Award Lecture Article

Control of Strain Hardening of Polymer Melts under Elongational Flow

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This paper includes two topics on the nonlinear elongational flow behavior from the viewpoints of a small amount of long relaxation time mode and physical gelation network structure. First one is polypropylene (PP). PP is a well-balanced material in terms of the physical properties such as the stiffness and heat resistance, and the cost. PP is, however, one of the linear polymers exhibit low melt strength and weak strain hardening. We focused on an introduction of a small amount of high molecular chain in order to enhance the strain hardening under elongational flow. This system showed unusual rheological behavior: strong elasticity, two-step nonlinear damping, strong strain hardening. This polymer system is very complex comparing with conventional PP in terms of the miscibility of the matrix and ultra-high molecular weight component. Another is poly(vinyl chloride)(PVC)/plasticizer systems. PVC forms physical gels in various solvents. We focused on the rheological behavior of high PVC concentration systems, since the physical properties and structure have been extensively studied mainly for low polymer concentration system. PVC/DINP system showed same relaxation exponent n with the value of the low concentration system reported previously. We observed change of the elongational flow behavior of sol-gel system such as PVC/plasticizer system with temperature. These behaviors from the view point of critical gelation phenomena has not been reported so far as much as we know.

Key Words: Elongational viscosity / Strain hardening / Polypropylene / Poly(vinyl chloride) / Physical gel

1. INTRODUCTION

Numerous efforts have been made on the study of the shear and elongational properties of polymer melts. The characteristics are used to describe the physical properties of a polymeric material so that we know what to expect when the polymer is processed by injection molding, film (or sheet) extruding, fiber-spinning apparatus. The two basic flows are used to characterize polymers: shear and shear-free flows. Usually polymer processings are a combination of these flows or sometimes are dominated by one or the other. The shear flow properties can be reported in many cases by manufactures and fabricators. Only this characteristic is sometimes insufficient for the processings to provide a complete picture of the relationship between the processability and the flow behavior when underwent free-surface processes in which the shape and thickness of the extrudate are determined by the rheological properties of the melt, the die dimensions etc. Therefore, we have focused attention on the melt rheology control and its processability. In this paper the methodology of control of elongational flow is discussed for two polymers. One example is PP which typically has very weak strain hardening. Large enhancements of the melt strength of

polypropylene (PP) were achieved by the introduction of high molecular weight polyethylene (PE) into PP. The viscoelastic properties of the high-melt-strength PP melts under shear flow were investigated. It was found that the rheological properties of the high-melt-strength PP were distinctly different from those of conventional PP. Another case is poly(vinyl chloride) (PVC)/ plasticizer system. PVC forms physical gels in various solvents. The dynamic viscoelasticity and elongational viscosity were measured for the relatively high polymer content system which is similar to commercial PVC compounds. The elongational behavior of PVC gels was studied in terms of critical sol-gel transition temperature. This paper is based in part on the papers presented previously.¹⁻³⁾

2. BIMODAL MOLECULAR WEIGHT DISTRIBUTION OF PP

Large amounts of polypropylene (PP) have been produced globally and applied to a wide range of products because of its various excellent properties, such as high stiffness and good heat and chemical resistances. PP is, however, one of the linear polymers that exhibit low melt strength and weak strain-hardening behavior. Thus, the resin has been difficult

to process with certain processing methods dominated by elongational flow, generally unsuitable for blow molding, foaming, and thermoforming. A representative methodology to improve the elongational behavior is an addition of long-chain branching or grafting onto backbone species.⁴⁻⁶⁾ It is possible to produce modified PP containing long side branches by the irradiation of an electron beam and the addition of peroxide, though PP usually has a tendency to decompose under a presence of radicals. Another option for improving the melt properties of a polymer is introducing a small quantity of high molecular weight components like a spike into a normal molecular weight distribution. Effect of high molecular weight component on the rheological properties was reported by some researchers.⁷⁻⁹⁾ Minegishi et al.⁹⁾ found that a large enhancement of the strain hardening could be obtained for polystyrene (PS) to which was added anionic PS with high molecular mass. When the concentration of the high molecular weight components reaches or exceeds the critical concentration for the entanglement of molecular chains, the strain-hardening property is distinctly enhanced. In these studies, the high molecular weight components were blended uniformly in a solvent with low molecular weight materials. With respect to PP, there was not successful report on enhanced melt properties via a small amount of high molecular weight components. In this study, high molecular weight PE was introduced as the long relaxation component in the polymerization process with a heterogeneous catalyst. This polymer system would be much complex than a simple mixture of amorphous resin blended with its analogous resin with a higher molecular weight because the polymer system consisting of PP and PE has been regarded as immiscible at least in the quiescent state. Here the effect of a small amount of ultra-high molecular weight component on the shear and elongational behaviors was studied.

