The linear viscoelastic properties of poly(propylene carbonate) (PPC) melts having different molecular weights and narrow molecular weight distributions were studied. Some linear viscoelasticity parameters, including the plateau modulus and zero shear viscosity of PPC, were evaluated. The entanglement molecular weight of PPC was estimated to be 5.9 kg/mol, which is considerably lower than that previously reported for PPC with a broad molecular weight distribution.

Key Words: Linear viscoelasticity / Plateau modulus / Poly(propylene carbonate)

1. INTRODUCTION

Nowadays, the environmental problem “white pollution” caused by common plastics makes people interested in biodegradable polymer materials. Carbon dioxide (CO₂) based polymers are in the class of emerging biodegradable polymers. Among them, poly(propylene carbonate) (PPC), an alternating copolymer of CO₂ and propylene oxide, has attracted attention. The production of PPC increases rapidly in recent years because of its low cost and good properties. The molar fraction of CO₂ is about 50 % according to the carbonate linkage, which dramatically reduces the consumption of petroleum-based materials. Because of the excellent biodegradability, transparency, and oxygen/water barrier property, PPC is used as adhesive agents, barrier and packaging materials.

Rheological measurements are sensitive and convenient methods to characterize the chain structure and flow behavior, and also important for processing and quality control. If we attempt quantitative analysis to compare the data with other known polymers, first, we need to study the linear viscoelasticity. In particular, the plateau modulus is one of the essential parameters because this parameter characterizes the entanglement properties of polymers. There have been several reports available in the literature for linear rheology of PPC. Thorat et al. synthesized a series of aliphatic polycarbonates from ring-opening polymerization and studied their linear rheology. They used a PPC sample with the weight average molecular weight of 28.9 kg/mol and the molecular weight distribution \(M_w/M_n = 3.83\). The results show that the crossover point of the storage and loss moduli of PPC, where Ning et al. defined this value as the plateau modulus, was lower than that of poly(ethylene carbonate) but higher than that of other polycarbonates with longer side chain carbon units. Cao et al. also reported the plateau modulus of PPC as 698 − 299 kPa, which depends on the molecular weight (91.9 − 48.2 kg/mol). Lin et al. studied the relation between thermal degradation and linear viscoelasticity of a commercial PPC. They obtained the plateau modulus of PPC as 150 kPa. However, in all those studies, comprehensive master curves of storage and loss moduli, including the Rouse relaxation, entanglement plateau, and terminal regions, were not obtained. The measurement is not technically difficult, but the precise and careful measurements have not been conducted for PPC to the best of our knowledge. As a result, the plateau modulus values reported in those papers are not consistent with each other. This problem is because the PPC samples used in the previous studies have broad molecular weight distributions or low molecular weight, which made it difficult to determine the linear viscoelastic parameters correctly. In addition, the difference in the determination method of the plateau modulus in those studies also causes the variations in the modulus values.

In this paper, we prepared PPC samples with different molecular weights and relatively narrow molecular weight distributions by precipitation fractionation and investigated their linear rheology. In particular, we examined five PPC
samples, where all of them have a molecular weight of over 100 kg/mol and their distribution less than 1.5. In linear rheology, small amplitude oscillation shear measurements were conducted over wide ranges of temperatures, and some linear viscoelastic parameters such as plateau modulus were estimated.

2. EXPERIMENTAL

2.1. Materials

A commercial PPC sample was purchased from Sigma-Aldrich, and the samples with different molecular weights were prepared by precipitation fractionation. Dichloromethane (DCM) and methanol were used as the solvent and non-solvent for PPC, respectively. The supplied PPC was dissolved in DCM (i.e., 10 g in 1 L) at room temperature, and then methanol was added until the solution became turbid. Afterward, the solution was heated up to 45 °C to be transparent. The temperature was then decreased to 35 °C, and the solution was kept overnight to precipitate. The first fraction was obtained from the precipitation. We repeated this procedure for the remaining supernatant solution to obtain five different fractions. Then we immersed the precipitates in methanol and stirred vigorously to remove the low molecular weight residues. Finally, the polymer samples were dried under a vacuum for several days.

We note that PPC generally has some polyether linkage generated from the side reaction homopolymerization of propylene oxide in its structure. For this issue, we performed $^1$H-NMR measurements and confirmed that the carbonate unit content in both commercial and fractionated PPCs in this study is higher than 95 %. This result means that the amount of polyether linkage is very small in the present PPC samples.

