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Electrospinning of the Solvents-resistant Nanofibers Based on Poly(acrylonitrile-co-glycidyl methacrylate)

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ABSTRACT: This article reports the preparation of a novel solvents-resistant nanofiber by electrospinning of poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) and subsequent chemical crosslinking. PANGMA nanofibers with the diameter range of 200 ~ 600 nm were generated from electrospinning of PANGMA/DMF solution of different solution concentrations. Different additives (citric acid and organic salt) were added to reduce the diameter and improve the morphology of the nanofibers. The as-spun PANGMA nanofibers were crosslinked by 27 wt.% ammonia aqua solution at 50 ℃ for 3h to gain the solvents resistance. Swelling test indicated that the crosslinked nanofibers swelled instead of dissolving in several different solvents. The weight loss of all the crosslinked nanofibrous mats immersed in solvents for more than 72 h was very low. The SEM photos of nanofibers after swelling test showed that no damage from solvents on the crosslinked nanofibers could be found and the structure of the nanofibrous mats also kept well. The pore size of the PANGMA nanofibers was also measured. These results all show that the crosslinked PANGMA nanofibers have good solvents resistance. These novel nanofibers have potential applications on the immobilization of homogeneous catalysts and enzymes.

Key words: electrospinning; crosslinking; solvent-resistance; poly(acrylonitrile-co-

glycidyl methacrylate) (PANGMA)

INTRODUCTION

Electrospinning has drawn widespread attention in recent years due to its distinguished versatility and simplicity in fabricating nanofibrous materials.[1-3] Electrospun nanofibers are very suitable as the support for the immobilization of homogeneous catalysts or enzymes because of their exceptionally long length, uniform diameter, huge surface area and highly porous structure.[4-6]

But a big problem is that normally lots of catalytical reactions must be performed in relatively harsh conditions, such as using DMF or THF as solvent and with a high reaction temperature. This requires that the supports should have a good solvents-resistance and thermo-resistance to guarantee the normal running of the supports during the whole reaction process.[7-9] However, most of the ordinary electrospun nanofibers have the common defects of poor solvents-resistance. For instance, electrospun poly(vinyl alcohol) (PVA) fibers even can dissolve in water easily. Chemical crosslinking is the most effectual method to solve the problem[10]. Polymer molecules in electrospun fibers can be chemically crosslinked so that the nanofibers will only swell instead of dissolve in solvents, thus can obtain the solvent-resistance and can be applied in a harsher working surrounding.[11,12]

Poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) is a new polymeric material which is the copolymer of acrylonitrile (AN) and glycidyl methacrylate (GMA). It has both the advantage of the chemical stability from the sturdy backbone of polyacrylonitrile and the advantage of the further reacting ability from the free and active epoxy group on GMA. The epoxy group offers the opportunity for the employment of PANGMA on a variety of activation/coupling chemistries for both crosslinking and chemical grafting of catalysts. An effectual chemical grafting of catalysts on the support not only can lower the leaching greatly but also can make the efficient reuse and recycling of the catalysts come to reality.[13,14]

In this paper, we describe the first results for a novel solvent-resistant electrospun nanofibrous mat, which can be obtained from PANGMA in two steps, first electrospinning PANGMA/DMF solution and second a chemical crosslinking via ammonolysis. This new nanofibrous mat has the potencial application as a stable support for covalent immobilization of homogeneous catalysts and enzymes.

EXPERIMENTAL

Materials

Poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) was synthesized by GKSS Forschungszentrum GmbH with a molecular weight (Mn) of ca. 100,000 and GMA contents of 7 mol.%. Ammonium hydroxide solution (27 wt.%) was purchased from Fluka Co. Citric acid and triethylbenzylammonium chloride (TEBAC) were purchased from Sigma-Aldrich Co. N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and toluene were purchased from Merck KGaA. All the chemicals were directly used without purification.

Preparation of PANGMA nanofibers via electrospinning.

PANGMA was dissolved in dimethylformamide (DMF) at room temperature with moderate stirring for 48 h to form a homogeneous solution. The solution concentration range was from 16 to 24 wt.% . The solution was placed in a 5 mL glass syringe with a metal needle with the inner diameter of 0.8 mm. A high voltage generator was connected to the middle of needle. A rectangler counter electrode covered with the aluminium foil was used as the collector. Typically, electrospinning was performed at applied voltage of 25 kV and the working distance (the distance between the needle tip and the collector) of 25 cm. The feed rate of the solution was controlled by a syringe pump (HARVARD PHD 4400, Harvard Apparatus.Co) to maintain at 1.5 mL/h and the electrospinning time was usually 4 h to obtain sufficient thickness of the mat. After electrospinning, the nanofibrous mat was detached and washed by methanol to remove the DMF and impurities, and then was dried under vacuum at 50 ℃ for 24 h to remove all the liquid.

