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Rheological Behavior of Hydrogen Bonding Miscible Blend: High Molecular Weight Poly(2-vinyl pyridine) and Low Molecular Weight Poly(4-vinyl phenol)

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We examined thermal and rheological behaviors for miscible polymer blends, poly(2-vinyl pyridine) / poly(4-vinyl phenol) (2VPy/VPh), in which intermolecular hydrogen bonds play an important role. The molecular weights of the 2VPy and VPh components are higher and lower than the critical sizes of the entanglement, respectively. In the mixture of these two polymers, only the 2VPy chains entangle each other, and the low molecular weight VPh is expected to act as a diluent. We found that the time-temperature superposition principle approximately held. The Williams-Landel-Ferry equation with a single parameter set (C_1 and C_2) could represent their shift factors by setting the reference temperatures to be $T_g + 64$ °C. From the comparison of the composite curves, we found that the intermolecular hydrogen bonds did not affect the entanglement densities but made the zero shear viscosities larger and the relaxation times longer.

Key Words: Miscible blend / Hydrogen bond / Rheology / Entanglement / Glass transition temperature

1. INTRODUCTION

A wide variety of polymer alloy materials have been developed over the past 70 years from the viewpoint that their physical properties can be controlled more easily than the synthesis of new polymers^{1,2)}. In general, there are two types of polymer alloys: miscible and immiscible systems. For the latter case, the phase-separated morphologies play an essential role in determining their properties³⁾. Therefore, the control of the morphologies has often been a topic in controlling their properties⁴⁻⁸⁾. On the other hand, for the former case, the parameters that can control properties are only two: the pure component properties and intermolecular interactions. Miscible blends or miscible block copolymers generally exhibit the average properties of the constituent polymers. In that sense, designing the material properties of miscible blends is more straightforward than the case of phase-separated ones. While this is an advantage, the difficulty in developing synergies in their properties is also a disadvantage. However, there is still a possibility to create synergistic effects by strengthening the intermolecular interactions.

We have reported some studies on the dynamics of miscible alloys, including miscible blends⁹⁻¹²⁾ and block

copolymers^{13,14)}. However, we have not thoroughly evaluated the effect of interaction strength on the component dynamics quantitatively. Many experimental studies revealed that miscible blends without specific interaction exhibit dynamic heterogeneity when the difference of the component T_g is larger than 25 °C^{9,15,16)}. On the other hand, Yang and Han¹⁷⁾ reported that H-bonding miscible blends are more dynamically homogeneous: they exhibit relatively sharp single glass transition in DSC, and the time-temperature superposition principle apparently holds. These dynamical homogeneities can be due to the suppression of the concentration fluctuation¹⁸⁾ and the coupling of two segmental dynamics¹⁶⁾. H-bonding polymer blends are sometimes called “polymer complex” due to their specific one-to-one interaction¹⁹⁻²³⁾.

Studies on the glass transition temperature T_g of hydrogen-bonding polymer blends revealed that intermolecular hydrogen bonds largely increase the T_g values, higher than the average values of the component T_g s²⁴⁻²⁷⁾. Poly(2-vinyl pyridine) / poly(4-vinyl phenol) (2VPy / VPh) blend examined in this study is one example of such systems. The increase of T_g due to the formation of one-to-one hydrogen bonds (H-bonds), as schematically shown in Fig. 1, slows down the component polymer dynamics in various spatial and time scales. Formation of the associated structure provides a variety of material characteristics, not only T_g but also other dynamical properties. Dielectric relaxation studies on H-bonded

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Fig. 1 Hydrogen bonding structure formed between VPh and 2VPy.

miscible blends showed that the segmental relaxation of both components occurred at the same rate even though their relaxation times were slower than the neat components, associated with the increase of T_g ²⁸⁾. However, it is still unclear how the slow dynamics in the rubbery and terminal regions are affected by such strong interaction. Yang and Han¹⁷⁾ demonstrated that the composition dependence of the zero-shear viscosity of the blend of VPh and 2VPy with similar molecular weights exhibited a maximum value at a certain blend composition w_{2VPy} as same with $T_g(w_{2VPy})$. However, since their systems are nearly unentangled, it is still unveiled how the entanglement dynamics is affected by hydrogen bonding. They also evaluated the average viscosity in the blends but could not evaluate the dynamics of each component. Therefore, in this study we have examined the rheological behavior of the 2VPy / VPh system, where the component molecular weights are largely different: the VPh component is non-entangled, and only the 2VPy component are entangled. In such systems, the complication due to the effect of entanglements between different species²⁹⁻³¹⁾ can be avoided. This paper discusses the blend composition dependence of the viscoelastic spectra in a wide frequency region including the terminal, rubbery, and glassy regions. We think the clarification of the rheological behavior is especially important from the perspective of the property control of such H-bonding polymer blends.

