



Influence of Polymer Blending on Crystalline Structure of Polyvinylidene Fluoride

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ABSTRACT

The changes in the crystalline structure of polyvinylidene fluoride (PVDF) were investigated via preparation of its blends with polymethyl methacrylate (PMMA), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) in molten states in an internal mixer at 10% to 40 wt% of the last two polymers. In all the blends, an increase in β -crystal content of PVDF was observed at different degrees and different morphologies. Polyvinylidene fluoride blends with PMMA showed a homogeneous morphology, whereas those with PET and PVC showed two-phase morphologies. These were accounted for the solubility parameter differences of the polymers. In the case of PVC the mismatch of processing conditions was found to be the main reason for the observed morphology. The technique of FTIR spectroscopy revealed that the relative β -crystal content of PMMA blend reached 70% at 30 wt% PMMA, whereas PET and PVC achieved 80% β -crystals by only 10 wt% modification. This was attributed to the interactions of the blended polymers with PVDF molecules in amorphous regions or at their interphases. The effects of PVC and PET on the beta-crystal content of PVDF are similar although the blends in the case of PET produce finer morphology as compared with those of PVC. It is desirable to find and maximize the content of PVDF in final piezoelectric article. The technique of WXR shows limited changes in shape and position of PVDF/PMMA and PVDF/PVC blends spectra and considerable changes in shape of PVDF/PET blends spectra. This is found to be related to the amorphous and semi-crystalline structures of PVC and PET, respectively. Due to the spherical symmetry of the PVDF spherulites the piezoelectric coefficient of the blends are found to be zero.

Key Words:

PVDF;
PMMA;
PET;
PVC;
blending.

INTRODUCTION

Poly vinylidene fluoride (PVDF) is a polymer of choice whenever the interests are directed towards piezoelectricity, toughness and chemical resistance. This polymer has an exceptional structure which is able to crystallize to at least five different crystalline forms; α , β , γ , δ and ϵ forms [1]. This is known as polymorphism. The most stable polymorph of PVDF is the α -form.

The PVDF chain conformation (TG⁺GTG⁻) makes the chains having a moderate dipole moment, but the symmetric packing of these chains in the unit cell nulls the overall dipole moment of the unit cell. The highest dipole moment of the unit cells belongs to the unit cell of β -form (*all-trans* conformation, TTTT). However, this conformation is thermodynamically unfavourable

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and therefore unstable. To overcome the energy barriers of the TGTG'-TTTT conversion many experimental techniques have been developed [1].

Two techniques of cold-drawing and blending are among important techniques to consider. In the first method, a PVDF film is subjected to a uni-directional or bi-directional tensile stress at a temperature range of 80-90°C. In this method the stress is transferred to the chains in crystallites via their segments in the amorphous phase of the film [3]. The mechanical stress directs the chains and crystallites along the tensile direction and would break some of them; while making the film properties quite anisotropic and reducing the total degree of crystallinity.

At the same time, blending PVDF with an amorphous polymer, e.g., polymethyl methacrylate (PMMA) which is miscible with PVDF results in the same form of crystallite conversion ($\alpha \rightarrow \beta$). Meanwhile, PVDF/PMMA blending was profitable for other reasons as well. Early research works on PVDF/PMMA blends were carried out via solution cast blending and the dielectric measurements were employed to investigate the phase behaviour and structure of the blend system [4]. These authors concluded that upto maximum composition ratio of 50/50, the blend is homogeneous in micro-scale as PVDF concentration increases.

The miscibility and crystallization kinetics were also studied in the case of PVDF/PMMA blends [5]. The crystallization dynamics was used to study the miscibility of the PVDF/PMMA blend [6]. The researchers found that with increasing the PMMA concentration, the rate of PVDF crystallization drastically decreases which is resulted from the rising glass transition temperature of the system. The blends of PVDF/PMMA were melt-extruded and the changes in the kinetics of crystallization were monitored via optical microscopy of the film blends [7]. It was found in this study that the diffusion of the PVDF chain from melt phase towards its spherulites is reduced. Consequently, the spherulite growth-rate was limited in the presence of PMMA molecules. The effect of tacticity of the PMMA has been also investigated [8] and it is found that PVDF interactions with the segments of isotactic PMMA is stronger than with those of syndiotactic PMMA. The

presence of fillers and pigments and their effects on the nucleation of PVDF crystals in its blends with PMMA were studied, and it was found that the chemical nature of the filler has an important impact on this property [9].

The amorphous blends of PVDF/PMMA were studied below T_g and it was found that the relaxations of two polymers occur independently [10]. It was concluded that the blends are heterogeneous under these conditions. The effect of high pressure CO_2 on the miscibility of PVDF/PMMA has been investigated by Walker et al. [11]. It was reported that after exposure to relatively high pressure CO_2 , PVDF crystallizes within the PMMA rich phase without any report on the structure of the crystals. Thermal and mechanical properties of PVDF/PMMA blends were investigated by Jarray et al. without any emphasis on the type of PVDF crystals [12]. Meanwhile, it was reported that PVDF crystals were formed in PMMA matrix and the amorphous phase was rich in PMMA. The miscibility of PVDF and atactic PMMA was studied by Huang et al. [13] using infrared technique and it was found that the miscibility of the blend originates from weak interactions of carbonyl groups of PMMA and hydrogens of PVDF methylene groups.

