

The effects of quenching on the phase structure of vinylidene fluoride segments in PVDF-HFP copolymer and PVDF-HFP/PMMA blends

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The phase characteristics of vinylidene fluoride (VDF) segments in vinylidene fluoride (VDF) and hexafluoropropylene (HFP) copolymer (PVDF-HFP) under different quenching temperature were investigated by infrared spectroscopy (FTIR) and X-ray diffraction (XRD) measurements. It was found that the α and β crystalline phases of VDF segments formed in PVDF-HFP as those in pure PVDF. Compared with pure PVDF, HFP segments affected the β phase formation obviously. Increasing of quenching temperature would decrease the fraction of β phase in the quenched PVDF-HFP films, and the films thicker than $8\ \mu\text{m}$ were not in favor of the β phase transformation. Blending PVDF-HFP with small amounts of PMMA ($\leq 10\ \text{wt}\%$) yielded great effects on the crystal phase of VDF segments. But higher blending degree of PMMA couldn't increase the formation of β phase further. © 2006 Springer Science + Business Media, Inc.

1. Introduction

Having extraordinary mechanical properties and complicated polymorphism, poly(vinylidene fluoride) (PVDF) has been well known since the 1960 s. There were at least four different crystallines including α , β , γ and δ form in PVDF, which could transform from one to the other under certain conditions [1, 2]. Among the four crystalline forms, the most common polymorph was α form, which could be produced during crystallization from the melt. β form was the most important polymorph with outstanding piezoelectric and pyroelectric properties. The β crystal in PVDF could be obtained from non-polar α modification by various processes such as mechanical deformation [3, 4], poling under large electric fields [5], crystallization from the melt under high pressure [6, 7] or very high cooling rates [8, 9]. The crystal phase of PVDF was also very sensitive to the blending with PMMA and the conformation of PVDF chains in the crystal phase depended on the composition and on the thermal history of the mixture, e.g., the β phase crystals can be obtained easily from the melt of PVDF-PMMA blends under ultra-high rate quenching [10]. The two polymers were also found to be compatible in the amorphous state, and the miscibility of the two polymers has been ascertained by various methods [11–14]. The major driving force for the com-

patibility resulted from hydrogen bonding involving the carbonyl groups of PMMA and the CH_2 groups of PVDF [15].

Copolymerization was an effective route to control the crystalline and improve the processibility of PVDF. Using PVDF as the main constituent blocks, the copolymer (PVDF-HFP) of vinylidene fluoride (VDF) and hexafluoropropylene (HFP) was contributing one of the important fluorine-containing polymer candidates in many fields. Especially, the role of PVDF-HFP in membranes, separators between the electrodes of batteries and gel electrolytes was generating great interests from academic and application aspects [16, 17]. With incorporating HFP units, the crystallinity of VDF segments was reduced greatly [18] and the flexibility was enhanced obviously as compared to net PVDF. At the same time, the remaining crystallinity devoted to the mechanical stability and the structural integrity of this copolymer. Currently, the crystallinity or polymorphism in PVDF-HFP has rarely been mentioned except investigating the effect of polar medium on γ form conformation during preparing the PVDF-HFP-based gel electrolytes [19].

Concerning the control of crystallization behavior of the PVDF-HFP copolymer is essential for preparing it

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into specific material, the polymorphism of VDF segments in PVDF-HFP copolymer and PVDF-HFP/PMMA blends will be studied in the present research.

2. Experimental

2.1. Materials and preparation of the samples

The PVDF-HFP ($M_w = 4 \times 10^5$) was purchased from Aldrich Co. Injection grade PMMA was kindly provided by LG Co. of Korea. PVDF-HFP copolymer and PVDF-HFP/PMMA blends were prepared into 2–13 μm thick films by casting their acetone solution (concentration from 1.5 to 20 wt%) onto a glass substrate and evaporating solvent at 50°C. If no special explanation, the films used in this paper were prepared from 3 wt% PVDF-HFP solution and the thickness was about 4 μm . The films were put onto thin mica sheets and melted at 190°C for 10 min and then plunged quickly into the water with temperature of 0 to 70°C (If no special explanation, the quenching temperature is at 0°C). The quenched films were then annealed at 100°C for 24 h.