2.2. Materials Characterization

Molecular characteristics for the fractionated PPC samples were determined by gel permeation chromatography (GPC; Shimadzu Co.) with polystyrene standards at 35 °C. Dichloromethane was used as the eluent, and the flow rate was 1 mL/min. The number and weight average molecular weights, $M_n$ and $M_w$, respectively, and the molecular weight distribution $M_w/M_n$ of the original and the fractionated PPC samples are summarized in Table I. The number in the sample codes for the fractionated samples denotes $M_w$ in the unit of kg/mol.

Differential scanning calorimetry (DSC) analysis was performed on a Q20 instrument (TA Instruments) under a N$_2$ atmosphere. The samples were first heated from −20 °C to 100 °C at 10 °C/min and then cooled to −20 °C at 10 °C/min, followed by the second heating process, which eliminates thermal history. The glass transition temperature was defined as the midpoint value of the transition in the second heating process.

Small amplitude oscillatory shear measurements were performed at various temperatures by a MCR301 (Anton-Paar) rheometer with the strain of 1 %. A parallel plate geometry with the diameter of 8 mm was used with the gap value of 1 mm. Angular frequencies $\omega$ of 0.1 – 100 rad/s were used.

3. RESULTS AND DISCUSSION

Figure 1 (a) shows the DSC profiles of the original and the five fractionated PPC samples. The glass transition temperature $T_g$ of the PPC samples estimated is listed in Table I. It can be seen that the fractionated PPC samples show higher $T_g$ values than the commercial one because the latter includes PPC oligomers as well as other low molecular weight components. In particular, propylene carbonate (PC) is generated by
the undesired backbiting reaction starting from the chain end of PPC\(^1\). We confirmed from \(^{1}H\)-NMR that the original commercial PPC includes ca. 5 wt% of PC, while the fractionated PPCs have almost no PC (data not shown).

The \(T_g\) value decreases with decreasing the molecular weight for the fractionated PPC samples. Although the value of \(T_g\) depends on the heating/cooling rate and the \(T_g\) estimation method from the DSC data, the molecular weight dependence is evident, and it follows the empirical Fox-Flory relation\(^{15}\) written as

\[
T_g = T_{g,\infty} - \frac{K_g}{M_n}
\]  

(1)

where \(T_{g,\infty}\) is the \(T_g\) value in the high molecular weight limit and \(K_g\) is a constant. Figure 1 (b) shows the \(1/M_n\) dependence of \(T_g\). Our fractionated samples (unfilled circle) exhibit an excellent linear relationship of \(T_g\) against \(1/M_n\), and the parameters in eq. 1 are determined as \(T_{g,\infty} = 44\) °C and \(K_g = 5.4 \times 10^5\) K g/mol. In contrast, the commercial PPC (filled circle) shows a considerably lower \(T_g\) value. This result strongly suggests that the low molecular weight compounds (e.g., 5 wt% of PC) in the commercial PPC, which are not reflected to \(M_n\) estimated in GPC, affect the \(T_g\).

We compare our \(T_g\) data with that reported by Li et al.\(^{16}\) earlier. See triangle in Fig. 1 (b). Note that the data by Li et al. covers a lower molecular weight range, where the decrease of \(T_g\) is observed more obviously than ours in the entire range of examined molecular weight, exhibiting the discrepancy in \(T_{g,\infty}\). Meanwhile, \(K_g\) value is essentially the same with each other. Although the exact reasons are unknown, this systematic discrepancy would be due to the measurement conditions such as heating/cooling rates as well as the estimation methods. Note also that the obtained \(K_g\) value for PPC (5.4 \times 10^5 K g/mol) is consistent with the reported values of other polymers, for which \(K_g\) values distribute within a range of \(K_g = 1 \times 10^4 - 5 \times 10^5\) K g/mol\(^{15,17,18}\).
Figure 2 (a), 2 (b) and 2 (c) show the master curves of storage modulus \(G'\), loss modulus \(G''\), and \(\tan \delta = G''/G'\), respectively, against angular frequency \(\omega\) for the fractionated PPC samples having different molecular weights. By applying the time-temperature superposition, we obtained the wide \(\omega\)-range master curves of the dynamic moduli including the Rouse relaxation, plateau and terminal regions, which have not been reported in previous studies on PPC\(^{(9-12)}\). Here, the reference temperature \(T_r\) is set as \(T_g,DSC + 60 \, ^\circ C\) to compensate the \(T_g\) difference among the samples. In the high \(\omega\) regime, the moduli, as well as \(\tan \delta\), overlap with each other for the five samples, while for the low \(\omega\), the terminal regime shifts to the lower \(\omega\) side with increasing the molecular weight. This behavior is entirely consistent with that established for other amorphous flexible polymers\(^{(4,19)}\).

