

Structure and Properties of PMP Foams Doped with Cu Nanopowders

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ABSTRACT: Poly-4-methyl-1-pentene (PMP) foams doped with Cu nanopowders have been prepared by thermally induced phase separation. Ultrasonic dispersal was exploited to increase dispersion uniformity of Cu nanopowders in the foam skeleton. With increase in the concentration of Cu nanopowders, the structure of the doped PMP foams becomes finer and the size of cells, smaller. The modulus data of the doped foams described by a scaling constant larger

than two significantly overestimate the predicted value. These indicate two roles of Cu nanopowders in PMP foams: fortifiers of foam structure and nuclei in polymer crystallization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5627–5632, 2006

Key words: poly-4-methyl-1-pentene; foams; Cu nanopowders

INTRODUCTION

Low-density open-cell polymer foams have been the subject of intense research in the past 20 years. Many applications of the foam can be found in the inertial confinement fusion (ICF) experiments.^{1–10} Poly-4-methyl-1-pentene (PMP), which contains only C, H atoms and poses minimum solid density (0.8 g/cm^3), is an ideal material for producing the foam. The PMP foams with a density of $10\text{--}100 \text{ mg/cm}^3$ and cell diameters of $4\text{--}30 \text{ }\mu\text{m}$ can be prepared by thermally induced phase separation (TIPS) technique, which is explained in detail elsewhere.¹ To meet the demand of diagnostic ICF experiment, some compounds, such as SiO_2 , TiCl_4 , Cr_2O_3 , etc., have been added into the PMP foam.^{11–13} It is important for the ICF experiments to use the foams with a uniform microstructure and well-dispersed dopants. However, there are still some problems in the doped foams. For example, dopants are not uniform and some unnecessary elements like oxygen and chlorine are introduced into the foams.

In this study, PMP foams doped with Cu nanopowders have been prepared by the TIPS technique. Ultrasonic dispersal was exploited to increase the uniformity of Cu nanopowders dispersed in foam skeleton. When compared with the refs. 11–13, only one expected dopant element is introduced into the foams. In practice, two or more elements can be doped into the foam according to the demand. The structure,

dopant uniformity, and mechanical properties of the doped foam were investigated.

EXPERIMENTAL

Poly-4-methyl-1-pentene (PMP) beads (high molecular weight, melt index 8) were obtained from Aldrich Chemical, and naphthalene and durene from Acros Organics. All reagents were used directly without further process. Copper nanopowders, with the average diameter of about 60 nm (measured by Mastersizer 2000, Malvern Instruments), was produced by the flow-levitation method.¹⁴

A sample of the Cu nanopowders-doped PMP foam was prepared as follows. PMP, nanometer copper powder, naphthalene, and durene were mixed together. The mass ratio of naphthalene and durene is 60 : 40. The content of PMP is dependant on the desired density of the foam. The mixture was heated to 160°C under reflux, until a homogeneous solution was obtained. The nanometer copper powders, in this solution, were ultrasonically dispersed for 2 h at 85°C in an ultrasonic bath. Then the solution was heated again to 160°C , and poured into a cylindrical aluminum mold with a diameter of 10 mm and a length of 50 mm. The mold was sealed in a weighing bottle and unidirectionally cooled to room temperature at a rate of about $1^\circ\text{C}/\text{min}$. The samples were machined into cylinders with a height of 10 mm and a diameter of 10 mm for mechanical tests and discs with a height of 1 mm and a diameter of 10 mm for measuring the density and the microstructure. After machining, the pieces were placed in vacuum ($<-0.08 \text{ MPa}$, 35°C) to remove the naphthalene and durene via sublimation.

