Fabricating Novel Thermal Crosslinked Ultrafine Fibers via Electrospinning

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ABSTRACT: In this article, we report the preparation of a kind of novel crosslinked ultrafine fiber by electrospinning of unsaturated polyester macromonomers (UPM) and subsequent thermal crosslinking. The UPM is prepared via a two-step reaction with poly(2-methyl-1,3-propyleneadipate) diol terminated (PMPA), isophoronediisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA). Poly(3-hydroxyl-butyrate-co-3-hydroxylvalerate) (PHBV) is chosen to improve the processability of the UPM. UPM/PHBV blend ultrafine fibers are successfully electrospun with a proper mass ratio of UPM to PHBV in dichloromethane solution. The fibers are thermally crosslinked after electrospinning. Measurement results indicate that the average diameter of the fibers is about 1 μm and the crosslinked fibers have good solvent-stability and thermal-stability. This novel fiber has potential applications in filtration and protective coating. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2142–2149, 2008

Key words: electrospinning; unsaturated polyester macromonomer (UPM); thermal crosslinking; stability

INTRODUCTION

In recent years, electrospinning has been drawing widespread attention due to its distinguished convenience and simplicity in fabrication fibrous materials with diameters ranging from several micrometers down to tens of nanometers. Because of their huge specific surface area and ultrahigh porosity, electrospun fibers and mats have great potential in such applications as filtration, protective coating, biosensor/chemosensor, and reinforcement in composite materials.[1–9] However, many applications have been limited for the common defects of electrospun fibers and mats such as poor thermal-stability, bad solvent-stability, and low mechanical strength.[10–12] For instance, electrospun poly(vinyl alcohol) (PVA) fibers can dissolve in water easily.[13,14] Lots of methods including surface modification,[15] heat treatment,[10,11,16] and chemical crosslinking[12,14,17–22] have been brought forward to solve these problems and

made improvements. In these methods, chemical crosslinking is an effectual one. Polymer molecules in electrospun fibers can be chemical crosslinked so that the fibers will not dissolve and also can be applied at a much higher ambient temperature. Several papers have reported on generating chemical crosslinked ultrafine fibers by electrospinning. Yi et al. reported that crosslinked eggshell membrane protein ultrafine fiber could be fabricated by dipping it in DCC (a catalyst) after electrospinning.[18] Zeng et al. prepared photocurable PVA derivative electrospun fiber and found that the fibers proved to be water stable after UV irradiation for more than 3 min.[19] Li and Hsieh reported that poly(acrylic acid) (PAA) electrospun fibers could be rendered insoluble in water by crosslinking with the addition of β-cyclodextrin and heating at 140°C for 20 min.[20]

Unsaturated polyester is one kind of extremely common thermosetting material. It has lots of good properties, such as good resistance against water, acids, oxidizing agents, organic solvents, light and weather. It is also one kind of nontoxic and environment-friendly material. Because of these merits, unsaturated polyester is wildly used in many different areas.[23–25]

Macromonomer and its preparing technique were firstly reported by Milkovich in 1980.[26] Macromonomer is a kind of polymer monomer whose terminal group can be further polymerized. Usually its molec-

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ular weight is in the range of several thousand to tens of thousands. Because of its relatively longer molecular chain, macromonomer has relatively less reactive groups that can participate in crosslinking reaction. Therefore macromonomer has the advantage of low shrinkage after crosslinking and can be used in those areas which request high size stability and high precision.[27,28]

In this study, a kind of diol-terminated acyclic polyester oligomer with average molecular weight of 2000 was selected as the primary experiment material. This polyester oligomer was functionalized with 2-hydroxyethyl methacrylate (HEMA) via a quantitative two-step reaction in order to change it into a kind of crosslinkable unsaturated polyester macromonomer (UPM). This UPM could not be electrospun directly as a result of its low solution viscosity which attributed to its low molecular weight, so poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), another acyclic polyester, was used to improve the processability of the UPM. After electrospinning, a crosslinked electrospun mat was prepared by thermally crosslinking the ultrafine fibers. Some relevant measurements were done to characterize the structure and crosslinking of the ultrafine fiber. To our knowledge, it is the first time that the thermal crosslinked ultrafine fibers from macromonomers were prepared via electrospinning.