Crosslinking of the as-spun nanofiber with ammonia

After washed by water, the PANGMA electrospun nanomat (PANGMA-ENM) was treated with 27 wt.% ammonium hydroxide solution to get sufficient crosslinking. The reaction was performed in at 50 ℃ for different crosslinking time. Finally the nanomats were carefully washed by water again and dried under vacuum at 50 ℃ for 24 h to remove all the liquid clearly.

Characterizations

The solvent-resistance of crosslinked PANGMA-ENM was tested by immersing them into different solvents (Toluene, THF, DMF, DMAc and DMSO) and the subsequent swelling test. A piece of well defined length and width (4 cm x 4cm) crosslinked nanomats were weighed first (W_0) and then immersed into different solvents for 72 h, then were taken out and weighed again (W_1). After weighing, samples were washed in methanol to remove the solvents and subsequently were put into vacuum oven to eradicate the solvents (50 ℃ for 24 h). Finally the nanomats were weighed (W_2) after drying. The swelling rate (S) and the weight loss rate (WL) were calculated by the following equations:

$$S = W_1 / W_2$$

$$WL = (W_0 - W_2) / W_0 \times 100\%$$

The structures of both the uncrosslinked and crosslinked PANGMA electrospun nanofibers were characterized by Fourier transform infrared (ATR-FTIR) which was performed on a FTIR spectrophotometer (Bruker Equinox 55, Bruker Optics) in the mid-infrared range from 4000 to 500 cm^{-1}.

The morphology of the PANGMA electrospun nanofibers and nanomats was observed with a scanning electron microscope (LEO Gemini 1550 VP, Zeiss) at 10 kV accelerating voltage after sputter-coating with gold. The average diameters of the nanofibers were calculated from 10 different single values randomly.

The pore size of the PANGMA-ENM was determined using the bubble-point method. It is based on the measurement of pressure necessary to blow air through a liquid-filled membrane. The relationship between the pore size and the corresponding pressure is given by the Young-Laplace equation:

$$R = 2\gamma \cos\theta / \Delta P$$

where R is radius of the pore, ΔP is the differential gas pressure, γ is the surface tension of wetting liquid, and θ is the wetting angle.[15,16]

The measurement was performed on a Porometer 4.900 from Porous Materials Inc. (PMI). The PANGMA-ENM stamps with diameter of 3 cm were immersed in the wetting fluid Porewick® from PMI (surface tension = 16×10^{-5} J/cm (16 dyn/cm)) for more than 15 min and then placed in the test cell. Then, by an automated procedure, a successively increasing pressure was applied across the membrane sample using nitrogen as pressurising gas. At a certain pressure, the surface tension of the pore filling liquid in the largest pores was exceeded. The liquid was displaced and the gas flow through the open pore could be monitored. Further pressure increase caused successive liquid displacement in smaller pores until all pores were open. The measured flow data allowed the calculation of the pore size distribution.

RESULTS AND DISSCUSSION

Electrospinning of PANGMA nanofibers

PANGMA/DMF solutions with different solution concentrations (16 ~ 24 wt.%) were electrospun. The morphologies of the obtained nanfibers are shown in Figure 1. The nanofiberous mats have uniform and beadless morphology and completely structure (Figure 1(a)). It is unexpected that the inside structure of these nanofibers seems to be nodular, instead of compact (Figure 1(b)). A possible reason of forming this structure is the phase inversion during the drying process of the nanofibers after electrospinning.[17-19] DMF is a low volatile solvent in room temperature (Vapor pressure: 490 Pa at 25 ℃). It can not evaporate completely during the electrospinning process and the residual DMF will spontaneously form some solvent rich regions inside the nanofibers. After these remaining DMF diffuses out, the original solvent rich regions transform into small pores and then such nodular structure forms.

Figure 1. SEM micrographs of PANGMA electrospun nanofibers with different morphologies: (a) structure of nanofibrous mat, (b) inside structure of single nanofiber

The diameter and the morphology of the PANGMA nanofibers could be further controlled by adding small amount of organic acid (citric acid) or organic salt (triethylbenzylammonium chloride (TEBAC)) into the spinning solution before electrospinning. Figure 2 shows the SEM photos of the nanofibers electrospun from solution with 1 wt.% citric acid (Figure 2(b)), with 0.5 wt.% TEBAC (Figure 2(c)) and without any additives (Figure 2(a)). The diameters of the neat PANGMA nanofibers are in the range of 400 nm to 600 nm and they are reduced to 250 to 350 nm after the additives added (Figure 3(a)), and also the morphologies of the nanofibers become more uniform.

Figure 2. SEM micrographs of PANGMA nanofibers electrospun from different solution: (a) without any additives, (b) with 1 wt.% citric acid, (c) with 0.5 wt.% TEBAC, the concentration of spinning solution is 22 wt.%

Some literatures have reported that additives can have influence on the diameters of nanofibers through the way of altering the conductivity of the spinning solution.[20,21] Generally, an electrical conductivity of a solution reflects a charge density on a jet, which will have big influence on the elongation level of a jet by in the manner of electrical force. Therefore, under the same applied voltage and spinning distance, a solution with a higher electrical conductivity may cause higher elongation of a jet along its axis and thus electrospinning fibers with smaller diameter. Experiments were performed to study the relationship between fiber diameters and the spinning solution conductivity to verify the hypothesis.

