

Plasticizer Effect of Dibutyl Phthalate on the Morphology and Mechanical Properties of Hard Elastic Poly(vinylidene fluoride) Fibers

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ABSTRACT: To improve the structure and hard elasticity of poly(vinylidene fluoride) (PVDF) fibers, a small amount of the plasticizer dibutyl phthalate (DBP) was added to PVDF. The PVDF/DBP blend fibers were prepared by melt spinning and subsequent annealing. The crystalline structure and thermal properties of the blend fibers were analyzed in terms of the long-period lamellar spacing, crystal structure, and degree of crystallinity with X-ray diffraction, differential scanning calorimetry, and small-angle X-ray scattering. The results indicated that stacked crystalline lamellae, which were aligned normal to the fiber axis, existed in the blend fibers, and they were in the form of an α -crystal phase. The total crystallinity of the blend fibers was higher than that of the pure PVDF fibers, and it reached its highest value when the DBP concentration was 2 wt %; then, it decreased with an increase in the

DBP content. The morphology and mechanical properties of the fibers were also investigated with scanning electron microscopy and electronic tensile experimentation. The results of scanning electron microscopy apparently exhibited a small porous structure on the surface of the blend fibers, and the more DBP there was in the PVDF fibers, the more porous structure was obtained. Mechanical experiments indicated that the fibers with a 5 wt % concentration of DBP had better elastic recovery and breaking strain than the pure PVDF fibers. These results all indicated that DBP-modified PVDF fibers have potential applications in preparing microporous membranes by a melt spinning and stretching process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3645–3651, 2009

Key words: fibers; mechanical properties; morphology

INTRODUCTION

Over the past years, hard elastic materials have attracted much attention because of their particular morphology, mechanical properties, and possible applications for preparing microporous membranes.^{1–7} These materials are characterized by a high modulus of elasticity, reversible deformation, energetic retractive forces, and a constant cross-sectional area during deformation.³ The unusual properties of hard elastic materials are due to the row-nucleated lamellar crystalline structures, which are aligned in the direction normal to the extrusion direction. This type of hard elastic behavior has been reported in polyoxymethylene,⁸ polypropylene (PP),¹

polyethylene (PE),⁷ poly(4-methyl-1-pentene),⁹ and so forth.

Recently, new hard elastic materials made by melt spinning and annealing, such as poly(vinylidene fluoride) (PVDF) fibers, were reported by Du et al.^{10,11} This kind of fiber has stacked crystalline lamellae, and the lamellar planes are perpendicular to the fiber axis. The long period of the lamellar spacing is 13.4 nm.¹¹ The fibers have a higher initial modulus of 3.5 GPa and an elastic recovery of 85% from 50% extension at room temperature. As for hard elastic PVDF fibers, the stacked crystalline lamellae favor their preparation into membranes by a subsequent stretching process.^{12,13} Crystalline polymers such as PP and PE have been successfully used to prepare microporous membranes by a melt spinning and stretching (MS-S) method.^{5–7} The micropore formation mechanism of the MS-S method is due to the stacked crystalline lamellae, which are aligned normally to the extrusion direction. When stretched, the crystalline lamellae will be separated, with a large number of voids forming, and the voids will be interconnected. Thus, the microporous structure is formed by stress, and then it is completed during annealing.¹⁴ Unlike PP and PE membranes, there are also some difficulties and

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problems in preparing PVDF membranes; for instance, the workability of the PVDF melt is poor, the crystallinity and breaking strain of the fibers are relatively low, and the pore size of the membranes is small. To improve the workability of the PVDF melt and the properties of PVDF fibers and membranes, some methods should be investigated. The addition of a plasticizing agent such as dibutyl phthalate (DBP) into PVDF fibers may be a good choice.

