

Experimental Observations of Time-Dependent Behaviors for Polycarbosilane Melt

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ABSTRACT: The distinct characteristics of thixotropic and viscoelastic phenomena of polycarbosilane (PCS) melt were reported first time based on experimental observations. The PCS was synthesized according to the Yajima process with the number of average molecular weight being ~ 1170 , followed by an appropriate preshear treatment to remove air bubbles encountered during the heating or pressing process of PCS specimens. A series of shear thixotropic loop, start-up, and step-down rate measurements were carried out at 280°C to systematically examine the time-dependent behaviors of PCS melt. It was

found that the PCS melt was nonlinear complex fluid with a strong time-dependent in viscoelasticity and apparent thixotropy. Compared with the conventional high-density polyethylene, the shear stress–shear time responses of PCS melt were more susceptible to the changes of shear rate, shear time, and standing time because of the nature of low-molecular-weight polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3395–3400, 2011

Key words: polycarbosilane; melt; viscoelastic properties; thixotropy; shear stress

INTRODUCTION

As a silicon-containing polymer, known as a good precursor for SiC ceramic products, polycarbosilane (PCS) normally has the number of average molecular weight (M_n) being <2000 and dispersion coefficient being 1.7–2.2. Although the exact molecular structure of PCS remains unclear, PCS can be characterized as a typical low-molecular-weight polymer. It is expected that the rheological properties of PCS melt would be notably different from those of conventional high-molecular-weight polymer melt or inorganic melt. Wang et al.¹ reported the rheological behavior of PCS melt in simple steady shear and showed that PCS melt is strong shear thinning non-Newtonian fluid. Unfortunately, no experimental results regarding the time-dependent PCS melt have been reported so far.

Thixotropy and viscoelasticity are regarded as two fundamental characteristics of complex fluids. The experimental methods commonly used to study thixotropic and viscoelastic properties of a non-Newtonian fluid are thixotropic loop (T loop), start-up, and step-down rate measurements. Two excellent review articles in detailed descriptions of thixotropy and viscoelasticity in various conventional polymer systems have been provided by Barnes² and, more recently, by Mewis and Wagner.³ Most of previous experimental investigations on complex time-dependent nonlinear behaviors of polymer melt have been limited to conventional polymer systems (usually $M_n > 10,000$) such as low-density branched polyethylene melt at 150°C,^{4,5} low-density polyethylene melt at 150°C,^{6,7} and aqueous poly(acrylamide) solutions.⁸ However, little information is available in the experimental observations on rheological properties of low-molecular-weight polymer melt, in particular, PCS melt with $M_n < 2000$ and less understood molecular structure.

The experimental measurements in study of polymer melt are challenged by accuracy and reliability of methods adopted. For example, air bubbles evolved from polymer decomposition because of heating process are extremely harmful in melt measurements and must be avoided. In this investigation, the characteristic viscoelastic and thixotropic phenomena of

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PCS were reported first time by performing a series of shear T loop, start-up, and step-down rate measurements at 280°C. The air bubbles possibly involved during the heating or pressing process of PCS specimens were removed by appropriate pretreatments before experimental measurements. A comparison between the time-dependent behaviors of PCS melt and conventional high-density polyethylene (HDPE) is presented, and the influence of molecular weight is evident from the experimental observations.

EXPERIMENTAL

Specimens

The PCS used in this investigation was prepared according to the Yajima process.^{9–11} The backbone structure of PCS may be represented by a simplified formula, $[\text{SiHCH}_3\text{CH}_2]_n$. The molecular weight of PCS melt was obtained by gel permeation chromatograph at 30°C with tetrahydrofuran as the eluant (1.0 mL min^{-1}) using Agilent 1100, and the spectrum was calibrated with polystyrene standards. The M_n and the dispersion coefficient of PCS were ~ 1170 and 2.004, respectively, with the initial softening point temperature of 197°C. The zero shear viscosity of PCS is 200 Pa s at 280°C.¹ The PCS samples were ground into powders and pressed into a button-shaped specimen that is 50 mm in diameter and 0.7–0.8 mm in thickness. A commercial grade HDPE resin with molecular weight of 200,000 and zero viscosity of 250 Pa·s at 280°C, designated as ML 57D075 (JHC260), a product from the Jilin Petrification of China Petroleum (Jilin, China) was also tested for a comparison.

