

Viscoelasticity and Morphology of Soft Polycarbonate as a Substitute for Poly(vinyl chloride)

Tadashi Inoue, Hiroshi Watanabe and Kunihiro Osaki

The soft polycarbonate resins, SPC, were newly developed as a substitute for soft poly(vinyl chloride). The soft polycarbonates are multiblock copolymers composed of bisphenol A polycarbonate, PC, and polydimethylsiloxane, PDMS. SPC resins are clear, transparent, and tough. Viscoelasticity and morphology of the resins were investigated to control physical properties of the resin. Electron microscope and small angle X-ray scattering experiments revealed that the SPC formed microdomain structures. Rheological measurements were used to discuss continuity of PC-rich phase domain, which determined the modulus around the room temperature.

Keywords : Substitute for Poly(vinyl chloride), Polycarbonate, Polydimethylsiloxane, Viscoelasticity, Strain-Induced Birefringence

Poly(vinyl chloride), PVC, is one of conventional polymeric materials in modern industry. Large amount of PVC is produced to consume chlorine produced in sodium hydrate synthesis process. Its mechanical properties are easily controlled by addition of plasticizers, and therefore PVC is used in many fields; lapping films, sheets for agriculture, building materials like pipes, and so on. However, recently there are some doubts about its safety. Dioxins may be produced by combustion, and additives like octyl phthalate are now known as environmental hormones.

Several approaches to develop substitutes for PVC are in progress. Among these approaches, a reasonable one is to capture properties of plasticized PVC by combi-

nation of rubbery and glassy polymers in microscopic level. In order to obtain a transparent material, it should be homogeneous in macroscopic scales unless an isorefractive polymer pair is selected. Obviously, in such an approach, properties of the obtained material would be strongly correlated with the starting polymers, and therefore selection of polymer pair is very important to obtain high performance substitute.

Soft polycarbonate resins, SPC, being multiblock copolymers composed of bisphenol A polycarbonate, PC, and polydimethylsiloxane, PDMS, are recently developed by Idemitsu Kohsan corporation. Neat PC is a very tough engineering plastic and PDMS is an excellent elastomer being chemically and thermally stable. Synthe-

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Rheology —

Scope of research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.



Prof
OSAKI, Kunihiro
(D Eng)



Assoc Prof
WATANABE, Hiroshi
(D Sc)



Instr
INOUE, Tadashi
(D Eng)



Techn
OKADA, Shinichi

Students:

KAKIUCHI, Munetaka (DC)
MATSUMIYA, Yumi (DC)
OGAWA, Takeshi (MC)
UEMATSU, Takehiko (MC)
YAMASHITA, Yasuhiro (MC)
FUKUMA, Eisai (UG)
MORI, Takuya (UG)
TAKAHASHI, Kazuhiro (UG)
OH, Gwan Kyo (RS)

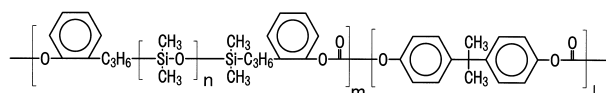


Figure 1. Molecular structure of soft polycarbonate.

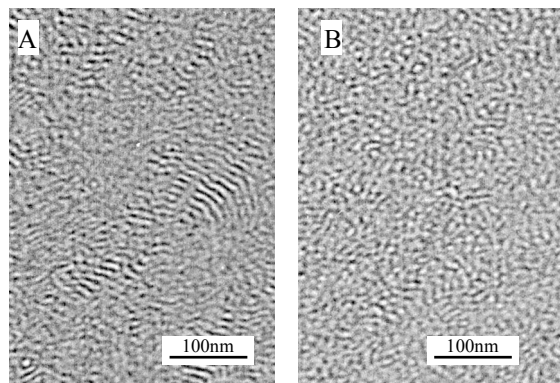


Figure 2. Electron micrograph of soft polycarbonates, A and B. Black domains correspond to PDMS rich phase.

sized SPC mimics plasticized PVC; clear, transparent, and tough. Thus, SPC is anticipated to be a good candidate for the substitute. In order to control physical properties and processability, SPC has been under investigation for a few years in our lab[1].