Figure 3. Average diameter of PAMGMA nanofibers (a), solution conductivity (b) with spinning solution with different concentration

Figure 3(a) shows the average diameter of the PANGMA nanofibers with and without adding additives and Figure 3(b) shows the solution conductivity before and after adding additives. It can be seen clearly that the solution conductivity increases while the average fiber diameter decreases after the additives are added. As mentioned above, nanofibers with thinner diameters can be obtained from the spinning solution with higher solution conductivity. A small amount of additives can change the solution conductivity greatly and thus reduce the diameters of the nanofibers.

Crosslinking and the solvents-resistance measurement

The as-spun PANGMA nanofibers must be crosslinked to gain the resistance against organic solvents, such as DMF and DMSO, otherwise its application would be greatly limited. The ammonolysis was performed at 50 ℃ and different crosslinking temperatures were attempted to obtain the best crosslinking conditions. The solvents-resistance of crosslinked PANGMA electrospun nanomat (PANGMA-ENM) was characterized by the weight loss rate of the ENM after immersed in solvents for 72 h.

Figure 4. Weight loss rate of crosslinked PANGMA-ENM crosslinked with different crosslinking time in different solvents

Figure 4 shows the weight loss rate of crosslinked PANGMA-ENM crosslinked with the crosslinking time of 1, 2, 3 and 6 h in DMF, DMAc and DMSO. PANGMA-ENM crosslinked with longer crosslinking time have lower weight loss rate in all the solvents, but there is no obvious difference of the data between crosslinking of 3 h and 6 h, which indicates that 3 h is already sufficient for obtaining stabilized PANGMA-ENM. Crosslinked PANGMA-ENM has excellent resistance against DMSO, also good resistance against DMF and DMAc. The weight loss rate in all the solvents does not exceed 2 wt.%.

Figure 5. FTIR spectrum of PANGMA nanofibers before (a) and after (b) crosslinking, samples prepared with ammonolysis at 50 ℃ for 3h

FTIR measurements were performed to structurally verify the crosslinking of PANGMA nanofibers. Figure 5 is the FTIR spectrum of neat (curve (a)) and crosslinked (curve (b)) nanofibers. On curve (a) there is a clear peak near 908 cm-1 (characteristic peak of epoxy group), which shows the existence of epoxy group in neat PANGMA nanofiber, meanwhile no obvious peak near 908 cm-1 can be found on the curve (b), which further proves that epoxy groups in PANGMA have been crosslinked by ammonia.

Figure 6. SEM micrographs of PANGMA nanofibers after immersed in different solvents for 72 h: (a) THF; (b) Toluene; (c) DMSO; (d) DMAc; (e) DMF

Figure 6 is the SEM photos of the crosslinked PANGMA nanofibers after solvents resistance measurements. Basically, the morphologies of nanofibers keep uniform after being immersed 72 h by solvents. For THF (a) and Toluene (b), PANGMA itself can not dissolve in them at all, so there is almost no change of the morphology and size of nanofibers. Fibers show cylindrical shape with a smooth surface and non-fractured body which is similar with the morphology of the original fibers. Also no deconstruction and deformation of the whole structure of the nanomats can be found. For DMSO (c) and DMAc (d), a slight swelling and distortion of the nanofibers can be observed because DMSO and DMAc can dissolve uncrosslinked PANGMA nanofibers and this sort of fiber morphology is the normal appearances of the swelling of the crosslinked fibers in solvents. The whole structure of these two nanomats keeps very well. For DMF (e), the morphology shows a moderate growth of fiber size and a little adhesion of the fibers. After all, DMF is the best solvent for PANGMA. It can also be observed from the macroscopic view that the weight loss rate (Figure 4) and swelling rate (data not shown) of crosslinked PANGMA-ENM in DMF is higher than those in other solvents. Conclusively, crosslinked PANGMA-ENM has good resistance against many commonly used solvents in catalysis reaction.

It is noteworthy that PANGMA nanofibers with only 7 mol% GMA content already have enough epoxide groups to obtain excellent solvents resistance. It is feasible to synthesize PANGMA with a higher GMA content (higher than 15 mol.%) and partially crosslink them after electrospinning in order to remain enough epoxy groups for providing an additional binding capacity for covalent immobilization of ligands of homogeneous catalysts. Moreover, the formed amino groups during the crosslinking can also be used, after activation with, e.g. glutaraldehyde, for the covalent immobilization of enzymes on to the PANGMA nanofibers.