Many polymeric materials in practical use contain plasticizers (low-molecular-weight additives) to tailor their physical properties for particular technical needs. Therefore, plasticizers may have great effects on fabricating the structure and properties of PVDF fibers. As for PVDF, plasticizers such as DBP,¹⁵ glyceryl triacetate,¹⁶ and a dimethyl phthalate (DMP)/dioctyl phthalate blend system¹⁷ are often used as diluents in preparing PVDF membranes by thermally induced phase separation (TIPS). In the TIPS process, the polymer and diluents are mixed to form a homogeneous solution above its melting point. Upon cooling, the system undergoes liquid-liquid or solid-liquid phase separation. The sites occupied by the diluents become micropores after the removal of the diluents. Gu et al.¹⁸ used DMP as a diluent to study the crystallization behavior of PVDF in a PVDF/DMP system via the TIPS process, and they found that DMP could affect the crystallinity and morphology of PVDF membranes. Moreover, a different crystal phase structure (α - or β -phase) was obtained through the control of the quenching temperature. In the TIPS process, a great amount of the diluent (ca. 40–80 wt % concentration) was used, so the crystallinity of the blends was very low.

In this study, a small amount of DBP (≤ 10 wt %) was added to PVDF to improve the mobility of the PVDF melt while not decreasing the crystallinity and elastic recovery of the PVDF fibers. The effects of the DBP concentration on the morphology and mechanical properties of the PVDF fibers are discussed in detail. The experimental results obtained from this study can be used to explore a new technique for preparing PVDF hollow-fiber membranes by the MS-S process.

EXPERIMENTAL

Materials

Extrusion-grade PVDF (1012), supplied by Solvay Solaxis Co. (Brussels, Belgium), had a melt flow index of 1.5 (230°C, 5 kg) and contained no nucleating agents. DBP (bp = 340°C), supplied by Guangdong Guanghua Chemical Factory Co., Ltd. (Guangdong, China), was used without further purification.

Preparation of hard elastic PVDF/DBP blend fibers

Hard elastic PVDF/DBP blend fibers were prepared with the following two steps. First, PVDF and DBP

were co-extruded by a twin-screw extruder (purchased from Nanjing Machinery Co., Ltd., Nanjing, China) at 180–220°C, and then the blends were granulated by a continuous granulator at room temperature. The DBP concentration in the blend system was controlled at 2, 5, or 10 wt %. Second, PVDF/DBP blends were melt-spun from a melting extruder at 230–260°C. The diameter of the spinneret die was 2 mm. The melt draw ratio, defined as the ratio of the take-up speed to the extrusion rate, was 130. The extruded fiber was taken up on a homemade roller and then annealed at 140°C under a constant-length condition for 4 h.

Scanning electron microscopy (SEM) measurement

The annealed PVDF/DBP blend fibers were first extracted by alcohol to remove the plasticizer DBP, and then the fibers were stretched at room temperature to 100% extension and finally annealed at 150°C for 30 min. The morphology of the samples was emission scanning electron microscope (FESEM, Sirion-100, Phillips, Eindhoven, Holland). The surfaces of the samples were coated with gold before examination.

Degree of crystallinity from differential scanning calorimetry (DSC)

A PerkinElmer Pyris-1 differential scanning calorimeter (Norwalk, CT) was used to measure the crystallinity of the sample at a heating rate of 10°C/min. The crystallinity (X_c) was defined as follows:

$$X_c(\%) = \frac{\Delta H}{\Delta H^0} \times 100 \quad (1)$$

where ΔH is the measured heat of fusion for the sample and ΔH^0 is the theoretical heat of fusion for the pure PVDF crystal (taken to be 104.7 J/g).¹⁹

X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS) measurements

The crystal phase structure of PVDF fibers was measured with an X-ray diffractometer (D/max-rA, Rigaku, Tokyo, Japan) with Cu K α radiation ($\lambda = 0.154$ nm). The SAXS patterns of PVDF fibers were determined with a Kratky small-angle scattering system produced by Anont Paar Co. (Graz, Austria) with Cu K α radiation ($\lambda = 0.154$ nm).

Mechanical testing

The mechanical properties of the PVDF fibers were measured with an electronic tensile tester (AG-1, Shimadzu Co., Kyoto Japan). All the tests were conducted at 20°C and 60% relative humidity. The elastic recovery was determined along the stretched