2.2. Sample characterization

FTIR spectroscopy was measured with an IR spectrometer (Bruker, vector 22) at a 1 cm^{-1} resolution and in the 400–4000 cm^{-1} wave number range. The fraction of α and β phase can be calculated using the procedure explained by Osaki and Ishida [20]. For a film sample with a thickness of d and an average total monomer concentration C using IR absorption bands, the following relation is held for each phase:

$$A_i = \log \frac{I_0}{I} = K_i C X_i d \quad (1)$$

where A_i is the absorbance of i phase, I, I^0 are the incident and transmitted radiation intensities, K_i is the absorption coefficient at corresponding wave number for i phase ($K_\alpha = 10.0 \times 10^3$ and $K_\beta = 8.1 \times 10^3 \text{ cm}^2/\text{mole}$), X_i is the degree of crystallinity of i phase. Thus, for a system containing α and β phase the relative fraction of the β phase, $F(\beta)$, can be calculated by the following equation [20].

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{0.81A_\alpha + A_\beta} \quad (2)$$

where X_α and X_β are the degree of crystallinity of the α and β phases, A_α and A_β are the absorbances of α and β phases at 530 and 510 cm^{-1} , respectively.

X-ray diffraction (XRD) measurements were performed on an X-ray Diffractometer (Rigaku D/max-RA) with Cu K_α radiation ($\lambda = 0.154 \text{ nm}$), and a scanning rate of 2°/min.

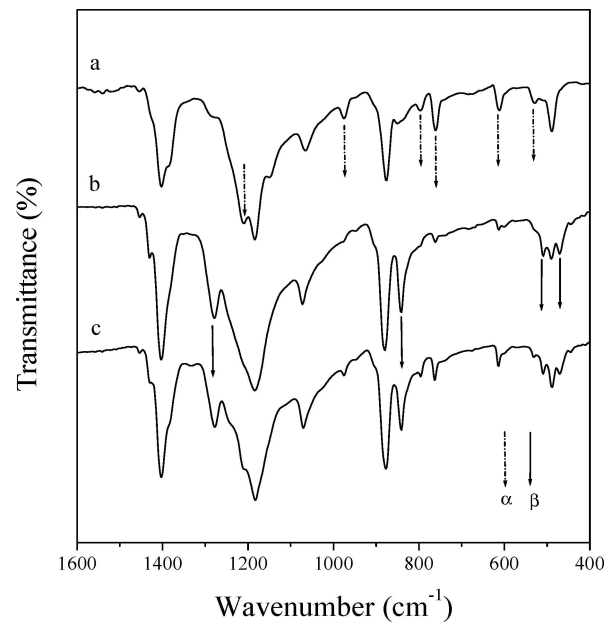


Figure 1 FTIR spectra of (a) the unquenched and (b) quenched PVDF-HFP, and (c) quenched pure PVDF.

3. Results and discussion

3.1. Effect of quenching temperature and film thickness

The FTIR spectra of the α and β phases of PVDF have been investigated extensively [10, 21–26]. It is known that the vibrational bands at 530, 615, 766, 795, 855, 976, 1214 and 1383 cm^{-1} referred to the α phase, while the bands at 470, 510, 600, 840, 1279 and 1431 cm^{-1} corresponded to the β phase [24]. The FTIR spectra of PVDF-HFP was shown in Fig. 1a and b, the bands corresponded to the α phase of PVDF appeared at 530, 615, 765, 795, 975, 1212 and 1384 cm^{-1} in the unquenched PVDF-HFP films, while the bands corresponded to the β phase of PVDF appeared at 470, 509, 840 and 1278 cm^{-1} in the quenched samples as shown in Fig. 1c. These results suggested that the α and β phases of PVDF were also existed in PVDF-HFP copolymer, and these phases were formed by the VDF segments in the copolymer.

As for the FTIR spectra of quenched PVDF-HFP and PVDF films shown in Fig. 1b and c, the α characteristic phase bands of quenched PVDF-HFP nearly disappeared with β phase characteristic bands appearing at 470, 509, 840 and 1278 cm^{-1} , while the α and β phases characteristic bands of pure PVDF coexisted in the samples. These results suggested that the α phase of PVDF-HFP could be transformed into β phase on quenching, and the incorporation of HFP with VDF would promote the formation of β phase.

