LAOS and uniaxial elongational flow behavior of Poly(vinyl chloride)/bis(2-ethylhexyl) phthalate blend

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1. Introduction:

Poly(vinyl chloride) (PVC) is widely used due to the ease with which its properties can be tuned by the addition of plasticizers. In fact, plasticized PVC remains elastic even upon addition of large quantities of plasticizer. This is because the PVC molecules undergo gelation into a three-dimensional molecular network. In addition, the crosslinks leading to the gel state are microcrystallites of PVC. Consequently, the gel that is formed is a physical gel and is thermoreversible.

A significant amount of research has been devoted to the elucidation of the variation of the physical properties of PVC gels with temperature [1], concentration [2], etc. The structure of the PVC gel is generally thought to be adequately described by the fringed-micelle model [3]. The model describes the gel as being composed of microcrystalline domains, which act as crosslinks with flexible chains connecting the microcrystalline domains. In spite of this, the mechanism of gelation in PVC and also the structure of PVC gels are hitherto only poorly understood. In order to shed further light on these topics here we study the variation of the gel properties with temperature, especially focusing on the connection between gel structure and rheological properties.

2. Material:

We used three different molecular weights of commercial poly(vinyl chloride) (labeled as PVC06, PVC10 and PVC17). The PVC was made using suspension polymerization by Mitsubishi Chemical Co. Three gelling systems of the PVC in bis(2-ehylhexyl)phthalate (DOP) were prepared at room temperature from THF solutions (about 80 wt% of THF). No stabilizers were added to the solutions. After the THF evaporated completely, the solid film obtained was used for further testing.

3. Experiment:

Linear viscoelastic measurements were carried out at various temperatures between 60ºC and 175ºC with a strain controlled rheometer (ARES, TA Instruments) using parallel plate geometry (diameter is 25 mm). Elongational viscosity measurements were performed with ARES using the elongational viscosity mode at several temperatures between 30ºC and 150ºC. The strain rates used were between 0.1 to 1.0 s^{-1}. Large amplitude oscillatory shear (LAOS) measurements were carried out with ARES using the parallel plate fixture at several temperatures between 30ºC and 172ºC. The strain amplitude ranged from 10 to 400% with the angular frequency fixed at 1 rad/s.

4. Result and Discussion:

Fig.1 shows G' versus ω curves for PVC06 at 6 different temperatures: 60, 80, 100, 120, 130 and 140ºC. The curves indicate that the behavior changes from that of a sol at high temperatures to that of a crosslinked gel at low temperatures. At the intermediate temperature of 130ºC, we found that

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

with n=0.75 [4]. This behavior is the well known rheological signature for the occurrence of a critical gel and was used to deduce the critical gel temperature of PVC10 and PVC17 also.

Fig.2 shows the start-up elongational viscosity of PVC06 at several strain rates at 60°C. It is clear that the material exhibits strain hardening and similar behavior was found for the other two PVC samples. Further, if we consider the start-up elongational viscosity of the different samples at the same fractional undercooling, α,

$$\alpha \equiv \frac{\left|T - T_{gel}\right|}{T_{gel}}$$

where T is the measurement temperature and T_{gel} is the critical gel temperature, we find that the different curves could essentially be superimposed. This behavior is showen in Fig.3 and suggests that the network structure in the PVC/plasticizer system is determined only by the value of α.

Moreover, we carried out LAOS measurements, and we examined the relation with gel structure. Details will be provided during the presentation.

5. Conclusion:

We carried out three kinds of measurements. Using the linear viscoelasticity measurement we determined the critical gel point of the samples. During the uniaxial elongational viscosity measurement, all of the blend systems showed strain hardening and the elongational curves could be superimposed by considering the relative distance from the critical temperature.

6. Reference:

[1] Lopes, D. Mijangos, C. Munoz, M. E. Santamaria, A. *Macromolecules*, **29**, 7108, 1996

[2] A. T. Walter, *J. Polym. Sci.*, **13**, 207, 1954

[3] A. Keller, *Faraday Discuss.* **1**, 101, 1995

[4] L. Li, Y. Aoki, *Macromolecules*, **30**, 7835, 1997

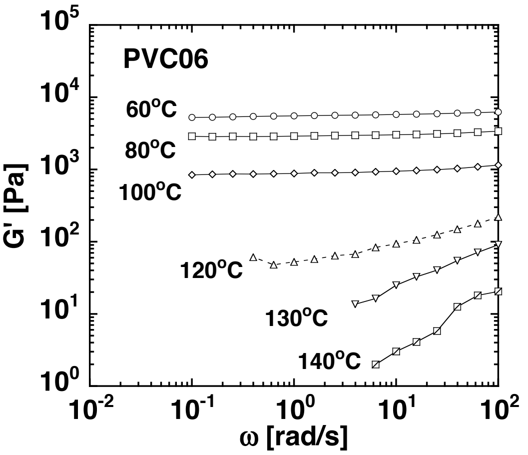

Fig.1 Strage modulus G' of PVC06 plotted against angular frequency ω for various temperature.

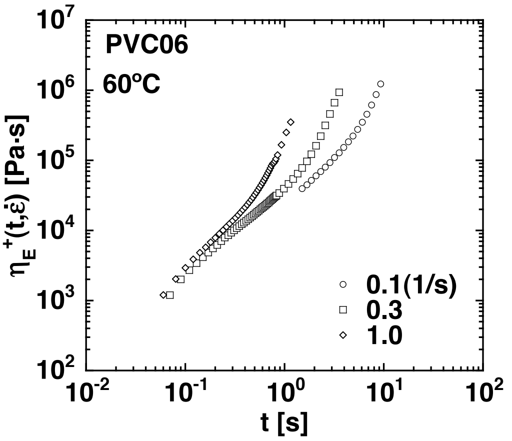

Fig.2 Time dependence of uniaxial elongational viscosity at various strain rates for PVC06 at 60°C

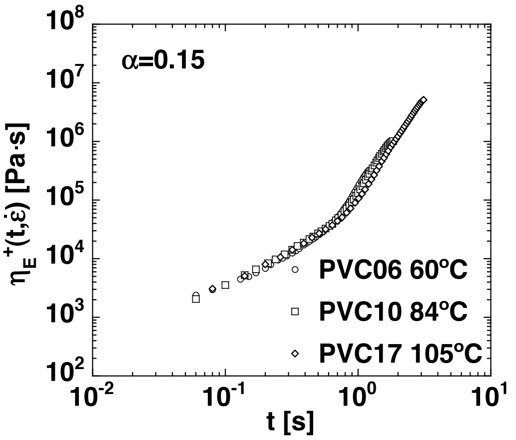

Fig.3 Time dependence of uniaxial elongational viscosity. strain rates: 1.0, for PVC06, PVC10 and PVC17 at same α.