Thermally-Induced Phase Separation Mechanism Study for the Preparation of Semicrystalline Polymeric Membranes

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Abstract : Thermally-induced phase separation mechanisms were investigated for the structure control of the semicrystalline polymeric membrane. Isotactic polypropylene showed the better resistance to the organic solvents than the other polymers for membrane materials tested in this work. Depending on the location in the phase diagram each sample had its own phase separation mechanism to result in the unique structure. The sample structure depended on the competitive liquid-liquid phase separation and polymer crystallization. The initial polymer composition, quench depth, cooling rate and the holding time in the liquid-liquid phase separation region had great influences on the structure formation. Interpretations of the structure formation based on the mechanism study were performed.

Introductions

Thermally-induced phase separation process (TIPS) is used for the fabrication of the microporous membranes from the semicrystalline polymers, which have superior chemical and thermal resistances to the conventional solvent cast membranes. Semicrystalline polymeric membranes are expanding their applications and expected to occupy the greater part of the conventional membrane market than ever. In TIPS process structure control of the membrane is the most important factor in membrane preparation process.[1-5]

Polymer and diluent are melt blended above the polymer melting temperature and upon cooling below the melting temperature polymer crystallization takes place, which is called as solid-liquid phase separation. The less miscible pair of the polymer and diluent undergoes the liquid-liquid phase separation originated from the thermodynamic instability of the system.[6-8] From the solid-liquid phase separation the sample forms the spherulitic lacy structure with the void which has been occupied by the rejected diluent during the spherulite formation. Liquid droplets of polymerlean phase are formed from the liquid-liquid phase separation either via nucleation and growth or spinodal decomposition followed by coarsening process.[9-11]

In this work isotactic polypropylene was selected as a semicrystalline polymer for membrane materials, and its chemical resistance was compared with those of the other commercially used membrane materials. Phase separation mechanism study was performed for the isotactic polypropylene/soybean oil system which undergoes both liquid-liquid and solid-liquid phase separations. Special interests were given to the liquid- liquid phase separation mechanism such as initial phase separation behaviors, droplet growth via coarsening, and coalescence of the droplets.[12-14] Interference of crystallization on the droplet growth was qualitatively investigated. Various cooling conditions were applied to the sample and the resulting structures were interpreted in terms of the phase separation mechanisms.

Experimental

Materials and Sample Preparation. Iso-

tactic polypropylene (iPP) (H730F, melt index= 10 g/10 min under the load of 5 kgf) was supplied from Yukong Co., Korea, and the commercial soybean oil from Cheiljedang Co. was used as a diluent. Nylon 12 was from Aldrich, polysulfone (PSf, Udel p-1700) from Amoco Co. and polyethersulfone (PES, Victrex) from ICI Co., and polyetherimide (PEI, Ultem 1,000) was from GE. All the organic solvents for chemical resistance test were from Junsei chemical Co., and Freon 113 from Dongyun Chemical Co. was used as an extractant. All the chemicals in this work were used as received with no further purification. Melt blending of iPP with soybean oil was performed for 2 hrs under the nitrogen atmosphere and the blended samples were quenched into the ice water and were stored in the refrigerator in order to prevent the migration of soybean oil to the sample surface.

Chemical Resistance Test. Chemical resistances of the membrane materials were tested to the common organic solvents. The popularly used membrane materials were selected such as iPP, nylon 12. PSf, PES, PEI and the organic solvents were toluene, acetone, N, N-dimethyl form amide (DMF), and tetrahydrofuran (THF). Each polymer sample was prepared as a film of 0.5 cm×0.5 cm with 3 mm thickness and was immersed in each organic solvent of 20 ml for 7 days. The sample was taken out from the solvent and rinsed with distilled water. Moisture on the surface was removed by using a filter paper. The swelling ratio was determined by measuring the thickness change of the sample.