EXPERIMENTAL

Materials

Poly(2-methyl-1,3-propylene adipate), diol terminated (PMPA) with average molecular weight of 2000 were purchased from Aldrich (Milwaukee, WI), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich (Germany). Isophorone diisocyanate (IPDI) (Fluka, Germany) and dibutyltin dilaurate (DBTDL) (catalyst) was purchased from Fluka (Italy). Acetone, dichloromethane and benzoyl peroxide (BPO) (initiator) were purchased from Sinopharm Chemical Reagent (China). All the chemicals above are of analytical grade and used without further purification. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) ($M_n = 460,000$, HV content = 3%) were kindly supplied by Ningbo TianAn Co. (China) as an injection-molding grade and were purified before being used.

Preparation of unsaturated polyester macromonomer

UPM in this study was prepared based on PMPA, IPDI and HEMA. First, PMPA was dissolved in acetone as desired content in a four-neck flask. After that, IPDI solution in acetone and DBTDL were added into the flask. The mixture was kept stirring under nitrogen atmosphere at 40°C for 6 h. Then the calculated quantity of HEMA and DBTDL were
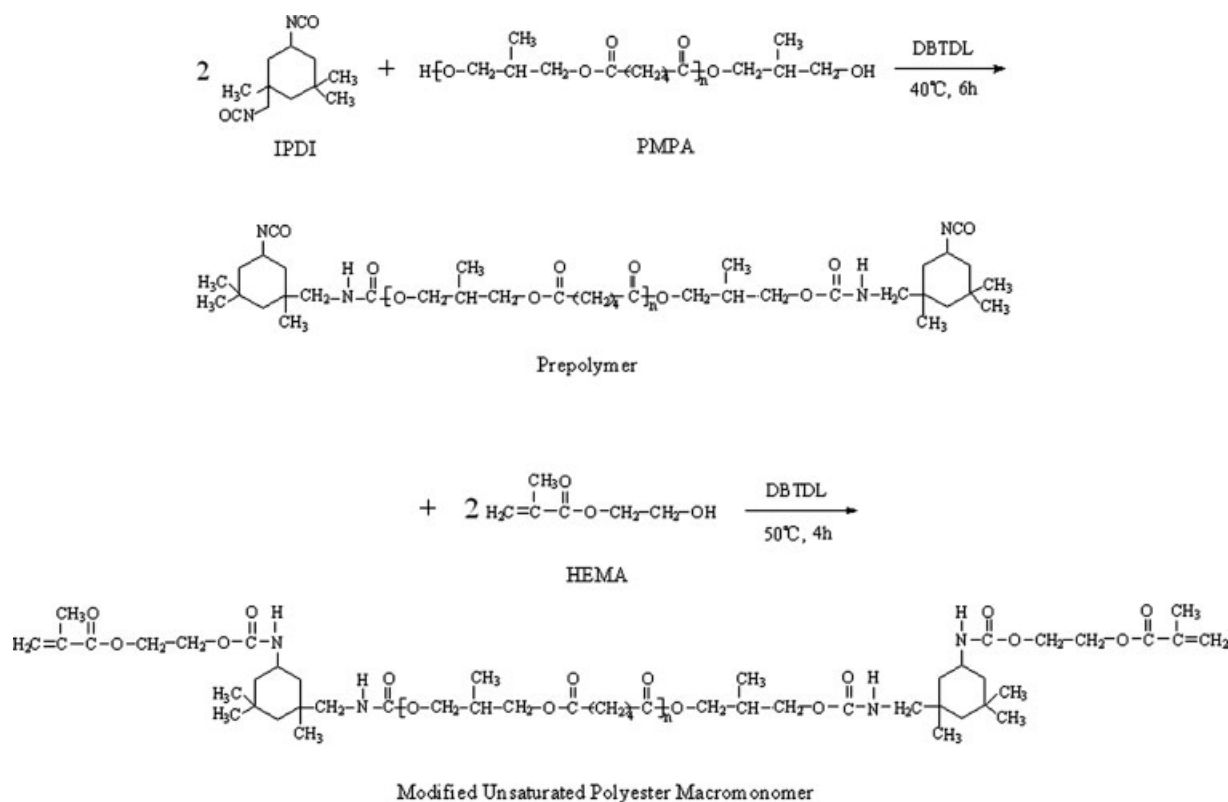
Scheme 1 Synthesis of unsaturated polyester macromonomer.
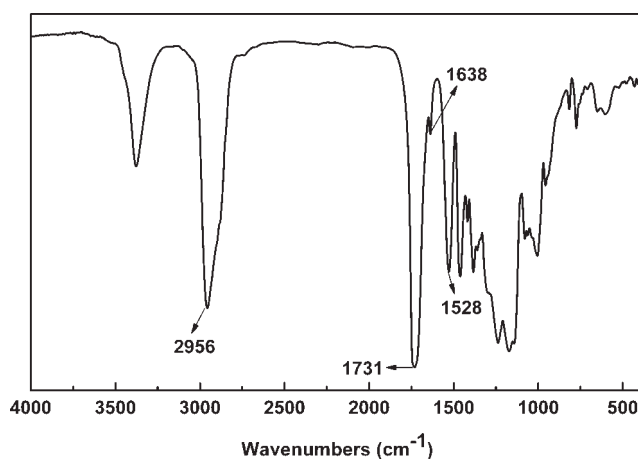
Figure 1 FTIR spectrum of the unsaturated polyester macromonomer prepared.

