Phase separation mechanism and morphology development during formation of ion-exchange membrane

Toshiaki Ougizawa, Keiichi Kuboyama, Yujiro Uchino
Department of Organic and Polymeric Materials, Tokyo Institute of Technology

Summary

Most of ion-exchange membranes are formed by polymerization of styrene and divinylbenzen and then the ion-exchange groups are introduced into the membrane. In the process of the polymerization, the phase separation takes place and it is considered that the formed morphology affects the performance of membrane remarkably. Usually rubber component is added to the mixture of styrene and divinylbenzen in order to improve the brittleness of the membrane and this may induce the phase separation. In this study, the morphology development during polymerization of styrene and divinylbenzen was measured by a light scattering and a transmission electron microscope. The phase separation mechanism was discussed.

Acrylic rubber was dissolved into mixture of styrene monomers and divinylbenzen monomers at room temperature to make up a 5/90/10 solution. As an initiator α,α'–azobis(isobutyronitrile) was added to the solution. The sample cell was placed in a hot chamber kept at a polymerization temperature, which was set horizontally on the light scattering stage. The change in light scattering profile with polymerization was measured. At first the solution was homogeneous. As the polymerization proceeded, a peek in light scattering profile appeared and then the intensity increased continuously with time. The peek position was almost constant. For polymerized sample, a regularly phase-separated structure was observed by the optical microscope. Characteristic features of this structure were the periodicity and dual connectivity of the phases. These are the hallmarks that the phase separation took place via spinodal decomposition mechanism. In order to specify the phase-separated phases, a measurement of differential scanning calorimeter was carried out. Two clear glass transition temperatures were observed; one corresponded to almost pure polystyrene-divinylbenzen and another almost pure acrylic rubber. Also it was confirmed that the styrene and divinylbenzene did not phase-separate. From the above, it is clearly shown that the morphology in the ion-exchange membrane is formed by phase-separation into styrene phase and rubber phase via the spinodal decomposition. It is also suggested that the phase-separated morphology can be controlled by changes of polymerization speed and miscibility between polystyrene and rubber.