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Confined crystallization behavior of PEO in silica networks

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Abstract

Poly(ethylene oxide) (PEO) and silica (SiO_2) organic–inorganic hybrid materials have been synthesized by sol–gel approach. The crystallization behavior of PEO in silica networks has been investigated by differential scanning calorimeter (DSC) and scanning electron micrograph (SEM). The degree of PEO crystallinity in PEO/SiO_2 hybrid networks reduces with the increase of SiO_2. PEO is in amorphous state when the concentration of PEO is lower than 50 wt% in the hybrid materials. The melting points of PEO in the networks are lower than that of pure PEO, but the melting point of PEO in the networks almost has the same melting point. WAXD and SEM results show that the crystalline behavior of PEO in PEO/SiO_2 hybrid system is sternly confined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Confined crystallization behavior; PEO/SiO_2 hybrid

1. Introduction

The design of new materials with enhanced properties continues to be a driver for the investigation of hybrid materials. In the past decade, organic–inorganic hybrid materials have been considered as innovative advanced materials showing an attractive field [1–12]. Most organic/inorganic hybrid composites can be prepared by introducing polymeric components into the sol–gel technology [10,13–17]. One indirect advantage of this technology including polymers is the facilitation to attain synergetic effects, specifically to produce materials that have optimized combination of the best properties of polymers with the best properties of inorganic materials.

Poly(ethylene oxide) (PEO) is a simple and representative linear polymer with interesting behavior both in the blending with other polymers and in the pure state. Because of the fundamental importance and wide applications, many authors have studied the phase structure, morphology and crystallization in the solid state and in solution [14,18–29]. These studies have been carried out both in the pure polymer and in its blending, but the behavior of PEO in a confined environment has been less quantitatively understood, when compared with that of PEO in free environment. An approach to design hybrid organic–inorganic materials with PEO by sol–gel method gives the limited environment for PEO. The behavior of polymers is affected by the blending, [18–20,22] cross linking [30] and block copolymerization [23,31]. We expected that the behavior of PEO in silica networks would also be affected.

We report the observation of confined crystalline behavior of macromolecules in the networks composed of PEO and SiO_2 which took the sol–gel approach to the synthesis of hybrid materials by designing PEO with tetraethyl orthosilicate (TEOS). The overall process is illustrated in Scheme 1. During this process the silica become system of pores, and PEO will be embedded in the pores at the low weight percentage of PEO. This approach allows us to study the confined behavior of PEO in a well defined inorganic networks intimately connected to a vary concentration of organic polymer and to investigate the morphology of organic polymer in the confined environment.

2. Experimental

The PEO here is a commercial product of polysciences lnc. The M_w and M_n determined by gel permeation chromatography (GPC) are 19 000 and 10 200, respectively, and their ratio is 1.86. TEOS is a commercial product of Aldrich Co. The general procedure for preparing the PEO/silica hybrids was to dissolve PEO in DMF at concentration of about 20 wt%. Measured amount of water and TEOS at molar ratios of 2.5:1 are mixed with DMF solution of PEO and a catalytic amount of HCl was added to adjust the pH to 2–3. A homogeneous solution was attained after