added and the whole mixture was stirred under nitrogen atmosphere at 50°C for another 4 h. After these reactions, the final UPM was gained and was dried in vacuum desiccator at 20°C for 12 h in order to remove acetone.

Electrospinning

The electrospinning apparatus used in this study consisted of a syringe with a flat-end stainless steel needle and a syringe pump (KD Scientific, Model 100) for controlling feeding rates, a collecting plate wrapped with aluminum foil and a high-voltage supply (Shanghai Shenfa, JG50-1) which was capable of generating DC voltage up to 60 kV. In a typical experimental process, UPM/PHBV blend solutions in dichloromethane with different ratio of UPM and PHBV were prepared and BPO was added. After completely stirred, the mixture was then transferred into the syringe. A 14 kV positive voltage was applied to the solution via the needle and a constant feeding rate of solution (0.8 mL/h) was given by the syringe pump. The distance between the tip of needle and aluminum foil was
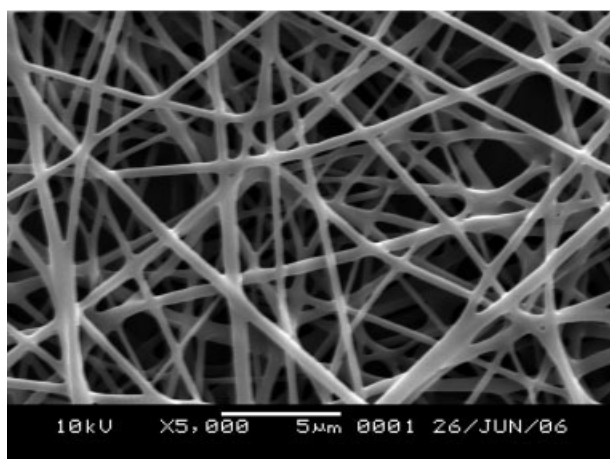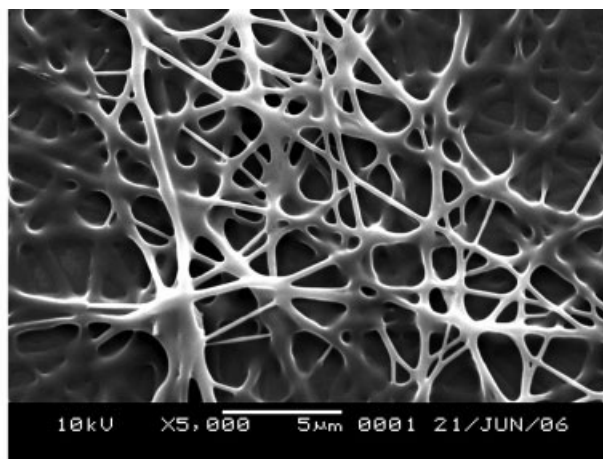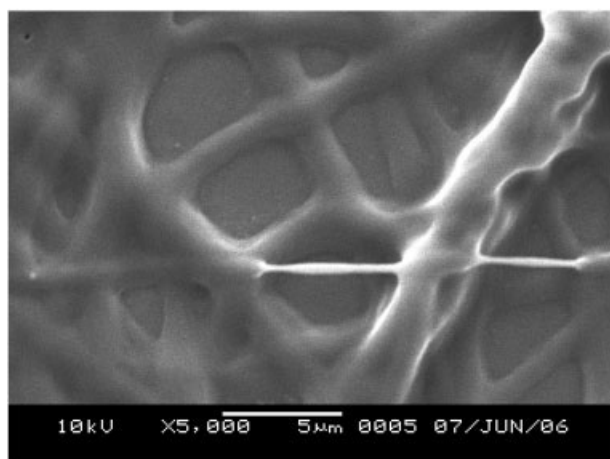
Figure 2 SEM micrographs of UPM/PHBV blend electrospun fibers with different UPM/PHBV ratio: (a) UPM/PHBV = 4/1; (b) UPM/PHBV = 7/1; (c) UPM/PHBV = 10/1, the PHBV concentration of all samples above is fixed to 0.8 wt %.
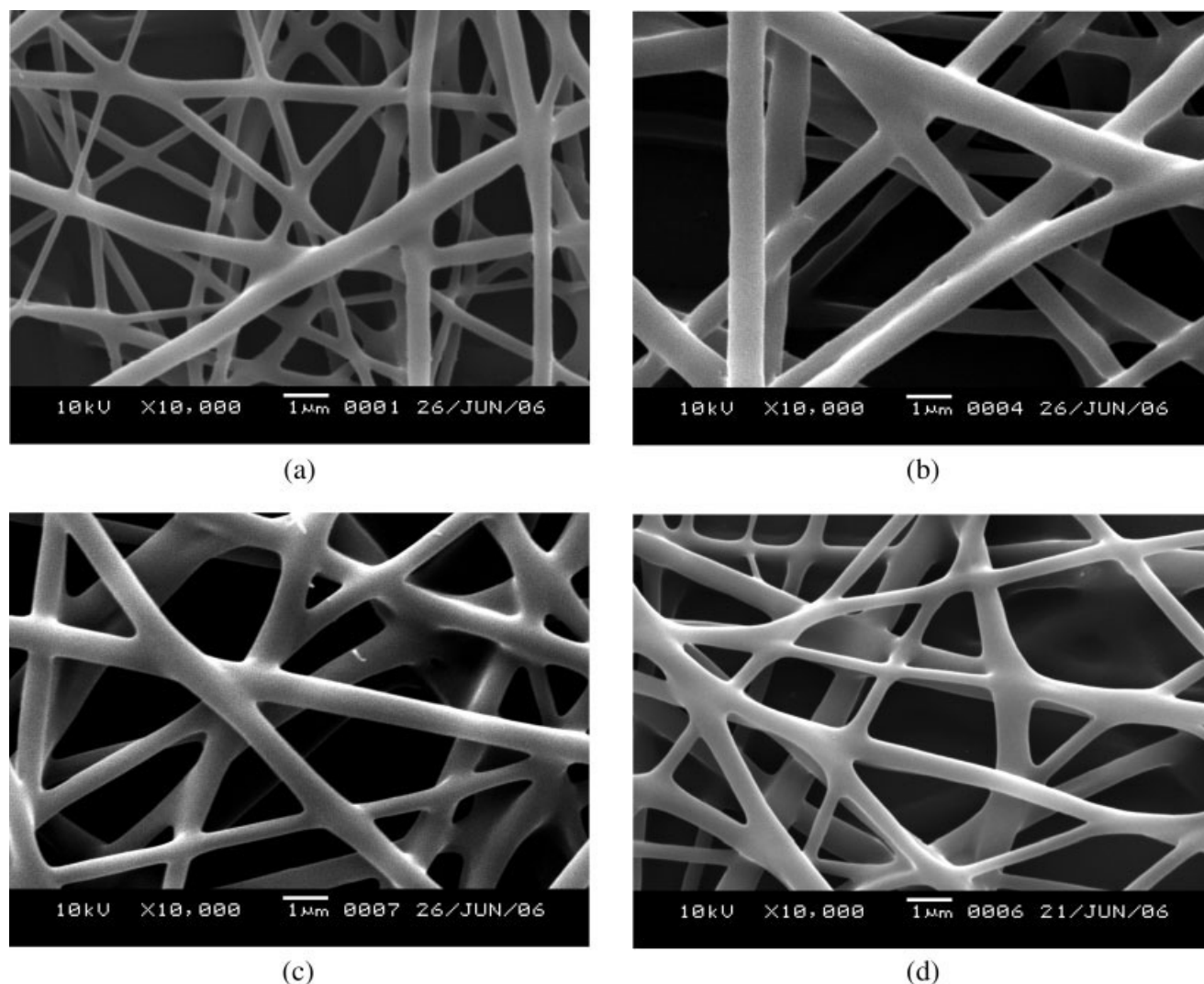
Figure 3 SEM micrographs of UPM/PHBV blend electrospun fibers from spinning solutions with different solid contents: (a) 4 wt % (UPM/PHBV = 3.2/0.8 wt %); (b) 5 wt % (UPM/PHBV = 4.0/1.0 wt %); (c) 7.5 wt % (UPM/PHBV = 6.0/1.5 wt %); (d) 10 wt % (UPM/PHBV = 8.0/2.0 wt %).

