Desalination and Water Treatment
www.deswater.com

34 (2011) 184–189
October

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doi: 10/5004/dwt.2011.2791

Properties and crystallization behavior of poly (vinylidene fluoride) (PVDF)/thermoplastic polyurethane elastomer (TPU) blends

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Received 3 September 2010; Accepted 3 January 2011

ABSTRACT

A series of poly (vinylidene fluoride) (PVDF)/thermoplastic polyurethane elastomer (TPU) blends were prepared with various mass ratios via melt blending. The miscibility and crystallization behavior of blends were characterized by scanning electron microscopy (SEM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), mechanical tests, wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). According to cross section morphological analysis, when the content of TPU was less than 25 wt%, PVDF appeared as a continuous phase while TPU appeared as a dispersed phase. The blend was a partially miscible system. With the further increase of TPU content, the presence of distinguishable boundaries at the polymer interfaces indicated that the PVDF/TPU blends were the immiscible systems. In addition, when the TPU content reached 50 wt%, the blend system displayed the lowest mechanical properties, which was attributed to the poor miscibility of the polymer blend. On the other hand, the samples presented predominantly α phase regardless of TPU content in the blends. Compared with neat PVDF, the melting and crystallization temperature of PVDF in the blends slightly decreased. It indicated no obvious interaction between the two polymers.

Keywords: Poly (vinylidene fluoride) (PVDF); Thermoplastic polyurethane elastomer (TPU); Miscibility; Crystallization; Blends; WAXD

1. Introduction

Poly (vinylidene fluoride) (PVDF) is widely used in microfiltration (MF) and ultrafiltration (UF) due to its excellent chemical properties, oxidation resistance and good thermal stability [1]. However, the high crystallinity and low surface tension properties limit its applications in many fields such as wastewater treatment, biomedical technology.

Blending is considered as the most effective and convenient way to enhance polymer materials and develop materials with desired performance [2]. Moreover, PVDF is highly miscible with oxygen-containing polymers, which is related to the interaction between the fluorine atoms and carbonyl groups of the partner polymer [3]. To improve the toughness of PVDF, thermoplastic polyurethane elastomer (TPU) is considered as a modifier to blend with PVDF, which is due to its excellent mechanical strengths, toughness and wear and low-temperature elasticities [4,5]. These unique properties of TPU are attributed to the unique molecular structure of the polymer chains. TPU is linear segmented block copolymers having soft segments and hard segments. The soft segments consist of the long flexible polyether or polyester chains which interconnect two hard segments. The hard segments are connected with each other by

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Presented at the AMS6/IMSTEC10, The 6th conference of the Aseanian Membrane Society in conjunction with the 7th International Membrane Science and Technology Conference, Sydney Australia, November 22–26, 2010

intermolecular hydrogen bonds and form physical crosslinks, while the soft segments form an elastomer matrix which accounts for the elastic properties of TPU. Thus, the addition of TPU is expected to enhance the toughness of PVDF. However, the effect of TPU on miscibility and crystallization behavior of PVDF/TPU blends has been rarely investigated.

In this work, a series of PVDF/TPU blends were prepared with various mass ratios via melt blending. The miscibility of blends was characterized by scanning electron microscopy (SEM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and mechanical tests. Simultaneously, the crystallization behavior of blends was investigated by wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

PVDF (Kynar K 760, $\bar{M}_w$ = 371,000) was supplied by Elf Atochem of North America. TPU (IROGRAN A80P4699) obtained from Huntsman was an amorphous polymer.

2.2. Melt blending and sample preparation

The melt blending of PVDF/TPU was carried out with a torque rheogoniometer (XSS-300, Shanghai Kechuang Machinery Co., Ltd, China) at 180°C and 50 rpm for 8 min. A series of the blends with various mass ratios of PVDF containing 100%, 75%, 50%, 25%, 0% (*w/w*) were prepared. Then, the blend samples were obtained by compression molding at 180°C with platen vulcanizing press for 15 min, and cooled freely at room temperature still under pressure (10 MPa). Thus the flat sheet samples (about 0.3 mm) with smooth surfaces were obtained. Afterwards, a series of measurements were performed.

