Chapter 4. RESULTS AND ANALYSIS

4. 1 Complex dielectric permittivity

4.1.1 Dielectric spectra

The complex dielectric function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$ relates the polarization **P** with the strength of a macroscopically averaged electric field **E** in a medium,

$$\mathbf{P} = [\varepsilon^*(\omega)-1]\mathbf{E} = \chi^*(\omega)\mathbf{E}, \qquad (4.\ 1)$$

where $\chi^*(\omega)$ is the dielectric susceptibility. The response of the polarization **P** to **E** can be separated in a fast ($\tau < 10^{-12}$ sec) and slow ($\tau > 10^{-12}$ sec) electronic contribution which originates from the orientation of dipoles.

A description of the relaxation spectra in glass-forming materials is still an active topic despite the great effort made in recent years. There are two well known functions that slow relaxation obey in frequency and time domain, so called Havriliak-Negami (HN) [33] and Kohlrausch-Williams-Watts (KWW) [44] function, respectively.

4.1.1.1 Expression in frequency domain

Assuming a simple exponential decay function of the polarization $\mathbf{P}(t) = \exp(-t/\tau)$, this results in the Debye formula for the complex dielectric function,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + i\omega\tau}, \qquad (4.\ 2)$$

where $\varepsilon_\infty = \varepsilon'(\omega)$ for higher limit of $\omega \gg \tau^{-1}$ and $\varepsilon_s = \varepsilon'(\omega)$ for lower limit of $\omega \ll \tau^{-1}$. τ is the relaxation time and $\varepsilon_s - \varepsilon_\infty$ is the dielectric strength $\Delta\varepsilon$.

Relaxation features are usually broaden and have a distribution of relaxation time. This can be described quantitatively by generalized relaxation function called the HN equation [33],

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\gamma}, \qquad (4.\ 3)$$

where α and γ are shape parameters denoting the symmetric and asymmetric broadening

of the relaxation function. The relaxation time τ depends to some extent on the shape parameters α and γ, respectively. It is closely related to the relaxation time τ_{max} with $\tau_{max} = (2\pi f_{max})^{-1}$, where f_{max} is the frequency at maximum dielectric loss of the relaxation function.

The broadband dielectric function is commonly described by the superposition of some relaxation processes which can be expressed in terms of HN functions and dc conductivity σ_{dc}.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_i \frac{\Delta\varepsilon_i}{[1+(i\omega\tau)^{\alpha_i}]^{\gamma_i}} - i\frac{\sigma_{dc}}{\omega\varepsilon_0}, \qquad (4.4)$$

where i = 1, 2, or 3 etc., and each relaxation time of each relaxation mode has a relationship of the type $\tau_1 < \tau_2 < \tau_3 \cdots$. The dc conductivity originates from the presence of charged impurities and is revealed at the lower frequency side of the dielectric loss.

Fig. 4.1 shows the dielectric losses, $\varepsilon''(f = \omega/2\pi)$, for nPrOH, as an example, at various temperatures against frequency f. The numbers above the spectra represent the measured temperatures. These spectra were normalized against the values, ε''_{max}, at the maximum peak position, f_{max}.

4.1.1.2 Expression in time domain

The decay of polarization is linked with the complex dielectric function through a half-sided Fourier transform,

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_S-\varepsilon_\infty} = \int_0^\infty e^{-i\omega t}[-\frac{d\psi(t)}{dt}]dt, \qquad (4.5)$$

where $\Psi(t)$ is the decay function. Assuming non-interacting dipoles in the materials under study the $\Psi(t)$ is equivalent to the correlation function of a fluctuating dipole $\mu(t)$,

$$\psi(t) = \frac{<\mu(0)\mu(t)>}{<\mu(0)\mu(0)>}, \qquad (4.6)$$

where the brackets indicate the ensemble average.

Relaxation which is not described by a simple exponential decay can be often fitted by the KWW function [44], which is also called a "stretched exponential ",

$$\phi(t) = \exp(-t/\tau)^{\beta_{KWW}} \qquad (4.7)$$

4.1.1.3 Relationship between HN and KWW functions

To some extent, the HN description in the frequency domain is equivalent to the KWW approach in the time domain. The connection among the parameters of the HN and the KWW functional forms has been suggested by the fact that both functions yield an accurate description of real data [45]. There are following analytical relations,

$$\ln[\frac{\tau_{HN}}{\tau_{KWW}}] = 2.6(1-\beta_{KWW})^{0.5}\exp(-3\beta_{KWW}), \quad (4.8)$$

for the characteristic times and

$$\alpha\gamma = \beta_{KWW}{}^{1.23}, \quad (4.9)$$

for the shape parameters. It is important to note that the HN function has four independent variables, while the latter has only three.