2.1 Materials

All the samples (conventional PP and Newstren/Newfoamer of high-melt-strength PP grades) were supplied by Chisso Petrochemica Co. (Chiba, Japan). PP-A is conventional homogeneous polymer, and PP-B-D are high-melt-strength PPs with high molecular weight component. The intrinsic viscosity of the high molecular weight component is 26 dL/g in tetralin at 135 °C. The content of the high molecular weight component of PP-B and C is 0.4 and 1.0 wt%, respectively. Figure 1 indicates the results of gel permeation chromatography (GPC) for PP-A, PP-B, and PP-C. The average molecular weights of PP-B and PP-C were similar to those of PP-A. Figure 1 shows a single peak and monomodal

curve, and so the peak of the high molecular weight component was detected for neither PP-B nor PP-C, resulting from that the level of the content was outside the limits of the measurements.

2.2 Dynamic Viscoelasticity

The samples were stable at 180 °C, as there were no changes in G' throughout the duration (~10 h) of the experiments. Figure 2 shows G' plotted as a function of frequency for PP samples. Even for a double-log plot of conventional PP (PP-A), the terminal flow regime where G' and G'' are proportional to ω^2 and ω , respectively, was not obtained within the frequency range examined. G' of PP-B and PP-C was significantly higher at low frequencies in comparison with that of PP-A and slightly lower than that of PP-A at relatively high frequencies. The height of the shoulder increased with the increasing content of uhmw PE. Figure 2 also exhibits an increase in the elastic response at low frequencies of high-melt-strength PP (PP-B and PP-C), that is, a decrease in $\tan \delta$. With decreasing frequencies, $\tan \delta$ curves of PP-B and PP-C culminated in

Fig. 1. Molecular weight distribution curves of PP-A, B and C.

Fig. 2. G' (left y axis, closed symbols) and $\tan \delta$ (right y axis, open symbols) curves plotted against the frequency measured at 180 °C for PP-A, PP-B, and PP-C.

the vicinity of 10^{-2} rad/s, whereas that of PP-A kept rising. The complex viscosity $|\eta^*|$ of PP-B and PP-C showed a slight increase below 10^{-2} rad/s. The activation energies of flow E_v were estimated by an Arrhenius plot of the shift factor against the reciprocal of the absolute temperature. The high activation energy can be related to a chain structure such as long-chain branching or a (partially) crosslinked structure. E_v values of PP-B and PP-C (37–38 kJ/mol) are almost the same as that of PP-A (38 kJ/mol). These values are significantly lower than that of long-chain-branching PP (55 kJ/mol), which was reported by Kurzbeck et al.¹⁰ for modified PP with electron-beam irradiation.

2.3 Nonlinear Stress Relaxation

Figure 3 shows the nonlinear relaxation modulus $G(t, \gamma)$ of PP-A for $\gamma = 0.3$ –6. The solid line represents the relaxation modulus in the linear regime, $G(t)$, which can be written by a sum of exponential functions as

$$G^0(t) = \sum_{i=1}^N G_i \exp(-t/\tau_i) \quad (1)$$

where τ_i and G_i are the i th relaxation time and corresponding relaxation strength, respectively, determined from dynamic viscoelastic measurements. In Figure 6, we note agreements between $G(t)$ and $G(t, \gamma)$ for a strain of 0.3 over the entire measurement time. Qualitative features observed in Figure 3 are similar to those already well known. When the shear strain was smaller than a certain values (0.5 in this article), $G(t, \gamma)$ was independent of γ over the entire range of time, representing $G(t)$ in the linear viscoelastic region. With an increasing magnitude of strain γ , $G(t, \gamma)$ decreased over the entire time range. We indicate the stress relaxation behavior of PP-C as an example of PP containing small amounts of high

