Dynamic Rheological Behavior and Microcrystalline Structure of Dioctyl Phthalate Plasticized Poly(vinyl chloride)

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ABSTRACT: The dynamic rheological behavior of poly(vinyl chloride) (PVC)/dioctyl phthalate (DOP) systems were studied as a function of DOP content and melting temperature. The dynamic rheological behavior of the PVC/DOP systems was found to be remarkably affected by the DOP content. The observed curves of storage modulus (G') versus frequency were well fitted to an empirical equation ($G' = G'_0 + K\omega^n$, where G'_0 is the low-frequency yield value of the storage modulus, the exponent n is a dependent index of frequency, K is a constant coefficient, and ω is the angular frequency). The loss tangent and/or phase angle increased remarkably at a higher DOP content. There was an apparent critical DOP content transition where the dynamic rheological behavior of the PVC/DOP systems changed greatly. Scanning electron microscopy observations revealed the existence of a multiscale particle structure in the PVC/DOP systems. For the PVC/DOP (100/70) system, with increasing melting temperature, its dynamic rheological behavior showed an apparent mutation at about 190°C. Differential scanning calorimetry (DSC) analysis confirmed that the high elastic networks in the PVC/DOP systems were closely related to the microcrystalline structure of PVC. The transitions in the curves of the gelation degree and crystallinity versus the DOP content corresponded well to the DOP content transition in the dynamic rheological behavior. DOP could inhibit the secondary crystallite of PVC and almost had no effect on the primary crystallite of PVC. The coexistence of the microcrystalline structure of PVC and the plasticizer (DOP) resulted in high elastic networks in the PVC/DOP systems. The DSC results explained the DOP content transition and the temperature transition in the dynamic rheological behavior of the PVC/DOP systems well. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1725–1733, 2011

Key words: crystal structures; gelation; poly(vinyl chloride); (PVC); rheology

INTRODUCTION

It is well known that there is a hierarchical morphology for poly(vinyl chloride) (PVC) grains obtained from suspension polymerization,[1] which results in a complex flow behavior during the processing. It is well agreed that PVC grains containing primary and subprimary particles are hard to plasticize into homogeneous melts at their processing temperature and shearing stress; therefore, PVC shows particulate flowing characteristics during its melt processing.[2,3]

Plasticized PVC is widely used in medical applications and automobile parts because of its excellent physical properties and low cost.[4–9] A lot of studies have been done on the mechanism of the plasticization and improvement of PVC products. The rheology, gelation, and sol–gel transition of PVC plastisols and gels have been studied by many researchers.[10–14] Otter et al.[15] measured the axial distribution of the pressures and temperatures at the inner wall of the barrel of an extruder, the axial temperature distribution in the hollow screw, and the radial temperature distribution of the melt close to the screw tip. They found that the properties of PVC extrudates depended on the processing temperature. Li and Aoki[16] studied the elasticity evolution of PVC/dioctyl phthalate (DOP) gels beyond the gel point and found that the gel elasticity developed as a function of the polymer concentration and molecular weight. Boudhani et al.[17] used oscillatory rheological experiments to investigate the gelation process and the sol–gel transition of PVC plastisols. They found that the sol–gel transition process was universal with respect to the temperature and solid

volume fraction. They also pointed out the variation of the gel time with temperature for the PVC plastisols could be predicted by Dickinson's model, and the moduli of the PVC plastisols depended on the PVC concentrations. With dynamic rheological testing, Nakajima and Harrelly[18–20] studied the relationship between the particle size distribution and viscoelastic properties, the formation of an immobilized layer in pseudoplastic flow, and the relationship between the storage modulus (G') and networks formed by particle contact.

It is generally recognized that the microcrystalline structure acts as the physical crosslinking points of the PVC elastomer. However, the rheological behavior and structure of the plasticized PVC melt have been reported less. Particularly, the effect of the DOP content on the microcrystalline structure and the melt elasticity of PVC and the relationship between the microcrystalline and dynamic rheological behavior of the PVC/DOP system are still far from being well understood. Obviously, the rheological behavior of the plasticized PVC melts and the development of microcrystallites of PVC during processing are very important for the application of the plasticized PVC elastomer. In this study, the relationship between the viscoelastic response and the evolution of the morphological structure of PVC/DOP melts were examined. The effects of the DOP content and melting temperature on the morphology, crystallization, and rheological behavior of the PVC/DOP systems were examined by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and dynamic rheological measurements.