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The density of the foam was calculated by dividing the mass of the disc with its volume. The mass was measured by a Sartorius analytical balance (LA230S). The volume was calculated from the dimensional measurement using TM-50 microscopy (Union Optical, Japan). The morphology of the foam was observed using a scanning electron microscopy (SEM, 1010B, Beijing Scientific Instruments). The dispersion of Cu powder in the doped foams was measured by Voyager II X-ray quantitative microanalysis system (Noran instruments). The Cu atom's percent content (P_{pra}) was calculated from mass percent content (w_{Cu}) determined by ICP according to eq. (1).

$$P_{\text{pra}} = \frac{w_{\text{Cu}}/64}{w_{\text{Cu}}/64 + 18 \cdot (1 - w_{\text{Cu}})/84} \times 100\% \quad (1)$$

All mechanical tests were conducted under ambient laboratory conditions on specimens with the foam density ranging from 0.04 to 0.09 g/cm³, Cu atom content from 0.5%–3.5%. Mechanical properties in compression were evaluated using a conventional Instron mechanical test frame. Tests were conducted in displacement control at a constant initial strain rate of 1.7×10^{-4} s. Modulus was calculated as the slope of the linear portion of the loading curves.

RESULTS AND DISCUSSION

Dopant uniformity

SEM photos of the doped foams with density 50 mg/cm³, Cu atom percent content 3% are shown in Figure 1,

and corresponding Cu powder dispersion pictures are illustrated in Figure 2. From Figure 1(a, b), no apparent influence of ultrasonic disperse on the structure of the doped foams can be observed. The same open interconnected morphology with a cell diameter less than 20 μm can be found in the foams prepared with or without ultrasonic dispersion, but it is seen that obvious difference exist in Figure 2(a, b). Ultrasonic dispersal improves the dispersion uniformity of Cu powder. But, a little aggregation of Cu nanoparticles occurred during the stages of the solution temperature rising from 85 to 160°C and following cooling. Therefore, nonuniform dispersion still exists in ultrasonic dispersal foam to some extent.

Morphology

SEM photos of doped PMP foams with Cu atom percent content 3% and different density are illustrated in Figure 3. According to eq. (1), when the Cu atom content in the foam is up to 3%, its PMP mass content is about 45%. So, the foamed polymer density (ρ_p) of the foam with density 30 mg/cm³ is only about 13 mg/cm³. Because of minor skeleton material, PMP, its morphology is quite weakly connected.

SEM photos of doped PMP foams with density 50 mg/cm³ and different Cu content are illustrated in Figure 4. Production of PMP foam involves formation of a gel-like low-density foam precursor and crystallization of the polymer phase.¹ The latter is necessary for the gel to have a sufficiently rigid structure. Nucleation is the first stage in the crystallization of polymer. Dur-

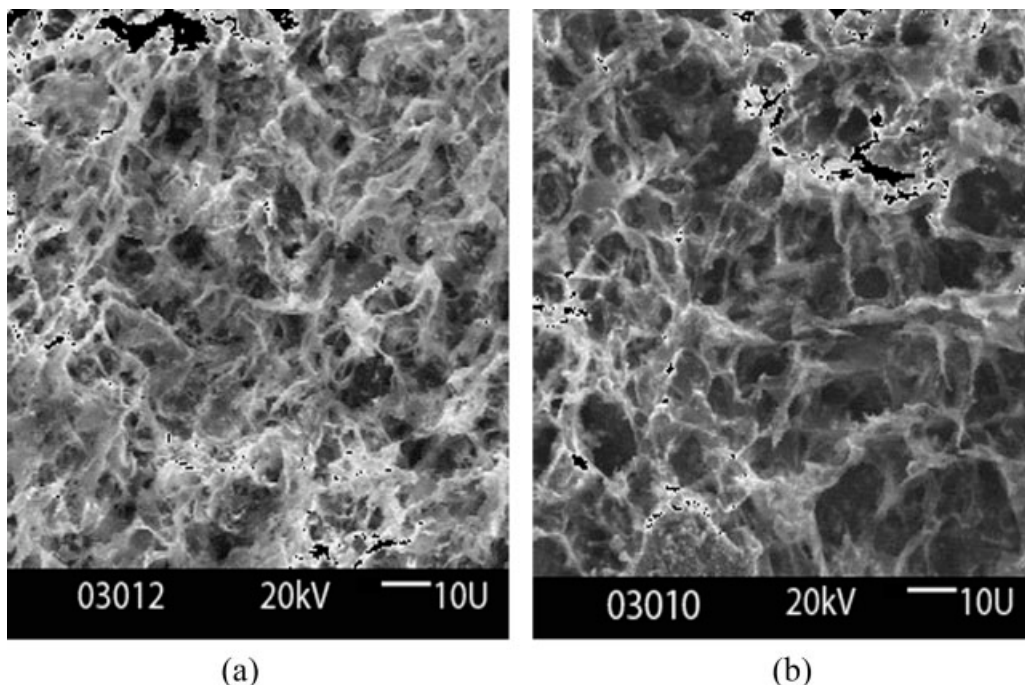


Figure 1 SEM photos of the doped foams with density 50 mg/cm³, Cu atom content 3% ($\times 700$): (a) ultrasonic dispersal, and (b) undispersal.

