Polymer Communication

Growing well-defined monodispersed silica in polyimide host membranes using a surfactant assisted sol-gel process

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ABSTRACT

Polyimide-silica membranes are interesting hybrid architectures that possess excellent mechanical, thermal and chemical properties. However, the dispersion of inorganic domains in the polymer matrix and the compatibility between the organic and inorganic phases are critical factors in these hybrid systems, due to the lack of favorable interactions between the hydrophobic polymer and hydrophilic silica. In this study, a new approach to forming hybrid membranes by the *in situ* generation of silica and functionalized silica in the polyimide matrix is presented. The new surfactant assisted sol-gel process improves the particle dispersion and the compatibility between the organic and inorganic phases. Moreover, this synthetic strategy allows the sol-gel process to proceed in the presence of a fully imidized, high molecular weight polyimide to generate a chemically well-defined silica phase. The importance of the polymer-silica and silica-surfactantaffinities and the influence of functionalization of silica in guiding the construction of the hybrid network are also examined here.

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1. Introduction

Organic-inorganic hybrid materials offer the promise of combining the superior mechanical integrity and thermal stability of inorganic phases with the flexibility and processibility of organic polymers. Polymer-silica hybrids are the most commonly reported hybrid systems in the literature [1]. Among the various possible polymer functionalities, polyimides (PI) are of particular interest because they have excellent mechanical properties, thermal stability and chemical resistivity. However, attempts at combining these high performance polymers with alkoxysilanes, using sol-gel chemistry, have met with several difficulties. Polyimides are virtually insoluble in the solvents (water and alcohol) that are essential for the hydrolysis and polycondenzation of alkoxides. Most of the previous reports [2–17] demonstrate a synthesis strategy involving a two-stage sol-gel process, wherein a poly(amic acid) (PAA) precursor is first synthesized from dianhydrides and diamines to which hydrolyzed silicon alkoxides, such as water-containing tetraethylorthosilicate (TEOS), are then added to facilitate the sol-gel process prior to thermal

imidization. This method not only involves the addition of a poor solvent for PAA but also generates large micron-sized inorganic domains that are inhomogeneously distributed in the polymer matrix. These PI-silica hybrid materials are brittle and contain large numbers of voids/cavities due to poor interfacial bonding between the silica and the polymer. The significant difference in the hydrophilic/hydrophobic properties of silica/polymer is the major reason for the gross inorganic phase separation and poor interfacial bonding. Only very few systems [7,8]. demonstrated good compatibility between the PI and silica phases. Homogeneous dispersion of silica was achieved in such systems by using partially imidized/low molecular weight PI matrices that have better physiochemical interactions with silica particles compared to those of fully imidized/high molecular weight PIs. Although such a fine dispersion of silica particles is suitable for coatings and supported films, the toughness of polymers is sacrificed in this method. Another popular method is to take advantage of a coupling agent with trialkoxysilyl groups to modify the preformed polymer before sol-gel process [9–13]. Although this method yielded transparent hybrid thin films with a fine dispersion of silica throughout the PI matrix, some of these materials are reported to be brittle [18], probably due to the interfacial defects between the silica domains and polymer matrix.

PI-silica hybrid systems made with high molecular weight polyimides and loaded with high contents of silica, are useful for

