

Flow Instability in Capillary Extrusion of Plasticized Poly(vinyl chloride)

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ABSTRACT: Flow instability in a capillary extrusion is studied for a high molecular weight, plasticized poly(vinyl chloride) (PVC). The onset of melt fracture correlates with the long time relaxation ascribed to the generation and/or growth of PVC crystallites. An increase in the residence time in the cylinder leads to this long time relaxation and results in the melt fracture, although the apparent shear stress remains constant, irrespective of the residence time. The extrudate temperature and the species of the plasticizer also have a significant influence on the apparatus of the extruded products. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1277–1283, 2001

Key words: viscoelastic properties; rheological properties; melt fracture; extrusion; poly(vinyl chloride)

INTRODUCTION

Plasticized poly(vinyl chloride) (PVC) compounds have been widely used in numerous applications because of their processability, mechanical properties, and relatively low production costs. The final properties in the solid state of the materials depend on the molecular weight of the PVC, as well as the species and contents of the plasticizer. In particular, it is well known that plasticized PVCs, which have a high degree of polymerization, exhibit excellent mechanical properties. Therefore, there is growing interest in their applications, although, they often show flow instability in extrusion, which limits productivity in processing.

The origin and mechanisms of flow instability for various polymers have been discussed extensively over at least 35 years.^{1–12} Nevertheless, it

is still one of the major problems in the field of polymer processing. Generally, the flow instabilities are classified into two groups. One is characterized as the small-amplitude and high-frequency distortion on the surface of the extrudates, which is often called “shark skin.” This phenomenon results in the dull appearance or loss of gloss of the products. The other is known as “melt fracture,” which is characterized as large-scale distortion.

The objective of this study is to clarify the origin of flow instability in a capillary extrusion for the mixture of a high molecular weight PVC and a plasticizer. In particular, the relationship between the melt fracture and linear viscoelastic properties, such as the oscillatory shear modulus and relaxation modulus, are discussed in detail. Furthermore, the effect of the plasticizer on the onset of the melt fracture is also studied.

EXPERIMENTAL

Materials and Sample Preparation

A commercial grade suspension PVC (TE2800, Taiyo PVC Corp.), which contains a small amount

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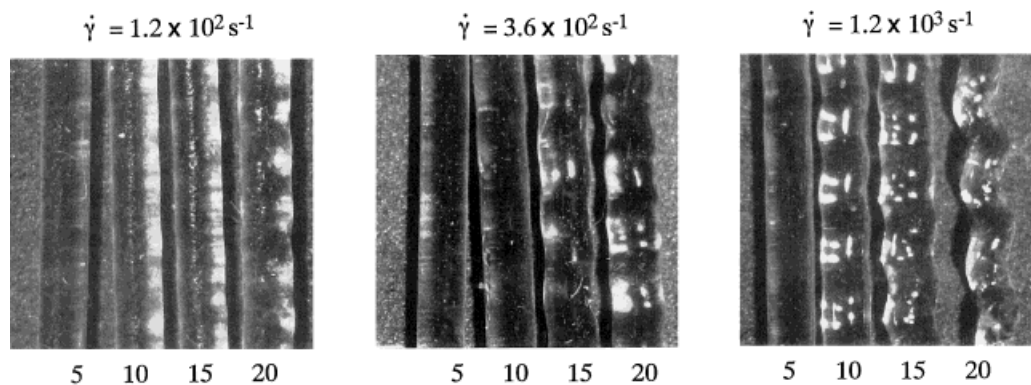


Figure 1 Extrudates of PVC/DOP obtained at 453 K. The shear rates ($\dot{\gamma}$) are 1.2×10^2 , 3.6×10^2 , and $1.2 \times 10^3 \text{ s}^{-1}$. The numbers in the figure denote the residence time (t_a , min) in the cylinder.

