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Polymer 42 (2001) 8265–8275

polymer

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An investigation on the microcellular structure of polystyrene/LCP blends prepared by using supercritical carbon dioxide

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Received 27 November 2000; received in revised form 21 March 2001; accepted 29 March 2001

Abstract

Foamed PS/LCP blends with cell diameter less than 7 μm are prepared by using supercritical CO_2, 25 MPa, and 80°C for 6 h. Characterization of the microcellular structure of these blends is conducted to reveal the influence of LCP addition, LCP ratio and compatibilizer used on the microcellular blends. Due to poor adsorption of supercritical CO_2 by LCP under the experimental conditions, the microvoids only exist in the polystyrene phase of the blends. Where in the LCP phase, the microfibrils and spheres retain their original morphology and a skin-core structure exist as in the unfoamed PS/LCP blends. The LCP ratio and the compatibilizer, zinc neutralized lightly sulfonated polystyrene ionomer (ZnSPS), influence the cell size of the microcellular blends. A significant decrease of cell diameter in low LCP composition is observed, and then the change is much less and levels off in higher LCP composition. An increase of cell size is found from skin to core, which is resulted from the effect of the skin-core structure of the PS/LCP blends and the effect of competition between gas diffusing in the cells and diffusing out of the skin. The microcellular blends with ZnSPS has larger cell size than those without ZnSPS, which is the consequence of the improvement of interfacial adhesion, where CO_2 could easily diffuse out through the gap between poor adhesion interface of blends without ZnSPS. It is also found that the cell density in the microcellular blends is slightly larger than that in the microcellular polystyrene. This implies an additional heterogeneous nucleation of LCP to the homogeneous nucleation of polystyrene.

Keywords: Microcellular polymer; Supercritical CO_2; Polystyrene/LCP blends

1. Introduction

Microcellular polymers are usually defined as closed-cell polymers with cell diameters in the range of 1–10 μm, cell densities in the range of 10^9–10^{12} cells per cubic centimeter and specific volume reduction in the range 5–95%. This kind of novel materials has received increased attention in the past two decades due to its unique ability to give new range of insulating and mechanical properties with reducing material costs [1–3]. The studies have revealed that microcellular polymers have the properties of high impact strength [4,5], high toughness [6], high stiffness-to-weight ratio [7], high fatigue life [8], high thermal stability [9], low dielectric constant [10], and low thermal conductivity. Thus, microcellular polymers find many potential applications such as food packaging, refrigerator linings, and sporting equipment. Moreover, the tiny size and uniform distribution of the microvoids make it possible to produce small-profile foaming parts for insulating purpose, such as microelectronic circuit board insulators, electronic signal wire insulation, read-only memory storage, which cannot be produced in traditional foaming processes. Furthermore, the preparation of microcellular polymers uses 'environmentally friendly' gases, such as CO_2 and N_2, rather than ozone-damaging CFCs or HCFCs, which makes them a viable alternative to current foam processes.

The preparation of microcellular polymers in the early researches is a batch process based on the principle of supersaturation [1–3]. The process consists of two steps in general. In the first step, the polymer sample is saturated by a high-pressure, non-reacting gas, such like CO_2, N_2, etc., in a pressure vessel at room temperature. This step is time-consuming and always takes hours or days to get uniform gas concentration in the sample. In the second step, the saturated sample is removed from high-pressure condition to atmosphere and get into supersaturation state. Then, the sample is heated to the temperature above the glass transition temperature of the polymer to initialize a great

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0032-3861/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00343-3

number of cell nuclei simultaneously. After several seconds to let cell grow, the microcellular structure is vitrified by temperature quench. By this simple process, numbers of commodity and engineering plastics have been made into microcellular structure, the list includes polystyrene [11], polyethylene [12], polypropylene [12], polycarbonate [13], high impact polystyrene [14], poly (ethylene terephthalate) [15], polyvinyl chloride [16], etc. Meanwhile the mechanism of cell nucleation and cell growth has also been studied [11,14,17].

The main advancement of making microcellular polymers in the 1990s is the application of supercritical fluids (SCFs) not only in the batch process but also in the traditional continuous process such as extrusion and injection molding [18–20]. It has been found that by using SCFs as the foaming agent, time is saved in the saturation step so that this new technology can be used for industrial practice. SCFs are materials above their critical temperature and pressure conditions, which exhibit interesting behavior by combining the properties of conventional liquids and gases. Specifically, their liquid-like densities allow for solvent power of orders of magnitude higher than gases, while gas-like viscosities lead to high rates of diffusion [21]. The application of SCFs in the area of polymer processing includes polymerization process, polymer purification and fractionation, ultrafine powder formation and environmentally preferable solvents for solution coatings [22,23]. In making microcellular polymers, supercritical CO_2 is chosen as the foaming agent due to its easily attainable critical parameters ($T_c = 31.05°C$, $P_c = 7.286$ MPa) as well as nontoxic, nonflammable and commercially available in high purity. The first attempt using supercritical CO_2 in making microcellular polymers was made by Cha et al. [18]. They used the same supersaturation method mentioned above. The essential difference was to increase the temperature and pressure to the state above the critical point of CO_2 while saturating polymers. The results were significant. Foamed polymers with cell sizes of less than 1.0 μm were made. The successful preparation of supermicrocellular materials, as Cha called them, gave a potential way to make transparent foamed materials, while cell sizes would be reduced to less than 0.1 μm and in the range of wavelength of light. After that, Beckman et al. [24] put forward a different route which was called pressure quench. Their method was taking advantage of the plasticization effect of polymers by CO_2 swelling. When polymers were saturated by supercritical CO_2, the glass temperature could be depressed to the room temperature in the case of PMMA, and the same for PS, PVC and PC [25]. Thus they found that microcellular structure could be achieved simply after rapid depressurization and did not need to heat the sample to the temperature above the glass transition temperature of pure polymers. McCarthy et al. [26,27] also used this method to make microcellular polystyrene. Recently, they studied the effects of molecular weight, polydispersity and low molecular weight components on the microcellular structure and tried to establish a new cell nucleation mechanism, other than the mechanism based on the classical nucleation theory [11], to illustrate these phenomena [28].