2. EXPERIMENTAL

The poly(2-vinyl pyridine) (2VPy) sample with molecular weight of $M_w = 1.82 \times 10^5$ was synthesized via living anionic polymerization. This sample was supplied by Profs Takano and Matsushita (Nagoya University). Two poly(4-vinyl phenol) (VPh) samples were supplied by JSR Corporation. Table I shows the characteristics of the samples used in this study.

The preparation method of the blends of 2VPy/VPh is as

Table I Characteristics of poly(4-vinyl phenol) (VPh) and poly(2-vinyl pyridine) (2VPy).

Code	$10^3 M_w$	M_w/M_n
VPh2	1.9	1.82
VPh5	4.5	1.77
2VPy182	182	1.06

follows. Firstly the prescribed amounts of VPh and 2VPy polymers were dissolved in DMSO (common solvent), and then the ternary solution was re-precipitated in deionized water. The obtained precipitates were dried in a vacuum for one day at 120 °C. Because of the precipitation operation in water, the blend compositions sometimes differed from those in the initially prepared DMSO solutions. Therefore, we determined the weight fractions of 2VPy (w_{VPy}) for the finally dried samples by the elemental analysis with the equipment of MT-6 (YANACO, Japan). The details of the blend sample preparation were reported previously³²⁾.

The glass transition temperature T_g for all the homopolymers and blend samples were determined with a differential scanning calorimeter (DSC 6220, Seiko Instruments Inc., Chiba, Japan). The rate of both heating and cooling processes was 10 °C min⁻¹. Three thermal scan cycles of 1st heating–1st cooling–2nd heating–2nd cooling–3rd heating were conducted in the temperature range of 30 °C ~ 230 °C. We determined T_g in the 2nd heating scan from the temperature at which the time derivative of the heat flow curve exhibited a peak. In the 3rd heating, we checked all the data to agree with the 2nd heating scan.

Linear viscoelastic measurements were performed with a strain-controlled rheometer ARES G2 (TA instruments) using a small-amplitude oscillatory shear mode. Stainless steel parallel plates with 4 mm diameter were used for the measurements. The temperature range was from 90 °C to 230 °C depending on the T_g of each sample. The angular frequency ω range was from 100 rad s⁻¹ to 0.1 rad s⁻¹. The applied strains were confirmed to be small enough to be within the linear response regime for all the measurements.

3. RESULTS AND DISCUSSIONS

3.1 Composition Dependence of Glass Transition Temperatures

Figure 2 shows the dependence of T_g on the weight fraction of 2VPy (w_{2VPy}) for the two blend systems, 2VPy182/VPh5 and 2VPy182/VPh2, examined in this study along with the previously reported data for 2VPy40 ($M_w = 3.9 \times 10^4$, $M_w/M_n = 1.66$) blends with VPh5 and VPh2. As reported

previously³²⁾, the w_{2VPy} dependence of T_g can be represented by the following modified Kwei equation using the component T_g values, $T_{g,2VPy}$ and $T_{g,VPh}$.

$$T_g = \frac{w_{2VPy}T_{g,2VPy} + kW_{VPh}T_{g,VPh}}{w_{2VPy} + kW_{VPh}} + qw_{2VPy}^\alpha w_{VPh}^\alpha \quad (1)$$

Here, $w_{VPh} = 1 - w_{2VPy}$, and k , q , and α are the parameters: (k , q , α) = (1.28, 158 °C, 1.17) for 2VP40/VPh5 and (1.35, 186 °C, 1.18) for 2VP40/VPh2 blends³²⁾. Regarding the VPh component, their T_g are different depending on the molecular weight: $T_{g,VPh} = 145.5$ °C (for VPh5) and 99.5 °C (for VPh2). However, those of 2VPy are the same: $T_{g,2VPy} = 98.9$ °C (for 2VPy40) and 98.7 °C (for 2VPy182). It can be said that the glass transition behavior of the high molecular weight 2VPy182 blend system used in this study is almost the same as that of the 2VPy40 blend system.