Lorec et al. [14] reported that with increase in PVDF content the system becomes heterogeneous and the resulting film becomes opaque. The inter-diffusion of PVDF and PMMA was studied and it was found that due to differences in chain stiffness the syndiotactic PMMA diffusion into PVDF matrix was faster than isotactic and atactic PMMA. The effect of PMMA on thermal crystallization of PVDF has been studied [15] and it is observed that these blends rapidly solidify with little or no crystals at all. This is a direct indication of the ability of PMMA inhibiting PVDF from crystallization. The effect of chain morphology (star or linear) on the PMMA/PVDF interaction and rate of crystallization was studied by Fan et al. [16]. It was found that star-PMMA shows lower degree of interaction with PVDF and consequently PVDF is crystallized faster in its corresponding blends.

The solution casting of PVDF/PMMA blends showed that addition of a small amount of PMMA promotes the crystallization of PVDF and increases

the thickness of its lamella [17]. The blends of PVDF and PMMA were solution cast using tetrahydrofuran (THF) as solvent [18]. The conclusive result of this work is that with increase in PMMA concentration in the blend composition the intensity of the FTIR peak at 877 cm^{-1} which corresponds to beta-phase crystal decreases. It is also reported that with increasing PMMA content of the blend both melting temperature and degree of crystallinity decrease. PVDF was melt-blended with PMMA in an extruder and it was observed that in the presence of PMMA the d-spacing of PVDF crystals decreases due to stress resulting from interactions between the components [19]. PVDF was solution blended with PMMA using *N,N*-dimethylformamide (DMF) as solvent and it was reported that smaller crystals and lower crystallinity were observed in PVDF phase [20].

PVDF is also melt blended with many other polymers such as nylons [21-23], polyolefins [24-27], polyethylene oxide [28], polystyrene [29,30], polyethylene terephthalate [31] and PVC [32,33] to impart some desirable properties such as thermal and electrical properties. Due to the fact that these research works were only concerned about the properties mentioned above and did not study crystalline structures in relation to the piezo- or pyroelectric properties of the resulting blends, the details of the reported works are not discussed further.

The technical importance of PVDF lies in its ability to be polarized under a strong electrical field. In the electrical field such as corona, the randomly directed polar crystals of a stretched PVDF film can be aligned in the direction of the applied field. The resulting sample (film or cylinder) can be metal coated and employed as a transducer in many different applications [1].

It is very important to find a way to convert non-polar crystals of PVDF to polar crystals without any stretching. In case the stretching step cannot be avoided then maximization of the β -crystal content of the starting PVDF preform would be the next preferred target. This would help to avoid or minimize the mechanical properties impairment or anisotropy development and makes it possible to prepare different shapes and profiles of piezoelectric or pyroelectric articles. As stated above, blending PVDF with amorphous polymers such as PMMA helps to

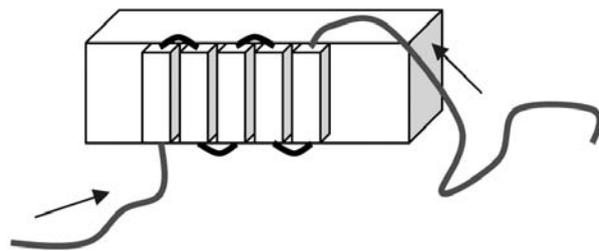


Figure 1. Schematic representation of polymer chain diffusion toward crystal front via reptation.

transform crystalline forms of PVDF [4-6]. This pair of polymers is thermodynamically miscible in molten state [13,18] and an active strong interaction occurs in the amorphous phase. The hydrogen bonding is responsible for this interaction and evolving miscibility. Due to this interaction in the amorphous regions a reduction in the radius of a rheologically confined virtual tube of PMMA is observed [34] which results in PVDF greater resistance towards chain reptation and lower rate of chain segment transfer onto crystal front during crystallization (Figure 1) [7]. This will exert an extra force on the PVDF chain while repeating towards the growth boundary of the crystallites and the PVDF chain is forced to assume its extended *all-trans* conformation which results in formation of β -crystals. The next question would be if other polymers have similar effects.

This work reports the effect of PET and PVC melt blending with PVDF on the morphology of the blends and the crystalline phase of PVDF. The properties of these blends are compared with those of PMMA counterpart. The novelty of the work is maintained on the effect of PET and PVC on formation of beta crystals in PVDF melt. The piezoelectric property (d_{33}) of the non-stretched and polarized films of the blends are determined and reported.

EXPERIMENTAL

Materials

Poly vinylidene fluoride (PVDF) Solef1010 grade from Solvay Co., USA ($M_v = 270,000\text{ g/mol}$, $PDI = 6.007$, $T_g = -30^\circ\text{C}$) [34]). Polymethyl methacrylate (PMMA, 100A grade) containing ethyl acrylate below 5 wt% was purchased from Aldrich (catalog no.

18,224-9, $M_w = 120,000$ g/mol, PDI = 1.05, $T_g = 105^\circ\text{C}$) [34]. Polyvinyl chloride (PVC) of S6058 grade with a K-value = 60 and IV = 580 dL/g was obtained from Bandar Imam Petrochemical Complex (BIPC), Iran, and polyethylene terephthalate (PET, CB-602 grade, IV = 0.8 dL/g, $T_g = 85^\circ\text{C}$ [35]) was purchased from Eastlon Co., Taiwan. All polymers were used without any further treatment.

Procedures

Polymers were melt-blended with PVDF using a Haake internal mixer equipped with a pair of sigma blades at 60 rpm for 5 min. The temperature of blending of PMMA and PET was fixed at 200°C and in order to minimize PVC thermal degradation the temperature of mixing was reduced to 180°C . The blends were taken out of the internal mixer and allowed to cool down to room temperature without any further temperature control.