2.3. Characterization techniques

Scanning electron microscopy micrographs of the cross sections of various blends coated with gold were obtained by a JSM-5900 instrument (JEOL, Japan) with an accelerating voltage of 15 kV. The cross sections were freeze-fractured in liquid nitrogen.

Fourier transform infrared spectroscopy spectra were obtained by a Nexus-670 (Nicolet, America). All spectra in the attenuated total reflection (ATR) mode were recorded from 4000 cm^{-1} to 600 cm^{-1}, with a resolution of 4 cm^{-1} and using 32 scans.

The tensile test was carried out on a universal testing machine (CMT5254, Shenzhen Sans Testing Machine Co., Ltd, China) at the constant temperature (20°C) and the extension rate was set as 50 mm/min. For each sample, several dumbbell shaped specimens were taken and averaged to determine the mechanical properties of the blends.

Wide angle X-ray diffraction was obtained by a XRD-6000 diffractometer (Shimadzu, Japan) to analyze the crystalline phase of PVDF/TPU blends at room temperature. The radiation source (Cu K_α X-ray) was operated at 40 kV and 30 mA, with the scanning angle ranging from 5 to 50° and the scanning velocity of 4°/min.

The lamellar thickness *L* was calculated using the Scherrer equation [6]

$$L = \frac{k\lambda}{B\cos\theta} \tag{1}$$

which *k* is a structure factor, taken as $k = 1.0$; $\lambda = 1.542$ Å is the wavelength of Cu K_α radiation; *B* represents the half-value breadth of the diffraction peak and θ is the Bragg angle.

Differential scanning calorimetry was done in a Q-200 thermal analysis apparatus (TA Instruments, America) under a dry nitrogen atmosphere. In order to remove the thermal history of sample, the polymer blend samples (ca. 10 mg) were heated from room temperature to 180°C at the rate of 40°C/min and maintained at 180°C for 5 min. Afterwards, all samples were cooled down to 40°C at the rate of 5°C/min. After 1 min at 40°C, the second heating was done upon to 180°C at a rate of 10°C/min. The degree of crystallinity (X_c) of PVDF was calculated by [7]

$$X_c = \frac{\Delta H_f/\phi}{\Delta H_f^*} \times 100\% \tag{2}$$

Where ΔH_f^* = 104.5 J/g is the melting enthalpy for a 100% crystalline PVDF, ΔH_f is the melting enthalpy of the blends measured in DSC, and ϕ is the weight fraction of PVDF in PVDF/PTU blends.

3. Results and discussion

3.1. The miscibility and interactions of the blends

3.1.1. Microscopy

The SEM observation of the cross section is a qualitative way to confirm the phase morphology of this polyblends. Fig. 1 showed the microscopic investigation of the cross section of the blends with various mass ratios of each component. It was obviously observed that the neat PVDF and TPU samples had only one homogeneous phase (Fig. 1A, E). When the content of TPU reached 25 wt%, PVDF appeared as a continuous

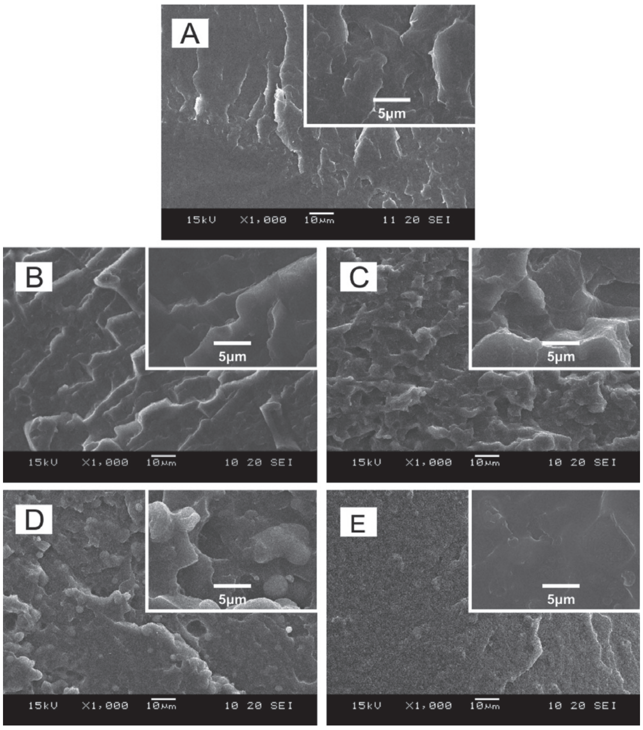

Fig. 1. SEM micrographs of cross section of PVDF/TPU blends with various mass ratios (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