14 cm. The ambient temperature was 22°C and the humidity was 50%.

Thermal crosslinking

The thermal crosslinking process was carried out by placing the UPM/PHBV blend electrospun mat on the aluminum foil in vacuum oven at 90°C for 8 h.

Characterizations

The structures of both the UPMs and the electrospun fibers were characterized by Fourier transform infrared (FTIR) which was performed on a FTIR spectrophotometer(NEXUS-670, Nicolet)in the mid-infrared range from 4000 to 500 cm^{-1}.

Morphologies of the electrospun fibers were observed under a scanning electron microscopy (SEM) (JSM-5600LV, JEOL) at 10 kV accelerating voltage after sputter-coating with gold.

Solvent-stability of crosslinked electrospun fibers was tested by immersing them into acetone for 24 h and then drying them for 24 h, followed by observation of the morphologies by using SEM. The microscopic morphologies of the fibers before and after immersion were compared.

Thermal-stability of crosslinked electrospun fibers was characterized by thermo-gravimetric analysis (TGA) which was performed on a Netzsch STA 409 PC thermal analyzer under nitrogen atmosphere from room temperature to 600°C at a heating rate 10°C/min.

RESULTS AND DISCUSSION

Preparation of unsaturated polyester macromonomer

The reaction process is shown in Scheme 1. UPMs were obtained by means of a two-step reaction
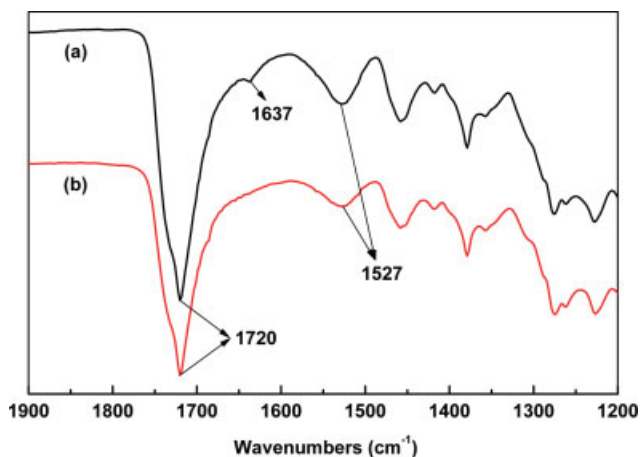
Figure 4 FTIR spectra of UPM/PHBV (3.2/0.8 wt %) blend electrospun fibers: (Curve a) before thermal crosslinking, (Curve b) after thermal crosslinking. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

among PMPA, IPDI and HEMA in acetone. The whole reaction was under the protection of nitrogen gas in order to exclude water.

The FTIR spectrum of the UPM prepared is shown in Figure 1. It can be found that the FTIR absorption peaks for N-H groups at 2956 cm^{-1}, ester group at 1731 cm^{-1}, $\overset{O}{\underset{||}{-C}}\,\overset{H}{\underset{|}{-N-}}$ group of urethane at 1528

cm^{-1} and C=C vinyl group at 1638 cm^{-1} were obvious. The existence of $\overset{O}{\underset{||}{-C}}\,\overset{H}{\underset{|}{-N-}}$ group makes clear that PMPA and HEMA were successfully reacted with IPDI. The absence of any peaks at 2272 cm^{-1}, 1783–1776 cm^{-1}, and 1410 cm^{-1} indicate that no NCO group, uretidindion and isocyanurate were detected by FTIR. The absence of NCO group illuminates that the graft reaction was gone along thoroughly and the absence of uretidindion and isocyanurate illuminates that seldom side-reactions were arisen.[29–32]

