

## 세그먼트화 블록 코폴리에스테르/용매/비용매 계의 상분리에 관한 연구

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### Phase Separation Behavior in Copolyetherester/Solvent/Nonsolvent Systems

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#### 1. Introduction

Phase transitions are responsible for microstructure formation during nonsolvent quenching of polymer solutions. Phase separation of polymer solutions can be induced in several ways, for instance, thermally induced phase separation (TIPS), air casting of the polymer solution, precipitation from the vapor phase and immersion precipitation. There have been commercial polymeric membranes manufactured by using the various phase transitions. Those processes also are used to form microporous coatings on textiles for producing breathability while retaining its external waterproofness.

Segmented block copolyetherester is the thermoplastic elastomer defined as copolymer having sequences of alternating polyester hard blocks and polyether soft blocks[1]. Since segmented block copolyetherester is semicrystalline, two types of phase separation process may occur during the preparation of films by immersion precipitation method. The liquid-liquid demixing results in a porous structure with pores that are formed from the nucleated polymer lean phase and the solid-liquid demixing occurs in the crystalline parts to form particles. There are already some applications in the copolyetherester film such as surgical drape, garment and article[2]. In case of the microporous copolyetherester film, it possesses the possibility in many applications such as breathable fabrics or synthetic leathers.

The objective for this study is to find a relationship between the various conditions and the final morphology of films induced by phase separation process.

We prepared films from the two different polymers and the quantitative data on turbidity were presented and cross-section morphology included.

## 2. Experimental

Segmented block copolyetherester based on poly(butylene terephthalate)(4GT) and poly(tetramethylene ether glycol)(PTMG) 2000 were synthesized. One copolyetherester having 35wt% and the other having 20wt% of hard segment were used. The two kinds of polymers were dissolved respectively in phenol with a various concentration range. Cloud point was measured by using titration method with a distilled water as a nonsolvent. We cast polymer solution on microglass and immersed in a coagulation bath containing phenol and distilled water. After sufficient coagulation time the films were removed and washed with distilled water and acetone at several times. The morphology was examined by scanning electron microscopy (Hitachi S-2350).

## 3. Results and Discussion

The cloud point curves are presented for two kinds of copolyetheresters in water-phenol system(*Figure 1,2*). The homogeneous liquid phase region, which is largely defined by the space between the polymer-solvent axis and the cloud point curve. We can see that cloud point curves for both of polymers lie in the almost same location for the each temperature due to the same hydrophobic characteristics[3]. The liquid homogeneous region lies mainly in the space between the polymer/solvent axis and the cloud point curve. The wide region was obtained at higher temperature, respectively.

The results of the morphology of films are presented in *Figure 3,4*. The two films having a skin layer with a lot of particle structure resembling crystallization are observed instead of a porous skin. However the cross-section of films demonstrates clearly the characteristics of a cellular morphology due to liquid-liquid demixing. In case of *Figure 4*, the polymer and the composition of bath used during the preparation of films are HSC 35% copolyetherester and 6:94 (solvent:nonsolvent by weight). This polymer has a higher crystallinity than HSC 20% copolyetherester does. The binodal line and the crystallization line are thought to be close to each other.

Liquid-liquid and solid-liquid demixing take place at the same time. In the skin layer, the polymer concentration is higher due to the loss of solvent. So polymer rich phase is supersaturated with respect to crystallization on the surface of films because of slow quenching by the mixed coagulation bath. And liquid-liquid demixing becomes to happen under the skin layer.

As the films was prepared with HSC 20% copolyetherester, liquid-liquid

demixing is expected to occur due to the low crystallinity of polymer. However, as shown in *Figure 3*, a phase separation process under conditions of fast out-diffusion of solvent and fast in-diffusion of nonsolvent takes place to give the dense skin structure instead of the porous morphology[4]. Underneath the skin is a region composed of closed pores which can be found in amorphous membranes.

#### 4. Conclusions

We can relatively find the information related to the interaction among polymer, solvent and nonsolvent through the cloud point curve. The morphology of films depended throughly on the crystallinity of the polymer used in the preparation of the films and kinetic effect as well as thermodynamic effect. In case the polymer has the low crystallinity, the porous structure was obtained due to liquid-liquid demixing.

However, the fast quenching during the precipitation of films result in a dense skin. As casting solution was immersed in the soft coagulation bath, the morphology presents a structure filled with particles on the skin of films.

#### 5. References

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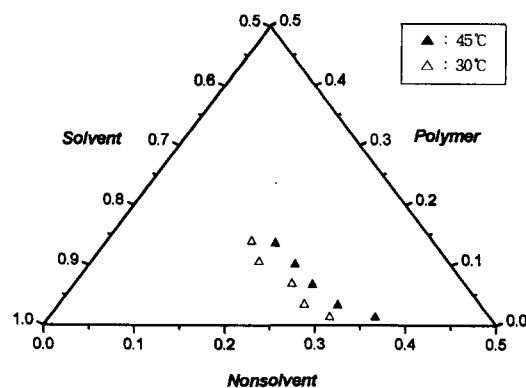


Fig. 1. Phase diagram of water/phenol/HSC20% copolyetherester system.

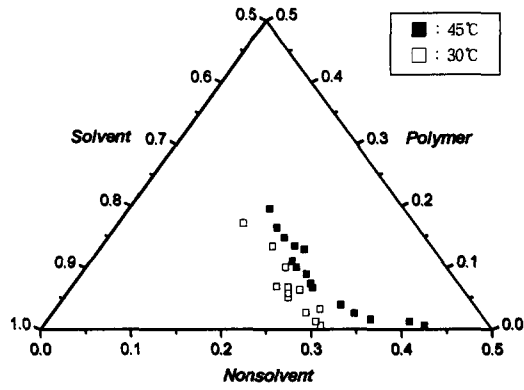


Fig. 2. Phase diagram of water/phenol/HSC35% copolyetherester system.

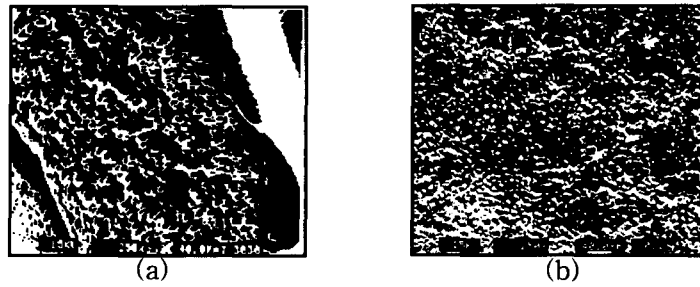


Fig. 3. The SEM photomicrograph of the HSC 20% copolyetherester films prepared by immersing 17% polymer solution into 100% distilled water bath at 45°C((a) cross-section, (b) surface).

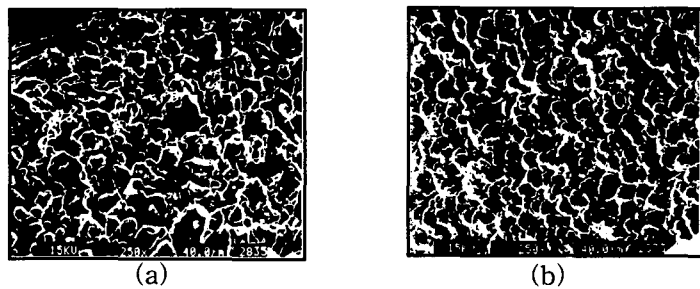


Fig. 4. The SEM photomicrograph of the HSC 35% copolyetherester films prepared by immersing 17% polymer solution into 6% coagulation bath at 45°C((a) cross-section, (b) surface).