Failure Mechanism of Time-Temperature Superposition for Poly(vinyl chloride)/Dioctylphthalate (100/70) System

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ABSTRACT: The failure behavior and its mechanism of time-temperature superposition (TTS) poly(vinyl chloride) (PVC)/dioctylphthalate (DOP) (100/70) system were studied from low to high temperatures with a step of 10°C. Arrhenius equation, WLF equation, mathematical nonlinear fitting, and manual shift were applied for TTS fitting. None of these methods could obtain the well-superposed master curves with either single horizontal shift or two-dimensional (horizontal and vertical) shift. The rheological data and differential scanning calorimeter (DSC) results were used to explain the failure mechanism of the TTS fitting. The curves of storage modulus versus frequency were well fitted to an empirical equation $G' = G'_0 + K\omega^n$. The yield behavior was used to analyze the influence of test temperature on the dynamic rheological behavior for the PVC/DOP (100/70) system. A transition of rheological behavior from the solid-like to the linear viscoelastic could be observed at 190°C because of the gradual melting of microcrystallites and the destruction of gel networks, which were confirmed by DSC analysis. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 452–458, 2012

Key words: poly(vinyl chloride); plasticized; time-temperature superposition; thermorheological complexity; rheology

INTRODUCTION

The temperature dependence of linear viscoelastic properties, for example, the modulus and the relaxation time, is described by the principle of time-temperature superposition (TTS),[1] which can characterize polymer materials and achieve satisfactory results about the actual processing behavior with no need of obtaining data over a wide angular frequency or shear rate range.[2–4] The resulting curve of superposing at different time (frequencies) and temperatures is the master curve that covers longer time or wider frequency domains.

This principle has been first proposed by Lenderman in 1943, in which time is equivalent to temperature for viscoelastic materials.[5,6]

TTS is based on the relation,

$$I(t', T_0) = \frac{\rho_0 T_0}{\rho T} I(t, T)$$

where $I(t', T_0)$ is the viscoelasticity function; $t = \alpha_T t'$, $\alpha_T = \frac{\tau_0}{\tau}$ is the shift factor; τ is the value of the relaxation time and τ_0 is the value of the relaxation time at the reference temperature T_0. Williams et al.[7] subsequently proposed a semiempirical formula to describe the principle well known as the Williams–Landel–Ferry equation in 1953.

Ward[8] and Van Gurp and Palmen have commented that TTS holds when (1) the exact matching of shapes of adjacent (time- or frequency-dependent) curves is obtained, (2) a_T has the same value for all viscoelastic functions, and (3) the temperature dependence of a_T has a reasonable form such as the Arrhenius and WLF equations [eqs. (1) and (2), respectively].

$$\ln a_T = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{1}$$

$$\log a_T = -\frac{B}{2.303 f_{T_0}}\left[\frac{T - T_0}{f_{T_0}/a_f + (T - T_0)}\right]$$
$$= \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \tag{2}$$

where T_0 is the reference temperature. As is known to all, eq. (2) comes from the free volume theory, in which f_{T0} is the free volume fraction at T_0, a_f is the volume expansion coefficient difference of the transition, B is a constant, C_1 and C_2 are empirical constants, and R is the gas constant [8.314 J (mol^{-1} K)]. When $T_0 = T_g$ (glass transition temperature), $C_1 = -17.44$ and $C_2 = 51.6$. If the reference temperature is

about 50°C above T_g, $C_1 = 8.86$ and $C_2 = 101.6$ (used in this work).

The TTS is valid only for materials with thermorheological simplicity.[9] The so-called thermorheological simplicity is such a characteristic of polymers that increasing the temperature and extending the observation time may make the same effect on the rheological property, such as linear flow of polymer melts. However, thermorheological simplicity requires the same temperature dependence of different unit relaxation, or else, the responding curve changes the shape in addition to the location with the change of temperature. As a result, curves at different temperatures cannot be superposed to a master curve. This phenomenon is defined as thermorheological complexity. This means that few polymers are completely in conformity with the principle.[10–13] Notwithstanding, the failure of the TTS could positively provide more information for determining temperature-dependence mechanisms of different molecular motions.[14,15]

There is a hierarchical morphology of poly(vinyl chloride) (PVC) grains that results in a complex flow behavior during the processing.[16] The plasticized PVC system has more complicated flowing units and morphology.[17] A lot of studies have been made on the dynamic property of the plasticized PVC solutions; however, the temperature dependence of the PVC/dioctylphthalate (DOP) products are still far from well being understood.[18–23] In this work, the failure of TTS fitting is systemically researched by analyzing the temperature response for the PVC/DOP (100/70) system. The superposition is determined by Arrhenius equation, WLF equation, and mathematic fitting. The failure mechanism of the TTS fitting is studied by rheological analysis and differential scanning calorimeter (DSC) data.