molecular mass chains. The non-linear relaxation moduli for PP-C are shown in Figure 4. $G(t, \gamma)$ for $\gamma = 0.3$ agreed with the linear function $G(t)$ evaluated with eq 1. When calculating $G(t)$ of PP-B and PP-C, authors have assumed a long relaxation mode (at $\tau = 10^5$ s) that is not observed for PP-A. The relaxation spectrum fitted the dynamic data well. Within a short time ($<10^2$ s), $G(t, \gamma)$ in all of the strains imposed here decreased monotonically as a function of time, and the shape was almost the same as that of PP-A. Note that the feature of $G(t, \gamma)$ for PP-C was distinctly different from that of PP-A over a certain time. Within a longer time region ($>10^2$ s), two-step relaxation processes attributed exclusively to the long relaxation mode were observed for the whole strain range examined. A similar behavior was obtained also for PP-B, although it is not shown here. We refer to the first relaxation step as the fast process and the second step as the slow process. These behaviors are observed for blends of styrene-isoprene diblock copolymers with homopolyisoprene.¹¹

2.4 Damping Function

It is important to note the dependence of the nonlinear modulus on strain. For large γ , $G(t, \gamma)$ deviated downward from $G(t)$. The amount of the decrease in $G(t, \gamma)$ for PP-A was almost independent of time. $G(t, \gamma)$ was still kept in shape if γ increased and the modulus was factorable into strain- and time-dependent functions; $G(t, \gamma) = G(t)h(\gamma)$, where $h(\gamma)$ is called the damping function. $h(\gamma)$ is a universal function of γ for a entangled flexible polymer with a narrow MWD and is independent of the molecular weight and concentration. For PP-B and PP-C, $G(t, \gamma)$ can be factored by the linear stress relaxation modulus at fast and slow relaxation processes:

$$G(t, \gamma) = G(t) h_f(\gamma) \quad (2a)$$

$$G(t, \gamma) = G(t) h_s(\gamma) \quad (2b)$$

Fig. 3. $G(t, \gamma)$ of PP-A at 180 °C for various strains, 0.3, 0.5, 0.7, 1, 2, 4, and 6, from top to bottom. The solid curve represents $G(t)$ determined from the dynamic viscoelastic data.

Fig. 4. $G(t, \gamma)$ of PP-C at 180 for various strains, 0.3, 0.5, 0.7, 1, 2, 4, and 6, from top to bottom. The solid curve represents $G(t)$ determined from the dynamic viscoelastic data.

where $h_f(\gamma)$ and $h_s(\gamma)$ are the damping functions at fast and slow steps, respectively.

The damping function of PP-A, PP-B, and PP-C are presented in Figure 5. $h_f(\gamma)$ of PP-A showed a slightly weaker dependence on strain than that predicted by Doi and Edwards¹²⁾ for a sharply distributed polymer. This may be due to the polydispersity of the polymer. For PP-B and PP-C, the fast and slow relaxation processes were observed over the entire range of γ . The nonlinear damping function for $h_f(\gamma)$ of PP-B and PP-C coincided with $h(\gamma)$ of PP-A. The strain dependence of $h_s(\gamma)$ was distinctly weaker than $h_f(\gamma)$, as shown in Figure 8. This demonstrates the presence of two different relaxation modes in PP-B and PP-C. This should be exclusively attributed to the motion or relaxation of very high molecular weight PE, as discussed later.

2.5 Uniaxial Elongational Viscosity

For uniaxial elongational viscosity the rod-like sample was used. Figure 6 (a) and (b) illustrate $\eta_E^+(t, \dot{\epsilon})$ for various $\dot{\epsilon}$ at 180 °C for PP-A and -C, respectively. The solid lines in the figure are the 3-fold linear viscosities $3\eta^+(t)$. The elongational viscosities of PP-A increased smoothly for various elongational strain rates. There was no upward deviation from the linear viscosity within the strain rate measured; $\eta_E^+(t)$ was independent of the strain rates. $\eta_E^+(t)$ of PP-A had a tendency to follow the linear viscoelasticity rule: $\eta_E^+(t) = 3\eta^+(t)$ in the limit of steady state ($t \rightarrow \infty$). Likewise, $\eta_E^+(t)$ for PP-B and -C increased smoothly with time within small strains. These samples which contain a small amount of PE with high molecular weight, however, exhibited remarkable upward deviations in η_E^+ called “strain hardening”, depending on the elongational strains. This is unexpected behavior for conventional linear PP as mentioned before.