Apparatus and Procedure. Thermo-optical microscope system was devised as shown in Figure 1. The melt blended sample was placed between the cover slips which were then sealed with vacuum grease for the prevention of the diluent vaporization during the experiment. The cover slips were loaded on the temperature programmed hot stage. Initial temperature of the hot stage was set at 210 °C to secure the homogeneity of the melt sample. Crystallization temperature of each sample was determined by using a differential scanning calorimeter (DSC, Perkin Elmer DSC7).

The phase separation was observed by the
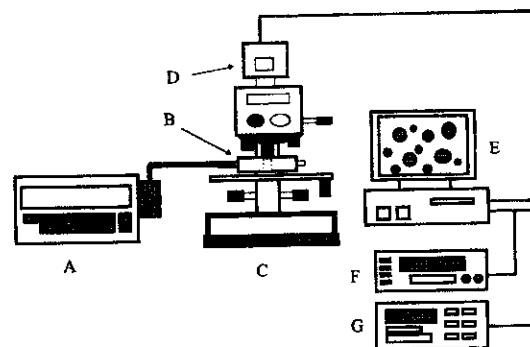
A: Central processor, B: Hot stage, C: Optical microscope,
D: CCD camera, E: Image analyzer, F: VCR recorder.
G: Color video printer

Figure 1. A schematic diagram of thermo-optical microscope system.

optical microscope on which the hot stage was placed. The images were monitored by using a CCD camera with a video cassette recorder and analyzed by an image analyzing system (IP lap spectrum). Several cooling conditions were applied to the samples such as constant cooling rate, quenching and holding. Thus obtained samples were immersed in Freon 113 for the extraction of the diluent for 24 hours. Then they were vacuum dried at 40 °C for 8 hours to make the microporous membrane sample. Structure of the membrane was examined by using a scanning electron microscope (SEM) after the fracture in liquid nitrogen.

Results and Discussions

Chemical Resistances of the Membrane Materials. As shown in Table I PSf. the most

Table I. Swelling Ratio of the Polymers for Membrane Materials in Organic Solvents

Polymer / Organic Solvent	Swelling Ratio (%)			
	Toluene	DMF	Acetone	THF
PP	6.9	1.1	0.8	6.5
Nylon-6	5.2	1.6	1.6	1.6
Nylon-12	0.0	0.6	1.3	0.0
PSf	dissolved	dissolved	50.0	dissolved
PES	2.3	dissolved	47.3	28.7
PEI	2.9	dissolved	4.6	dissolved

widely used membrane material, was dissolved in toluene, DMF, and THF, and its swelling ratio to acetone was 50%. Since PSf membrane was prepared by the solvent casting method, its poor resistance to chemicals was inherent. PES was developed to improve the PSf membranes and it showed the better chemical resistance than PSf. However, it was still weak to chemicals. PEI was quite resistant to toluene and acetone, and was weak to DMF and THF. Nylon 12 and iPP showed the best resistance to the organic solvents tested in this work. iPP is much cheaper and has better processability than Nylon 12. Therefore, iPP was chosen as the best materials for the chemical resistant membrane preparation.

Phase Diagram of iPP and Soybean Oil System. The phase diagram of iPP and soybean oil system was experimentally determined as shown in Figure 2. Thermo-optical microscope system detected the decrease of the light transmittance at cloud point, and it was confirmed by the presence of the cellular structure in the SEM images of the sample held at that temperature. The crystallization curve was determined by using a DSC. In both cases the cooling rate was set as 10 °C per minute. The monotectic composition of the system was located at 60 wt% of iPP and 112 °C, which is the border of the liquid-liquid and solid-liquid phase separation region. The crystallization line below the cloud point was nearly flat regardless of the
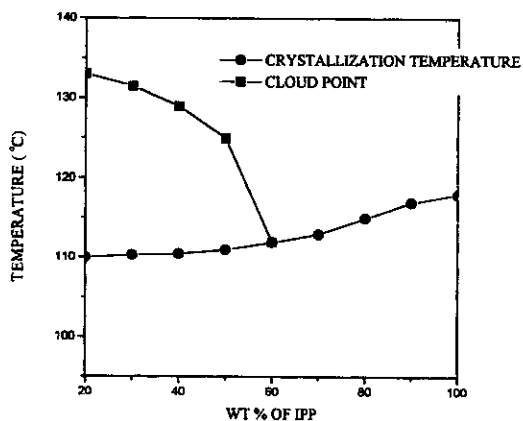
composition. which is the characteristic of the liquid-liquid phase separating system.