Electrospinning of UPM/PHBV blends

Solutions with different concentrations and ratios of UPM to PHBV were electrospun. The ratio of UPM to PHBV played an important role in the formation and controlling morphology of the fibers. High UPM/PHBV ratio made the electrospinning process unstable. Most of the fibers in the elecctrospun mat were sticky and conglutinated together. The meshy structure collapsed in many parts of the mat [as shown in Fig. 2(b)]. If the UPM/PHBV ratio increased to 10 : 1, the conglutination was very severe and spread over the mat. Hardly any fibers apart could be observed by SEM [Fig. 2(c)]. When the
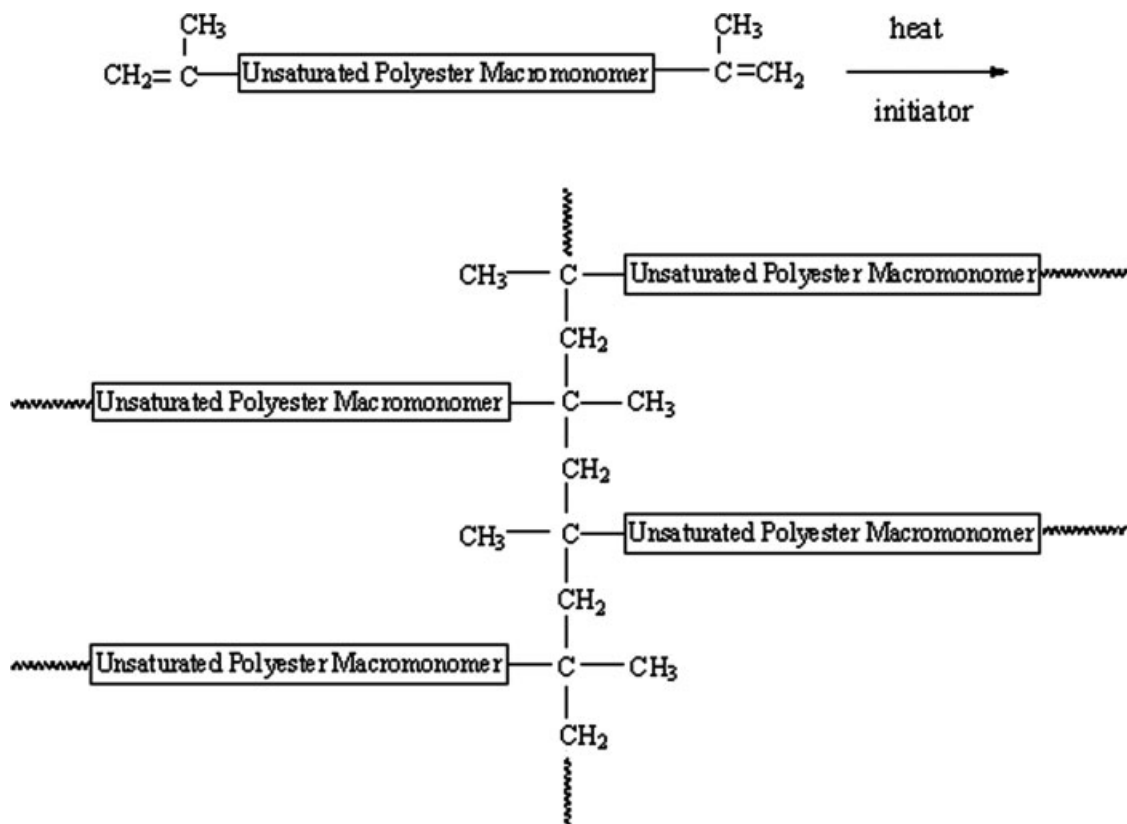
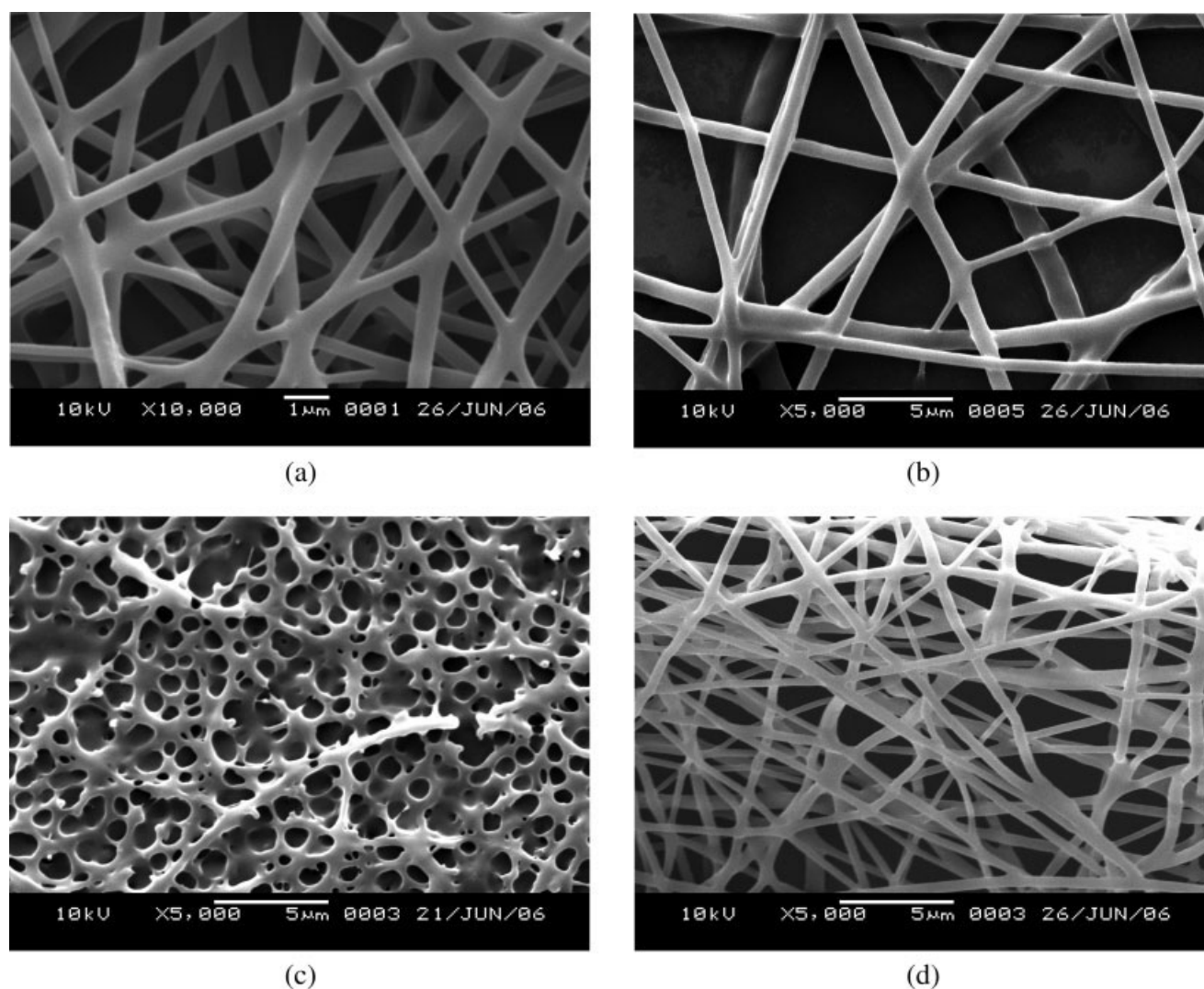**Scheme 2** Thermal crosslinking of unsaturated polyester macromonomer.

