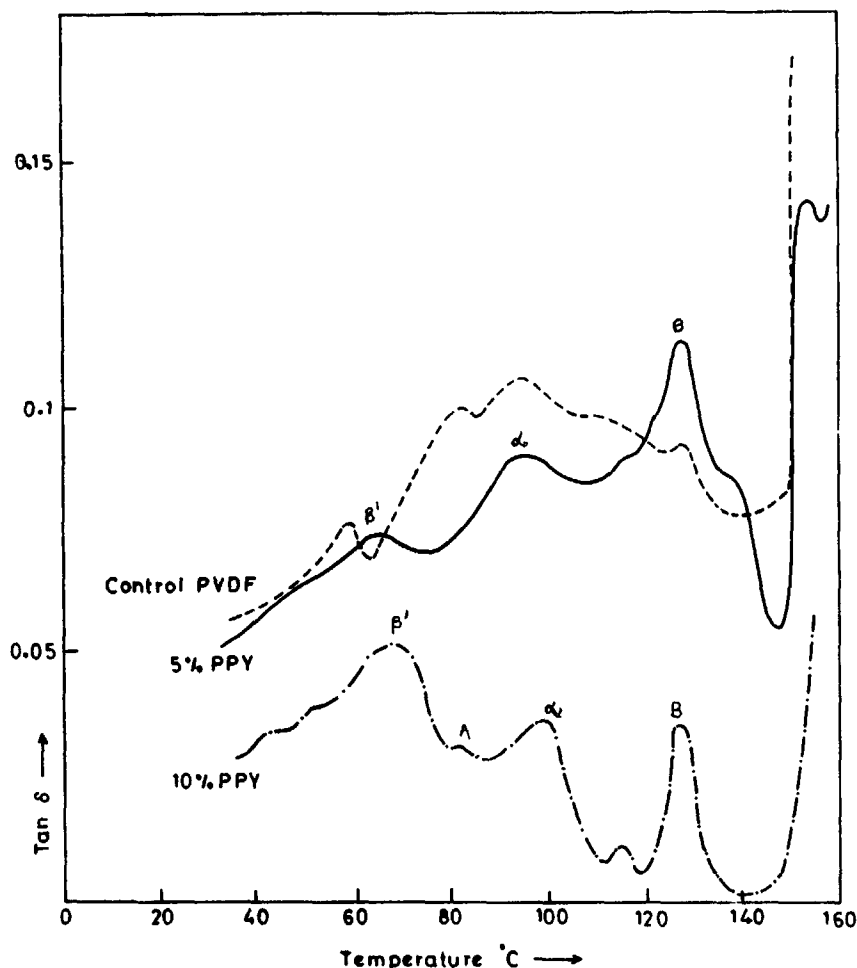
of chains and is the glass transition temperature;  $\gamma$  at  $-70^{\circ}\text{C}$  is due to segmental motion of side chains; and  $\beta'$  at  $50^{\circ}\text{C}$  can be assigned due to molecular motion in the amorphous phase.

The mechanical loss spectrum,  $\tan \delta$  vs. temperature, observed in the present investigation is shown in Figure 2. We did not carry out the experiment at subzero temperature and, therefore, our observations are only from room temperature to  $120^{\circ}\text{C}$ . It may be seen that in the case of pure PVDF films a small

relaxation peak is observed at  $58^{\circ}\text{C}$  followed by another large peak centered at  $93^{\circ}\text{C}$ . These peaks can be designated as  $\beta'$  and  $\alpha$ , respectively. The relaxation spectra for pure PVDF and PVDF/PPy composites are also shown in Figure 2. The peak positions corresponding to these two relaxations have been given in Table II, from which it can be seen that the increase of PPy content shifts these peaks to higher temperatures. The increase of PPy content to 20% PPy leads to the shift of  $\beta'$  peak to  $75^{\circ}\text{C}$ ,

Table I Melting and Crystallization Temperatures of PVDF/PPy Composites

Sample	Melting Temp. $T_m$ ( $^{\circ}\text{C}$ )	Crystallization Temp $T_c$ ( $^{\circ}\text{C}$ )	Heat Capacity (J/g)
Pure PVDF	163.9	139.7	76.1
PVDF + 5% PPy	178.5	140.0	32.3
PVDF + 10% PPy	174.9	142.6	54.1
PVDF + 20% PPy	173.9	143.9	38.9
PVDF + 50% PPy	172.8	144.8	31.2



**Figure 2** Dynamic mechanical spectrum ( $\tan \delta$  vs. temperature) of control PVDF and its composites with PPy: (a) pure PVDF; (b) 5% PPy; (c) 10% PPy.

and for the 50% PPy composite, it shifts to 82°C. Similarly, the  $\alpha$  peak for the composites having 20 and 50% PPy shift to 120 and 102°C, respectively.

The progressive shift of the  $\alpha$  peak to higher temperature can be attributed to the lesser amount of chain flexibility. This tendency is similar to the an-

tiplasticizing action observed for other polymers. Since the  $\alpha$  relaxation peak has been attributed to the crystalline regions, the shift of the  $\alpha$  relaxation peak to higher temperature means that the PPy affects the crystalline regions. We have, indeed, observed a slight decrease in the percentage crystal-

**Table II** Temperatures of Relaxation Peaks of PVDF/PPy Composites from Dynamic Mechanical Spectra

Sample	Temperature for $\tan \delta_{\max}$			
	$\beta'$ Peak	$\alpha$ Peak	Peak A	Peak B
Pure PVDF	58	93	82	—
PVDF + 5% PPy	64	94	—	125
PVDF + 10% PPy	68	98	80	127
PVDF + 20% PPy	75	120	88	135
PVDF + 50% PPy	82	102	—	160

linity and partial transformation to phase I when the samples were probed by WAXD.

The diffusion of PPy in the crystalline region must naturally be preceded by interaction with the amorphous phase. It is, therefore, expected that the peak  $\beta'$  attributed to the amorphous region should also change correspondingly. Our observation of the steady shift of the  $\beta'$  peak to higher temperatures with increase in PPy content confirms our hypothesis.

It is interesting to observe from Figure 2 that in addition to the  $\beta'$  and  $\alpha$  peaks we also observe the additional maxima in the relaxation spectra around 80 and 130°C. These peaks are designated as A and B in Table II. It can be seen that there is a slight variation in the temperature corresponding to the maxima of these peaks. The main important characteristics of peak B is that the peak intensity increases rapidly with pyrrole content. The high intensity and the sharpness of this peak indicates a new phase due to the complex formation of PVDF and PPy. Its higher value of the temperature shows improved thermal stability of the composites.

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