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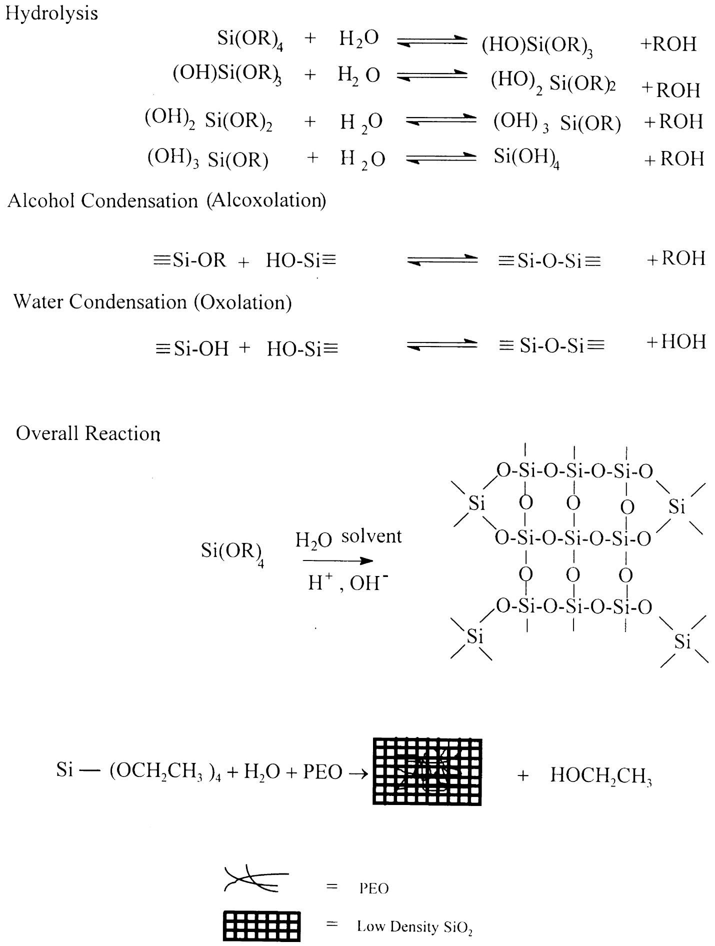

Scheme 1.

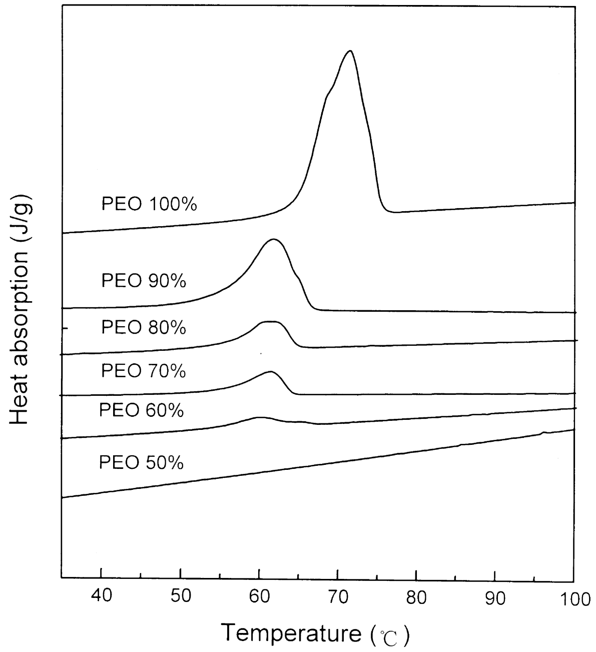

Fig. 1. DSC curves of PEO/SiO$_2$ hybrid materials at a heating rate of 10°C/min.

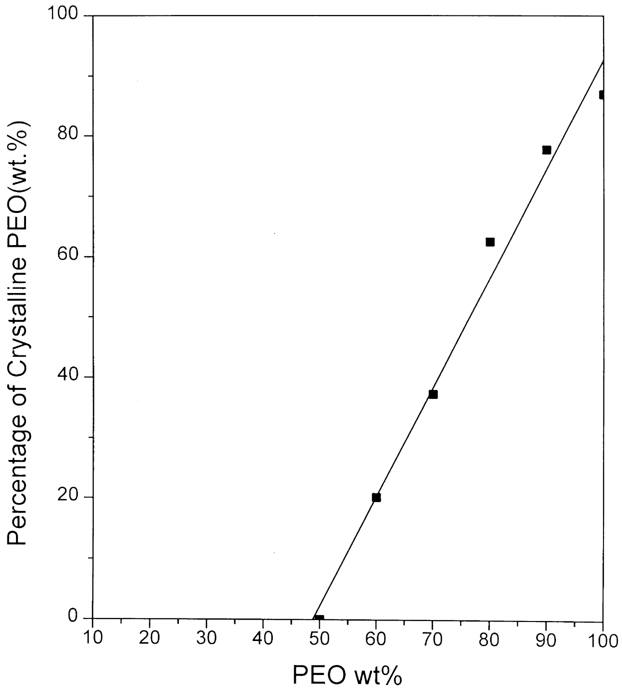

Fig. 2. The weight percentage of crystalline PEO vs. PEO concentration in PEO/SiO$_2$ hybrid system.

