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Formation of nanoporous poly(aryl amide ether) (PAAE) films by selective removal of poly(ethylene glycol) (PEG) from PEG/PAAE composite films

Daoji Gan [a], Shiqiang Lu [a], Wendy W. Cao [b,*]

[a] *Department of Materials Science and Engineering, Nanchang Institute of Aeronautical Technology, Nanchang, Jiangxi 330034, People's Republic of China*
[b] *Longtan Scientific, C-310, 8704 Broadview Road, Broadview Heights, OH 44147, USA*

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Abstract

Poly(aryl amide ether) (PAAE) thin films with nanometer-sized pores have been prepared in two steps: (1) solution casting of partially miscible poly(ethylene glycol) (PEG)/PAAE blends from one of their common solvents, dimethyl sulfoxide (DMSO), results in formation of PEG/PAAE nanocomposite films; (2) selective removal of PEG component by water washing yields nanosized, porous PAAE films. The pores have been found to have a small size variation and cover the whole surface homogeneously. With an increase in PEG contents, the sizes of the pores increase but the size distributions do not have much changes. This has been ascribed to formation of small PEG domains in PEG/PAAE composite films, which is facilitated by the strong interactions, mostly hydrogen bonds, between PEG and PAAE macromolecular chains.

Keywords: Poly(aryl amide ether); Poly(ethylene glycol); Nanocomposite films; Nanometer-sized pores

1. Introduction

Interest in high-performance aromatic polyamides arises from their ever-increased potentials in modern industries [1,2]. These polymers exhibit excellent thermal and mechanical properties, which are ascribed to the strong hydrogen bonding among amide groups and high stiffness of the polymer chains rendered by aromatic phenyl groups [3–5]. As further development of those materials, poly(aryl amide ether), due to insertion of flexible ether linkages into the polymer backbone, not only maintains the excellent physical properties, but also yields significantly improved processibility/solubility that cannot be attained from aromatic polyamides [3,4,6,7]. The enhanced solubility in organic solvents makes it possible to generate high-quality free-standing films by a simple technique—solution casting.

Porous polymeric thin films with well-defined, nanometer-sized structures are very much needed for use as electronic devices and nanofiltration membranes [2,8]. These films can be produced by either using blowing agents [9,10] or selectively eliminating a second component that forms nanodomains in composite films [8,11,12]. The latter method has been extensively

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[*] Corresponding author. Tel./fax: +1 440 526 5327.
E-mail address: stephengandj@yahoo.com (W.W. Cao).

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developed and a number of techniques have been employed to remove the second component from the major component matrix. Selective removal of PMMA from PS-b-PMMA film by UV etching has been reported to yield porous films with well-ordered periodic structures [12]. Nanoporous films can also be produced by selectively decomposing, at appropriate temperature, block copolymer films that contains both thermally stable and liable components [8,11]. As an alternative to the synthesis of entirely new block copolymers that contains two components, polymer blends wherein a second component can be removed by selective solvents provide a unique and elegant approach to produce porous films. This method requires that the two components in blending be able to form strong molecular interactions to yield homogeneous distribution of nanodomains that are then removed to produce nanosized pores. Hydrogen bonds have been used for this type of applications; i.e., taking advantage of strong hydrogen bonding between 4-vinylpyridine and a second minor additive, nanoporous films of poly(styrene-block-4-vinylpyridine) (PS-PVP) have been successfully prepared by blending with either 3-pentadecyl phenol [13] or 2-(4′-hydroxybenzeneazo)benzoic acid [14], and then by washing with selective solvents.

In this contribution, we report formation of nanoporous PAAE thin films by washing PAAE/PEG composites with water to remove water-soluble PEG. The strong hydrogen bonding between amide groups of PAAE and oxygen of PEG units [15,16] is expected to result in well-defined nanoscopic morphologies and thereby, removal of PEG leaves nanoporous PAAE film. Whereas our approach bears some similarity to the one used for the preparation of PS-PVP nanoporous films [13,14], this is, according to our knowledge, the first report on the production of nanoporous films of aromatic polyamides by this simple technique. Moreover, our method takes advantage of a simple homopolymer, which is sharply different from the complicated block copolymer of PS-PVP.

