PVDF/PMMA Composite Nanofiber Fabricated by Electrospray Deposition: Crystallization of PVDF Induced by Solvent Extraction of PMMA Component

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ABSTRACT: The crystallization of poly(vinylidene fluoride) (PVDF) was observed after the poly(methyl methacrylate) (PMMA) component was extracted from the PVDF/PMMA (50/50) composite nanofiber fabricated by electrospray deposition, even though the original composite showed a completely amorphous pattern in the wide-angle X-ray diffraction. The content of the β-crystal form in the crystalline region depended on the PVDF/PMMA composite ratios and the type of solvents used for the extraction of the PMMA component, e.g., chloroform and toluene. Thus, the content of the β-crystal form can be controlled by selecting the original PVDF/PMMA composition and the solvent used to extract the PMMA component. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1868–1872, 2009

Key words: poly(vinylidene fluoride); poly(methylmethacrylate); composite; nanofiber; electrospray deposition; extraction; wide-angle X-ray diffraction; IR; β crystal form; solubility parameter

INTRODUCTION

Recently, nanofibers have gained much attention in the research fields of science and technology.[1,2] Electrospray deposition (ESD), or electrospinning, is a versatile method for the preparation of nano-microscaled fibers.[3,4]

Poly(vinylidene fluoride) (PVDF) has been intensively studied because of its excellent chemical and dielectrical properties.[5–8] PVDF exists in at least four main crystalline structures; α-, β-, γ-, and δ-crystal forms.[5,6] They are distinguished by the conformation of the C—C bond along the chain backbone. The crystalline structure of PVDF influences the polarity of PVDF. The α-crystal form is nonpolar, whereas the β-crystal form has polar properties. Each phase of this polymer can be used for specific applications.[9] In our previous research study, we demonstrated that the diameter, morphology, and crystalline structure of the PVDF nanofiber were controllable by changing the polymer concentration of the spray solution or by adding surfactants to the solutions.[10,11]

The PVDF/polymer composite has gained the attention of many researchers, for example, the blending of PVDF with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(vinyl pyrrolidone) (PVP), etc.[8,12,13] The PVDF/PMMA polymer composite is a type of miscible blend polymer in a melt.[12] Blending of PVDF with PMMA can combine the advantageous properties of PVDF and PMMA and also enhance the economic value of these materials. However, as most of the previous studies have been carried out about the bulk composite system, such as the advantageous properties of PVDF/PMMA have not been achieved effectively. Especially, the selective extraction of the PMMA component expects the formation of the porous material, if the effective extraction could be achieved. Because of these reasons, we developed the PVDF/PMMA composite nanofiber.
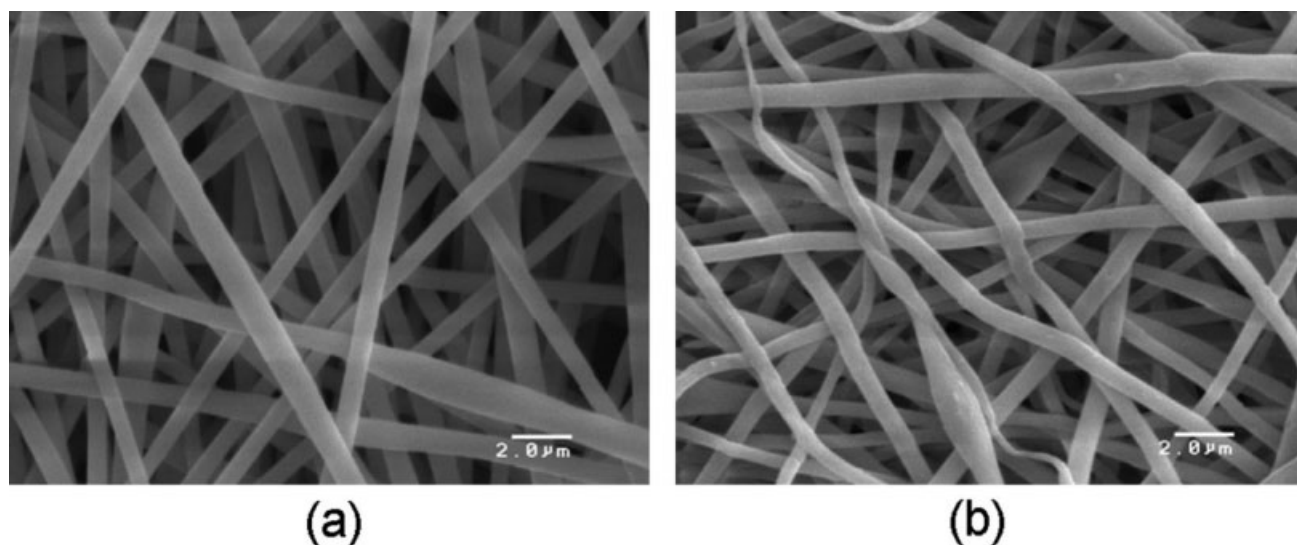
The objective of this article is to report the crystallization of the PVDF component induced by the solvent extraction of the PMMA component from the PVDF/PMMA composite nanofiber fabricated by ESD.