Figure 7. Pore size distribution histogram of PANGMA-ENM

Figure 7 is the histogram of the pore size distribution of uncrosslinked (green), crosslinked (red) and immersed (purple) PANGMA-ENM. It can be found from the histogram that the pore size of the nanomats slightly reduces after crosslinking and further obviously reduces after immersed in DMF. Some reasonable explanations for the reduction of pore size after crosslinking are: crosslinking happens not only inside nanofibers but also inter nanofibers and this cause a more close inter-linkage of fibers. In addition, a crosslinking temperature of 50 ℃ may induce a slight shrinkage of nanomats. For the reduction after immersion in DMF, the swelling of the crosslinked nanomats will alter both the shape of nanofibers and the structure of the nanomats. The growth of the nanofibers caused by swelling will occupy part of the pore space, resulting in the reduction of pore size, and the shrinking of nanomats during the drying process after swelling will reduce the pore size too.

CONCLUSIONS

In summary, we have demonstrated the preparation of a novel solvents-resistant nanofiber based on the electrospinning of poly(acrylonitrile-co-glycidyl methacrylate) (PANGMA) and the subsequent crosslinking of the nanofibers. The results of relative characterizations indicate that the diameter of the PANGMA nanofibers is in the range of 200 ~ 600 nm and can be controlled by adding different additives into the electrospinning solution. The as-spun PANGMA nanofibers can be successfully crosslinked by 27 wt.% ammonia aqua solution at 50 ℃ for 3h. The pore size of the PANGMA electrospun nanomat (PANGMA-ENM) will reduce after crosslinking and immersion into the solvents. The crosslinked PANGMA nanofibers have good resistance against most of the solvents which are commonly used in catalysis reaction. They have potential applications on the immobilization of homogeneous catalysts and enzymes.

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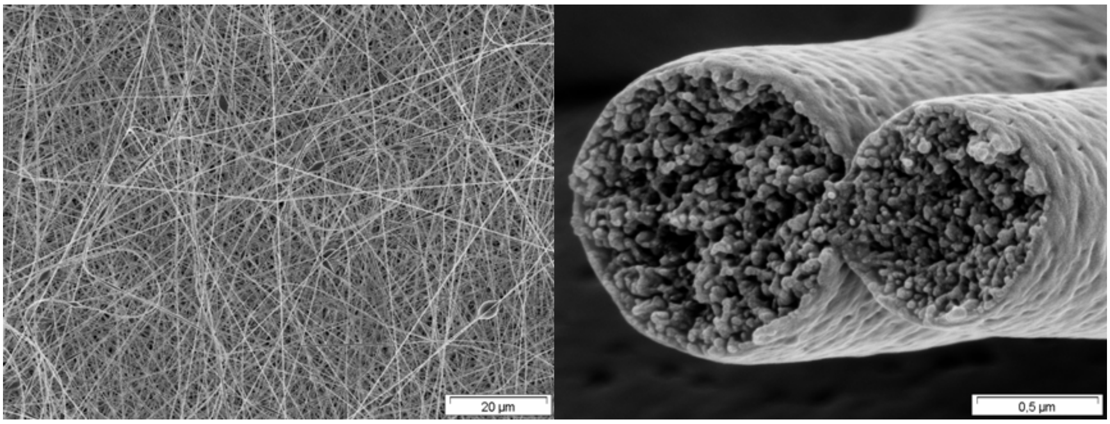
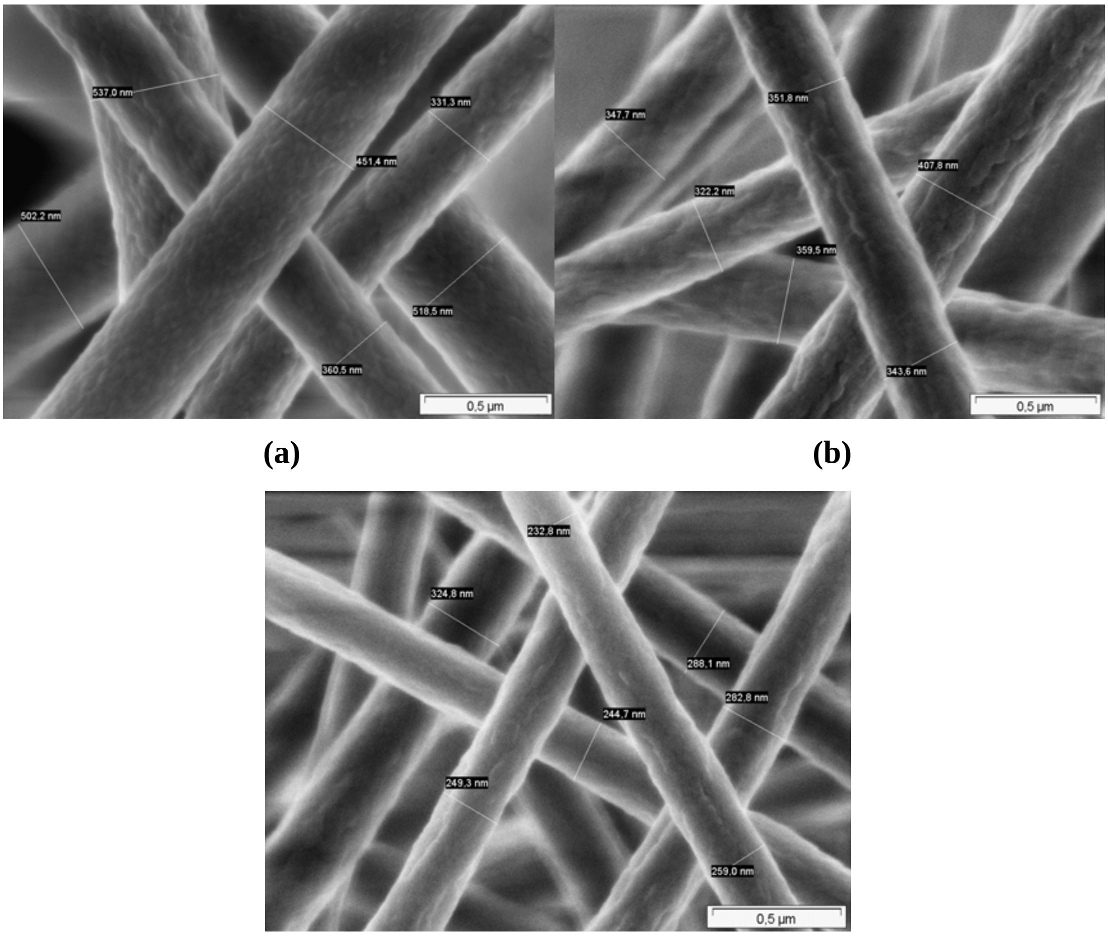