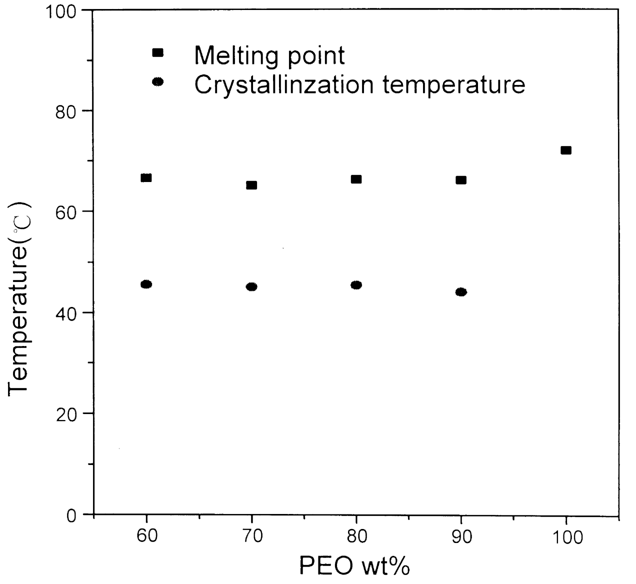

Fig. 3. Melting point and crystallization temperature of PEO in PEO/SiO_2 hybrid system vs. PEO wt%.

attiring for 2 h and then casted the solution into covered PTFE dishes and placed them in an oven at 40°C for one week until they became gel. The solvent was evaporated slowly over 1 week at 80°C keeping PEO in the melting state. The specimens thus prepared were further dried in a vacuum oven at 80°C until a constant weight was attained. A DSC experiment was performed with Perkin–Elmer DSC-7 differential scanning calorimeter for the observation of melting and crystallization of PEO, a Philips PW1700 automatic powder diffractometer with Ni-filtered CuKα radiation was used for the wide-angle X-ray diffraction (WAXD) measurements (the scans were obtained by using a 0.05° step programmed with a collection time of 10 s per step) and a scanning electron microscope (SEM) (Jeol JXA-840) was used to invest the morphology of PEO and SiO_2 hybrid fracture surface which were sputter-coated with gold.

Table 1
Crystalline size of L_{120} of PEO in PEO/SiO_2 hybrids with different PEO content

PEO (wt%)	2θ[a]	B[b]	β[c]	L_{120} (nm)
100	19.09	0.83	0.816	9.87
90	19.14	1.56	1.553	5.18
80	19.19	2.17	2.165	3.72
70	19.22	2.76	2.756	2.92
60	19.14	3.27	3.267	2.46

[a] Bragg angle.
[b] Measured half-width of the experimental profile (in radians or degrees).
[c] Pure line broadening (in radians or degrees).