2. Experimental

2.1. Materials

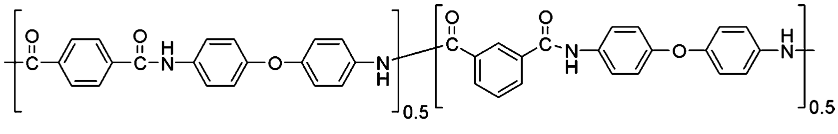
Dimethyl sulfoxide (DMSO) was of analytical grade and used without further purification. Poly(ethylene glycol) (PEG) having a weight-averaged molecular weight (M_w) of 3400 was purchased from Aldirch. Poly(aryl amide ether) (PAAE) (Scheme 1) was synthesized by polycondensation of 4,4′-diaminodiphenyl ether (DAPE) with terephthaloyl chloride (TPC)/isophthaloyl chloride (IPC) (molar ratio: 0.5/0.5) in presence of *N*-methyl-2-pyrrolidone (NMP) as a solvent [17]. The polymer has an inherent viscosity (η_{inh}) of 1.10, as determined by using Ubbelohde-type viscometer at 25 °C in H_2SO_4. Prior to use, mica (New York Mica Company, New York, USA) was peeled off the top layers to yield a fresh surface [18]. Water used in all experiments was double-distilled and then purified by a E-Pure system.

2.2. Film preparation

Blend of PAAE with appropriate amount of PEG was prepared by dissolving both polymers in a common solvent, DMSO. The thin film was produced by spin-coating a 20 μl of polymer(s)/DMSO solution (10 mg/mL) onto a mica surface at a speed of 4000 rotation per minute (rpm). It was dried under vacuum at 80 °C for 2 days. To remove possible residual solvent and, in some cases, to selectively remove PEG to yield porous film, the sample was immersed into water for 8 h, with frequent replacement of fresh water. The film was then dried at 80 °C in vacuum for another 2 days. The relatively thick film was obtained by casting the polymer solution onto a glass slide, followed by the above-mentioned drying procedure.

2.3. Characterization

The ^{1}H NMR of the polymer in DMSO-d_6 was recorded by a 500 MHz Bruker NMR spectrometer, using solvent proton signal as a reference. A Perkin–Elmer thermogravimetric analyzer (TGA) (system 7) was used to measure the thermal stability of the polymers. About 20 mg finely grounded samples were used for all measurements, which were performed in nitrogen atmosphere at a heating rate of 20 °C/min from 50 to 700 °C. The morphologies of the thin films were examined by an atomic force microscope (AFM) (Nanoscope III Scanning Probe Microscope, Digital Instruments, Santa Barbara, CA, USA) [19,20]. The instrument was equipped with a J-type vertical engage scanner and the measurements were performed under a dry nitrogen atmosphere to minimize the effect of air humidity. Approximate film thickness was measured by contact AFM *via* applying a large force (~150 nN) in a 1 × 1



Scheme 1. Chemical structure of poly(aryl amide ether) (PAAE).

μm area of the polymer surface until no further materials were displaced by the AFM tip. The force was then minimized and a larger square of the AFM image was collected to show a height profile across the undisturbed area and the machined field [19,20].

3. Results and discussion

Porous polymer films are prepared first by formation of composite films via blending with a second component, followed by washing off the second component. To yield films with homogeneous distribution of pores, the second component that will be selectively removed should be homogeneously distributed in the major polymer matrix that will serve as the component of the porous films. As required by this way, the second component should have strong interaction with the major component to avoid formation of large and inhomogeneous domains. Optimization of PEG as a second component is based on an assumption that the oxygen in PEG units is capable of forming hydrogen bonds with