Thin films (100 microns) of the pure PVDF and its blends were prepared via a laboratory hot press at 200°C . These films were used for crystalline

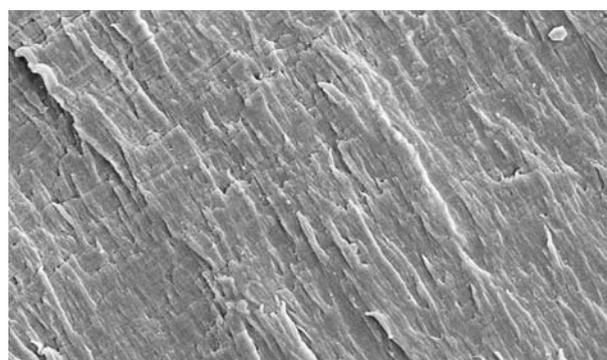
structure characterization on a Bruker FTIR spectrophotometer (model IFS48, Germany). The same hot press was used to prepare disks of 1-mm thickness and 25 mm diameter for crystallography studies on a Siemens diffractometer (model D5000), Germany. The morphology of cryogenically fractured and gold coated surfaces of the blend samples were viewed using a scanning electron microscope, SEM (LEO, model 1455VP, UK).

The polymer thin films were polarized using a laboratory made corona charging oven for 10 min at 103°C under 1.8 MV/cm and after 48 h the piezoelectric coefficient (d_{33}) of the films was measured on an APC Int., Ltd., d_{33} -meter (model 8000, USA) at a working frequency of 1000 Hz.

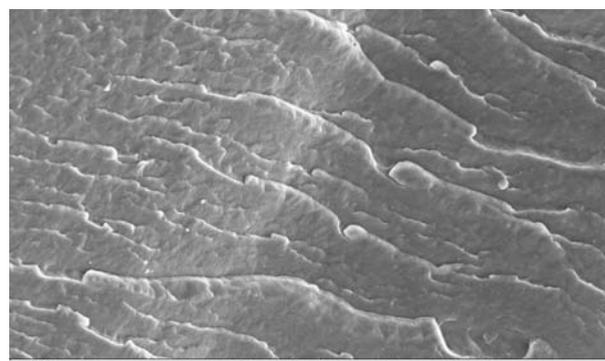
RESULTS AND DISCUSSION

Blends Morphology

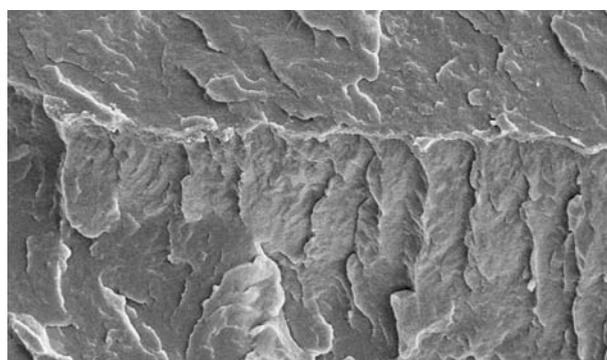
The miscibility and the effect of PMMA on crystalline structure of PVDF are widely studied



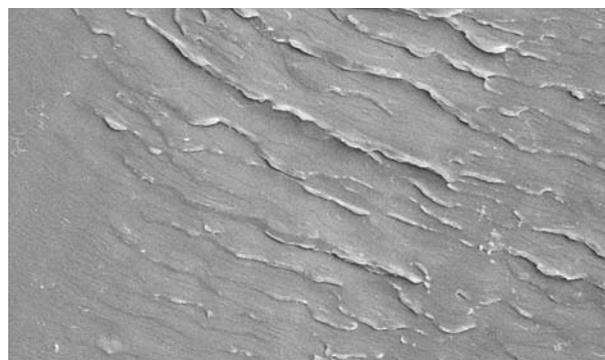
(a)



(c)



(b)



(d)

Figure 2. The SEM micrographs show morphology of polyvinylidene fluoride blends with: (a) 10 wt%, (b) 20 wt%, (c) 30 wt% and (d) 40 wt% of PMMA.

[5,17-20]. Based on literature sources and to retain PVDF in its semi-crystalline form, 10 to 40 wt% PMMA blends of PVDF were prepared as reference blends. The morphology of the prepared PVDF/PMMA blends is shown in Figure 2. According to Shams Es-Haghi et al. [34] the PVDF/PMMA pair is fully miscible and homogeneous blend and a fine morphology are anticipated in the entire range of concentrations. Figure 2, for the given resolution, presents a single-phase morphology for 10 to 40 wt% blends of PMMA in PVDF matrix. However, it is known that this blend is homogenous down to the nanometer scale [34]. Another important factor is that the viscosities of these polymers are close to each other at different mixing temperatures [34]. This also helps to have a fine morphology and intimate mixing of the PVDF and PMMA chains. Once polymer

chains come to such close contacts effective interactions start to play a major role in amorphous molten state and retard the PVDF chain diffusion towards the crystal fronts [6,7,15]. The PVDF chains are forced to assume their most extended conformation (*all-trans*) to balance the forces stemming from crystallization of PVDF and PVDF-PMMA interactions [34] (Figure 1). Solidification of chains with the most extended conformation (*all-trans*) at the interface of crystals and molten phase (crystal front) results in formation of beta crystals. This is a favourable phenomenon which finally produces PVDF spherulites with a spherical symmetry which after being stretched can be converted to electroactive polymer parts.