(a) **(b)**

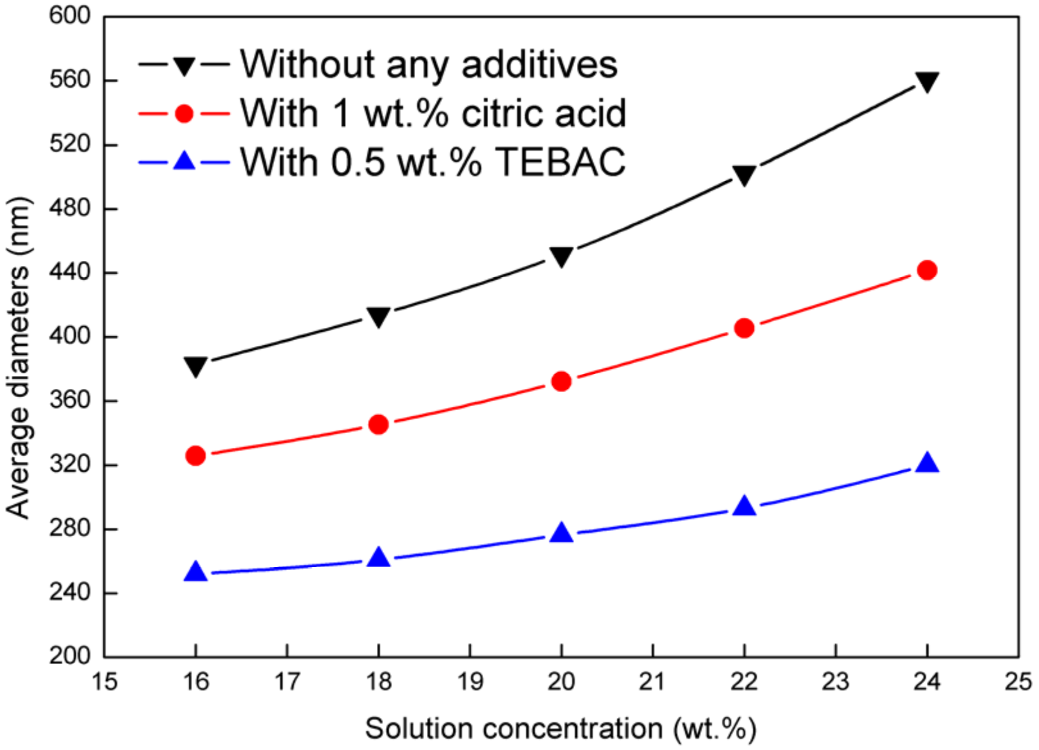
Figure 1. SEM micrographs of PANGMA electrospun nanofibers with different morphologies: (a) structure of nanofibrous mat, (b) inside structure of single nanofiber