Fig. 2 Weight fraction dependence of T_g for 2VPy182 / VPh5, 2VPy39 / VPh5, 2VPy182 / VPh2, and 2VPy40 / VPh2 blends. The data of 2VPy40 blends were already reported³²⁾. The solid and dashed lines represent the modified Kwei equation (Eq 1).

The $T_g(w_{2VPy})$ of the VPh2 blend system has its peak position at $w_{2VPy} \sim 0.4$, even though the component T_g s are almost the same. As discussed in our previous paper, we believe this is because the VPh component forms hydrogen bonds between OH—OH groups (self-H-bonding), which reduces the contribution to the hetero-hydrogen bonds with pyridine groups of VPh shown in Fig. 1. The stoichiometric ratio of the hydrogen bond formed between VPh and 2VPy is 1:1 in the monomer units. However, due to the effect of self-H-bonding of the VPh component, an ideal hydrogen bonding structure having the stoichiometric ratio of 1:1 may be formed at $w_{2VPy} < 0.5$. As will be discussed later, this effect also appears in the rheological behavior.

3.2 Viscoelastic Spectra of 2VPy/VPh Blends

The frequency ω dependence of the storage modulus G' and loss modulus G'' were measured for the two blend systems, 2VPy182/VPh5 and 2VPy182/VPh2, with three compositions, and the composite curves were constructed: Fig. 3 and Fig. 4, respectively show the reduced frequency dependence of G' and G'' of all the blend data, including those of the neat 2VPy182, VPh5, and VPh2. The reference temperature was set at 160 °C. It should be noted that this is the first time that the viscoelastic spectra of 2VPy/VPh blends have been measured from the glass to the termination region. In the construction of these master curves, we found that the time-temperature superposition principle apparently held for these systems over a wide temperature range except for VPh2 and VPh5 homopolymer systems. In particular, for the VPh2 system, a slight temperature-dependent change in the shape of G' is observed at the lowest frequency side: the higher the temperature, the stronger the ω -dependence of G' . This may reflect the dissociation of the self-hydrogen bonds between OH groups at high temperatures. On the other hand, such

Fig. 3 Composite curves of G' (open markers) and G'' (filled markers) for 2VPy182 / VPh5 blends with $w_{2VPy} = 0, 0.295, 0.551, 0.734$, and 1 at 160 °C. Those of $w_{2VPy} = 0$ are plotted on the right-hand axis to avoid data overlapping.

Fig. 4 Composite curves of G' (open markers) and G'' (filled markers) for 2VPy182 / VPh2 blends with $w_{\text{VPy}} = 0, 0.258, 0.498, 0.748$, and 1 at 160 °C. The data of $w_{\text{VPy}} = 1$ is the same as that shown in Fig. 3. Those of $w_{\text{VPy}} = 0$ and 0.258 are plotted on the right-hand axis to avoid data overlapping.

behavior was not observed in the blend systems, suggesting that the H-bonding between VPh and 2VPy (hetero-hydrogen bonding) is strong. In other words, the associated structure does not change much in the measurement temperature range. This behavior is consistent with the literature data¹⁷⁾.

From the shapes of the G' and G'' spectra for VPh2, VPh5, and 2VPy182 homopolymer systems, we can find that 2VPy is well entangled because of the appearance of the plateau region at $\log(\omega a_T) = 0 \sim 2$, while the two VPhs are non-entangled systems. Furthermore, VPh5 shows the Rouse mode as the shoulders in both G' and G'' on the low ω side, but for VPh2 no such shoulder exists. This is also consistent by considering that VPh2 consists of only two or three Rouse segments, whose molecular weight is reported for polystyrene having a similar structure to VPh to be 850³³⁾. For the spectral shapes of the blend systems, they are broader compared with that of 2VPy. We will discuss this point in section 3.4.