The polymer PET is not quite amorphous and its crystallinity is moderate with its viscosity also close

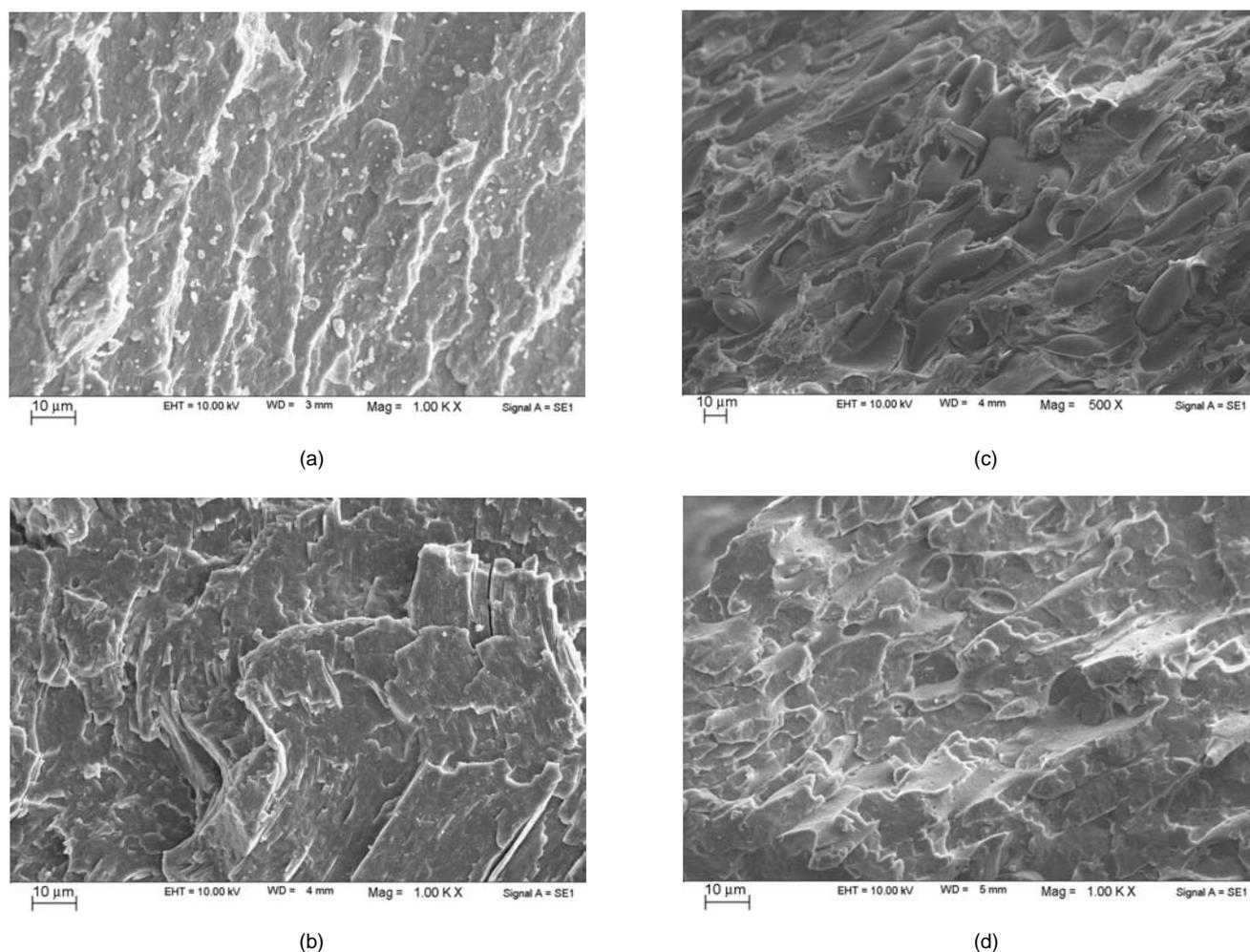
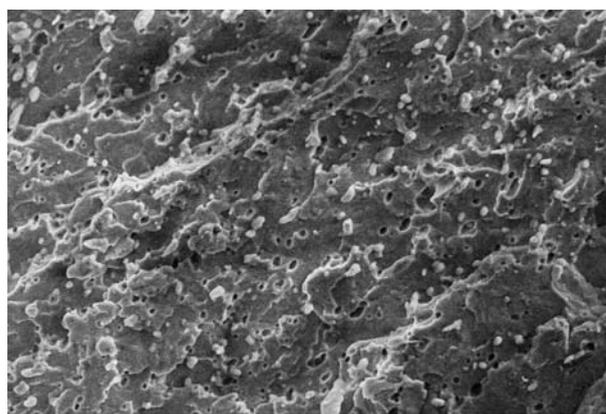


Figure 3. The SEM micrographs show morphology of polyvinylidene fluoride blends with: (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt% of PET.