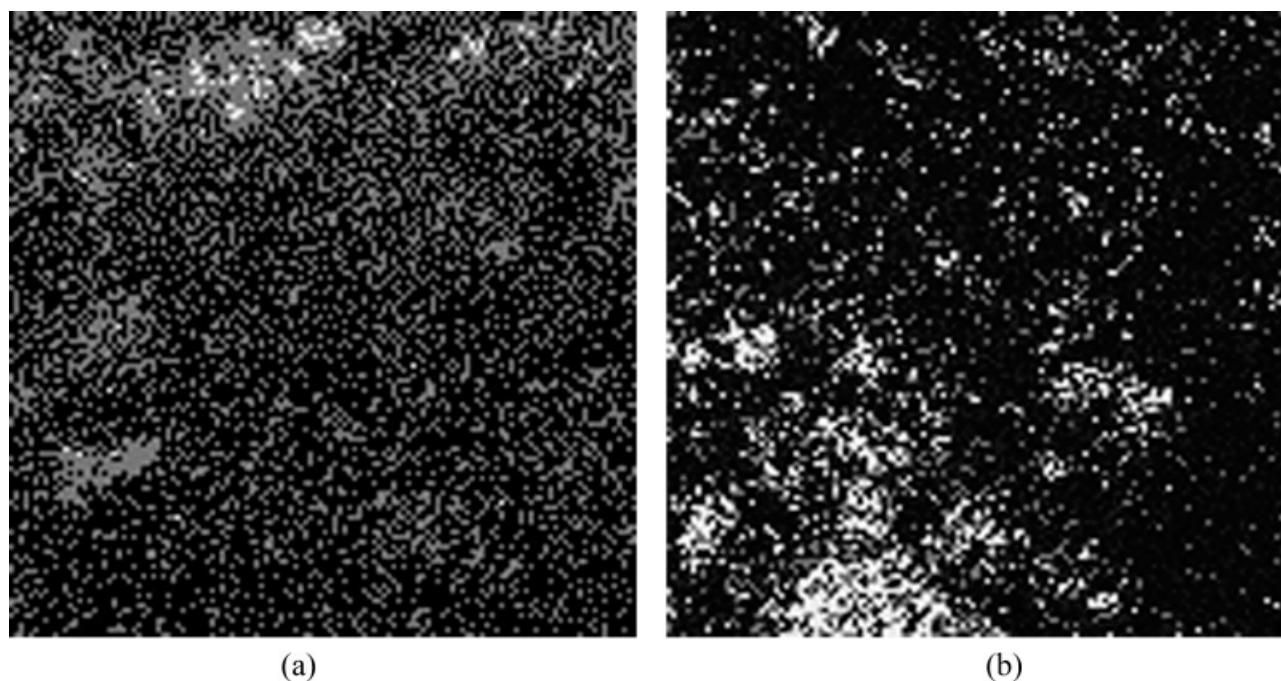


Figure 2 Cu powder dispersion pictures of the doped foams corresponding with Figure 1: (a) ultrasonic disposal, and (b) undisposal.

ing nucleation, molecules overcome an energy barrier and gather to form embryos of the new phase. If the size of the embryos exceeds a critical size, further increase of embryo size leads to a reduction in free energy. Thus, stable nuclei are generated. Cu nanopowders doped in the polymer solution can act as “nuclei.” With the increasing of Cu content, the growth of nuclei can occur

at more positions. Under the same crystallization condition (such as polymer composition, crystallization temperature, cooling rate, and so on), finer foam structure and higher cell density can be obtained with higher Cu atom content. From the Figure 4, we can see that the cells of the doped foam become smaller with increasing Cu nanopowder content.