3. Results and discussion

Fig. 1 shows the DSC curves of PEO/SiO_2 hybrid

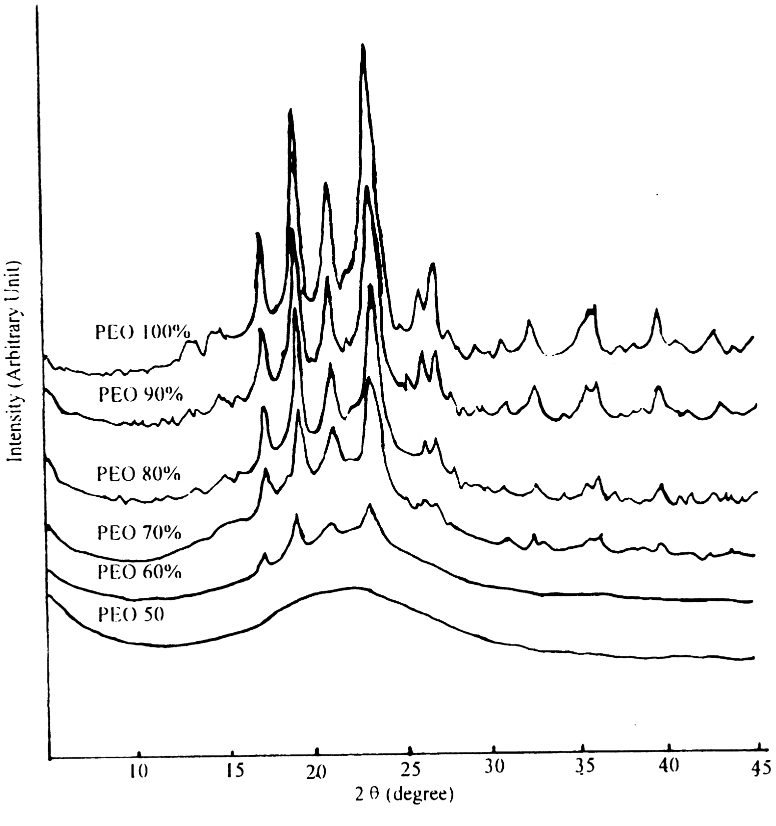

Fig. 4. WAXD patterns for PEO/SiO_2 hybrid system with different weight ratios.