Fig. 5. Comparison of $h(\gamma)$ of PP-A and $h_f(\gamma)$ and $h_s(\gamma)$ for the fast and slow relaxation processes of PP-B and PP-C, respectively. The solid line represents $h(\gamma)$, as predicted by Doi and Edwards¹²⁾, for a polymer with a narrow MWD.

2.6 Temperature Rising Elution Fractionation

To further discuss the relationship between the rheological properties and the role of uhmw PE for high-melt-strength PP consisting of two components with different crystallizabilities (i.e., PP and PE), we performed TREF for PP containing 0.9 wt % high molecular weight PE ($[\eta] = 26$). TREF is a technique for separating a semicrystalline polymer according to differences in the molecular structure or composition. The fractions were collected at predetermined temperatures (ranging from 10~130 °C) intervals and were recovered by evaporation of the ortho-di-chlorobenzene and drying *in vacuo*. As shown in Table I, the sample was fractionated into nine fractions according to the crystallization temperature of each component at elution temperatures. The presence of PE was seen in Fr. 3 and 4 with DSC analyses, although the whole polymer before fractionation did not reveal the presence of PE. Figure 7 shows the DSC thermograms of Fr. 3 and 4. The presence of PE was seen in Fr. 3 and 4 with DSC analyses, although the whole polymer before fractionation did not reveal the presence of PE. In Table I, the peaks correspond to the melting points of PE (~130 °C) and PP (~149 °C, Fr.3; 160 °C, Fr. 4) with low tacticity. Figure 8 indicates the results of high temperature (HT)-GPC of Fr. 3, which showed a larger

Fig. 6. Variation of transient uniaxial extensional viscosity with time at constant strain rates and temperature of 180 °C for (a) PP-A and (b) PP-C. The solid line indicates 3 times the dynamic viscosity, $3\eta^+$, at 180 °C.

melting enthalpy corresponding to PE than that of Fr. 4. The bimodal curve can be clearly seen. It is reasonable to suppose that the peak at a higher molecular weight in Fr. 3 corresponds to PE from the results of DSC and HT-GPC.

A Fr. 5-9 mixture, in which PE was not detected by DSC, was again dissolved and mixed in solvent. TEM micrograph of Fr. 5-9 exhibits morphology typical of conventional PP, that is, a lamellar structure without a domain. The result of the dynamic testing is presented in Figure 9. This fractionated sample (a Fr. 5-9 mixture) distinctly exhibits a high elastic response at low frequencies, characterizing the viscoelastic behaviors of PP-B and PP-C, although the presence of PE was not detected by DSC and TEM for Fr. 5-9. This behavior is unexpected for conventional PP. The results found here support our hypothesis discussed previously; the shoulder of the high-melt-strength PP cannot be related to the PE domain. Thus, we conclude that the PE chains (less than half the amount of the whole polymer) dissolved in PP cause the unusual rheological properties of the high-melt strength PP, such as the second plateau and weak damping, and that the domain structure assigned to PE is almost independent of the long relaxation mode.

Table I. Molecular characteristics and melt properties of PP samples.

Code	$[\eta]^a$ dl/g	PE content wt%	$[\eta]^b$ dl/g	MFR g/10min	$\bar{M}_w/10^5$	$\bar{M}_w/\bar{M}_n$	T_m^c °C	Melt strength cN	Ev kJ/mol
PP-A	-	-	3.1	0.4	5.4	4.7	166	4.7	38
PP-B	26	0.4	3.0	0.3	5.0	5.1	167	9.3	38
PP-C	26	1	3.0	0.4	5.0	4.4	166	n.d. ^d	37
PP-D	26	0.9	-	4.8	2.7	4.0	166	6	-

a: Intrinsic viscosity in tetralin at 135 °C of polyethylene.

b: Intrinsic viscosity in tetralin at 135 °C of whole polymer.

c: Melting temperature obtained from DSC thermogram.

d: not determined owing to rupture.