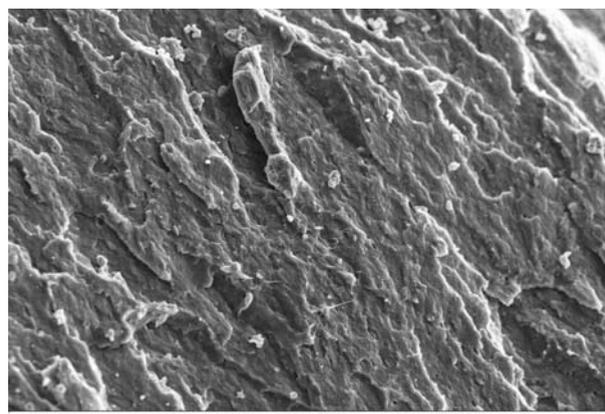
to that of PVDF [36], which makes it possible to simply melt blend PVDF and PET together. In Figure 3, the morphology of four different blend compositions of these two polymers is shown. A two-phase morphology is clearly observable for all compositions of the blends. For this relatively high resolution, it seems that these two polar polymers cannot establish sufficiently strong interactions and phase separation leads into gross domains. Meanwhile, as it is seen in SEM micrographs the interphase adhesion is good enough to keep PET particles unmoved after cryogenic fracture. Almost no void and pull out is observable. Regardless of the crystalline structure of PVDF, it seems quite interesting as far as the mechanical properties of the blends are concerned. This could be considered as a favourable morphology during the stretching of PVDF segments towards induced

oriented beta-crystals. In Figures 3b and 3d with 20 and 40 wt% PET, the morphology of the blends is more homogeneous which seems very favourable for stretching.

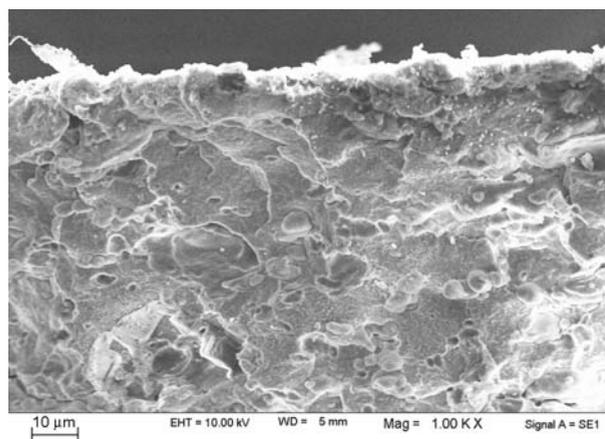
The morphology of the blends of PVDF and PVC blends is very different. Like other blend systems, four samples containing 10 to 40 wt% PVC were prepared and scanned using SEM technique. As seen in Figure 4, many non-homogeneities and voids have appeared in the films of the blends. Therefore, from morphological and mechanical properties points of view, blending PVDF with PVC at high concentration of PVC is not favourable as PVC domains dominate over other polymer when its concentration in the blend increases. It seems that PVC is able to interact with PVDF chain at the inter-phase and provide some solid surfaces for initiation and nucleation of the



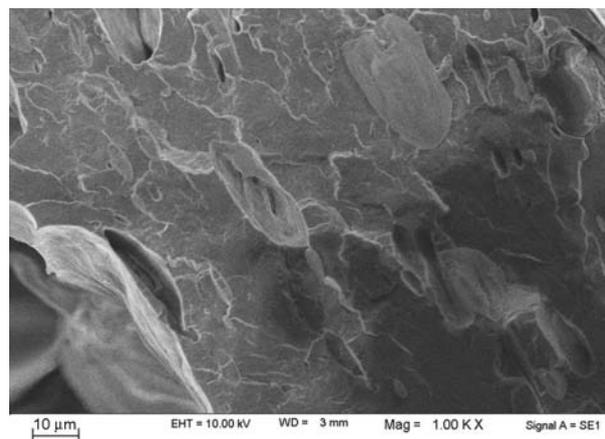
(a)



(c)



(b)



(d)

Figure 4. The SEM micrographs show morphology of polyvinylidene fluoride blends with: (a) 10 wt%, (b) 20 wt%, (c) 30 wt% and (d) 40 wt% of PVC.

Table 1. Solubility parameters for used polymers.

Polymer	PVDF [37]	PMMA [38]	PET [38]	PVC [38]
Solubility parameter (δ), (MPa) ^{0.5}	19.2	19.0	20.5	19.5

PVDF crystals. It is explained in the next section that the inter-phase-based interactions would lead into PVDF crystal transformation. However, it is clear that the blends do not tolerate extensive elongations needed for orientation of beta crystals due to their two phase morphology.

As it is evident in Table 1 [37,39] the solubility parameter of the PVDF and PMMA is very close to each other and a homogeneous morphology is expected for the blends of this polymer pair. This is confirmed by SEM micrographs (Figure 2). Meanwhile, the solubility parameter of PVDF and PET are far enough to generate two-phase morphology (Figure 3). In the case of PVDF/PVC blends the solubility parameters are not very different but the processing conditions especially the temperature (180°C) are not in favour of good mixing and as a result a gross-phase separated morphology develops (Figure 4). A point is constantly persistent in case of all three blends that the interactions between polymeric components, rheological properties and mixing conditions play a major role in morphology development.

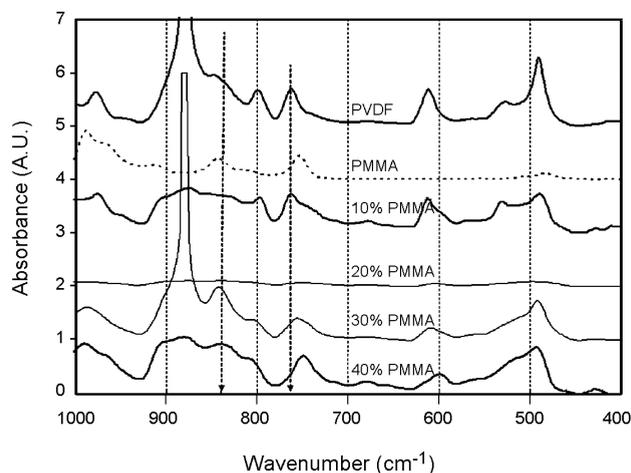
Crystalline Structure Studies

FTIR technique

The technique of FTIR spectroscopy has been successfully used in quantitative determination of different PVDF polymorph contents [39,40]. In this technique different absorption bands are assigned to different crystalline PVDF polymorphs. According to the technique cited above, the peak heights (areas) at 763 cm⁻¹ (α -form) and 840 cm⁻¹ (β -form) were excerpted from the spectra shown in Figures 5 to 7 and using equation 1, the beta content of the blends was calculated.