Regarding the glass mode peaks in the G'' spectra observed on the high-frequency side, we can see that the peak frequencies for the VPh5 blend with $w_{\text{2VPy}} = 0.295$ and for the VPh2 blend with the $w_{\text{2VPy}} = 0.498$ locate at the lowest ωa_T . These behaviors are consistent with the functional forms of $T_g(w_{\text{2VPy}})$ shown in Fig. 2: the highest T_g values among the three compositions in the VPh5 and VPh2 systems were $w_{\text{2VPy}} = 0.295$ and $w_{\text{2VPy}} = 0.498$, respectively, *i.e.*, the $T_r - T_g$ values are the lowest for these compositions. The relationship between T_g and the rheological spectra will be discussed based on the shift factors in the next section.

3.3 Temperature Dependence of Shift Factors

Figure 5 shows the temperature dependence of the shift factors a_T for (a) 2VPy182 / VPh5 and (b) 2VPy182 / VPh2 blends with various compositions used to construct the

Fig. 5 $T - T_r$ dependence of the shift factors for (a) 2VPy182 / VPh5 and (b) 2VPy182 / VPh2 blends with various compositions. The solid lines represent the fit curves by the WLF equation.

composite curves shown in Figs. 3 and 4. Reflecting the large T_g difference for the blend samples, $\log a_T$ curves at the same reference temperature ($T_r = 160$ °C) are largely different. First, we fitted the a_T data of the neat 2VPy182 using the Williams Landel Ferry (WLF) equation.

$$\log a_T = -\frac{C_1(T - T_r)}{C_2 + T - T_r} \quad (2)$$

We obtained the values of $C_1 = 6.805$ and $C_2 = 124.03$ °C with $T_r = 160$ °C. In general, the C_1 and C_2 values become almost universal even for different T_g samples by setting the appropriate reference temperatures: $T_r = T_g + \text{constant}$. Based on this property, we moved the WLF curve fitted to the 2VPy

Table II T_r^* and T_g for 2VPy182/VPh5 and 2VPy182/VPh2 blends at several compositions.

System	w_{2VPy}	$T_r^*/^{\circ}\text{C}$	$T_g/^{\circ}\text{C}$
2VPy182 / VPh5	1	160	98.7
	0.734	196.0	127.5
	0.551	220.1	161.2
	0.295	232.0	170.9
	0	209.1	145.5
2VPy182 / VPh2	1	160	98.7
	0.748	185.5	129.9
	0.498	212.3	146.9
	0.258	197.0	136.0
	0	165.5	99.5

 Fig. 6 Universal shift factors obtained by setting an appropriate reference temperature T_r^* for each blend.

data onto the other data through the horizontal and vertical shifts. The precise method has been reported previously³⁴. The fit-results are shown by the solid lines in Fig. 5, demonstrating that a single WLF function can represent almost all the data.

This operation enables us to determine a new reference temperature T_r^* for each sample. Namely, by changing T_r (160 °C) to T_r^* , the a_T curves can be superposed. The results are shown in Fig. 6, indicating that the superposition works well. Thus obtained T_r^* values are listed in Table II along with the T_g values determined by DSC. The plot of T_r^* vs. T_g is shown in Fig. 7, demonstrating a reasonable correlation between T_r^* and T_g : the relation of $T_r^* = T_g + 64^{\circ}\text{C}$ approximately holds. This result suggests that the strong hydrogen bonding between 2VPy and VPh contributes equally to the change in T_g and the change in complex modulus. In other

 Fig. 7 Comparison of T_r^* obtained by the rheological shift factors with T_g determined by the differential scanning calorimetry.

words, the WLF analysis based on the free volume theory, which is valid for polymer systems without specific interactions, can be applied to the H-bonding miscible blend, although the H-bonding interaction strongly affects the glass transition and the molecular motion of polymers.

3.4 Comparison of the Viscoelastic Spectra in the Iso-Frictional State

Figures 8 and 9 show (a) $G'(a_T\omega)$ and (b) $G''(a_T\omega)$ at T_r^* , *i.e.*, in the iso-frictional state. Here, the horizontal shifts from 160 °C to T_r^* were calculated from the shift factor shown in Fig. 6. In these figures, the $G'(a_T\omega)$ and $G''(a_T\omega)$ curves at 160 °C were moved only horizontally, not vertically, meaning that the absolute values of G' and G'' are those of 160 °C. These comparison indicates that the glass modes observed in the frequency range higher than 10^6 s^{-1} overlap each other in the iso-frictional state. This is a natural result since the glass mode is a local relaxation, and its relaxation time is supposed to be the same under iso-frictional condition. In the glass to rubber transition region ($10^4 \sim 10^6 \text{ s}^{-1}$), both G' and G'' of the blends are slightly broadened compared to the 2VPy homopolymer. This suggests that the association and dissociation of hydrogen bonds may occur in this region. In the rubbery plateau region ($10^0 \sim 10^4 \text{ s}^{-1}$), the height of G' decreases as increasing the VPh content. In the terminal region (below 10^0 s^{-1}), both the heights of G' and G'' are decreased, but the peak positions of G'' does not seem to change much with w_{2VPy} .