of ethylene, was employed. The number- and weight-average molecular weights, which were determined by gel permeation chromatography (GPC, 150-C, Waters) at 313 K using tetrahydrofuran as a solvent, were $M_n = 1.38 \times 10^5$ and $M_w = 2.66 \times 10^5$, respectively, using a polystyrene standard. Di-2-ethylhexyl phthalate (DOP) and dibutyl phthalate (DBP) were employed as the plasticizers. The blend composition of the components in the PVC/plasticizer was 50/50 (w/w). The PVC and plasticizer were blended with a small amount of the thermal stabilizer using a two-roll mill in which the surface temperature was kept at 443 K. Observing the morphology of the compounds by an electron microscope, we confirmed that the samples blended at this temperature had no primary particles of PVC. Therefore, in this study, we do not have to discuss the difference in the degree of "gelation," which is the degree of collapse of the primary particles, even though it is generally accepted that the degree of gelation has a serious influence on the processing of PVC compounds.^{6,13}

Measurements

A capillary rheometer (Capilograph, Toyo Seiki) was used for the evaluation of the flow instability in a capillary extrusion. The capillary die employed was 60 mm in length and 0.5 mm in radius with an L/D ratio of 60 and an entrance angle of $\pi/2$. The extrudate temperatures were 453 and 463 K, which are conventional for processing. In this study the effect of the residence time in the cylinder of the rheometer, as well as the apparent shear stress, on the onset of flow instability was examined.

The oscillatory shear moduli, such as storage shear modulus (G') and loss modulus (G''), were

measured at 453 and 463 K using a parallel-plate type rheometer (MR-500, Rheology). The stress relaxation measurements were also carried out at 453 and 463 K in order to investigate the long time relaxation mechanism. The applied shear strain was 0.4. All measurements were carried out under a nitrogen atmosphere. We also confirmed by GPC that molecular degradation did not take place during the measurements.

The endotherm profile was investigated by using a differential scanning calorimeter (DSC-7, Perkin-Elmer). The samples of about 10-mg weight were sealed in aluminum pans and kept at various annealing temperatures ($T_a = 373, 403,$ and 433 K) for 20 min and cooled to room temper-

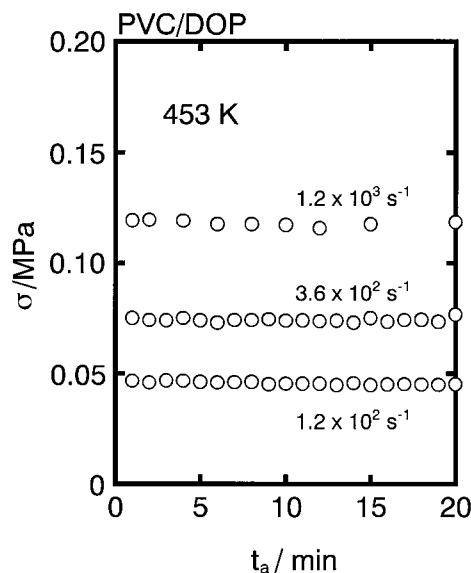


Figure 2 The time dependence of the apparent shear stress (σ) at 453 K for PVC/DOP. The numbers represent the apparent shear rates ($\dot{\gamma}$).