Pretreatments

To remove any air bubbles that may be generated during the heating or pressing process, the PCS samples were first heated to 440°C and then kept at the same temperature for 1 h under nitrogen atmosphere to evolve air bubbles produced by possible decomposition of smaller molecules from PCS during the heating process. In addition, the air bubbles may also be encountered during the preparation of button-shaped PCS specimens by pressing process; and it is proved by experimental results that a preshearing treatment of a continuous and steady shearing at a constant shear rate of 0.1 s^{-1} for 300 s before each rheological measurement would eliminate the bubbles.

Rheological measurements

All the rheological measurements of PCS melt including shear T loop, start-up, and step-down rate tests were carried out at 280°C after preshearing treatment and standing for additional 30 min using

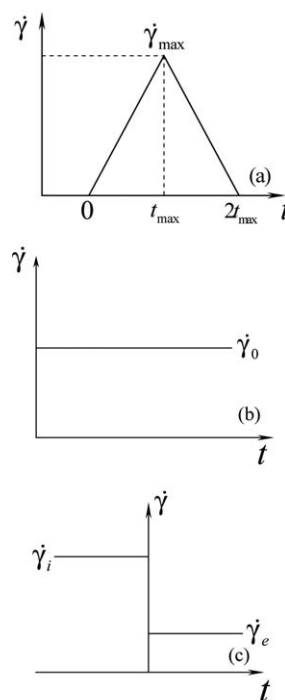


Figure 1 (a) T loop test. (b) Start-up shear test. (c) A step-down in shear rate test.

an advanced rheological extended system (TA Instruments). The T loop [Fig. 1(a)] was measured under a triangular loop mode, i.e., the shear rate increased linearly from 0 to a maximum value ($\dot{\gamma}_{\max}$) at t_{\max} and then decreased from $\dot{\gamma}_{\max}$ to 0 in a time range of t_{\max} . Thus, the T loop is characterized by two parameters, the loop time t_L and $\dot{\gamma}_{\max}$. The start-up tests were performed by suddenly applying a constant shear rate to the sample at rest for a period of time as shown in Figure 1(b). The step-down rate tests as shown in Figure 1(c) were performed by a sudden reduction in shear rate from $\dot{\gamma}_i$ to $\dot{\gamma}_e$. The shear stress–shear time responses of HDPE were also measured at 280°C using the same experimental procedures as PCS. A new sample was used for each test.

RESULTS AND DISCUSSION

Removal of air bubbles

As air bubbles may be generated during the rheological measurements of PCS melt due to sample heating or pressing process, it is necessary to remove any air bubbles encountered during the measurements to guarantee accuracy of data. The preheating of PCS samples was performed and preshearing of PCS melt was applied before each rheological measurement to remove air bubbles and to ensure uniform distribution of PCS melt. The photos taken before and after the pretreatments are given in Figure 2. It clearly shows that the air bubbles [lighter

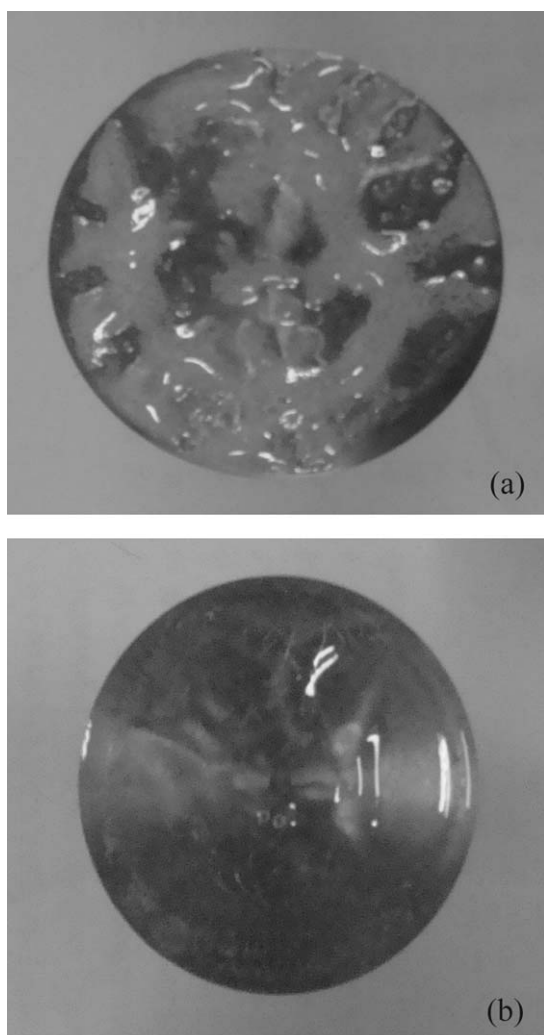


Figure 2 Photos of PCS specimen (a) before the preshearing treatment and (b) after the preshearing treatment.

color in Fig. 2(a)] were almost completely removed and the PCS melt became uniformly distributed after the pretreatments. However, the reasons for the effects of preshearing treatment on the specimen remain unclear and need to be further investigated.