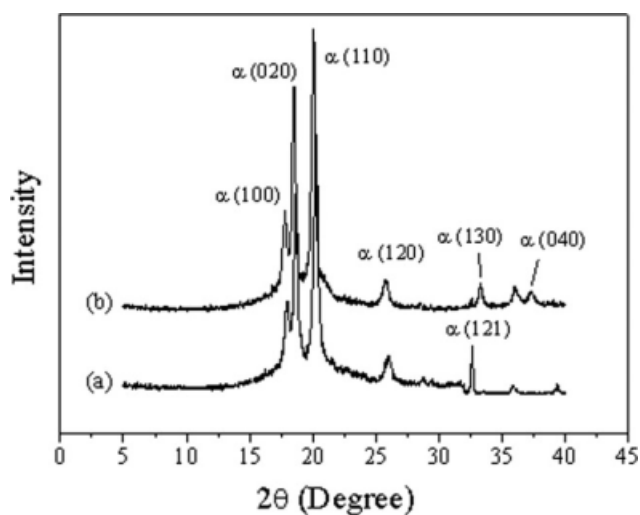


Figure 1 XRD patterns of PVDF fibers with DBP concentrations of (a) 0 and (b) 10 wt %.

direction of the fiber under the first cycle of loading and unloading at a deformation rate of 120%/min. The percentage of elastic recovery of the fiber was calculated according to our former report.⁴

RESULTS AND DISCUSSION

Crystal structure

XRD was used to investigate the crystal structures of the pure PVDF and PVDF/DBP blend fibers; the results are shown in Figure 1. Only the α -crystal phase was found in the fibers. In comparison with the pure PVDF fibers, several new crystal peaks such as $\alpha(130)$ and $\alpha(040)$ appeared in the PVDF/DBP blend fibers, and they indicated that DBP favored the formation of a new α -crystal phase in the blend fibers. According to our previous study,⁴ only an α -crystal structure is helpful for the hard elasticity of PVDF fibers. Therefore, the addition of DBP to PVDF has a potential effect on the hard elasticity of PVDF fibers.

The thermal properties of the PVDF/DBP blend fibers were also investigated. The DSC curves of the blend fibers are presented in Figure 2; the melting peak temperature of the blend fibers decreased with the DBP content, as shown in Figure 3. The total crystallinity of the blend fibers exhibited an interesting phenomenon: it increased with the addition of DBP, and its value was higher than that of the pure PVDF fibers. When the DBP concentration was 2 wt %, its crystallinity reached the highest value, and then it decreased with an increase in the DBP content (5–10 wt %). These phenomena indicated that the plasticizer DBP could increase the crystallinity of the PVDF fibers. This might be explained by the solubility parameters of DBP and PVDF. The

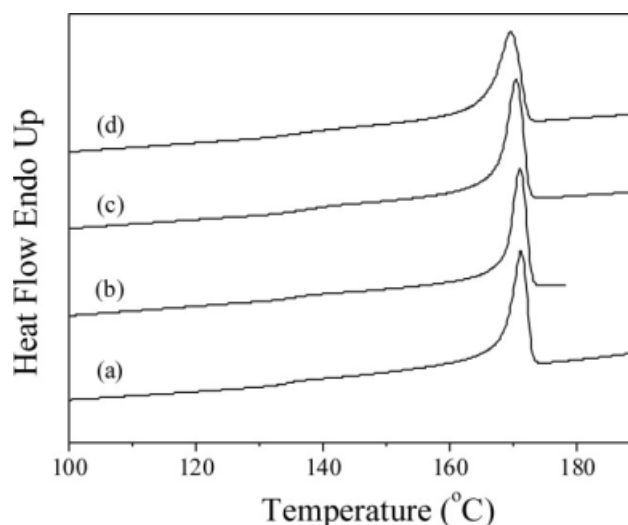


Figure 2 DSC curves of PVDF/DBP fibers with DBP concentrations of (a) 0, (b) 2, (c) 5, and (d) 10 wt % (annealing time = 4 h).

common viewpoint is that when the solubility parameters of the solvent and the polymer approach each other or their difference is not greater than 3.7, the polymer will dissolve in the solvent.²⁰ In this study, the solubility parameters of PVDF and DBP were 23.2 and 20.3, respectively,^{20,21} so DBP and PVDF had a certain compatibility, DBP could permeate the molecular chains of PVDF, and they mixed into a homogeneous phase above their melting point. Accordingly, the addition of a small amount of DBP (≤ 10 wt %) to PVDF could improve the mobility of the molecular chains of PVDF, and it generated more free volume between the molecular chains. Thus, during the crystallization process, DBP had the function of ordering the molecular segments