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several applications, such as: microelectronics, optics, aerospace, fuel-cell membranes etc [12]. In this communication, we report a new method for the *in situ* generation of chemically well-defined silica structures in a fully imidized PI matrix by employing a sol-gel process involving PI and alkoxide precursors. To avoid segregation and sedimentation of the inorganic precursors, the synthesis requires an appropriate solvent with specific physico-chemical properties; THF was chosen as a compatible solvent to bridge the alkoxide and water and avoid polyimide precipitaion. In order to circumvent the inherent incompatibility between PI and silica, two different polyimides, containing vastly different quantities of hydroxyl functional groups that can form hydrogen-bonding interactions with silica have been studied as the PI matrixes. In addition, the mutual affinity between the hydrophilic silica particles, which may lead to gross inorganic phase separation during the concentration step, has been reduced by means of a non-ionic surfactant, Brij® 35. Previously, Ha et al reported [17] a surfactant-silica-polyimide system wherein mesoporous silica prepared using surfactant and a water soluble poly (amic acid) ammonium salt precursor were used to prepare PI-mesoporous silica hybrid composites. In another recent article, Lee et al [19] described a surfactant treatment of preformed silica particles to improve the dispersion of SiO_2 in sulfonated polyimides: although, they could achieve nano-level dispersion, it was at a low silica loading ($\leq$3wt %). The present method achieves very fine dispersion of silica particles in the PI matrix at significantly high silica contents (30 wt %). Apart from the role of surfactant and the copolymer effect, the influence of functionalization of silica in guiding the construction of the hybrid network is also demonstrated here using two silica precursors Tetraethylorthosilicate (TEOS) and 3-mercaptopropyltriethoxy silane (MPTES).

2. Experimental section

2.1. Materials

2,2′-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (bisphenol-A dianhydride or BPADA), 4-phenylphenol, and the silica precursors: TEOS ($\geq$99%), and MPTES ($\geq$80%) were purchased from Aldrich, USA. BPADA was recrystallized from a mixture of toluene and acetic anhydride. Monomer grade 3,3′-dihydroxy-4,4′-diaminobiphenyl (HAB) was obtained from TCI Chemical Co., and dried at 50 °C under vacuum. The surfactant Brij® 35 (water $\leq$1%) from ACROS and all other reagents obtained commercially were used as received.

2.2. PI synthesis

2.2.1. BPADA-DAPP polyimide (D-series) polymers

2, 6-Diamino-4-phenylphenol (DAPP) was prepared from 4-phenylphenol by a two-step process involving nitration followed by reduction, as per a previously published procedure [20]. BPADA-DAPP polyimide was prepared by a conventional two-step process involving the formation of the poly(amic acid) followed by thermal dehydration to the polyimides in solution. In a typical synthesis, to a 100 ml flask purged with nitrogen was added DAPP (2.00 g, 9.990 m mol) and 1-methyl-2-pyrrolidone (NMP, 15 ml). The mixture was stirred to form a clear, brown solution at room temperature. To this solution of diamine, was added BPADA (5.200 g, 9.990 m mol) and NMP (20 ml) with mechanically stirring for 4 h to give a viscous yellow PAA solution that was thermally cyclized in solution by refluxing for 3 h to yield the hydroxy-containing polyimide. The polymer solution was cooled, diluted with 100 ml NMP and filtered. The filtrate was precipitated in methanol to give a white solid.

2.2.2. BPADA-HAB polyimide (H-series) polymers

BPADA-HAB polyimide was prepared by a similar procedure, adapted for BPADA-DAPP as above, with DAPP replaced by HAB. Complete imidization was achieved in this case after refluxing the PAA solution for 20–24 h. The polymer solution was cooled to 60 °C and was used for composite membrane preparation after proper dilution.

2.3. Preparation of PI-silica hybrid membranes

TEOS, MPTES or a mixture of these was used as the silica precursor for the preparation of hybrid membranes. A constant concentration of the surfactant Brij® 35 ($CH_3-(CH_2)_{11}-(OCH_2CH_2)_{23}-OH$), at a molar ratio of SiO_2/Brij® 35 = 1:0.0167, was used throughout the work unless otherwise mentioned.