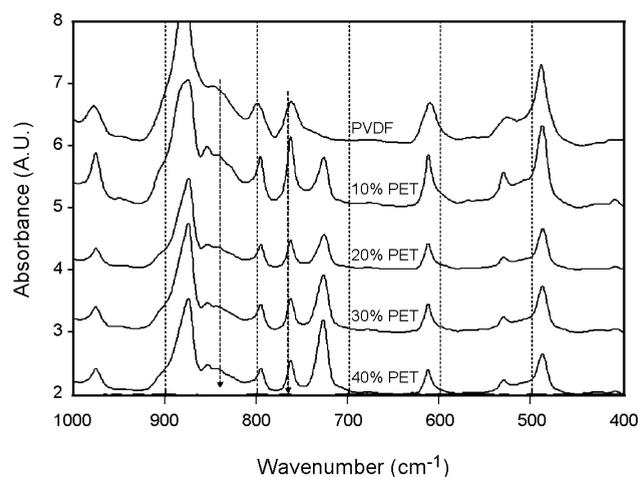
$$F(\beta) = \frac{A_{\beta}}{(1.26)A_{\alpha} + A_{\beta}} \quad (1)$$

where, A_{α} and A_{β} correspond to the height of

**Figure 5.** FTIR Spectra of PVDF and its blend with PMMA.

absorption bands at 763 and 840 cm⁻¹, respectively. The results are reported in Table 2. In Figures 5 to 7, the position of these absorption bands is shown by the arrows. In Figure 5 the spectra of PVDF and its blends with PMMA are shown and the related extracted information is reported in Table 2.

In PMMA spectrum of Figure 5 two absorption peaks are observed in the vicinity of the alpha and beta peaks. These peaks do not make any interference

**Figure 6.** FTIR Spectra of PVDF and its blends with PET.

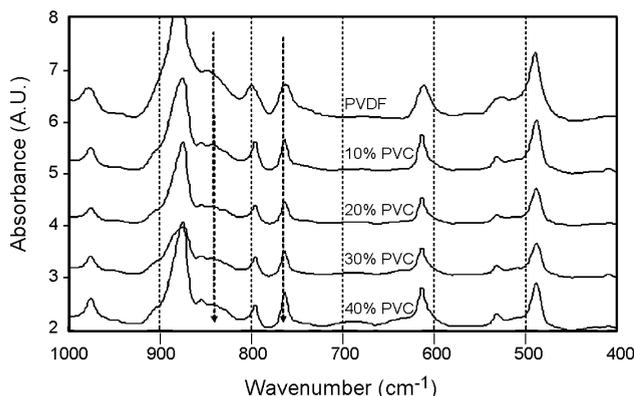


Figure 7. FTIR Spectra of PVDF and its blends with PVC.

and we observe that with increasing PMMA content of the blend, absorption at 763 cm^{-1} sharply decreases whereas the absorption intensity increases at 840 cm^{-1} . As it is evident in Table 2, in case of 10/90 PMMA/PVDF blend a 40% increase in beta-crystals of PVDF is observed. The maximum value for beta content of the blend is obtained for PVDF/PMMA (70/30) blend and a reduction in $F(\beta)$ is observed beyond 30 wt% PMMA. According to literature sources [34] and our result at high PMMA concentrations, PVDF is prohibited to crystallize and an amorphous blend is formed. This shows that the blend containing 30 wt% PMMA is the optimum composition as far as crystal form and electroactive properties are concerned.

Table 2. Spectral parameters, beta-content and d_{33} of pure PVDF and its blends.

PVDF blends	$F(\beta)$ (%)	d_{33}
PVDF	6.45	0
10 wt% PMMA	43.07	0
20 wt% PMMA	57.65	0
30 wt% PMMA	70.83	0
40 wt% PMMA	68.10	0
10 wt% PET	81.60	0
20 wt% PET	79.59	0
30 wt% PET	80.94	0
40 wt% PET	81.11	0
10 wt% PVC	76.60	0
20 wt% PVC	80.36	0
30 wt% PVC	81.19	0
40 wt% PVC	81.97	0

In Table 2 the data of PVDF and PET blends are also included (Figure 6). As it is observed the beta-content of PVDF crystal is highly increased as compared with that of pure PVDF and even its blends with PMMA. In Figure 6 it is observed that no interfering peak is shown by PET and PVDF peaks position do not shift, whereas their relative height and area are changed. By taking experimental errors into account it seems that PET blends contain around 80% beta crystal and it is concluded that the optimum PET concentration is 10%. This is a very important result that at a very low PET concentration a higher PVDF beta crystal content, better mechanical properties and higher piezoelectric properties after stretching are achieved. This result nominates PET as the best candidate for PVDF crystal transformation and further studies.

The beta crystal contents of PVDF/PVC blends are reported in Table 2 (Figure 7). The position and shape of the peaks are changed but their relative height is by no means changed. It is observed that the beta content is highly augmented as compared with that of pure PVDF. In case of these blends the beta crystal content starts from 76% and finally reaches 82% of the total PVDF crystals. It is very important to obtain such a high-beta crystal content using polymer blending technique. However, due to the limitations in the processing conditions of PVC and over 100°C processing temperature difference between this polymer and PVDF along two-phase blend morphology, PVC is not recommended for blending with PVDF.