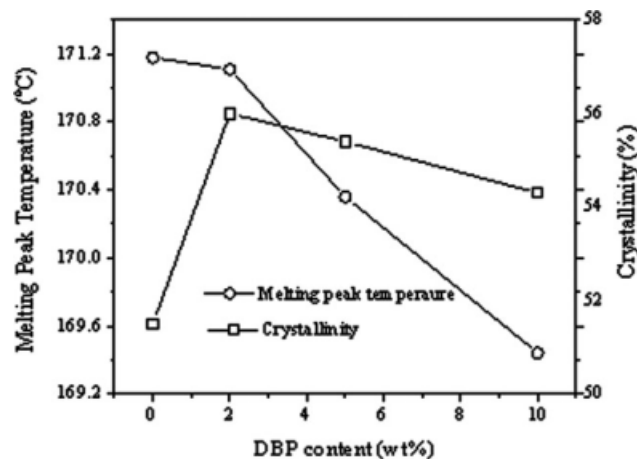


Figure 3 Effects of the DBP content on the melting peak temperature and crystallinity of PVDF fibers (annealing time = 4 h).

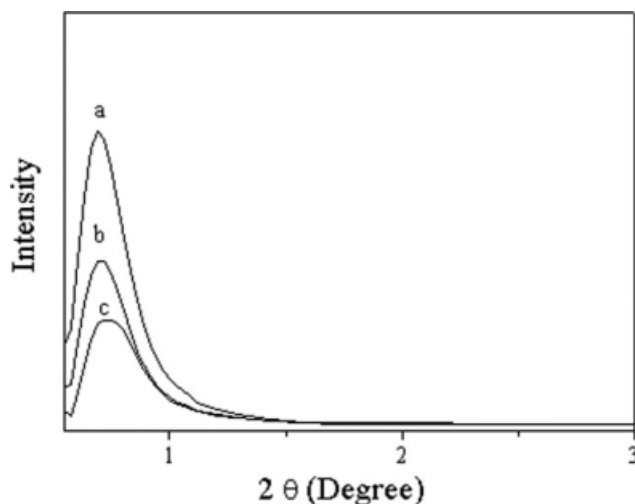


Figure 4 SAXS curves of PVDF fibers with DBP concentrations of (a) 0, (b) 5, and (c) 10 wt %.

of PVDF in both the crystalline region and the amorphous region and finally increased the total crystallinity of the fibers.

SAXS experiments were used to measure the long periods of the crystalline lamellae in the fibers. Figure 4 shows SAXS curves of PVDF/DBP fibers with different DBP contents. The corresponding scattering intensity curves of the samples all indicated their primary scattering peak was at 2θ values of approximately 0.68, 0.70, and 0.72°, as shown in Figure 4(a–c), which correspond to long periods of 11.3, 11.6, and 10.9 nm, respectively. These results also indicated that in the PVDF/DBP fibers the crystals existed in the form of stacked crystalline lamellae, and the lamellar planes were perpendicular to the fiber axis.⁴ The long-period lamellar spacing of the samples were not affected greatly by the addition of DBP, whereas the scattering intensity decreased with the increasing DBP content, and this indicated that the number of crystalline lamellae decreased with increasing DBP content in the fibers.

Morphology of the PVDF fibers

To investigate the effects of stretching on the morphology of PVDF and PVDF/DBP blend fibers, SEM experiments were carried out. The results indicated that no porous structure appeared on the surface of the pure PVDF fibers; only a raised structure was found, as shown in Figure 5(a,b). The raised structure might be related to the stacked crystalline lamellae in the fibers.¹ As for the stretched PVDF fibers, the raised structure disappeared, and some submicroscopic cracks existed on the surface of the fibers [Fig. 6(a)]. These cracks might be related to the hard elasticity of the fibers; when these fibers

were stretched, the stacked crystalline lamellae were separated with the formation of the submicroscopic cracks, and then these cracks could be heat-set by the following annealing process.¹³ In comparison with the PVDF fibers, there was apparently a small porous structure on the surface of the stretched PVDF/DBP blend fibers, and the greater the DBP content was, the more porous structure was obtained, as shown in Figure 6(b,c). This indicates that DBP is favorable for the formation of a porous structure in hard elastic PVDF fibers.