The synthetic technique was based on creating two individual homogeneous inorganic and organic solutions, which were then mixed and the solvent evaporated under carefully controlled conditions. The homogeneous inorganic solution was a partially acid-hydrolyzed alkoxide sol in tetrahydrofuran (THF), while the organic solution was a 10% solution of PI in NMP. Since the silica precursor does not dissolve well in water, it is often necessary to add an organic solvent; in the present work, THF was chosen as the co-solvent, taking into account its: solubility, hydrophilicity and volatility. In a typical preparation, TEOS (or MPTES or a mixture of the two), water, THF and HCl (molar ratios 1:4:10:0.002) were mixed and stirred at room temperature for 20 h. The surfactant Brij® 35 was added to the sol to prevent the segregation and sedimentation of the inorganic network during condensation. The silica sol containing surfactant was then added to 10% PI solution in NMP and heated at 60 °C for 10 h. These solutions were cast in petri dishes and heated at 80 °C for 10 h to remove the solvent.

It was found that the BPADA-DAPP (D-series) polymer could accommodate only up to 20 wt% silica content, since beyond this limit a separately grown silica phase was visible in the SEM images. But, interestingly, the BPADA-HAB (H-series) polymer could

Table 1
Typical starting compositions for D-series and H-series polymer-composites prepared using surfactant.

Sample	Silica content	SiO₂/Brij® 35 (mol ratio)	TEOS	MPTES
H30–0.0167S–1.50T/0M	30 wt%	0.0167	1.50 m mol	–
H30–0.0167S–1.125T/0.375M	30 wt%	0.0167	1.125 m mol	0.375 m mol
H30–0.0167S–0.75T/0.75M	30 wt%	0.0167	0.75 m mol	0.75 m mol
H30–0.0167S–0.375T/1.125M	30 wt%	0.0167	0.375 m mol	1.125 m mol
H30–0.0167S–0T/1.50M	30 wt%	0.0167	–	1.50 m mol
D20–0.0167S–1.0T/0M	20 wt%	0.0167	1.0 m mol	–
D20–0.0167S–0.75T/0.25M	20 wt%	0.0167	0.75 m mol	0.25 m mol
D20–0.0167S–0.50T/0.50M	20 wt%	0.0167	0.50 m mol	0.50 m mol
D20–0.0167S–0.25T/0.75M	20 wt%	0.0167	0.25 m mol	0.75 m mol
D20–0.0167S–0T/1.0M	20 wt%	0.0167	–	1.0 m mol

Table 2
Details of H-series composites prepared without surfactant and presented in this communication.

Sample	Silica content	TEOS	MPTES
H30−1.50T/0M	30 wt%	1.50 m mol	–
H30−1.125T/0.375M	30 wt%	1.125 m mol	0.375 m mol
H30−0.75T/0.75M	30 wt%	0.75 m mol	0.75 m mol
H30−0.375T/1.125M	30 wt%	0.375 m mol	1.125 m mol
H30-0T/1.50M	30 wt%	–	1.50 m mol

accommodate up to 30 wt% silica. The silica weight % here refers to the total silica content derived from both TEOS and MPTES, assuming total conversion of silica precursors to silica. In order to study the effect of silica functionalization, the molar ratios of the silica precursors were varied and the samples were prepared with different starting compositions of TEOS and MPTES. The starting compositions for different samples and their designations are given in Table 1. For example, the BPADA-DAPP polymer-composite containing 20 wt% silica and the surfactant (in the molar ratio of $SiO_2/Brij^® 35 = 1{:}0.0167$) prepared from 0.75 mM TEOS and 0.25 mM MPTES is designated as D20−0.0167S−0.75T/0.25M. PI-silica composites with no surfactant were also prepared for comparison, and the details are listed in Table 2.