While numerous aspects of microcellular processing have been studied over the last two decades for pure polymers, little work has been reported on polymer blends and composites. Suh et al. [1] used HIPS, a blend of polystyrene and rubber, in their pioneer work on making microcellular polymers. Then Campell et al. [14,29] has also investigated the microcellular processing of HIPS and patented a heterogeneous nucleation method. Park et al. has reported the microcellular structure of PE/iPP blend [30] and PVC/wood fiber composite [31]. Nevertheless, no systematic works have been reported on microcellular polymer blends. It is well known that polymer blending is a common and versatile way to develop new materials with a desirable combination of properties. Thus, it can be expected that better performance of microcellular polymers will be achieved by simply introducing another minor component into the polymer matrix. Among polymer blends, in situ composite containing a thermotropic liquid crystalline polymer (LCP) is one group of particularly attractive materials, owing to their specific rheological and mechanical performance. Therefore, in this paper, the work on the preparation of microcellular polystyrene/LCP blends is reported.

Although some new approaches have been used recently, such like sintered method [32] and gelation of CO_2 [33], to make microcellular materials, the work presented here still follows the method invented by Beckman [24] due to its versatility. Polystyrene is chosen due to a fully understanding of its behavior in the field of microcellular polymers study [11,26–28]. Thus, the effect of LCP in the blends can be clearly identified and studied. In immiscible polymer blends, a third compatibilizer is usually added to improve the compatibility and properties of the system. In this work, a third component is used in the blends to reveal the effect of compatibilizer on the microcellular structure and improve the poor interfacial adhesion between PS phase and LCP phase [34,35]. The compatibilizer is zinc neutralized lightly sulfonated polystyrene ionomer (ZnSPS). It is known that ionomers have unusual effect for the compatibilization in many immiscible polymer blends. Ionic groups, especially acid groups and metal ionic groups, in ionomers can cause several interactions with polar groups of polar polymers in blends. These possible interactions include dipole–dipole, ion–dipole, ion–ion and hydrogen bond. These interactions can serve as physical crosslinks at the interface, reduce interfacial tension and improve interfacial adhesion. Weiss et al. [36,37] has reported that ZnSPS is miscible with LCP (VA950) and Hara et al. [38–40] has reported that metal neutralized lightly sulfonated polystyrene (SPS) ionomers have good adhesion with their parent polymer. Therefore, ZnSPS is added to the blends as a compatibilizer. The effect of LCP ratio, ZnSPS content and miscibility between

two components on the microcellular structure is reported here.

2. Experimental

2.1. Materials

The polystyrene used was PS 666D ($M_w = 243,000$, measured by gel permeation chromatography), supplied by Yanshan Petrochemical Corporation, China. The LCP used was Vectra A950, a commercial, wholly aromatic copolyester of 73% hydroxybenzoate (HBA) and 27% hydroxynaphthanoate (HNA) from Hoechst-Celanese. Vectra A950, hereafter simply referred to as LCP, has a T_g of 100°C and a crystalline solid to nematic liquid transition (T_{KN}) of 280°C by differential scanning calorimetry (DSC). Lightly sulfonated polystyrene was prepared by the procedure described by Makowski et al. [41]. The sulfonation level was 3.3 mol%, calculated from the elemental analysis of sulfur. The zinc neutralized lightly sulfonated polystyrene ionomer, hereafter referred to as ZnSPS, was prepared by neutralizing solution of the SPS with a 20% molar excess of zinc acetate. The ZnSPS was then precipitated in a large excess of ethanol, filtered, washed several times with ethanol. The remaining organic solvent was removed by steam stripping in boiling water and followed by drying at 80°C for several days [38]. The CO_2 with a purity of 99.9%, was supplied by Beijing Analytical Gas Factory.

2.2. Blending and injection molding

All the material to be used were dried at 80°C under vacuum for 24 h before melt processing. The blending ratio of PS/LCP was 90/10, 80/20, 70/30 and 40/60 by weight. The proportion of ZnSPS, if used in blends, was 10% of LCP weight fraction in PS/LCP blends of all ratios, and 20, 30, 40, 50% of LCP weight fraction in the case of PS/LCP 80/20 blends in addition. Binary and ternary blends were prepared on a CS-194 Mini-Max extruder at 285°C. Each blend was extruded twice to get the better mixing effect. Then the plate samples of blends as well as pure PS and LCP were injection molded with the dimension of 1.54 mm thick and 15.4 mm wide at 285°C on a CS-183 Mini-Max injection-molding instrument.

2.3. Foam preparation

The foaming process followed the method described by Beckman et al. [24]. Plate samples of 1.54 mm thick were enclosed in a high-pressure vessel. The vessel was flushed with low-pressure CO_2 for about 3 min and preheated to 80°C. Then the pressure was increased to 25 MPa and maintained for 6 h to ensure equilibrium absorption of CO_2 by the samples [26]. After saturation, a rapid quench of pressure to atmosphere was adopted in about 20 s. The microcellular structure was allowed to a full growth at the experimental temperature and atmospheric pressure for 30 min before the vessel was slowly cooled to room temperature in about 2 h.

2.4. Foam characterization

The samples, either foamed or not, were fractured in liquid nitrogen, coated with an approximately 10 nm thick layer of gold on the fractured surface and observed with a Hitachi S-530 scanning electron microscope.

The cell structure parameters, such as cell diameters and cell densities, were characterized by using the method suggested by Kumar et al. [42]. The cell diameter (D) is the average of all the cells on the SEM photo, usually more than 100 cells. The cell density (N_f), which is the number of cells per cubic centimeter of the foam, is calculated as

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2}, \quad (1)$$

where n is the number of cells seen on the SEM photo, A the area of the micrograph (cm^2), and M is the magnification factor. In addition, the cell density (N_0) based on the pristine unfoamed sample is calculated as

$$V_f = \frac{\pi}{6} D^3 \times N_f, \quad (2)$$

$$N_0 = \frac{N_f}{1 - V_f}, \quad (3)$$

where V_f is the volume fraction occupied by the microvoids. Though some errors exist in this process of converting the flat properties to cubic ones, the accuracy is acceptable for a comparison of the microcellular structure of different blend ratio under the same foaming conditions.