Time-dependent characteristics of PCS melt

Typical T loops of PCS melt obtained at different t_{\max} values ranging from 200 to 600 s are presented in Figure 3. The arrows indicate the forwarded and reversed loading directions, corresponding to the loading path of shear rate shown in the inlet scheme. In all the cases, the shear stress–shear rate curves display identical hysteresis with the counterclockwise type, in the sense that the shear stress–shear rate curve for the loading path is underneath the shear stress–shear rate curve for the unloading path. It is apparent that the shear stress (τ) increased rapidly with the increase of shear rate ($\dot{\gamma}$) and reached the maximum shear stress (τ_{\max}) at the largest shear

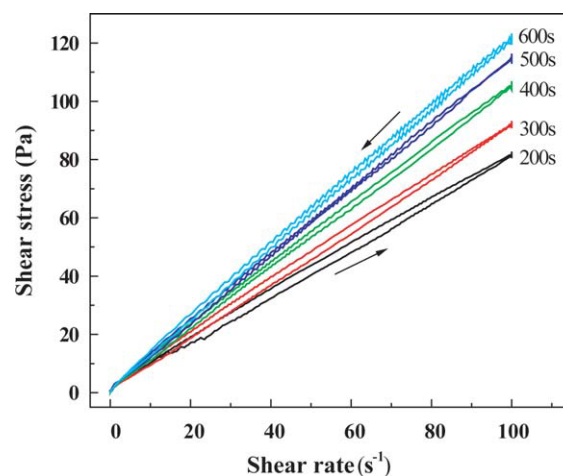


Figure 3 Typical T loops of PCS melt under different t_{\max} values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rate ($\dot{\gamma}_{\max}$) via the forwarded direction, then reduced significantly with the decrease of $\dot{\gamma}$ along the reversed direction, which forms characteristic PCS T loop. Although the shapes of T loops obtained for different t_{\max} values appeared similar, the areas within the T loops denoted by A and the τ_{\max} values varied noticeably with t . Table I summarizes the values of τ_{\max} and A for various shear times evaluated from Figure 3. As evident in Table I, the τ_{\max} values went up from 81 to 122 Pa when t_{\max} extended from 200 to 600 s, an increase of 50% of τ_{\max} ; whereas, the A values were negative as a loop was formed in the counterclockwise direction, and the absolute values slightly lowered with a total reduction of 15.7% from 200 to 600 s. These observations suggest that the PCS melt exhibited strong time-dependent behavior, which are remarkably different from those of conventional polymers. The low-molecular-weight and the specific structure of PCS melt ($M_n = 1170$, in this study) may be responsible for the particular behaviors.

Turning now to the start-up experiment, which is instructive for examining stress-growth response of the test melt, Figure 4 demonstrates stress-growth data for the shear rate ranging from 0.1 to 80 s^{-1} . At low shear rates, it seems that there is no stress overshoot and the stress slightly decays as the time elapses. But as the shear rate increases, the stress starts to deviate from the “steady” plateau. After the critical time corresponding to “overshoot” peaks, the

TABLE I
The Maximum Shear Stress and Area of Thixotropic Loop Obtained From Figure 3

t_{\max} (s)	200	300	400	500	600
τ_{\max} (Pa)	81	92	105	114	122
A	– 230	– 214	– 177	– 110	– 194

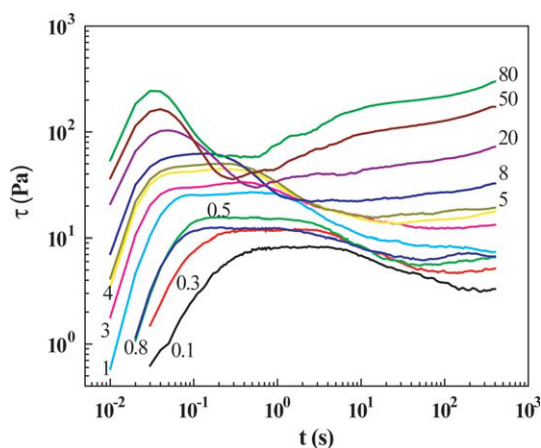


Figure 4 Typical shear stress–shear time responses of PCS melt during the applications of various shear rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress decreases first and then continuously increases until the end of the experiment. For the critical time corresponding to the overshoot, the larger is the