Fig. 7. MWD curves of neat PP, Fr. 3 and 5-9.

2.7 Estimation of the High-Molecular-Weight Chain Stretching

As the data in Figure 6 illustrated, PP-B and -C have a large strain hardening. The distinct strain hardening of the PP-B and -C suggest entanglement of PE with high molecular mass. Enhancement of the strain hardening via the high molecular weight chain is valid only for the miscible system. PP and PE are generally believed to be an immiscible system, at least under the quiescent state. The results (in part 1 and this study), however, implied the presence of dissolved PE chains into PP and phaseseparated PE (domains). It is reported that the phase dissolution is induced by high shear flow field in an injection machine even for PP and PE.⁴² However, PP-B and PP-C did not undergo such high shear flow. The unusual flow behavior cannot be attained by a simple mixing via an extruder. One possible explanation could be that high-molecular-mass PE dispersed finely within PP during the polymerization process. The average molecular weight of PE introduced into PP is not definite, but it is clear that the PE has higher molecular weight and thus much higher relaxation mode than those of PP. The intrinsic viscosity $[\eta]$ in tetralin at 135 °C of the high-molecular-weight PE (solo polymerization of ethylene

Fig. 8. DSC thermograms of Fr. 3 and 4 as a function of temperature.

Fig. 9. G' , G'' , and $\tan \delta$ as a function of ω at 180 °C for a mixture of Fr. 5-9 fractionated by TREF.

without no polymerization of propylene) was 26 dL/g. Extrapolation of the relationship between $[\eta]$ and the weight-average molecular weight M_w gave $M_w \approx (4-5) \times 10^6$. $[\eta]$ and M_w of whole polymer (PP-B and PP-C) are 3.0 dL/g and $M_w \approx 5 \times 10^5$, respectively. In figure 8, the bimodal molecular weight distribution could be clearly seen for some fractionated sample, though there were not two peaks for the whole polymer. Here, for elongational flow, we attempt to estimate the role of a small amount of higher molecular weight chain that is dissolved into lower molecular weight polymer.

Osaki et al.¹³⁾ reported an estimation on the nonlinear flow properties (two-step stress overshoot in shear flow and strain hardening in uniaxial flow) for binary polymer blends (PS and its high-molecular-weight analogue). The elongational stress caused by the high molecular weight chain (H-chain) was calculated via a simple dumbbell model. They utilized constitutive equations proposed for the comb-shaped branch polymer by McLeish and Larson¹⁴⁾ to estimate the chain orientation and stretching independently. We shall show an example calculating the elongational stress growth function of the binary system containing small amounts of uhmw-components by this method, assuming that all the H-chain (high-molecular-weight PE) can dissolve into the low molecular mass chain (L-chain, viz. PP) matrix and the H-chain can entangle each other within the L-chain. Assuming a characteristic time for the orientation as the maximum relaxation time, the orientation tensor $\mathbf{S}$ of the end-to-end vector $\mathbf{r}$ obeys following equations:

$$\frac{\partial \mathbf{r} \mathbf{r}}{\partial t} = \mathbf{K} \cdot \mathbf{r} \mathbf{r} + \mathbf{r} \mathbf{r} \cdot \mathbf{K}^T - \frac{1}{\tau_H} \left(\mathbf{r} \mathbf{r} - \frac{1}{3} \mathbf{I} \right) \quad (3a)$$

$$\mathbf{S} = \frac{\mathbf{r} \mathbf{r}}{tr \mathbf{r} \mathbf{r}} \quad (3b)$$

$$\mathbf{K} = \frac{1}{2} \begin{bmatrix} 2\dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & -\dot{\epsilon} \end{bmatrix} \quad (3c)$$

where $\mathbf{K}$ is the deformation rate tensor, $\mathbf{I}$ is the unit tensor, τ_H is the maximum relaxation time of H-chain, and $\mathbf{S}$ is the orientation tensor. The time evolution of the stretch ratio of the H-chain is given by a characteristic time for the chain stretching τ_R as

$$\frac{\partial \lambda}{\partial t} = \lambda \mathbf{K} : \mathbf{S} - \frac{1}{\tau_R} (\lambda - 1) \quad (4)$$