Mechanical properties of the PVDF/DBP fibers

The stress–strain behavior of PVDF/DBP blend fibers at a strain rate of 120%/min is shown in Figure 7. The breaking strain of the blend fibers increased with the DBP content, whereas the breaking strength decreased from 150 to 90 MPa with increasing DBP content, and the initial modulus of

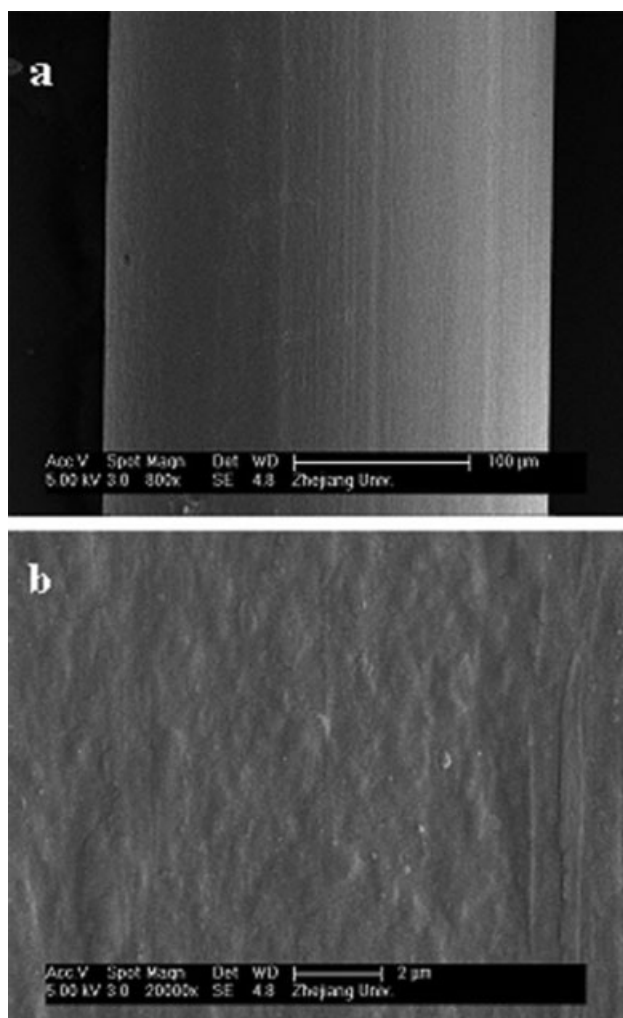


Figure 5 SEM photographs of pure PVDF fibers without stretching.

