Sol-Gel Transition and Equilibrium Shear Modulus of Poly(vinyl chloride) and Plasticizers

M. A. Semsarzadeh, S. M. Barikani**

Summary: The elasticity of poly(vinyl chloride) gels with molecular weight distribution (M_w/M_n), of 2.16 have been studied in the region beyond their gel points. Dynamic storage modulus G', and equilibrium gel shear modulus of elasticity G_e, at low frequencies (ω) have specific developments as a function of polymer concentrations c, and plasticizers. The scaling elasticity from $G_e = k\varepsilon^z$ equation holds at different PVC plasticizer gels. The scaling exponent z, and constant k. ε is defined as the relative distance, $\varepsilon = (|c - c_g|)/c_g$, the calculated $z = 2.45 \pm 0.15$. Furthermore, this analysis provides constant k with certain informations about the dependency of gel elasticity on the kind of plasticizer. Near the sol-gel transition temperature T, G_e decreases rapidly with increasing temperature. The normalized moduli G_eM/cRT, of the gels at different temperature, and/or c were dependent on the relative distance from the gelation point ε, and PVC and plasticizers concentration respectively. These results suggested mesh size of gel network near the gelation point for PVC with bis(2-ethylhexyl) phthalate (DOP) or di-n-butyl sebacate (DBS) plasticizers that has been newly reported.

Keywords: equilibrium shear modulus; gel elasticity; mesh size; plasticizer; poly(vinyl chloride)

1. Introduction

Poly(vinyl chloride) (PVC) forms physical gels in various plasticizers, and the structures [1–3] and physical properties [1,2,4] of those gels have been investigated. The gels are generally classified as randomly cross-linked networks of flexible PVC strands, and the PVC crystal domains work as the cross-linking domains. Some properties of the gels such as the equilibrium modulus are unequivocally related to this network structure: for example, for a well developed gel forms a densely connected network throughout the whole system, the equilibrium elasticity is related to orientation/deformation of the PVC gel strands [5–9]. The term ‘‘quasi-equilibrium’’ refers to the difficulty (or even sometimes impossibility) of obtaining the thermodynamic equilibrium modulus of a physical gel. However, details of the structure of the crosslinking domains, either fibrous crystals [1,2] or small crystallites [5] have not been elucidated completely, and the structures of the gel strands themselves PVC chains or their fibrous aggregates [4,6] may change with temperature, concentration and solvent quality. In this paper, the sol-gel transition and polymer concentration with scaling law is studied and the affect of the plasticizer, on the stable system of gelation, the equilibrium modulus and the critical behavior reported.

2. Experimental

2.1. Materials

The polymer used in this work was commercial poly(vinyl chloride) $(PVC)_E$

Polymer Group, Department of Chemical Engineering, Tarbiat Modarres University, P.O. Box 14155/4838, Tehran, Iran
Tel.: +98-21-8011001; fax: +98-21-8006544
E-mail: semsarzadeh@modares.ac.ir; fmpi_419@yahoo.com

produced through emulsion polymerization by SABIC (K = 70), Arabia petrochemical company. The weight-average molecular weight is 128×10^3 determined from GPC. 2 wt % of a tin-type stabilizer were added to the samples at a PVC concentration higher than 7 wt %. The Poly(vinyl chloride) (PVC) prepared by using of bis(2-ethylhexyl) phthalate (DOP) and di-n-butyl sebacate (DBS) plasticizers were prepared at room temperature (about 25 °C) from tetrahydrofuran (THF), solutions of PVC/plasticizer (Table 1). Using of this method allows samples physically to be mixed at room temperature and equilibrated with time instead of high temperature and each sample was stable with time. On the other hand, the residual THF concentration (1–3 wt.ppm by Headspace Gas Chromatography) was found to be too low to affect the viscoelastic properties of PVC gels [19]. The evaporation of THF from each solution proceeded at room temperature for 2 to 3 weeks, depending on the polymer concentration. Within 3 weeks, the weight of the system became constant and the evaporation of THF was completed. The sufficiently long time was taken for the evaporation and the equilibrium of gelation prior to each measurement, to ensure sample stability [7,17,19]. The PVC chains began to form crystal domains at some point during the above evaporation procedure, and a soft but well-developed PVC gel system was recovered on completion of this procedure. This gel was highly deformable at room temperature. The final concentration soft/solid gel samples are 45 to 500 g/l for the PVC/plasticizer.