EXPERIMENTAL

Materials and sample preparation

In this study, PVC was suspension grade with an average degree of polymerization of 650–750, and a DOP absorption of 12 g/100 g of PVC (SG-8, Sichuan Province Jinlu Resin Co., Ltd, Deyang, China). The particle size of the PVC powder ranged from 60 to 160 μm, and the particle size distribution is shown in Figure 1. In a high-speed mixer, PVC was mixed with 2 phr (parts per hundred resin) organotin stabilizer, 0.5 phr stearic acid, and different amounts of DOP, ranging from 5 to 70 phr before use. Organotin stabilizer, stearic acid, and DOP were commercial products. The dry blend powders were processed in an internal mixer (Haake Rheocord 90, Gebr. Haake GmbH, Karlsruhe, Germany) at 140°C (chamber temperature) at 30 rpm for a period of 8 min. The specimens for dynamic rheometry were compression-molded at 180°C into disks 25 mm in diameter and about 1 mm thick.
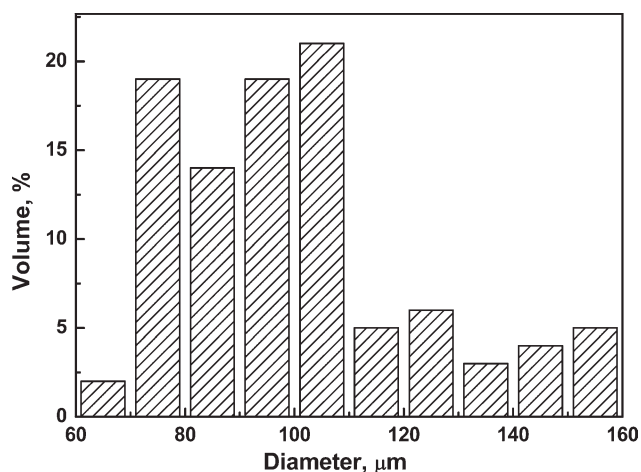
Figure 1 Particle size distribution of pure PVC powder from SEM graphs.

Measurements and characterization

The viscoelastic properties of the specimens were measured with an oscillatory rheometer (AR1500EX, TA Instruments, New Castle, DE, US) under a nitrogen atmosphere. For PVC/DOP systems with various DOP contents, the measurements were performed in frequency sweep of 0.0628–628.3 rad/s at 180°C, and the strain amplitude was 3% to maintain the measurement in the linear viscoelastic region. For the PVC/DOP (100/70) system, dynamic rheological measurements were carried out at 140–190°C with a step of 10°C.

The cryofractured surfaces of the processed PVC/DOP systems were observed by a scanning electron microscope (XL30FEG, Philips, Amsterdam, The Netherlands).

The gelation level and crystallinity (X_c) of the specimens were determined through the data of a differential scanning calorimeter (TA Instruments, Q20, US). During the test, the specimens were first isothermal at 25°C for a period of 3 min and were then heated to 240°C at a heating rate 20°C/min. All tests were performed under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Dynamic rheological behavior

Effect of the DOP content on the rheological behavior of the PVC/DOP systems

The G' and loss modulus (G'') versus angular frequency (ω) of the PVC/DOP systems are shown in Figure 2. As shown, with increasing DOP content, G' and G'' decreased, and the relationship between G' and G'' changed from solidlike ($G' > G''$, PVC with 0–10 phr DOP) to gel-like ($G' \approx G''$, PVC with 15–30 phr DOP) and then liquidlike ($G' < G''$, PVC with 50–70 phr DOP) in the partial or whole measured frequency range; this indicated that as the DOP
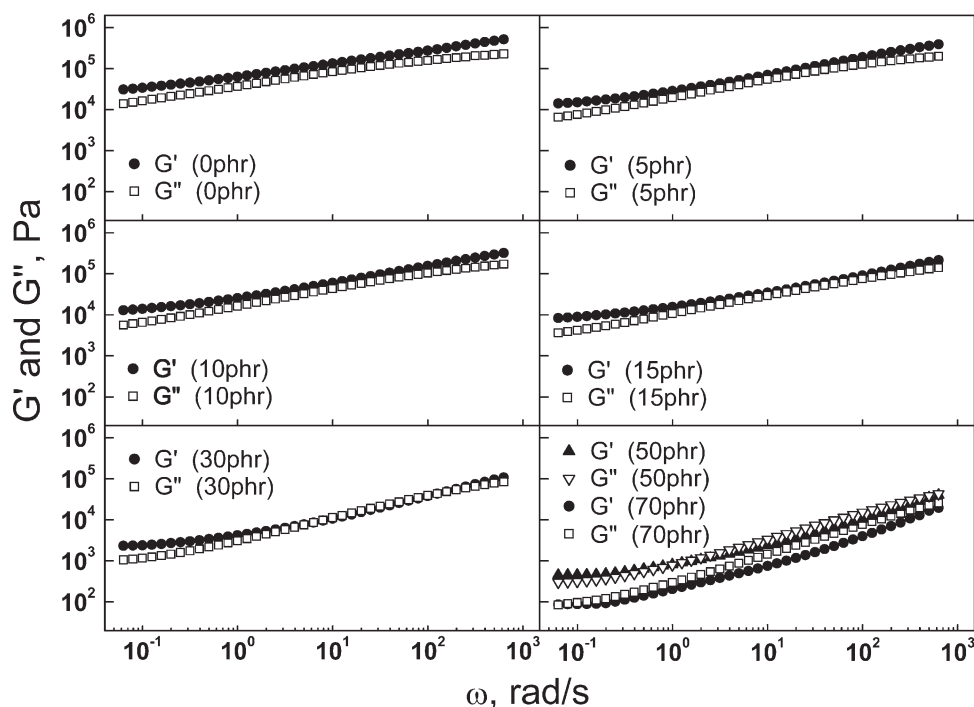
Figure 2 G' and G'' versus ω of the processed PVC/DOP systems at 180°C.

