

Structure and piezoelectricity in blends of PVDF films

دراسة التركيب و البيزوكهربائية لأغشية من مخلوطات بوليمر PVDF

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Abstract

The crystalline structure, band vibration and piezoelectric properties of PVDF (neat and blend) oriented in the γ -phase have been investigated utilizing X-ray diffraction, infrared spectroscopy and piezoelectric measurements respectively. The γ -phase and α -phase always exist in the solvent cast films, but with fading orientation caused by the blending content of PMMA and PVAc. Miscibility in the PVDF-PVAc blend was confirmed by vibrational band shift. It was found that the piezoelectricity of PVDF blends might strongly be affected by the final crystal structure of PVDF resulted from blending process and on the nature of blending polymer. However, the magnitude of piezoelectric constant d_{33} was found to be decreasing with the content of blending polymer for both PVDF-PMMA and PVDF-PVAc blends.

الخلاصة

تم دراسة التركيب البلوري، اهتزاز الحزمة، خواص البيزوكهربائية لبوليمر PVDF (النظيف و المخلوط) بطور- كما باستخدام حيود الأشعة السينية، مطيافية الأشعة تحت الحمراء و قياسات البيزوكهربائية على التعاقب. تبين بان الطورين بطور كما و ألفا تتواجد دائما بالأفلام المصبوبة من المذيب، و لكن توجيهها يختفي بسبب محتوى الخلط من بوليمري PMMA و PVAc. تم تثبيت قابلية الامتزاج في مخلوط PVDF-PVAc من خلال ترحزح حزمة الاهتزاز. وجد أن البيزوكهربائية لمخلوطات PVDF تتأثر بشدة بالتركيب البلوري ل PVDF الناتج من عملية الخلط و من طبيعة البوليمر المخلوط. و قد وجد بان مقدار ثابت البيزوكهربائية d_{33} يتناقص و بمقادير متفاوتة مع محتوى الخلط لكلا المخلوطين PVDF-PMMA و PVDF-PVAc.

1. Introduction

Within the last decades, polyvinylidene fluoride (PVDF) has been widely investigated due to its important piezo- and pyroelectric properties. In addition to these properties, PVDF is known for its poly-morphism of five crystalline phases with different conformations α , β , γ , δ and ϵ phases [1].

A rather strong electric moment in the PVDF monomer unit arises because of strong electro-negativity of fluorine atoms compared to those of hydrogen and carbon atoms. Thus each chain possesses a dipole moment perpendicular to the polymer chain [2, 3]. If the polymer chain pack in crystals to form parallel dipoles, the crystal possesses a net dipole moment as in polar form β , γ and δ ; whereas, in antiparallel chain dipoles, the net dipole moment vanishes as in non- polar α and ϵ phases. Amongst others, β -phase in addition to γ -phase contain the largest spontaneous polarization (P) per unit cell [3].

PVDF is known to have various crystalline modifications depending on the type of solvents used in a solvent casting. PVDF has the α modification when cast from acetone or cyclohexanone, the β modification when cast from hexamethyl phosphoramidate, and γ modification when cast from dimethylformamide, dimethylacetamide [4, 5] or dimethylsulfoxide [6].

The interest in PVDF as a piezo- electric material stems from the fact that it can be readily prepared in the form of the flexible sheets. The transducer made from PVDF are characterized by a broad band behavior, high voltage out put, low acoustic impedance, high flexibility and toughness and ease of fabrication [7]. To achieve piezoelectric polymer systems that can be capable of adopting complex shapes, PVDF blending with other polymers, such as polymethylmethacrylate (PMMA) and polyvinyl acetate (PVAc) which posses good mechanical properties, in addition, are inexpensive [8].

It has been apparent that the piezoelectric properties of PVDF may depend in a very complex way, on the molecular and supermolecular structure as well as on the mechanical and electrical properties of the crystalline and amorphous regions [9].

The main objective of this paper is to study the dependence of piezoelectric constant d_{33} for PVDF-PMMA and PVDF- PVAc blends as a function of the structure and coexistence of α -, β - and γ -phases. These should facilitate more understanding about the mechanism of dependence of the piezoelectric properties of PVDF blends on their structures.

2. Experimental

2.1. Materials and films preparation

Pipe fittings produced by George Fischer Company were used as a source of pure PVDF material. These fittings are produced according to ASTM-D3222; sheets of PMMA (Perspex) produced by ICI company were used and commercial PVAc was used too.

Films of neat PVDF and PVDF- PMMA and PVDF-PVAc blends with different weight percentages were cast from 6% by wt. of N, N' dimethyl- formamide (DMF) solutions onto glass slides. The films were dried at $50 \pm 3^\circ\text{C}$ for 3-4 hours.