The dependences of the α to β phase transformation on the quenching temperature were shown in Fig. 2. When the quenching temperature was below 30°C, the samples of PVDF-HFP exhibited mainly the β phase. When the quenching temperature approached to 40°C, the bands appearing at 530, 615, 765, 795, 975 and 1214 cm^{-1} , also at 510, 840, 1280 cm^{-1} indicated the co-existence of α

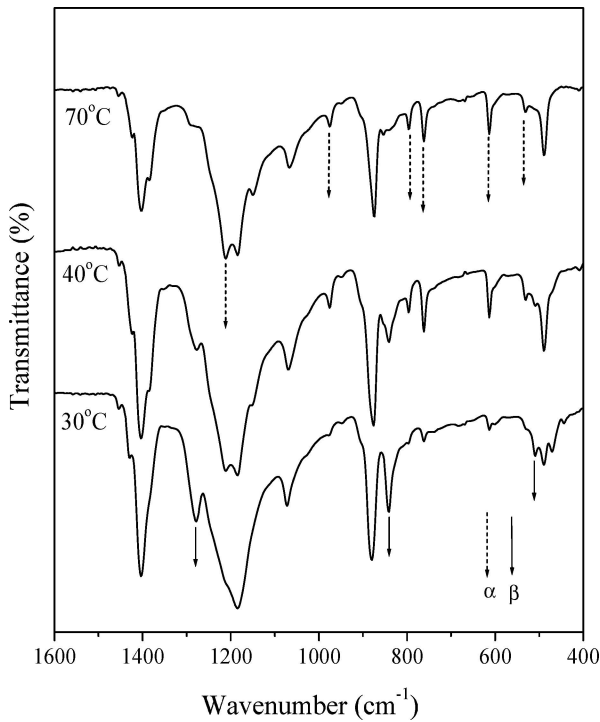


Figure 2 FTIR spectra of PVDF-HFP films quenched at various temperatures.

and β phases. When the quenching temperature was near 70°C , the bands of the β phase at 510 , 840 and 1280 cm^{-1} almost disappeared with the α phase characteristic bands mainly exhibiting. Fig. 3 showed the dependence of the fraction of β phase ($F(\beta)$) on the quenching temperature. The $F(\beta)$ value decreased from 87 to 5% with the quenching temperature increasing from 0 to 70°C . The critical quenching temperature of the β phase formation was near 40°C , which was approaching to the critical quenching temperature of pure PVDF [9]. Similarly, it could be suggested that the growth rates of the α and β phases in PVDF-HFP upon quenching were also quite different below and above the critical quenching temperature. When the quenching temperature was below the critical value, the growth rate of the β phase was much higher than that of the α phase. On the other hand, the growth rate of the α phase was higher than that of the β phase when above the critical value.

The phase structure of quenched PVDF-HFP samples also depended on the film thickness as shown in Fig. 4. It was indicated that the relative content of the β phase was higher than that of the α phase when the film thickness was below $8\ \mu\text{m}$. But when the film was thicker than that, the α phase would become the predominant crystals in the films. The reason might be that the quenching temperature in the thicker films was quite different on the surface and in the inner of the films during quenching from the melt. The quenching temperature in the inner of the films would be higher than that on the surface, which would result in the α crystals in the bulk and the β crystals on the surface. With the increasing of the film thickness, the α phase

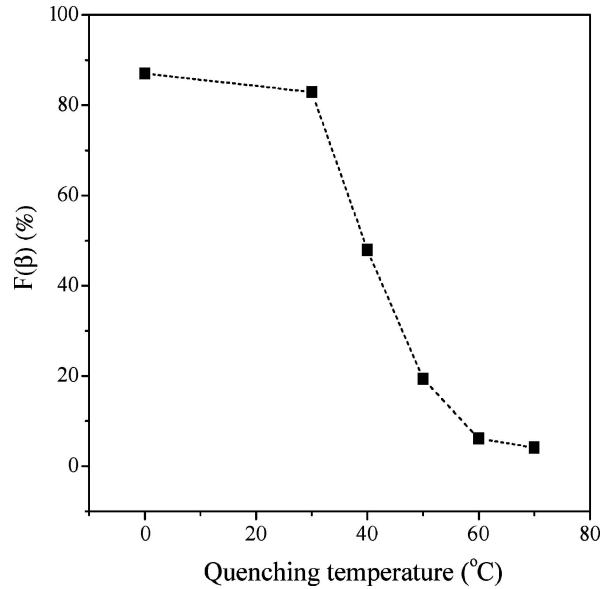


Figure 3 Dependence of relative amount of β phase, $F(\beta)$, on quenching temperatures.