3. Results and discussion

3.1. Morphology of microcellular blends

Fig. 1 shows the SEM micrographs of the fracture surfaces of microcellular PS/LCP blends and PS/ZnSPS/LCP blends. It should be pointed out that the samples are cut along the injection flowing direction other than the transverse direction. To give more details on the microcellular structure, SEM micrographs of higher magnification and different compositions are shown in Figs. 2–5, with one micrograph of microcellular pure polystyrene for reference shown in Fig. 6. From these figures, a two-phase system is clearly observed where the microfibrils and spheres, which believed to be LCP, are surrounded by the foamed material. The morphological difference between the microcellular PS/LCP blends and PS/ZnSPS/LCP blends is not remarkable. These two blends show same trends of variation in cell sizes and LCP morphology. It is found form Fig. 1 that cells have clear distribution of size from skin to core. Cell

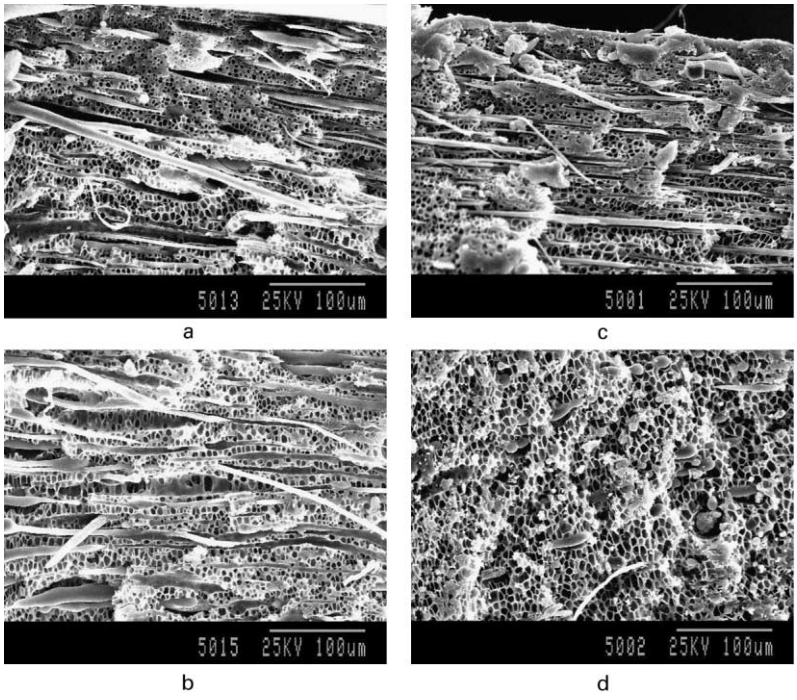

Fig. 1. SEM micrographs illustrating cell distribution from skin to core of microcellular blends foaming at 25 MPa, 80°C, and the effect of ZnSPS on the microcellular structure: (a) PS/LCP, 70/30, skin; (b) PS/LCP, 70/30, core; (c) PS/ZnSPS/LCP, 80/2/20, skin; (d) PS/ZnSPS/LCP, 80/2/20, core.

diameter increases from outer area to inner area in the skin region then turns to uniform in the core region. It is also found that a skin-core structure of LCP is obtained in these blends. In the skin region, LCP enriches in content and prefers to form microfibrils along the flowing direction. In the core region, LCP turns to poor in content and prefers to form spheres with respect to LCP composition. This is the common phenomenon in in situ composites. From the higher magnification photos, it is clearly seen that the sizes of the voids in the blends are in the same range of the microcellular pure polystyrene in qualitative comparison. Therefore, microcellular polymer blends can be prepared using the

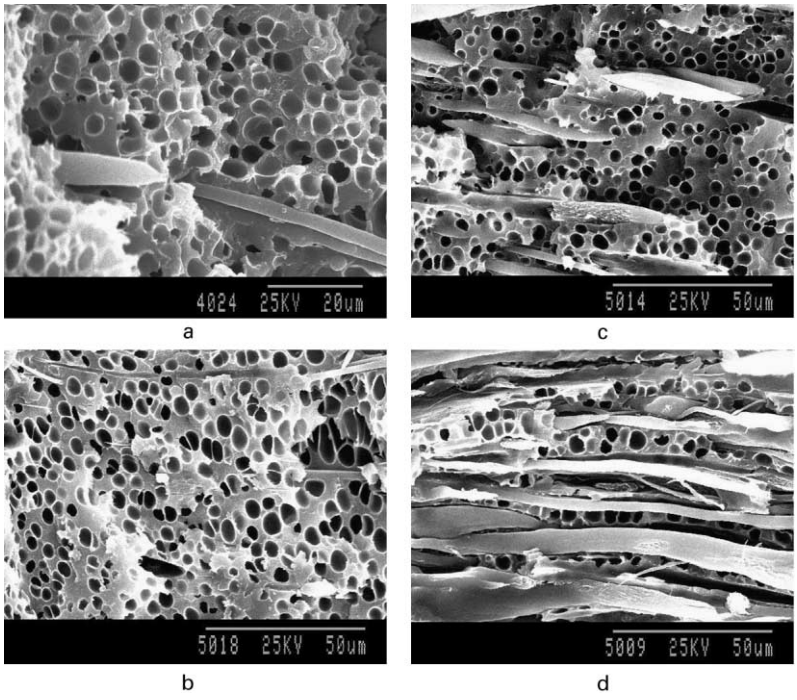

Fig. 2. SEM micrographs illustrating the skin region of microcellular PS/LCP blends foaming at 25 MPa, 80°C. The PS/LCP blend ratios are: (a) 90/10; (b) 80/20; (c) 70/30; (d) 40/60.