First, in order to evaluate the concentration dependence of the entanglement density, the plateau modulus G_N was determined as the value of G' when $\tan \delta (= G''/G')$ shows a minimum. This method enables us to unambiguously determine the representative modulus values even when the G' does not show a clear plateau region. Some other methods

Fig. 8 (a) G' and (b) G'' spectra for 2VPy182 / VPh5 blends with w_{2VPy} indicated in the figure at $T = T_r^*$.

Fig. 9 (a) G' and (b) G'' spectra for 2VPy182 / VPh2 blends with w_{VPy} indicated in the figure at $T = T_r^*$.

have been reported so far³⁵⁾, but most of them cannot be used unless G'' shows a clear peak in the terminal region. Therefore, it is difficult to apply such methods to these blend systems where G'' does not exhibit a clear peak except for neat 2VPy. Only Wu's method³⁶⁾ using the crosspoint (G_x) of G' and G'' ($G_x = G' = G''$) at a frequency ω_x given by Eq 3 is applicable for the data shown in Figs. 3 and 4 to determine the plateau modulus.

$$\log G_N = \log G_x + 0.38 + \frac{2.63 \log \frac{M_w}{M_n}}{1 + 2.45 \log \frac{M_w}{M_n}} \quad (3)$$

This equation relates the M_w/M_n ratio and G_x to G_N . In the

blends examined here, hydrogen bonding interaction rather than the molecular weight distribution affects the shapes of G' and G'' ; however, we use the M_w/M_n ratio of 2VPy (1.06) to estimate G_N for the confirmation of the G_N values. The w_{2VPy} dependences of G_N determined from the above-mentioned two methods are shown in Fig. 10. We can see that both ways give similar G_N values, and they are nearly proportional to w_{2VPy}^2 . In the entangled polymer solution (polymer / low molecular weight diluent system), the plateau modulus is known to be proportional to the 2 ~ 2.3 power of the polymer volume fraction ϕ ^{37, 38)}. (Because the densities of 2VPy and VPh are nearly equal, 1.16 g cm⁻³ and 1.15 g cm⁻³, respectively, it is not necessary for these blends to distinguish the volume fraction from the weight fraction.) From the w_{2VPy}^2 dependence of G_N , we think that the entanglement network consists of only 2VPy182 chains, and the low molecular weight VPh can be simply regarded as a plasticizer. In other words, non-entangled VPh does not help increase the entanglement density even if it forms hydrogen bonds with 2VPy.

Next, we focus on the terminal relaxation region. In the low frequency region, the relaxation of the entangled network of the high molecular weight 2VPy182 component is observed. For the 2VPy182 homopolymer system, the terminal flow behavior, $G' \sim \omega^2$, and $G'' \sim \omega$ appears. However, for the blend systems, the terminal spectra are slightly broadened, and the terminal exponents are somewhat weaker. This means that a long relaxation time component exists in the blend systems, suggesting the existence of hydrogen-bonded aggregates even at high temperatures where termination relaxation appears.

Since the behavior of $G'' \sim \omega$ is barely observed for some blend samples, we plotted G''/ω against ω for all the data and superimposed them by the vertical shift to estimate the plateau values at $\omega \rightarrow 0$, which correspond to the zero shear viscosity $\eta_0 (= \lim_{\omega \rightarrow 0} G''/\omega)$. As for the relaxation time, we examine two different average relaxation times. One is the crosspoint relaxation time τ_x defined as the inverse of the frequency ω_x at which G' and G'' intersect each other (close to the peak position of G''). The other is so-called the first-moment relaxation time τ_n defined as $\tau_n = \eta_0/G_N$ ³⁹⁾. Figure 11 shows the w_{2VPy} dependence of thus determined η_0 , τ_x , and τ_n . In these values, there is no apparent difference between the two blend systems: 2VPy182/VPh5 and 2VPy182/VPh2. This is because of the small viscosity difference between VPh5 and VPh2 at T_r^* ($\eta_0 = 398$ Pa s for VPh5 and 281 Pa s for VPh2). In Fig. 11, linear approximations were made for the w_{2VPy} dependences of these three valuables, and the slopes obtained by the least-squares method are also shown. In an

Fig. 10 Weight fraction dependence of the plateau modulus G_N determined from two methods: $\tan\delta$ minimum method (hexagonal markers) and Eq 3 (asterisk and cross markers) for 2VPy182 / VPh5 and 2VPy182 / VPh2 blends.