content increased, there was an apparent solid–liquid transition in the rheological behavior of these PVC/DOP systems. In addition, in the low-frequency region, G' and G'' declined with increasing DOP content and showed terminal platforms or quasi-equilibrium moduli in the systems with DOP contents of 30–70 phr. This indicated the existence of a high-elastic network. However, the description of a transition from solidlike to liquidlike rheological behavior for the PVC/DOP system does not mean the motion of the PVC molecular chains; it just indicates that the viscous flow started to predominate in the rheological behavior rather than the elastic deformation.
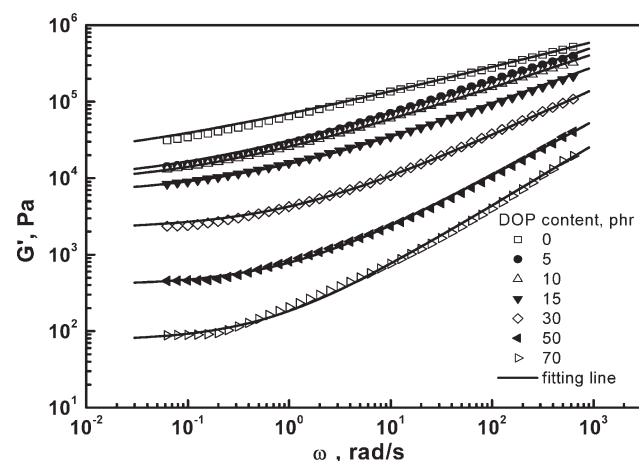
From further analysis, we found that an empirical equation [eq. (1)] could be used to fit the observed curves (Fig. 3):

$$G' = G'_0 + K\omega^n \qquad (1)$$

where G'_0 may be interpreted as the low-frequency yield value of the storage modulus and $G'_0 + K$ can be regarded as G' when $\omega = 1$. The exponent n is a dependent index of the frequency. A bigger n indicates a higher dependence of G' on the frequency. The data listed in Table I show that G'_0 decreased remarkably with increasing DOP content; this indicated that the network of the PVC system with a higher DOP content was softer and apt to deform. On the other hand, n increased remarkably with increasing DOP content; this indicated that for the

Figure 3 G' and fitting line versus ω of the processed PVC/DOP systems at 180°C.

TABLE I
Rheological Parameters of Eq. (1) for the PVC/DOP Systems

DOP content (phr)	G' (Pa)		
	G'_0	K	n
0	1.33×10^4	5.67×10^4	0.34
5	8.58×10^3	2.26×10^4	0.45
10	7.57×10^3	1.84×10^4	0.45
15	6.02×10^3	9.43×10^4	0.49
30	2.17×10^3	2.11×10^3	0.61
50	4.00×10^2	3.85×10^2	0.72
70	7.50×10	1.09×10^2	0.80

Figure 4 Dependence of η* on the frequency of the processed PVC/DOP systems at 180°C.

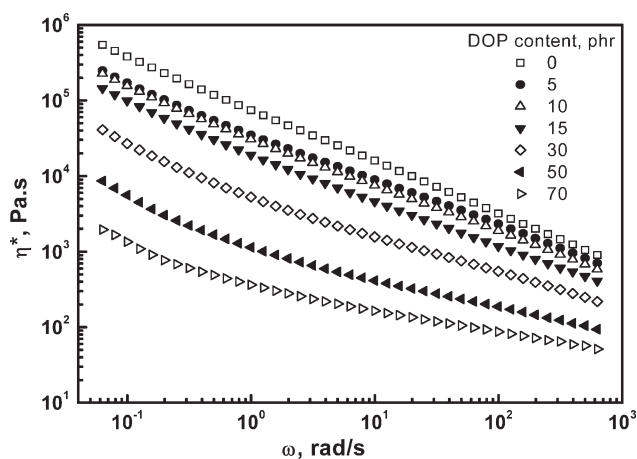**Figure 5** Tan δ versus frequency of the processed PVC/DOP systems at 180°C.

PVC/DOP system, a higher DOP content resulted in a stronger dependence of G' on the frequency. Equation (1) was originally used to simulate the particle suspension system.[21] Here, eq. (1) describes well the rheological behavior of the plasticized PVC systems; this indicated the existence of particulate flowing characteristics in the PVC/DOP systems due to the undestroyed PVC particles and the gel networks formed by the microcrystallite.

