

## The rheological properties of poly(vinylidene fluoride-co-hexafluoropropylene) solutions in dimethyl acetamide

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### Abstract

The effects of temperature on the rheological properties of the solutions of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) in dimethyl acetamide (DMAc) were investigated in terms of frequency and concentration. The effects of temperature on the intrinsic viscosity of the solutions were discussed. In dynamic rheological measurement, the concentrated solutions showed a little unexpected rheological response; as temperature was increased dynamic viscosity was increased and the solutions exhibited more noticeable Bingham body character over the temperature range, 30 to 70°C. In addition, the solution gave longer relaxation time, lower value of loss tangent and higher value of yield stress at higher temperature and at higher concentration. On the other hand, the dilute solutions revealed that intrinsic viscosity was decreased and its Huggins constant was increased with increasing temperature. These physical parameters suggested that the increase of viscosity with increasing temperature resulted from the localized gelation of PVDF-HFP due to reduced solubility to the solvent.

**Keywords** : poly(vinylidene fluoride-co-hexafluoropropylene), dimethyl acetamide, solution, rheological properties, intrinsic viscosity

### 1. Introduction

In the cases of polymer solutions, the rheological properties are expected to be affected by complicated factors such as polymer-polymer interactions, polymer-solvent interactions, polymer concentration, temperature, and solution phase. Particularly in a polar polymer solution, the intermolecular interactions between components in the solution would have a very crucial effect on the rheological properties of the solution (Lee *et al.*, 2004; 2006). In the cases of the solution of poly(vinyl alcohol) (PVA), the tacticity of the polymer also has a profound effect on the physical properties (Kim *et al.*, 2000; Lyoo *et al.*, 2001; Choi *et al.*, 2001). Only a little difference in the syndiotactic diad content brought about a dramatic change in rheological responses of PVA solutions because an increase of syndiotactic diad content increases the effectiveness of inter- and intra- hydrogen bonding of polymer chains (Lyoo *et al.*, 1998). A 2 wt% syndiotactic PVA solution exhibits a strong Bingham flow behavior and spontaneously forms a fibrillar gel structure even by very low shear force (Kim *et al.*, 2000; Lyoo *et al.*, 2001). It is also expected that temperature would affect the rheological

properties of polar polymer solutions on condition that a change in temperature brings about a change in solubility of the solvent to the polymer or a change in phase morphology.

Nano fibrous polymeric membranes which have highly porous mesh and large surface area-to-volume ratio are finding their applications in industrial fields such as high-efficiency filter, biomedical scaffolds, and secondary battery separators (Ramakrishna *et al.*, 2006). Most of the applications require an excellent chemical resistance. Fluoropolymers such as poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) are known as chemically inert materials with high temperature resistance (Dargaville *et al.*, 2003). They are being used for materials under harsh chemical environment. Hydrophobic property enables them to be applied to the membrane-based gas absorption and oil/water separation fields (Zhang and Cussler, 1985; Wang *et al.*, 1999).