Fig. 11 Weight fraction dependence of the zero share viscosities and two different averaged relaxation times, τ_n (asterisk and cross markers) and τ_x (square markers) for 2VPy182 / VPh5, and 2VPy182 / VPh2 blends at $T = T_r^*$.

entangled polymer solution system without any specific interaction, the concentration dependence of the viscosity and relaxation time under iso-frictional conditions is expressed by the following equations (in the concentrated to bulk region)³⁸⁾.

$$\eta_0 \sim \phi^{3.6}, \tau \sim \phi^{1.3} \quad (4)$$

The observed slopes for η_0 , τ_x , and τ_n in Fig. 11 (1.8, 0.53, -0.13) are much smaller than the powers in Eq 4 (3.6 and 1.3). These weak concentration dependences observed here can be qualitatively explained by considering that 2VPy chains aggregate via multiple H-bonds with VPh chains. For example, if the H-bonded association structure becomes larger by an increase in VPh concentration (a decrease in w_{2VPy}) at T_r^* , the relaxation time and viscosity will increase. The stoichiometric ratio of the association between 2VPy and VPh is 1:1, but as discussed in section 3.1, the 1:1 aggregation is expected to occur at $w_{2VPy} < 0.5$. Therefore, the associated

structure of 2VPy via the H-bonding with VPh may be initially developed with decreasing w_{2VPy} , but below a certain w_{2VPy} (< 0.5), it will remain unchanged. The decrease in the entanglement density by increasing the VPh content competes with the increase of the aggregation size, resulting in a weaker w_{2VPy} dependence of η_0 , τ_x , and τ_n than that for typical entangled polymer solution systems. It is noted that the w_{2VPy} dependence of τ_x and τ_n are different. This can be understood by considering that τ_n is the average relaxation time with higher weight on the long-time component than τ_x . The difference between the two relaxation times slightly increases with decreasing w_{2VPy} , indicating that the relaxation time distribution becomes somewhat broader at lower w_{2VPy} .

The aggregation size should be a function of temperature, which means that the time-temperature superposition principle does not hold⁴⁰⁾. However, in this experiment, at least no significant breakdown of the time-temperature superposition principle was observed. This suggests that the hydrogen-bonded aggregates are retained without dissociation even at the high temperatures where the termination region was measured. We think a more detailed experimental investigation of the aggregate formation is necessary in the future.

4. CONCLUSIONS

We conducted DSC and rheological measurements on the two blend systems, 2VPy182/VPh5 and 2VPy182/VPh2, with composition from 1:0 to 0:1. The glass transition temperatures of these blends were consistent with our previously reported results for 2VPy40/VPh5 and 2VPy40/VPh2, and the modified Kwei equation could represent the functional form of $T_g(w_{2VPy})$.

By using the time-temperature superposition principle, we could construct composite curves of $G'(\omega)$ and $G''(\omega)$. WLF analysis of the temperature dependencies of the shift factors for all the blend compositions enabled us to obtain appropriate reference temperatures T_r^* s, which were approximately represented by $T_r^* = T_g + 64$ °C.

From the comparison of the composite curves for both blends at $T = T_r^*$ (iso-frictional state), we found the following relations: (1) $G_N \sim w_{2VPy}^2$, (2) $\eta_0 \sim w_{2VPy}^{1.8}$, and (3) $\tau_x \sim w_{2VPy}^{0.53}$, $\tau_n \sim w_{2VPy}^{-0.13}$. The relation (1) indicated that the low molecular weight VPh component works just as a plasticizer for the entangled 2VPy component. However, the relations (2) and (3) suggested that the terminal flow of the 2VPy component is affected by the hydrogen bonding with the VPh component.

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