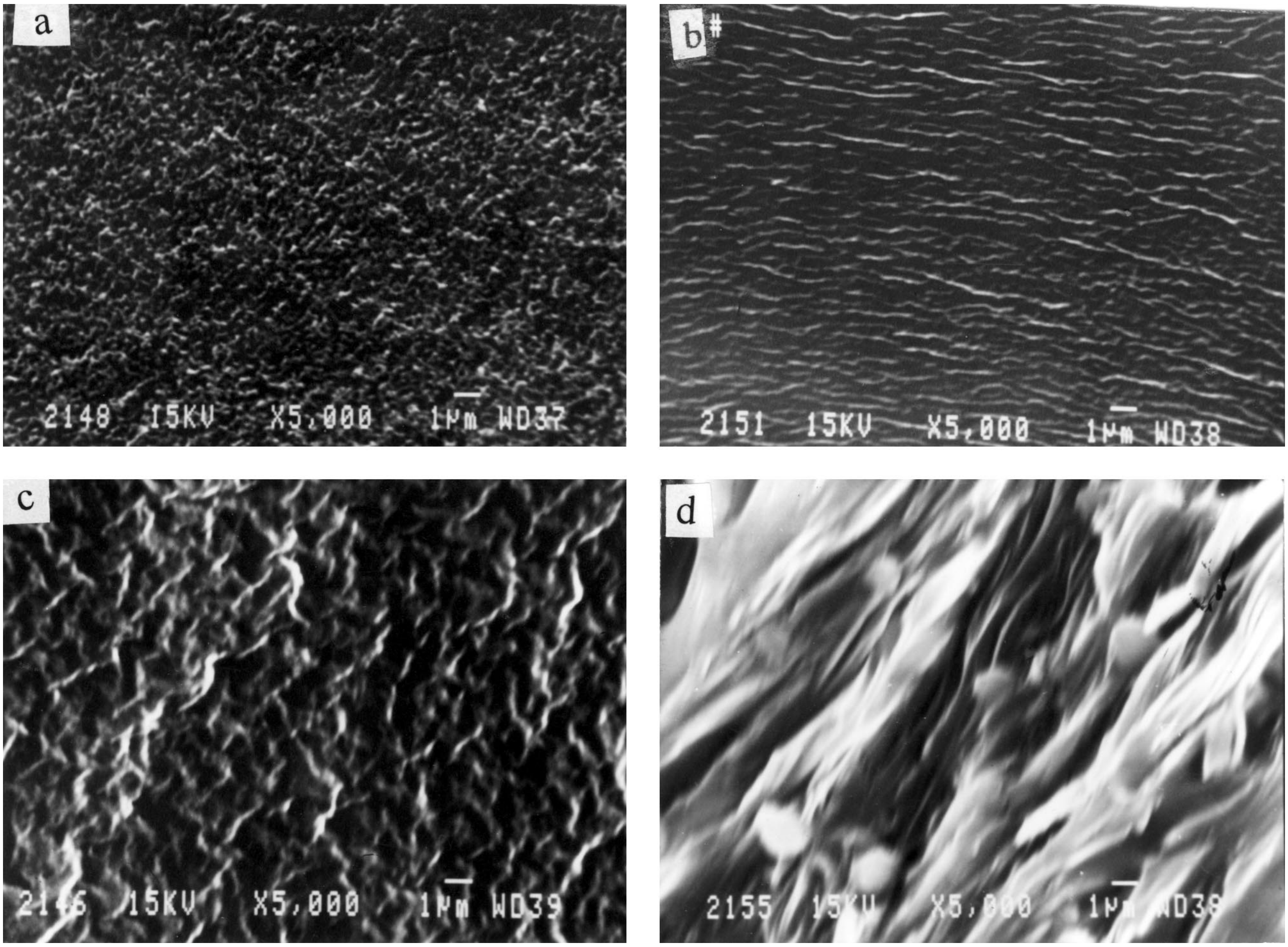

Fig. 5. SEM photographs of the fracture surface of PEO/SiO_2 hybrid system: (a) 50 wt% PEO; (b) 60 wt% PEO; (c) 70 wt% PEO; (d) 90 wt% PEO.

materials with different ratios on heating. The samples were heated from 0 to 100°C with a heating rate of 10°C/min. In Fig. 1 the hybrids of PEO with silica exhibit no peak when the PEO weight percentages is under 50%. This result indicates that the crystallization of PEO in the hybrids is strictly confined.

Fig. 2 shows the DSC result of hybrid materials. The weight percentage of crystalline PEO evolved was recorded vs. the concentration of PEO in the composited samples. The heat of fusion obtained is directly proportional to the weight percentage of crystalline PEO. The weight percentage of crystalline PEO (C_r) (wt%) was calculated from the following relation:

$$C_r = \Delta H_f/(\chi_A \times \Delta H^\circ_f) \times 100\% \tag{1}$$

where ΔH_f is the apparent heat of fusion per gram of the hybrids, χ_A is the concentration of PEO wt% in the hybrid networks and ΔH°_f is the thermodynamic heat of fusion per gram of completely crystalline PEO [32]. The amount of crystallizable PEO in the PEO/SiO_2 hybrid networks is reduced with the increase of SiO_2, as shown in Fig. 2. PEO is not able to crystallize when the PEO concentration is lower than 50 wt%. We also have investigated the crystallization behavior of some other crystalline polymers in the hybrids with silica, and found the same trend such as shown in Fig. 2 (unpublished results). From the experimental process we know that the PEO here crystallized from the melting state, and the DSC studies indicate that the reduction of weight percentage of crystalline PEO results from the confined movement of macromolecular chains in the silica networks. At the low weight percentage of PEO in the hybrid system, the PEO is thoroughly embedded in the pores of silica, the PEO chains are absorbed on the surface of the porous silica gel, the movement of macromolecular chains is limited in the micropores, it is difficult to crystallize. On the contrary, at the higher weight percentage of PEO in the hybrid system, part of the polymer is out of the pores and becomes the crystalline phase in this system.