EXPERIMENTAL

Materials and preparation of solution

PVDF, $M_w = 1.41 \times 10^5$, KF1100T was obtained from Kureha, Tokyo, Japan, and PMMA with $M_w = 1.68$

Figure 1 SEM image of as-deposited PVDF/PMMA (50/50) nanofiber (a) and residual PVDF nanofiber after extraction by chloroform (b). Scale = 2.0 μm.

$\times 10^5$ from Mitsubishi Chemical, Tokyo, Japan. N,N-Dimethyl acetamide (DMAc) (Wako, Japan) was used as a solvent. The PVDF/PMMA bulk blends were prepared by milling the PVDF and PMMA pellet with a uniaxial melt extruder[12] for the PVDF/PMMA blends of 20/80, 50/50, 60/40, and 90/10. The concentration of the PVDF/PMMA blends in the DMAc solution was fixed at 30 wt %. For example, for the PVDF/PMMA (50/50) solution, the polymer viscosity was 2500 mPa s and the surface tension of the solution was 37 mN/m.

Electrospray deposition

The ESD device is the same as that used in a previous study.[14] The polymer solution was contained in a syringe having a stainless steel nozzle (1.0-mm internal diameter). The nozzle was connected to a high-voltage regulated DC power supply (HDV-20K 7.5STD, Pulse Electronic Engineering, Japan). A constant volume flow rate was maintained using a syringe-type infusion pump (MCIP-III, Minato Concept, Japan). The grounded target used for the counter electrode was an aluminum plate (15 × 15 cm² area). The distance between the nozzle tip and the substrate surface was 15 cm, the applied voltage was 15 kV, and the flow rate was 2 μL/min. Deposition was carried out at 25°C under a 25–30% relative humidity.

Extraction of PMMA from PVDF/PMMA nanofiber

To extract the PMMA, the as-deposited PVDF/PMMA fiber was treated in chloroform or toluene by ultrasonication at 60°C for 60 min and then vacuum-dried for 1 day. Over 99 wt % of the PMMA

component was extracted from the composite nanofiber by this treatment.

Characterization

The surface morphologies of the deposited nanofibers were observed using a scanning electron microscope (SEM, SM-200, Topcon, Japan) operated at 10 kV. All samples were sputter-coated with Au.

The wide-angle X-ray diffraction (WAXD) intensity was measured at a scattering angle from 5° to 50° using Ni-filtered Cu Kα radiation from a Rigaku RINT2550 Diffractometer with a fiber-specimen holder.

The FTIR spectra were recorded using a FT/IR-410 Spectrometer from JASCO in the transmittance mode.