2.4. Characterization

SEM images of the hybrid composites were recorded using a Jeol Model JSM 6700F field emission scanning electron microscope. All samples were gold-coated and mounted on copper strips. A Philips/FEI Tecnai G20 transmission electron microscope (TEM) operating at 110 kV was used to examine the hybrid morphology. The sample preparation involved embedding membranes in an Epon[TM]-Araldite mixture followed by ultramicrotomy with a diamond knife to obtain thin sections which were placed on copper grids for TEM analysis. Solid-state ^{29}Si NMR experiments were conducted on a Varian Infinity[plus] 400 MHz spectrometer operating at a frequency of 79.5 MHz, the chemical shifts are given with reference to
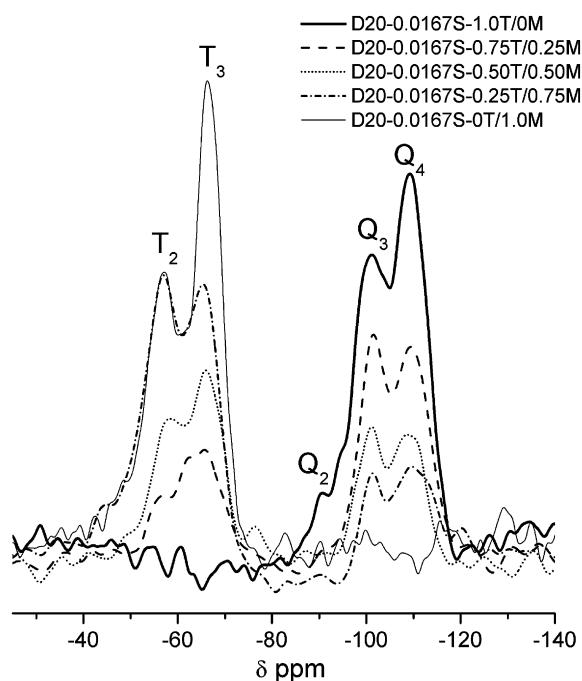
tetramethylsilane. In order to study the extent of silica condensation before solvent evaporation, FTIR spectra of the liquid samples applied on KBr pellet were recorded before the solution-casting.

3. Results and discussion

3.1. Silica precursor effect in presence of surfactant

The ^{29}Si CP/MAS NMR spectra of D-series polymer-composites are shown in Fig. 1. The D20−0.0167S−1.0T/0M sample prepared from the silica precursor TEOS alone displays prominent Q_4 and Q_3 resonances with a minor Q_2 resonance. The characteristic peaks at −109 and −101 ppm indicate that the *in situ* sol-gel reaction has generated a well-condensed silica network inside the PI matrix. When the precursor MPTES was added for thiol-functionalization of silica matrix, keeping the total silica content constant at 20 wt%, additional T resonance peaks appear (T_2 at −58 ppm and T_3 at −66 ppm for the D20−0.0167S−0.75T/0.25M sample), indicating the incorporation of mercapto functionalized silica in the inorganic network. The Q and T resonances observed here are close to the corresponding values reported in the literature [21]. With further increase in the extent of functionalization of the silica matrix, the intensity of T resonance peaks increases proportionately at the expense of Q peaks; and, for the sample generated from MPTES alone, only T resonances are observed.

The scale-expanded FTIR spectra (Fig. 2, see supplementary data for spectra in the range $1000-3600$ cm^{-1}) of liquid samples obtained before solution-casting for D-series polymer-composites show characteristic imide peaks at 1780, 1730 and 1365 cm^{-1}. The absence of a polyamic acid peak in the range $1650-1690$ cm^{-1} reveals that the construction of a hybrid network was achieved in a completely imidized matrix [22]. The peaks corresponding to different silica structures such as Si−O−Si ($1000-1100$ cm^{-1}) and Si−OH ($1020-1040$ cm^{-1}) [15,18] are also observed in the FTIR spectra. It must be noted that the intensity of silanol peaks increases with the MPTES content of the casting sol. In an earlier study [18], it was found that the degree of condensation of
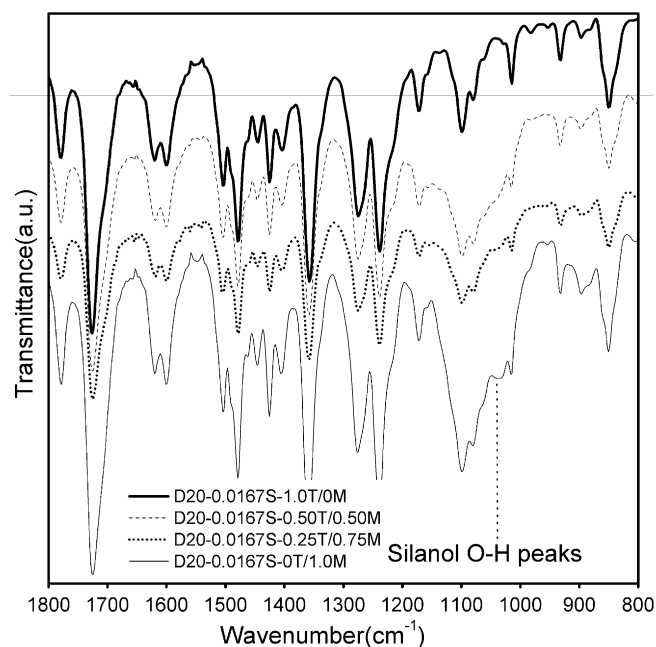