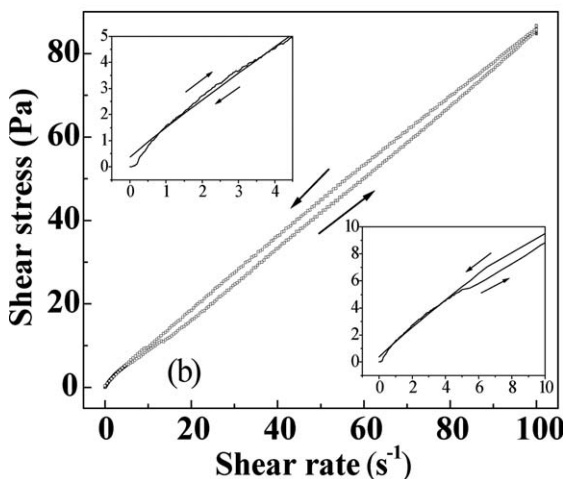
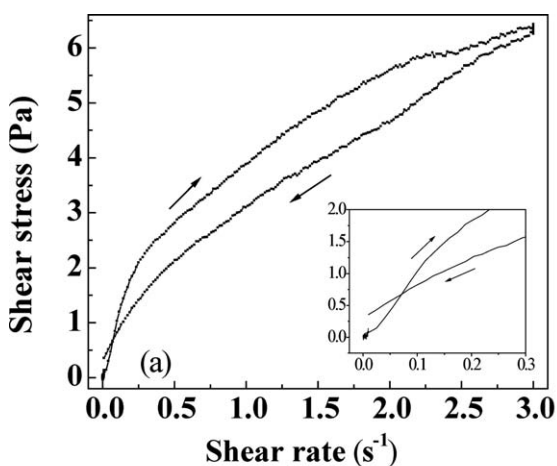


Figure 5 T loops of PCS melt: (a) $\dot{\gamma}_{\max} = 3 \text{ s}^{-1}$, $t_{\max} = 100 \text{ s}$; (b) $\dot{\gamma}_{\max} = 100 \text{ s}^{-1}$, $t_{\max} = 300 \text{ s}$.

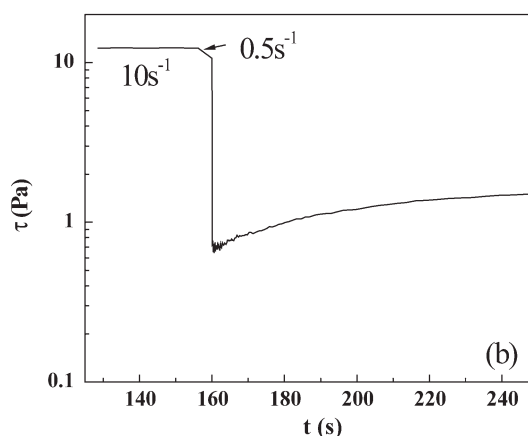
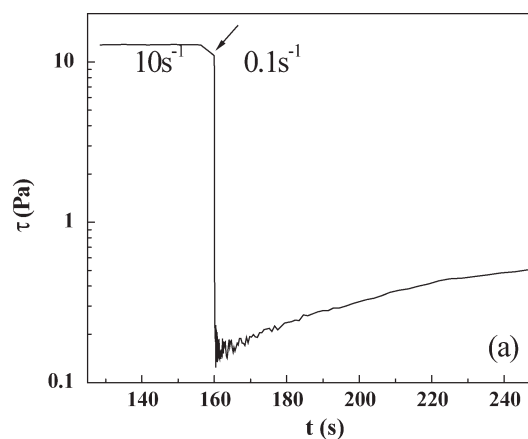


Figure 6 The shear stress as a function of shear time for PCS melt during the sudden reduction in different shear rates after the constant applications of the same shear rate (10 s^{-1}) for the same time.

shear rate and the shorter is the critical shear time. As the products of critical shear time and shear rate are not constant for the experiment, the stress growth of PCS melt in shear could not be predicted by Mewis and Wagner model.³ This discrepancy should be viewed as a strong time-dependent viscoelastic behavior of PCS melt. In this work, we only consider overshoot, and in the further work, we will encounter the long time behavior of stress growth of PCS melt.