Effect of the Polymer Solution Composition. Three homogeneous melt samples with different compositions (30, 50, and 70 wt% of iPP) were quenched from 210 °C to 120 °C.
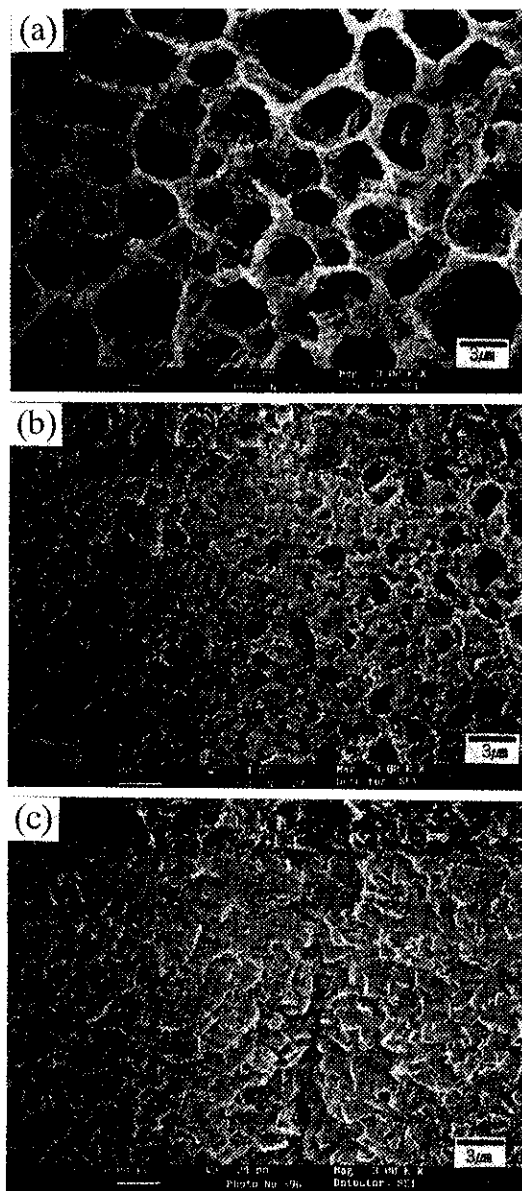

Figure 3. Cross sectional images of the samples with different initial compositions quenched from 210 °C to 120 °C and held for 10 minute before quenching to ice water ((a) 30 wt% iPP. (b) 50 wt% iPP. (c) 70 wt% iPP).

Figure 2. Phase diagram of iPP/soybean oil system determined at 10°C/min.

held for 10 minutes and requenched to ice water. As shown in Figure 3, 30 and 50 wt% samples have cellular structure while 70 wt% sample showes spherulitic structure without any cells. At 120 °C 30 and 50 wt% samples were below the cloud point curve and 70 wt% sample was above it. Though the crystallization temperature locates below 120 °C, the equilibrium melting temperature must be much higher than this. Therefore, all the samples can be thermodynamically crystallized at this temperature. 30 and 50 wt% samples underwent the liquid-liquid phase separation to result in the cellular structure followed by the crystallization, and 70 wt% sample underwent only the crystallization to result in the spherulitic structure only. Once the sample was crystallized there was no room for liquid-liquid phase separation, since the sample got solidified already.