Fig. 1. ^{29}Si MAS NMR spectra of PI-silica and PI-modified silica membranes of D-series polymer.

Fig. 2. FTIR spectra of hybrid systems revealing the extent of silica condensation in D-series composites. The casting sols were applied on KBr crystal for the analysis.
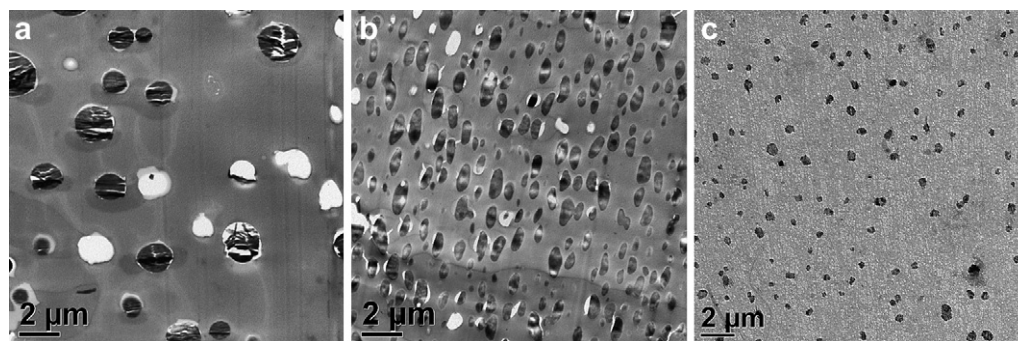
Fig. 3. TEM images of D-series composite membranes prepared using surfactant (SiO$_2$/Brij® 35 = 1: 0.0167 molar ratio) and (a) TEOS alone (D20−0.0167S−1.0T/0M) (b) equal molar quantities of TEOS and MPTES (D20−0.0167S−0.50T/0.50M) and (c) MPTES alone (D20−0.0167S−0T/1.0M).

organotrialkoxysilanes (methyltrimethoxysilane (MTMS)) is lower than that of tetraalkoxysilanes (tetramethylorthosilicate (TMOS)) due to the lower functionality ($f = 3$), and the steric hindrance introduced by the organic group. It can therefore be anticipated that silica generated from MPTES is hydrolyzed, but condensed to a lesser extent before the evaporation step. These silica structures, bearing large numbers of hydroxyl groups (silanol groups), can associate with surfactant molecules and play an important role in dispersing silica within the polymer matrix, as revealed by Transmission electron microscopy (TEM) images of PI-silica hybrid materials.

Fig. 3 shows the TEM micrographs of BPADA-DAPP based hybrids (D-series) with different starting quantities of MPTES. The silica particles present in the hybrid polymer prepared with TEOS alone (D20−0.0167S−1.0T/0M) consist of large micron-sized silica spheres dispersed throughout the polyimide matrix (Fig. 3a). When thiol-functionalization of the silica was effectively carried-out, the resulting hybrid polymer, D20−0.0167S-0.50T/0.50M, prepared with equal quantities of silica precursors 0.50 mM TEOS:0.50 mM MPTES shows fairly homogeneously dispersed smaller silica particles (Fig. 3b), indicating that the mercapto functionalization allows the growth of silica particles with better dispersion and size homogeneity. As an extension of this, when the PI-silica hybrid is prepared with MPTES alone, D20−0.0167S−0T/1.0M has silica particles further reduced in size as shown in Fig. 3c. Thus, improved dispersion and size homogeneity are obtained with the fuctionalization of silica structures.