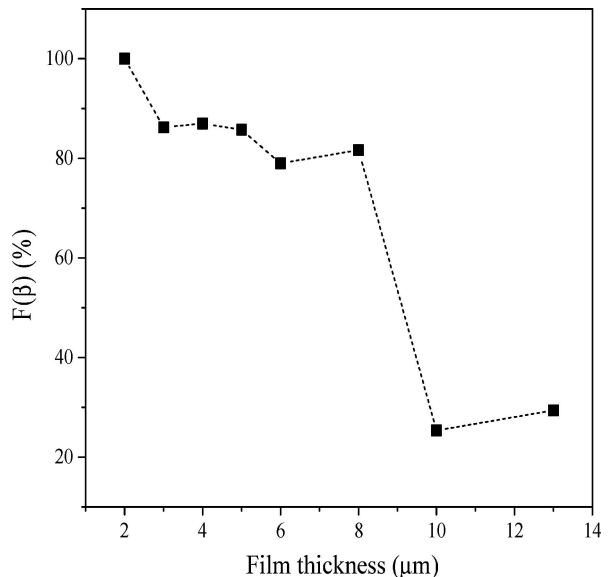


Figure 4 Dependence of relative amount of β phase, $F(\beta)$, on film thickness.

would become the predominant results with little amount of β phase on the surface.

3.2. Effect of blending with PMMA

FT-IR spectra of unquenched and quenched PMMA/PVDF-HFP blends of various compositions were shown in Fig. 5. The unquenched samples only showed the α characteristic bands of VDF segments at 530 , 615 and 795 cm^{-1} . The quenched samples with PMMA content in $10\text{ wt}\%$ exhibited the characteristics of VDF segments in β phase at 470 , 510 , 840 and 1280 cm^{-1} . When PMMA content in the blends was $20\text{ wt}\%$, there were no obvious characteristic bands of β phase, but several weak characteristic bands of

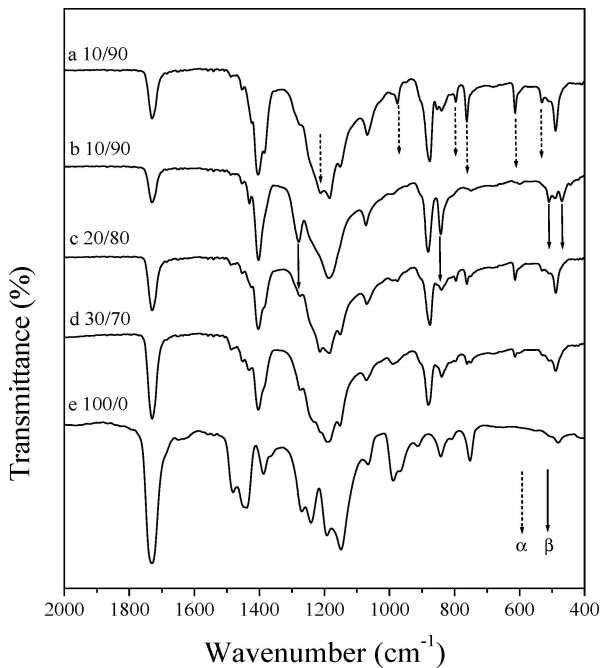


Figure 5 FTIR spectra of unquenched (a) and quenched (b, c, d, e) PMMA/PVDF-HFP blend films.

α phase appeared at 530, 615, 762 and 795 cm^{-1} . When PMMA content in the blend was further lifted to 30 wt%, the characteristic bands of α phase became very weak. The reason for these results may be that quenching can lead to the nucleation of β phase at lower temperature, and the β phase will grow further in the annealing stage. For the blends with PMMA content ≥ 20 wt%, however, the imperfectness of crystallinity in the as-quenched samples, annealing will induce further crystallization of VDF segments at 100°C, including both nucleation and growth. Hence in this case the blends exhibited an increase in the α phase though it was very weak.

In order to further reveal the phase structure of VDF segments in PVDF-HFP copolymer and PVDF-HFP/PMMA blends under quenching and subsequent annealing, X-ray analysis was performed.

The XRD pattern of PVDF-HFP copolymer was shown in Fig. 6, two peaks at $2\theta = 17.8$ and 19.7° were observed in the unquenched PVDF-HFP films, which corresponded to the reflections of α (100), (110) crystal respectively. After the copolymer was quenched at 0°C , the reflection peaks at $2\theta = 19.7^\circ$ disappeared completely, only a strong peak at $2\theta = 20.5^\circ$ was observed presenting the reflection of β (110) and (200) crystal [27] as shown in Fig. 6b. Consistent with the findings in FT-IR spectra, XRD results indicated that the β phase could be transformed effectively by quenching.