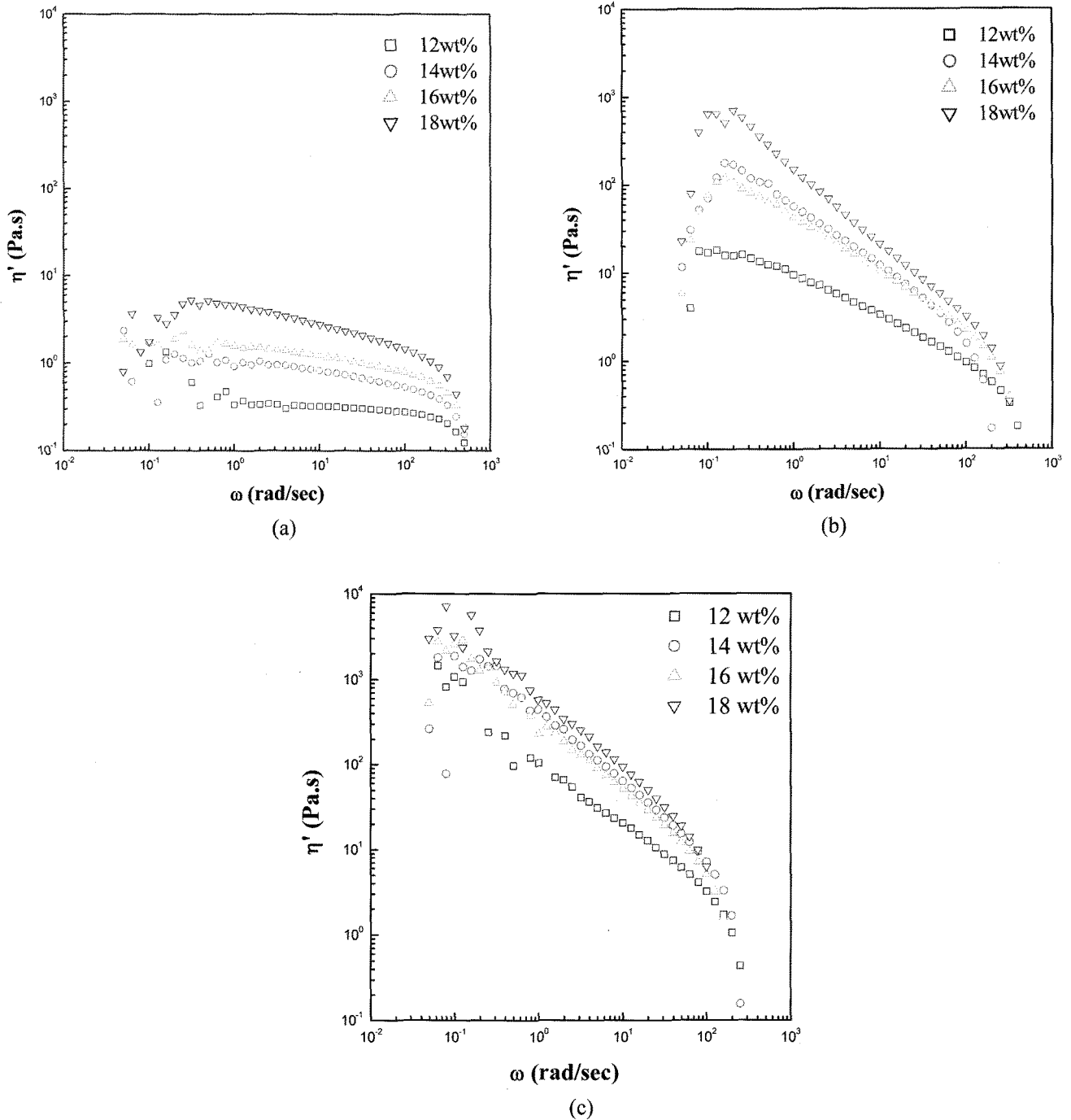
Recently intensive efforts have been made to develop new materials for electrochemical cells which can be used for portable electronics, mobile phones, electric vehicles, and other electronic devices (Nicotera *et al.*, 2002). The capacity of electrochemical cells is mainly determined by electrode materials. It is well recognized that the separator has a significant influence on the charge/discharge capacity as a channel for ion conduction. PVDF-HFP has been

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attempted to be used in the field of secondary lithium battery because it can give rise to higher ion conduction rate in ionic channel than PVDF due to lower crystallinity (Michot *et al.*, 2000). Electrospun PVDF-HFP webs are expected to be effectively utilized as separators in the secondary lithium batteries. The rheological properties of polar PVDF-HFP solutions in dimethyl acetamide (DMAc) are expected to be very complicated, which is crucial to design the solution dopes for electrospinning. Up to now,

**Table 1.** Values of  $[\eta]$ ,  $C^*$ , and  $K_H$  of PVDF-HFP solutions in DMAc

Temp.	$[\eta]$	$C^*$	$K_H$
30°C	3.32	0.301	0.284
50°C	3.12	0.320	0.291
70°C	2.82	0.355	0.301



**Fig. 1.** Viscosity curves of PVDF-HFP solutions in DMAc at; (a) 30, (b) 50, and (c) 70°C.

however, little study on the rheological properties of the solutions has been disclosed. In this study we investigated the rheological properties of PVDF-HFP solutions in DMAc.