3.2. Effect of nature of polyimide host matrix

Fig. 4 displays the TEM images of BPADA-HAB (H-series) based PI-silica hybrids, prepared using increasing concentrations of MPTES:

(a) H30−0.0167S−1.1250T/0.375M, (b) H30−0.0167S−0.75T/0.75M, (c) H30−0.0167S−0T/1.50M. It is clear that in this system silica particles with a reduced size are generated with an increase in the quantity of the thiolated silica precursor, MPTES, similar to that observed with BPADA-DAPP polymer earlier (Fig. 3). However, marked differences can be noticed in the morphologies of these two hybrid systems.

A comparison of H-series composites prepared from equal molar quantities of TEOS and MPTES (H30−0.0167S−0.75T/0.75M, Fig. 4b) and MPTES alone (H30−0.0167S−0T/1.50M, Fig. 4c) with those corresponding samples of D-series composites (D20−0.0167S−0.50T/0.50M (Fig. 3b) and D20−0.0167S−0T/1.0M (Fig. 3c)) show that hybrid membranes of H-series polymer exhibit a homogeneous surface at the micronic (length) scale as opposed to the dispersed-particle morphology of D-series membranes. Such a promising effect by H-series polymer can be associated with its increased hydrophilic properties owing to the presence of greater number of −OH groups, which facilitate hydrogen-bonding interactions between the polymer and particle, allowing homogeneity (at the micronic scale) and better molecular compatibility.

Another salient feature of the BPADA-HAB polymer with a higher number of hydroxyl groups, is that it supports PI-silica hybrids with silica contents as high as 30%, while still maintaining good homogeneity and uniform silica particle dispersion, unlike BPADA-DAPP polymers which show the growth of a separate silica phase when the silica content exceeds 20%.

3.3. Brij® 35 surfactant effect

The Morphology obtained for the BPADA-HAB polymer-based composite, prepared by surfactant assisted sol-gel process involving TEOS and MPTES silica precursors (H30−0.0167S−0.375T/1.125M),
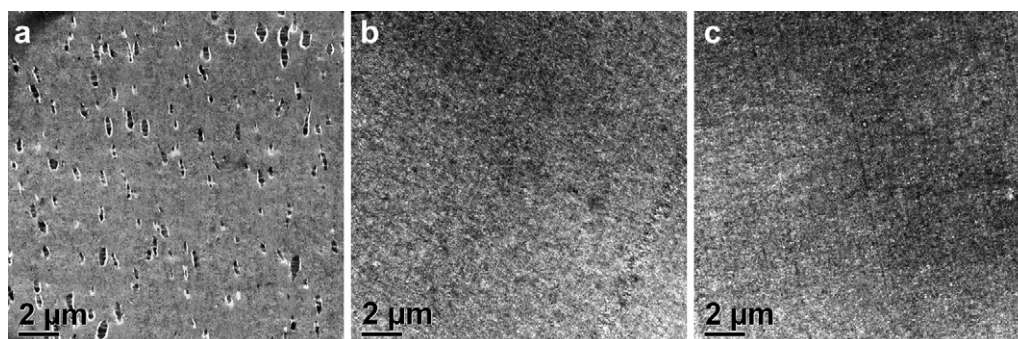