phase while TPU appeared as a dispersed phase. Compared with immiscible PVDF/polycarbonate (PC) system [8] with obvious interface between two polymers, the blend (containing 25 wt% TPU) was considered as a partially miscible system. With the further increase in TPU content, there appeared to be two materials coexisting as the continuous phase. And the layered and ridge-like structures exhibited a typical immiscibility of the two polymers. When the content of TPU was 75 wt%, it was obviously observed that TPU became a continuous phase and some PVDF particles dispersed in the TPU amorphous matrix. Therefore, as the TPU content was more than 25 wt%, the PVDF/TPU blends were the immiscible systems, whereas the blend with the TPU content <25 wt%, the system can be considered as the partially miscible one.

3.1.2. FTIR spectroscopy

FTIR is an effective way to character different groups and their interactions in the blends, and it can also distinguish the different crystalline phases of PVDF. In this work, FTIR spectra of PVDF/TPU blends with various mass ratios were shown in Fig. 2.

Samples containing PVDF have well-defined absorption bands at 613, 761, 854, 974, 1178, 1208, 1381 cm^{-1} (Fig. 2A). As reported [2], all of these absorption bands represented the characteristic spectrum of α phase of PVDF crystal. It indicated that α phase of PVDF predominated in the work. In the inset of Fig. 2C-E, the absorption bands at 2850 and 2937 cm^{-1} were associated with symmetric and asymmetric CH_2 stretching vibrations of TPU, respectively. Moreover, the peaks of 3314 and 1530 cm^{-1} were assigned to the vibrations of NH and CN groups in TPU. The carbonyl absorption band of TPU was split distinctly into two peaks, one at 1730 cm^{-1} and the other at 1700 cm^{-1}, which were attributed to free and hydrogen-bonded carbonyl groups, respectively [5]. However, the increase of TPU resulted in a decrease in the intensity of the characteristic bands of PVDF (some even disappeared). This phenomenon could be explained by two reasons: (i) The FTIR spectroscopy in ATR mode was used, and the density of PVDF is much higher than TPU, as they were blended, the low density component shifted to the surface. (ii) Some physical interactions between two polymers leaded to a decrease in the intensity of the characteristic bands of PVDF. This is a unique phenomenon that the characteristic band at 840 cm^{-1} emerged as the 25 wt% content of TPU added, this could be attributed to the γ or β phase of PVDF. Whereas the bands at 776, 812 and 833 cm^{-1} characteristic for the γ phase were absent in all samples. Thus, it may be anticipated that the peak at 840 cm^{-1} referred to the β phase [2,3].

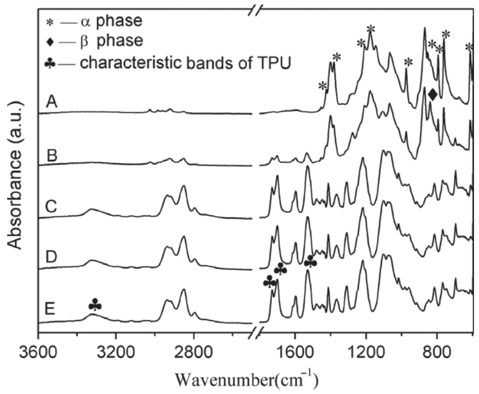

Fig. 2. FTIR spectra of PVDF/TPU blends with various mass ratios (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

In general, miscibility in polymeric blends arises from specific interactions between the two polymers. Infrared spectroscopy can be used to establish the nature and level of such molecular interactions in polymer blends. However, with the increase in the content of TPU, no shift of each characteristic band and no new bands like hydrogen bands were found except some intensity changes. It can be concluded that no obvious interaction between the two polymers.