Finally, a contribution of the H-chain to stress is expressed as

$$\sigma_H = 3G_N \phi_H^2 \lambda^2 \mathbf{S} \quad (5)$$

Here ϕ_H is the concentration of the H-components, and G_N is the plateau modulus. When the molecular weight of H-chain is much larger than that of L-chain, eqs 3 and 4 lead to respectively

$$\frac{\partial \mathbf{r} \mathbf{r}}{\partial t} = \mathbf{K} \cdot \mathbf{r} \mathbf{r} + \mathbf{r} \mathbf{r} \cdot \mathbf{K}^T \quad (6)$$

$$\frac{\partial \lambda}{\partial t} = \lambda \mathbf{K} : \mathbf{S} \quad (7)$$

We used eqs 6 and 7 for the estimation of σ_H under an assumption of $\dot{\epsilon} \tau_H \gg \dot{\epsilon} \tau_R \gg 1$. We utilized the stress growth function data of PP-A as that of the L-chain. The result for the case of $\phi_H = 0.01$ is shown in Figure 10 as an example. The reduced viscosity growth function, $\eta^+ / G_N \tau_L$, is plotted against reduced time, t / τ_L , at various reduced elongational rates, $\dot{\epsilon} \tau_L$. It indicates the strong strain hardening regardless of a very small amount of H-chain at each strain rate, where the L-chain does not exhibit any nonlinear features.

Figure 11 shows the reduced stress growth, σ / G_N , against the Hencky strain for the polymer with a bimodal molecular

Fig. 10. Reduced uniaxial extensional viscosity of a bimodal polymer with H-component ($\phi_H = 1$ wt %) as a function of time at various reduced rates of extension: 0.5, 0.1, 0.05, 0.01, and 0.005 from left to right. The broken line depicts the contribution of the L-component.

Fig. 11. Reduced stress growth obtained from Figure 10 as a function of Hencky strain at various reduced rates of elongation.

weight distribution obtained from Figure 10. In Figure 11, the reduced stress increases with strain. Over an elongational strain, the reduced stresses at various rates converged on a single value, independent of strain rates ($\epsilon \geq 4$). In this region, we may say that the stress growth is predominantly governed merely by the strain, because of extremely long relaxation time of the H-chain. Figure 12a,b indicates stress growth against ϵ for PP-A and PP-C containing uhmw-PE. In Figure 12b, the elongational stress curves at various rates tend to converge at large strain. This behavior would correspond to that of the result of Figure 12 ($\epsilon \geq 4$). Of course, this behavior is not observed for conventional PP which uhmw-PE is not introduced (see Figure 12a). From the above-mentioned, the eminent elongational behavior of PP containing uhmw-PE at large strain may result from the stretch of the uhmw-PE chain.

2.8 Processability of Rheology-Controlled PP

The extrusion foaming was carried out with butane as a physical blowing agent to examine the effect of strain hardening of the rheology-controlled PP on the processability. Figure 13 a,b shows optical micrographs of foamed cells of conventional PP and PP incorporated with a small amount of ultra-high molecular weight component, in which both foamed samples have same apparent specific gravity. Figure 13b indicates homogeneous and closed cells for PP

with outstanding strain hardening, because the steep increase of elongational viscosity stabilized bubble expansion growth. On the contrary, Figure 13b shows inhomogeneous and open cells for standard PP due to unstable deformation of cell walls and coalescence of bubbles. It should be concluded, from what has been said so far, that a small amount of ultra-high molecular weight chain has strong impact to enhance the strain hardening, which leads excellent processability under free surface.