RESULTS AND DISCUSSION

Figure 1 shows the surface structure of the as-deposited PVDF/PMMA (=50/50) fiber and the residual PVDF fiber after extraction of the PMMA by chloroform. The 900-nm averaged diameters of both nanofibers were similar to each other, although more heterogeneity of the diameter was observed at the residual PVDF fiber. The BET-specific surface areas of the residual PVDF fiber and the original PVDF/PMMA composite fiber were 3.04 and 2.75 m²/g, respectively. The mercury porosimetry measurements showed that the residual PVDF fiber did not have porous structure inside the fiber. Furthermore, the size of the specimens decreased after ultrasonication, corresponding to the PVDF/PMMA composition ratio. These results suggest that shrinkage of the fiber might occur after the PMMA extraction along

the fiber axis and, as a result, the diameter did not apparently change. Figure 2 shows the WAXD intensity curves for the as-deposited PVDF/PMMA (= 50/50) fiber and the residual PVDF fiber after extraction of the PMMA by chloroform. The as-deposited nanofiber showed almost the amorphous pattern with the peak ca. $2\theta = 16°$, which corresponds to the result reported by Horibe et al.[12] On the contrary, the sample after the PMMA extraction (residual PVDF nanofiber) showed a clear crystalline structure. The curve showed the strongest peak at ca. 18° and 20° and also with characteristic peaks at ca 26°, 35°, and 40°. From a comparison with the previous studies by Hasegawa et al.[6] and Horibe et al.[12] concerning the peak position and intensity, the peaks 20°, 35°, and 40° were assigned to the β-crystal form (Form-I) and the peaks 18° and 26° were assigned to the α-crystal form (Form-II). Thus the residual PVDF nanofiber would be formed by the mixture of the α-crystal form (Form-II) and β-crystal form (Form-I). The total crystallinity of the residual PVDF nanofiber was 53% using the DSC measurement.