In the last column of Table 2, the piezoelectric coefficients of PVDF and its blends are reported. The beta crystal content of the PVDF is low and the films are not stretched. Due to the presence of non-oriented beta crystals, a zero piezoelectric coefficient is expected. For the blends, however, a zero piezoelectric coefficient is observed. Here, also the spherical symmetry of the spherulites cancels the electrical activity of the blend. It is already observed that the highly beta crystalline pure PVDF is electrically inactive [41].

WXR D Technique

The crystalline structure of polymers is qualitatively studied using wide angle X-ray diffraction (WXR D) technique. The typical diffraction spectrum of PVDF

and peaks of alpha crystals are assigned elsewhere [1,2,18,40]. The principal peak of α -PVDF appears at $2\theta = 19.5^\circ$. However, for a non-stretched or highly β -containing PVDF, the position of the peaks does not change [41] with respect to those of the α -PVDF, although the shape of the peaks does change. As a matter of fact, the shape and peaks of oriented β -crystals are different from those of α -crystals. In fact oriented β -crystals are responsible for piezoelectric activities that exist only in uni-axial or biaxial stretched PVDF films and profiles which appear at $2\theta = 20.5^\circ$ [41,42]. Meanwhile, incorporation of solid nano-particles (nanotubes and modified nanoclay) in PVDF has recently been confirmed to form oriented beta-crystals proved by WXRd technique [43-45]. In this study a clear change in the WXRd patterns is evident, which proves the qualitative conversion of alpha to beta crystals. The determination of the content of β -crystals of the blends is not possible using WXRd technique. In spite of that, it is useful to follow the changes in WXRd patterns of the blends.

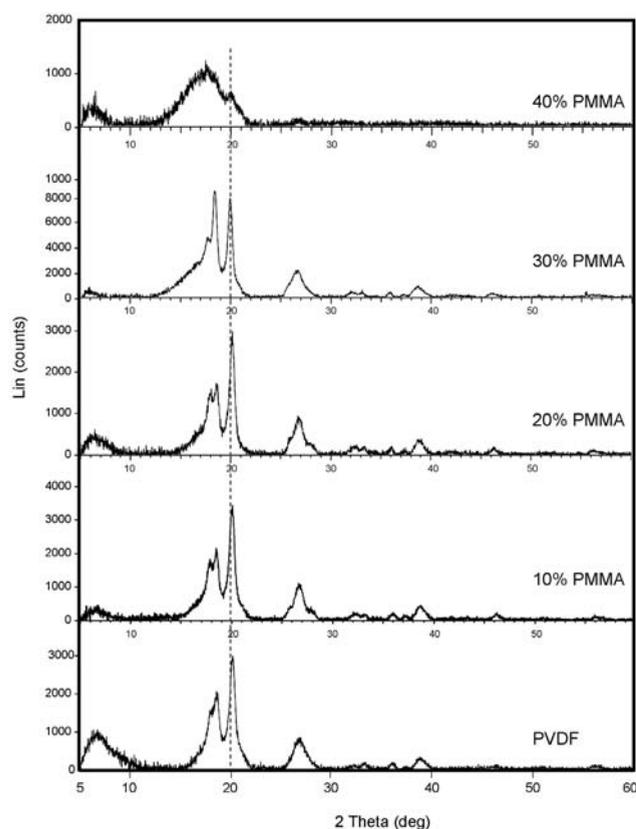


Figure 8. WXRd Spectra of PVDF/PMMA blends with 0, 10, 20, 30 and 40 wt% PMMA.

The WXRd patterns of pure PVDF and its blends with PMMA are compiled in Figure 8. The three peaks of alpha phase are evident at 17.5, 18.3 and ~ 20 degrees. The patterns of 10 wt% and 20 wt% PMMA blends are similar to that of PVDF. Due to the fact that all compositions contain some degrees of beta crystals, a large peak appears around 20° . Upon increasing the PMMA content to 30 wt%, the peak at 18.3 starts to increase in height and beyond this concentration the patterns are similar to amorphous hollow along with an additional shoulder around 20° . This is an indication of losses in PVDF crystallinity at higher PMMA concentrations. It should be noted that the technique of FTIR only quantifies the relative amount of different PVDF polymorphs and does not measure the absolute degree of crystallinity.

One important observation is that the shape of blend's peaks between $2\theta = 15-20^\circ$ is different from those normally observed for pure PVDF films (comparing Figure 8 with Figures 9 and 10). As it is clearly evident, in case of PVDF/PET blends the some