EXPERIMENTAL

Materials and sample preparation

In this work, the PVC (SG-8, Sichuan Province Jinlu Resin Co., Deyang, China) was of suspension grade with K-value 55–59, viscosity number 73–86 g/mL, and DOP absorption 12 g/100 g PVC. In a high-speed mixer, the PVC was mixed with 2 phr (parts per hundred parts of resin) organotin stabilizer, 0.5 phr stearic acid, and 70 phr DOP. Organotin stabilizer, stearic acid, and DOP were commercial products. The formula of the neat PVC system is almost the same except for the addition of DOP.

Dry blend powders were processed in an internal mixer (Haake Rheocord 90, Gebr. Haake GmbH, Karlsruhe, Germany) at 190°C (chamber temperature), 30 rpm (rotation speed of the blade) for a period of 8 min. These specimens were compression-molded at 180°C and cut into disks 25 mm in diameter and about 1 mm in thickness.

Measurements and characterizations

The viscoelastic property of the molded specimens was measured using an oscillatory rheometer (AR1500EX, TA Instruments, New Castle, DE). Measurements were performed in a frequency sweep of 0.0628–628.3 rad/s at test temperatures from 140 to 190°C with a step of 10°C, and the strain amplitude was 3% to maintain the measurement in linear viscoelastic region. All tests were performed after a preheating step about 3 min and in nitrogen atmosphere during the whole process.

The enthalpy of microcrystallites in molded specimens was determined through the measurement by the DSC (Q20, TA Instruments). During the test, the temperature of specimens was first maintained at 25°C for a period of 3 min and then raised to 250°C with a heating rate of 20°C/min. All tests were performed under nitrogen atmosphere.

RESULTS AND DISCUSSION

As argued by Harper and Weitsman,[24] the viscoelastic property of thermorheologically complex materials can be well defined with both horizontal and vertical shift factors, a_T and b_T. A two-dimensional (horizontal and vertical) shift is adopted for the PVC/DOP (100/70) system, which is more complicated and peculiar than other thermorheologically complex, to show the detailed failure conditions of different TTS-fitting methods.

First of all, the single horizontal shift is adopted for the PVC/DOP (100/70) system. Four methods are used to obtain a_T including Arrhenius equation [eq. (1)], WLF equation [eq. (2)], nonlinear mathematical fitting [eq. (3)], and manual shift, respectively.

$$\log(\tan \delta) = \sum_{k=0}^{k=m} C_k [\log(a_T \cdot \omega)]^k \quad (3)$$

