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Crystallization behavior of PCL in hybrid confined environment

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Abstract

Poly(ϵ-caprolactone) (PCL) and silica (SiO_2) organic–inorganic hybrid materials have been synthesized by the sol–gel method. The crystallization behavior of PCL in silica networks has been investigated using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The degree of PCL crystallinity in PCL/SiO_2 hybrid networks reduces with increase of SiO_2. PCL is in an amorphous state when the concentration of PCL is lower than 40wt% in the hybrid system. The melting point of PCL in the networks is lower than, but close to that of pure PCL. WAXD and SEM results show that the crystalline behavior of PCL in PCL/ SiO_2 hybrid system is strictly confined.

Keywords: PCL crystallization behavior; PCL/SiO_2 hybrid

1. Introduction

The field of confined liquids, in particular that of confined polymers, has developed rapidly in the last ten years [1]. Confinement complicates the physics of such films and may alter their properties drastically. Recently, computational and experimental efforts have begun to examine effects of similar small dimensions on polymer structure. Molecular dynamics simulations of chains near structureless solid surfaces show that although there is a significant enhancement of segmental density very close to the surface, this enhancement is less than that found with atomic liquids.

It is now generally accepted that the presence of a confining boundary induces local ordering of a fluid to an extent greater than is normally found in a bulk liquid radical distribution function. This local surface structure has been predicted for hard-sphere liquids by a large number of molecular dynamics simulations and has been confirmed experimentally by surface force measurements of liquids trapped in a narrow slit between two confining boundaries.

At present, most of the work on confined polymers is focused on the polymer films and ultrathin polymer films [2–10]. 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 hybrids have been considered as innovative advanced materials given an attractive field [11–22]. Most organic–inorganic hybrid composites can be prepared by introducing polymeric components into sol–gel technology [20,23–27]. One indirect advantage on including polymers is that synergistic effects may be attained, specifically to produce materials that have an optimized combination of the best properties of polymers with the best properties of inorganic materials.

The biodegradability and nontoxicity of poly(ϵ-caprolactone) (PCL) are of great interest for the controlled release of drugs from subdermally implanted polymer devices. However, the technological development of PCL in this area is limited by its short useful lifespan (about one year) and high crystallinity. Thus, several studies have been devoted to PCL blends and copolymers with the aim to control the biodegradation rate of this polymer and its crystallinity [28,29]. Organic–inorganic hybrid materials of PCL are an attractive means to control simultaneously these properties, and the behavior of PCL in a confined environment has been less quantitatively understood, when compared with that of PCL in a free environment. An approach of designing hybrid organic–inorganic materials with PCL and by the sol–gel method gives the confined environment necessary to study the behavior of PCL.

We have taken the sol–gel approach to the synthesis of hybrid materials by designing PCL with tetraethyl orthosilicate (TEOS), and the material composed of PCL and SiO_2