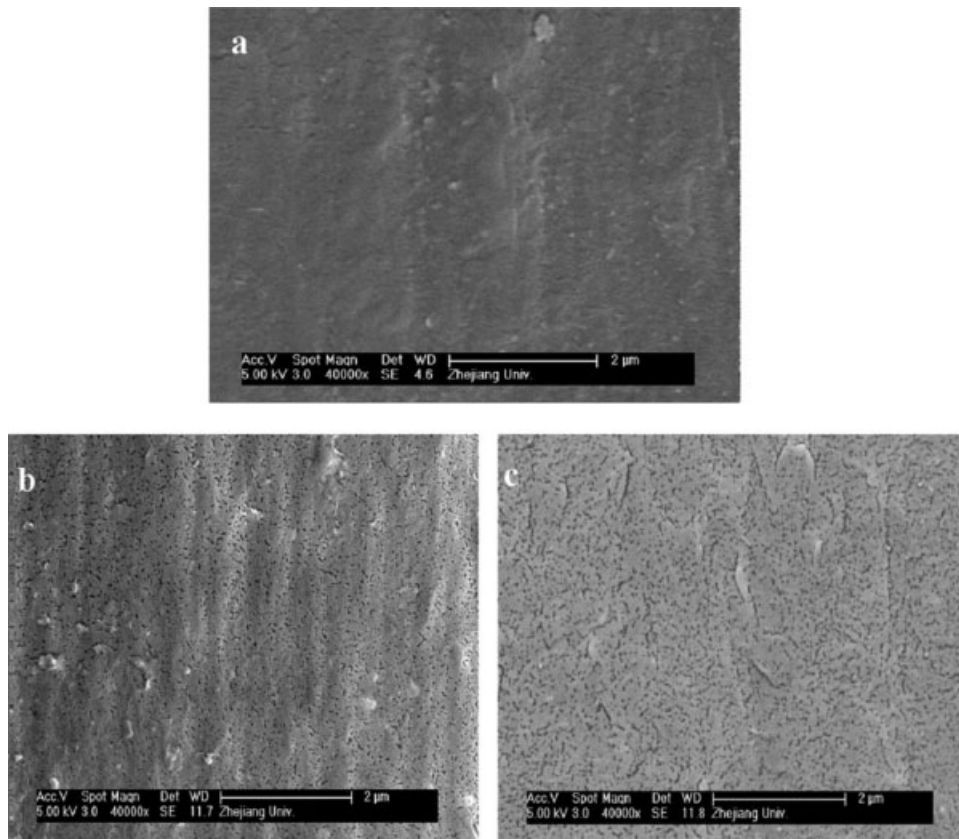


Figure 6 SEM photographs of PVDF fibers with DBP concentrations of (a) 0, (b) 5, and (c) 10 wt % (elongation of the fibers = 100%).

the fibers also decreased from 2.2 to 1.3 GPa. These results indicated that the blend fibers had higher breaking strength and initial modulus. This phenomenon (i.e., the breaking strain of the fibers increasing with increasing DBP content) could be used to improve the stretching ratio of PVDF fibers, which is important for the preparation of PVDF membranes by the MS-S method.

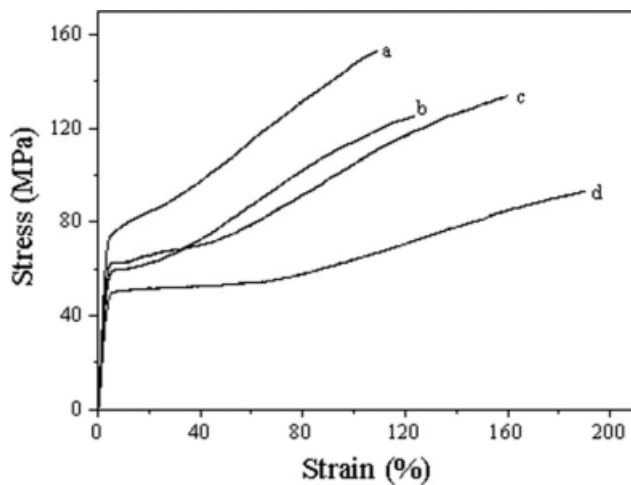


Figure 7 Stress-strain curves of PVDF fibers with DBP concentrations of (a) 0, (b) 2, (c) 5, and (d) 10 wt %.

The effect of the cyclic loading on PVDF/DBP fibers with different DBP concentrations was also studied. During the experiment, PVDF fibers were first drawn to 50% extension and then returned to the original gauge length for five successive times.

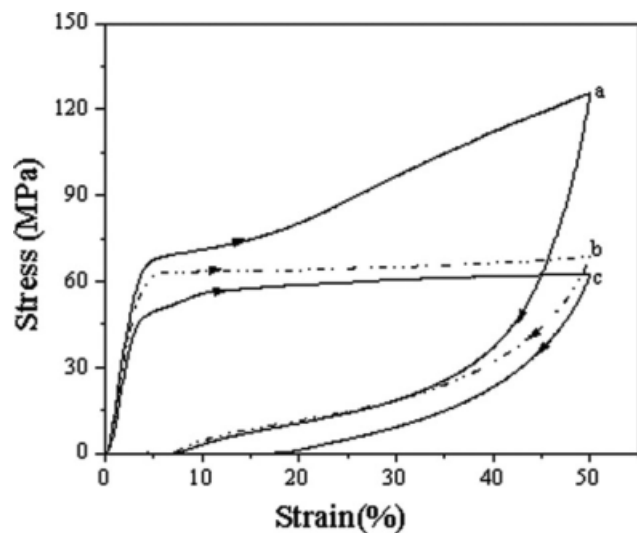


Figure 8 Cyclic loading to 50% extension of PVDF fibers with DBP concentrations of (a) 0, (b) 5, and (c) 10 wt % (rate = 120%/min).