In Fig. 3 (a), the horizontal shift factors \(a_T\) used for the time-temperature superposition are plotted against \(T - T_r\). All the \(a_T\) values fairly lie on a single curve expressed by the Williams-Landel-Ferry (WLF) relation written as\(^{(4)}\):

\[
\log a_T = -\frac{C_1(T - T_r)}{C_2 + (T - T_r)}
\]

with the parameter values of \(C_1 = 6.59\) and \(C_2 = 121.9\) K at \(T_r = T_g,DSC + 60\) \(^\circ C\). The \(a_T\) values for PPC reported by Lin et al.\(^{(12)}\) are also plotted for comparison. Note that Lin et al. employed \(T_r = 100\) \(^\circ C\), and we converted their data according to our choice of \(T_r\). Nevertheless, our \(a_T\) values are consistent with the earlier result. In addition to the horizontal shift, a vertical shift factor \(b_T\) was also multiplied by the moduli at each temperature to attain the best overlapping. Fig. 3 (b) shows the temperature dependence of \(b_T\). With a scattering, \(b_T\) decreases with an increase of temperature, as reported earlier for other polymers. This scattering is probably due to a small variation in the sample loading. Meanwhile, we note that the magnitude of data scattering is similar to that for \(a_T\), and it is magnified in panel (b), in which the range of the vertical axis is much narrower than that in panel (a).

Figure 4 shows a direct comparison of the dynamic moduli for PPC with similar \(M_w\) values, which are 236k in this study and 235k for Lin et al.\(^{(12)}\). Here, Lin’s data were horizontally shifted to set the reference temperature as \(T_r = T_g + 60\) \(^\circ C\). In contrast, the vertical shift was not conducted to the data. Obviously, the moduli by Lin et al. are lower than ours in the entire observation \(\omega\) range. This discrepancy cannot be compensated even if the vertical shift is considered, mainly because of the molecular weight distribution, which strongly affects the zero-shear compliance. The discrepancy may also be due to low molecular weight compounds that affect \(T_g\). Yet, further discussion is difficult because the high-frequency data were not reported in the earlier study.

From Fig. 2, the plateau modulus \(G_0^{\infty}\) and the zero-shear viscosity \(\eta_0\) for the PPC samples were estimated, and they are summarized in Table II. \(G_0^{\infty}\) was determined by two methods\(^{(7)}\); one is from the integration of \(G''\) in the terminal region,
shows a minimum, $G''$ where $\tan \delta$ is similar to that for $b_m$ molecular weight dependence, the magnitude of the variation subtracted from the overall $G''$. The other is from the $G'$ value where $\tan \delta$ shows a minimum, $G'_{\text{N,Int} - \text{min}}$. Because the $G'_{\text{N,Int}}$ values obtained in these two methods show a good agreement within an error of 10 % for our samples, $G'_{\text{N,Int}}$ values for PPC are used for further discussion hereafter.

Figure 5 (a) plots the $G'_{\text{N,Int}}$ values against the molecular weight. Although the $G'_{\text{N}}$ values in this study exhibit a weak molecular weight dependence, the magnitude of the variation is similar to that for $b_1$ reported in Fig. 3 (b). Hence, we take the average of $G'_{\text{N,Int}}$ to determine the $G'_{\text{N}}$ value for our PPC as 670 kPa. The $G'_{\text{N}}$ values reported previously$^{1, 12}$ are also plotted in Fig. 5 (a). The $G'_{\text{N}}$ data by Cao et al.$^{11}$, which were estimated by the integration method of $G''$ in the terminal region, exhibit a steep molecular weight dependence in the low molecular weight range ($M_a = 91.9 - 48.2$ kg/mol), whereas the values for two samples with higher $M_a$ are similar to ours. The $M_a$-dependence of $G'_{\text{N}}$ for small $M_a$ is consistent with the earlier studies$^{7, 8, 20, 21}$, and the high $M_a$ samples in both studies are sufficiently entangled exhibiting the saturated $G'_{\text{N}}$ value in the high-$M_a$ limit.