3. PHYSICAL GEL OF PVC / PLASTICIZER SYSTEM

Poly(vinyl chloride) (PVC)/various solvents systems is typical physical gels in which micro crystallines behave as crosslinking junctions, and the structures and physical properties of these gels have been extensively investigated.^{15,16)} Recently, Aoki et al. have conducted a series of rheological studies for PVC in bis(2-ethylhexyl) phthalate¹⁷⁻²²⁾ and in various plasticizers.²³⁾ These studies are mainly devoted to the properties of PVC systems with low polymer concentration. However, commercial PVC compounds are generally used for rigid and flexible

Fig. 12. Stress growth as a function of Hencky strain at various strain rates for (a) PP-A and (b) PP-C.

Fig. 13. Optical micrographs of foamed cell (a) conventional PP and (b) PP with strain hardening.

applications with high PVC concentration. It has been reported that these PVC compounds have a microcrystalline structure whose melting range is about 120-210 °C and can extend to somewhat higher temperatures.²⁴⁾ Therefore, the melting and recrystallization occurs in the range of temperatures at which processing is normally conducted. Viscoelastic properties of commercial PVC compound were reported at temperatures below and above the processing temperature.²⁵⁻²⁷⁾

The viscoelastic behavior of PVC/plasticizer system is characterized with the power-law relationship as well as chemical crosslinked polymers^{28, 29)},

$$G' = G''/\tan \delta \propto \omega^n \quad (8)$$

$$\tan \delta = \tan(n\pi/2) \quad (9)$$

It is very interesting to know whether the PVC systems exhibit the critical gel behavior at high PVC concentrations and then the relaxation exponent n changes by the concentration. Furthermore, elongational flow behavior of sol-gel system such as PVC/plasticizer system has not been reported as much as the authors know.

3.1 Materials

We used PVC (weight-average polymerization degree of 1,300) and di-isononyl phthalate (DINP) as a plasticizer. The PVC powder was blended with prescribed amounts of DINP, a small amount of Ca-Zn type stabilizer, and 5 pph of CaCO₃, calendered on a hot roller for 5 min at 150 °C, compression molded at 180 °C under a pressure of 15 MPa, and cooled gradually to room temperature. The weight ratio of PVC/DINP in PVC8 shown here was 0.455/0.545.

3.2 Linear Viscoelastic Behavior of PVC/DINP Systems

Figures 14, 15, and 16, respectively, show the ω dependence of G' and G'' , and $\tan \delta$ for the PVC8 at different six temperatures: 150, 160, 170, 180, 190, and 200 °C. Each measurement was performed for the freshly prepared PVC8 to avoid the influence of thermal history and the thermal degradation. At low temperature, $T = 150\sim 180$ °C, PVC8 behaves as a well-developed gel; G' and G'' tend to level off with decreasing ω and exhibit a plateau at low ω . This behavior suggests that a network structure of PVC molecules is formed in PVC8. At the highest temperature of 200 °C, this system behaves as a sol, although the terminal flow behavior ($G' \propto \omega^2$ and $G'' \propto \omega$) cannot be observed. At the intermediate temperature of 190 °C, the slopes of $\log G'$ and $\log G''$ versus

$\log \omega$ curves become linear, indicating behavior of critical gels. These curves apparently correspond to the curves at the gel point. Figure 3 shows the plots of $\tan \delta$ versus ω at various temperatures. Specifically, it suggests that the ω -independent $\tan \delta$ is observed at 190 °C. This “flat” phase angle region covers a wide frequency window, as marked by a horizontal line. Only the low frequency “flat” region is associated with the gel point.

Fig. 14. Storage modulus G' of PVC8 plotted against angular frequency ω for various temperatures.

Fig. 15. Loss modulus G'' of PVC8 plotted against angular frequency ω for various temperatures.

Fig. 16. Loss tangent $\tan \delta$ of PVC8 plotted against angular frequency ω for various temperatures.