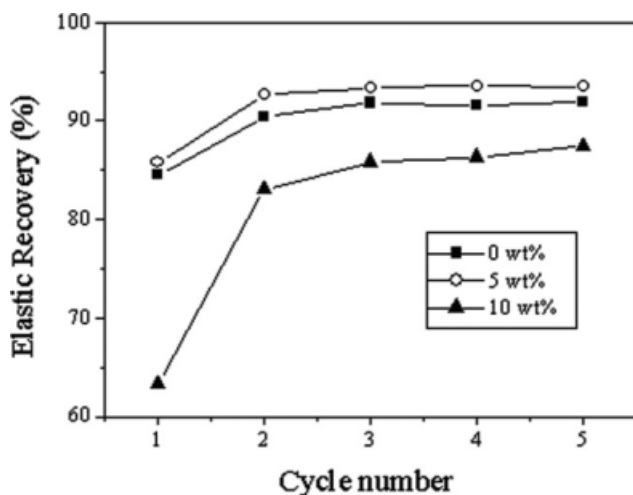


Figure 9 Elastic recovery of PVDF/DBP fibers with different DBP concentrations.

Figure 8 shows the effect of the DBP concentration on the behavior of the first cycle of PVDF fibers. The elastic recovery of pure PVDF fibers was about 85% in the first cycle, and the initial elastic modulus was 2.2 GPa. As for the PVDF/DBP samples, the initial modulus and stress at 50% extension both decreased with increasing DBP content, as shown in Figure 8. Moreover, DBP also had a great effect on improving the elastic recovery of the fibers, as shown in Figure 9. The fibers with a 5 wt % concentration of DBP had higher elastic recovery than the pure PVDF fibers; the elastic recovery was 86% in the first cycle, then increased from 86 to 93%, and tended to level off after several repeated loading cycles at 50% extension at room temperature, as shown in Figure 9. When the DBP content was 10 wt %, the elastic recovery of the fibers was only 63% in the first cycle, and this was much lower than that of the pure PVDF fibers; then, it increased with repeated loading cycles. This phenomenon (i.e., PVDF/DBP blend fibers having a higher elastic recovery and initial modulus) suggested that these fibers had the characteristics of hard elasticity.

As for the effect of the DBP content on the elastic recovery of the samples, it could be explained that although PVDF and DBP had a certain compatibility, the difference between their solubility parameters indicated that their compatibility was not very good. Therefore, during the crystallization process, DBP could permeate only into the noncrystalline region and not into the crystalline region of the PVDF fibers; this increased the mobility of the PVDF molecular chains in the amorphous region. In our previous study,⁴ we found that a perfect crystal structure and a noncrystalline region with good mobility could improve the elastic recovery of PVDF fibers. Similarly, the good mobility of the noncrystalline

region could improve the elastic recovery of the PVDF/DBP blend fibers, so the fibers with a 5 wt % concentration of DBP had the highest value. However, the amount of DBP added to PVDF was not very much; when the DBP concentration was higher than 5 wt %, the elastic recovery of the fibers decreased. Therefore, PVDF with a 5 wt % concentration of DBP may be a good choice for preparing hard elastic PVDF fibers.

CONCLUSIONS

The effects of DBP on the morphology and mechanical properties of PVDF fibers were discussed. The following conclusions were reached from the examination of these data.

XRD results showed that the addition of a small amount of DBP to PVDF fibers favored the formation of an α -crystal structure. The total crystallinity of the fibers was higher than that of the pure PVDF fibers, and it reached its highest value when the DBP concentration was 2 wt %; then, it decreased with increasing DBP concentration (<10 wt %). However, the melting peak temperature of the samples decreased with increasing DBP content. SAXS results showed that stacked crystalline lamellae, aligned in the direction normal to the fiber axis, existed in the fibers, and their long periods were about 11 nm; they were not affected greatly by the addition of DBP. SEM results showed that there was apparently a small porous structure on the surface of the PVDF/DBP blend fibers, and the more DBP content there was in the PVDF fibers, the more porous structure was obtained. The mechanical properties showed that the breaking strain of PVDF/DBP blend fibers increased with increasing DBP concentration, whereas the breaking stress decreased accordingly. The elastic recovery curve indicated that the fibers with a 5 wt % concentration of DBP had better elastic recovery than pure PVDF fibers, and the elastic recovery increased from 86 to 93% after three repeated loading cycles at 50% extension at room temperature.

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