2.2. Measurements

The PVC/DOP and PVC/DBS softs or solids were transferred from the flat laboratory dish into the dynamic rheometer (UDS200). A parallel plate fixture with a diameter of 25 mm was used. Depending on the viscoelastic properties of each sample, the linearity of dynamic viscoelasticity was ensured by applying the suitable amplitude of shear strain. The oscillatory strain amplitude was kept small (2%) and the linear responses were detected. All frequency sweep measurements were carried out by using a variable temperature step from 40 °C to the complete flow temperature or 180 °C. The shear storage modulus G′ and loss modulus G″ were measured as a function of angular frequency (ω) and temperature. During this heating procedure, the temperature T was kept constant at several selected points where the moduli were measured. Prior to each measurement, the samples were kept at 40 °C for reasonable time in order to reach constant temperature and was chosen to minimize the effect of the gel forming temperature. The data on the temperature dependence of the viscoelastic behavior were obtained from the frequency sweep data measured at various temperatures by a heating procedure [7,12,16,19].

Table 1.
Amounts of using materials

PVC/plasticizer (g/l)	45	70	80	100	200	300	500
THF (wt %)	68.5	74.5	76	79	82	86	91

3. Results and Discussion

3.1. Dynamic Viscoelastic Behavior of PVC Gels Through the Sol-Gel Transition

The critical behavior in the vicinity of the sol-gel transition in this studies, and the scaling exponent n = (0.75 – 0.77) has been used for PVC/DOP or PVC/DBS gels. Since the phase angle δ varies from 0 to π/2 as n takes a value between 0 and 1, n measures the viscoelasticity distance from a completely viscous liquid (δ = π/2) or from a completely elastic solid (δ = 0).

In general, a lower value of n implies formation of a more highly elastic gel, and the same value of n means an equivalent viscoelasticity. The absolute values of G′(ω) or G″(ω) for comparison of the viscoelasticity are not taken because n does not directly contain the information about the dynamic moduli [7–12].

The universal value of n found for the PVC/DOP and PVC/DBS samples may suggest a similarity in the gel structure at the gel point. Around the sol-gel transition, PVC clusters with sizes ranging from a few tens to hundreds of nanometers were observed in solution using light scattering [4,7,13], this shows that the PVC clusters contribute to the subsequent crystal junctions of gels. The X-ray diffraction measurements were carried out by Lemstra et al [7,10]. It confirmed the crystallinity of the stretched PVC gels, and showed patterns similar to those in the commercial bulk PVC. The crystallinity of commercial PVC usually possesses within 10% [7,14]. The conclusion drawn from the small-angle neutron scattering (SANS) experiments support the model of fibrous crystal structure and rodlike sections in the PVC gels [6,7]. Rheology provides one with a convenient tool to view the particular behavior of a gelling system from the liquid state to the solid state.