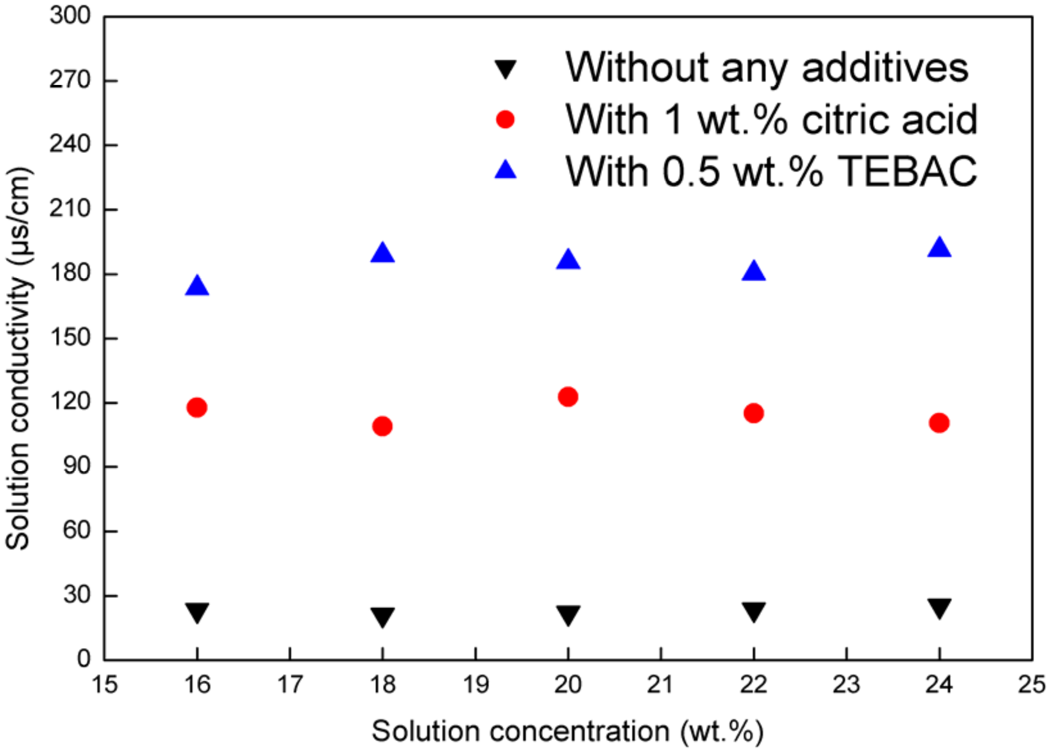
(a) **(b)**

(c)

Figure 2. SEM micrographs of PANGMA nanofibers electrospun from different solution: (a) without any additives, (b) with 1 wt.% citric acid, (c) with 0.5 wt.% TEBAC, the concentration of spinning solution is 22 wt.%



(a)



(b)

Figure 3. Average diameter of PAMGMA nanofibers (a) and solution conductivity of spinning solution (b) with solution concentration

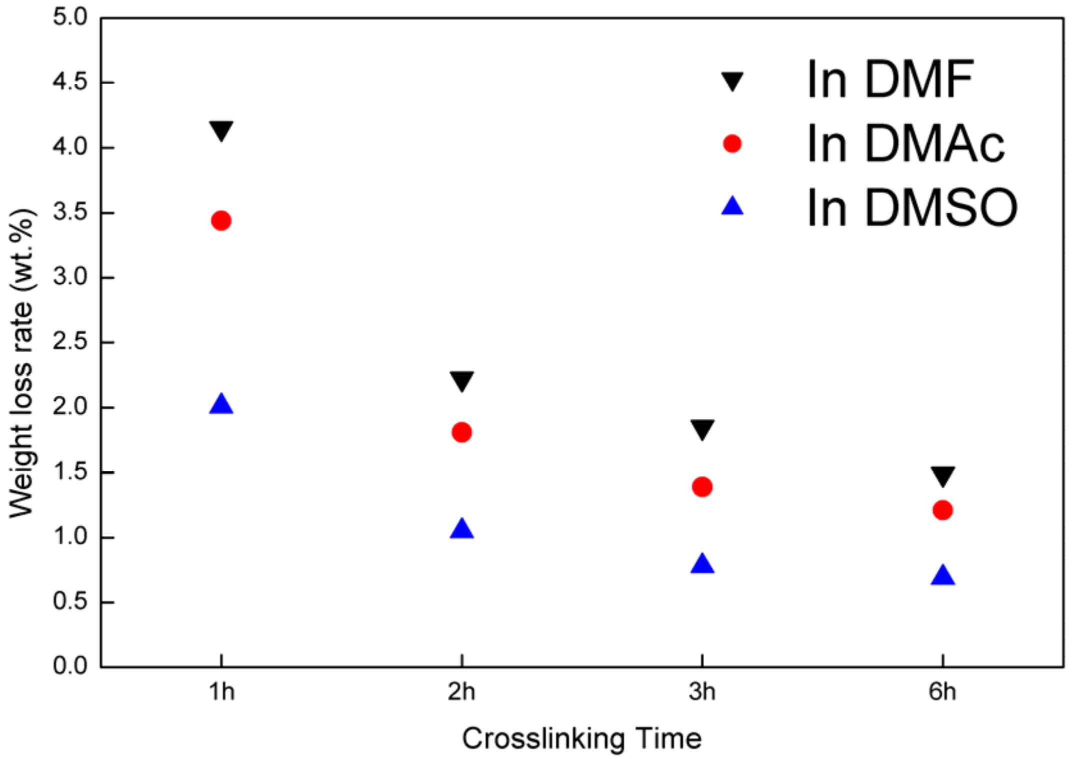


Figure 4. Weight loss rate of C-PANGMA-ENM crosslinked with different crosslinking time in different solvents

