Thermo-stabilized, porous polyimide microspheres prepared from nanosized SiO₂ templating via *in situ* polymerization

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Abstract. In this article, we addressed a feasible and versatile method of the fabrication of porous polyimide microspheres presenting excellent heat resistance. The preparation process consisted of two steps. Firstly, a novel polyimide/nano-silica composite microsphere was prepared via the self-assembly structures of poly(amic acid) (PAA, precursor of PI)/nanosized SiO₂ blends after *in situ* polymerization, following the two-steps imidization. Subsequently, the encapsulated nanoparticles were etched away by hydrofluoric acid treatment, giving rise to the pores. It is found the composite structure of PI/SiO₂ is a precondition of the formation of nanoporous structures, furthermore, the morphology of the resultant pore could be relatively tuned by changing the content and initial morphology of silica nano-particles trapped into PI matrix. The thermal properties of the synthesized PI porous spheres were studied, indicating that the introduction of nanopores could not effectively influence the thermal stabilities of PI microspheres. Moreover, the fabrication technique described here may be extended to other porous polymer systems.

Keywords: thermal properties, porous polyimide, microspheres, template, self-assembled composites

1. Introduction

In the last decades, owing to several special added-value applications in the area of catalysts, separation, chromatographic carriers, adsorbents, low-dielectric fillers, storage and deliver carriers for drugs, phonics crystals, nanoelectronics, or biotechnology [1–4], porous polymer materials, especially spherical ones, have been the hotspot of active study area in the development of new materials and some of them have been shown to be of practical use. Herein, an excellent porous polymer matrix should satisfy a variety of requirements, such as desirable thermal stability, chemical resistance and high modulus to support the void structure.

Polyimide (PI) is considered as the most promising candidates that could satisfy the above requirements with high thermal stability, good mechanical properties, excellent adhesion properties and out-

standing dimensional stability [5–7]. Up to now, several studies have been contributed to the preparation of well-defined porous PIs, such as PI membranes and PI foams; however, few reports have focused on preparing porous PI microspheres. Among those methods, reprecipitation method and thermal decomposition of the labile component are two of the most widely used techniques. Kasai *et al.* [8] proposed a route to fabricate porous PI nano-particles involving the use of LiCl, polymeric porogens (poly(acrylic acid) [9, 10], poly(vinyl alcohol) [9], poly(methyl methacrylate) [11], polyvinylpyrrolidone and polyelectrolyte [12]) as porogens. They investigated the effect of the porogen species and the reprecipitation conditions on the porous structures of the PI nano-particles. Unfortunately, the method they established requires precise control over the processing conditions, and cannot be employed for mass production

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of porous particles. Besides, the final nanopore structure is still superficial, and it seems difficult to control the pore size and/or the pore number. Additionally, another alternative approach has been employed to fabricate meso- and macro-porous polymer materials using block copolymers that have two or more chemically immiscible blocks covalently linked together (e.g. the IBM Almaden Research Center, 1990s [13–15]; Chung *et al.* [16] (2006); Olson *et al.*, [17] (2008); Wu *et al.*, [4] (2012)). In these studies, the morphological structure of porous PI was determined by the initial morphology of the microphase separated structures of the copolyimides [17]. But the decomposition technique could plasticize the PI and generate the chain mobility during the pore formation, which made the pores collapse, particularly when the processing temperature is too close to the softening temperature (the minimum temperature of glass transition) of the PIs [18, 19]. Furthermore, thermal degradation is adverse to the molecular weight and certain critical mechanical properties.

Based on their contribution and theoretical support on the preparation of porous PI spheres, we attempted to introduce a simple and reproducible approach to prepare porous PI micro-particles using nano-silica particles as inorganic template. Through the typical self-assembly structures of poly(amic acid) (PAA, precursor of PI)/nano-SiO₂ sol blends, nano-porous PI spheres could be obtained after the removal of the silica component. Compared to the above method, the key advantage of the method lies in the mechanical and thermal properties of resultant porous PI spheres are little influenced and prevent the collapse of the porous structure during thermolysis. Furthermore, in this way, the whole process is easily controlled and applicable for mass production of porous PI particles, moreover, the pore size and pore struc-

ture of the porous polyimide spheres could be relatively controlled by adjusting the content and size of silica [20, 21]. The overview of the synthesis of the porous PMDA-ODA PI microspheres was shown in Figure 1.