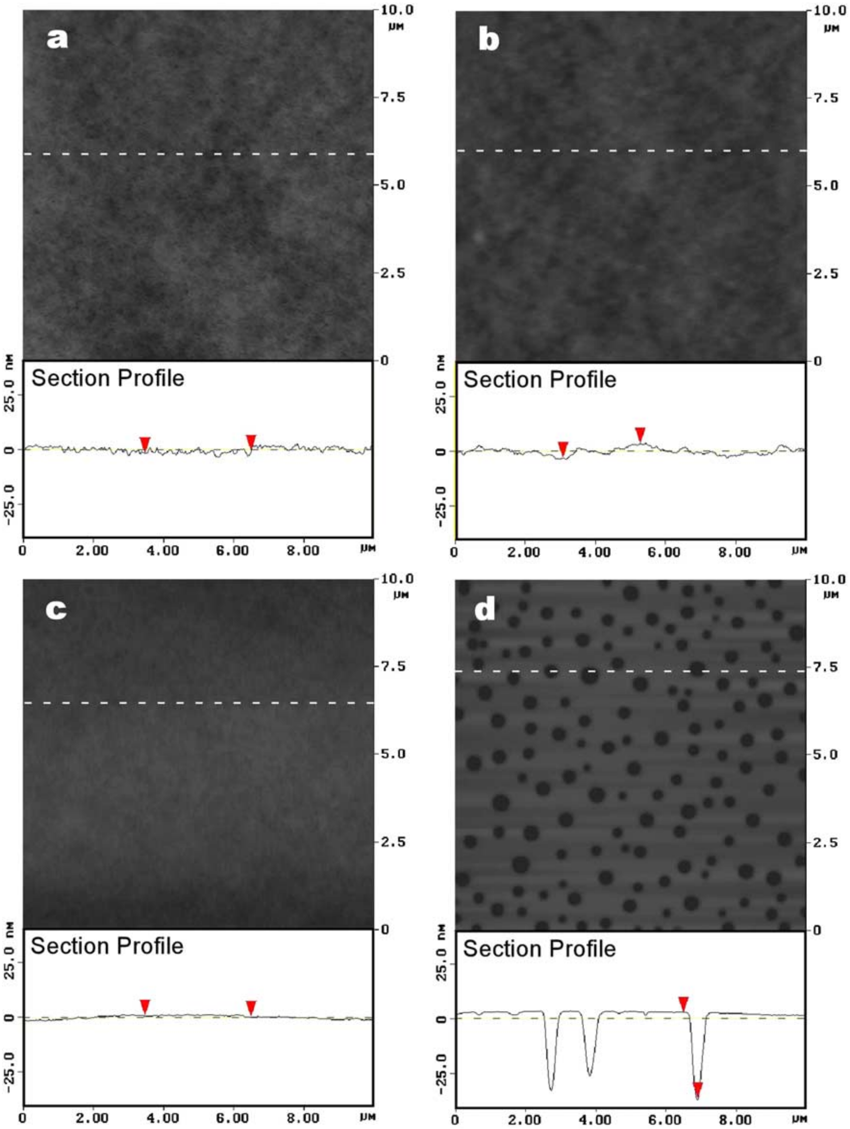


Fig. 1. AFM height images (*Z*: 20 nm) of thin films prepared by spin-coating PAAE onto mica from DMSO (a), followed by immersing the film into water and drying in vacuum (b); and spin-coating PEG/PAAE blend (1/9 by weight) from DMSO (c), followed by selective removal of PEG via water washing (d). A section profile cross the image as indicated by the dash line is shown below each AFM height image.

the amide groups in PAAE [15,16]. As a result, the expected partial miscibility between PEG and PAAE will prevent large phase separation and thereby inhibit formation of non-uniform PEG domains in the PEG/PAAE composite films. The uniform PEG domains are then removed by using water, which is a good solvent for PEG but a non-solvent for PAAE.

The morphologies of the polymer films were examined by AFM (Fig. 1). The PAAE film prepared without using PEG shows a featureless surface, where a root mean square (RMS) roughness in 1 × 1 μm area is 0.34 ± 0.04 nm (Fig. 1a). The section profile, where the representative height variations are presented, reveals a very smooth surface. It thus suggests that spin-coating from PAAE solution in DMSO is able to produce very homogeneous polymer films. It is worth mentioning that evaporation of solvent under vacuum does not give rise to pores in the films. In addition, due to insolubility of PAAE in water, immersion of the PAAE film into water did not lead to change of the film morphologies (Fig. 1b). A very smooth and homogeneous thin film can also be obtained by spin-coating a blending solution of PAAE/PEG onto mica surface (Fig. 1c). However, nanometer-sized pores are observed after the film was washed by water to remove PEG component (Fig. 1d). The pores display a relatively small size variation and cover the whole surface homogeneously. Since the pores are the results of removing PEG domains dotted in the PEG/PAAE composite films, the AFM observations confirm the above-mentioned assumption that strong interactions, mostly hydrogen bonding, exist between PEG and PAAE molecules. The averaged pore sizes were found to be around 550 nm in diameters and 30 nm in depth. By a scratching contact AFM [19,20], the original film was found to be about 32 nm thick, thereby some pores almost go deep to the substrate.