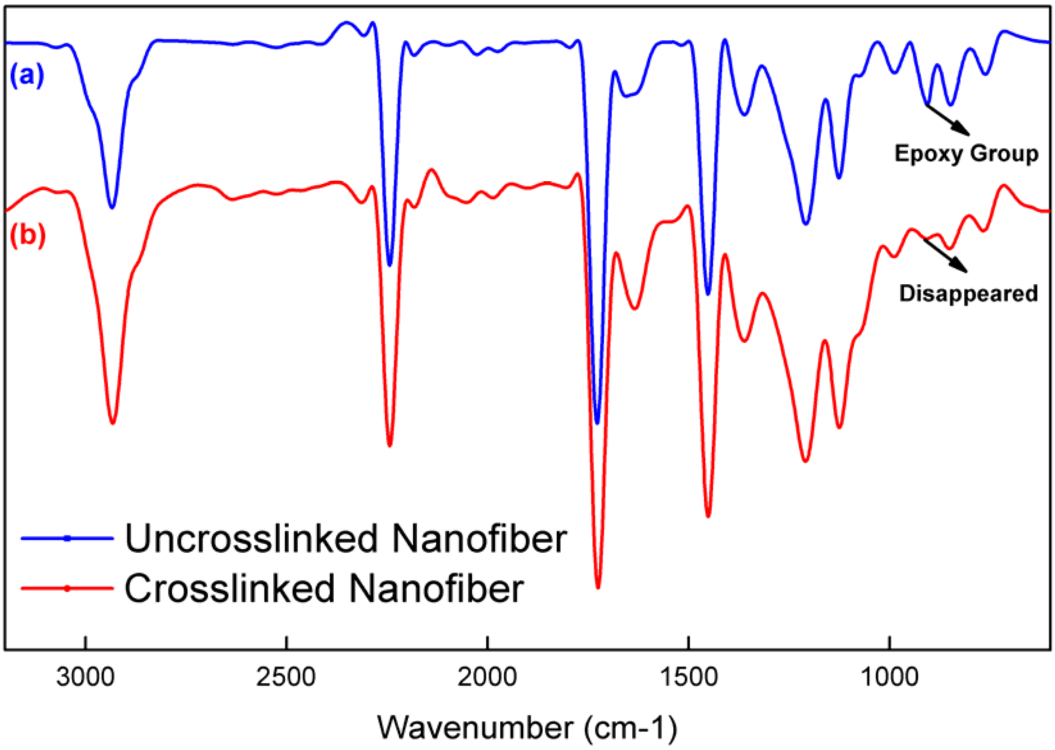
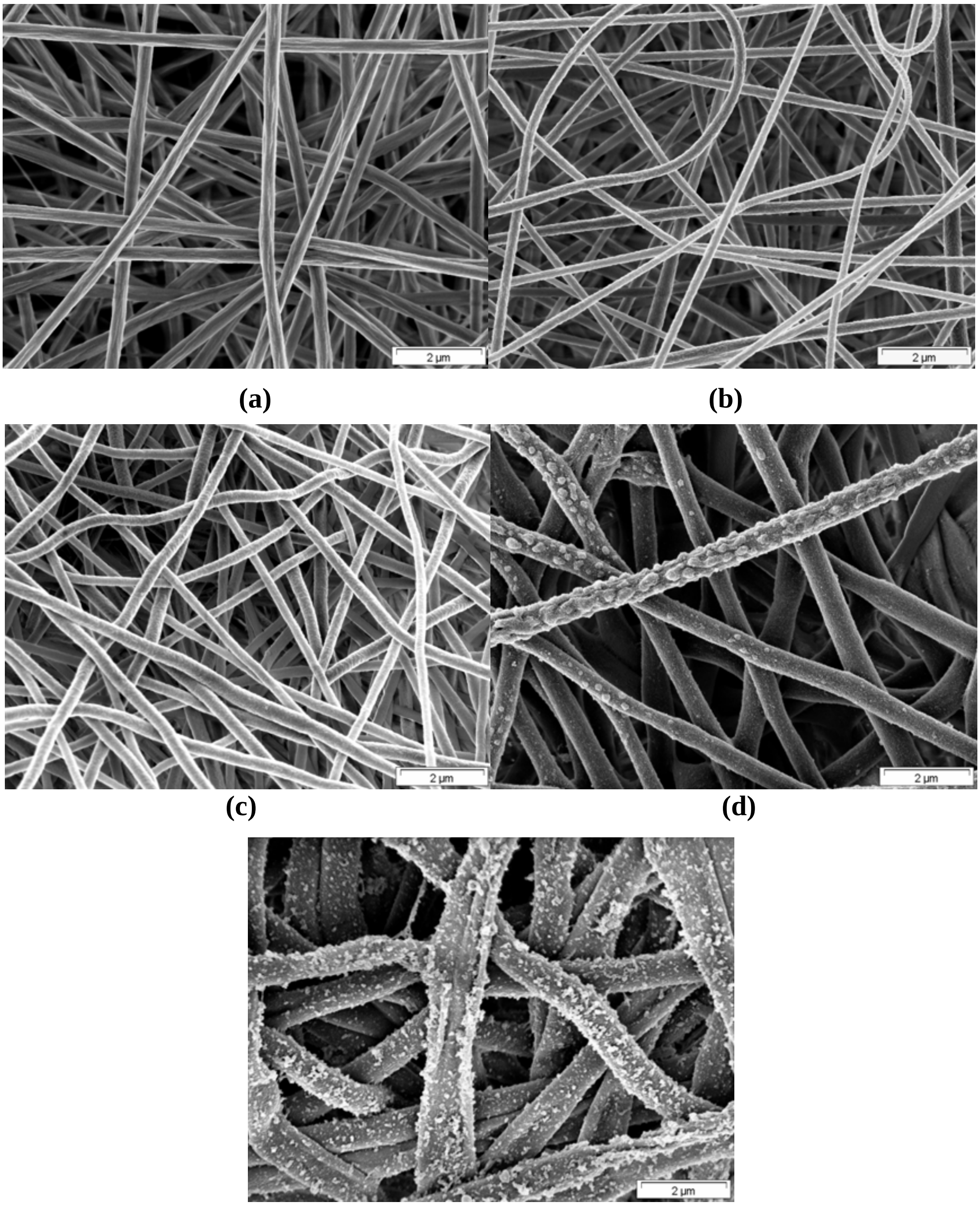