In the measured frequency range, there was no Newtonian plateau in the complex viscosity (η*) for all of the PVC/DOP systems, and η* steadily decreased with increasing DOP content (Fig. 4). In a low-frequency range, η* of the PVC/DOP systems with a 30–70 phr DOP content showed a higher increase with decreasing frequency; this also indicated the appearance of a gel network. It was apparent that for a given frequency, η* showed a linear decrease with increasing DOP content. η* showed a faster decrease in the low-frequency range than in the high-frequency range; this indicated that η* depended more on the DOP content in the low-frequency range.

The dependence of the loss tangent (tan δ) on the frequency and the van Gurn–Palmen plots are shown in Figures 5 and 6. Tan δ and the phase angle δ increased apparently with increasing DOP content, and when the DOP content was equal to or greater than 30 phr, tan δ and δ were greater than 1 and 45°, respectively. For the PVC/DOP (100/70) system, there were two tan δ peaks; this indicated an increase in the viscosity and the appearance of new flowing segments of PVC.

In fact, as a kind of plasticizer, the DOP penetrated into the PVC grains [Fig. 7(a)], swelled them, increased their size, glued the particles together, and existed in a free state with a transition process [Fig. 7(b)], and the DOP molecular could weaken the interaction of the PVC molecular chains and result
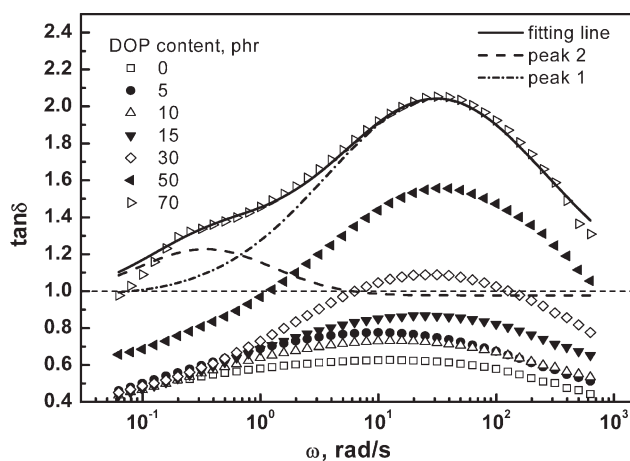
in a high mobility of the PVC molecular chains or a low resistance to deformation, that is, a low G'. During the heating process, the PVC particles and DOP fused together. The grains, agglomerates, and primary particles of PVC were successively destroyed to form a homogeneous material with a morphological structure, which packed grains and primary particles. When the DOP content was low, the dynamic rheological behavior of the PVC/DOP systems showed the feature of a solid filler-filled system; this indicated the formation of a homogeneous material with a morphological structure of grains and primary particles. This was verified by some researchers and our studies [Fig. 7(c)]. However, the dynamic rheological behavior of the PVC/DOP systems showed the feature of a high elastic network at a high DOP content. From the SEM observation [Fig. 7(d)], we observed that there was a homogeneous phase with a morphological structure of a packing of grains and primary particles. As a whole, the
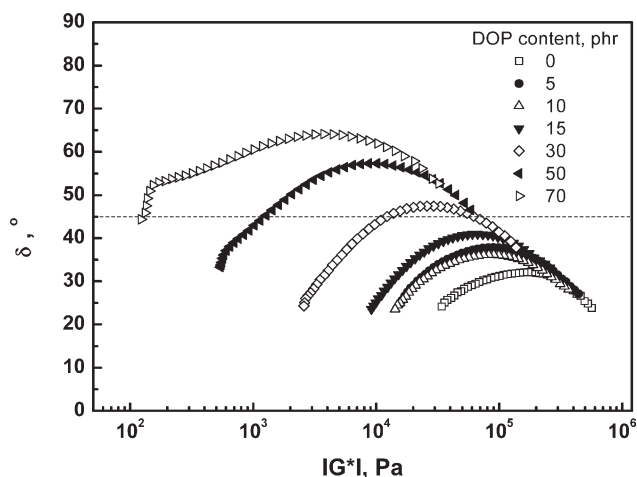

Figure 6 van Gurn–Palmen plots of the processed PVC/DOP systems at 180°C. G* is the complex modulus.

(a) PVC resin

(b) PVC dry blend powder (100/70)

(c) Processed PVC/DOP (100/5)