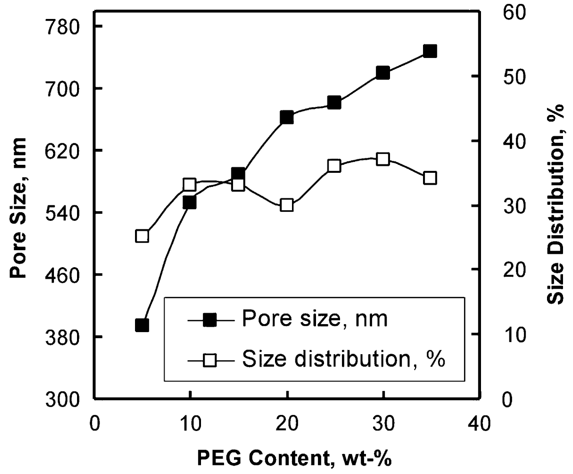


Fig. 2. Dependence of averaged pore sizes and size distributions on the content of PEG used for film preparations.

Since PEG is the source of pores in the films, the effect of PEG contents on the pores should be investigated in more detail. A dependence of the pore sizes and size distributions on the PEG contents used for film preparations is shown in Fig. 2, where the sizes are averaged diameters of pores measured by AFM and, the size distributions are calculated as percentages that represent standard deviations about the mean pore sizes (for example, a measured diameter of 90 ± 9 nm would be defined as having 10% size distribution). Apparently, the pore sizes of the films increase with the contents of PEG used for the film preparation, but the size distributions do not show regular changes since the values fluctuate around 30–40%. The increased pore sizes are the results of increased domain sizes of PEG in the PEG/

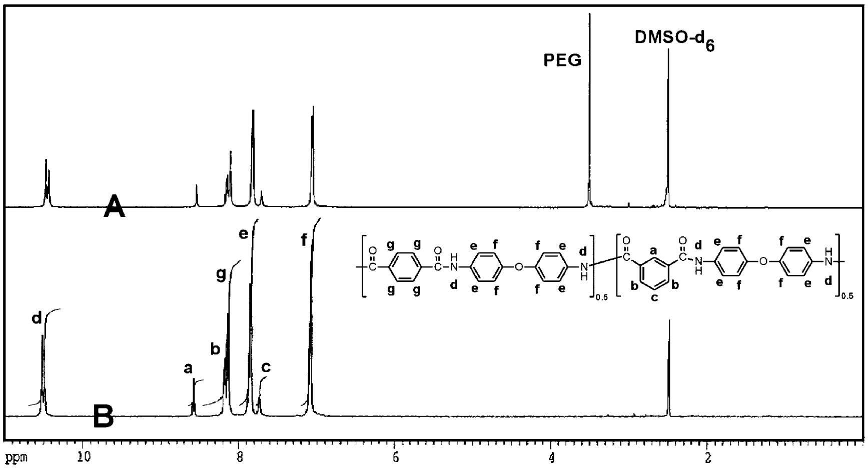


Fig. 3. ^{1}H NMR of PEG/PAAE (1/9 by weight) blend before (A) and after (B) removal of PEG by water washing.

PAAE composite films as the PEG contents increase. In another word, the increased PEG domain sizes, once removed by water washing, lead to an increase in pore sizes in the porous PAAE films. The fact that no large variations of pore size distributions are observed suggests that large phase separation does not occur as the PEG content is kept in this range [16]. Otherwise, increased PEG domain size distributions in PEG/PAAE composite films and consequently increased pore size distributions in PAAE films should be observed as a result of non-uniform PEG domains. Very high content of PEG was not used since it would result in very large portion of pores in the films, which ultimately may lead to very poor mechanical properties of the porous films, especially for thin films.