2.2. Analytical methods

Wide-angle X-ray diffractometry (WXR). The crystalline structure of the films was analyzed using X-ray diffraction spectra obtained from Cu $K\alpha$ radiation on Philip automated system (PW 1832).

Fourier Transform infrared spectro- scopy (FTIR). Infrared spectra were obtained in transmission mode at room temperature on a Shimadzu 8400S FTIR spectrometer from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} .

Piezoelectric measurements. Static piezometer (designed and constructed ingeniously) was used to measure the piezoelectric constant d_{33} of the films at room temperature. By loading the films with known weight perpendicular to the surface of the films (direction 3), the surface charges manifested at the same direction were measured then.

3. Results and discussion

3.1. X-ray diffraction results

3.1.1. Neat Pure PVDF

WXR was performed to identify the crystalline phase of PVDF used in this study. Figure (1) shows the X-ray spectrum of the as-cast PVDF film. The spectrum indicates that the PVDF film of this work is in the γ -phase. Reflections due to α -phase are also present in the structure. γ -phase can be characterized by the major peak [(110) (201)] at $2\theta = 20.2^\circ$ and minor peak (004) at 39.3° which agreed with those reported by Prest et. al. [6] for the γ -phase film cast from dimethylsulfoxide. In

addition, reflections for α -phase can be characterized by (100) and (110) at 18.1° and 18.8° respectively [10].

3.1.2. PVDF blends

Figures (2 and 3) display the WXR D spectra from different weight percentages for blends of PVDF-PMMA, and PVDF-PVAc respectively. The observed spectra, for both blends, signify diminished intensity in the major peaks characterize a semi-crystalline structure in comparison with neat PVDF. In addition that peaks which belonged to α - and γ -phases, peaks with low intensity for β -phase have been appeared. These peaks are (001) and [(020)(310)] at 35.6° and 37° respectively. From these figures (2 and 3), it can be noted that the crystalline content in both types of PVDF blends decrease with increasing concentration of the blending polymers PMMA and PVAc, due to the amorphous nature of the two polymers.

3.2. γ/α ratio

The integrated intensities i.e. the area under the peaks of the α - and γ - phases can be taken as a measure for the degree of crystalline orientation each phase bear subject to the effect of blending content. Figure (4) shows the dependence of normalized γ/α ratio on weight percentages of blending polymer for the two blends. It is clear those blends and for all compositions have normalized γ/α lower than that for neat PVDF.

It can be noted from this figure, that the normalized γ/α for PVDF-PMMA blends drastically decreased with the addition up to 10 wt. % PMMA, then decreased with a slightly manner with higher PMMA content. This result can be explained as follows: When blending PVDF with PMMA by solvent cast method, the crystalline modification is determined wholly by the type of solvent more than of the blending polymer, in determining the final crystalline modification of the PVDF blends [4]. In this work, final modification from DMF solvent, always result in γ -phase, but the existence of a little amount of PMMA in the blend cause an induced stress on the PVDF chains that change the conformation of some segments from γ - to β -modification.

Since, phase transition from γ - to β -phase can be activated by mechanical deformation [11], it will thus lead to a decrease in the normalized γ/α with blending polymer content along with a weak appearance for β -phase. However, blending more PMMA inhabit the rotation of these segments which carry the dipoles in the crystalline regions or at least strongly hindered. Therefore, normalized γ/α will be slightly decreased with PMMA content larger than 10 wt. %.

In the case of PVDF-PVAc blends, the behavior is similar to that for PVDF-PMMA blends but with larger values of normalized γ/α for all compositions. Increasing of γ -phase content with composition may be attributed to the good miscibility in the PVDF-PVAc blends.

3.3. FTIR results

Figs.5, 6 and 7 show the typical IR spectra of neat PVDF, PVDF-PMMA (80-20) wt.% and PVDF-PVAc (80-20) wt.% blend films respectively. Though the IR spectrum of the γ -phase is very similar to that of β -phase [12], the γ -phase has the characteristic bands at 776 and 430 cm^{-1} and does not has the β characteristic band at 467 cm^{-1} [4]. In addition, the bands, such as 530 , 765 and 795 cm^{-1} are considered as the α -phase [13]. In fact, there appears a strong band at 601 cm^{-1} due to the noncrystalline part of PVDF [14] indicated by the arrow in Figures (5 - 7). The IR spectrum (see Fig.5) shows that neat PVDF is composed mainly of γ -phase.