2. Experimental procedures

2.1. Materials

4, 4'-diaminodiphenyl ether (ODA, CP) and pyromellitic dianhydride (PMDA, CP) were supplied by Aladdin Industrial Corporation and used with grinding and without further purification. Acetic anhydride (Ac₂O, dehydrating agent, AR), pyridine (catalyst, AR), N, N-Dimethylformamide (DMF, AR), Paraffin Liquid (LP, CP), hydrofluoric acid (HF, 40%, AR) and other solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, China. Surfactants (Span 85 and Tween 80, CP) were obtained from Aladdin Industrial Corporation and dried at 80°C in a vacuum oven over night. Silica sol (JN-40, 100 nm, $\rho_{\text{SiO}_2} = 1.2 \text{ g/cm}^3$, pH = 8–10) and γ -glycidyloxypropyltrimethoxysilane (GOTMS) were industrial grade reagent from Shandong Baxter new materials Co., Ltd and used as received.

2.2. Preparation of the PI/SiO₂ composite microspheres

2.0 mL GOTMS, in volumetric amount, was suspended in 20 mL SiO₂ sol with ultrasonic agitation. Subsequently, the mixed solution was stirred for 2 h at 40°C. Then, the GOTMS-stabilized silica sol was stored in room temperature for use.

In a 100 mL flask, 0.5000 g of ODA was dissolved in 15 mL of DMF solution with agitation at room temperature. Then the ODA dissolved completely, 0.5555 g of PMDA (1:1.02 molar ratio) was introduced into the solution in increments. After 15 min, 3.5 mL of the GOTMS-stabilized silica sol was added dropwise to the stirring mixture in batches. After magnetic agitation for 1 h and ultrasonic dispersion for 2 h, the reaction mixture was further stirred for 48 hours at room temperature to yield a homogeneous PAA/Si solution. Then the homogeneous PAA/Si solution was dispersed dropwise into 60 mL of vigorously stirred paraffin liquid containing 11.25 mL of surfactants ($V_{\text{span85}}:V_{\text{tween80}} = 2:1$), following by stirring over 2 h. Subsequently, a mixture of pyridine and Ac₂O (1:1, molar ratio) was added dropwise into the above emulsion system. After 2 h, the chemically imidized solid particulate product was

Figure 1. Overview of the synthesis of the porous PMDA-ODA PI microspheres

extracted by centrifugal separation and washed several times with petroleum ether and acetone to purify by removing any unreacted monomers and surfactants. Immediately following this, the solid particulate was placed in an air circulating oven with the curing procedure: 80°C (for 2 h), 120°C (for 2 h), 160°C (for 2 h), 200°C (for 2 h), 240°C (for 4 h), 280°C (for 4 h), 320°C (for 2 h).

2.3. Preparation of the porous PI microspheres

The detached PI/SiO₂ composite spheres were immersed in hydrofluoric acid solution with concentration of 25 wt% to remove the encapsulated silica particles. The etched spheres were collected by filtration, washed with distilled water to neutral, and dried under vacuum for 5 h at 200°C to remove traces

Figure 2. Reaction scheme for preparing the porous polyimide microspheres

of water. The porous PI microspheres were obtained. The typical reaction scheme for preparation the porous PMDA-ODA PI microspheres were presented in Figure 2.

2.4. Characterization

Chemical structure analysis was performed with a Bruker FT-IR Spectrometer model Equinox-55, USA. The changes of the characteristic absorption bands and corresponding functional groups were analyzed. Surface morphology characterization was evaluated using a FEI Navo Nano SEM-430 (FEI-SEM) at accelerating of 20 kV. The TGA instrument model Netzsch STA 409C under nitrogen at a heating rate of 10°C/min from room temperature to 900°C was used to characterize the differences in the thermal stability of the three type spheres.

3. Results and discussion

3.1. Chemical structure analysis

Previously, our laboratory research group prepared pure PI microspheres with a high solid content in a non-aqueous emulsion. Analogously, the porous spheres were obtained in the manner as mentioned in the experimental chapter. FT-IR was used to evaluate the presence of silica in the composite spheres and disappearance in the porous spheres. The FT-IR spectra of pure PI (Figure 3a), PI/SiO₂ (Figure 3b) and porous PI (Figure 3c) are illustrated in Figure 3. As shown in the obtained spectra, the characteristic imide group stretching vibrations were observed at 1721, 1777 cm⁻¹ (stretching vibration of cyclic C=O), 1373 cm⁻¹ (C–N stretching vibration) and 723 cm⁻¹ (bending vibration of C=O), which confirmed the complete conversion of the PAA precursor to PI and suggested they possessed of the same chemical basic

