

Polymer Communication

Flexible bi-continuous mesostructured inorganic/polymer composite membranes

Jin Ma^a, Zhenglong Yang^a, Xiaocong Wang^a, Xiaozhong Qu^a, Jiguang Liu^a,
Yunfeng Lu^b, Zhibing Hu^c, Zhenzhong Yang^{a,*}

^a State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

^b Department of Chemical and Biomolecular Engineering, University of California at Los Angeles, Los Angeles, CA 90095-1592, USA

^c Departments of Physics, Chemistry and Materials Science, University of North Texas, Denton, TX 76203, USA

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Abstract

Flexible bi-continuous mesostructured polymer/inorganic composite membranes have been synthesized by undertaking co-assemblies of surfactants and inorganic sol–gel processes inside pores of a preformed porous polymer membrane such as PP porous membrane Celgard[®] 2400. The pores are interconnected across the membranes, therefore the continuity of the inorganic mesopores across the membranes is guaranteed in principle. The solvent ethanol used for silica sol is conducive to the synthesis of inorganic materials such as silica within the pores although the PP membrane is hydrophobic. The composite membranes show new properties such as transparency, flexibility, uniform nanosized pores and enhanced permeability.

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1. Introduction

Mesostructured inorganic such as silica with defined channel pore geometry and chemistry have been extensively studied using both inorganic precursors and organic surfactants [1–4]. Functional composites are achieved by incorporation of functional materials either within mesopores or onto pore surfaces [5]. These mesostructured materials are promising for applications in catalysis, chemical and biological separation, adsorption, drug delivery and energy storage [6–8]. Aiming for their practical applications, the materials should be processed into desired macroscopic morphologies such as particles, fibers and thin films [9–15]. Silica is inherently fragile, and usually requires to be supported by proper matrices. We and other groups have recently prepared composite

membranes of mesostructured silica/anodic porous alumina [16–20], which display unique channel morphologies. The mesoporous inorganic phases are continuous across the membranes thus are promising in potential applications such as separation of nanoparticles. Unfortunately, they are rather fragile and difficult to obtain desired shapes.

It is urgently required to prepare flexible bi-continuous mesostructured composite membranes, in which all mesoporous inorganic phases are accessible to nanosized species to pass through. Flexible composites with enhanced mechanical properties have been prepared by mixing preformed silica particulates with polymers or by *in situ* generation of mesostructured inorganic phases inside a hydrophobic polymeric host matrix [21–24]. Mesostructured inorganic domains are dispersed and isolated within the polymer matrices, it is difficult for nanosized particles to pass through the mesopores.

In this communication, we report the synthesis of flexible bi-continuous mesostructured polymer/inorganic composite membranes by undertaking co-assemblies of surfactants and

* Corresponding author. Fax: +86 10 62559373.

E-mail address: yangzz@iccas.ac.cn (Z. Yang).

inorganic sol–gel processes inside pores of a preformed porous polymer membrane. The pores are interconnected across the membranes, therefore the continuity of the inorganic mesopores across the membranes is guaranteed in principle. The solvent ethanol used for silica sol is conducive to the synthesis of inorganic materials such as silica within the pores although the PP membrane is hydrophobic. The composite membranes show new properties such as transparency, flexibility, uniform nanosized pores and enhanced permeability.

2. Results and discussion

Polypropylene (PP) porous membranes are flexible and chemical resistant with good mechanical properties. They are commercially available and have been extensively used in separation and lithium battery [25]. PP porous membrane Celgard® 2400 of about 25 μm thickness was used as an example membrane to synthesize composite membranes. The

PP membrane is prepared by uniaxial stretching PP membrane, and the resulted pores are slit-like with the orientation parallel to the stretching direction (Fig. 1a). The pores are interconnected across the membranes ensuring an easier matter transportation. They are polydispersed in a size centered at about 40 nm \times 200 nm, with PP microfibrils bridged across the pore walls. After the incorporation of silica/template block copolymer Pluronic F-127, no remarkable interfaces were found between the mesostructured silica and PP matrix (Fig. 1b), indicating that the PP membrane pores were completely filled with silica. They formed silica/PP microfibrils interpenetration networks. The composite membranes changed from opaque to transparent after the incorporation of silica (Fig. 2). The appearance change from opaque to transparent is resulted from the substitution of air with mesoporous silica inside the pores of the porous membrane. The refractive index difference between mesoporous silica and PP matrix becomes smaller even close to zero, thus the membrane becomes transparent.