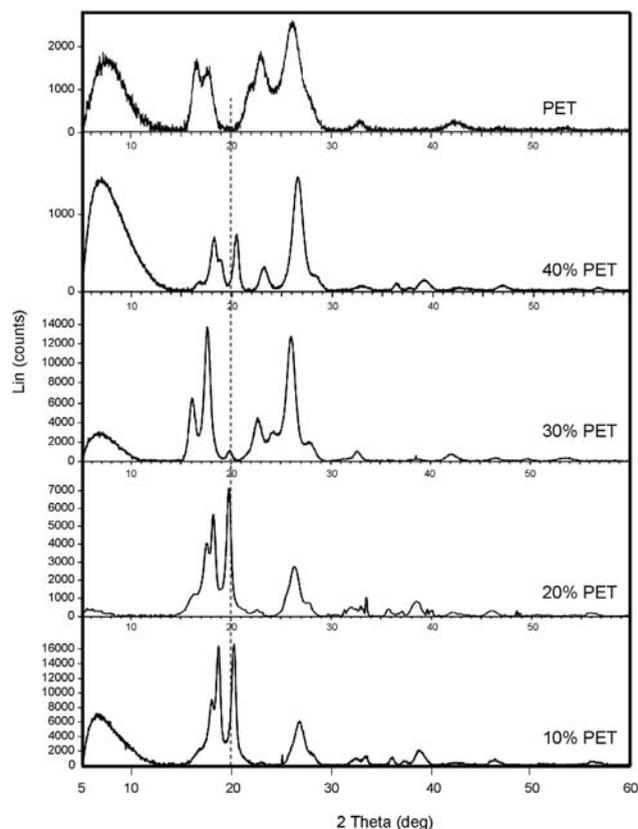


Figure 9. WXRd Spectra of PVDF/PET blends with 10, 20, 30, 40 and 100 wt% PET.

other peaks are observed in Figure 9. This is mainly related to the diffractions of the PET crystals (Figure 9). This makes interpretation of the patterns of these blends impossible. According to Figure 10, only at 10 wt% PET concentration, a peak is detected at 20.5° which confirms the effectiveness of this concentration as optimum level. This is in good agreement with FTIR measurements.

Meanwhile, in the case of PVDF/PVC blends no other peaks appear in the spectrum. The only differences in the shape of the peaks and the relative height at 18.5° are drastic increases with respect to that of 20° . This is interesting that the observed increase in 18.3° peak at low PVC concentration (e.g., 10 wt%) happens for PMMA blends only at 30 wt% of the blend. This simply can be attributed to the amorphous structure of the PVC and interaction of its polar chlorine groups with CH_2 groups of PVDF. This can be simply appreciated on the difference between the electronegativities of the chlorine and fluorine atoms of PVC and PVDF. Therefore, a stronger H-bond between PVC and PVDF is expected as compared to that of PVDF/PMMA and PVDF/PET systems. According to the findings by Pawde et al. [19] this may lead to stress changes during mixing

process which results in increase in d-spacing of the crystals and reduction of diffraction angles. It can be concluded that a very low concentration of PVC (e.g., 2-3 wt%) can be used to induce extensive crystal transformation in PVDF.

CONCLUSION

In this research two polymers, i.e., PET and PVC were melt blended with PVDF to increase the latter's β -crystal content. SEM Micrographs reveal a fine and homogeneous morphology mainly for PVDF/PMMA blends and to a lesser extent for PVDF/PET blends, whereas a two-phase morphology was observed for PVDF/PVC blends. These differences in morphology were accounted for using the differences in solubility parameter of the polymer pairs. PMMA and PVC have similar solubility parameters with that of PVDF, whereas with PET it is basically different. Meanwhile, PMMA and PET blends show fine morphology whereas that of PVC blends are phase separated. According to FTIR spectral analysis pure PVDF contains a very low content of β -crystals. Upon incorporation of PMMA, the β -content of the blend reaches 70% at PMMA concentrations higher than 30 wt%. Meanwhile, the β -crystal content of PVDF/PET and PVDF/PVC blends reach 80% at very low counterpart polymer concentrations (i.e., 10 wt%). These polymers are able to interact with PVDF chains in the amorphous regions and at inter-phases to prohibit PVDF segments diffusion towards the crystallization fronts. This causes a kind of stretching at molecular level which results in the end-to-end orientation of PVDF chains and produces *all-trans* conformations which chiefly crystallize to beta crystals.

This technique shows the development of two new blends for increasing β -crystal content of PVDF. The WXR D spectra also reveal some changes in the crystal structure of PVDF. Both PVC and PMMA are fully amorphous polymers whereas PET is a semi-crystalline polymer. Therefore, PVC and PMMA induce very limited changes in the WXR D of the blends whereas PET changes the diffraction pattern drastically. The piezoelectric coefficient of the blends is zero which is due to the spherical symmetry of the PVDF spherulites.

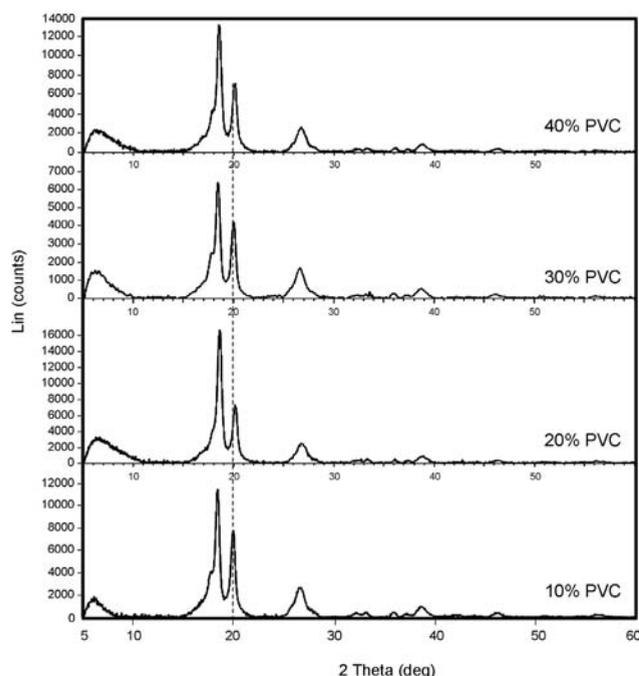


Figure 10. WXR D Spectra of PVDF/PVC blends with 10, 20, 30 and 40wt% PVC.

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