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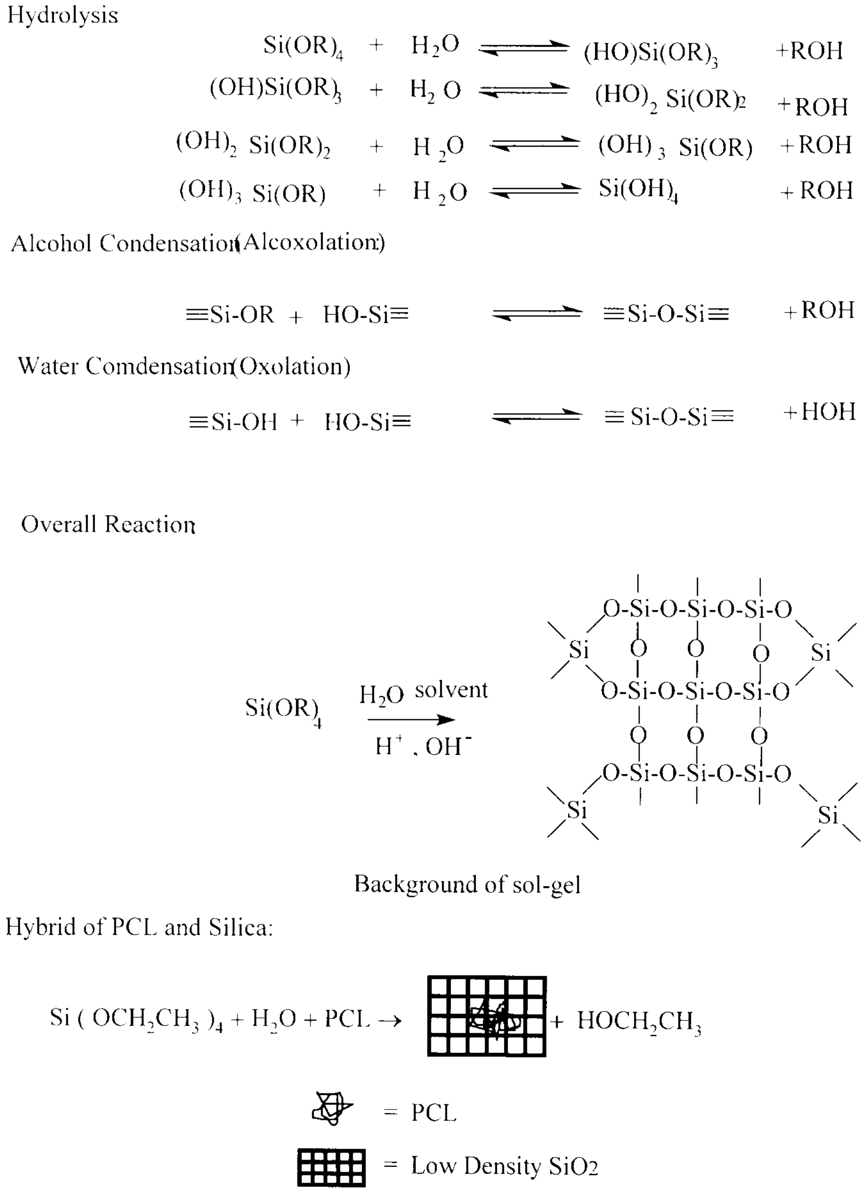

Scheme 1.

hybrid to introduce a network. This overall process is illustrated in Scheme 1. During this process the silica becomes a system of pores, and PCL will be embedded in the pores at a low weight percentage of PCL. This approach allows us to study the behavior of a well defined inorganic network intimately connected to an organic polymer of variable concentration and to investigate the morphology of an organic polymer in the nanoscale environment.

The crystallization of polymers is affected by crosslinking, the block copolymers and their blending with other polymers. We expected that the weight percentage of crystalline PCL in silica networks would also be affected. In order to investigate the behavior of PCL in silica networks we did an experiment and found interesting results.

2. Experimental

The PCL here are commercial products of Polyciences Inc. The M_w and M_n determined by gel permeation chromatography (GPC) are 22,000 and 11,300, respectively, and their ratio is 1.95. TEOS is a commercial product of Aldrich Co. The general procedure for preparing the PCL/silica hybrids was to dissolve PCL in THF at a concentration of about 20 wt%. Measured amounts of water and TEOS at a molar ratio of 2.5:1 are mixed with THF solution of PCL and a catalytic amount of HCl was added to adjust the pH to 2–3. A homogeneous solution was attained after 2 h and cast into covered PTFE dishes and placed in an oven at 40°C for one week, when a gel was formed. The solvent was evaporated over a week at 70°C, keeping PCL at the