The cell size of the 50 wt% sample is smaller than that of 30 wt% sample for the two reasons. Since 50 wt% sample has greater amount of the iPP, it should have less porosity and smaller cell size than 30 wt% sample. The 50 wt% sample is closer to the cloud point and has smaller quench depth for liquid-liquid phase separation (temperature difference between the cloud point and holding temperature) and greater quench depth for crystallization (temperature difference between the cloud point and the equilibrium melting temperature) than 30 wt% sample. Therefore, the liquid drop growth was interfered by the crystallization at that temperature to form the cells with smaller sizes.

Effect of Quench Depth. The melt samples were quenched to several holding temperatures below the cloud point curve and held there for 10 minutes before they were quenched to ice water. Each holding temperature has its own quench depth for liquid-liquid phase separation and quench depth for crystallization. As shown in Figure 4. the samples held at 130, 125 and 110 °C made cellular structure. while those held at 100 and 25 °C have spherulitic lacy structure. For 30 wt% sample the cloud point was 131 °C and the crystallization temperature was 110 °C as shown in the phase diagram. and the temperatures of 130, 125 and 110 °C were within

the liquid-liquid phase separation region above the crystallization temperature. Therefore, the samples quenched to these temperatures underwent the liquid-liquid phase separation without much interference of crystallization to result in the cellular structure.

The sample held at 130 °C has less number of cells than the other cellular structured samples. At this location the sample is likelihood to be in the metastable region, since it is very close to the cloud point. Within the metastable region, the polymer-lean phase droplets are formed via nucleation and growth mechanism and the smaller quench depth induced lower droplet growth rate.[9,10] Therefore, the cellular structure with isolated cells was obtained for the sample quenched at 130 °C, whose number of cells should be less than those of the spinodally decomposed samples.

The cell size of the 110 °C sample was smaller than that of 125 °C sample, which does not follow the general trend that size and growth rate of the droplet increase with the increase of quench depth.[14] Though the quench temperatures were above the crystallization temperature, the samples were below the equilibrium melting temperature. Therefore, each sample was under the thermodynamic driving force for crystallization. The 110 °C sample underwent the faster crystallization than the 125 °C sample, and the crystallization interfered the growth of the droplet of the 110 °C sample, which otherwise might have grown much bigger and faster than the 125 °C sample.

For the quench temperatures of 100 and 25 °C, the crystallization rate was more accelerated than that of the liquid-liquid phase separation for the greater quench depth. Then the polymer crystallization rates were much higher than the liquid-liquid phase separation rate, and there were no time for droplet formation and growth due to the interference of crystallization.