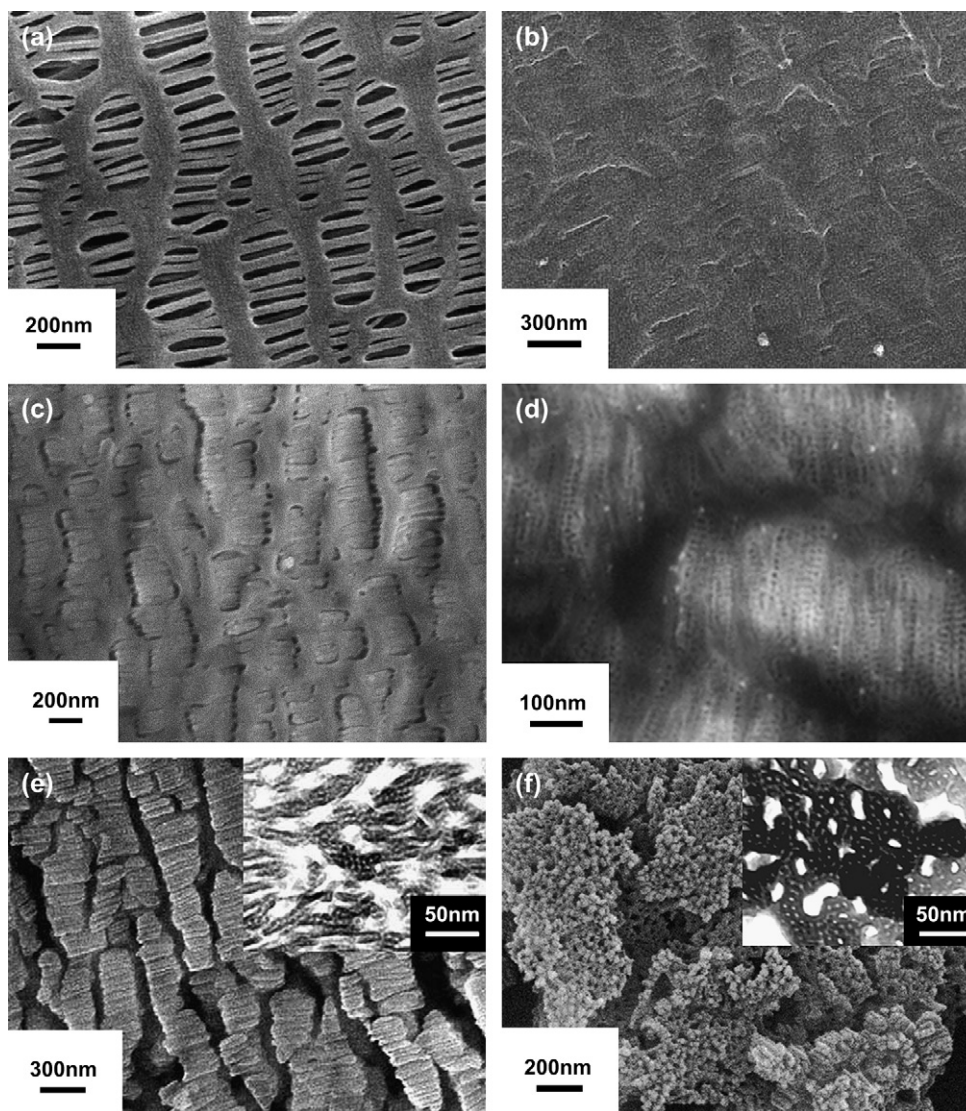


Fig. 1. Morphologies of some representative samples. (a) SEM image of the PP porous membrane; (b) PP/silica/F-127 mesostructured composite membrane; (c) and (d) SEM and TEM images of mesoporous PP/silica composite membrane after F-127 being dissolved; (e) and (f) top view and side view of SEM images of the calcined membrane, inset TEM images.

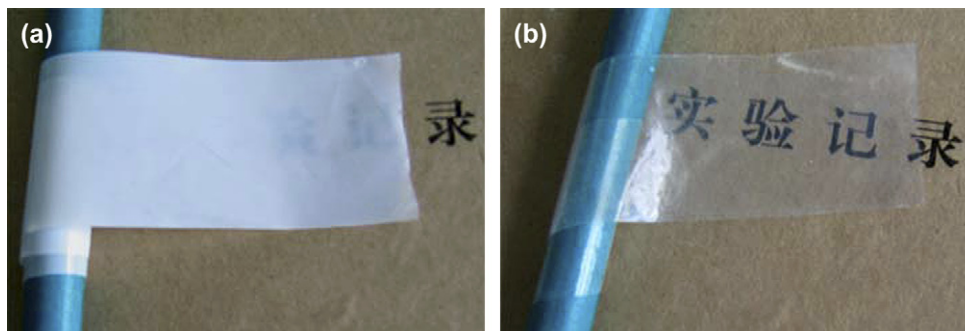


Fig. 2. Optical images of (a) PP porous membrane; and (b) PP/silica composite membrane.

