Study on the Viscoelastic Properties of Cellulose in Dilute Ionic Liquid Solutions

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論　文　内　容　の　要　旨
Thesis Summary

We aim to clarify the molecular characteristics of cellulose which will be important to develop new commodity plastic and elastomeric materials from natural resources without chemical reactions to preserve bio-degradation ability. The object of this study are (i) to examine how to get uniform solutions without severe degradation of cellulose molecules, (ii) to apply Rouse-Zimm model to the dynamic viscoelastic properties and propose a molecular estimation method and (iii) to examine how the molecular weight changed by changing the dissolution conditions.

Dissolution conditions of cotton, linter pulp, avicel, and nadelholz sulfur pulp (NSP) into 1-butyl-3-methylimidazolium chloride (BmimCl), 1-allyl-3-methylimidazolium chloride (AmimCl), and 1-ethyl-3-methylimidazolium acetate (EmimAc) are examined to obtain colorless and high viscosity uniform solutions. The tested dissolution conditions are inadequate for EmimAc. Degradation of cellulose was suppressed by choosing adequate dissolution temperatures for BmimCl (130 ℃) and AmimCl (110 ℃) solutions at depressed conditions without mechanical stirring,

though it was difficult to obtain colorless uniform solutions for avicel and linter. Dynamic viscoelastic properties of uniform solutions of cotton and NSP in BmimCl and AmimCl showed typical terminal region behavior. Lowering the bubble burst speed in the early stage of dissolution by keeping at 0.1 atm was effective compared to high vacuum. Moreover, preheating at lower temperature resulted in more mild bubble burst and the higher relative viscosity, denoting that the molecular weight of cellulose change with the swelling condition and bubble burst speed by changing the temperature and pressure.

As a molecular weight (M) estimation method for cellulose in ionic liquid solution, fitting procedure of dynamic viscoelastic data to Rouse-Zimm (RZ) model with a correction term (LT term), introduced by Osaki *et al*. and examined for standard polystyrene samples, is examined in this study. Since the RZ model calculation with and without LT term for loss modulus G" almost coincide, the data are first fitted to RZ model to get the best fit of G" by using M as a single fitting parameter, while fixing other parameters from experimental conditions and using experimentally determined relaxation time τ_{RZ}. Then the LT term, calculated from intrinsic viscosity $[\eta]$ and two adjusting parameters, is employed to judge the appropriateness of the estimation of molecular weight by further fitting storage modulus G'. The measured G' and G" can be well fitted with RZ model plus LT term in the terminal region though small discrepancy in the transition region was observed. The estimated M showed ±10% error due to ±15% error of τ_{RZ}. It is concluded that this procedure is

useful when τ_{RZ} can be determined within a small error. The estimated *M* can be used at least for the comparison of cellulose/IL solutions differently prepared.

The change in water content (*WC*) of cellulose/ILs during the preheat treatment were examined and found that *WC* became almost constant for later stage of the treatment, which increased with amount of cellulose. To investigate the influence of initial *WC*, different water content samples are examined and found that the correlation between initial *WC* and resulting M_w of cellulose is poor. Moreover, reproducibility of M_w is poor for each concentrations. However, M_w of cellulose in AmimCl can be controlled on a certain extent under 0.1 atm with different dissolving temperature. It is concluded that controlling the bubble-burst speed is essential factor for the M_w of cellulose dissolved in ILs solution.