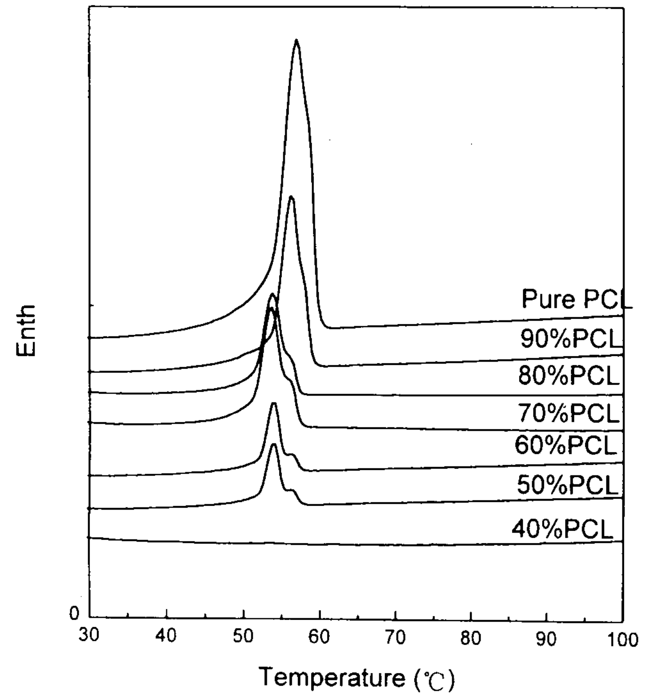

Fig. 1. DSC curves of PCL/SiO_2 hybrid materials at a heating rate of $10°C/min^{-1}$.

melting state. The specimens thus prepared were further dried in a vacuum oven at 70°C until a constant weight was attained. A DSC experiment was performed with a Perkin-Elmer DSC-7 differential scanning calorimeter for the observation of PCL crystallization, and a Philips PW1700 automatic powder diffractometer with Ni-filtered CuK_α 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) (model JXA-840, Japan) was used to invest the morphology of PCL and SiO_2. The test specimens were first cold-fractured in liquid nitrogen. In order to investigate the morphology of the silica in the hybrid system, half of the specimens were extracted by chloroform ($CHCl_3$) three times (each time keeping the samples in $CHCl_3$ for one day and filtering off the solution) and dried in an oven for three days. The samples to be investigated by SEM were coated with a thin layer of gold–palladium alloy to avoid charging under the electron beam.

3. Results and discussion

Fig. 1 shows the DSC curves of PCL/SiO_2 hybrid 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 hybrid of PCL with silica exhibits no peak when the PCL weight percentage is under 40 wt%. This result indicates that the crystallization of PCL in the hybrids is strictly confined.

Fig. 2 shows the weight percentage of crystalline PCL in the hybrid plotted against the concentration of PCL. It is the DSC result of the hybrid materials. The samples as attained were heated from 0 to 100°C at a heating rate of 10°C/min. The heat of fusion obtained is directly proportional to the weight percentage of crystalline PCL. The weight percentage of crystalline PCL(C_r) was calculated from the following relation,

$$C_r = \Delta H_f/(\chi_A \times \Delta H_f^{\circ}) \times 100\%, \qquad (1)$$

where ΔH_f is the apparent heat of fusion per gram of the hybrids, χ_A is the concentration of PCL (wt%) in the hybrid materials. ΔH_f° is the thermodynamic heat of fusion per

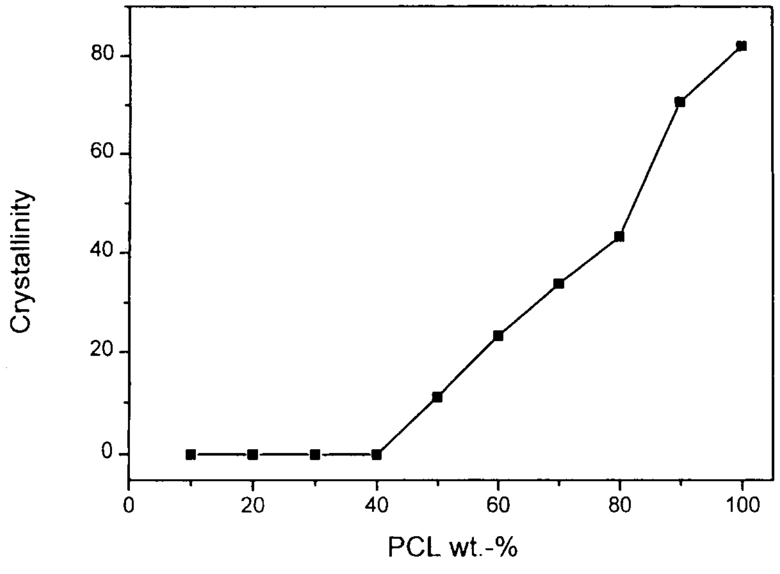

Fig. 2. PCL crystallinity against PCL wt% in the hybrids.