Figure 5 SEM micrographs of UPM/PHBV (3.2/0.8 wt %) blend electrospun fibers: (a) before thermal crosslinking; (b) after thermal crosslinking for 8 h; (c) after thermal crosslinking for 2 h, dipped in acetone for 24 h; (d) after thermal crosslinking for 8 h, dipped in acetone for 24 h.

UPM/PHBV ratio decreased to 4 : 1, a successful electrospinning proceeded and a uniform fiber structure was observed by SEM [Fig. 2(a)]. At a constant ratio of UPM to PHBV as 4 : 1, solutions with different solid contents were electrospun (as shown in Figure 3).

Figure 3 shows SEM images of the UPM/PHBV blend fibers with solution concentration from 4 to 10 wt % (UPM/PHBV = 4 : 1). The effect of concentrations on the diameters of UPM/PHBV blend electrospun fibers was not obvious. Fibers electrospun from solutions with relatively low concentration (4 wt %) [Fig. 3(a)] have almost same diameters as those from solutions with relatively high concentration (10 wt %) [Fig. 3(d)]. The average diameter of the samples was about 1 μm. This phenomenon was very similar with that of electrospinning pure PHBV solution in dichloromethane with low concentration (from 0.8 to

4 wt %).[33] So it was considered that the UPM, which had much lower molecular weight, contributed little to the diameter variation of the electrospun fibers. The diameter was mainly controlled by the PHBV content.

