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主 論 文 の 要 旨

論文題目 **Linear and Nonlinear Rheological Properties of Poly(Propylene Carbonate)**
(ポリ(プロピレンカーボネート)の線型および非線型粘弾性特性)

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論 文 内 容 の 要 旨

Poly(propylene carbonate) (PPC) is a CO₂-based biodegradable material. Although its rheology is important for processing, the rheology of PPC has not been fully elucidated. This thesis is dedicated to the rheology of PPC, and it consists of 5 chapters. Chapter 1 is introduction. Chapter 2 is sample preparation and characterization. Chapter 3 and Chapter 4 are linear and nonlinear rheological properties of PPC. Chapter 5 is summary.

In Chapter 1, I introduce the background and literature research of the rheology of PPC and other reported polymers. For linear rheology, the chemical structure of polymers determines the so-called linear rheological parameters: entanglement molecular weight, plateau modulus and relaxation time. After normalizing the linear viscoelastic curves with these parameters for different polymers, linear rheology exhibits universality. The situation becomes complex for nonlinear rheology of polymers. Shear and elongational flows are two typical deformations and are often utilized in the processing. It has been established that shear rheology follows the universality like linear rheology, however, elongational rheology has not been fully explored due to the difficulty of measurements. According to the data for several polymer melts, elongational behaviors seem to depend on the chemical structures of polymers. Concerning PPC, there has been limited number

of studies on the linear rheology of commercial PPC. Besides, reported linear rheological parameters are inconsistent between different studies due to insufficient measurement and sample problems. For nonlinear rheology, only a few shear data are available and no extensional data have been reported. Thus, I set up the research target of this thesis to systematically explore the linear and nonlinear rheology of PPC.

In Chapter 2, PPC samples were prepared and characterized. Commercial PPC synthesized from heterogeneous catalyst has large molecular weight, broad molecular weight distribution and massive low molecular weight impurities propylene carbonate (PC). By fractionation precipitation method, impurities in commercial PPC can be removed and molecular weight distribution becomes much narrower. Six PPC samples covering a wide molecular weight range having relatively narrow molecular weight distribution are prepared from a commercial PPC. The PPC samples were characterized by several methods such as nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), multi-angle light scattering (MALS) and differential scanning calorimetry (DSC). From NMR it was confirmed that fractionated PPCs didn't have low molecular weight impurities PC and the carbonate units on the backbone are more than 95%. From GPC and MALS, molecular weight and distribution of PPCs were obtained. It was confirmed that fractionated PPCs have various molecular weights (68.8k - 344k) and relatively narrow distribution (~ 1.4). From DSC, the glass transition temperatures for fractionated PPCs were determined and were found to be weakly dependent on the molecular weight.

In Chapter 3, linear rheological properties of PPC were investigated and compared with previous studies. The fractionated PPCs were measured by a rotational rheometer at various temperatures. Master curves of G' and G'' of the PPCs were obtained by the empirical time-temperature superposition (tTS) principle. In the transition region, G' and G'' overlapped irrespective of the molecular weight. In the plateau region, G' showed a rubbery plateau and this plateau region became wider when the molecular weight increased. The plateau modulus values of PPCs were extracted from G' and G'' curves by the two different methods. The results do not depend on the evaluation method and the

value is essentially insensitive to the molecular weight. The plateau modulus G_N of PPCs was thus estimated as 0.67 MPa, and the entanglement molecular weight M_e as 5.9 kg/mol. This G_N value coincides with the data by Cao et al. (0.3-0.7 MPa), but is much higher than the data by Lin et al. (0.15 MPa). The discrepancy may be due to the problem in the sample and the evaluation method in the previous study. In the terminal region, G' and G'' of the PPCs show slower relaxation with increasing molecular weight. The zero-shear viscosity η_0 values of PPCs were obtained from G'' . η_0 increases obviously with increasing the molecular weight and follows the relationship $\eta_0 \propto M_w^{3.4 \pm 0.2}$, which is consistent with that for other polymers. The entire G' and G'' curves were compared with the Likhtman-McLeish (LM) model prediction. The results of PPCs are in reasonable agreement with the LM model prediction like polystyrene, polyisoprene and polybutadiene.

In Chapter 4, nonlinear shear and uniaxial elongational rheological properties of PPC were investigated. The shear rheology was measured by a rotational rheometer with a cone-plate geometry at various shear rates. The elongational properties were measured by a filament stretching rheometer at various elongational rates. The empirical tTS principle was examined for the nonlinear viscoelastic data, and it was applicable in the measured nonlinear shear and elongation data. For shear, the PPCs show shear thinning behavior. The Cox-Merz rules between dynamic complex viscosity and steady-state viscosity were not violated. For elongation, at the low elongational rate, elongational viscosities of PPCs follow the linear viscoelastic curves. At high elongational rates, elongational viscosities of PPC deviate from the linear viscoelastic curves to the higher viscosity side. The steady-state elongational viscosities η_E of PPCs decrease with elongation rate. After normalizing η_E by $3\eta_0$ and plotting the normalized η_E against elongational rate $\dot{\epsilon}$ to the relaxation time τ_d , we found a relation $(\eta_E/3\eta_0) \sim (\dot{\epsilon}\tau_d)^{-0.5}$. This behavior is similar to earlier experimental results for PS, polyisoprene (PI) and polymethyl methacrylate (PMMA), but clearly different from poly(tert-butylstyrene) (PtBS) and poly(n-butyl acrylate) (PnBA). In addition, a direct comparison was conducted between PPC and PS with a similar M_w/M_e value and similar molecular weight distribution. Normalized transient elongational viscosity at the same Weissenberg number $\dot{\epsilon}\tau_d$ for PPC and PS show good

agreement. Because the elongational behavior of PS has been discussed in terms of the orientation-induced reduction of the monomeric friction, the obtained similarity of PPC to PS suggests that a similar friction change may happen to PPC, in spite of the difference of the chemical structure.

Finally, in Chapter 5, I summarize the results related to the research purpose. The linear and nonlinear rheological properties of PPC are similar to typical polymers such as PS.