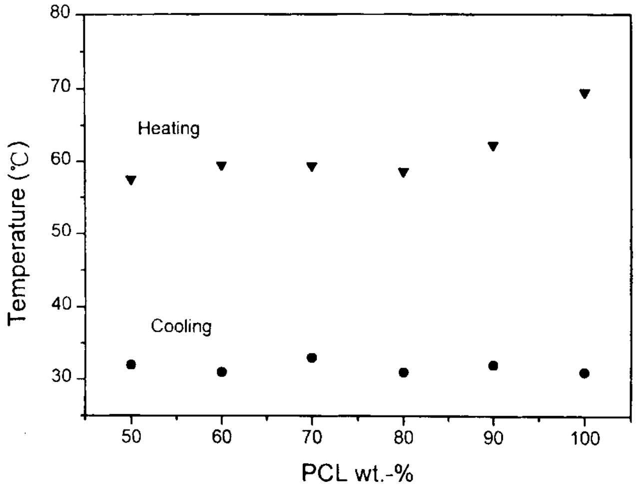

Fig. 3. Melting temperature and crystallization temperature against PCL wt% in the hybrids during the heating and cooling processes.

Table 1
Crystallite size of $L200$ and L_{110} of PCL in silica network at different ratios

	PCL (wt%)	2θ[a]	B[b]	β[c]	L_{hkl} (nm)
L_{110}	100	21.18	0.30	0.26	31.07
	90	20.97	0.30	0.26	31.06
	80	20.87	0.30	0.26	31.06
	70	20.85	0.30	0.26	31.06
	60	20.95	0.30	0.26	31.06
	50	20.88	0.30	0.26	31.06
L_{200}	100	23.54	0.40	0.37	21.92
	90	23.30	0.40	0.37	21.91
	80	23.21	0.40	0.37	21.91
	70	23.18	0.40	0.37	21.91
	60	23.29	0.40	0.37	21.91
	50	23.28	0.40	0.37	21.91

[a] Bragg angle.

[b] Measured half-width of the experimental profile.

[c] Pure line broadening.

gram of completely crystalline PCL and was assumed to be 135.31 J/g [30]. The weight percentage of crystalline PCL in the PCL/SiO_2 hybrid networks is reduced with the increase of SiO_2, as shown in Fig. 1. PCL is non-crystallizable at concentrations lower than 40 wt%. The weight percentage of crystalline PCL in the hybrid almost forms a straight line when it is plotted against PCL wt%. We have also investigated the behavior of some other crystalline polymers that hybrid with silica, and found the same trend as shown in Fig. 2. From the process of experimentation we know that the PCL crystallized here from the melting state, and the DSC results indicate that the reduction in weight percentage of crystalline PCL results from the confined movement of macromolecular chains in the silica networks. At low weight percentages of PCL, the PCL is thoroughly embedded in the pores of silica and the PCL chains are absorbed on the surface of the porous silica gel, and the movement of macromolecular chains is limited in the micropores and it is difficult to crystallize. On the other hand, at the higher weight percentages of PCL in the hybrid system, part of the polymer is out of the pores and forms the crystalline phase in this system. Fig. 3 shows the DSC result of the melting points and the crystallizing temperature of PCL in the PCL/SiO_2 hybrid — when the PCL can crystallize in the networks for a concentration of PCL (wt%). The melting temperature T_m was taken as the temperature corresponding to the maximum of the melting peak when the samples were heated from 0 to 100°C, and the crystallizing temperature T_c was taken as the temperature corresponding to the minimum of the crystallization peak when the samples were cooled from 100 to 0°C. The melting points of PCL in the networks are lower than that of pure PCL, as shown in Fig. 3. We can infer that the crystalline phase of PCL in the networks will be different from the crystalline phase of pure PCL and block copolymers and that of blends with other polymers. The crystalline morphology of PCL in the confined environment will be different. We observed it by SEM as described in the following, which supports our idea.