Figure 5. FTIR spectrum of PANGMA nanofibers before (a) and after crosslinking (b), crosslinked samples prepared with ammonolysis at 50℃ for 3h



(a) **(b)**

(c) **(d)**

(e)

Figure 6. SEM micrographs of PANGMA nanofibers after immersed in different solvents for 72 h: (a) THF; (b) Toluene; (c) DMSO; (d) DMAc; (e) DMF

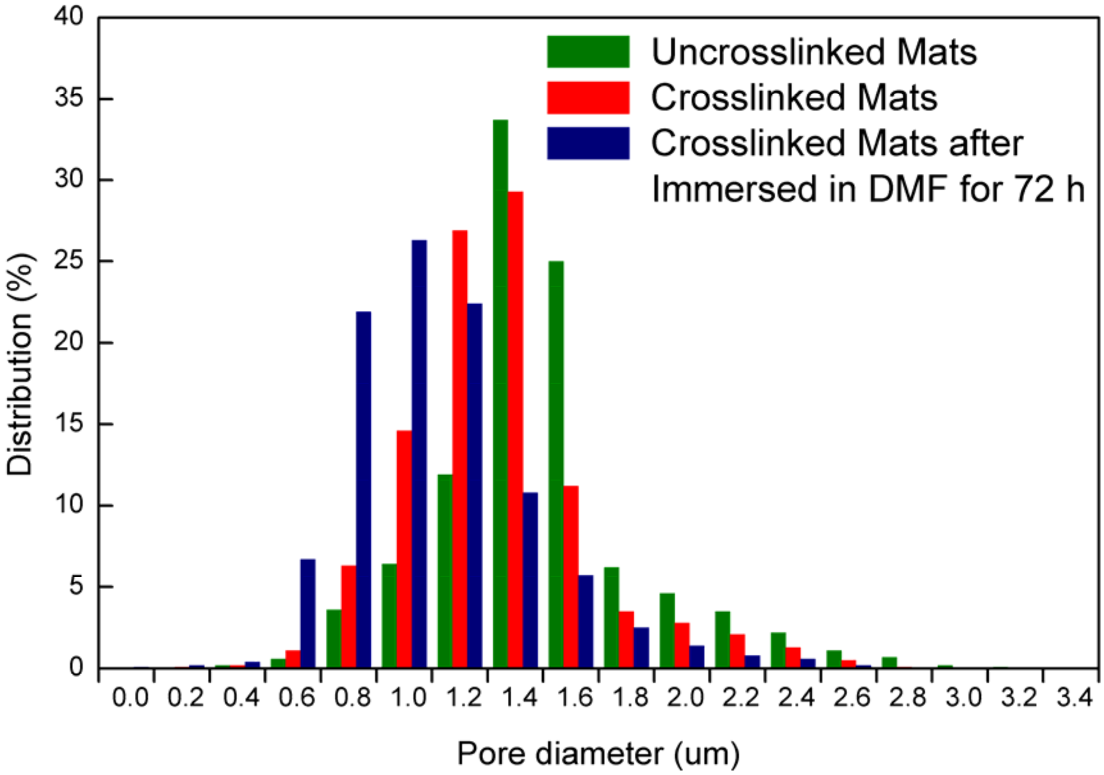


Figure 7. **Pore size distribution histogram of PANGMA-ENM**