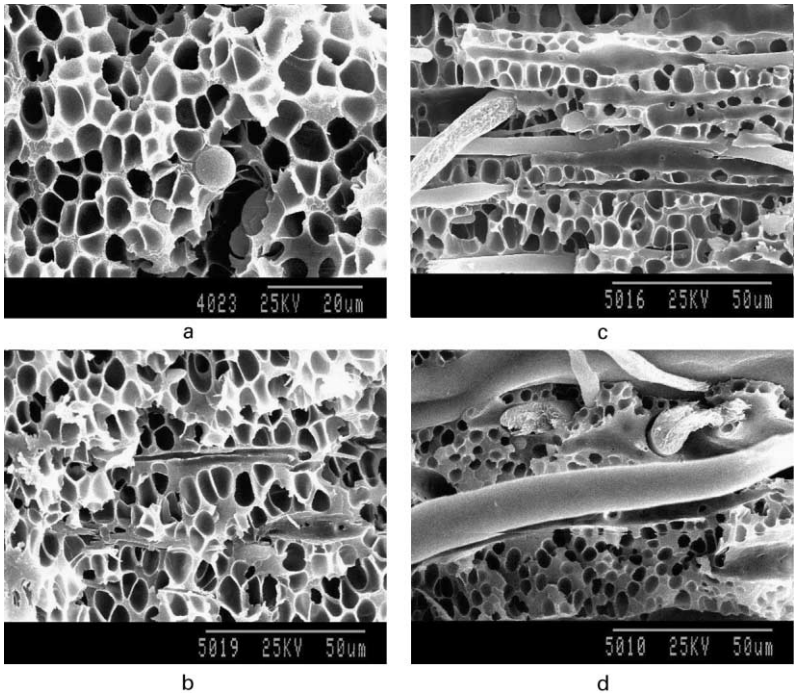

Fig. 3. SEM micrographs illustrating the core region of microcellular PS/LCP blends foaming at 25 MPa, 80°C. The PS/LCP blend ratios are: (a) 90/10; (b) 80/20; (c) 70/30; (d) 40/60.

same method and experiment conditions used for making microcellular pure polymers.

In addition, two interesting phenomena are observed in these microcellular blends. One is that foaming structure extensively exists in the polystyrene phase in all compositions even if LCP has higher content than PS. While the LCP phase is retaining its shape of microfibrils or spheres as in the unfoamed materials. To illustrate this phenomenon, absorption and desorption test of CO_2 in pure LCP and the blends is taken by following the method used by McCarthy

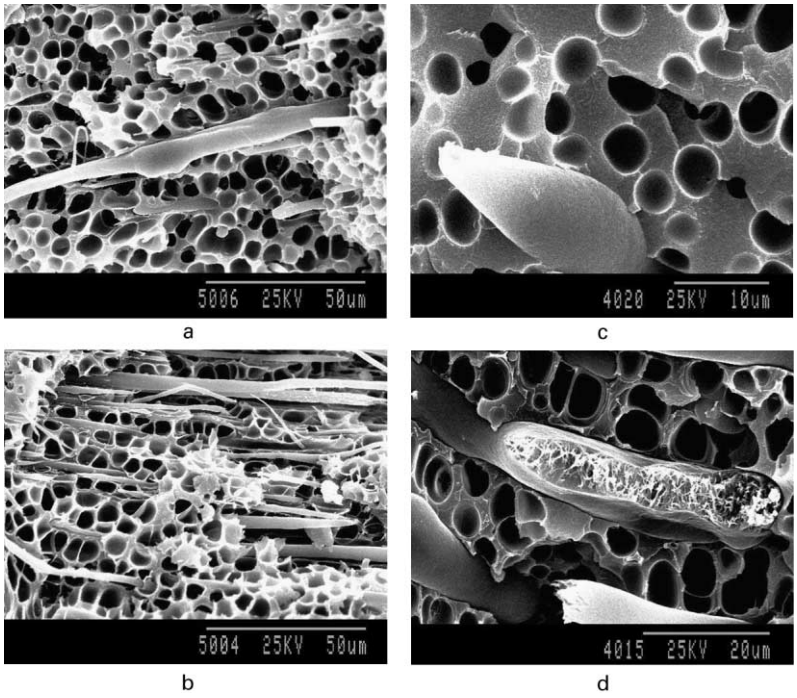

Fig. 4. SEM micrographs illustrating the skin region of microcellular PS/ZnSPS/LCP blends foaming at 25 MPa, 80°C. The PS/ZnSPS/LCP blend ratios are: (a) 90/1/10; (b) 80/2/20; (c) 70/3/30; (d) 40/6/60.

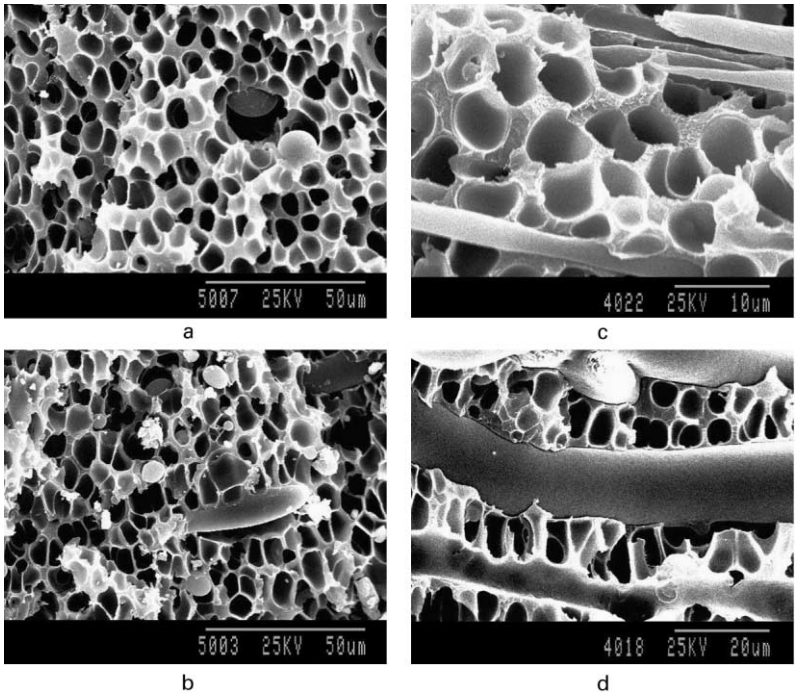

Fig. 5. SEM micrographs illustrating the core region of microcellular PS/ZnSPS/LCP blends foaming at 25 MPa, 80°C. The PS/ZnSPS/LCP blend ratios are: (a) 90/1/10; (b) 80/2/20; (c) 70/3/30; (d) 40/6/60.