In view of the strong interactions between PEG and PAAE, it becomes a critical concern if or not the PEG component in the composite films can be completely removed by water. This was checked by using a relatively thicker film sample prepared by solution casting on a glass slide, followed the same water washing procedure as employed for the thin film preparations. Shown in Fig. 3 are the ^{1}H NMR of the film sample before and after water washing. The proton signal of PEG is observed at 3.60 ppm in the PEG/PAAE composite film (Curve A). Water washing leads to complete disappearance of PEG proton signals (Curve B), indicating that the PEG component can be efficiently removed by the water washing procedure. Moreover, the integral ratios of proton signals are consistent with the chemical structure of PAAE, suggesting no chemical damage of the PAAE component occurred during the preparation of porous films. Since PEG can be removed even from the thicker film as evidenced from ^{1}H NMR, removal of PEG from the thin films used for AFM measurements should be much easier and thus expected.

PAAE, as a wholly aromatic polymer, is known to display excellent thermal stability. It is thereby expected that the porous PAAE films exhibit the same thermal properties. This is demonstrated by TGA measurements (Fig. 4), and for comparison a TGA curve of PEG is also shown in Fig. 4. PEG, as an aliphatic polymer, is much less thermally stable compared to PAAE. It should be emphasized that PEG decomposes in a very complete fashion (nearly 0 wt% residue after decomposition) in a very narrow temperature range from 350 to 430 °C. Decomposition of PAAE starts at 450 °C, and by 700 °C about 50 wt% material is decomposed and evaporated. Porous PAAE film shows exactly the same thermal behavior as the powder PAAE that was used for the film preparation. It also suggests no PEG residue in the films because, otherwise, a decomposition curve at lower temperature for the PEG component should be observed, given the complete degradation behavior of pure PEG as mentioned before. This is in agreement with the conclusion drawn from the ^{1}H NMR measurements.

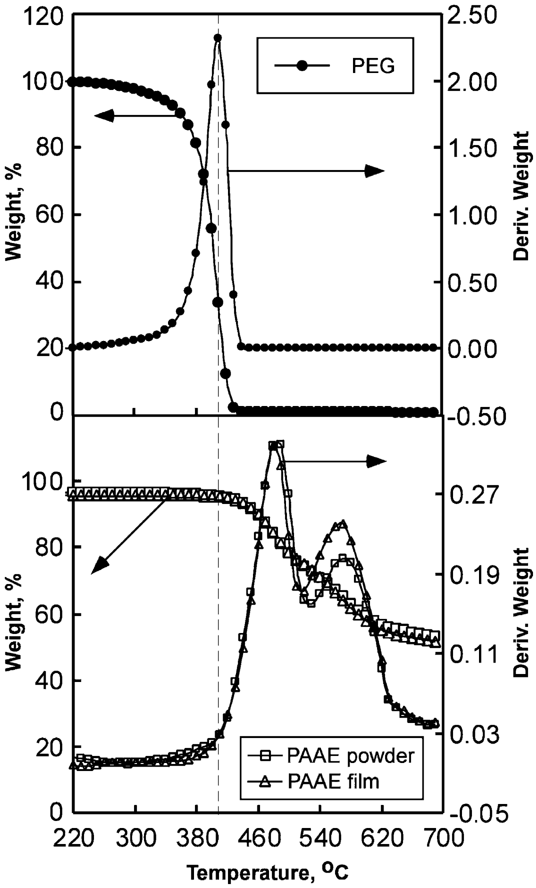


Fig. 4. TGA curves of PEG (solid circle), original PAAE powder (open square) and porous PAAE film (open triangle) (heating rate: 20 °C/min; in nitrogen). The porous film was prepared by selective removal of PEG from PEG/PAAE (1/9 by weight) composites.

4. Conclusions

It has been demonstrated that the nanoporous PAAE films can be produced from PEG/PAAE composite films. The pores with a small size variation homogeneously cover the whole surface area and, the pore sizes but not size distributions increase with the content of PEG used for the preparation of PEG/PAAE composite films. The pores are originated from small domains of PEG in the composite films, whose formations are facilitated by the strong intermolecular interactions between PEG and PAAE. Nevertheless, complete removal of PEG from the composite films is still achievable by using water. This method has been proved to be a simple approach to produce nanoporous PAAE films.

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