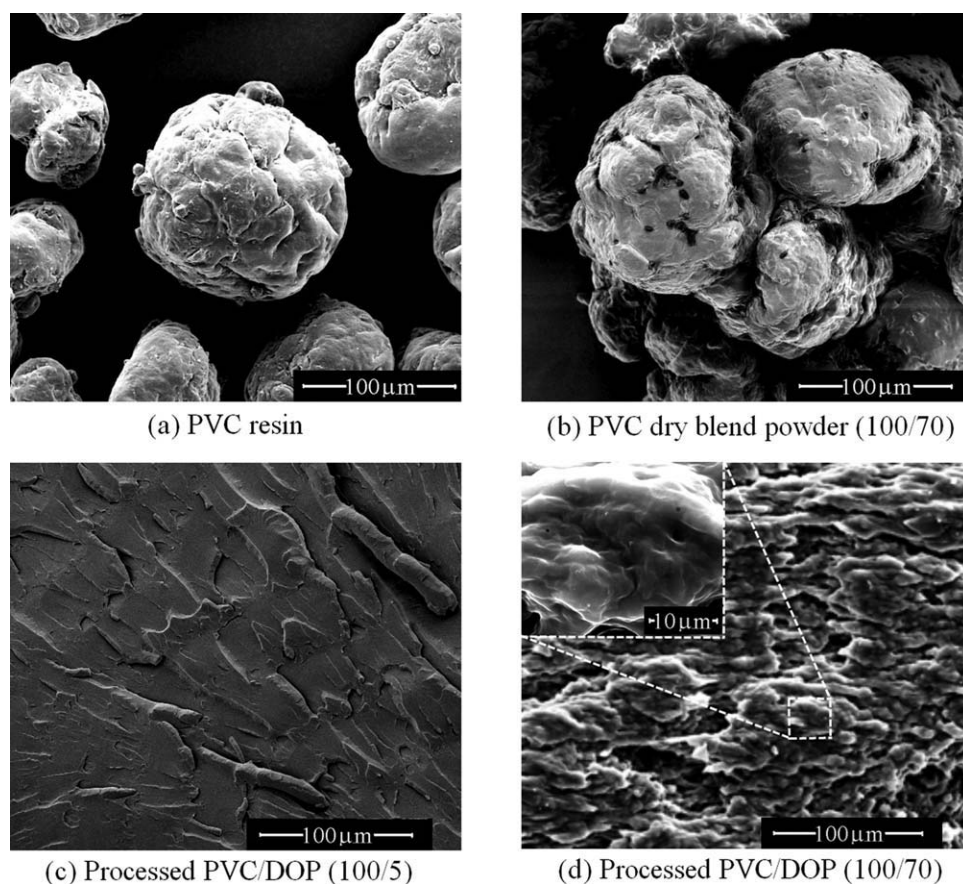(d) Processed PVC/DOP (100/70)

Figure 7   SEM observations of the morphologies of the processed PVC/DOP systems.

PVC was plasticized or fused better when a continuous phase was formed; this linked all multiscale structures together and predominated in the dynamic rheological behavior of the PVC/DOP systems. With 30–70 phr DOP, the mobility of the PVC molecular chain segments improved, and some molecular chains could even move. Accordingly, the gel network, which acted as the main unit of the high elastic flow, had an excellent deformability. Then, the gel network resulted in a comparatively low moduli and the appearance of quasi-equilibrium moduli, low viscosity, and high tan δ in the PVC/DOP systems. On the other hand, when DOP was added to PVC, the DOP first interacted with PVC and was absorbed by PVC. When the DOP content was high enough, the free DOP molecular may have existed in the PVC/DOP systems. All those would have resulted in an appearance of new flowing segments and a solid–liquid transition in the rheological behavior with higher DOP content.

Effect of the melting temperature on the rheological behavior of the PVC/DOP (100/70) system

In addition to plasticizers, the temperature also influenced the mobility of the PVC molecular and

microcrystalline structure in PVC. Only the PVC/DOP (100/70) system was studied at various melting temperatures because the linearity of the dynamic viscoelasticity was not reachable at low or all temperatures for the other PVC/DOP systems,.

For the PVC/DOP (100/70) system, the effect of the melting temperature on the dynamic rheological behavior is shown in Figure 8. Clearly, the dynamic rheological behavior of the PVC/DOP (100/70) system depended on both the frequency and melting temperature. The relation between G' and G'' changed from solidlike (140–150°C) to gel-like (160–170°C) and then to liquidlike (180–190°C) in the partial or whole measured frequency range, especially at 190°C. G'' was much higher than G'. Clearly, there was a transition temperature for the G' of the PVC/DOP (100/70) system, especially at a low frequency. All of this indicated that the increase in the melting temperature also led to an apparent solid–liquid transition in the rheological behavior of the PVC/DOP (100/70) system.