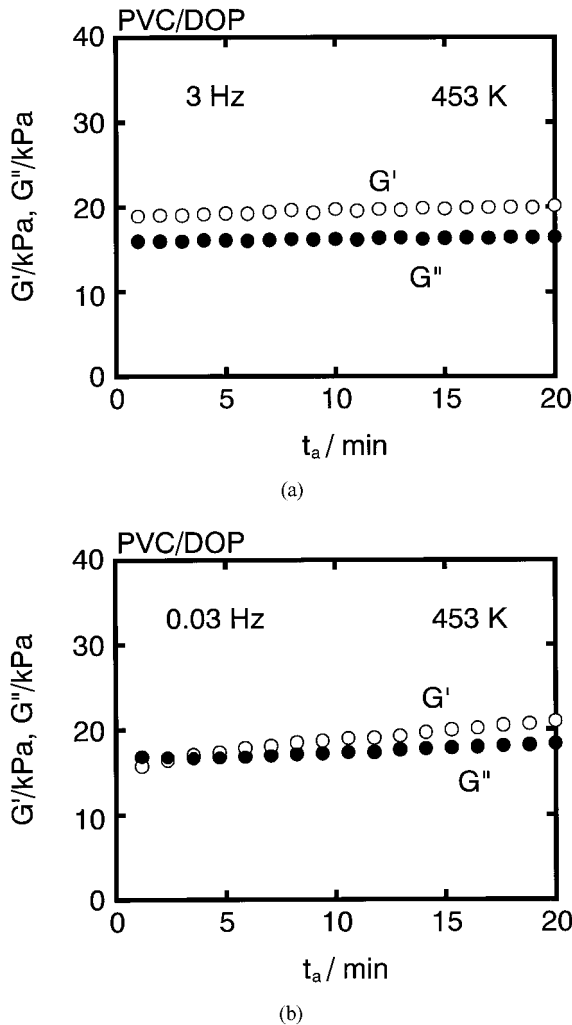


Figure 3 The time variation of (○) shear storage modulus (G') and (●) loss modulus (G'') at 453 K for PVC/DOP. The frequencies used were (a) 3 and (b) 0.03 Hz.

ature at a rate of 10 K min^{-1} . Then the heating thermograms were examined at a rate of 10 K min^{-1} . All of the procedures were performed under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Flow Instability of PVC/DOP

Figure 1 shows the photographs of the PVC/DOP extruded at 453 K. The apparent shear rates ($\dot{\gamma}$) are 1.2×10^2 , 3.6×10^2 , and $1.2 \times 10^3 \text{ s}^{-1}$. The numerals in the figure denote the residence time (min) in the cylinder, which is considered the annealing time (t_a). As seen in the figure, some of the extrudates exhibit a wavy shape known as the

typical distortion pattern of melt fracture. Moreover, the melt fracture takes place prominently for the extrudates with a longer residence time, irrespective of the shear rate.

Figure 2 shows the time variation of the apparent shear stress (σ) at various shear rates. It is found from the figure that the apparent shear stress remains constant in the experimental time region. According to numerous studies, melt fracture often takes place when the shear stress is above the critical one. Furthermore, the onset of melt fracture is noticed as a change in the slope of a log-log plot of shear stress versus shear rate.^{3,4,6} In this study, however, it is obvious that the onset of melt fracture is independent of the shear stress and significantly affected by the residence time t_a in the cylinder. Considering the results, we must control the residence time in a capillary rheometer or an extruder in the evaluation of the flow instability of a plasticized PVC.

The time dependence of the oscillatory shear modulus for the PVC/DOP was measured at 453 K to comprehend the variation of the rheological properties during the stay in the cylinder of the capillary rheometer. As shown in Figure 3(a), both moduli are little changed at 3 Hz. On the other hand, G' increases rapidly at 0.03 Hz as shown in Figure 3(b), which demonstrates that the oscillatory shear modulus, as well as the appearance of the extrudates, depends on the thermal history.

By measuring the time variation of oscillatory moduli at various frequencies, we obtained the

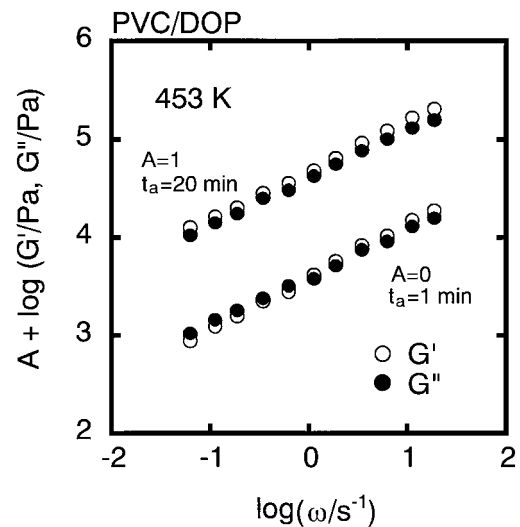


Figure 4 The frequency dependence of (○) shear storage modulus (G') and (●) loss modulus (G'') at 453 K for PVC/DOP with $t_a = 1$ and 20 min.

frequency dependence as shown in Figure 4. In the figure, the results of the samples with residence times t_a of 1 and 20 min are exemplified. For the sample with $t_a = 20$ min, G' is larger than G'' , which is $\tan \delta < 1$ in the frequency range, whereas G' is smaller than G'' at the lower frequency region for the sample with $t_a = 1$ min. These facts indicate that the annealing procedure at 453 K really enhances the long time relaxation mechanism, although conventional PVC compounds are often processed at this temperature.