et al. [26]. The results show that nearly no detectable amount of CO_2 is absorbed in pure LCP under the experimental conditions, 25 MPa, 80°C and 6 h. The results of PS, PS/LCP blends (80/20) and PS/ZnSPS/LCP blends (80/2/20) are shown in Fig. 7. From Fig. 7, it is found that an amount of CO_2 nearly proportional to the blending fraction of PS is absorbed in the blends under the same conditions. As reported in the literatures [24,26], two basic factors should be met in the pressure quench process for preparing microcellular polymers. One is the absorption of sufficient amount of CO_2 to let cell nucleation and growth while depressurization. The other is the depression of T_g of the sample below the experiment temperature upon CO_2 absorption. These two factors qualitatively represent the thermodynamics and kinetics demands for microcellular structure formation. The classical nucleation theory is used to describe it more clearly. This theory is suggested by Colton et al. [16–18] to model the rate of nucleation of cells in microcellular foams. The nucleation rate N is given by

$$N_i = f_i C_i \exp(-\Delta G_i^*/kT), \tag{4}$$

where the subscript i denotes whether the nucleation is homogeneous ($i = 0$) or heterogeneous ($i = 1$), f_i is a frequency factor of gas molecules merging in the nucleus, C_0 is the concentration of gas molecules in the polymer, C_1 is the concentration of heterogeneous nucleation sites, ΔG_i^* is the Gibbs free energy associated with the formation of a

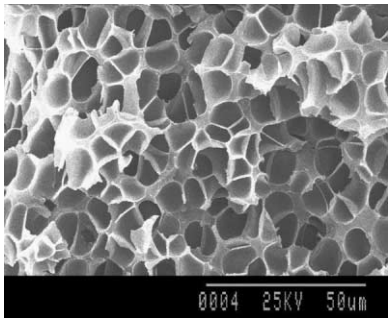

Fig. 6. SEM micrograph showing the microcellular PS foaming at 25 MPa, 80°C.

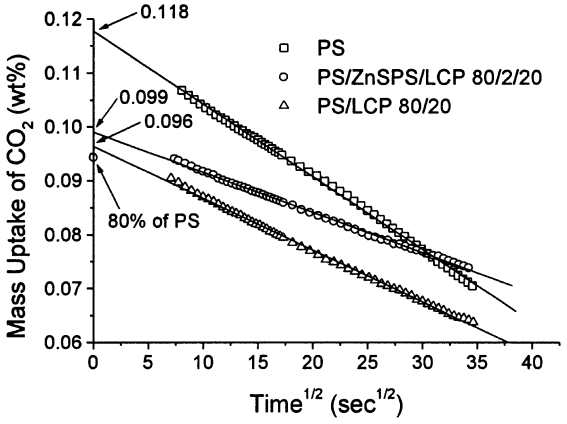

Fig. 7. Mass uptake of CO_2 by PS, PS/LCP and PS/ZnSPS/LCP.

nucleus. If the nucleation is homogeneous

$$\Delta G_0^* = \frac{16\pi\gamma^3}{3\Delta P^2}, \tag{5}$$

where γ is the surface energy at the cell–polymer interface and ΔP is the pressure exerted by the supercritical CO_2 on the cell walls. In the case of heterogeneous nucleation

$$\Delta G_1^* = \frac{16\pi\gamma^3}{3\Delta P^2} S(\theta), \tag{6}$$

$$S(\theta) = (1/4)(2 + \cos\theta)(1 - \cos\theta)^2, \tag{7}$$

where θ is the contact angle of the polymer/cell/gas interface.

From formula (5) and (6), little absorption of CO_2 in the LCP phase will result in approximate zero ΔP while pressure quenching. Then the energy barrier for forming a nucleus in the material will be quite large. This high-energy barrier accompanying with nearly zero C_0 means that it is impossible to initiate nuclei in the LCP phase. Moreover, it has been observed that the depression of T_g by CO_2 is nearly linear proportional to the amount of absorption [25]. Little absorption means the LCP phase will retain in glass state under the experiment temperature (80°C). So cell growth is impossible as well. Therefore, the LCP microfibrils and spheres retain their morphology as in the unfoamed blends and the polystyrene phase has the microcellular structure as in the case of microcellular pure polystyrene.

The other interesting phenomenon found in the microcellular blends is the shape of microvoids. In the skin region of PS/LCP blends, the cells retain spherical shape; while in the core region of them, the cells have a polygonal structure. In the case of PS/ZnSPS/LCP blends, the cells have the polygonal structure either in the core region or in the skin region. This phenomenon will be discussed in the next section.

3.2. Cell sizes in microcellular blends

It has been shown that cell size increases from the outer area to the inner area in the skin region of microcellular blends. Moreover, cells in the skin region of PS/LCP blends have a spherical shape, while polygonal shape in the core region. Statistics on cell diameter is taken to reveal the nature of these phenomena. The average cell sizes in the skin and core region are shown in Fig. 8 for blends of different composition, with error bars indicating the cell size distribution. A significant decrease of cell diameter in low LCP composition is observed, compared with microcellular pure polystyrene. Upon higher LCP composition the change is much less and level off. Cells in the skin region have smaller cell diameter than those in the core region. Concerning the difference between cell sizes of PS/LCP blends and PS/ZnSPS/LCP blends, it is found that the former has smaller cell diameters for the same composition either in the skin region or in the core region, and has more quickly reduction of cell sizes with increasing LCP content.

Usually, it is considered that cell size is related to two factors. One of them is the competition between the gas diffusing out of the skin and diffusing into nucleated cells. Park et al. [43] has shown that the real expansion ratio of the microcellular polymers is far less of the ideal expansion ratio. The ideal volume expansion ratio (R_I) can be estimated as

$$R_I = \frac{\text{Volumn}_{\text{polymer}} + \text{Volumn}_{\text{gas}}}{\text{Volumn}_{\text{polymer}}} = 1 + \frac{m_{CO_2}}{m_{\text{polymer}}} \frac{\nu_{CO_2}}{\nu_{\text{polymer}}}, \tag{8}$$