structure. Whereas, there were also obvious differences among the spectra (as shown in spectra by * marks). For example, the wavenumbers from 1000 to 1100 cm⁻¹ were attributed to typical absorption bands for Si–O–Si network vibrations derived silica, overlapping with absorption stretches associated with the in-plane C–H bending vibration band present in the 1080–1090 cm⁻¹ region, and the weak C–H peaks derived from GOTMS occurred in the 2867–2925 cm⁻¹ range in Figure 3b. Interestingly, it could be easily seen that the wavenumber of 1722 cm⁻¹ (C=O symmetric stretching) shift to higher frequencies at 1726 cm⁻¹, which was connected with change of the force constant, implying that there existed a few chemical bonds between organic molecules PI with functional groups such as carbonyl and ether bond and inorganic ingredient SiO₂ comprising a few hydroxyl groups. On the other hand, the coupling agent (GOTMS) also supplied many physical and chemical cross-linking points between the two phases, producing an increase of inter-chain interactions and ultimately higher frequencies. In Figure 3c, the spectra of porous PI is similar to the pure ones, and the disappearance corresponding to the Si–O–Si stretching band, ranging from 1000–1100 cm⁻¹, revealed the presence of only polyimide phase in porous spheres, and unveiled that the silica had been removed completely from the PI matrix and the HF chemical treatment did not affect the chemical structure of PI.

3.2. Microstructure analysis

Prior to discussion, the porous PI spheres were prepared successfully from nano-silica templating via *in situ* polymerization. SEM was performed to give details on the morphological changes of the various PI spheres. For the pure PI spheres (Figure 4a, 4b), they appear to be spherical perfectly with a smooth and dense surface and a narrow size distribution. Figure 4c, 4d represent a self-assembly composite spheres. It is noticed that the composites exhibit nearly fractal with the bumpy surface and non-uniform size. The amount of SiO₂ particles on the PI spheres obtained did not change after further product purification, in which the product were washed in petroleum ether and acetone under ultrasonic conditions. It can be seen that a large number of inorganic particles are deposited throughout outer surface of the PI microspheres (Figure 4d). Herein, only a small part volume of silica particles chemically

Figure 3. FT-IR spectra of the resulted PI spheres: (a) pure PI, (b) PI/SiO₂ composites, (c) porous PI

Figure 4. SEM images of the resulted PI spheres: (a) and (b) pure PI, (c) and (d) PI/SiO₂ composites, (e) and (f) porous PI

grafted to the organic phase exposed on the surface of PI spheres. In addition, a few granular aggregates derived from agglomeration of nano-particles occurred on the surface of composite spheres. The self-assembled PI/SiO₂ composite spheres were etched by HF acid to obtain the porous PI structure (Figure 4e, 4f). Compared to the composite spheres, the inorganic domains disappear and shape of spherical structure are conformed to be unchanged before and after the etching process, again indicating that HF etching have little influence on the structure of PI domains. Here, template method was applied to replace traditional thermal decomposition technique to prevent the collapse of the pore structure during thermolysis at the softening temperature. Because the size and distribution of pores strongly depended on the morphology of silica particles in PI matrix, estimated from the SEM overview, the resulted pores are randomly distributed and the average size locates approximately in the range of 70–100 nm and is consistent with the morphology of SiO₂ (Figure 4f). Interestingly, some meso- and macro- pores caused by the agglomeration of the nano-SiO₂ that are opening at the external surface of the PI spheres. Thus, much effort should be also put into attempt to develop the miscibility of the two phases with reducing the agglomeration of the inorganic particle, moreover, improve the uniformity of the pore distribution and size.

These phenomena could be explained as follows: During the process of the chemical imidization, the PI chains twisted, encapsulated the whole SiO₂ par-

ticles, dissolved out gradually and formed the composites. In preparing composite process, the functional groups of the GOTMS provided the bond link between the inorganic domains SiO₂ network and the phase PI matrix, leading to the formation of a considerable fine interconnected network system [22]. Furthermore, because the solubility of PI in DMF decreased rapidly, the small part of inorganic particles has not been trapped into the organic phase, giving rise to the demi-exposition of silica particles. Meanwhile, the compatibility between the two phases was low, leading to the intertwists between the PAA chains and silica three-dimensional networks were not enough dense compared to the intertwists among the single PAA chains. Moreover, as a result of nanometer effect, the inorganic particles of small size down to nanometer were easy to develop into very large ones through the condensation with neighboring particles, commonly, when the inorganic component content of PAA/Si solution was excessively high, the inorganic phase should present obvious agglomeration.

To further observe the variation of internal morphologies of the spheres, we searched for the broken spheres in SEM field-of-view (Figure 5a, 5b). We observed that the SiO₂ particles at the range of 70–100 nm appeared to be interconnected by the thin-wall of PI substrate to form groups of larger objects. The composites were acid treated to produce porous structure. Compared to the former, the interpenetrating network disappears and converts to a mass of disordered pores. Unfortunately, the collapse of

Figure 5. SEM images of the internal morphologies of the resulted PI spheres: (a) PI/SiO₂ composites, (b) porous PI

the thin-wall produced the macropores and may deteriorate the mechanical properties. Apparently, developing the dispersibility of the inorganic particles in PI matrix with reducing the agglomeration is the key of the method.