In eq. (3), C_k is the polynomial coefficient and the value of m is taken as 4. This method does not depend on other parameters that need to be determined extra and provides a more convenient and accurate calculation. The subscripts $-A$, $-W$, $-f$, and $-M$ denote Arrhenius equation, WLF equation, mathematical fitting, and manual shift respectively. The fitting curves of $a_{T\text{-}f}$ with eq. (3) are shown in Figure 1. The horizontal shift factors (a_T) calculated by different methods are listed in Table I, where the $a_{T\text{-}W}$ is calculated by WLF equation [eq. (2)] directly. The $a_{T\text{-}A}$ at 150°C is assumed to be equal to the $a_{T\text{-}W}$
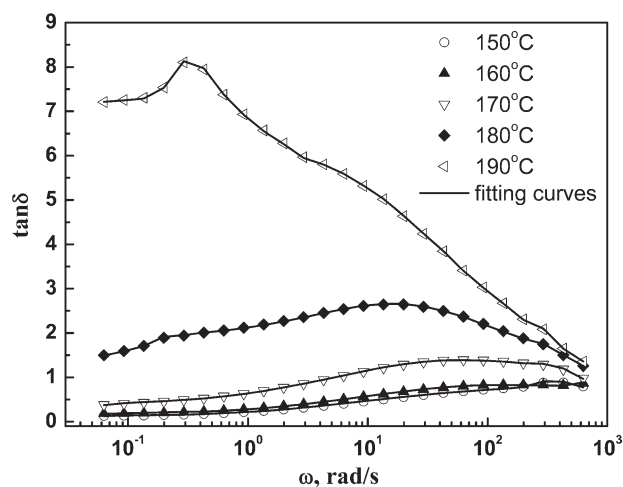
Figure 1 Fitting curves of a_T according to eq. (3) for PVC/DOP (100/70) system at different melt temperatures: 140, 150, 160, 170, 180, and 190°C.
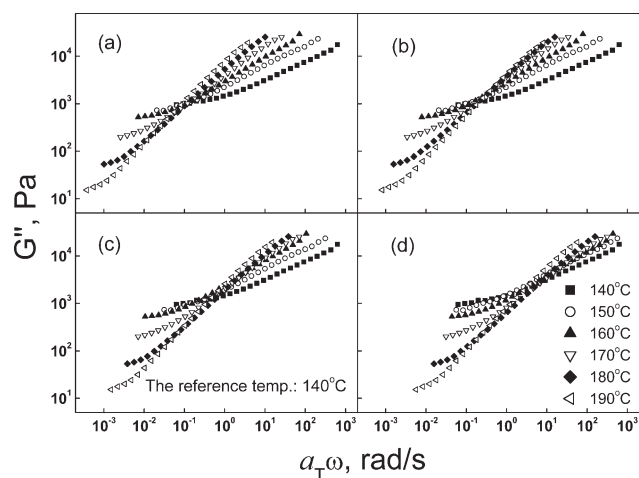

Figure 2 Master curves of PVC/DOP (100/70) system with the horizontal shift factor (a_T) obtained from Arrhenius equation (curve a), WLF equation (curve b), eq. (3) (curve c), and manual shift (curve d).

at 150°C, then a_{T-A} at other temperatures are calculated based on the a_{T-A} at 150°C. a_{T-f} and a_{T-M} are obtained by the fitting calculation and manual shift, respectively. The master curves obtained from different methods are shown in Figure 2. Obviously, none perfectly smooth master curve can be obtained, and deviations appear in high frequency and/or low frequency areas for the PVC/DOP (100/70) system. From Figure 2(a,b), only an intersection of curves can be observed in whole frequency regions. However, the superposed curves by mathematical fitting and manual shift show some limited modifications in high frequency region. The appearance of quasi-plateau rheological behavior in terminal region is the main reason for the separation in low-frequency area.

To compensate for the limitation of horizontal shift, the vertical shift is introduced into TTS to measure the diverge degree from TTS. As similar as a_T, b_T can also be obtained by nonlinear polynomial fitting using eq. (4),

$$\log(\tan\delta) = \sum_{k=0}^{k=m} D_k[\log(G^* \cdot b_T)]^k \qquad (4)$$

TABLE I
The Horizontal Shift Factor (a_T) Obtained with Different Methods at Various Temperatures for PVC/DOP (100/70) System

T (°C)	150	160	170	180	190
a_{T-A}	0.329	0.114	0.041	0.016	0.006
a_{T-W}	0.329	0.125	0.054	0.025	0.013
a_{T-f}	0.501	0.169	0.113	0.061	0.024
a_{T-M}	0.9	0.7	0.5	0.25	0. 09

The subscript $-A$, $-W$, $-f$, and $-M$ denotes Arrhenius equation, WLF equation, mathematical fitting, and manual shift, respectively.

where D_k is the polynomial coefficient and the value of m is taken as 4. Fitting curves are illustrated in Figure 3. The vertical shift factor (b_{T-f}) of Arrhenius equation, WLF equation, and mathematical fitting are calculated by eq. (4), and both the horizontal shift factor (a_{T-M-1}) and vertical shift factor (b_{T-M}) are obtained by manual shift, which are listed in Table II. With these obtained shift factors, the master curves of different methods are exhibited in Figure 4, in which Curves 4(a–c) represent b_{T-f} versus a_{T-A}, a_{T-W}, and a_{T-f}, respectively, and curve (d) represents b_{T-M} versus a_{T-M-1}.