η^* of the PVC/DOP (100/70) system at various melting temperature is shown in Figure 9. η^* of the PVC/DOP (100/70) system decreased with increasing melting temperature and frequency. The slower decrease of η^* appeared more clearly at high
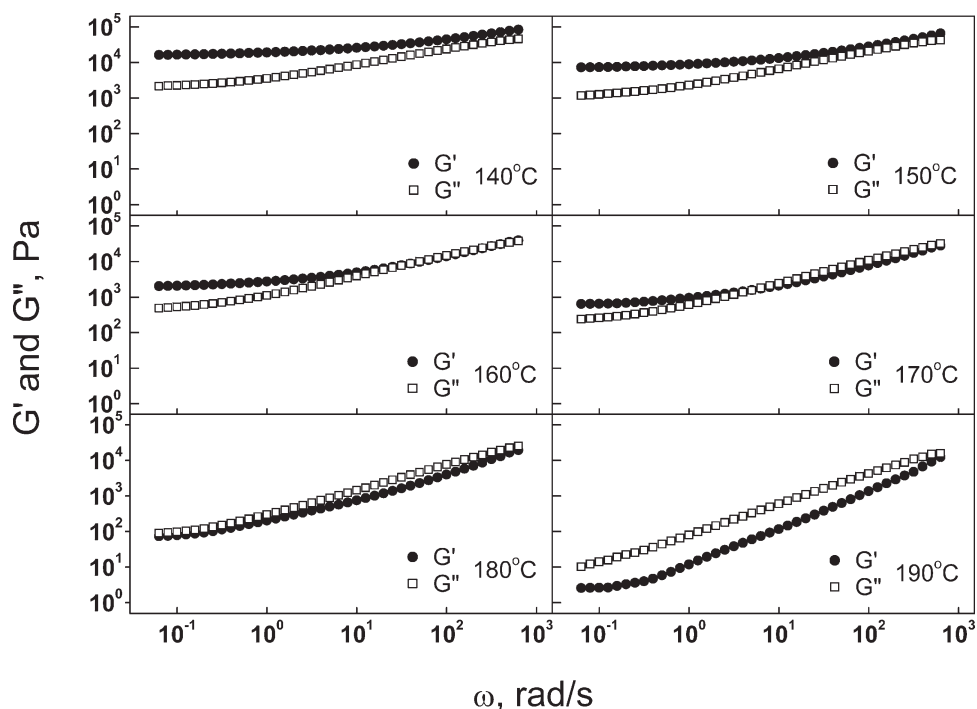
Figure 8 Effect of the melting temperature on the dynamic rheological behavior of the processed PVC/DOP (100/70) system.

melting temperatures than at low melting temperatures. With the increase in the melting temperature, there was an apparent decrease in η^* of the system at low frequency and a little decrease in η^* at high frequency; this indicated that the dynamic rheological behavior at low frequency was more sensitive to microstructural changes in the polymer materials.

The dependence of tan δ on the frequency and the van Gurn–Palmen plots are shown in Figures 10 and 11. The tan δ and phase angle increased apparently with increasing melting temperature. At 180

and 190°C, there were two loss peaks in the curve of tan δ versus frequency; this may have been caused by different flowing regimes. However, in the van Gurn–Palmen plots, the curves showed characteristics similar to a monodisperse polymer to some extent. Tan δ and δ were much greater than 1 and 45°, respectively.

As a matter of fact, we suggest that because of the existence of a microcrystalline structure in PVC, there was a high elastic network in the PVC/DOP (100/70) system. The mobility of the molecular chain segments and even some molecular chains was improved in the PVC/DOP (100/70) system. When
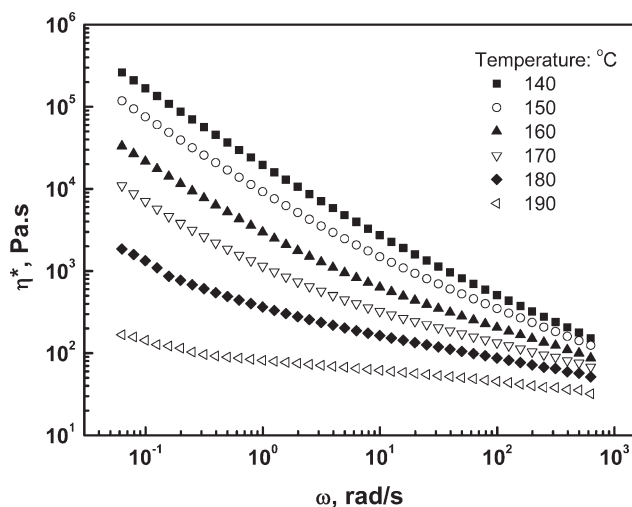

Figure 9 Dependence of η^* on the frequency of the processed PVC/DOP (100/70) system at various melting temperatures.
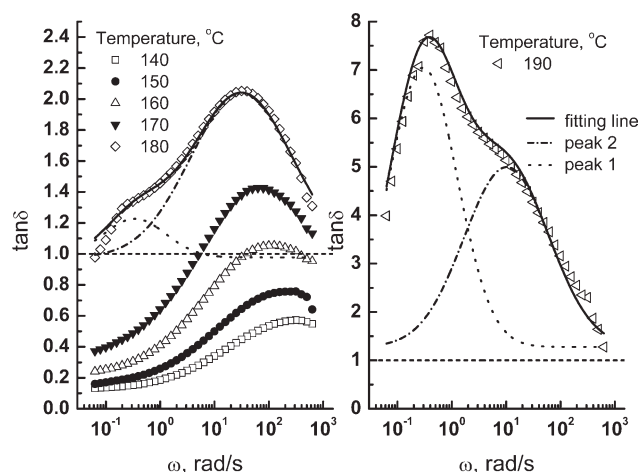