In comparison, the difference between air and PP is remarkably high to cause opaque appearance. In addition, they are rather flexible to be curled into tubular shapes. After Pluronic F-127 was removed from the composite membrane by dissolution with ethanol, silica phase was slightly contracted but the transparency preserved (Fig. 1c). The completion of F-127 dissolution was confirmed by FT-IR spectra (Fig. 3). Before dissolution, the characteristic vibration peaks at 850 and 1270 cm^{-1} (curve b) were attributed to R–O–R' of F-127. The peaks disappeared (curve c), indicating F-127 has been completely dissolved. Ultramicrotomed cross-section TEM image of the composite sample confirmed the presence of mesopores of about 4 nm (Fig. 1d), which were duplicated from F-127. To further characterize their interior structure, the composite membrane was calcined at $450\text{ }^{\circ}\text{C}$ forming hierarchically structured silica with the original shape of the composite membrane well preserved. This process is similar to the previously reported synthesis of bimodal porous inorganic materials using a small molecular porogen and a polymer membrane as dual templates [26,27]. The slit channels of about $10\text{--}30\text{ nm}$ in diameter were formed by duplication of the PP microfibrils (top view, Fig. 1e), and the silica skeletons were mesoporous of about 3.9 nm as shown by an inset TEM image. Side view images (Fig. 1f) also revealed the presence of the bimodal pores.

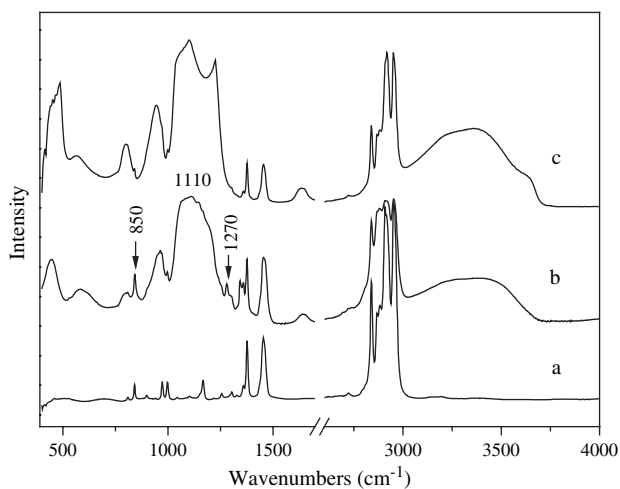


Fig. 3. FT-IR spectra of (a) PP porous membrane; (b) and (c) PP/silica/F-127 composite membrane before and after the dissolution of F-127.

The pore size and size distribution were further characterized by N_2 adsorption/desorption isotherms (Fig. 4). PP membrane templated with silica possessed a broad pore size distribution around 13 nm and a specific BET surface area $75\text{ m}^2/\text{g}$, whose pores were resulted from the PP microfibrils.