The XRD patterns of unquenched and quenched PMMA/PVDF-HFP blends were shown in Fig. 7. Similar to the copolymers, two peaks were found at $2\theta = 17.9$ and 19.7° in the unquenched blend films, which represents the (100) and (110) reflections of the α phase.

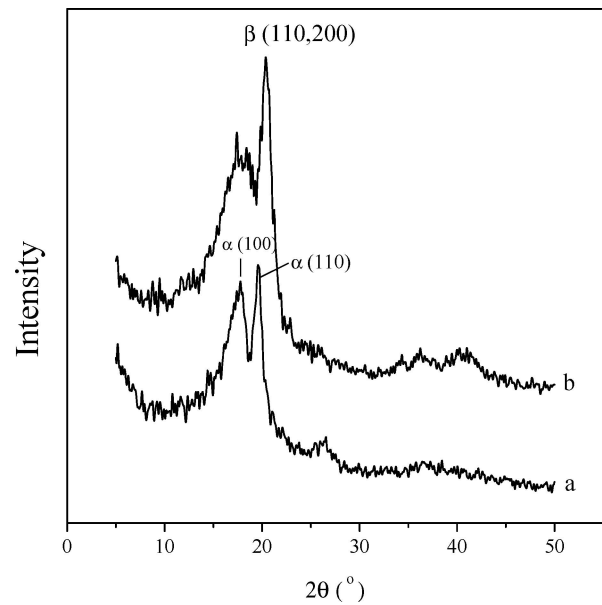


Figure 6 X-ray diffraction patterns of (a) unquenched and (b) quenched PVDF-HFP films.

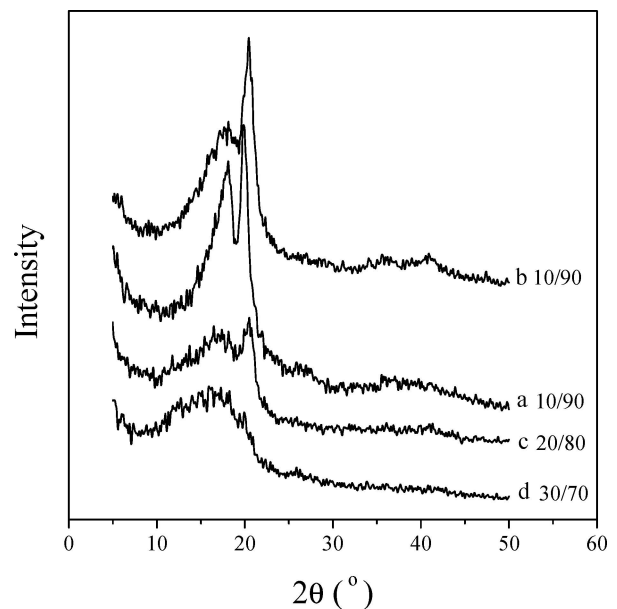


Figure 7 X-ray diffraction patterns of unquenched (a) and quenched (b, c, d) PMMA/PVDF-HFP blend films.

After quenched, a strong peak which represented the characteristic reflection of β (110) and (200) crystal planes appeared at $2\theta = 20.5^\circ$. When the content of PMMA was 20 wt%, the reflection of β crystal planes became weak and another relative weaker reflection peak of α phase appeared at $2\theta = 17.6^\circ$ at the same time. When the content of PMMA was 30 wt% or above, the absence of reflection peaks at $2\theta = 17.6$ and 20.5° indicated the VDF segments in blends turned to the amorphous state. These observations also coincided with those in FT-IR measurements.

4. Conclusions

Through the investigation of the phase structure of VDF segments in the PVDF-HFP copolymer and PVDF-HFP/PMMA blends under quenching and annealing process, it has been approved that the β phase, rather than the total crystallinity, of VDF segments in copolymer could be enhanced by the HFP segments in comparison with those in pure PVDF. The phase structure of the films was greatly influenced by quenching temperature and the film thickness. The $F(\beta)$ value of the quenched PVDF-HFP films decreased from 87 to 5% with the quenching temperature increasing from 0 to 70°C for the film with thickness of 4 μm . The critical quenching temperature of the β phase transformation was around 40°C. The films thicker than 8 μm didn't tend to the β phase transformation. Blending PVDF-HFP with small amounts of PMMA (≤ 10 wt%) would promote the growth of β phase.

Acknowledgments

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