Even though the number of specific interactions in the polymer blend is much less than in solvent-solvent or polymer-solvent mixture system, the nature of interactions such as hydrogen bonding in the polymer blends can nevertheless be identified by IR spectroscopy. These specific intera-

molecular interactions in the binary mixture result in the shift of IR absorption bands and/or new IR absorption peaks. PVDF-PMMA blends are known to be miscible in the amorphous state over the whole composition range by various methods [4], but when cast from DMF they are totally immiscible as indicated by both the NMR and DSC techniques [15]. Furthermore the addition of PMMA does not affect the final crystalline phase of PVDF in PVDF-PMMA blends. A glimpse on Figure (6) confirms that PVDF-PMMA blend remain in the γ -phase.

Inspection of absorption bands in the IR spectra of PVDF-PVAc, figure (7), reveal that there is a shift in position of the band at 610 cm^{-1} as compared with 601 cm^{-1} for neat PVDF (not observed in PVDF-PMMA blends). This shift indicates the existence of an interaction between PVDF and PVAc, and it may be attributed to the interaction between the acidic protons of the PVDF and the basic carbonyl groups for PVAc, which is responsible for the miscibility of PVDF-PVAc blends [15, 16].

3.4. Piezoelectric constant

Piezoelectric constant d_{33} of neat and blended PVDF, are shown in Figure (8). Some remarks are drawn from this figure. The neat PVDF film has $d_{33} = 4\text{ pC/N}$, identical to the value reported by Gerliezy et al [17]. As PVDF is blended with PMMA or PVAc, the general trend of the d_{33} for the blends appear to be decreasing with the content, and the decrease in PVDF-PMMA blends is more pronounced than PVDF-PVAc blends having same different weight percentages of PMMA and PVAc.

Many factors affect the value of measured d_{33} for PVDF blends. In the case of PVDF-PMMA, the blend consists from neat PVDF crystals (polar and nonpolar) which grow within an amorphous matrix, containing both PVDF and PMMA [9]. The increase of PMMA concentration in the blend lead to increase in the amorphous regions, and consequently, d_{33} is decrease with it. In addition, d_{33} does not depend only on the concentration of polar crystals but is strongly governed by the electrical and mechanical properties of the amorphous phase and crystalline regions [18]. This is why nonlinearity is observed between d_{33} and blending content, see Figure (8).

Also, it can be noted that d_{33} for PVDF-PVAc is decreased with concentration of PVAc, but with values smaller than that for PVDF-PMMA for all blending content. This behavior can be attributed to two factors: firstly, the larger relative γ -phase content in PVDF-PVAc blends by comparison with that for PVDF-PMMA for all blending content. Secondly, PVAc has a weak piezoelectric activity [19], that may be contribute to the piezoelectric response in the blend.

4. Conclusions

The main conclusions that can be drawn from this investigation: γ -phase always exist in the neat PVDF and in the blends PVDF-PMMA and PVAc cast from DMF solvent.

In contrast to PMMA, PVAc show a tendency to be miscible with PVDF.

The piezoelectric activity of PVDF blends is strongly dependent on the concentration of polar crystals and on the nature and content of the blending polymers. The normalized γ/α ratio in PVDF blends is decreasing with blending content, but with a value for PVDF-PVAc larger than that for PVDF-PMMA at a certain blending content. These results reveal that the crystalline phase of PVDF could be controlled by blending with amorphous polymers having certain interaction with PVDF. This is demonstrated by recognizing different d_{33} values not only for PMMA or PVAc but also with their blending content.

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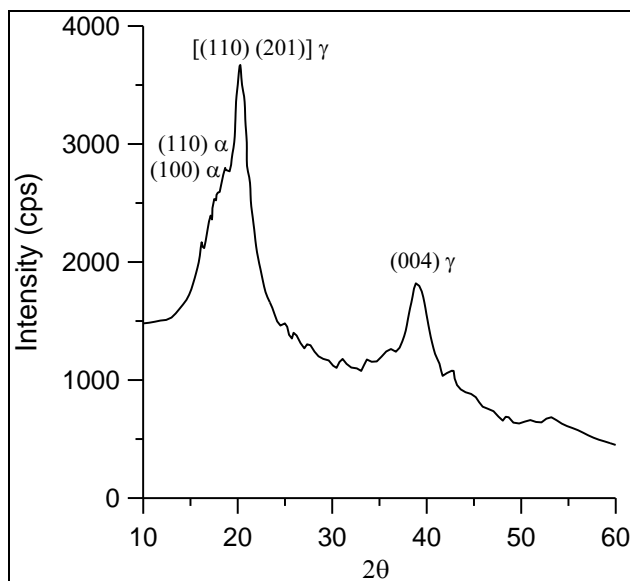


Fig (1) WXR D spectra of as-cast PVDF.