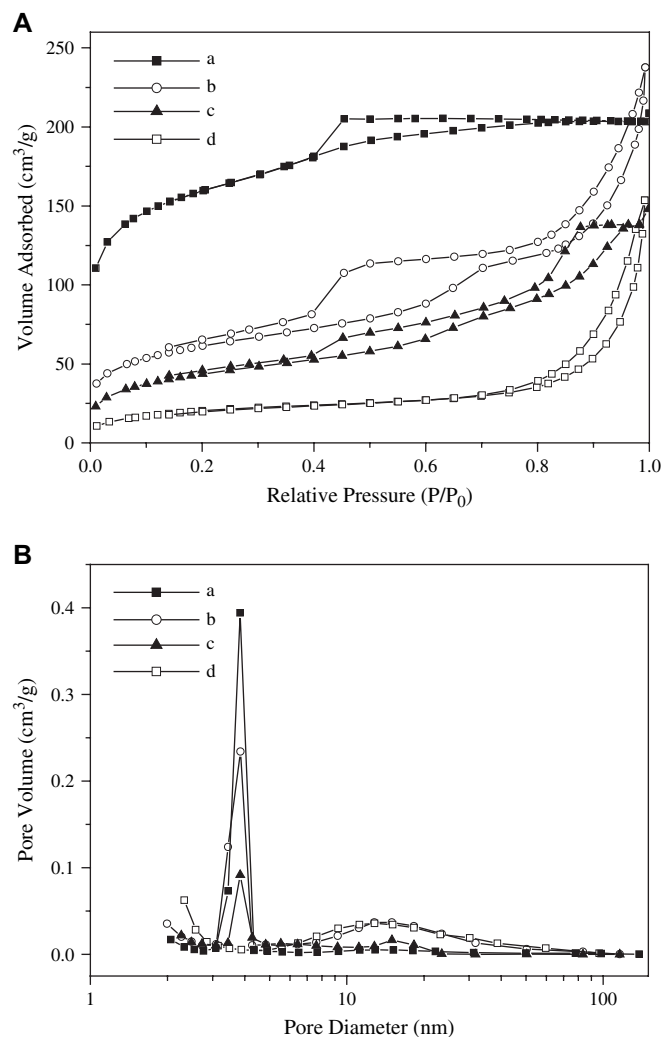


Fig. 4. N_2 adsorption/desorption isotherms (A) and the pore size distribution (B) of four representative samples. (a) Calcined mesoporous silica prepared outside; and (b) inside the PP membrane with F-127; (c) PP/mesoporous silica after dissolution of F-127 by ethanol; (d) calcined porous silica from PP/silica composite membrane without F-127.

The mesoporous silica synthesized outside the PP membrane, had a narrow pore size at 3.9 nm, which resulted from the block copolymer F-127. The specific BET surface area was 540 m²/g. For the composite membrane after being calcined, there existed bimodal pores centered at 13 and 3.9 nm, respectively. The small pore size was also consistent with SAXS result (Fig. 5). Higher order diffraction peaks were weak, indicating the pores were not well arranged orderly. This was consistent with TEM results (Fig. 1e and f). The specific BET surface area was 409 m²/g. TGA results indicated that the contents of F-127 and silica were 7 and 28 wt%, respectively, with respect to the composite membrane (Fig. 6). Both the specific surface area and pore size can be tuned by varying template structure and concentration. As listed in Table 1, the pore size can be decreased from 5.7 nm using F-127 to 2.2 nm using CTAB. The specific surface area was changed from 200 to 1160 m²/g. The pore size and specific surface area can also be tunable by the mixture of different templates, for example F-127/CTAB.

After the introduction of mesostructured silica within the PP pores, wettability and permeability have been significantly enhanced. Both the composite membranes before and after the removal of the templates became hydrophilic with water contact angles at 66° and 78°, respectively, whilst the PP porous membrane was hydrophobic with water contact angle at 113°. The synergetic effect of hydrophilic silica and high capillary force by the mesopores cause the increased hydrophilicity of the composite membranes. The wettability inversion facilitated faster transportation thus separation of species can be performed under low pressure. As proof of the concept, permeation of aqueous hydrochloric acid was tested (Fig. 7). The aqueous solution immediately penetrated through the mesoporous composite membrane upon the addition of the solution. This was verified by a rapid color change from orange to red of the pH indicator methyl orange contained in the bottom solution. The composite membrane before F-127 removal had comparably fast diffusion rate as the mesoporous membrane. Although PP

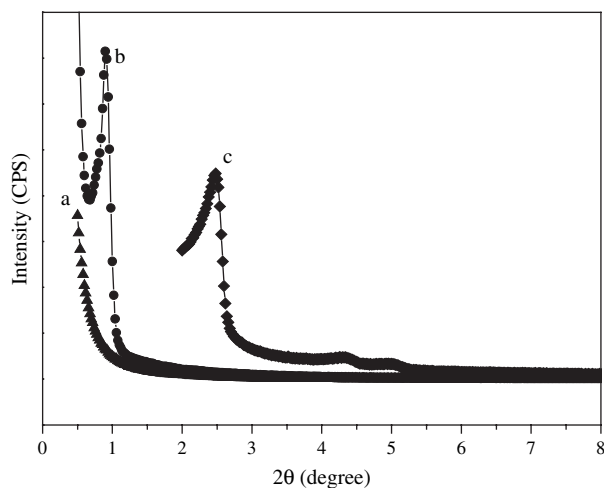


Fig. 5. SAXD patterns of the mesoporous silica produced by calcination of PP/silica composite membrane: (a) without using surfactant; (b) using F-127; (c) using F-127/CTAB.