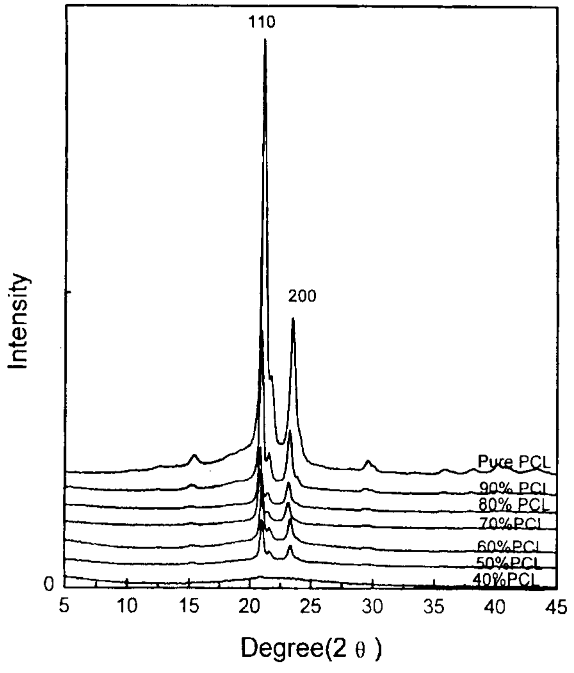

Fig. 4. WAXD patterns for PCL/SiO_2 hybrid systems with different weight ratios.

Fig. 4 shows the WAXD reflection patterns of the same samples. The DSC result showed that the PCL could not crystallize in the hybrid system when the PCL ratios are lower than 40 wt%, and its crystallinity reduces with increase in silica weight ratio while the PCL weight ratios are higher than 50 wt%. The WAXD patterns in Fig. 4 correspond well with this result. But the crystal structure of PCL in silica has not changed. The crystallite size perpendicular to the (hkl) plane, L_{hkl} in nm, is usually given by the

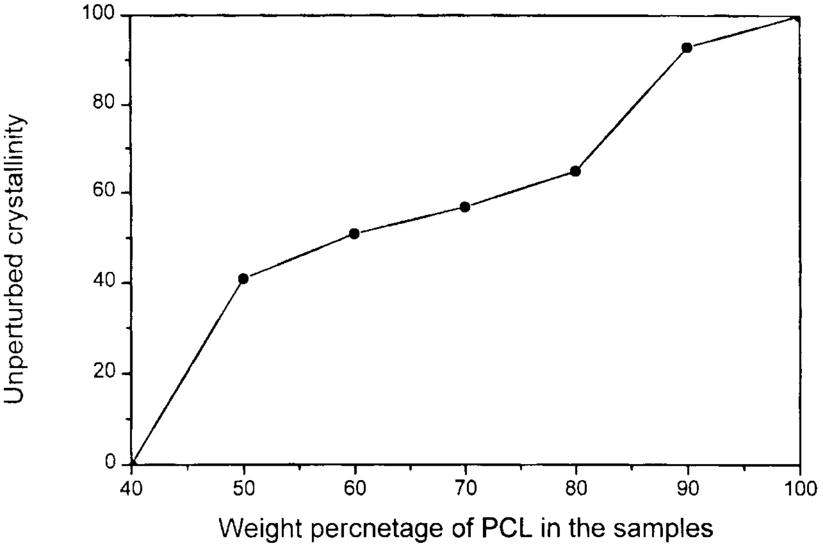

Fig. 5. Unperturbed PCL crystallinity vs PCL wt% in the hybrids.