One may argue that small molecular weight compounds may affect $G'_{\text{N}}$. According to the Rubinstein-Colby theory$^{22}$, the plateau modulus of well-entangled solutions depends on the polymer volume fraction $\Phi$ as $\Phi^{-3}$. This theory tells that even if the sample includes 5 % of low molecular weight compounds, the decrease of the plateau modulus is just about 10 %. Although the details of the samples by Cao et al. were not described in their paper, we suppose that their samples did not include a large amount of oligomers and low molecular weight compounds.

In contrast, our $G'_{\text{N}}$ values are considerably higher than that reported by Lin et al.$^{12}$, who reported $G'_{\text{N}} = 150$ kPa according to the $G'_{\text{N,Int} - \text{min}}$ method. This discrepancy is rationalized from the comparison of $G'$ and $G''$ in Fig. 4, in which the crossover modulus between $G'$ and $G''$ reported by Lin et al. is significantly lower than our data, due to the sample polydispersity and low molecular weight compounds.

To demonstrate that the variation of our $G'_{\text{N,Int}}$ with respect to $M_a$ is within a reasonable experimental error, in Fig. 5 (b), we compare the normalized plateau modulus of PPC in this study with that of other flexible amorphous polymers: polybutadiene (PBD), polyisoprene (PI), and polystyrene (PS)$^7$. Here, for our PPC, $G'_{\text{N,Int}}$ is normalized by the averaged $G'_{\text{N}}$ value for the five samples ($= 670$ kPa). The reported data for PBD, PI, and PS data are also normalized by the average $G'_{\text{N}}$ value among the samples with different molecular weights$^7$, that is, 1.16 MPa for PBD, 0.38 MPa for PI and 0.195 MPa for PS. The normalized $G'_{\text{N}}$ values for PPC are within a similar scattering with the other polymers.

According to Ferry’s book$^4$, the entanglement molecular weight $M_e$ can be calculated from the plateau modulus as follows.

$$M_e = \rho RT / G'_{\text{N}}$$

(4)

Here, $\rho$ is the melt density, for which we employ the value reported earlier$^{22}$ as $\rho = 1.26$ g/cm$^3$ at room temperature. Note that here we do not consider the temperature dependence of $\rho$ assuming that the variation is not large as reported for other polymers$^{39}$. For $G'_{\text{N}}$, we use the averaged value determined as 670 kPa. The resultant $M_e$ value with $T = 100$ °C is calculated to be 5.9 kg/mol. The $M_e$ value of PPC in this study is evidently lower than that reported by Lin et al. (21.2 kg/mol)$^{22}$ because of the difference in $G'_{\text{N}}$ values as explained above. Note also that the previous study$^{12}$ considered the prefactor of 4/5 in eq 4 to estimate $M_e$ based on the

| Sample       | $10^{-5}G'_{\text{N,Int}}$ | $10^{-3}G'_{\text{N,Int} - \text{min}}$ | $Z$ | $10^{-5}\eta_0$ |
|--------------|-----------------------------|----------------------------------------|-----|-----------------|
| PPC460k      | 6.4                         | 6.2                                    | 78  | 300             |
| PPC361k      | 6.5                         | 6.2                                    | 61  | 140             |
| PPC236k      | 7.1                         | 6.7                                    | 40  | 32              |
| PPC144k      | 6.9                         | 6.2                                    | 24  | 4.5             |
| PPC105k      | 6.3                         | 6.0                                    | 18  | 1.6             |

* Estimated from eq. 3 at $T_g + 60$ °C. * Estimated from the $G'$ value where $\tan \delta$ is minimum. * Calculated from $Z = M_e / M_a$ . * Estimated from eq. 5 at $T_g + 60$ °C.
Doi-Edwards theory\textsuperscript{5}). Nevertheless, according to the $M_e$ value thus determined, we confirmed that our PPC samples have the entanglement numbers $Z = M_w / M_e$ within a range of $18 - 78$ as tabulated in Table II.