Fig. 3 shows the DSC result of the melting points and crystallization temperature of PEO in PEO/SiO_2 hybrid samples, when the PEO can crystallize in the networks corresponding to the concentration of PEO wt%. The melting temperature T_m was taken as the temperature corresponding to the maxim of the melting peak, and the crystallization temperature T_c was taken as the temperature corresponding to the minimum of the crystalline peak when

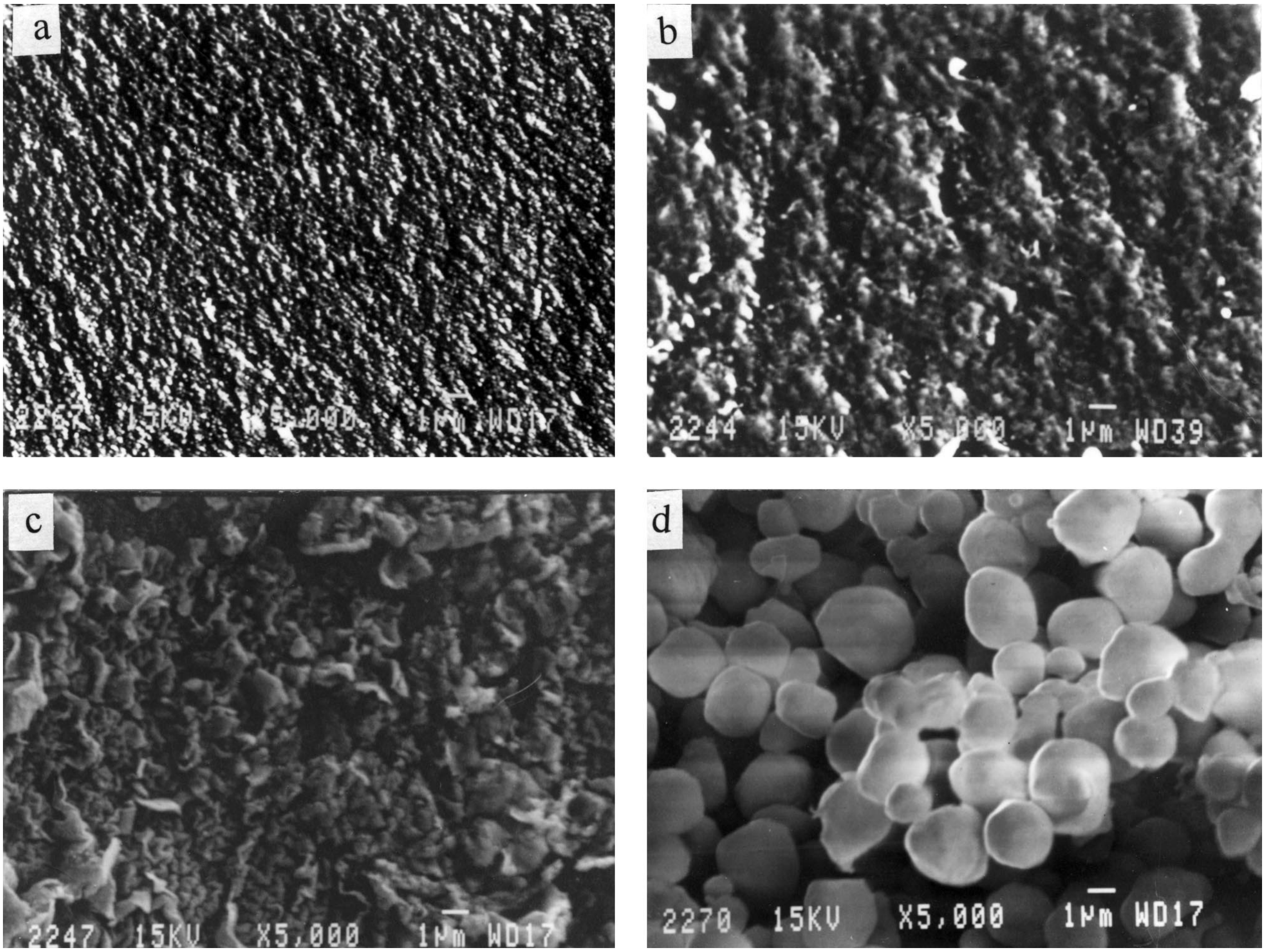

Fig. 6. SEM photographs of the fracture surface of PEO/SiO_2 hybrid system after being extracted by $CHCl_3$: (a) 50 wt% PEO; (b) 60 wt% PEO; (c) 70 wt% PEO; (d) 90 wt% PEO.