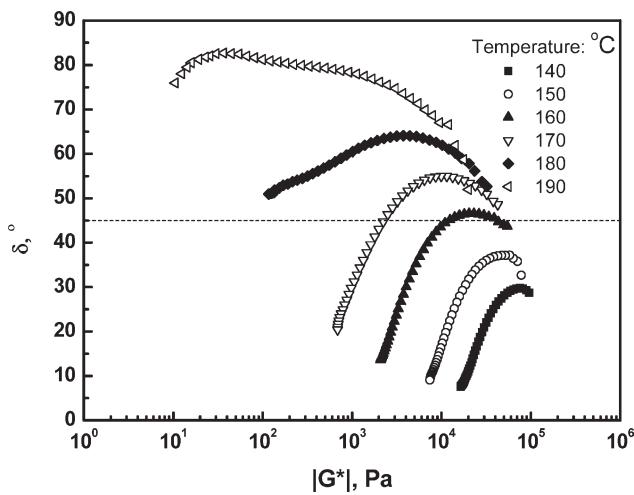**Figure 10** Tan δ versus frequency of the processed PVC/DOP (100/70) system at various melting temperatures.

Figure 11 van Gurn–Palmen plots of the processed PVC/DOP (100/70) system at various melting temperatures.

Figure 12 DSC behavior of the processed PVC/DOP systems.

the melt temperature was low, only chain segments could move, and molecular chain motion was limited by the network. Because the network was a kind of physical crosslinking network, with increasing melting temperature, the crosslinking density became lower; this resulted in the motion of some molecular chains. In the melting temperature range used in this study, the destruction and formation of a physical crosslinking network was reversible. This resulted in the existence of a high elastic state of the dynamic rheological behavior. Of course, the resistance to motion of molecular chains was much bigger than that of the chain segments; this led to a bigger value of tan δ at a higher melting temperature. In addition, the existence of activation energy for the motion of molecular chains also led to the transition temperature for the change in the dynamic rheological behavior.

DSC analysis of the microcrystallite of PVC in the PVC/DOP systems

To verify the suggestion that the microcrystalline structure or primary crystallite played an important role in the crosslinking network of the PVC/DOP systems, the gelation degree (G) and X_c of the PVC/DOP systems were analyzed through DSC.

Gilbert and Vyvoda[22] were the first to identify two endothermic peaks (the A and B enthalpies) on the DSC patterns of processed PVC. Then, eq. (2), involving the A and B enthalpies, was proposed by Potente[23] to quantitatively calculate G of PVC through DSC data:

$$G = [\Delta H_A / (\Delta H_A + \Delta H_B)] \times 100\% \quad (2)$$

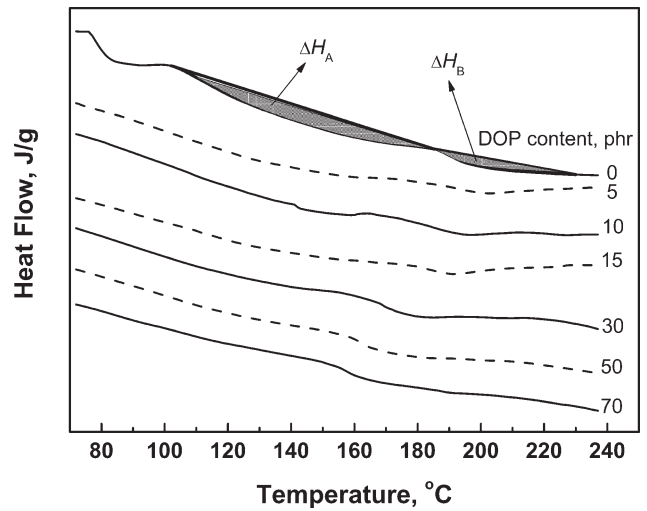where ΔH_A and ΔH_B are the melting enthalpy of the secondary and primary crystallites, respectively

(Fig. 12). At the same time, X_c could be calculated with eq. (3):

$$X_c = \Delta H_u / \Delta H_u^0 \quad (3)$$

where $\Delta H_u = \Delta H_A + \Delta H_B$, represents the actual heat enthalpy of the sample and $\Delta H_u^0 = 43.9$ J/g, represents the heat enthalpy of samples with 100% crystallinity.[24,25] In this study, the changes in ΔH_A and ΔH_B with the DOP content are shown in Figure 13.

From those figures, we observed that ΔH_A decreased monotonously and ΔH_B almost remained unchanged subsequent to a slight increase in the DOP content; this verified that the primary crystallite indeed existed in those PVC/DOP systems. In fact, when the mixing temperature was 140°C, the real melting temperatures of these PVC/DOP systems were lower than the melting temperature range of the primary crystallite, and the DOP molecular mainly
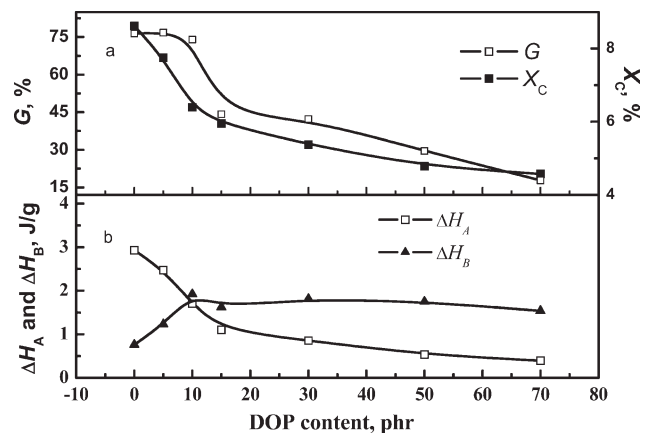

Figure 13 Effects of the DOP content on (a) G and X_c of the processed PVC/DOP systems and (b) the melting enthalpy of the processed PVC/DOP systems.