Stress relaxation measurements are also carried out for a better understanding of the viscoelastic properties in the long time region. Figure 5 shows the relaxation modulus $[G(t)]$ at 453 K. In the figure the circles represent the experimental values and the lines denote the calculated ones from the oscillatory moduli using the following equation proposed by Schwarzl¹⁴:

$$G(t) = G'(\omega) - 0.560 G''\left(\frac{\omega}{2}\right) + 0.200 G''(\omega) \Big|_{\omega=1/t} \quad (1)$$

The reasonable agreement between the experimental relaxation moduli and the calculated ones is observed, suggesting that the rheological properties at the applied strain of 0.4 are within the linear viscoelastic region. Furthermore, $G(t)$ falls off rapidly in the long time region for the sample with $t_a = 1$ min whereas it relaxes with a constant slope of a log-log plot for the sample with t_a

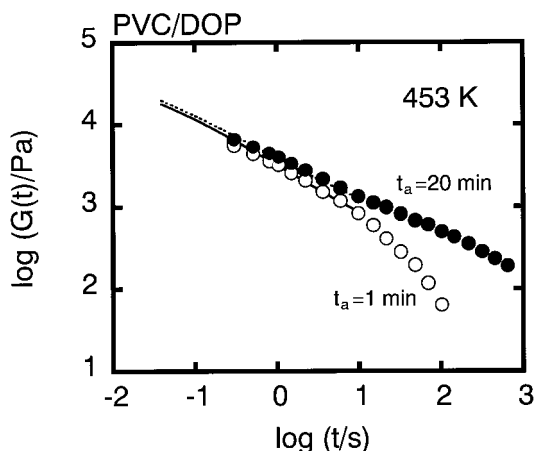


Figure 5 The relaxation modulus $[G(t)]$ at 453 K for PVC/DOP at $t_a = (\circ)$ 1 and (\bullet) 20 min. The values were calculated by eq. (1) for the sample with $t_a = (---)$ 1 and (\cdots) 20 min.

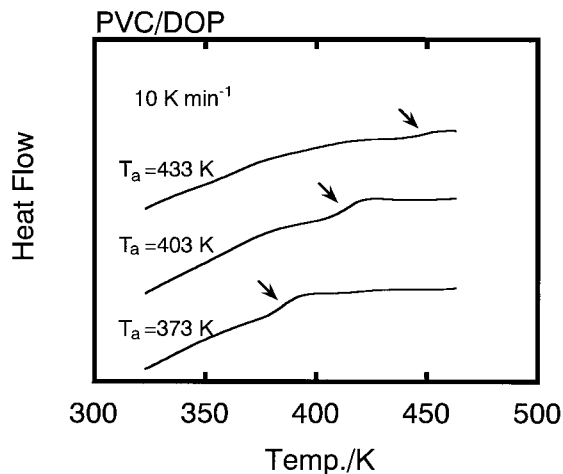


Figure 6 The DSC thermograms for PVC/DOP at a heating rate of 10 K min^{-1} ; T_a , the annealing temperature; the arrows denote the shoulder ascribed to the fusion of the crystallites produced during the annealing.

$= 20$ min. According to Chambon and Winter,^{15,16} the linear viscoelastic properties of a critical gel can be described as follows:

$$G' \propto G'' \propto \omega^n \quad (2)$$

$$G(t) = S_0 t^{-n} \quad (3)$$

where S_0 is the gel strength.

It is apparent from Figures 4 and 5 that the oscillatory shear moduli (Fig. 4) and relaxation modulus (Fig. 5) of the sample with $t_a = 20$ min obey eqs. (2) and (3) in the experimental frequency or time region. The facts suggest that the sample with $t_a = 20$ min behaves like a critical gel from the rheological point of view, which exhibits strong elasticity compared to conventional thermoplastics.¹⁷ Therefore, it is taken for granted that the marked melt fracture takes place. In other words, the onset of melt fracture is attributed to the strong melt elasticity.