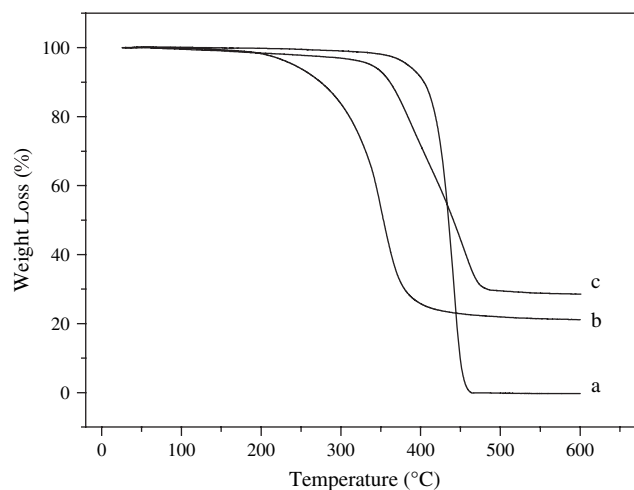


Fig. 6. TGA traces of representative membranes. (a) PP porous membrane; (b) and (c) PP/silica/F-127 composite membrane before and after removal of F-127 by dissolution.

membrane had larger pores, the permeation was rather slow. The solution started to gradually become red after 40 min and became completely red several hours later. An example electrolyte sodium chloride can also rapidly diffuse through the composite membrane, which was verified by the abrupt increase in conductivity across the membrane. In comparison, the conductivity across PP membrane increased slowly. The mesoporous composite membrane can be used in nanoparticle separation. An aqueous dispersion of 2 nm CdTe can easily pass through membranes, while 30 nm Fe₃O₄ nanoparticles were not. By using series composite membranes with varied pore size, nano-sized species can be separated and purified.

The inorganic components can improve thermal deformation of polymer materials [28,29]. The dependence of storage moduli with temperature of the composite membrane was characterized with DMTA (Fig. 8). The storage moduli of PP membrane along two directions parallel and perpendicular to microfibrils orientation decreased progressively with temperature. The decrease became less pronounced for the composite membrane with the storage moduli at the same level up to 130 °C (1373 MPa) as those of PP membrane at the maximum utilization temperature 70 °C (255 MPa). This indicated that the composite membranes can be used at higher temperatures up to 130 °C. Although the onset melting temperature for PP at 140 °C (Fig. 9) was less influenced, the melt peak of the composite membranes became

Table 1
Properties of the mesoporous silica prepared under different conditions

Surfactants	Concentration ratio (surfactant:TEOS)	Pore size (nm)	Pore volume (cm ³ /g)	Surface areas (m ² /g)
F-127	1:6	5.7	0.58	209
	1:3	3.9	0.67	409
Brij-56	1:6	3.7	0.55	734
	1:3	2.7	0.53	700
CTAB	1:8	3.0	0.72	659
	3:8	2.2	1.12	1163
F-127 + CTAB	1:1:3	3.3	0.73	958

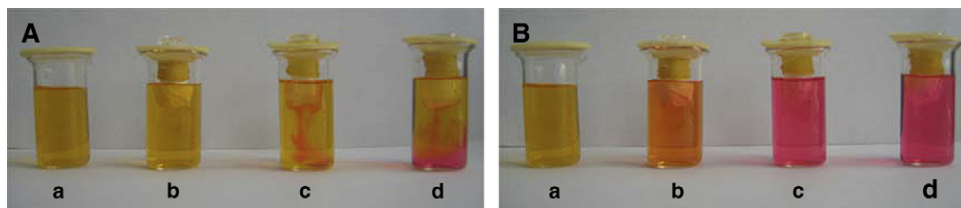


Fig. 7. Permeation test of three representative membranes for varied time: (A) after 20 s, and (B) after 40 min. (a) Methyl orange contained aqueous solution; (b) PP membrane; (c) and (d) mesostructured PP/silica composite membrane before and after F-127 was dissolved.

broad and asymmetric compared with PP membrane, indicating the PP chain is greatly confined by silica.