DOP content (phr)	T_{ini} (°C)	T_c (°C)	T_{ter} (°C)
0	110.04	180.96	228.16
5	112.16	181.17	230.14
10	100.66	172.78	223.85
15	105.06	178.13	228.56
30	100.21	154.99	216.82
50	99.16	152.31	212.70
70	82.72	149.54	208.53

T_{ini}, initial temperature of enthalpy A; T_c, dividing temperature of enthalpies A and B; T_{ter}, terminal temperature.

interacted with the PVC molecular in the amorphous region and almost did not diffuse into the primary crystalline region. Therefore, the primary crystallite of PVC was hardly destroyed by DOP and did not depend on the used processing conditions. However, the secondary crystallite was inhibited by DOP because of the increase in the chain mobility of PVC induced by the DOP molecules. At the same time, when the DOP content was low, the primary crystallite of PVC could be partly destroyed because of the shear stress and friction heat or a higher real melting temperature. With increasing DOP content, the primary crystallite of PVC was almost fully preserved, so ΔH_B first increased slightly and then stayed almost unchanged. G and X_c also decreased with increasing DOP content. There were apparent transitions in the curves of ΔH_A, G, and X_c versus the DOP content; these corresponded to the DOP content transition in the dynamic rheological behavior and verified that the dynamic rheological behavior of the PVC/DOP systems were closely related to the microcrystalline structure of PVC. In fact, the DOP molecule combined first with the PVC molecule and then existed as a free molecule in the PVC/DOP systems if the DOP content was high enough. All those resulted in the transitions in the curves of ΔH_A, G, and X_c versus the DOP content. In addition, notably, with increasing DOP content, the melting temperature range for the primary crystallite shifted to a lower temperature range (Table II). This phenomenon may be explained well by the interaction between the DOP and PVC molecules. When the DOP content was higher, the primary crystallite of PVC was encapsulated by DOP molecules. When the PVC/DOP systems were heated, the DOP molecules more easily penetrated into the primary crystallite because of its solvation to PVC molecules; this resulted in the shift in melting temperature. From another point of view, this phenomenon also verified the suggestion that the higher tan δ and the appearance of a new tan δ peak at a low frequency for the PVC/DOP (100/70) system at 180 and 190°C were due to the motion of some PVC molecular chains.

Notably, the results of DSC and dynamic rheological behavior analysis seemed to agree well. In fact, the DSC analysis measured the fusion enthalpy of the crystal, which revealed a partial structure of the PVC/DOP systems. Comparatively, the dynamic rheology analysis revealed the response to the stress and the moving of different units in the PVC/DOP systems generally. When the DOP content was low, G was high, and the mobility of the PVC molecular chains was low. Simultaneously, the PVC molecular chain segments could move along with the primary particles and showed a dynamic rheological behavior of a filler-filled system. When the DOP content was high, it was still a typical homogeneous material with a hierarchical morphology for the PVC/DOP systems. However, the particles swollen by enough DOP had a high deformability, and the PVC molecular chains were highly mobile as well. Therefore, those PVC/DOP systems behaved as high elastic networks in which the reserved microcrystallite acted as the physical crosslink points.

CONCLUSIONS

The addition of DOP remarkably affected the dynamic rheological behavior of the PVC/DOP systems. With increasing DOP content, G', G'', and η^* of the PVC/DOP systems decreased, tan δ and/or the phase angle increased, and there was an apparent DOP content transition in the dynamic rheological behavior of the PVC/DOP systems. For the PVC/DOP (100/70) system, the change in the melting temperature also resulted in a change in the dynamic rheological behavior with an apparent temperature transition at about 190°C. All of the dynamic rheological behavior revealed the existence of high elastic networks in the PVC/DOP systems. The DSC data verified that the high elastic networks in the PVC/DOP systems were influenced by the primary crystallite of PVC and the DOP content. There were apparent transitions in the curves of ΔH_A, G, and X_c versus the DOP content, which corresponded to the DOP content transition in the dynamic rheological behavior and verified that the dynamic rheological behavior of the PVC/DOP systems was closely related to the crystallite of PVC. The DOP inhibited the formation of the secondary crystallite of PVC and hardly influenced the primary crystallite of PVC. The melting temperature range for the primary crystallite shifted to a lower temperature range with increasing DOP content.

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