3.1.3. Mechanical properties

Measurement of the mechanical properties is one of the efficient ways to estimate the interfacial adhesion of the polymer blends [9]. The effects of the content of TPU on hardness, tensile strength and elongation at break of PVDF/TPU blends were listed in Table 1. TPU exhibited the typical behavior of an elastomer with a higher elongation at break. With the addition of 75 wt% TPU in the blend, the elongation at break of PVDF/TPU blend dramatically increased to about 614%, more than six times of that of neat PVDF. It confirmed that the addition of a mass of TPU effectively enhanced the toughness of PVDF. As the content of TPU further deceasing to 50 wt%, both the PVDF and TPU coexisted as the continuous matrix and the weak interfacial adhesion led the tensile strength and elongation at break of the blend decreased rapidly. The addition of PVDF caused disruptions to the TPU interchain hydrogen bonding by acting as particulate barriers between TPU chains. Owing to little or no interactions between the two polymers, this disruption resulted in the tensile strength significantly decrease. Moreover, the blend was found to have the lowest mechanical strength. This phenomenon may also be interpreted by the conclusion of SEM and FTIR analyses, PVDF and TPU just blended simply without new interactions appearing in the blends, resulting in a low interfacial strength.

Table 1
Mechanical properties of the PVDF/TPU blends (mean ± S.D.)

PVDF/TPU blends	Hardness Shore D	Tensile strength (MPa)	Elongation at break (%)
100/0	74	46.4 ± 0.8	90 ± 40
75/25	58	14.0 ± 2.4	7 ± 1
50/50	44	5.8 ± 0.6	25 ± 3
25/75	34	19.5 ± 0.8	614 ± 22
0/100	30	36.2 ± 0.5	629 ± 39

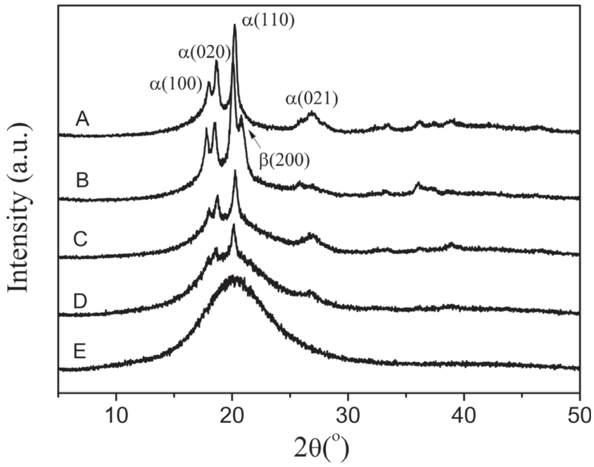

Fig. 3. WAXD diffractograms of PVDF/TPU blends with various mass ratios: (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

3.2. Crystallization behavior of the blends

PVDF is a semi-crystal polymer presenting pronounced polymorphic crystalline forms. It can crystallize into three principal conformations (namely, α, β , γ), depending on different crystallization conditions [2,3,10]. WAXD measurement was employed to confirm the crystalline phase of the samples, as shown in Fig. 3. According to the Gregorio's work [2], peaks at $2\theta = 17.9$, 18.5, 20.2, 26.6° in the curve for neat PVDF (Fig. 3 A), presented the diffractions in planes (100), (020), (110), (021), respectively, which were all character of the α phase of PVDF [10]. Neat TPU exhibited an amorphous feature which was characterized by an amorphous halos centered at $2\theta = 20°$ with no sharp peaks (Fig. 3 E). With the increase of TPU addition, the blends presented predominantly α phase as shown in Fig. 3 (B–D). However, new diffraction peak at $2\theta = 20.7°$ appeared as the content of TPU was 25 wt% in the blend. As reported [2], it could be attributed to the β phase, corresponding to the reflections from the (200) planes. This is totally agreed with the result of FTIR, and absorption band at 840 cm^{-1} was the characteristic band of β phase. On the other hand, as the TPU content increased in the blend, all peaks had a decrease in their intensity, especially for the ones at $2\theta = 17.9°$, 18.5°, the peaks could be hardly observed with 75 wt% TPU addition. This could be related to the content of crystal PVDF in the blends, the less PVDF was, the lower intensity was. Moreover, the intensity of the amorphous halo of TPU increased, which concealed the diffraction peaks of PVDF.