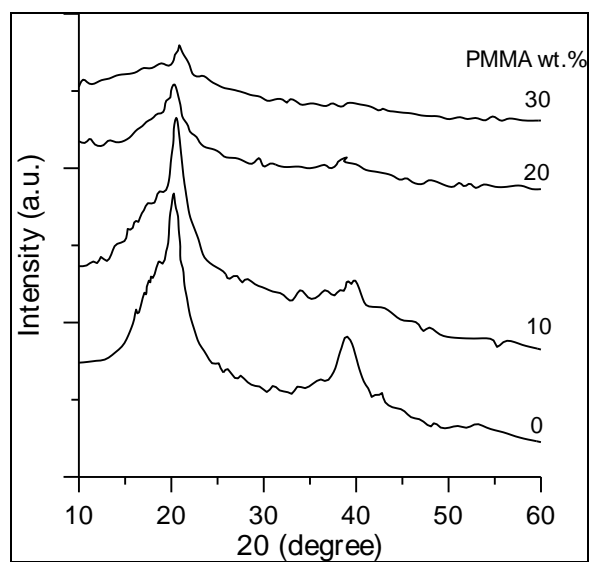


Fig (2) WXR D spectra for different weight percentages of PVDF-PMMA blends.

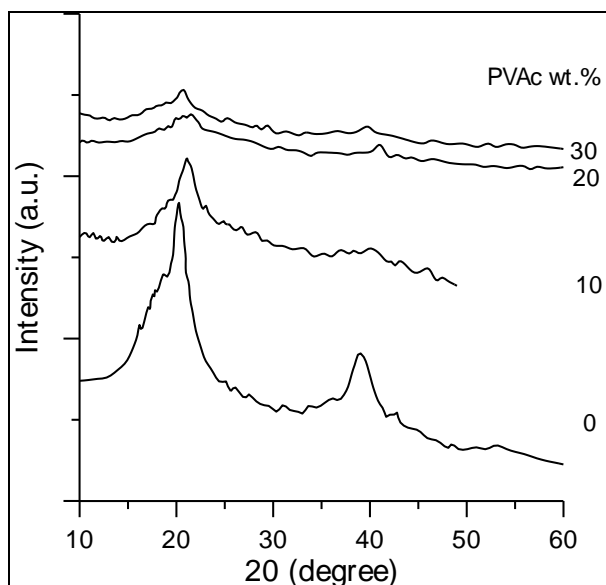


Fig (3) WXR D spectra for different weight percentages of PVDF-PVAc blends.

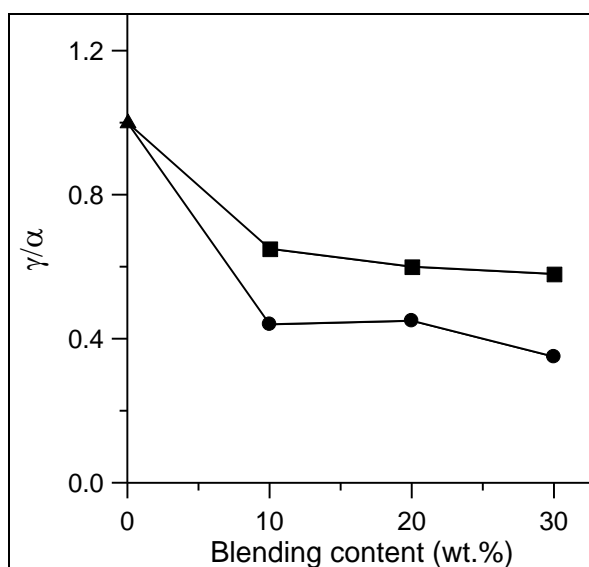


Fig (4) Normalized β/α ratio for PVDF-PMMA (●) and PVDF-PVAc (■) versus blending content.

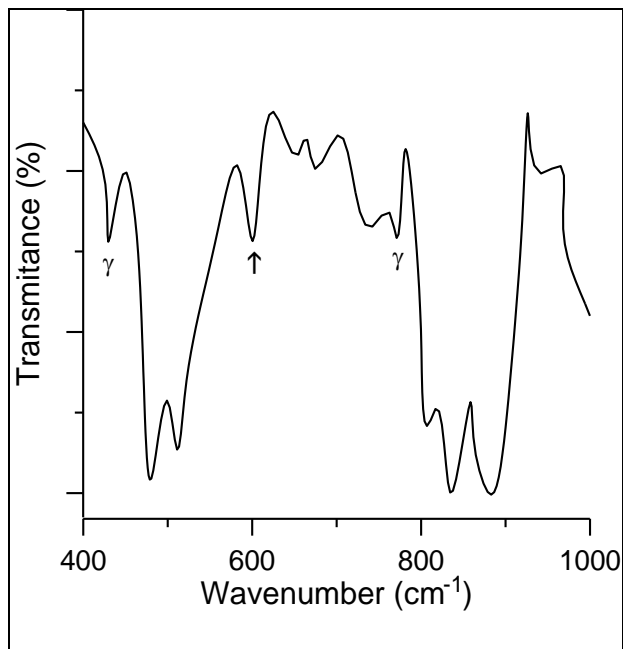


Fig (5) IR spectrum of DMF cast PVDF.