In this work dynamic behavior of PVC/DOP and PVC/DBS systems at $T \geq 100\,^{\circ}C$ in Figure 1(a) shows the storage modulus G' of a PVC gel system ($c = 200$ g/l) at different temperature. The PVC gel is well developed at 100 °C to exhibit ω-independent G' (and much smaller G''; not shown). At constant G', the equilibrium modulus G_e is calculated. Equilibrium modulus decreases with increasing temperature slowly and then rapidly decreases at the sol-gel transition temperature. The shear storage moduli G' is illustrated in Figure 1(a) as a function of angular frequency for the PVC/DOP and PVC/DBS series. The polymer temperature ranges from 100 to 180 °C ($c = 200$ g/l) as indicated. The PVC gel is well developed at 100 and 120 °C for PVC/DOP and PVC/DBS and 140 °C for PVC/DBS to exhibit ω-independent G'. At the sol-gel transition temperature T_{gel}, the Winter-Chambon [15] relationship $G'(\omega) \sim G''(\omega) \sim \omega^n$, $0 < n < 1$ is valid and the loss tangent ($\tan\delta$) is independent of angular frequency ω. This ω-independence at the gelation point, confirmed for various chemical and physical gels [16–19], was used to determine T_{gel} of our PVC systems. The effect of concentration of PVC/DOP and PVC/DBS in the pre and post gel states is shown in Figure 1(b). The equilibrium modulus G_e and storage modulus G' different angular frequency ω for PVC/DBS gel systems than PVC/DOP, have bean increased at the high temperature (<120 °C) and low concentration (>100 g/l) in Figure 1.

3.2. Gel Elasticity

The experimental and theoretical methods of the gelation are based on the scaling law. Like many physical parameters of poly-

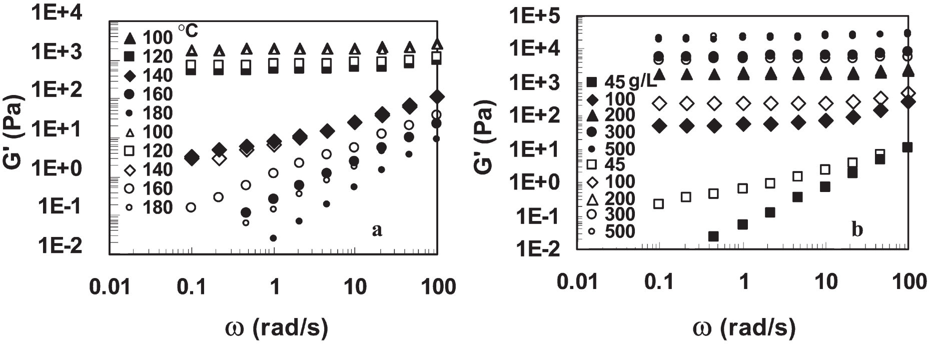

Figure 1.
(a) Plots of storage modulus G' against angular frequency ω for the PVC gels ($c = 200$ g/l) at various temperatures as indicated. (b) Plots of storage modulus G' against angular frequency ω for the PVC gels ($T = 100\,^{\circ}C$) at various concentrations as indicated. The filled symbols indicate c of the PVC/DOP gel and the open symbols are for the c of the PVC/DBS gel obtained in this study.

mers, rheological behavior of a gelling polymeric system is approximated by power laws. Various power laws have been proposed and examined to explain or predict rheological features of gelling systems, especially for the sol-gel transition [16–18]. The equilibrium modulus G_e follows equation 1:

$$G_e \propto \varepsilon^z \quad \text{for } p > p_g \tag{1}$$

The relative distance of a variable p from the sol-gel transition point p_g, is defined $\varepsilon = (|p - p_g|)/p_g$ and p is degree of cross-linking, concentration, time or temperature in a gelation process. z is the critical exponent determining the critical characterized in the vicinity of the sol-gel transition.

Theoretically, the values of the critical exponent z have been predicted by many models [7,17,18]. The classic theory based on the Bethe lattice (the tree approximation) gives $z = 3$, while the models using percolation theory predict different value of z are considered. For example, $z = 8/3$ is reported when of hydrodynamic interactions [7]. The range of polymer concentration in which G_e was not clearly observed may be more interesting because the gel network structure would be expected to develop in other concentration ranges. On the other hand, as the PVC concentration increased, the G_e was clearly observed in the low-frequency regions. In Table 2 the quasi-equilibrium modulus G_e was obtained from the G' in the frequency independent range. Table 2 excluded the samples which did not exhibit the frequency independent G' in the observed frequency range. We are now going to examine the elasticity evolution and the scaling law based on the data in Table 2.