According to the three strong peaks observed in the diffractograms (Fig. 3), the values of 2θ and the interplanar distance d were listed in Table 2. The lamellar L in the direction perpendicular to the (*hkl*) crystal plane was calculated by Bragg equation and Scherrer equation [3,6] (Table 2). The value d of all planes was nearly unchanged with different content of TPU in the blends, i.e., the lattices parameter of α phase was not affected. However, the values L_{100}, L_{020} and L_{110} decreased with the addition of TPU content. As reported, in miscible binary blend system such as PVDF/PMMA, the amorphous polymer could be sandwiched in inter-lamellar regions, leading to an increase trend of L [3]. Compared with the PVDF/PMMA blends, the contrary results were obtained in this work. In particular, the values L_{100}, L_{110} were not observed as the weight fraction of TPU addition. It indicated that TPU retard the lamellar growth of PVDF in the blends.

Table 2
Values of 2θ and respective *d* spacing observed in the WAXD diffractograms

PVDF/TPU blends	*hkl*(100)			*hkl*(020)			*hkl*(110)			*hkl*(021)		
	2θ(°)	*d*(Å)	*L*(Å)	2θ(°)	*d*(Å)	L(Å)	2θ(°)	*d*(Å)	*L*(Å)	2θ(°)	*d*(Å)	*L*(Å)
100/0	17.98	4.93	115.3	18.59	4.77	142.6	20.20	4.39	181.4	26.62	3.34	53.8
72/25	17.82	4.97	107.0	18.50	4.79	122.4	20.06	4.42	142.0	26.62	3.34	52.0
50/50	17.98	4.93	61.1	18.66	4.75	–	20.21	4.39	80.4	26.84	3.32	59.0
25/75	–	–	–	18.54	4.78	34.7	20.06	4.42	–	26.78	3.33	73.2
0/100	–	–	–	–	–	–	–	–	–	–	–	–

–: not observed; θ: Bragg angle; *d*: the interplanar distance; *L*: the lamellar thickness (1 Å = 10^{-10} m).

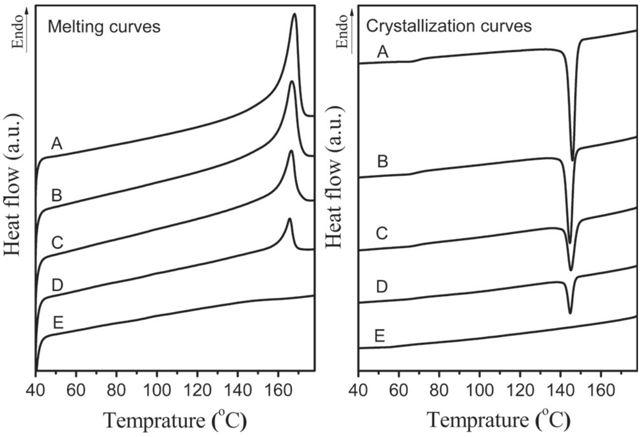

Fig. 4. DSC melting and crystallization behavior of PVDF/TPU blends with various mass ratios: (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, (E) 0/100.

3.3. Thermal analysis

As described in the Experimental, all samples were first melted at 180°C for 5 min to eliminate any thermal history. The data of the DSC melting and crystallization results of PVDF/TPU blends from Fig. 4 were summarized in Table 3. It was easy to find that the onset (T_m^{on}) and final melting temperature (T_m^f) of PVDF were unchanged, as a result, the value $\Delta T_m (= T_m^f - T_m^{on})$ was hardly changed. The steady value ΔT_m suggested that the crystal size of PVDF was not affected by TPU addition, i.e., the homogenous crystal size was formed in the process [11]. On the other hand, the melting temperature of PVDF/TPU blends was slightly decreased as the TPU content increased. According to the researchers' work [12–13], the miscibility of a blend system with semi-crystalline polymer was achieved by the interaction between the amorphous of each component. This interaction would lead to a decrease in the melting temperature of the crystalline component. Compared with neat PVDF, the melting temperature slightly decreased by 2.4°C as the content of TPU was 75 wt% in the blend. However, with respect to PVDF/PMMA miscible blends [3], the decrease value in melting temperature of PVDF which reduced by 27°C as PVDF/PMMA = 70/30, was more than PVDF/TPU blend system. This observation can be explained by the poor miscibility of the PVDF/TPU blend. With an increase of TPU content in the blend, although the melting enthalpy of PVDF was reduced from 52.9 to 14.9 J/g, the degree of crystallinity based on the PVDF content of the blend was increased from 50.6% to 57.0%.

