EFFECT OF PHYSICAL CROSSLINKING OF PVC/DOP GEL ON SHEAR AND ELONGATIONAL FLOW: UNIVERSALITY OF ELASTICITY

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ABSTRACT

Shear and elongational behavior of mixtures of poly(vinyl chloride) (PVC) and dioctyl phthalate (DOP) were studied using different molecular weights of PVC. PVC/DOP showed behaviour typical of a gel below a critical temperature and the gel was thermoreversible. The shear moduli and apparent start-up elongational viscosity of the PVC/DOP gels were examined at a fixed relative distance to the gelation temperature, α. The moduli and the apparent viscosity exhibited universality, i.e., the data for all three molecular weights could be superposed at a fixed α.

1. INTRODUCTION

PVC forms physical gels in various solvents. Gelation can be induced either by varying the concentration or the temperature [1-3]. At the critical gel point, the storage modulus (G′) and the loss modulus (G′′) exhibit power-law dependence on the angular frequency, ω, with identical power-law exponents [4]:

$$G'(\omega) = G''(\omega)/\tan \delta \propto \omega^n \qquad (1)$$
$$\tan \delta = \tan(n\pi/2). \qquad (2)$$

The power-law exponent, n, is a characterstic property of the network and is between 0 and 1. For PVC, the relaxation exponent $n \approx 0.75$ and has been found to be independent of the molecular weight, the molecular weight distribution, concentration of the polymer, temperature, solubility of the plasticizer in the PVC, see [2,3] and the references therein. This suggests that, in general, PVC critical gels possess roughly similar fractal network structures.

In this study, we investigate the temperature induced gelation in PVC/DOP mixtures at a fixed polymer concentration. In order to remove the complications arising from the processing and thermal history and various additives, we used the method introduced by Aoki [5] to prepare the PVC/DOP samples. The dynamic modului and the elongational viscosities were measured and analyzed.

2. EXPERIMENTAL

PVC of weight-average molecular weights 61.9, 102 and 173 kg/mol (denoted as PVC6, PVC10 and PVC17 respectively) and polydispersity approximately were used. The suspension polymerized PVCs were supplied by Mitsubishi Chemical Coorporation.

PVC/DOP mixtures with 20 wt% of polymer were prepared by Aoki's method [5] mentioned above. We confirmed that the method could remove the processing history of the sample by noting that no detectable change in the rheological data was observed when the measurements were repeated after 1 and 2 months. The reproducibility of all of the data reported here was confirmed in this way.

The dynamic oscillation measurements and uniaxial elongational tests were carried out at different temperatures using a rotational rheometer (Ares, TA instruments).

3. RESULTS AND DISCUSSION

In order to probe the linear rheology, dynamic viscoelastic measurements of three PVC/DOP mixtures were carried out at various temperatures. For all of the samples, the behaviour that was sol-like at high tempertures became gel-like as the temperature was reduced. At T_{gel}, the dynamic moduli obey Eqs. (1) and (2). Therefore, for each of the samples, we plotted tan δ versus ω at different temperatures, T. Using the plots, we determined the gelation temperature, T_{gel}, as the temperature at which the tan δ became independent of ω. The determined T_{gel} increased with an increase in the molecular weight of the PVC.

The dynamic modului of the gels were found to be a function of both the molecular weight of the PVC and the temperature. Using the value of the storage modulus at low frequencies and classical rubber elasticity, we calculate the approximate molecular weight of the network strands (see Fig. 1). Note that the calculated molecular weight between strands is significantly larger than the molecular weight of the PVC chains. Further, the strand molecular weight depends only on the relative distance from T_{gel}, α = |T − T_{gel}|/T_{gel}, except for α = 0.05. The reason for the lack of universality for α = 0.05 is currently unclear.
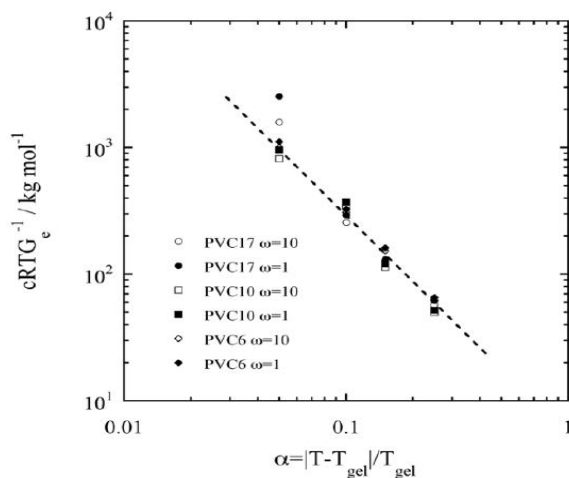

Fig. 1 Universality of Linear Viscoelasticity: "molecular weight of the network strand" as a function of α.

We also performed start-up uniaxial elongation experiments at various temperatures using the same three PVC/DOP mixtures. The samples displayed strong strain hardening below their respective gel points. At a given temperature, the higher molecular weight sample displayed stronger strain hardening. However, similarly to the linear moduli, the apparent viscosity under start-up uniaxial elongations for all of the samples could also be superimposed at a fixed α, except for α = 0.05.

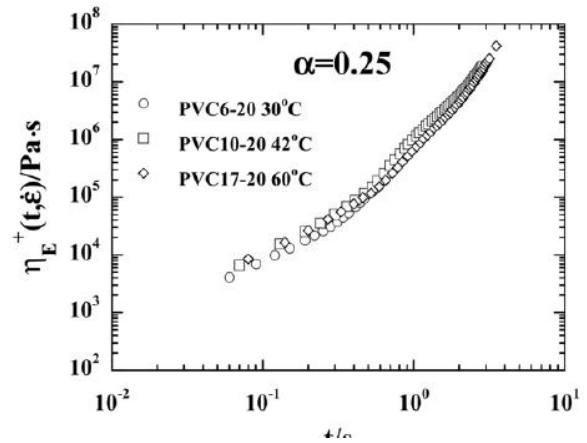Fig. 2 Universality of noninear Viscoelasticity: Apparent viscosity during start-up uniaxial elongation for α = 0.25.

4. SUMMARY

We studied the rheological behavior of PVC/DOP gels for three molecular weights of PVC but at an identical polymer concentration. For the three samples investigated, the dynamic moduli and the apparent viscosity during start-up uniaxial deformation could be superimposed at equal α, except for α = 0.05. In addition, the molecular weight of the gel calculated using classical rubber elasticity is significantly larger than the molecular weight of the PVC chains.

5. REFERENCES

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