To further confirm the influence of hysteresis in time-dependent viscoelasticity of PCS melt under different shear rates, two T loops were also measured with the low and high shear rates, respectively, as shown in Figure 5. It is interesting to note that the shapes of hysteresis loops were distinguishably different from each other. A hysteresis loop in clockwise type with an area of 1.9 was obtained at $\dot{\gamma} = 3 \text{ s}^{-1}$ [Fig. 5(a)]. Two hysteresis loops with the areas of 1.7 [a small loop in clockwise type as shown in upper-left inset in Fig. 5(b)] and -232 [a larger loop formed in a counterclockwise type as shown in bottom-right inset in Fig. 5(b)] were obtained at $\dot{\gamma} = 100$

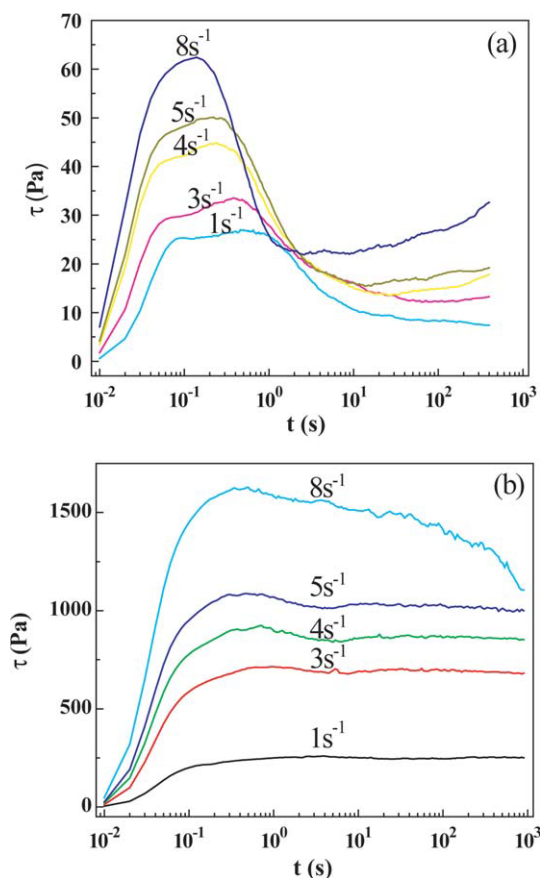


Figure 7 Shear stress–shear time responses during the applications of various shear rates: (a) PCS melt; (b) HDPE melt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

s^{-1} . This provides strong evidence that the hysteresis of PCS melt depends not only on shear time but also on shear rate. Smaller shear rate and shorter shear time resulted in positive hysteresis, indicating an increase of viscosity. Very large shear rate and longer shear time led to both positive and negative hysteresis, suggesting the alteration of viscosity by varying shear rate, i.e., increasing viscosity at lower shear rate then decreasing at higher shear rate. This observation is consistent with those observed in Figure 4.

The time-dependent viscoelastic behaviors of PCS melt were further studied by applying dynamic shear rates starting from the constant applications of 10 s^{-1} for 160 s then switched immediately to shear rates of 0.1 and 0.5 s^{-1} . The results are compared in Figure 6. It can be seen that the PCS melt exhibited a characteristic viscoelastic behavior. According to noncontroversial determination of thixotropy in Mewis and Wagner's review,³ the PCS melt showed weak thixotropy because, in the step-down rate test, the stress dropped instantaneously to a lower value, followed by a subsequent fast relaxation to the lowest value, and finally went up slowly and gradually. It is clear from Figure 6 that the PCS melt demon-

strates a joint response of the thixotropic and viscoelastic behaviors. However, whether a PCS melt has a strong viscoelasticity in the sense that the viscoelastic behavior dominates in the step-down rate test is still unclear, because the nonlinear viscoelasticity of melts is normally characterized by the magnitude of storage modules and the normal stress effects or the Weissenberg number,¹² which will be explored in a further work. The shear stress dropped rapidly on imposing the variable shear rate and then slowly resumed with time.