Table 3
DSC melting and crystallization results of PVDF/TPU blends with various mass ratios

PVDF/TPU blends	T_m^{on} (°C)	T_m^p (°C)	T_c^{on} (°C)	ΔT_m (°C)	ΔH_m (J/g)	X_c (%)	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c (°C)	ΔH_c (J/g)	$t_{1/2}$ (min)
100/0	156.6	168.0	171.2	14.6	52.9	50.6	149.5	145.9	142.1	7.4	46.8	0.87
75/25	156.7	166.8	170.8	14.1	39.8	50.8	148.1	144.7	141.2	6.9	35.1	0.85
50/50	156.3	166.5	170.2	13.9	26.8	51.4	152.6	145.1	142.1	10.5	22.4	1.58
25/75	156.2	165.6	170.0	13.8	14.9	57.0	148.0	144.8	141.5	6.5	11.5	0.74
0/100	–	–	–	–	–	–	–	–	–	–	–	–

T_m^{on}: onset melting temperature of PVDF; T_m^p: peak melting temperature of PVDF; T_m^f: final melting temperature of PVDF; $\Delta T_m = T_m^f - T_m^{on}$; ΔH_m: melting enthalpy; X_c: crystallinity of PVDF; T_c^{on}: onset crystallization temperature of PVDF; T_c^p: peak crystallization temperature of PVDF; T_c^f: final crystallization temperature of PVDF; $\Delta T_c = T_c^{on} - T_c^f$; ΔH_c: crystallization enthalpy of PVDF.

In the crystallization process, the value enthalpy of crystallization (ΔH_c) for PVDF decreased significantly as the content of TPU addition, which was due to the decrease in PVDF in the blends. In Table 3, the crystallization half time ($t_{1/2}$), which is defined as the half time of crystallization, was used as a characteristic parameter of the crystallization process [11]. As reported [14], the smaller the value $t_{1/2}$ was, the faster the crystallization rate was, and vice versa. In the blends, the value $t_{1/2}$ of blend containing 50 wt% TPU was obviously higher than other samples. When the TPU content reached 50 wt%, TPU and PVDF were coexisting as the continuous phase, and the TPU chains disturbed PVDF chains to arrange into the lattice, resulting in the rate of crystallization of PVDF remarkably reduce.

4. Conclusions

When the content of TPU was less than 25 wt%, PVDF appeared as a continuous phase while TPU appeared as a dispersed phase. The blend was considered as a partial miscible system. With the further increase in TPU content, the PVDF was evident as the dispersed phase in the TPU matrix. The immiscibility of these two polymers could be seen by the presence of smooth boundaries around the PVDF particulates. Additionally, when the TPU content reached 50 wt%, the blend system displayed the lowest mechanical properties. On the other hand, as the addition of 75 wt% TPU in the blend, the elongation at break of PVDF/TPU blend dramatically increased to about 614%, more than six times of that of neat PVDF. It confirmed that the addition of a mass of TPU effectively enhanced the toughness of PVDF. As demonstrated by WAXD and FTIR, the samples presented predominantly α phase. However, only when the content of TPU reached 25 wt%, a small amount of the β phase crystal of PVDF was observed. According to DSC analysis, the melting and crystallization temperature of PVDF in the blends were slightly decreased. When the content of TPU was 75 wt%, the crystallinity of PVDF reached the highest to 57%.

Acknowledgement

The authors thank the National Basic Research Program of China (2009CB623404) and the Priority Academic Program Development of Jiangsu Higher Education Institutions for their financial support of the research.

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