3. Conclusions

In summary, we have presented synthesis of flexible bi-continuous mesostructured polymer/inorganic composite membranes by co-assemblies of template surfactants and sol–gel processes of inorganic materials inside pores of PP porous membranes. The mesopores are rather narrow with their sizes tunable between 2 and 10 nm. The mesopores are continuous across the membranes, the resultant new properties such as enhanced wettability and permeability facilitate the potential applications in nanosized species separation and purification. The utilization temperature of the composite membrane is increased to 130 °C much higher than the previous upper limit of about 70 °C of PP membrane. The mesoporous membranes are flexible and can be easily constructed into desired shapes. The concept can be extended to other inorganic materials, for example titania and porous polymer membranes with varied compositions, a huge family of flexible mesostructured composite membranes is expected.

4. Experimental

A 25 μm thick PP porous membrane Celgard[®] 2400 was purchased from Celgard LLC. Block copolymer Pluronic

F-127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was purchased from BASF. A typical silica–surfactant sol was synthesized as follows: Pluronic F-127 (2.0 g) was dissolved in ethanol (5.5 g) followed by the addition of hydrochloric acid (1.5 g, 0.2 mol L^{-1}) under stirring; tetraethyl orthosilicate (TEOS, 6.0 g) was added to the mixture and stirred for 2 h at room temperature. PP membrane was immersed in the sol for 24 h until becoming transparent to ensure complete infiltration. After the sol soaked membrane was taken out of the sol, residual silica sol was completely scratched with a rubber blade. Following a further sol–gel process in air (humidity 60–80%) for 48 h, mesostructured composite membranes were formed.

Characterization: JE forming OL JSM-6700F field emission scanning electron microscope (SEM) and JEM-100CX transmission electron microscope (TEM) were used to investigate the morphologies. Nitrogen adsorption isothermal was performed on a Micromeritics ASAP-2020M porosimeter. BRUKER EQUINOX 55 FT-IR was used for recording the infrared spectra. Differential scanning calorimetry (DSC) was conducted using a DSC822[°] METTLER TOLEO with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Thermogravimetric analysis was performed with Perkin Elmer Pyris 1 TGA at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. X-ray diffraction (XRD) analysis was carried out on a Siemens X-ray spectrometer with Cu K α radiation at 0.154 nm. Dynamic mechanical thermal analysis (DMTA-MKIII) was performed on a Rheometric Scientific DMTA instrument.

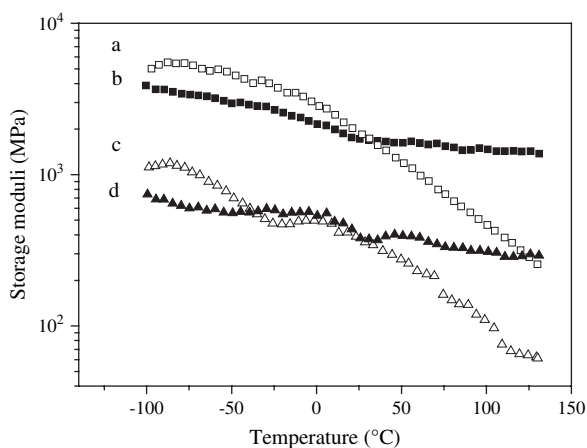


Fig. 8. Storage moduli dependence on temperature of the representative membranes. (a) and (b) PP and PP/silica composite membranes, respectively, along the direction parallel to the microfibrils; (c) and (d) PP and PP/silica composite membranes, respectively, along the direction perpendicular to the microfibrils.

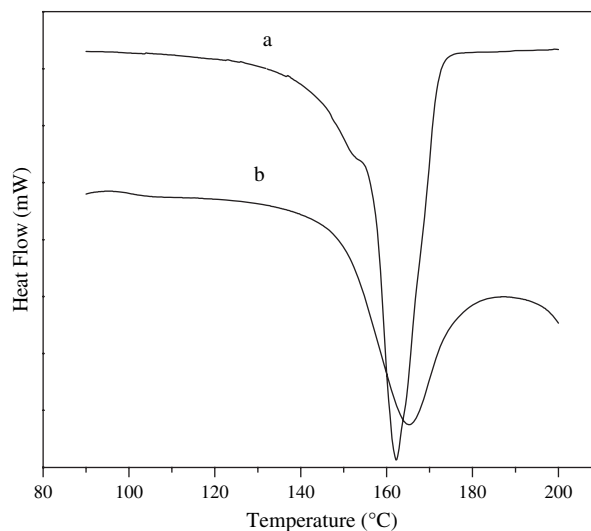


Fig. 9. DSC traces of (a) PP porous membrane; (b) PP/silica composite membrane after F-127 being dissolved.

Acknowledgements

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