Fig. 4. TEM images showing morphology of H-series composites. (a) H30−0.0167S−1.125T/0.375M (b) H30−0.0167S−0.75T/0.75M (c) H30−0.0167S−0T/1.50M.
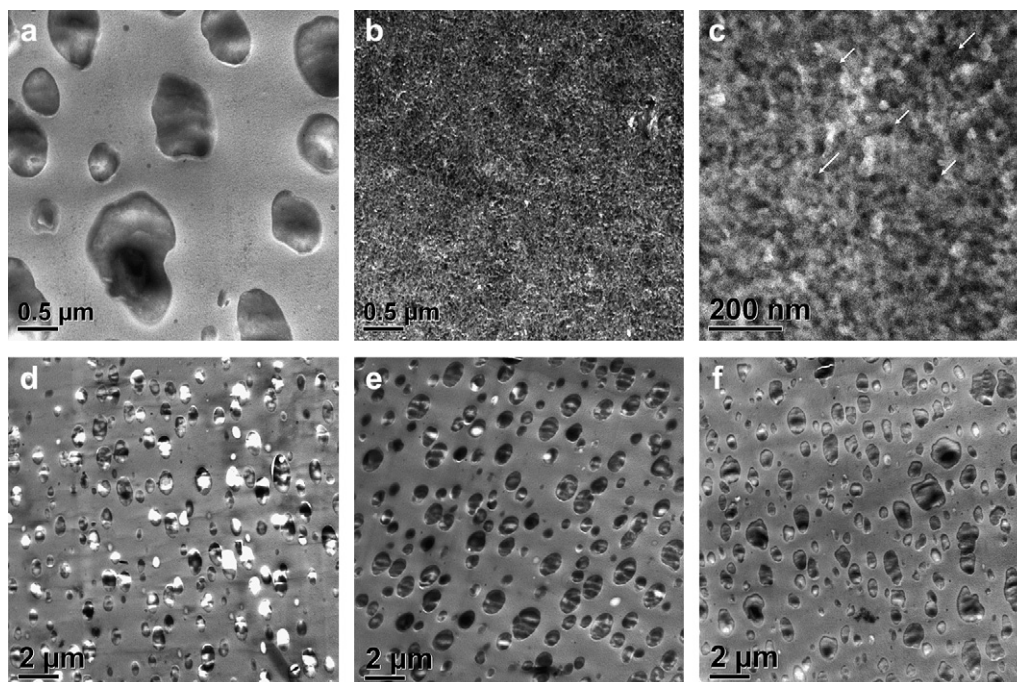
Fig. 5. TEM images showing morphology of (a) the sample prepared without surfactant (H30−0.375T/1.125M) and the corresponding sample prepared using surfactant assisted method (H30−0.0167S−0.375T/1.125M) (b) at low magnification(c) at a higher magnification (arrows point out silica particles). (d−f) TEM images of H-series composites prepared without using surfactant (d) H30−0.0167S−1.125T/0.375M (e) H30−0.0167S−0.75T/0.75M (f) H30−0.0167S−0T/1.5M.

was compared with that of the corresponding composite prepared without using surfactant (H30−0.375T/1.125M). It is clear that the sample without surfactant exhibits phase separated morphology (Fig. 5a), while surfactant added to the polymer-composite results in a significant particle size-reduction and a uniformly-distributed silica phase (Fig. 5b). The TEM image at higher magnification (Fig. 5c) shows clearly distinguishable nano-sized silica particles (∼20 nm), uniformly embedded throughout the PI matrix, highlighting the beneficial effects of the surfactant additions for finer and uniform distribution of the silica in hybrid materials..