Effect of Cooling Rate. Cooling condition plays the most important role in TIPS process. Four cooling conditions were applied to 30 wt% iPP samples at 210 °C. As shown in Figure 5, the three samples cooled at 1, 10, and 20 °C/min formed the cellular structure, and the direct-
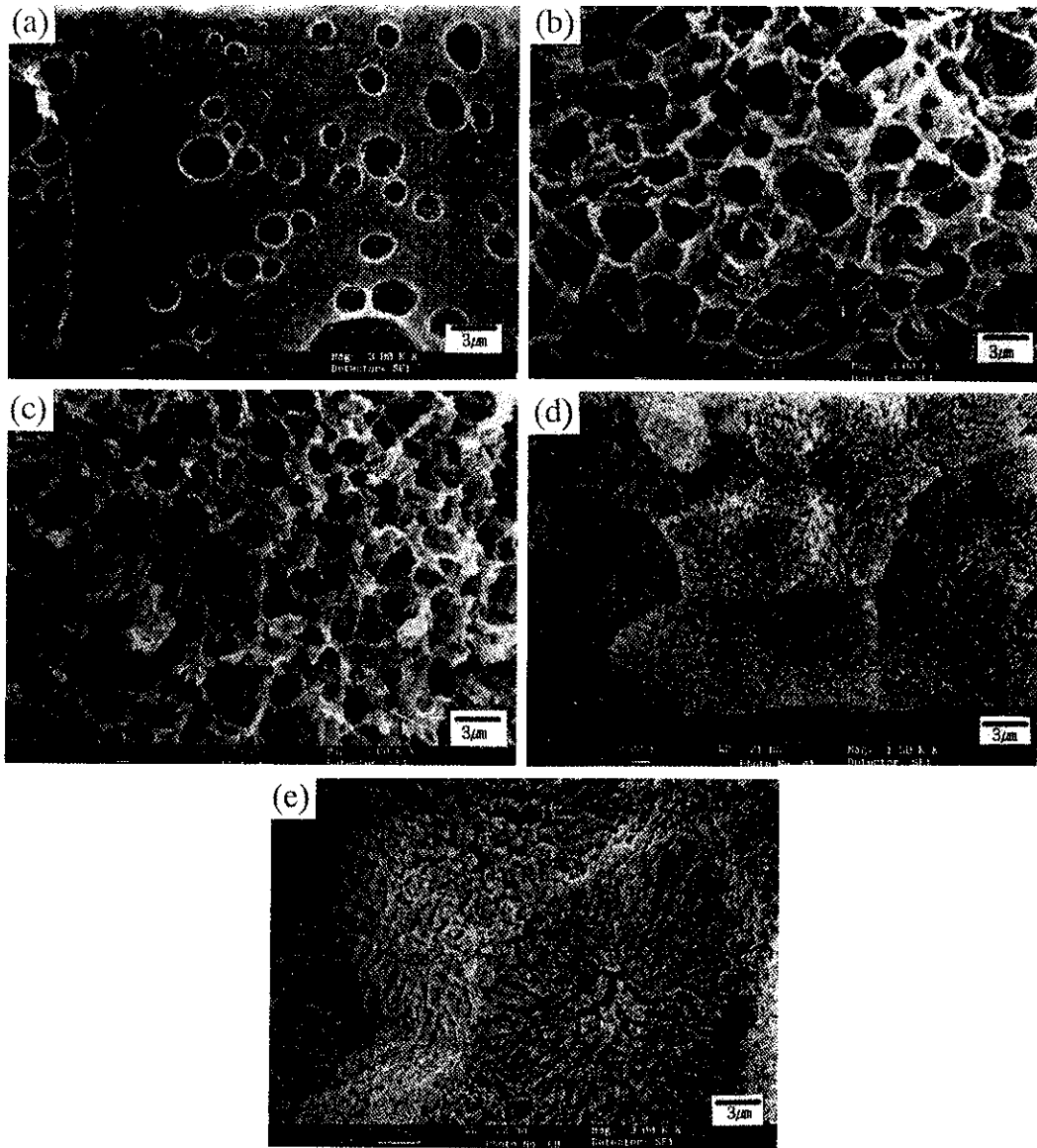
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Figure 4. Cross sectional images of the 30 wt% samples quenched from 210 °C to different temperatures with 10 minute of holding time before quenching to ice water ((a) 130 °C. (b) 125 °C. (c) 110 °C. (d) 100 °C. (e) 25 °C).

ly quenched sample formed the spherulitic structure without cells. As the cooling rate increased, the cell size decreased. The lower cooling rate allowed the sample to stay in the liquid-liquid phase separation region longer before the crystallization begins to result in the greater cell size. However, the lower cooling rate induced the smaller quench depth and the growth rate and the size of the droplet should be reduced,[14]

which is opposite to the observation. In this case interference by crystallization was more important factor than the quench depth.

Effects of Holding Time in the Liquid-Liquid Phase Separation Region. In order to support the argument that the droplet grew in the liquid - liquid phase separation region. 30 wt% sample was quenched from 210 °C to 120 °C, where the sample was held for various intervals.