Thermal crosslinking of UPM/PHBV blend electrospun fibers

The electrospun fibers (the UPM/PHBV ratio of mass concentration was 3.2 : 0.8 wt %) were put in vacuum oven and then heated at 90°C. After thermal crosslinking for 8 h, the fibers were characterized by FTIR spectroscopy to verify the change in the structure of the crosslinked fibers. Figure 4 shows the FTIR spectra of UPM/PHBV blend electrospun fibers before and after thermal crosslinking. The major peaks for UPM/PHBV blend at 1637 cm^{-1} in curve
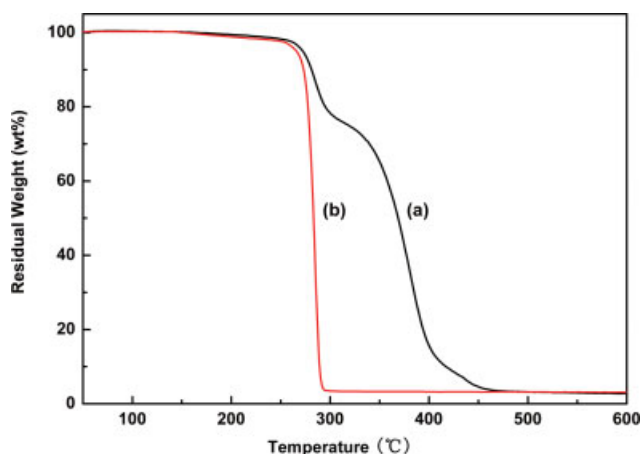
Figure 6 Thermogravimetric curves of crosslinked UPM/PHBV blend electrospun fibers and pure PHBV: (a) crosslinked UPM/PHBV blend electrospun fibers with UPM/PHBV ratio of 3.2/0.8%; (b) pure PHBV. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(a), 1720 and 1527 cm^{-1} in both curve (a) and curve (b) were attributed to C=C vinyl group, ester group and

$$\begin{matrix} O & H \\ \| & | \\ -C & - N - \end{matrix}$$

group of urethane. After thermal crosslinking, the C=C stretching peak disappeared, as shown in curve (b). It indicates that the double bonds at the terminals of the UPM were reacted after heating (as shown in Scheme 2).[30,31,34,35]

UPM was freely soluble in acetone, so the thermal crosslinked electrospun fibers (the UPM/PHBV ratio of concentration was 3.2 : 0.8 wt %) were dipped into acetone for 24 h to test their solubility, and then the SEM micrographs of the fibers before and after thermal crosslinking were taken. It can be found that no obvious changes of the morphology of the fibers took place, only the surface of the fibers turned to be a slightly rougher [Fig. 5(b)].

The degree of crosslinking and the acetone stability of the electrospun fibers were closely related to the thermal treatment time, as shown in Figure 5(c,d). With insufficient thermal crosslinking (2 h), parts of the electrospun mat were dissolved in acetone and a porous structure was formed, while sufficient thermal crosslinking (8 h) resulted in the fibers with good acetone- stability. The morphology of the fibers kept well and no dissolving, swelling, breaking and shrinking were observed by SEM.

The TGA thermograms of both crosslinked UPM/PHBV electrospun fibers (the UPM/PHBV ratio of concentration was 3.2 : 0.8 wt %) and pure PHBV are compared in Figure 6. It can be observed from curve (a) that crosslinking of UPM/PHBV electrospun fibers occurred in two weighted-loss steps. The first step started at about 230°C, the curve had a smooth decline to 280°C and then sharply declined

to 300°C, at which the removed weight reached 20%. This proportion of weight loss was consistent with the PHBV content in UPM/PHBV blend, in the same way, the initial and final decomposition temperatures were in agreement with those of pure PHBV (curve (b)). It is believed that the weight loss was caused by the thermal decomposition of PHBV. The second step was between 320°C and 450°C. A sharp decline of the weight occurred near 350°C and 10% weight remained when the temperature reached 400°C. This was the result of thermal decomposition of the crosslinked UPM in the blend. The blend fibers were totally decomposed after 470°C.

CONCLUSIONS

UPM based on acyclic polyester was prepared by means of successfully modification of the polyester with the double bonds. UPM/PHBV blend solution in dichloromethane could be electrospun well when the UPM /PHBV ratio reached 4 : 1. The average diameter of the fibers was about 1 μm. Crosslinked UPM/PHBV blend ultrafine fibers could be generated with subsequent thermal treatment. After thermal crosslinking for 8 h, the UPM/PHBV blend fibers exhibited good acetone-stability. They had a good potential for application in those areas where solvent-stable and thermal-stable materials were required, such as filtration, protective coating etc. Further research will be focused on the investigation of phase distribution of the crosslinked UPM/PHBV fiber.

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