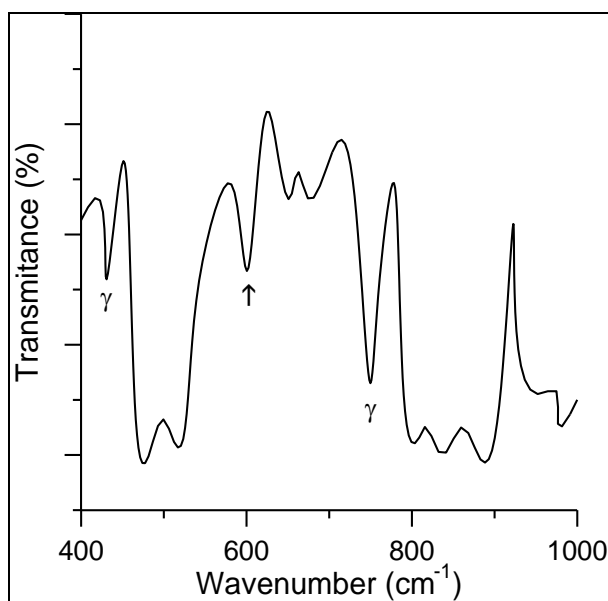


Fig (6) IR spectrum of PVDF-PMMA (80-20) wt.% blend.

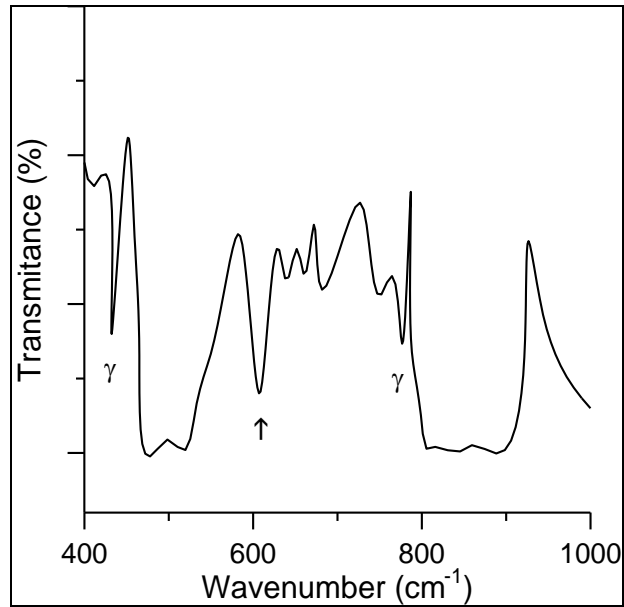


Fig (7) IR spectrum of PVDF-PVAc (80-20) wt.% blend.

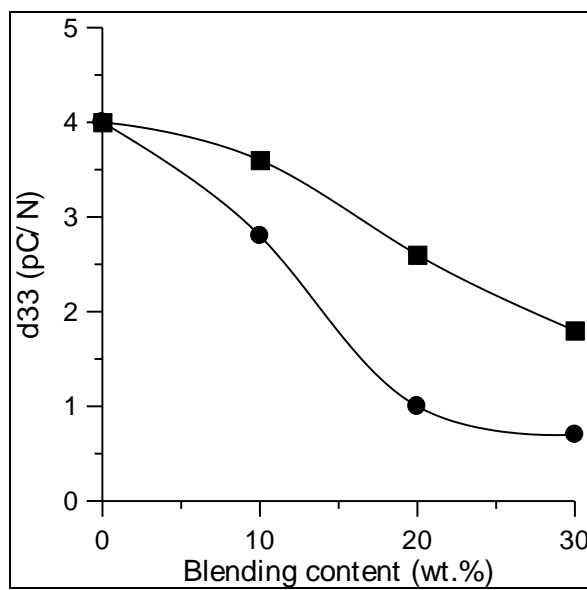


Fig (8) Piezoelectric constant d_{33} for PMMA (●) and PVAc (■)-PVDF films with blending content.