Figure 3 shows the IR spectra of the residual PVDF nanofiber after extraction by chloroform and toluene of the PVDF/PMMA = 50/50 composite nanofiber. The two spectra were significantly different. This suggests that the solvent, which was used for the extraction of the PMMA component, produced a different mechanism of swelling and crystallization of the PVDF component during the extraction.
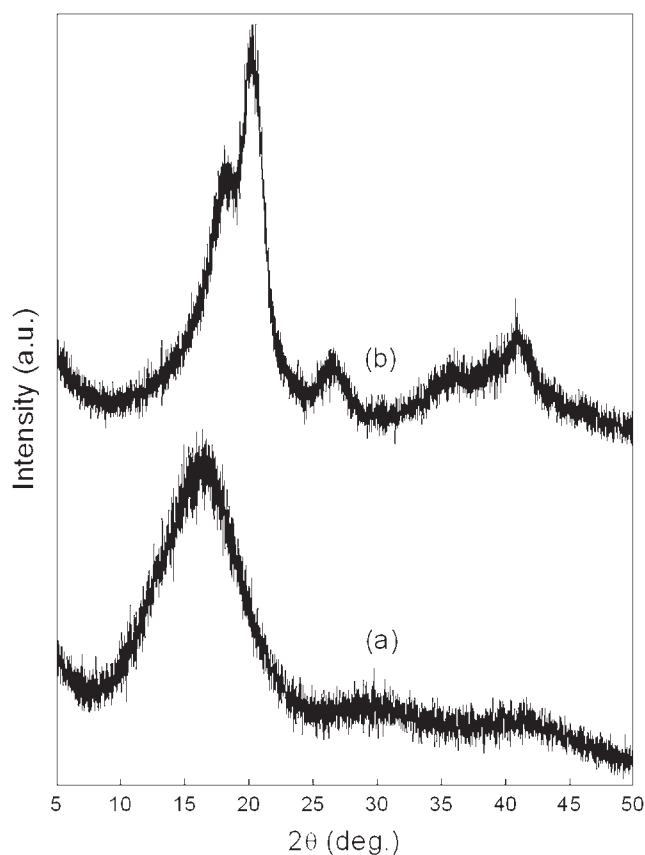
Figure 2 WAXD intensity curves of as-deposited PVDF/PMMA (50/50) nanofiber (a) and residual PVDF nanofiber after extraction by chloroform (b).
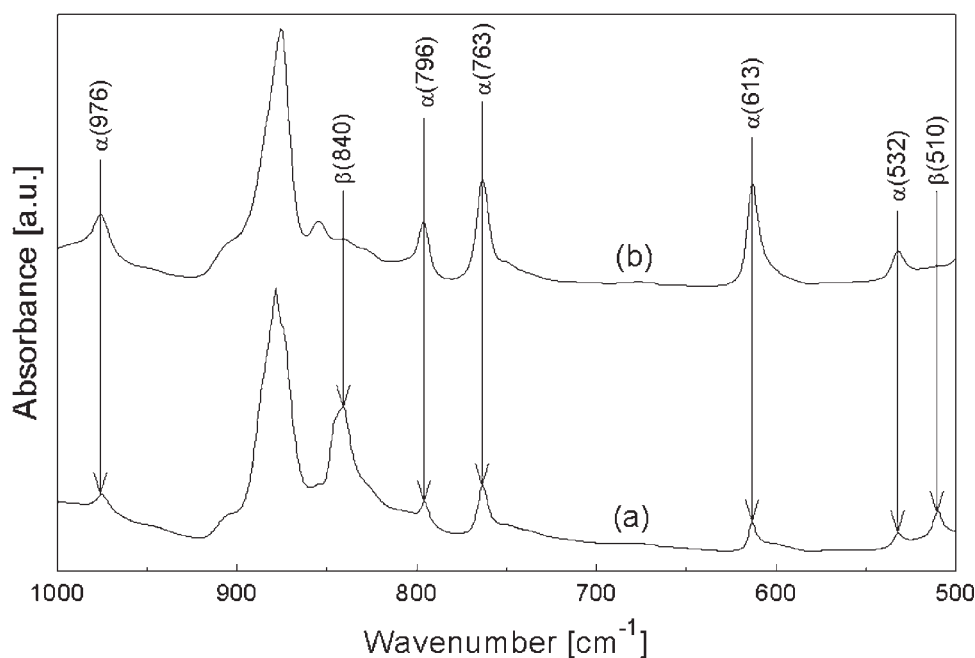
Figure 3 IR spectra of residual PVDF nanofibers extracted by chloroform (a) and by toluene (b), wavenumbers and crystal forms inside are based on the previous studies.[7,15]
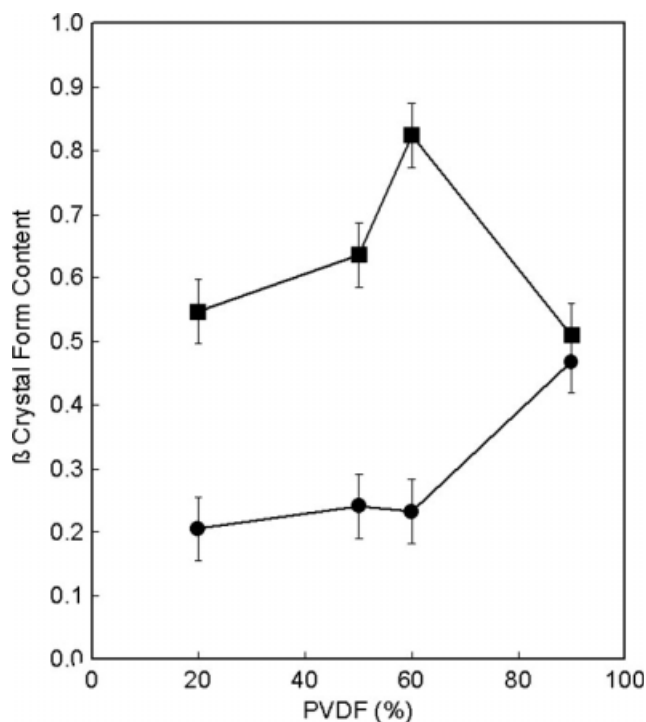
Figure 4 β-Crystal form contents of residual PVDF nanofiber after solvent extraction as a function of PVDF composition: ■, chloroform; ●, toluene.