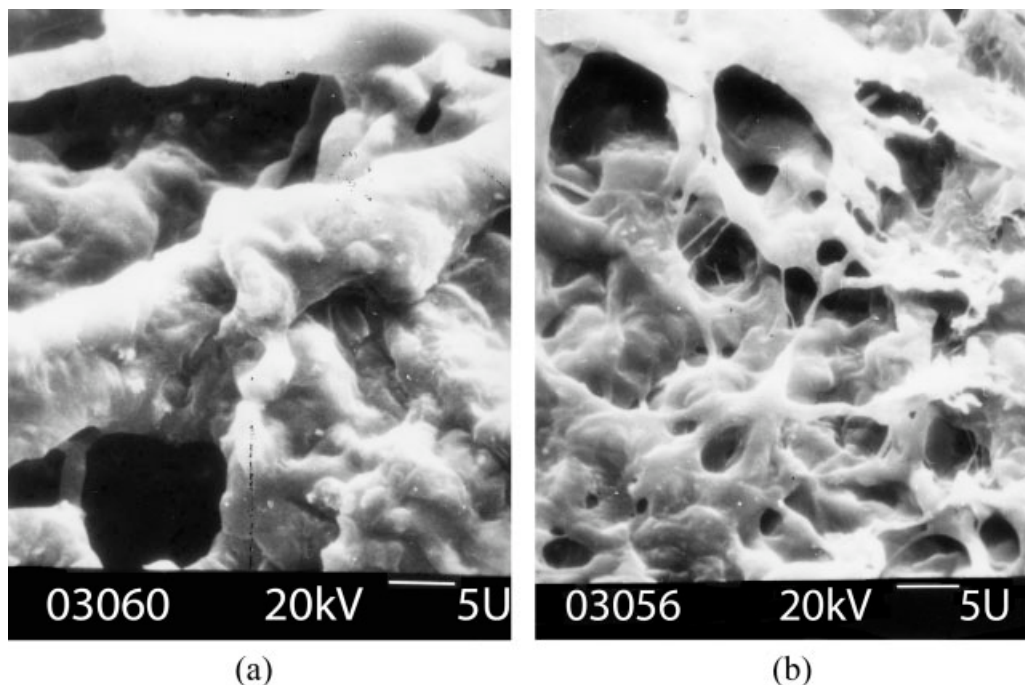


Figure 3 SEM photos of doped PMP foams with Cu content 2.2% and different density ($\times 1400$): (a) 30 mg/cm^3 , and (b) 50 mg/cm^3 .