4.1.2 Dielectric strength

The temperature dependence of the dielectric strength, $\Delta\varepsilon(T) = \varepsilon'_s(T) - \varepsilon'_\infty(T)$, is shown for iPrOH in Fig. 4. 2 as an example. The dielectric strength is obtained from the fit of the HN equation. It is the difference of the dielectric constant between the lower and higher frequency limit or the integrated area of the dielectric loss.

The dielectric strengths obtained from the Impedance/Gain-phase analyzer was calculated using the earlier reported results and are in agreement with those determined by the TDR system.

It is found that the main $\Delta\varepsilon(T)$ for all kinds of material in this study can be well described by the modified Onsger equation,

$$\Delta\varepsilon(T) = -A + B/T \quad (4.10)$$

According to Eq. (4. 10), it should be noticed that the extrapolation of $\Delta\varepsilon(T)$ indicates no divergence at 0 K due to the existence of A. The case of A = 0 is usually called Onsager's law. The negative sign of A in Eq. (4. 10) is an indication that the molecular behavior of alcohols in this study is not free but cooperative each other, so that the experimental values are deviated from the prediction of Onsager's law. If the second term can be expressed by B/(T-To) or B/(T-TK), where To = TK, it is called as Curie-Weiss law. It is not fulfilled for alcohols even if the relaxation frequency looks like diverging at To.

4.1.3 Temperature dependence of relaxation

As shown in Fig. 4. 1, the loss peak broadens and the maximum shifts to lower frequency when temperature decreases. Involving the cooperative behavior between molecules, the shift rate of the f_{max} against temperature, namely inverse relaxation time τ, is one of the important topics in the study of liquid-glass transition. The temperature dependence of the different relaxation frequency is complex and not at present completely understood. There are common expressions for the temperature dependent relaxation obtained from the viscosity measurements, NMR system, light scattering, dielectric spectroscopy [3, 5].

The most widely used empirical expression is that established by VTF [46],

$$f_{max} = f_0 \exp [-B/(T-T_0)], \qquad (4.\ 11)$$

where T_0 (> 0 K) is the Vogel-Fulcher temperature where the relaxation frequency diverges. This VTF expression was derived theoretically in terms of CRR by Adam and Gibbs [9] or free volume [7] as explained in detail in the Chapter 2. According to the Adam and Gibbs, the VTF law is equivalent to the Williams-Landel-Ferry (WLF) expression [8].

When $T_0 = 0$ in VTF expression, it can result in the Arrhenius (ARR) expression,

$$f_{max} = f_0 \exp (-E/T), \qquad (4.\ 12)$$

where E is the activation energy. This ARR expression is the result of thermal activation feature.

There is an expression which stems from the mode coupling theory (MCT) [17],

$$f_{max} = A (T - T_c)^{\gamma}, \quad \gamma > 0 \qquad (4.\ 13)$$

This expression is valid only above T_c.

It is very hard to make only a dynamic scenario to cover the entire liquid and supercooled region. The above Eqs. (4. 11), (4. 12) and (4. 13) have their own range of validity. Which model can well express the behavior in the specific temperature range unambiguously and precisely? The method of temperature derivative analysis was employed to determine the temperature dependence of relaxation [47]. For instance, the VTF expression can be linearized by the following derivative equation:

$$[-d\log(f_{max})/d(1/T)]^{-1/2} = (T - T_0)B^{-1/2} \qquad (4.\ 14)$$

The parameters, B and T_0, and fitting range are precisely determined with the aid of the representation $[-d\log(f_{max})/d(1/T)]^{-1/2}$ vs. 1/T. In the case of $T_0 = 0$, this relationship is reduced to ARR expression and appears as a horizontal line.

In the observed temperature windows as shown in Fig. 4. 3, an expression of linear dependence of Eq. (4. 14) against 1/T in the lower temperature ranges was obtained. In

the higher temperature range where the line deviates from the extrapolation of the VTF law, ARR fitting is applied.

4.2 Complex heat capacity

The typical real and imaginary schemes of complex heat capacity $C_p^*(\omega, T) = C_p'(\omega, T) - iC_p''(\omega, T)$ for PG and tPG are shown in Figs. 4. 4a) and b), respectively. These scans were carried out in the condition of 5 K/min underlying heating rate, 100 sec modulation period and 1.33 K modulation period. The conventional heat capacity with 5 K/min heating rate is identical to the value of $|C_p^*| = (C_p'^2 + C_p''^2)^{1/2}$ in this case.

As shown in Fig. 4. 4 a), the real part of heat capacity has an abrupt increase near T_g which reveals the increase of the degree of freedom in the supercooled state. The midpoint of the $|C_p^*|$ was traditionally defined as the calorimetric glass transition temperature T_g. It is ambiguous to define the end point of glass transition due to the small increase of $|C_p^*|$ near the end point.