The generation and growth of PVC crystallites is responsible for the enhancement of long time relaxation.^{6,18-23} PVC crystallites, which are composed of syndiotactic sequences within the polymer chain, are believed to form a fringed micelle structure.¹⁹ Because of the coexistence of the isotactic sequences, however, the melting point is far below the equilibrium melting point²⁴ ($T_m^0 = 473 \text{ K}$) and the degree of crystallinity is very low. Moreover, PVC crystallites have very broad melting points, depending on the size. Further, the

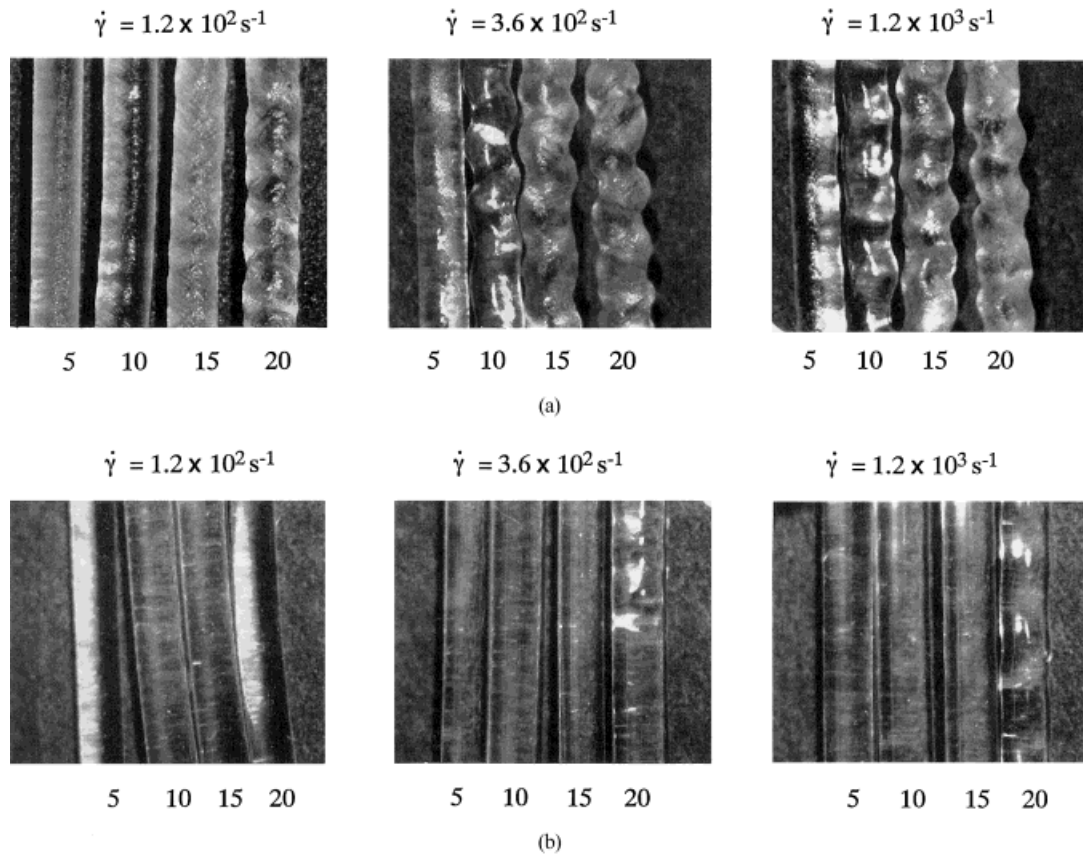


Figure 7 Extrudates of (a) PVC/DOP and (b) PVC/DBP obtained at 443 K. The shear rates ($\dot{\gamma}$) are 1.2×10^2 , 3.6×10^2 , and $1.2 \times 10^3 \text{ s}^{-1}$. The numbers in the figure denote the residence time (t_a , min) in the cylinder.