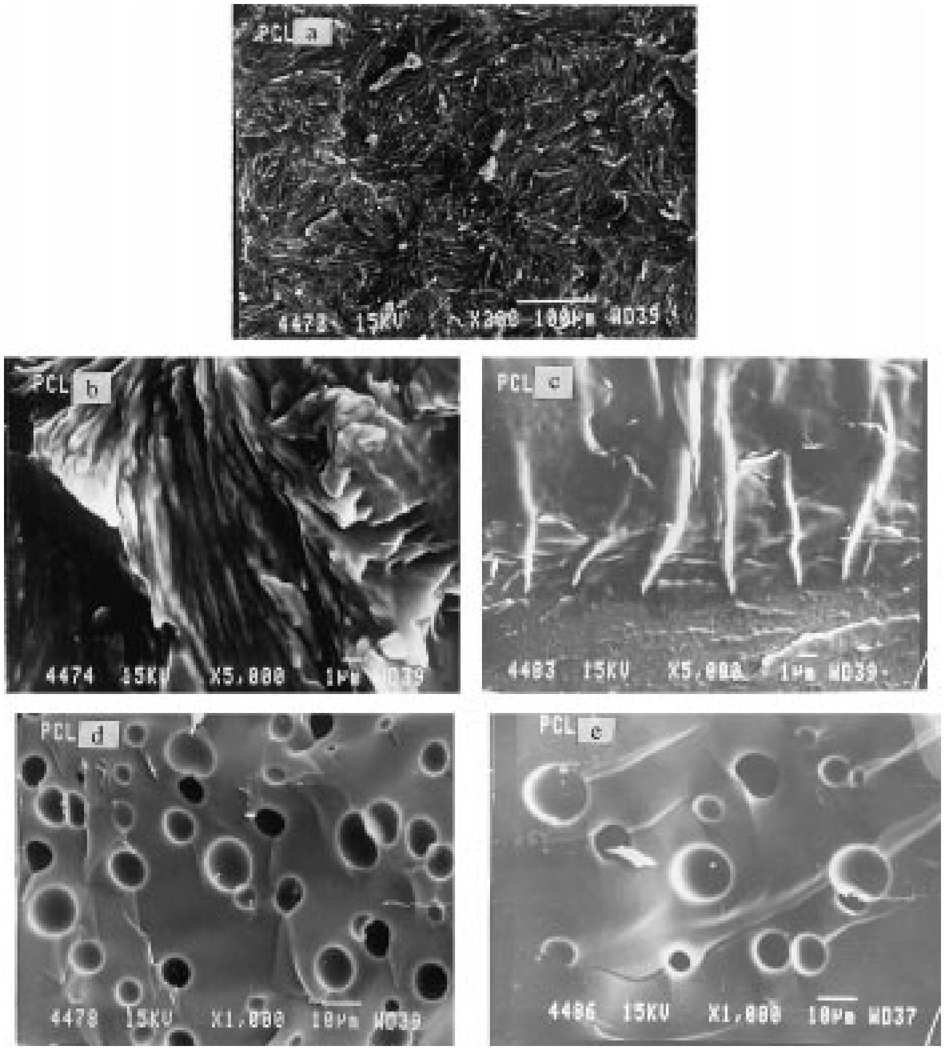

Fig. 6. SEM photograph of PCL/SiO$_2$ hybrid networks' fracture surfaces (a — 90 wt% PCL, b — 90 wt% PCL, c — 70 wt% PCL, d — 50 wt% PCL, e — 40 wt% PCL).

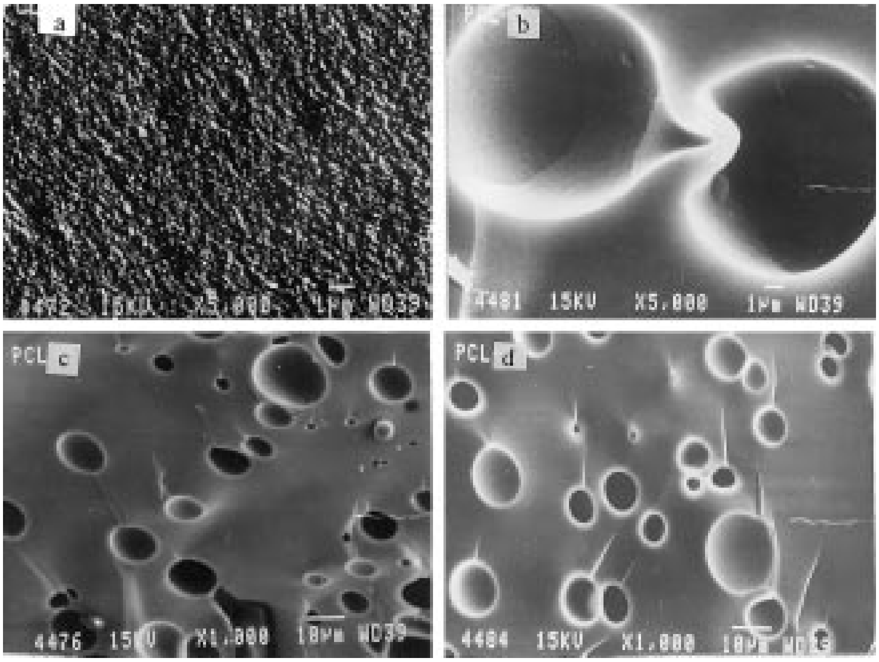

Fig. 7. SEM photograph of PCL/SiO_2 hybrid networks' fracture surfaces after extraction by $CHCl_3$ (a — 90 wt% PCL, b — 70 wt% PCL, c — 50 wt% PCL, d — 40 wt% PCL).