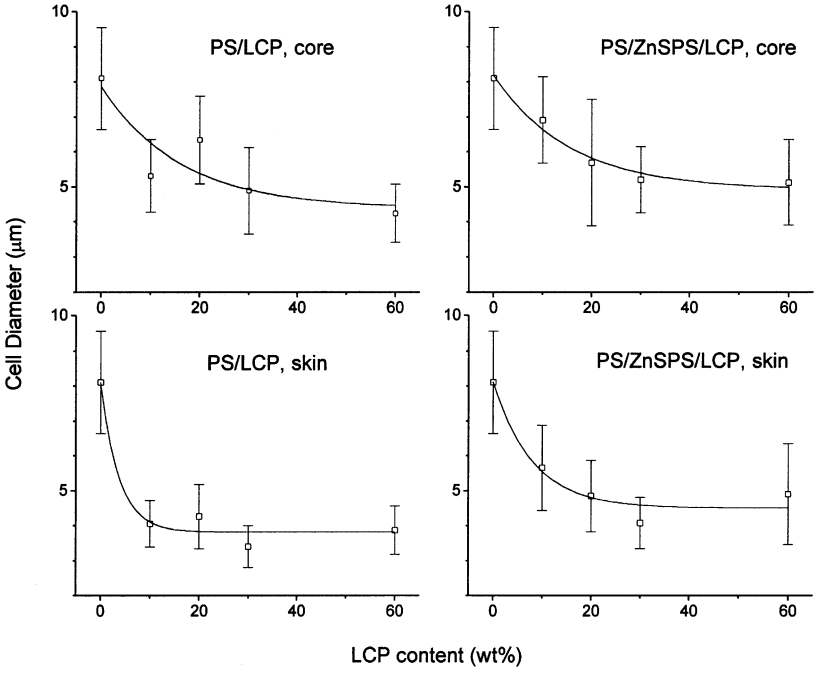

Fig. 8. Effects of LCP content and ZnSPS on the average cell diameter of microcellular PS/LCP blends foaming at 25 MPa, 80°C.

where $m_{CO_2}/m_{polymer}$ is the mass uptake of CO_2 in the polymer, ν is the specific volume. Using this formula, Park estimated the ideal expansion ratio of HDPE, which absorbed 7 wt% CO_2 at 121°C. The R_I calculated is about 55.4 and the real expansion ratio is only 36% of that at the highest volume expansion ratio achieved. This implies that most of absorbed CO_2 is not efficiently used for cell growth. Most of the gas has escaped out to the environment through the skin, or the polymer matrix is solidified too quickly before all the dissolved gas diffused into the cells to fully expand the foams. The other factor influencing the cell size is the cell growth process. Once the cells have nucleated, they continue to grow as available gas diffuses into cells, provided that little resistance is encountered. The cell growth rate is limited by the diffusion rate and the stiffness of the polymer matrix. In general, the cell growth process is controlled primarily by the time allowed for the cell growth, the temperature of the system, the state of supersaturation, the hydrostatic pressure or stress applied to the polymer matrix, and the viscoelastic properties of the polymer matrix [44]. In the system investigated, the first four can be neglected, due to the same experiment condition for all samples, so the viscoelasticity of the polymer should be the major factor affecting the cell growth. As mentioned above, a combining effect of these two factors, i.e. the competition between the gas diffusing out of the skin and diffusing into nucleated cells and the viscoelasticity of the polymer matrix, is supposed to illustrate the phenomena observed in microcellular blends.

Firstly, for showing the effect of viscoelasticity of the blends, the dynamic mechanical analysis (DMA) test is taken with the heating rate of 5°C/min using a Perkin–Elemer DMA-7e. In Fig. 9, the E' at 80°C is drawn vs. LCP composition. It is shown that the stiffness of polymer matrix increases with increasing LCP addition and the PS/ZnSPS/LCP blends show more increases than PS/LCP blends at the same LCP composition. Therefore, upon LCP addition, the stiffness of polymer matrix increased so that cell diameter in the blends is smaller than that of pure microcellular polystyrene. In addition, the effect of the viscoelasticity on the cell growth should reach a critical value as the LCP content increases, so the cell size increase is level off as LCP ratio increases.

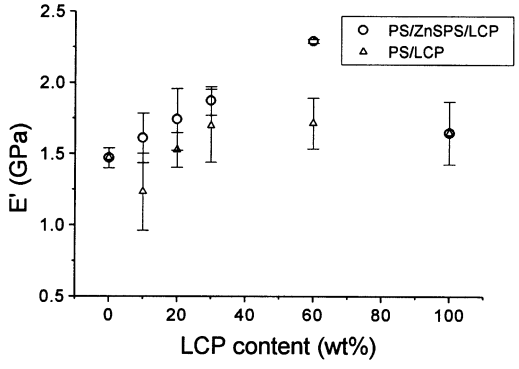

Fig. 9. Effect of LCP content and ZnSPS on the viscoelasticity of blends at 80°C.

Secondly, it is believed that the skin-core structure of the unfoamed blends and the gas diffusing out of the skin are the main causes responsible for cell sizes increasing from surface to core. Fig. 10 shows the SEM micrographs of the fracture surfaces of the unfoamed PS/LCP blends and the unfoamed PS/ZnSPS/LCP blends. The samples are also cut along the injection flowing direction so the microfibrils formed by LCP about 4–8 μm in diameter along the flowing direction are clearly seen. In this selected 90/10 ratio and others not presented here, a typical skin-core structure is observed, where LCP microfibrils are enriched in the skin region. This is the common phenomenon of polymer/LCP blends, especially in the processes involving higher shear field like injection molding and extrusion. After the foaming of the polystyrene phase, this skin-core structure still retains as shown in Fig. 2. From the DMA results, it is clear that LCP is the reason for the increasing stiffness of polymer matrix. However, the DMA results reflect the viscoelasticity information of the entire sample. Therefore, it is supposed that the enrichment of LCP and the formation of microfibrils in the skin will result in more resistance to cell growth. On the other hand, the gas in the skin region escapes out of the skin easier than that in the core area. This is usually used to explain the formation of unfoamed skin of microcellular polymers [45,46]. And it is also responsible for the smaller cell size in the skin region.

Thirdly, it is supposed that the poor interfacial adhesion between PS and LCP is responsible for the much smaller cell sizes found in the microcellular PS/LCP blends than those in the PS/ZnSPS/LCP blends. It is known that ionomers have an unusual effect for the compatibilization in many immiscible polymer blends. In the case of lightly SPS ionomers, Weiss et al. [36] has reported that ZnSPS was miscible with LCP (Vectra A950) based on the experimental facts from DSC and DMA. In the subsequent study [37], they found that the sulfonation level and the choice of the cation used to neutralize the ionomer influence the miscibility. They attributed this miscibility to a repulsive interaction within the ionomer, although the origin of miscibility was not yet clear. On the other hand, it is known that ionomers are immiscible with their precursor polymers due to the aggregation of the ionic groups [47]. But a much better adhesion is expected at the interface because they share the same type of segments. Thus in such systems, the blending should not result in weakening of the mechanical properties of the homopolymers as it may in other two-phase systems. Hara et al. [38–40] conducted a series of investigations on polystyrene-sulfonated polystyrene blends and found good adhesion between the ionic cross-linked particles and the matrix. Because ZnSPS is miscible with LCP and have good interfacial adhesion with polystyrene, so it would be a good compatibilizer in PS/LCP blends. Although DMA test cannot distinguish the T_g changes in the PS/LCP blends due to small difference