crystalline size, which is responsible for the melting point, is affected by the annealing and/or the processing temperature, which demonstrates that the thermal history decides the distribution of melting points.^{6,13,23,25} Furthermore, some of crystallites exist even at the processing temperature. In other words, the melting points of part of the crystallites are higher than the processing temperature. According to Barendswaard et al.,²² the degree of crystallinity for a PVC/DOP (50/50) compound is about 5%, even at 453 K. The modulus in the low frequency or in the long time region are enhanced as a result of the existence of the crystallites, because they act as crosslink points.²³ In particular, high molecular weight PVC, which is polymerized at a lower temperature, has increased syndiotacticity, which enhances the degree of crystallinity.²⁰ Consequently, these compounds, including high molecular weight PVC, often show melt fracture.

To confirm the generation and growth of PVC crystallites during the stay in the cylinder, DSC heating measurements are carried out for the PVC/DOP annealed at various temperatures for 20 min.

Figure 6 shows the results of the DSC heating run. The endothermic shoulder, denoted by the arrows in the figure, is observed at a temperature just above the T_a , which is ascribed to the fusion of the PVC crystallites. According to previous studies,^{6,13,23,25,26} the DSC pattern of PVC fusion does not appear as a sharp peak but as one or two shoulders like those in the figure. The results in Figure 6 show that the PVC used in this study crystallizes during the annealing, even at the processing temperature. The shoulder becomes distinct as the annealing temperature decreases. This is reasonable because deep supercooling promotes the growth of crystallites at temperatures well above the glass-transition temperature.

Effect of Species of Plasticizer on Flow Instability

Figure 7(a) shows the extrudates obtained at 443 K for the PVC/DOP. Compared with the extrudates at 453 K shown in Figure 1, even the samples with a short residence time exhibit the marked melt fracture at this temperature. Thus,

the extrudate temperature, as well as the residence time, has a significant effect on the onset of melt fracture. This phenomenon corresponds with the degree of crystallinity, which decreases with increasing temperature.

The extrudates of the PVC/DBP at 443 K are shown in Figure 7(b). The aspect of the extrudates is found to depend on the species of the plasticizer. When the DBP is used as a plasticizer, the melt fracture takes place only for the extrudate that has a long residence time ($t_a = 20$ min) at $\dot{\gamma} = 3.6 \times 10^2$ and $1.2 \times 10^3 \text{ s}^{-1}$. The apparent shear stress (not presented) is independent of the residence times for the PVC/DOP and PVC/DBP, which are the same as that observed for the PVC/DOP at 453 K shown in Figure 2.

Figure 8 shows the frequency dependence of the oscillatory shear modulus for the PVC/DOP [Fig. 8(a)] and PVC/DBP [Fig. 8(b)]. Both G' and G'' for the PVC/DBP are lower than those for the PVC/DOP. Moreover, G' is always larger than G'' in the experimental frequency region for the PVC/DOP at 443 K. On the other hand, G'' is always larger than G' in the lower frequency region for the PVC/DBP with $t_a = 1$ min. The difference between the PVC/DOP and the PVC/DBP is attributed to the difference in the solvating property of the plasticizer. According to Bigg,²⁷ the solubility parameter between PVC and DBP is lower than that between PVC and DOP. It is generally accepted that the melting temperature of the polymer is lowered by a good solvent.²⁸ Accordingly, the melting temperature of the PVC crystallites in the PVC/DBP is lower than that in the PVC/DOP, which leads to the difference in the degree of crystallinity at the processing temperature.

Figure 9 shows the relaxation modulus at 443 K. The order of the magnitude of $G(t)$ at longer times is as follows: PVC/DOP ($t_a = 20$ min), PVC/DOP ($t_a = 1$ min), PVC/DBP ($t_a = 20$ min), and PVC/DBP ($t_a = 1$ min). This corresponds to the aspect of the extrudates as shown in Figure 8, demonstrating that the flow instability of the plasticized PVC can be predicted by the linear viscoelastic properties, such as the oscillatory modulus and relaxation modulus. In particular, the relaxation modulus gives useful information on the onset of the melt fracture.