Scherrer equation,

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta}, \tag{2}$$

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

Based on the DSC and WAXD results, we assume that one sample is composed of two parts — one part is unperturbed PCL, the other part is confined PCL and silica, which is composed of 60 wt% silica and 40 wt% PCL. This is reasonable when the sample that has the same composite and PCL cannot crystallize. On the basis of this hypothesis, we can analyze the crystallization behavior of PCL in the hybrid system. At low (under 49 wt%) weight percentages, the PCL chain is completely in silica and its movement is strictly confined by the rigid silica network; at high (over 50 wt%) weight percentages, PCL is in an unperturbed state, so that it can crystallize and the crystalline PCL has the same melting point and the same crystalline structure. After all the unperturbed PCL is in confined space, its crystallinity and the melting temperature are different from the pure PCL. So we can calculate the crystallinity of unperturbed PCL in the PCL/SiO_2 hybrid system from the following equation,

$$C_r' = \Delta H_f / \left(\left(1 - \frac{1 - \chi_A}{1 - n} \right) \times \Delta H_f' \right) \times 100\%, \tag{3}$$

where C_r' is the crystallinity of the unperturbed PCL in the hybrid system, ΔH_f is the apparent heat of fusion per gram of the hybrids, χ_A is the concentration (wt%) of PCL in the materials, n is concentration of PCL when it is uncrystallizable in the samples (here $n = 40\%$), and $\Delta H_f'$ is the apparent heat of fusion per gram of pure PCL. The calculated results show in Fig. 5 that there is an obvious transition of C_r' in the system. The PCL crystallinity does not change not very much from 50 to 80 wt% in the system, but when the PCL weight percentage is higher than 90 wt%, there is a mutation of C_r'. This indicates there must be a transition in the structure of the samples.

Fig. 6 shows the scanning electron micrographs of PCL/SiO_2 hybrid fracture surfaces at 40, 50, 70, and 90 wt% of PCL. Fig. 6a shows the SEM photographs observed for 90 wt% in the hybrid. The morphology of PCL had clear spherulite, but no spherulite was observed for other PCL weight percentages in this experiment as shown in Fig. 6b–6e. Fig. 6e shows a hybrid of 40 wt% PCL, which has no crystalline phase, as shown in Fig. 1. No apparent PCL phase can be seen, indicating that the PCL is fully embodied in silica networks and its molecular chain movement is so highly confined by the networks that it is uncrystallizable. Fig. 6b, 6c and 6d show the PCL crystalline phase is decreasing with increasing silica in the hybrid networks. It corresponds to the melting temperature of the samples as shown in Fig. 2 and the mutation of $C_r^\prime$ in Fig. 5 of this system.

Fig. 7 shows SEM photographs of PCL/SiO_2 hybrid fractures surfaces after being extraction by $CHCl_3$. The morphology of SiO_2 was also influenced by the percentage of PCL in the networks. PCL supplied a relatively soft environment for the silica to form networks as shown in Fig. 7. The solvent left holes in the samples after drying as we find in Fig. 6d and 6e. Through Fig. 7 we can explain Fig. 5 easily. Fig. 7a is the silica fracture surface of the PCL/SiO_2 (90:10) hybrid. In this sample, silica is the discrete phase, and will have less influence on the PCL. In others the silica is a continuous phase, and will confine the movement of PCL molecular chains in those systems. All of these features imply that the silica networks confined the behavior of PCL and interface adhesion exists between PCL and SiO_2. This is in good agreement with the DSC result and the morphology observed by SEM.

3. Conclusions

The present study of organic–inorganic hybrid materials of PCL/SiO_2 networks enables us to recognize the effects of the confined environment on PCL behavior. PCL in the hybrid system is not able to crystallize at weight ratios below 40 wt%. On the other hand the crystallite size of PCL in the hybrid materials increases with increase in weight percentage of PCL. When PCL is crystallizable, the movement of PCL molecular chains in the PCL/SiO_2 hybrid system is rigidly confined by the silica networks, and the silica is also affected by the PCL in this system. The melting temperature of crystalline PCL in the hybrid materials is lower than that of pure PCL.

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