EFFECT OF PHYSICAL CROSSLINKING OF PVC/DOP GEL ON SMALL AMPLITUDE OSCILLATORY SHEAR

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Abstract - Dynamic viscoelasticity of PVC/di-octyl phthalate (DOP) contained 20 wt% of PVC was measured for several PVCs which had different molecular weight at various temperatures. The equilibrium modulus, Ge, of various PVC/DOP gels showed the temperature dependencies. However, at a constant relative distance from the gel point, the frequency dependencies of Ge for the different molecular weight sample were almost identical. Assuming classical rubber elasticity, these results suggest that the structure of the gel essentially does not depend on the molecular weight of PVC, but only on the relative distance.

Keywords: Physical crosslinking, PVC, Rheology

Introduction

Poly(vinyl chloride)/di-octyl phthalate (DOP) gels with PVC content of 20 wt.% was prepared by a solvent evaporation method. The dynamic viscoelsticity was measured at various temperatures. The gel exhibited a typical sol–gel transition behavior with elevating temperature. At a critical temperature the PVC gel showed the sol-gel transition behavior: the characteristic power-law dependence of storage and loss modulus, G' and G'', on the angular frequency ω,

$$G'(\omega) = G''(\omega) / \tan(n\pi) \propto \omega^n \qquad (1)$$

$$\tan \delta = \tan(n\pi / 2) \qquad (2)$$

It is reported that PVC gel is classified as randomly crosslinked networks of flexible PVC strands and the crystal domains play an important role as crosslinking junctions. The physical properties of PVC gels are strongly influenced by the network structure. In fact, the PVC gel shows a pronounced increase of transient elongational viscosity over a critical strain under constant strain rate below the critical sol-gel transition temperature T_{gel} [1,2]. This results from the network structure and cannot be expected behavior for linear polymers. When increasing temperature, the PVC gel still shows the steep increase of the elongational viscosity. Over T_{gel} it does not show, however, any strain hardening. This change is attributed to the change of network structure. Below T_{gel}, the gradual melting of the PVC crystallites takes place with elevating temperature depending on the melting temperature of the crystal domain. Above T_{gel}, a densely connected network throughout the whole system disappears. The melting behavior of PVC crystals worked as crosslinking junction in the physical gel dominates the rheological properties. The temperature, concentration of polymer, solvent and molecular weight may affect the network structure, thereby a change of the rheological behaviors. So far the study on the crosslinking structure has not been fully understood, however. Kakiuchi et al. [3] examined the equilibrium modulus Ge of PVC/ DOP gels in terms of molecular weight and concentration of PVC. They found that the equilibrium modulus normalized by concentration, temperature and molecular weight was universally dependent on the relative distance from the gelation point in terms of PVC concentration. This suggests that the mesh size of crosslinked network in the gels near gelation point is universally determined by the relative distance and molecular weight.

In this study we investigated the gel structure of PVC/DOP gels with constant polymer concentration. The equilibrium modulus and the elongational viscosity were analyzed in terms of the relative distance from T_{gel}.

Experimental

PVC/DOP gels having 20 wt% of PVC was used. The suspension polymerized PVC was supplied from Mitsubishi Chemical Coorporation. Weight-average molecular weights are 61.9, 102 and 173 kg/mol and denoted as PVC6, 10, 17, respectively. The molecular weight distributions are approximately 2 for all the samples. Prior to the sample preparation, the PVC sample was purified through precipitation from a tetrahydrofuran (THF)/methanol mixture. For preparation of the PVC/DOP gel, prescribed amounts of the purified PVC samples and DOP were dissolved in THF (70% in weight), and then THF was allowed to thoroughly evaporate from a shallow container (glass dish) at room temperature. During a long evaporation period (>3 weeks), the PVC/DOP gel was wellstabilized/equilibrated. Thus, no detectable change was observed for the rheological data obtained from repeated measurements with intervals of 1 and 2 months. The reproducibility of the data reported in this paper was confirmed in this way.

The dynamic oscillation measurements and uniaxial elongational tests were carried out by rotational rheometer (Ares, TA instruments).

Results and Discussion

The dynamic viscoelastic measurements of PVC6, 10, 17 gels with DOP were carried out at various temperatures. We determined T_{gel} by tan δ vs T plots at various frequencies. All curves converged on a certain

values at T_{gel}. At this temperature the relationships of Eq. 1 and 2 were valid. For the gels of various molecular weight at various temperatures, G' was shown in Fig. 1. Here we defined the relative distance from the T_{gel};

$$\alpha = \left| (T - T_{gel}) \right| / T_{gel} \qquad (3)$$

At the same α (0.25, 0.15, 0.1) G' of various molecular weight showed frequency-independency and those were similar values. As decreasing α (approaching to T_{gel}) G' decreased. G' at $\alpha = 0.05$ scatter of the data was observed. It can be said that this is due to the experimental error since the physical crosslinking junction became temperature sensitive by the fluctuation at the temperature close to T_{gel}.