As a low-molecular-weight polymer, PCS melt is more susceptible to the change of shear rate; this is verified by a comparison of shear stress–shear time responses between PCS and HDPE melt as given in Figure 7. The magnitude of shear stress for HDPE melt [Fig. 7(b)] was almost 20 times as that of PCS melt [Fig. 7(a)], and the shear stress of HDPE became less time-dependent except in the case of $\dot{\gamma} = 8\text{ s}^{-1}$, where the shear stress started to drop with the increase of time. As compared with HDPE melt, the shear stress of PCS melt was much more sensitive to the change of shear rate with time,

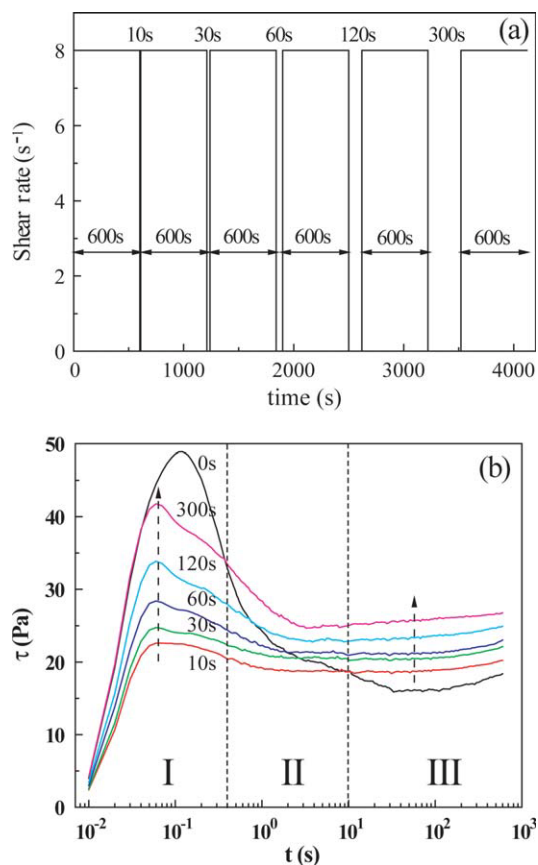


Figure 8 (a) The loading path for the experiment; (b) the shear stress–shear time responses of a PCS melt by applying constant shear rate of 8 s^{-1} for 600 s with a various waiting time indicated between two measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

implying a stronger time-dependent viscoelastic behavior of PCS than that of HDPE. A detailed investigation concerning the correlations between structure and time-dependent behaviors will be conducted in the future.

Effects of standing time during the interval of the two identical shear rate applications on the time-dependent responses of PCS melt are presented as τ - t curves measured from the same PCS specimen in Figure 8. It is clear that the τ - t curve may be essentially divided into three distinct regions. The initial τ - t curve (0 s) was obtained at $\dot{\gamma} = 8 \text{ s}^{-1}$ and showed a strong peak maximum, which gives $\tau_{\text{max}} = 48.9 \text{ Pa}$ at 0.12 s. The τ - t curves were measured subsequently for the same PCS specimen after standing for 10, 30, 60, 120, and 300 s, respectively, between the two subsequent measurements. The shear stress greatly decreased at first (10 s), then gradually went up with the increase of standing time in Region I ($t < 0.4 \text{ s}$). The peak maximum appeared earlier as compared with the initial curve and could not resume to the value observed in the initial curve. However, the values of shear stress measured after various standing times were all larger than that of the initial curve in Region III. The variations in the magnitude of shear stress with time in Region II were somehow between the high and low values of the initial curve. The phenomena observed from Figure 8 suggested that even for the same PCS specimen, when applying the same magnitude of shear rate, the standing time between the two subsequent measurements also strongly influenced the time-dependent behaviors. The minimum standing time required for the τ - t curve to recover the initial τ - t curve in Region I must be longer than 300 s; however, with the extension of measuring time, it still remains questionable that the initial τ - t curve could be recovered. Apparently, the thixotropic mechanism for common suspension or emulsion systems could not be employed to well describe the

PCS melt. More systematical study is undergoing to understand the causes of complex time-dependent responses of PCS melt by clarifying the exact microstructure and chemical composition of PCS.

SUMMARY

The time-dependent rheological behaviors of PCS melt were systematically studied by performing shear T loop, start-up, and step-down rate measurements at 280°C. The pretreatments were applied to effectively remove air bubbles produced during the heating or press process and to ensure accuracy of experiments. The time-dependent behaviors of PCS were significantly affected by shear rate, shear time, and standing time between the two subsequent measurements. The PCS melt exhibited strong time-dependent behavior with a weak thixotropy, which is remarkably different from those observed for common polymer melt like HDPE.

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