3.3. Thermal analysis

As shown in Figures 6 and 7, the thermal stabilities of the pure PI spheres, the PI/SiO₂ spheres and its corresponding porous PI spheres were compared by using TGA and DTGA curves in the range of 40–900°C. The thermal stabilities of the spheres are expressed by the temperature for 5 and 10% weight loss, and the temperature for maximum mass loss rate, $T_{5\%}$, $T_{10\%}$ and $T_{\max}$, which are listed in Table 1. As expected, one may notice that the thermal stability of porous spheres presented less lower than the other ones. It is natural since the thermal stability of inorganic moiety is higher than organic resins, the inclusion of the inorganic component will enhance the thermal stability of polymer [23, 24]. Besides, when the inorganic component content was enough large, a duplex-continuous interpenetrating network

Table 1. Thermal stabilities of the three type spheres

Sample code	$T_d(5\%)$ [°C]	$T_d(10\%)$ [°C]	$T_{\max}$ [°C]	Char yield at 900°C [wt%]
(a)	499	566	601	48.11
(b)	499	552	569	73.97
(c)	455	519	562	52.49

had formed after *in situ* polymerization, hindering the movement of polymer molecules and enhancing the thermal conductivity. The factors all cooperated to increase the thermal decomposition temperature of the composites. However, the incorporation of pores will impair the regularity and the crystallization of the chain segments, and increase the free volume of polymer, which are adverse to the thermal stability of PI matrix. The two elements resulted in the lowest thermal stability of the three spheres. But, there was no apparent weight loss before 455°C for the porous PI, and until 562°C the obvious changes of weight loss were brought about. Therefore, the obtained porous PI spheres are still high heat resistance, being of central importance to the practical applications. Moreover, this conclusion unveiled that the HF etching process did not affect the backbones of polyimide, which was in good agreement with FT-IR results.

3.4. The mechanism for formation of the porous PI microspheres

On the basis of the above results, we audaciously propose a mechanism of formation for porous structures, which is a much more complicated process. Firstly, the uniform solution of PAA-DMF containing SiO₂ particles was obtained after polymerization, following by dispersing into Paraffin Liquid to form emulsion system. Immediately, most of the PAA and SiO₂ molecules gradually formed dispersion phase. Then the fine DMF droplets containing PAA and SiO₂ particles were initially generated in the Paraffin Liquid medium. Herein, the dispersibility of inorganic particles was a crucial condition for the uniformity of pore network. Secondly, upon the process of the chemical cyclization, the solubility of PI in DMF decreased rapidly, the PI chains bonded with nano-SiO₂ began to twist, dissolve out gradually, solidify and form composite spheres of PI and SiO₂. Finally, the discontinuous inorganic SiO₂ particles were eluted perfectly from composite system by the HF rinse procedure, providing porous PI microspheres with closed pore structure.

Figure 6. TGA curves of the resulted PI spheres: (a) pure PI, (b) PI/SiO₂ composites, (c) porous PI

Figure 7. DTGA curves of the resulted PI spheres: (a) pure PI, (b) PI/SiO₂ composites, (c) porous PI

Indeed, the dispersibility of inorganic particles is influenced by the complicated interactions, the rate of solidification and the inorganic particles content of composites, which should determine directly the resulted pore structure. It is well known that on the surface of silica particles, there exist many hydroxyls which could have strong hydrogen bonding interaction with carboxyl of PAA, moreover, the coupling agent also provide more bond sites between the PAA chains and SiO₂ network. The PI/SiO₂ composite spheres resulted from a balance between the varied interactions and the diffusion of the molecules, namely, after chemically imidization, most of inorganic particles were complexed into organic phase and the composites were obtained. By the removal of SiO₂, the PI porous structures having clear interfaces were formed successfully. Nevertheless, the compatibility of two phases is the most dominant factor affecting the fabrication of the porous PI micro-particles. Furthermore, considering the diversity of polymers, we suspect that it will be suited to prepare other porous polymer micro-particles possessing anomalous structures through judicious selection of the combination of organic polymer and the inorganic components.

4. Conclusions

In conclusion, a simple methodology of the fabrication of porous polyimide microspheres with pore size in the nanometer regime was presented. This is a novel, versatile paradigm in the production of porous PI spheres with high heat resistance, based on a self-assembly composite structure comprised of a polyimide as the matrix or dominant phase with silica as the templates, which have been designed primarily via *in situ* polymerization route. Upon a HF etching treatment, the silica particles tripped into the matrix were released, leaving the pores in the range of 70–100 nm. The resultant porous morphology of the as-synthesized PI spheres could be involved in variety of factors (e.g. the initial morphology and weight content of the silica, the complicated interactions in two phases). The prepared thermo-stabilized, porous PI microspheres make it promising in the high temperature resistance of microelectronics. Furthermore, the various inorganic particles, in this way, could be self-assembled into versatile polymer matrix, allowing the preparation of the multifarious porous polymer materials not only porous polyimide materials.

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