In Figure 3(a), in the case of chloroform, a strong absorption from the β-crystal form at 840 cm^{-1} and weaker absorptions from the α-crystal form are observed, whereas absorptions almost only from the α-crystal form are observed in Figure 3(b), in case of toluene.[7,15] This suggests that the PVDF component consists of the proper mixture of the α- and β-crystal forms when the PVDF/PMMA composite was treated with chloroform, while a lower amount of the β-crystal form is contained in the PVDF when using toluene.

Therefore, we manufactured a series of PVDF/PMMA (20/80, 60/40, 90/10) composite nanofibers under conditions similar to the 50/50 one. Thereafter, the PMMA components were separately extracted by chloroform and toluene from the PVDF/PMMA composite nanofibers. From each IR measurement, the contents of the β-crystal form, i.e., ratio of the β-crystal form to the total crystalline region, were calculated using the absorbance at 763 cm^{-1} for the α-crystal form and at 840 cm^{-1} for the β-crystal form proposed by Salimi and Yousefi.[16]

Figure 4 shows the contents of the β-crystal form in the residual PVDF nanofibers after the PMMA extraction as a function of the PVDF/PMMA composition. Although a considerable absolute uncertainty is unavoidable, when the composite nanofibers were extracted by chloroform, higher contents of the β-crystal form were obtained, whereas with toluene, lower contents of the β-crystal form were obtained

over the wide range of PVDF/PMMA compositions, except at 90/10. At the 90/10 composition, however, comparable contents of the β-crystal form were observed for both solvents. The solubility parameters of PVDF, PMMA, chloroform, and toluene have been reported as 10,[17] 9.1, 9.3, 8.9 (cal$^{1/2}$ cm$^{-3/2}$),[18] respectively. When the as-deposited nanofiber was treated at 60°C for 1 hr in an air oven, which is the same temperature condition with the solvent extraction, no change of the WAXD and IR were observed. Thus, the crystalline form of PVDF would be affected just by swelling with the two solvents used upon ultrasonication. When the PVDF contents are below 60 at the as-deposited nanofiber, amorphous PVDF component might be swollen stronger by chloroform than by toluene, since the solubility parameter of chloroform is closer than that of toluene to the one for PVDF. As a result, the trans-zigzag molecular conformation that forms the β-crystal form could be easily generated in chloroform rather than toluene. At the 90/10 composition, since WAXD of the as-deposited fiber already showed crystalline pattern of PVDF to some extent, swelling of solvent to the crystalline region is weaker than the case of lower PVDF compositions, which show complete amorphous pattern in WAXD. Thus, the comparable contents of the β-crystal form were observed regardless of the solvents used.

The above mentioned speculation can be guaranteed if the total degrees of crystallinity of all the samples are the same. Actually, we have measured the degree of crystallinity of the series of the residual PVDF nanofibers extracted by chloroform using DSC. The results were 52, 53, 52, 55, 49% for PVDF/PMMA = 20/80, 50/50, 60/40, 90/10, respectively. These data should be seemed almost identical concerning the measurement errors of DSC. Therefore, in the case of chloroform extraction, total crystallinity of the residual nanofibers is the same, and we can discuss the β- and α-form content as mentioned earlier. However, for toluene, we have no evidence about the total crystallinity, and further studies are expected. The mechanisms of the crystallization are still open to discussion, but with the above mentioned treatments, the ratio of the β-crystal form to the α-form can be controlled. It is one of the advantages of using the PVDF/PMMA composite nanofiber, because it is difficult to control the crystal form and its content in the PVDF bulk and single material.

CONCLUSIONS

The crystalline PVDF nanofibers were prepared by the ESD of PVDF/PMMA composite nanofibers and successive removal of PMMA. The WAXD and FTIR analyses of the residual PVDF nanofiber

demonstrated that the crystal PVDF region was obtained from almost the entire amorphous composite nanofiber by extracting the PMMA. Furthermore, the crystal region consisted of a mixture of the α- and β-crystal forms. Thus, the contents of the β-crystal form can be controlled by selecting the PVDF/PMMA composition ratios and solvents, e.g., chloroform and toluene, for the extraction.

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