SPC is synthesized from copolymerization of end phenol-modified poly(dimethyl siloxane), PDMSOH, and bisphenol A. Molecular structure of SPC is shown in Figure 1. Controlling parameters for physical properties of SPC are; content of PDMS(w_{PDMS}), molecular weight of PDMSOH(M_{PDMS}), and total molecular weight(M). As shown later, SPC has microdomain structures. M_{PDMS} affects the miscibility of two microdomains. The reported results were mostly taken with SPC having $M_{\text{PDMS}} = 1980$. Depending on w_{PDMS} , rubber-like (sample A, $w_{\text{PDMS}} = 0.387$) and glass-like (sample B, $w_{\text{PDMS}} = 0.552$) specimens were obtained.

Figure 2 shows examples of electron micrograph of rubber-like (soft) and glass-like (hard) SPC. In both cases, *similar* microdomain structures were observed. For the lower PDMS content polymer(A), lamellar like structure is partially observed. Small angle x-ray scattering experiments, indicating relatively narrow Bragg's peak, also support existence of the microdomain structure.

Details of the microdomain structures were examined through dynamic mechanical measurements using oscillatory deformation. The strain-induced birefringence was also examined to detect structural changes (chain orientation). Figure 3 shows temperature dependence of the complex modulus for the two samples. There are two glass transition temperatures(100°C , -100°C (not shown

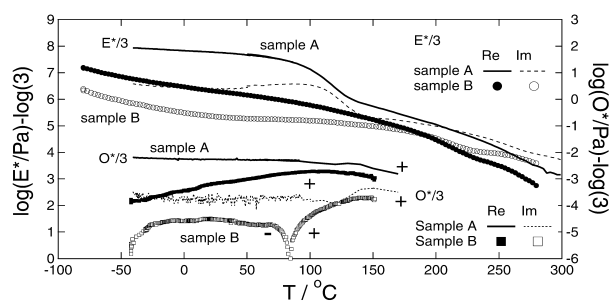


Figure 3. Temperature dependence of the complex modulus, $E^* = E' + iE''$, and the strain optical coefficient, $O^* = O' + iO''$, for SPC.

in Figure 3)), which indicates the system has a phase-separated structure. The higher glass transition temperature is identified with PC and lower one with PDMS. The two glass transition temperatures are almost constant for these polymers. Temperature dependence of modulus around the room temperature is weak, which means that SPC is much more thermally stable than PVC.

The modulus between the two glass temperatures was found to show a steep change around $w_{\text{PDMS}} \sim 0.5$. This result suggests that the continuity of the PC-rich phase changes around $w_{\text{PDMS}} \sim 0.5$: If PC domains are continuous, glassy PC domains are deformed affinely, and therefore glassy behavior is observed. On the other hand, if the glassy PC domains are not continuous and soft PDMS domains are mainly deformed, rubbery behavior is observed. This speculation is confirmed with dynamic birefringence measurements, which reflects strain of PC domain. (Negative birefringence is due to large deformation of PDMS domains.)

Tensile properties at large deformations were also examined. Strain-stress curve for sample A having higher PDMS content shows rubber-like behavior; the stress increases monotonically with strain. On the other hand, sample B shows the glass-like behavior; stress yielding is observed at few percent elongations. These results also can be explained with continuity of glassy PC domains. Thus, rheological measurements are sensitive to continuity of PC domain, which is hardly discussed with ordinary structural analysis in detail.

In conclusion, continuity of PC domains is a key factor to control mechanical properties of well phase-separated SPC. Effect of miscibility of the two phases will be discussed in near future by using lower M_{PDMS} samples.

References

- [1] T. Inoue, K. Osaki, H. Morishita, H. Tamura, and S. Sakamoto, *Zairyo*, **49**, 1298(2000).