CONCLUSION

In the present study, the flow instability was investigated, especially the onset of melt fracture,

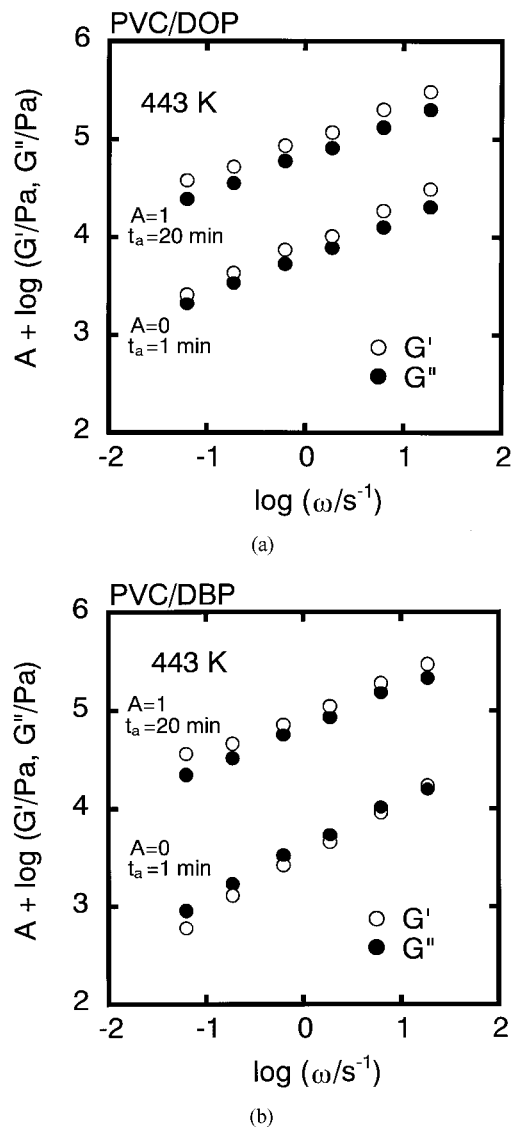


Figure 8 The frequency dependence of (○) shear storage modulus (G') and (●) loss modulus (G'') at 443 K for (a) PVC/DOP and (b) PVC/DBP. The results for the samples with $t_a = 1$ and 20 min are shown.

in a capillary extrusion of a mixture of high molecular weight PVC and a plasticizer, in which two kinds of plasticizers, DOP and DBP, were employed. The onset of melt fracture depended on the residence time in the cylinder of the capillary rheometer. The extrudate with a long residence time exhibited a marked melt fracture, although the apparent shear stress remained constant, irrespective of the residence time. The result demonstrated that there is no critical shear stress for the onset of melt fracture for the plasticized PVC.

The melt fracture was found to correlate with the linear viscoelastic properties. The sample, which exhibited marked melt fracture, had a long

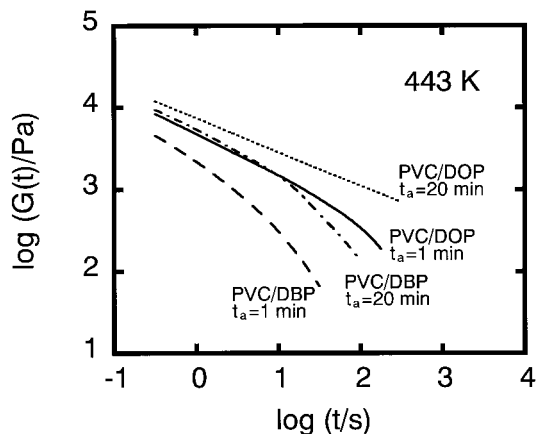


Figure 9 The relaxation modulus at 443 K for PVC/DOP, $t_a =$ (—) 1 and (\cdots) 20 min $G(t)$; and PVC/DBP, $t_a =$ (- - -) 1 and (- · -) 20 min.

relaxation time. The annealing enhanced the long time relaxation ascribed to the growth of PVC crystallites. The solubility parameter between PVC and the plasticizer also affected the melt fracture, because the ability of the dissolution of PVC crystallites depends on the species of the plasticizer. In this study, PVC/DBP exhibited less melt fracture than PVC/DOP, because DBP has the stronger solvating property of the PVC crystallites.

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