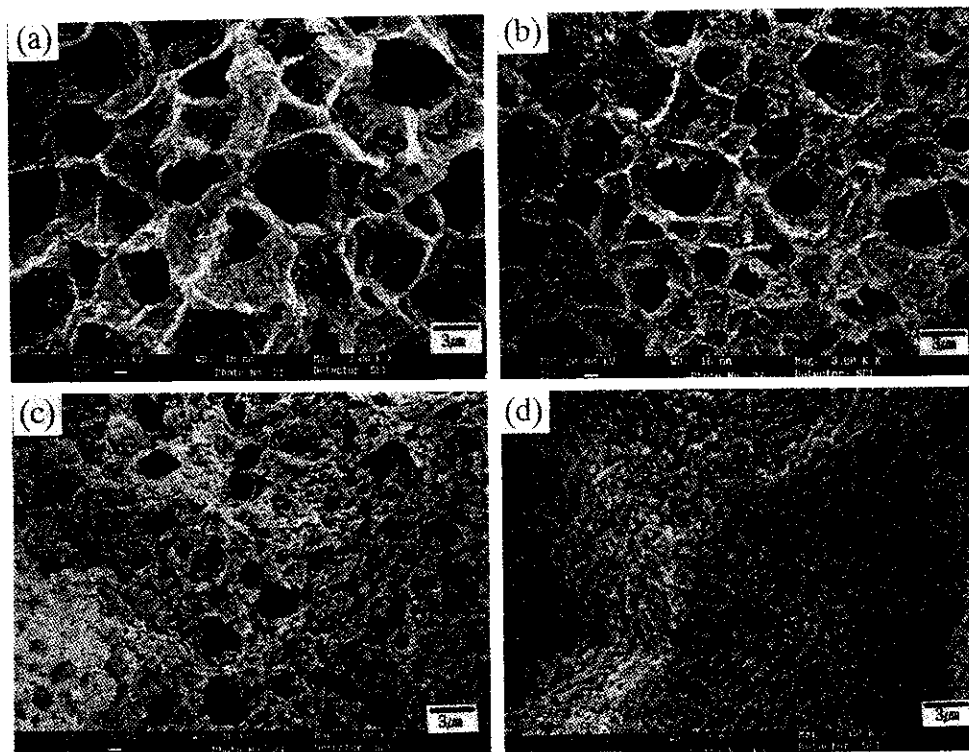Korea Polym. J., Vol. 5. No. 3. 1997

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Figure 5. Cross sectional images of the 30 wt% samples cooled at different cooling rates from 210°C to room temperature ((a) 1 °C/min, (b) 10 °C/min, (c) 20 °C/min, (d) direct quenching to room temperature).

Chou and Sigga proposed that droplet grows with time within the liquid-liquid phase separation region via coarsening process as shown in the equation below.

$$d \propto (kT/\eta)^{1/3} t^{1/3}$$

where d is droplet diameter, k is Boltzmann constant, T is temperature, η is viscosity, and t is time.[13,14]

With the increase of the holding time, the cell size increased as shown in Figure 6. After 10 minutes even coalescence occurred to make huge cell by the agglomeration of the droplets. However, the cell size did not changed after 10 minutes due to the onset of the crystallization, which was proved by using an optical microscope and a DSC.