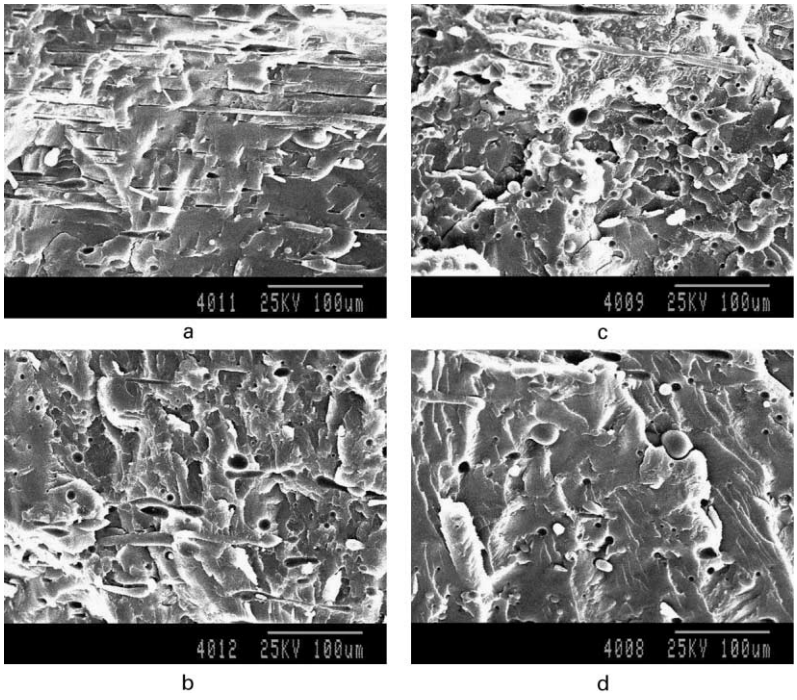

Fig. 10. SEM micrographs illustrating the skin-core structure of PS/LCP (90/10) blends and the effect of ZnSPS on miscibility: (a) PS/LCP, skin; (b) PS/LCP, core; (c) PS/ZnSPS/LCP, skin; (d) PS/ZnSPS/LCP, core.

between them, there are still many evidences found in the experiment that the addition of ZnSPS can improve the miscibility of the blends. For PS/LCP blends, Fig. 10 clearly shows smooth surfaces of the microfibrils in the skin region and those of remaining holes after pulling away of LCP spheres in the core region. These indicate a rather poor interfacial adhesion between the LCP and PS. Upon ZnSPS addition, clear signs of improved interfacial adhesion between the LCP spheres and microfibrils with the matrix are observed. Although a skin-core structure still exists, it is found that less microfibrils formed in the blends. These phenomena are believed concerning with the improvement of miscibility. Moreover, from DMA results, Fig. 9 shows the increase in E' value of PS/ZnSPS/LCP blends. This also indicates the improvement of interfacial adhesion. Furthermore, this improvement is also observed in the higher magnification SEM photo of microcellular structure shown in Figs. 2–5. For instance, Fig. 3d shows that the LCP microfibril is pulled out of the matrix and clear gap can be observed, while Fig. 5d, the counterpart with ZnSPS, shows that the LCP microfibril connects well with the matrix. Since CO_2 has much larger diffusion coefficient in air than in polymer. It is believed that more CO_2 has diffused out of the system in the cell growth process through the gap at the interface between polystyrene and LCP. This is also confirmed by the desorption test. In Fig. 7, the slope of the desorption curve is proportional to the diffusion coefficient. It is clearly seen that CO_2 diffuses out of PS/ZnSPS/LCP more slowly than out of PS/LCP. So less amount of CO_2 is available for cell growth in PS/LCP blends than in PS/ZnSPS/LCP blends. These would be the reasons for smaller cell size in PS/LCP blends than its counterpart in PS/ZnSPS/LCP blends. In addition, the spherical cells are usually considered as not fully-grown whereas the fully-grown cells usually have polygonal shape. So it is not surprising to find spherical cells in the skin of PS/LCP blends due to less CO_2 diffusing into the cells. Park et al. [44,45] have reported similar phenomenon in the PVC/wood-fiber composites where low volume expansion found in the composites using fibers without surface treatment.

Fourthly, to find more evidences, a series samples with different ZnSPS content and constant LCP ratio (PS/LCP 80/20) are prepared under the same experiment conditions. The statistic results on cell diameters are plotted vs. ZnSPS content in Fig. 11. It should be pointed out that cells taken from the skin area, about 200 μm depth, are different from those results reported before (about 300 μm depth). So the cell diameters are smaller than the previous results). From Fig. 11, there is a distinctly increasing trend of cell sizes with increasing ZnSPS content. It is believed that this trend is also resulted from the improvement of the interfacial adhesion.

Finally, the phenomenon found in Fig. 8 that cell diameter of PS/ZnSPS/LCP decreasing with increasing LCP content more slowly than those of PS/LCP can be attributed to the combining effects of the improvement of interfacial adhesion by ZnSPS and the enhancement of stiffness by LCP. It has been discussed that the enhancement of stiffness results in cell sizes decreasing while the improvement of interfacial adhesion results in cell sizes

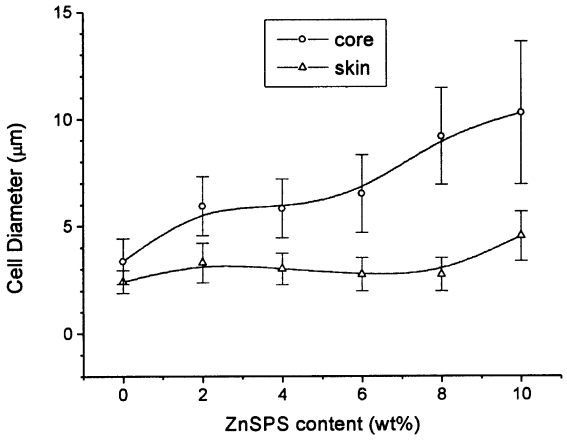

Fig. 11. Effects of ZnSPS content on the average cell diameter of microcellular PS/ZnSPS/LCP blends (PS/LCP 80/20) foaming at 25 MPa, 80°C.