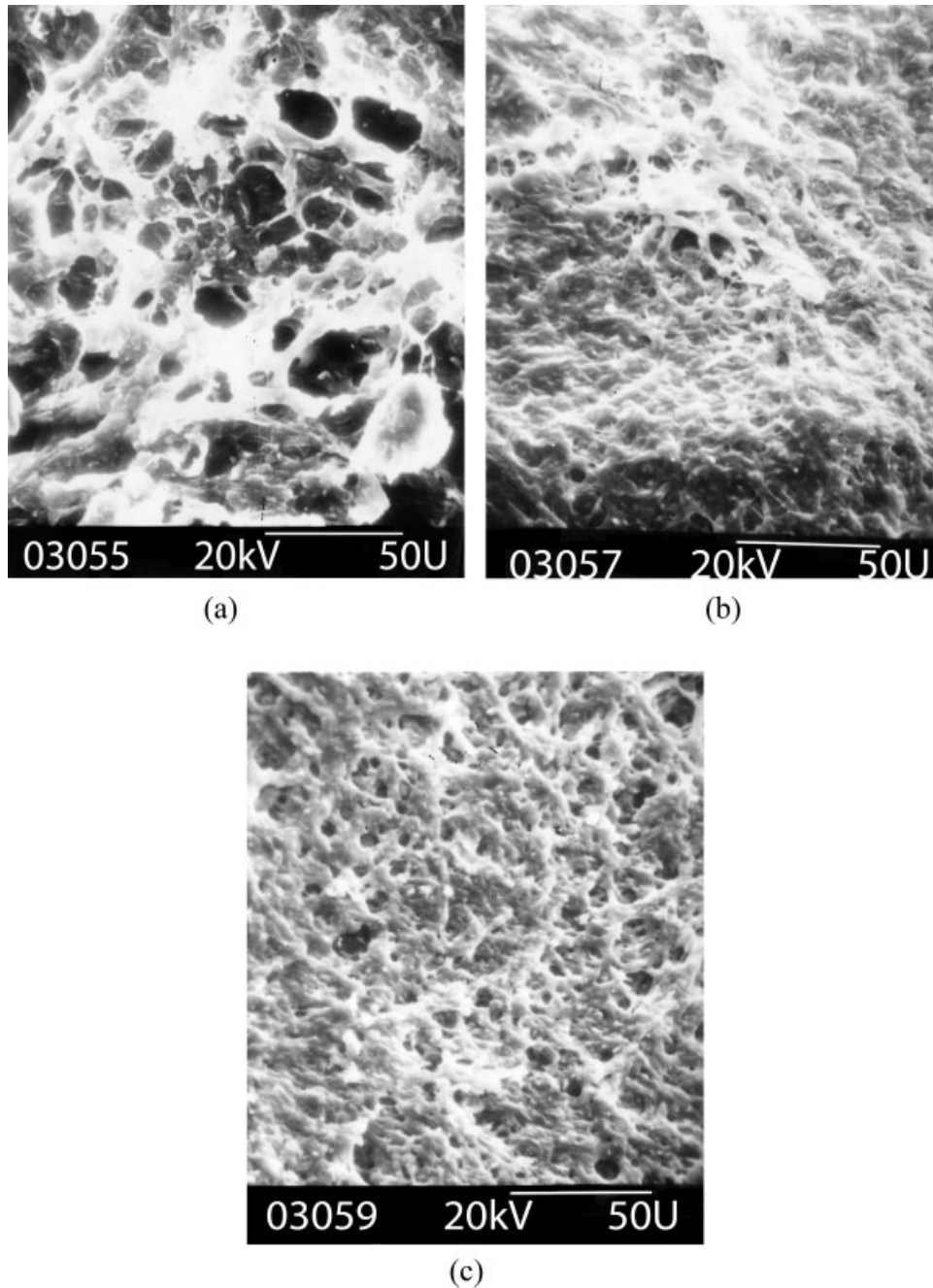


Figure 4 SEM photos of doped PMP foams with density 50 mg/cm^3 and different Cu content ($\times 350$): (a) 0, (b) 2.5%, and (c) 3.6%.

Mechanical properties

To investigate the influence of the Cu additive on the mechanical properties of the foam, ρ_p is chosen as a reference to compare the behavior between the undoped and doped foam. For the doped foams, ρ_p is calculated from the densities of foam specimen and the weight fraction of the Cu nanopowders as given in eq. (2).

$$\frac{\omega_{\text{Cu}}}{\rho_{\text{Cu}}} + \frac{1 - \omega_{\text{Cu}}}{\rho_p} = \frac{1}{\rho_f} \quad (2)$$

where ρ_f is the density of foam specimen, ρ_{Cu} the density of the Cu nanopowders (8.96 g/cm^3), and ω_{Cu} the weight fraction of the Cu nanopowders.

On the basis of comparison, the influence of Cu nanopowders on mechanical properties is shown in Figure 5. It is clear from Figure 5 that the doped specimens have greater moduli than the undoped PMP foam.

According to the current theory for conventional foams, the relative mechanical property of foam can be related to its relative density by the formula¹⁵

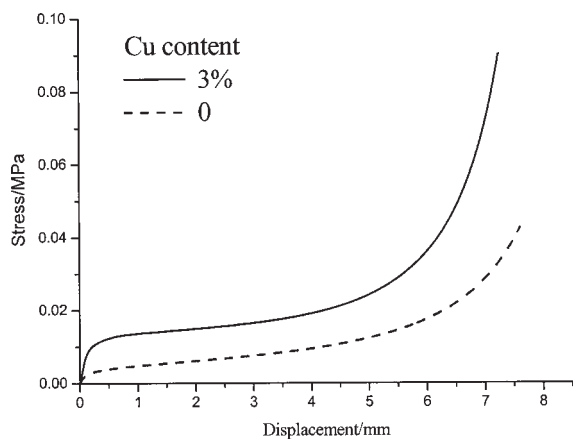


Figure 5 Comparison of compression stress–strain curves of the Cu doped foams to the undoped foam.