It can be observed that master curves with double shift factors are better superposed than those with single horizontal shift factor, especially in the high-frequency region (higher than 5 rad/s). The curves with best fitting effect that are cut from Figure 4(d) are shown in Figure 5. Indeed, for these curves, the
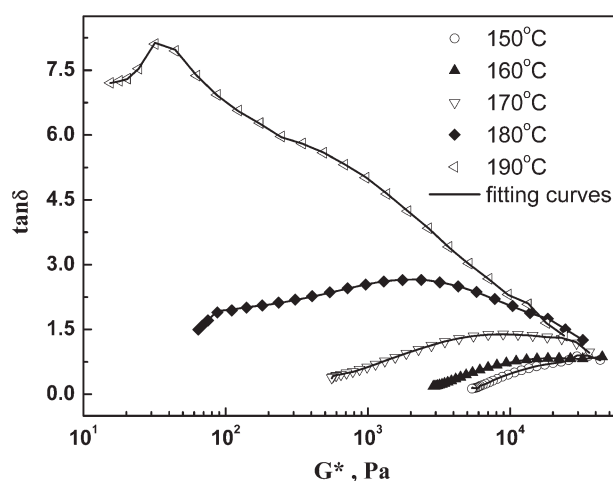

Figure 3 Fitting curves of b_T according to eq. (4) for PVC/DOP (100/70) system.

TABLE II
The Shift Factor (a_T, b_T) Calculated with Different Methods at Various Temperatures for PVC/DOP (100/70) System

T (°C)	150	160	170	180	190
$b_{T\text{-}f}$	0.784	0.535	0.452	0.324	0.222
$a_{T\text{-}M\text{-}1}$	0.8	0.6	0.2	0.05	0.01
$b_{T\text{-}M}$	0.8	0.7	0.4	0.22	0.1

superposition is acceptable when the data is in rather high frequency region, which is about 10^{-2} – 10^{3} rad/s. Moreover, the frequency range of the master curve is much narrower than that of the normal master curve or even the normal test frequency range. However, in lower frequency region, the fitting curves (Fig. 4) are still clearly separated, from which the information related with microstructure is mainly obtained. Therefore, the improved master curve in high frequency region does not make much sense. Besides, it can be obtained that the value of b_T with no obvious tendency is higher than a_T and much lower than 1 (without vertical shift), indicating that the vertical shift in TTS for the PVC/DOP (100/70) system plays an important role.

These commonly used TTS fitting methods are inadequate for the PVC/DOP (100/70) system and exhibit different degrees of deviation. A master curve cannot be obtained by WLF equation, because the parameters C_1 and C_2 are not suitable for this system because of both the improper temperature, which is much higher than $T_g + 50$ and the flow condition. The Arrhenius equation can provide a little better superposition curve than WLF equation, but the shift energy cannot be obtained as a constant, suggesting that there are multilevel flowing
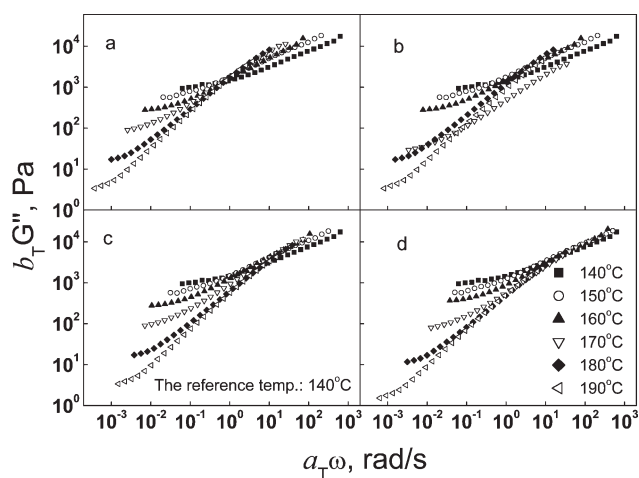