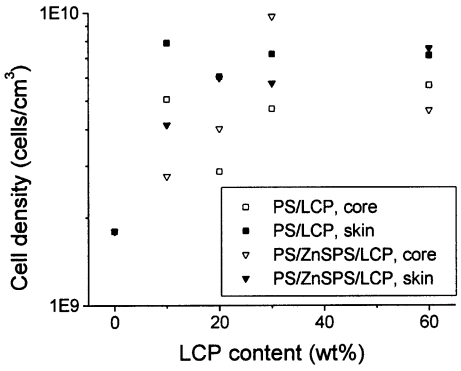

Fig. 12. Effects of LCP content and ZnSPS on the cell densities of microcellular PS/LCP blends foaming at 25 MPa, 80°C.

increasing. With higher LCP content, the enhancement of stiffness has the dominant effect on cell sizes that covers the effect of improvement of interfacial adhesion. So the curves of the cell sizes vs. LCP content level off at higher LCP content end. While at lower LCP content end, the effect of improvement of interfacial adhesion on cell sizes cannot be covered. Therefore, it is found that the reduction of cell sizes at lower LCP content is smaller than that at higher LCP content in the case of PS/ZnSPS/LCP. And the curve of PS/ZnSPS/LCP shows more slowly reduction rate than those of PS/LCP.

3.3. Cell densities in microcellular blends

In the study of the cell nucleation mechanism, cell densities are usually regarded as a representative parameter for cell nucleation in the foaming process. In the present study, statistics of cell densities is conducted to reveal the cell nucleation mechanism in this pressure quench process. The experimental phenomenon that no microcellular structure exists in LCP phase has been reported. Another fact is that the microcellular blends still retain the skin-core structure of LCP, which responds that LCP content is enriched in skin region. Based on these facts, an approximate method should be used to calculate the cell densities in polystyrene phase. The method involves subtracting the measured LCP occupied area from the total area in SEM micrographs, i.e. A in formula (1). Thus, the resulted cell densities are supposed to be the cell densities in polystyrene phase and can be compared with that of microcellular pure polystyrene directly. The corresponding cell densities based on the unfoamed materials are shown in Fig. 12.

From Fig. 12, it is found that cell densities of different compositions are at the same order of magnitude with microcellular pure polystyrene's produced under same conditions and have only a slightly increase in absolute value, about 2–5 times. From classical nucleation theory, formula (4)–(7), the parameters, i.e. f_i, ΔP, and T, relating to the material property and the experimental conditions can be thought as the same to all the blends investigated. Therefore, the only two variables in the system are C_i and θ. It has been reported in this work that the nucleation occurs only in the polystyrene phase and CO_2 concentration in the polystyrene phase has no distinct change comparing with the pure polystyrene. As reported in the literatures [11,26], the nucleation is believed to be homogeneous in microcellular polystyrene. So obviously, the nucleation in the microcellular blends is not simply a homogenous one. The increased cell density in the blends seems resulted from an additional heterogeneous nucleation by LCP. In addition, smaller γ and θ are expected in the PS/ZnSPS/LCP blends. That would result in a low energy barrier in cell nucleation process so that more cell densities would be expected. However, this increase of cell densities is much small and believed to be covered by the errors introduced when the statistics is conducted. Furthermore, Colton [11] has pointed out that one of the main factors in the heterogeneous nucleation is the concentration of heterogeneous nucleation sites, which is not proportional to the secondary phase added. The nucleation sites will be the same after reaching a critical amount of secondary phase and then no increase of cell densities will be observed. This is also the case in the system investigated where cell densities are not significantly influenced by the LCP ratio. That suggests the LCP content is far beyond the critical amount. Nevertheless, in those works concerning the heterogeneous nucleation in the microcellular polymers, such like HIPS where rubber particles act as nucleation sites [14,29], PET and CPET where the polyolefin particles and domain of PET crystals act as nucleation sites [15], PE/iPP blends where the minor component acts as nucleation sites [30], a typical morphology of cells nucleated and grown around small particles can be clearly observed in the SEM micrograph. This typical structure does not exist in the microcellular blends studied here. Cells nucleated and grown around LCP spheres and microfibrils cannot be observed in any blends of different compositions. Thus, there are still lacks of experimental evidences to study the nature of cell nucleation in the system studied and further experiments should be designed to investigate the mechanism of cell nucleation in the microcellular polymer blends.

4. Conclusions

The microcellular PS/LCP blends with cell diameter less than 7 μm are successfully prepared by using supercritical CO_2 pressure quench process, under the same experimental conditions, 25 MPa, 80°C and 6 h of saturation, as those for making microcellular polystyrene. The addition of LCP has several effects on the foam structure of these microcellular blends. Firstly, it is found that the microvoids only exist in the polystyrene phase of the blends, where in the LCP phase, the microfibrils and spheres retain their original morphology and a skin-core structure exist as in the unfoamed PS/LCP blends. The fact that no identified amount of CO_2 can be absorbed by LCP under the experimental condition is responsible for this phenomenon. Secondly, the addition of LCP increases the viscoelasticity of the blends and restricts the growth of the microvoids, which causes the cell diameter in microcellular blends (<7 μm) smaller than that in the microcellular polystyrene (≈ 8 μm). Thirdly, it is found that a significant decrease of cell diameter in low LCP composition, then the change is much less and levels off in higher LCP composition. Fourthly, the effect of the skin-core structure of the PS/LCP blends on the viscoelasticity of the matrix, accompanying with the effect of competition between CO_2 diffusing out of the skin and diffusing in the nucleated cells, makes the microcellular blends a distinct increase of cell size from skin to core. Fifthly, the cell density in the microcellular blends is greater than that in the microcellular polystyrene. This should be resulted from an additional heterogeneous nucleation of LCP phase, although more experimental evidences are required. At last, the addition of compatibilizer, ZnSPS, improves the interfacial adhesion between PS and LCP. The improvement of the interfacial adhesion decreases the amount of CO_2 escaping from the gaps between PS and LCP, which results in larger cell sizes found in microcellular PS/ZnSPS/LCP blends.

Acknowledgements

This work was supported by the National Natural Science Foundation of China, 59873026.

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