Table 2.
Quasi-equilibrium modulus G_e (Pa) as a function of polymer concentration c and temperature for gel systems

Gel	c (g/l) T (°C)	60	80	120	140
PVC/DOP	45	18.3	1.017	—	—
	80	340	188.6	—	—
	100	575	318	—	—
	200	3454	3042	510	—
	300	12412	10111	2114	230.9
	500	31650	30148	8740	2401
PVC/DBS	45	13.4	6.376	—	—
	70	136	83.8	—	—
	100	536	298.3	13.7	—
	200	2927	2328	694	3.53
	300	10110	8752	2784	931.76
	500	36458	32539	8925	3467

The PVC gel is well developed at the more of concentration to exhibit ω-independent G'. The same was used investigated the gel structure in a wide ranges of concentration and temperature. For this purpose, we focused our attention to the equilibrium modulus G_e, and looked for a universal relationship between G_e and ε in equation 2. In fact, we used the relationship for a normalized modulus G_eM/cRT in equation 3 and discussed the gel structures of PVC/DOP and PVC/DBS. For the PVC/DOP and PVC/DBS gels at various temperatures, Figure 2 shows plots of G_e against concentration. The concentration dependence of G_e becomes weaker for larger concentration. The scaling law were examined by plotting the equilibrium modulus G_e against the relative distance, $\varepsilon = (|c - c_g|)/c_g$ in the double logarithmic scale from equations 2 and 3. The scaling law of equations 2 and 3 were examined by plotting the equilibrium modulus G_e and the normalized moduli G_eM/cRT against the relative distance, $\varepsilon = (|c - c_g|)/c_g$ in the

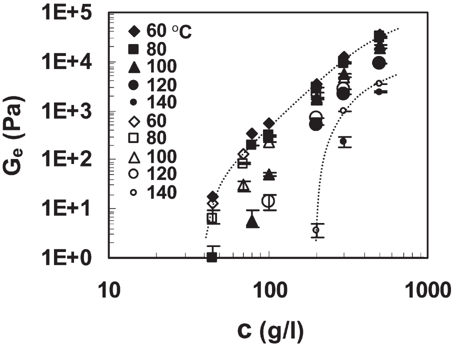

Figure 2.
Plots of equilibrium modulus G_e of the PVC/DOP (filled symbols) and the PVC/DBS (open symbols) gels against the PVC concentration c at various temperatures T as indicated.

double logarithmic scale as shown in Figures 2(a) and 2(b) To obtain the scaling exponent z and n, with a linear fitting of data for each series of the gel systems.

$$G_e = K\varepsilon^z, \quad z = 2.45 \pm 0.15 \tag{2}$$

and

$$G_eM/cRT = B\varepsilon^n, \quad n = 1.8 \tag{3}$$

R is the gas constant.

The results are shown in Figure 3 the equilibrium modulus G_e and normalized modulus G_eM/cRT against ε. This modulus is almost determined by ε irrespective of the concentration and temperature. Equation 4 suggests that the effective mesh size M_g (Table 3) of the randomly cross-linked PVC gel network, not very far from the gelation point c_g is determined by ε and M [12].

$$G_e = cRT/M_g, \quad M_g = Mf(\varepsilon) \tag{4}$$

Here, f(ε) is a function of only ε. The data in Figure 3(b) suggest that f(ε) is approximately proportional to $\varepsilon^{-1.8}$ in the range of ε examined, although f(ε) is not clear in the close vicinity of the gelation point (for small ε).

4. Conclusions

Poly(vinyl chloride) (PVC) gels were prepared from THF solutions. DOP and DBS were used as the solvent or plasticizer for the gels. Dynamic viscoelastic measurements were carried out to allow us to observe the elasticity evolution of the PVC gels as a function of polymer concentration, temperature and plasticizer. It was found that the evolution of gel elasticity defined as the quasi-equilibrium modulus G_e followed the scaling law $G_e \propto \varepsilon^z$, the scaling exponent z (=2.45 ± 0.15) also the normalized moduli $G_eM/cRT \propto \varepsilon^{1.8}$ was dependent to type of plasticizer (B for PVC/DOP ≈ 0.05 and PVC/DBS ≈ 0.03). In the vicinity of the gel point, however, the frequency independent equilibrium modulus was not experimentally observed in the frequency range studied.