$$\frac{P_f}{P_s} = C \left(\frac{\rho_f}{\rho_s} \right)^n \quad (3)$$

where P_f is some property of the foam, and P_s is the same property for the bulk polymer. The quantities ρ_f and ρ_s are the densities of foam and bulk polymer, respectively. C is a constant that is equal to 1.0, when the property is the modulus, and 0.3, when it is the collapse stress. The exponent n equals 2 and 3/2 for the modulus and collapse stress, respectively. Some related properties of the bulk PMP are listed as follows: $\rho_s = 0.83 \text{ g/cm}^3$, $E_s = 1.25 \text{ MPa}$.

Figure 6 shows compression stress–strain curves for Cu nanopowders doped PMP with Cu atom content 2.2% and different densities. Double logarithmic plots of the relative modulus against the relative foam polymer density are shown in Figure 7. Dashed line is the predication of theory given in eq. (3) for $C = 1$ and $n = 2$. Similar to that reported by LeMay,¹⁶ it appears that the modulus data are

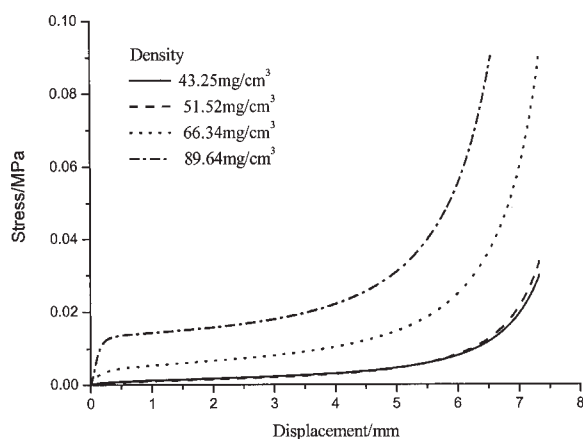


Figure 6 Compression stress–strain curves for the doped PMP foams with Cu content 2.2 at % and different density.

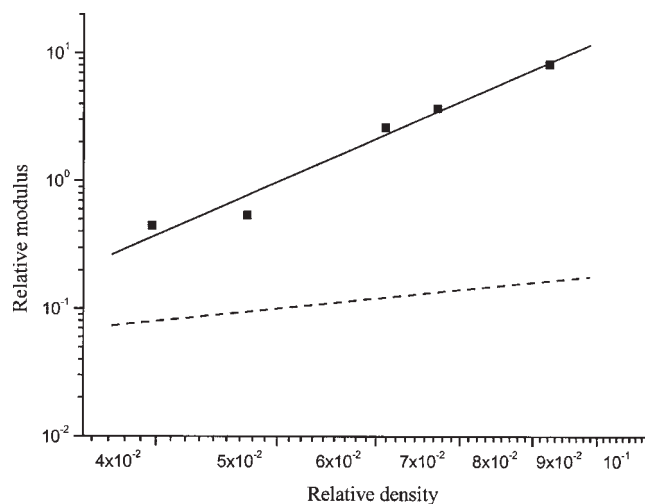


Figure 7 Variation of the relative modulus against the relative foam polymer density.

described by scaling constants larger than the predicted value $n = 2$. But it is opposite to the previous results that the moduli of the doped foams significantly overestimate the dashed line. It is caused by two functions of Cu nanopowders doped in foams: (1) intensifier of foam structure; (2) nuclei. The stiffness of a porous material is determined by the degree of interconnectivity of the solid material comprising its structure. Being nuclei doped in the polymer solution, Cu nanopowders greatly increase the degree of interconnectivity of the PMP foam skeleton, as mentioned earlier.

CONCLUSIONS

Cu nanopowders doped PMP foams have been prepared by TIPS. Ultrasonic dispersal above melting point of solvent can improve the uniformity of Cu powders in foam skeleton. The doped foam has greater module than the undoped PMP foam and significantly overestimate the predicted value by current theory for conventional foams. It indicates two roles of Cu nanopowders in PMP foams: intensifier of foam structure and nuclei in polymer crystallization. It is testified that the finer structure and smaller size cells can be formed with Cu content increasing by SEM.

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