the samples were cooled from 100 to 0°C. Even though the melting points of PEO in the networks are lower than that of pure PEO, they have little difference from each other in the hybrid samples. We can conclude that the crystalline phase of PEO in the hybrid system would be different from the pure crystalline phase of PEO and its blending with other polymers and block copolymers. Because the rigid silica network confines the growth of fine PEO lamella, and the melting points of the crystalline PEO do not correspond to the size of the lamella, they are just the melting points of crystalline phase of PEO in the hybrid materials.

Fig. 4 shows the WAXD reflection patterns of the same samples. The DSC results showed that the PEO cannot crystallize in the hybrid samples when the PEO weight ratios are lower than 50%, and its crystallinity reduces with the increase in silica weight ratio while the PEO weight ratios are higher than 60%. The WAXD pattern in Fig. 4 corresponds well to this result. But the crystal structure of PEO in silica has not changed. The crystallite size perpendicular to the (*hkl*) plane, L_{hkl} in nm, is usually given by the Scherrer equation

$$L_{hkl} = 5.73\frac{K\lambda}{\beta \cos \theta} \qquad (2)$$

where K is the Scherrer shape factor, here $K = 0.9$, λ is the wavelength of X-ray, θ is the Bragg angle, β is the pure line broadening, B is the measured half-width of the experiment profile (in degrees), b_0 is the instrumental broadening, which was obtained to be 0.15° from scans of standard silicon power, using the above definitions of B and b_0 and assuming peak shapes, then $\beta^2 = (B^2 - b_0^2)$. As an example, the values of the crystallite size perpendicular to (120) plane L_{120} at several selected ratios are presented in Table 1. It shows that L_{120} systematically increases as PEO wt% increases. The reason given to such a phenomenon is probably that the poorly crystallized macromolecules or small and metastable crystals were strictly confined by the rigid silica networks.

Fig. 5 shows the SEM of the fracture surface PEO/SiO_2 hybrid at 50, 60, 70, and 90 wt% PEO. The micrographs in Fig. 5 show, that increase the amount of PEO used in the hybrids cause an increase in the dimensions of the domains due to the separation of the polymer phase. PEO/SiO_2 hybrid with a weight ratio of 1:1 has no clear PEO phase as shown in Figs. 1 and 4. It seems reasonable to conclude that the movement of the PEO is highly confined in the porous silica, consequently, PEO cannot crystallize in the silica networks. Fig. 5(b)–(d) shows the PEO layer phase becomes thicker and thicker with the increase of PEO amount in the hybrid networks, and that means the PEO still crystallize when it is out of the porous silica.

Fig. 6 shows SEM photographs of the fracture surface of PEO/SiO_2 hybrid after being extracted by $CHCl_3$. The morphology of silica in the hybrids becomes gradually finer and finer with increasing silica contents in the hybrid system. The size of SiO_2 was also influenced by the increase of PEO. PEO in the networks supplied a relatively soft environment for silica to become beads as show in Fig. 6(d). On the contrary, the silica in hybrids can confine the behavior of PEO more strictly than PEO can affect silica in this system.

4. Conclusions

The present study of organic–inorganic hybrid materials of PEO/SiO_2 networks enables us to recognize the effect of PEO behavior in the confined environment. PEO in the hybrids is not able to crystallize at the weight ratio that is lower than 50%, on the contrary, crystalline PEO in the hybrid has almost the same melting temperature. The movement of PEO molecular chain in the PEO/SiO_2 hybrid system can be strictly confined by the rigid silica networks and the silica is also affected by PEO in this system. The melting temperature of crystalline PEO in the hybrid system is lower than that of pure PEO.

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