Figure 4 Master curves of PVC/DOP (100/70) system with double shift factors [b_T obtained from eq. (4) and a_T obtained from Arrhenius equation (curve a), WLF equation (curve b), eq. (3) (curve c), respectively, and $a_{T\text{-}M\text{-}1}$ and $b_{T\text{-}M}$ both obtained from manual shift (curve d)].
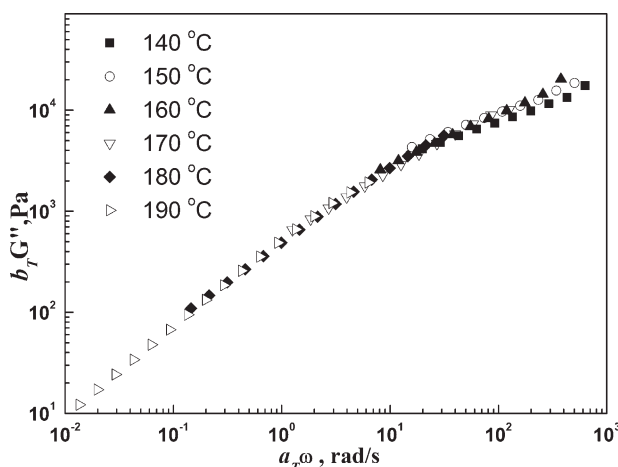

Figure 5 Master curve of the PVC/DOP (100/70) system with double shift factors [b_T obtained from eq. (4) and a_T obtained from eq. (3)].

behaviors. The mathematical fitting equation and the manual shift provide the best fitting effect, which is still far from that of a typical master curve. The results are closely related to the microstructure of the PVC/DOP (100/70) system.

From the above results, it can be found that the TTS fitting cannot be used for the PVC/DOP (100/70) system, and the reason for the failure of TTS fitting maybe due to the multiple flow units and microcrystallites. To make further analysis of these rheological data, an empirical equation [eq. (5)] can be used to fit observed curves (Fig. 6).

$$G' = G_0' + K\omega^n \qquad (5)$$

where, G_0' can be interpreted as the low-frequency yield value of the storage modulus and ($G_0' + K$) can be regarded as the storage modulus when $\omega = 1$. The exponent, n, is a dependent index of the storage modulus on the frequency acting as a measure
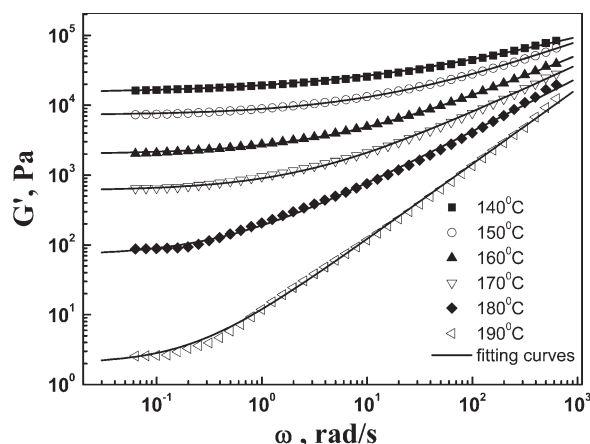

Figure 6 Storage modulus (G') and fitting line versus angular frequency (ω) of the PVC/DOP (100/70) system.

TABLE III
Rheological Parameters of eq. (5) for the PVC/DOP (100/70) System

Test temperature (°C)	G'_0	K	n
140	1.50×10^4	4.42×10^3	0.42
150	7.20×10^3	1.67×10^3	0.55
160	2.00×10^3	6.94×10^2	0.62
170	6.00×10^2	3.00×10^2	0.70
180	7.00×10^1	1.20×10^2	0.77
190	2.00×10^0	1.00×10^1	1.08

of the non-Newtonian behavior. This equation was originally used to simulate the particle suspension system.[25] However, the equation well describes the storage modulus behavior of the PVC/DOP (100/70) system without the filler, indicating that there is a particulate flowing characteristic in this system at all test temperatures. The data listed in Table III shows that G'_0 and K decrease remarkably with the increase of test temperature, indicating that the elastic property of the PVC/DOP (100/70) system weaken at higher temperature. Simultaneously, n increases remarkably when the test temperature increases, indicating that the filled-like behavior disappears gradually. Those results reveal that the existence of multilevel flow units, manifold particles, or/and gel networks of the plasticized system have a significant impact on the flowing behavior. Considering that the structure of samples is not changed during the test within linear strain region in which sublevel particles cannot be destroyed, the rheological change should mainly attributes to the change of the gel networks.