The zero-shear viscosity $\eta_0$ for the five PPC samples is determined from the following relationship:

$$
\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad \text{at} \quad T = T_g + 60 \ ^\circ\text{C} \quad (5)
$$

Figure 6 shows the molecular weight dependence of $\eta_0$, in comparison with various kinds of polymers such as PBD, PI, and PS\textsuperscript{19,24-28}. Here, the horizontal axis is normalized by $M_e$ and the vertical one is normalized by the critical viscosity $\eta_c$, which is the viscosity for the sample with the critical molecular weight defined as $2M_e = M_c$. We used $M_e = 2M_c = 11.8$ kg/mol and $\eta_c = 62$ Pa s, where the latter is estimated from the $\eta_0 - M_w$ dependence of our PPCs. Our PPC data exhibits $\eta_0 \propto M_w^{3.6 \pm 0.2}$ dependence, which is consistent with the established $M_e^{3.4}$ dependence\textsuperscript{4} within an error. Indeed, our PPC data overlaps well with the literature data.

Finally, the universality of the master curves of $G'$ and $G''$ for our PPC is examined by comparison to those predicted by the Likhtman-McLeish (LM) model\textsuperscript{6}). This model is the quantitative theory for linear dynamics of linear monodisperse entangled polymers based on the de Gennes-Doi-Edwards reptation model\textsuperscript{5,29}). The details of this model are explained elsewhere\textsuperscript{6}). According to the theory, we can describe the linear viscoelasticity of entangled polymers using four parameters, i.e., the unit modulus $G_e$, the Rouse relaxation time of one entanglement segment $\tau_e$, the number of entanglement per chain $Z_{LM}$, and the constraint release parameter $c$. As shown in Table II, our PPC samples are reasonably entangled, and in this regard, the LM model is applicable.

Figure 7 (a) and 7 (b) show the normalized $G'/G_e$ and $G''/G_e$ data, respectively, against the normalized $\omega\tau_e$ for the five PPC samples compared with the LM model predictions\textsuperscript{6}). We determined the two parameters, $G_e = 900$ kPa and $\tau_e = 2.0 \times 10^{-4}$ s, to fit the data for the two highest $M_w$ samples (i.e., PPC460k and PPC361k) in the plateau and Rouse relaxation regions. Then we determined the value of the characteristic molecular weight as $M_{e,LM} = \rho RT / G_e = 4.3$ kg/mol.

Note that $G_e$ is different from and higher than $G_N$, and the resultant entanglement molecular weight $M_{e,LM}$ is smaller than $M_e$ as established earlier. From $M_{e,LM}$, we obtained $Z_{LM} = M_w / M_{e,LM}$, which is larger than $Z$ shown in Table II. In principle, we have to use $Z_{LM}$ to draw the theoretical curves. However, we found that the use of $Z$ instead of $Z_{LM}$ attains better agreement with the experimental results. Such a
separate optimization of $G_e$ and $Z_{LM}$ has been made by Auhl et al.\textsuperscript{30} for monodisperse polyisoprenes. We chose the remaining parameter $c_{\nu} = 1$, and the results are shown in Fig. 7. PPC data exhibit a good agreement with the model from the high to middle $\omega\tau_e$ range, while in the low $\omega\tau_e$ regime, the data shows slightly slower and broader terminal relaxation. This slower relaxation is due to the molecular weight distributions of the PPC samples used in this study. Concerning the value of $c_{\nu}$, $c_{\nu} = 1$ is used for the best fitting of polystyrene and polybutadiene\textsuperscript{6} and $c_{\nu} = 0.1$ for polyisoprene\textsuperscript{30}. Note that $c_{\nu}$ is the fitting parameter, which depends on the fitting procedure, and the difference of $c_{\nu}$ could be compensated by other parameters. We also note that our samples are not monodispersed, and the molecular weight distribution affects the parameter determination.

4. CONCLUSION

The linear viscoelasticity of the fractionated PPC samples with the narrow molecular weight distributions and different molecular weights was studied. $G_0^*$ of PPC was obtained as 670 kPa, and $M_c$ as 5.9 kg/mol. These values are significantly different from those reported previously\textsuperscript{12}. The discrepancy is because the examined PPC samples have narrow molecular weight distributions, which is clearly different from the previous studies on PPC\textsuperscript{6-12}. The linear viscoelasticity and its characteristic values of our PPC samples are consistent with the other polymers, demonstrating the validity of the obtained viscoelastic data.

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