The imaginary part of heat capacity has a peak at T_g as illustrated in Fig. 4. 4 b). The peak position corresponds to the glass transition temperature. The broadening of the peak is related to the resolution of the equipment as explained in Chapter 3.

4.3 Glass transition temperature

The glass transition usually can be obtained from the calorimetric measurement. In the conventional manner, the midpoint of the $|C_p^*|$ is T_g. In MDSC version, on the other hand, the peak of imaginary heat capacity can be defined as T_g. This T_g is called as the calorimetric glass transition temperature.

There are other kinds of definition for Tg from the mechanical or relaxation point of view. The temperature, where the viscosity reaches 10^{13} poise or the relaxation time is 100 sec, is also defined as the glass transition temperature for the engineering use.

Fig. 4. 5 shows the relationship between the calorimetric T_g and dielectric T_g where dielectric relaxation time is 100 sec. The dielectric T_g was calculated from the extrapolation of the VTF fitting in the lower frequency range. Whereas the calorimetric T_g includes total degree of freedom such as rotation or diffusion, the dielectric T_g originates

only from the α relaxation. Two glass transitions lie within the experimental uncertainty. This strongly indicates that the glass transition in alcohol is related to the α relaxation phenomenon.

4.5 Combination of Adam-Gibbs theory and the domain model

Domain model proposed by Matsuoka et al. [10] originated from the idea of cooperative motion between molecules and supports the VTF law. From the identification of the VTF expression from Adam-Gibbs theory and domain model, the parameters in these equations may be determined by comparing them. The VTF expression from Adam-Gibbs theory contains the calorimetric information and the VTF from the domain model contains dielectric information.

The VTF equation for relaxation frequency comes from the following equation,

$$\ln\frac{f_{max}}{f_0} = -\frac{\Delta\mu^*}{R}\frac{1}{T-T_0}, \qquad (4.\ 15)$$

where $\Delta\mu^*$ is the activation energy for independently relaxing conformers or Vogel-Fulcher energy in kcal/mol, which is expressed as the repeat chain unit in the case of oligomers or polymers and R is the gas constant. $\Delta\mu^*$ is related to the $\Delta\mu$ which is the total activation energy including intermolecular interaction with the following relationship:

$$\Delta\mu^* = \Delta\mu\frac{T^*-T_0}{T^*}, \qquad (4.\ 16)$$

where T* is the temperature where the relaxation time is 3×10^{-11} sec.

From the comparison between Eqs. (4. 11) and (4. 15), the parameter B is related to the activation energy in following way:

$$B = \frac{\Delta\mu^*}{R} = \frac{\Delta\mu}{R}\frac{T^*-T_0}{T^*} \qquad (4.\ 17)$$

The relationship between the heat capacity change at Tg, $\Delta C(T_g)$, and the fragility was discussed by Angell [2, 13] and Hodge [48]. For VTF equation, the Adam-Gibbs relation between $\Delta C(T_g)$ and B is

$$\frac{B}{T - T_0} = \frac{s^* \Delta\mu}{RTS_c(T)}, \tag{4. 18}$$

where s* is the minimum configurational entropy required for the rearrangement larger than Rln(2), $\Delta\mu$ is the activation energy hindering the rearrangement of one mol of conformers and $S_c(T)$ is the configurational entropy. To calculate $S_c(T)$, the hyperbolic postulation, $\Delta C_p(T) = T_g\Delta C_p(T_g)/T$, was used, i.e., the configurational entropy is

$$S_c(T) = \int_{T_0}^{T} \frac{\Delta C_p(T)}{T} dT = \int_{T_0}^{T} \frac{T_g \Delta C_p(T_g)}{T^2} dT \tag{4. 19}$$

For the linear approximation of heat capacity at glass and liquid state, $C_{pg}(T) = A_g + B_gT$ and $C_{pl}(T) = A_l + B_lT$, the difference in heat capacity is $\Delta C_p(T) = (A_l - A_g) + (B_l - B_g)T$. For the several calorimetric fitted values by both $\Delta C_p(T) = T_g\Delta C_p(T_g)/T$ and $\Delta C_p(T) = (A_l - A_g) + (B_l - B_g)T$, it is noted that there were no significant differences in either the quality of the fits or the values of the fitting parameters [49].

From the Eqs. (4. 18) and (4. 19), the parameter B is

$$B = \frac{s^* \Delta\mu T_0}{RT_g\Delta C_p(T_g)} \tag{4. 20}$$

From the comparison between the two equations, i.e., from both dielectric and thermal, Eqs. (4. 17) and (4. 20), s* can be derived,

$$s^* = \frac{T_g \Delta C_p(T_g)}{T_0} \frac{T^* - T_0}{T^*} \tag{4. 21}$$

The minimum configurational entropy for a mol of conformer s* is

$$s^* = R \ln (W), \tag{4. 22}$$

where W is the number of states that a conformer can take.