In addition, the yield behavior is usually used to determine the percolation transition point for filled system.[26] From Figure 7, it can be observed that although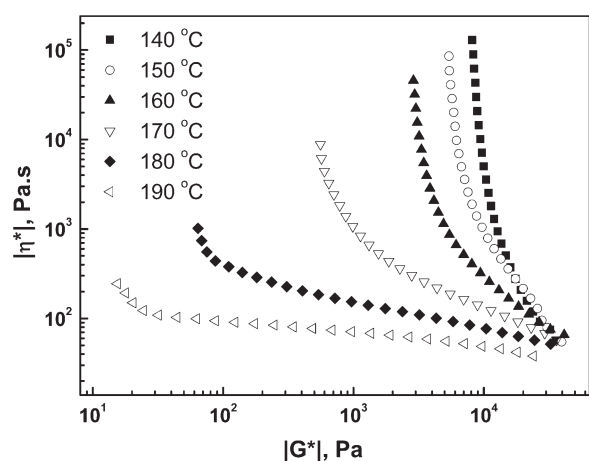 yield behaviors are weakened by the temperature increase, there are obvious yield behaviors in the rheological behavior of the PVC/DOP (100/70) system at different melt temperatures, confirming that there is a strong network structure in the PVC/DOP (100/70) system, which could not be destroyed completely in test temperature range.

The dependence of loss tangent (tan δ) on frequency is shown in Figure 8. It is obvious that the loss tangent increases apparently, and the peak moves to low frequency region with the increase of melt temperature. At 180 and 190°C, there is a new loss peak in the low frequency range ($10^{-1} - 10^0$ Hz), and tan δ is much greater than 1. Simultaneously, when the melt temperature continues rising, the value of new loss peak in low frequency region greatly increases; however, the original peak is weakened. It means that when the melt temperature is high enough, besides the gel network and multilevel particles, the chain segment motion gradually plays a more important role in the PVC/DOP (100/70) system.

It is well known that the microcrystallites in the PVC matrix act as the crosslink points to form the high-elastic gel network. Therefore, the decrease of the amount of microcrystallites could induce an imperfect network. Besides, the melt temperature can affect the mobility of PVC chain segments and the salvation of DOP to PVC. When the melt temperature is low, only few microcrystallites melt and the molecular chain motion is limited by gel networks in the PVC/DOP (100/70) system. The mobility of molecular chain segments and even some molecular chains is good with the increase of temperature. Because the network is a kind of physical crosslinking network, with the increase of melt temperature, the crosslinking points' density becomes lower, resulting in the motion of some molecular chains. In the melt temperature range used in this study, the destruction of the physical crosslinking points is
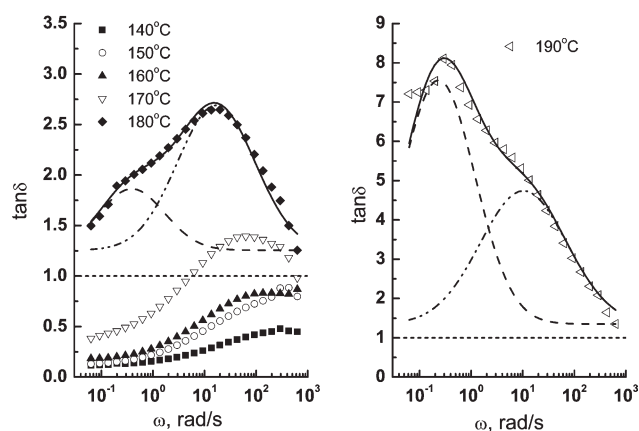
Figure 7 Dependence of the complex viscosity (η*) on complex modulus (G*) of the PVC/DOP (100/70) system at various melt temperatures.