Conclusions

IPP showed the better resistance to the organic solvents than the other polymers for membrane materials tested in this work. Depending on the location in the phase diagram each sample had its own phase separation mechanism to result in the unique structure. The samples with the initial composition less than the monotectic composition formed the cellular structure while the sample with greater composition formed just spherulitic lacy structure. The samples held at the temperatures between the cloud point and crystallization temperature formed the cellular structure. When holding temperature was close to the cloud point the sample underwent the liquid-liquid phase separation via nucleation and growth mechanism to produce the isolated cells. For the greater quench depth crystallization rate was more accelerated than the liquid-liquid phase separation rate. With the increase of the cooling rate the cell size was reduced to reveal that interference by crystallization was more important factor than the quench depth in structure formation. With the increase of the hold-
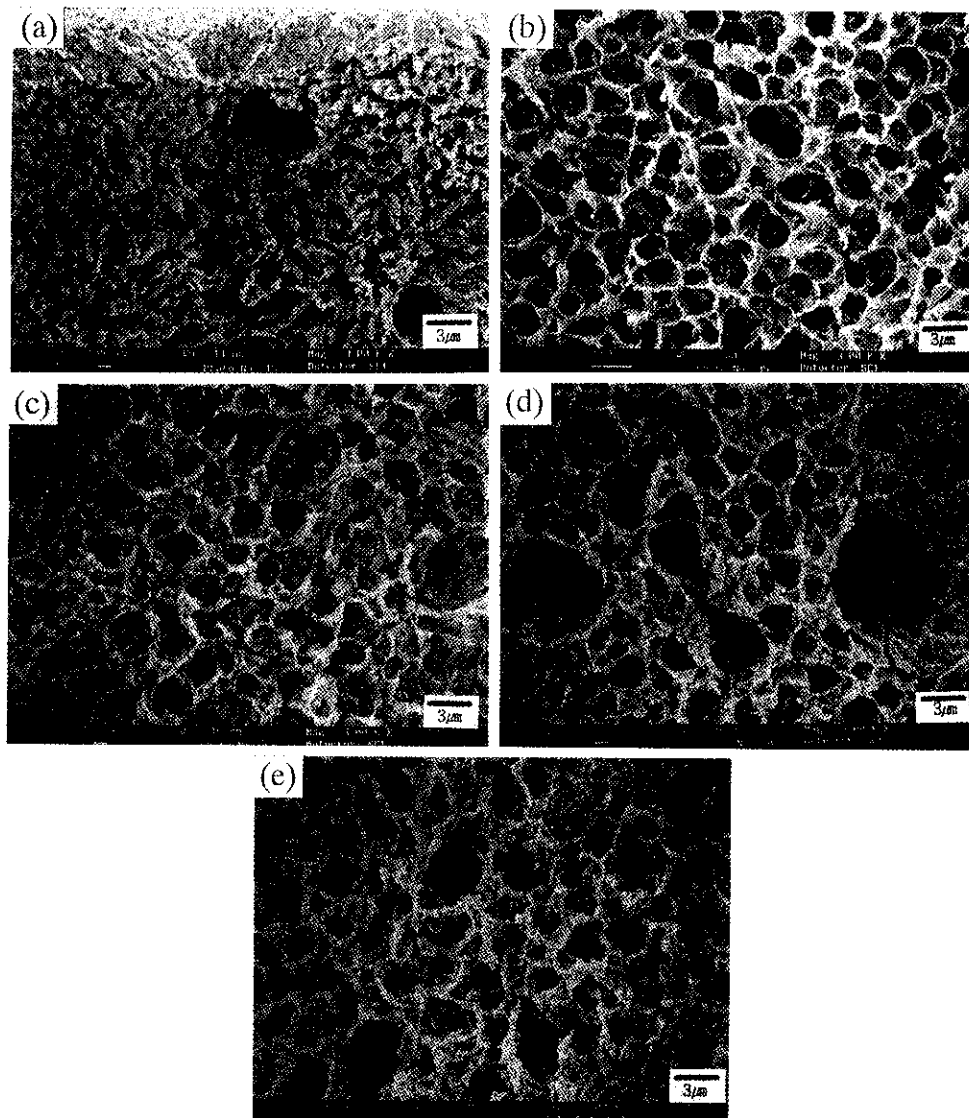
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Figure 6. Cross sectional images of the 30 wt% samples quenched from 210 to 120 °C and held for different intervals ((a) 1 min. (b) 5 min, (c) 10 min. (d) 30 min. (e) 60 min).

ing time within the liquid-liquid phase separation region, the cell size increased and even coalescence occurred to make huge cell by the agglomeration of the droplets.

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