The equilibrium modulus G_e of PVC/DOP and PVC/DBS gels at T ≥ 60 °C were also studied and near the gelation point, G_e decreases rapidly. We have examined the

Table 3.
Constants of equations 2 and 3 as a function of temperature T for gel systems and mesh size

Gel	T (°C)	K	Z	B	n	ε	$M\varepsilon^{-1.8}$ (kg/mol)
PVC/DOP	80	117	2.42	0.05	1.8	0.2	2319
	100	155	2.4			0.5	445.7
	120	298	2.51			0.8	191.3
	140	385	2.6				128
PVC/DBS	80	37	2.3	0.03	1.8	12.5	24.6
	100	81	2.38			5	7
	120	113	2.4			10	2.03
	140	275	2.37			20	0.583

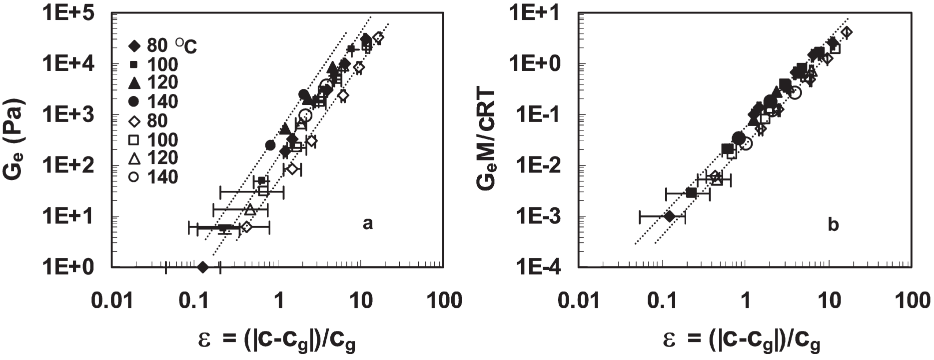

Figure 3.
(a) Equilibrium modulus G_e, (b) normalized equilibrium modulus $c^{-1}R^{-1}T^{-1}MG_e$ of the PVC/DOP and PVC/DBS gels plotted against the relative distance from the gelation point, $\varepsilon = (|c - c_g|)/c_g$: filled and non-filled symbols respectively, are for the PVC/DOP and PVC/DBS gels.

Table 4.
Mesh size obtained from equation 2 and Table 3 as a function of temperature T for gel systems ($c = 300$ g/l)

Gel	c (g/l)	T (°C)	G_e (Pa)	ε	$M\varepsilon^{-1.8}$ (kg/mol)
PVC/DOP	300	80	10111	1.842	42.63
		100	5627	1.5	61.69
		120	2114	0.78	200.2
		140	230.9	0.195	2427
PVC/DBS	300	80	8752	2.376	26.96
		100	4736	1.71	48.73
		120	2784	1.335	76.1
		140	931.76	0.515	422.63

dependence of G_e on the distance ε from the gelation point in normalized form and the mesh size of the randomly cross-linked network in the gels near the gelation point has determined by ε and plasticizer. More specifically, an effective gel network strand appears to be composed of several PVC chains (associating with each other at the cross-linking crystal domains) to have the size $Mf(\varepsilon)$, where $f(\varepsilon) \sim \varepsilon^{-1.8}$ gives the association number. The molecular picture, derived from the observation that G_eM/cRT is dependent on ε and has the value smaller than unity for $\varepsilon < 5$ in the PVC/DOP and $\varepsilon < 8$ in the PVC/DBS, is consistent with the expected similarity of the bifurcated gel network structure for various c and plasticizer (Table 4).

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