The equilibrium modulus G_e of chemically crosslinked network polymer can be described as follows;

$$G_e = cRT / M_x \qquad (4)$$

where c, R and M_x are concentration, gas constant and molecular weight of crosslinking strand. We apply this concept to PVC/DOP gels. Fig. 2 shows the equilibrium modulus determined from 1 and 10 rads^{-1} plotted against α. According to Eq. 4 the molecular weight of crosslinking strand of our gel system can be demonstrated by cRT/G_e as shown in Fig. 3. This suggests that the molecular weight of crosslinking junction which is effective for elasticity of gel decreases with increasing α and depends only on α irrespective of M of PVC. We should note that cRT/G_e is smaller than M_w of PVC in some cases. For example at $\alpha = 0.1$, 2-5 chains for PVC6, 10, 17 systems at least associate each other and form independent network strand which can sustain elasticity of the gel.
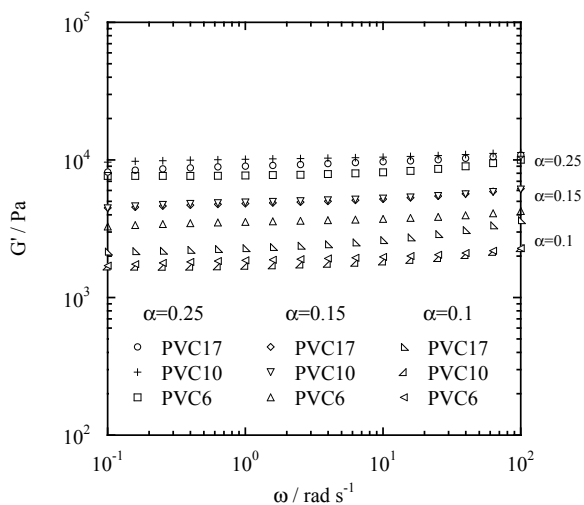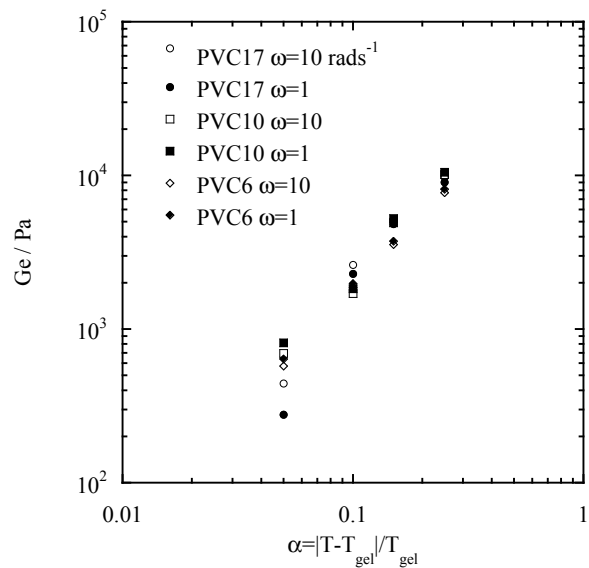
Figure 2 Equilibrium modulus Ge of PVC-6, 10, 17 plotted against relative distance from T_{gel} at angular frequency of 1 and 10 rads^{-1}.
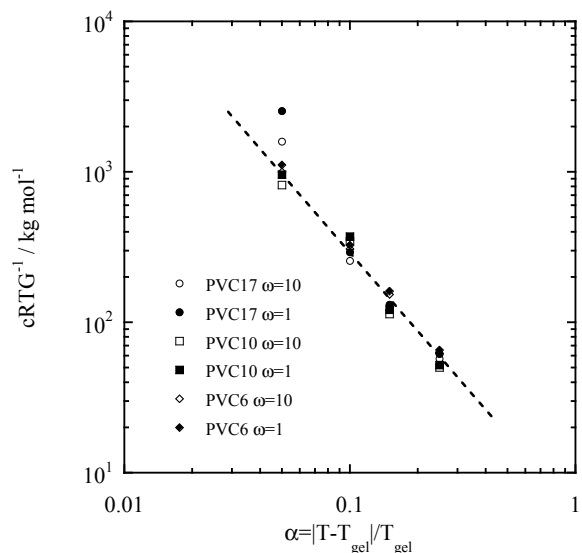
Figure 3 Molecular weight between crosslinking points of PVC-6, 10, 17 plotted against relative distance from T_{gel} at angular frequency of 1 and 10 rads^{-1}.

Conclusions

We studied the rheological behavior of PVC/DOP gels having same concentration but different molecular weight. G' of the PVC gels shows similar G' as comparing at same relative distance from T_{gel}. When we compared G_e as a function of α, G_e increased with an increase with α. The molecular weight of gel network strand based on Eq.4 decreased with increasing α. This suggests that gel network strand can be formed by at least 2-5 molecular chains associate each other to sustain elasticity of the physical gel.

Figure 1 Storage modulus G' of PVC-6, 10, 17 plotted against angular frequency at the relative distance from the T_{gel}, $\alpha = \left| (T - T_{gel}) \right| / T_{gel}$.

References

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