Figure 8 Loss tangent (tan δ) versus frequency of the PVC/DOP (100/70) system at various melt temperatures.
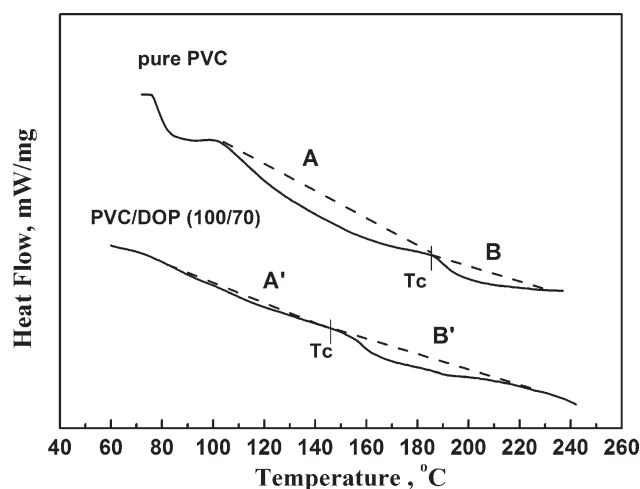
Figure 9 DSC curves of the PVC/DOP (100/70) system and neat PVC.

irreversible, which results in the increase of the proportion of the viscous behavior in the dynamic rheological behavior of the PVC/DOP (100/70) system. On the other hand, the plasticizer (DOP) molecular can hinder PVC molecular from forming microcrystallites and with the increase of melt temperature the salvation of DOP increases, resulting in an increase of the destruction of the networks to some extent. All these verify the existence of the complexity of dynamic rheological behavior, which can explain the failure of TTS fitting for the PVC/DOP (100/70) system.

To understand deeply into the evolution of microcrystallites with the increasing temperature, DSC analysis was carried out, and the result is shown in Figure 9. There are the secondary microcrystallites (expressed as A') and the initial microcrystallites (expressed as B') in PVC/DOP (100/70) system as common PVC system (expressed as A and B, respectively). For the PVC/DOP (100/70) system, the melting enthalpy of secondary microcrystallite is small, and the melting enthalpy of initial microcrystallites is comparatively larger.[27] Although the enthalpy value may be not quite accurate by some system and human errors, it still can be used to semiquantitatively explain the change of microcrystallites. From this figure, it can also be observed that at a comparative low temperature, the microcrystallites cannot be completely destroyed, resulting in the appearance of rheological behavior like network system. With the increase in the test temperature, the microcrystallite volume (the sum of A and B) of the PVC/DOP (100/70) system decreases. Here, T_c denotes as the temperature of the end of A and the start of B. Among the test temperature range, the second microcrystallites have almost entirely melted for the PVC/DOP (100/70) system, because the T_c is about 142°C, much lower than that of neat PVC (181°C).

Therefore, there are only the original microcrystallites acting as the crosslinking points to form the gel networks. The melting enthalpy of secondary microcrystallites is 0.458 J/g, which is much smaller than that of neat PVC as 2.932 J/g. The melting enthalpy of primary microcrystallites is 1.980 J/g, much larger than that of pure PVC as 0.761 J/g. At 190°C, the proportion of the residual primary microcrystallites takes only about 4 and 14% of total microcrystallite for the PVC/DOP (100/70) system and for pure PVC system, respectively, which is insufficient to form the gel networks, and the rheological behavior of linear polymer appears. All these verify that the microcrystallites of PVC are the most important factor for the rheological property of the PVC/DOP (100/70) system.

CONCLUSIONS

The failure behaviors of four TTS fitting methods as Arrhenius equation, WLF equation, mathematical nonlinear fitting, and manual shift are systemically studied and compared for the PVC/DOP (100/70) system in this work. From our results, it can be concluded that a good master curve during whole frequency region cannot be obtained from the four methods, and the addition of vertical shift provides scarcely any melioration. An acceptable fitting curve is obtained by data in rather high frequency through nonlinear fitting, but the frequency range is no wider than the normal test region. It indicates that the existing TTS methods are inadequate to carried out for the PVC/DOP (100/70) system. The reason is researched by rheological data and DSC results. Complex flow units as gel network and multiple particles are considered as the major causation. Further analysis of rheological data reveals that with the increase of test temperature, the melting of microcrystallites in PVC leads to the apparent transition in the rheological behavior. An empirical equation usually describing the filler-filled polymer systems can be used to well fit the curves of the storage modulus versus the frequency, indicating that there are particulate flowing characteristics in this plasticized system. The DSC result reveals that at the transition temperature (190°C), almost the whole microcrystallites melt, leading to a notable weakness of the networks. It verifies that it is the networks that dominate the rheological behavior below the transition temperature in the PVC/DOP (100/70) system.

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