In order to understand the action mechanism of the surfactant, surfactant-free H-series composites were prepared from different starting compositions of TEOS and MPTES silica precursors (Table 2), and then compared with the corresponding samples containing a constant concentration of the surfactant. Fig. 5 (d−f) shows TEM images of three surfactant-free polymer-composites prepared with increasing contents of MPTES in the starting compositions. It is interesting to see that all the samples prepared without surfactant exhibit a phase separated morphology. Bigger inorganic domains are observed with an increase in silica functionalization by MPTES, due to coalescence of hydrophilic silica particles. Thus, the functionalization of silica results in coarse dispersion and poor homogeneity of the embedded silica structures in the PI matrix. These observations agree quite well with the findings by Cornelius and Marand [18] that tetramethylorthosilicate (TMOS)-based PI-silica hybrid materials display quite homogeneous morphologies with very fine dispersions of silica particles, while methyltrimethoxysilane (MTMS)-functionalized silica structures appear as phase separated in the PI matrix. They postulated that TMOS is more reactive than MTMS and quickly underwent hydrolysis and condensation before phase separation could take place, leading to the formation of a highly interpenetrating network of PI and silica structures at 22.5 wt% silica content. In short, their study and our results in Fig. 5 d−f show that functionalization of silica favors phase separation and poor dispersion in the absence of surfactant. This tendency is reversed when

surfactant is present in the system (see Figs. 3 and4), where silica functionalization enhances the size-reduction and fine dispersion of silica particles in PI matrix. Thus, it is concluded that the surfactant molecules owing to their surface active properties adsorb on the surface of the functionalized silica particles and modify their hydrophilic nature to prevent the particle-aggregation and subsequent phase separation.

The homogeneous microstructures in which inorganic silica phase is finely dispersed in the polyimide matrix are potentially interesting morphologies. Moreover, this approach using surfactant opens further possibilities offered by the versatile organic functionalization of the inorganic phase.

Acknowledgment

Appendix. Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.polymer.2010.09.064.

References

[1] Zou H, Wu S, Shen J. Chem Rev 2008;108:3893−957.
[2] Nandi M, Conklin JA, Salvati Jr L, Sen A. Chem Mater 1991;3:201−6.

[3] Joly C, Goizet S, Schrotter JC, Sanchez J, Escoubes M. J Membr Sci 1997;130:63−74.
[4] Morikawa A, Iyoku Y, Kakimoto M, Imal Y. Polymer 1992;24:107−13.
[5] Wahab MA, Kim I, Ha CS. J Polym Sci Polym Chem 2004;42:5189−99.
[6] Ha CS, Park HD, Frank CW. Chem Mater 2000;12:839−44.
[7] Morikawa A, Iyoku Y, Kakimoto M, Imal Y. J Mater Chem 1992;2:679−90.
[8] Chang CC, Chen WC. Chem Mater 2002;14:4242−8.
[9] Kioul A, Mascia L. J Non-Cryst Solids 1994;175:169−86.
[10] Wang S, Ahmad Z, Mark JE. Chem Mater 1994;6:943−6.
[11] Shang XY, Zhu ZK, Yin J, Ma XD. Chem Mater 2002;14:71−7.
[12] Park HB, Kim JH, Kim JK, Lee YM. Macromol Rapid Commun 2002;23:544−50.
[13] Musto P, Ragosta G, Scarinzi G, Mascia L. Polymer 2004;45:1697−706.
[14] Ohtani O, Goto Y, Okamoto K, Inagaki S. Mater Lett 2006;60:177−9.
[15] Mo TC, Wang HW, Chen SY, Dong RX, Kuo CH, Yeh YC. J App Polym Sci 2007;104:882−90.
[16] Kim Y, Ha CS, Chang T, Lee WK, Goh W, Kim H, et al. J Nanosci Nanotechno 2009;9:4633−43.
[17] Lee T, Park SS, Jung Y, Han S, Han D, Kim I, et al. Eur Polym J 2009;45:19−29.
[18] Cornelius CJ, Marand E. Polymer 2002;43:2385−400.
[19] Lee CH, Park HB, Park CH, Lee SY, Kim JY, McGrath JE, et al. J Power Sources 2010;195:1325−32.
[20] Tullos GL, Powers JM, Jeskey SJ, Mathias LJ. Macromolecules 1999;32:3598−612.
[21] Glaser RH, Wilkes GL, Bronnimann CE. J Non-cryst Solids 1989;113:73−87.
[22] Wahab MA, Kim I, Ha CS. Polymer 2003;44:4705−13.