The relaxation exponent n , obtained from eqs. 8 and/or 9, was 0.75 for PVC8. This was confirmed for more high PVC concentration system. It should be noted that these n values are in agreement with the values obtained previously for the PVC/plasticizer systems with low PVC concentrations.^{16, 18-20, 23)} These facts indicate that the fractal structure of PVC gels have a same fractal dimension irrespective of polymer concentration, as the relaxation exponent n characterizes the fractal dimension reflecting this magnitude.³⁰⁻³³⁾

3.3 Elongational Viscosity Behavior of PVC/DINP Systems

Figures 17, 18, and 19 show the time evolution of the elongational viscosity $\eta_E^+(t, \dot{\epsilon})$ of the PVC8 at various strain rates at 160, 180, and 190 °C. In these figures, the numerals denote strain rates and the solid lines indicate $3\eta^+(t)$. In this paper, $\eta^+(t)$ is the shear stress growth function in the linear viscoelastic region calculated from the G' and G'' using an approximate equation proposed by Osaki et al.³⁴⁾

On the start-up of elongational flow at a rate $\dot{\epsilon}$, the viscosity growth function η_E^+ of PVC8 followed the linear $3\eta^+(t)$ at a short time scale and then deviated from $3\eta^+(t)$. At 160 °C of the PVC8, the curve obtained at strain rate of 0.05 s⁻¹ agrees with $3\eta^+(t)$ below 10 s. At longer time, the η_E^+ curve increases with time. The η_E^+ curves at higher strain rates increase steeply with time. None of the curves approaches steady-state values. At 170 °C (not shown here) and 180 °C, the flow behavior under elongational flow was very similar to those at 160 °C, although the absolute values at 170 and 180 °C showed a decrease according to the temperature. It is clear that below 180 °C, the PVC8 exhibited strong strain hardening. At the critical gel temperatures (190 °C of PVC), we note that all η_E^+ curves at various rates did not show large deviation from linear viscoelastic region anymore, although the data were scattered because of low viscosity. We can say that there is a critical change in the elongational flow behavior in the vicinity of the temperature, where the loss tangent shows independency of the frequency (see Figs. 16). Above 190 °C η_E^+ measurement was very difficult because of the small tensile tension. It is experimentally demonstrated that the rheological behavior of PVC/DINP systems not only shear, but elongational flows changes drastically before, near, and beyond the sol-gel transition as a function of temperature.

We found that the elongational viscosity behavior of the PVC8 exhibited strong strain hardening below T_{gel} , although it did not show strong strain hardening above T_{gel} . Below T_{gel} , the PVC crystal domains are stable and act as a strong cross-linking point. Then the flexible PVC strands between

the crosslinking points behave as a crosslinked rubber. These flexible strands are elongated the same as a crosslinking rubber and exhibit higher nonlinear stress as rubber elasticity beyond a certain strain. This should be the reason for strong

Fig. 17. Time dependence of uniaxial elongational viscosity at various strain rates for PVC8 at 160 °C. The solid line is $3\eta^+(t)$ calculated from dynamic viscoelastic data in shear.

Fig. 18. Time dependence of uniaxial elongational viscosity at various strain rates for PVC8 at 180 °C. The solid line is $3\eta^+(t)$ calculated from dynamic viscoelastic data in shear.

Fig. 19. Time dependence of uniaxial elongational viscosity at various strain rates for PVC8 at 190 °C. The solid line is $3\eta^+(t)$ calculated from dynamic viscoelastic data in shear.

strain hardening of the gels.

The polymer at the gel point is a critical state. The critical gel has no intrinsic size scale and includes from the small cluster to the infinite cluster. At the gel point, the infinite clusters are very few and may not be stable. The unstable clusters will be broken under the large strain. Then, we cannot observe the strain hardening at T_{gel} . Sol-gel transition of PVC and PVC/plasticizer systems is associated with the melting of some crystallites and consequent loosening of the network in the high-temperature range where the strain hardening under elongational flow vanishes. We can conclude that the unusual rheological behavior of PVC8 results from the continuous change of morphological state occurring in the temperature range from 150 to 220 °C. Therefore, the time-temperature superposition principle cannot be applied for the systems exhibiting the sol-gel transition.

4. CONCLUSION

This study shows control of nonlinear elongational behavior and its important role in terms of processing operation. We demonstrated that the strain hardening can be controlled by a presence of long relaxation time components such as very high molecular weight chain and/or physical crosslinks connected polymeric chains into three-dimensional network. These are exceptional methodology to enhance rheological behavior and have a potential to design new polymer and find further application. Recently, considerable progress has been made in polymer dynamics and precision polymerization. This study would be also expected as a guiding principle in designing new materials with desirable processability.

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