## 2. Experimental

### 2.1. Materials

Fluoropolymer, Kynar 2801, was purchased from Elf Atochem Co. Kynar 2801 was a copolymer of vinylidene fluoride (VDF) and hexafluoro-propylene (HFP) (88/12 by mol %) whose number-average molecular weight was 120,000. The PVDF-HFP was dissolved in dimethyl acetamide (DMAc) (12 to 18 wt%) with stirring for 3 hrs at 30°C to obtain homogenous solutions.

### 2.2. Measurement of rheological properties

Intrinsic viscosity ( $[\eta]$ ) was determined from the inherent viscosities measured over the concentration range 0.01 and 0.8 g/dl by Ubbelohde viscometer (Schott Co.). An advanced rheometric expansion system (ARES, rheometric Scientific, Inc.) was used to measure the rheological properties of concentrated solutions. Parallel-plate geometry, with a diameter of 50 mm for solutions, was used. The plate gap and strain level were 1 mm and 10%, respectively. The strain level was adjusted by pretest. The specimen was kept for 5 min prior to measurement in a nitrogen atmosphere. To prevent the evaporation of the solvent during measurement, heavy mineral oil (Aldrich Co.) was coated on the edge of the plates. Dynamic frequency sweep measurement was conducted over the angular frequency range of 0.05 to 500 rad/s.

## 3. Results and discussion

### 3.1. Physical properties of dilute solutions of PVDF-HFP in DMAc

The viscosities of the extremely dilute solution of a polymer offer important information on the physicochemical nature of the polymer because it reflects the physicochemical state of individual polymer chains. The critical concentration ( $C^*$ ), the concentration at which entangling and overlapping of polymer molecules begin to take place, is calculated by Eq. (1).

$$C^* = \frac{1}{[\eta]} \quad (1)$$

Huggins constant ( $K_H$ ), the degree of polymer-solvent interaction, is calculated by Eq. (2).

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \quad (2)$$

The values of  $[\eta]$ ,  $C^*$ , and  $K_H$  of PVDF-HFP solutions in

DMAc at three different temperatures are given in Table 1. It is noted that the value of  $C^*$  and  $K_H$  is increased but that of  $[\eta]$  is decreased with increasing temperature. It is recognized that the value of  $K_H$  is equal to 0.52 in a  $\theta$  solvent, less than 0.52 in a good solvent, and between 0.8 and 1.3 in a poor solvent.  $K_H$  values indicate that DMAc is a good solvent for PVDF-HFP. However, the increase of  $K_H$  with temperature suggests the solubility of PVDF-HFP to DMAc is decreased with increasing temperature. This is further ascertained by the reduction of  $[\eta]$  with increasing temperature because  $[\eta]$  is a measure of the coil dimension of individual polymer chain in the solution (Park *et al.*, 2004).

### 3.2. Rheological properties of concentrated solutions of PVDF-HFP in DMAc

The dynamic rheological properties of PVDF-HFP solutions in DMAc are shown in Fig. 1. It should be noted that viscosity is increased with increasing temperature. In addition, the shear thinning behavior gets more and more dom-

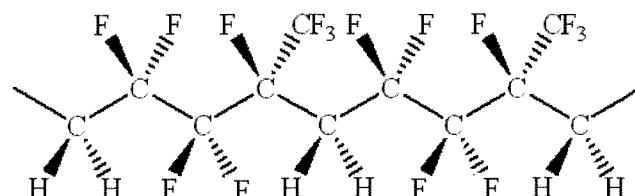


Fig. 2. The chemical structure of PVDF-HFP.

Table 2. Power-law index of PVDF-HFP solutions in DMAc

Concentration (wt%)	Power-law index ( $n$ )		
	30°C	50°C	70°C
12	0.919	0.432	0.239
14	0.804	0.344	0.151
16	0.797	0.209	0.129
18	0.693	0.099	0.044

Table 3. The value of yield stress of PVDF-HFP solutions in DMAc

Concentration (wt%)	Yield stress ( $G_0''$ ) (Pa)		
	30°C	50°C	70°C
12	0.0014	1.0023	2.018
14	0.0336	1.6459	2.5234
16	0.2173	1.7685	2.6596
18	0.6803	2.1635	2.8299

inant with increasing temperature. This seems to originate from the reduction of solubility to the polymer with increasing temperature as given in Table 1. Unlike in the dilute solution systems in which solubility plays a dominant role in determining viscosity, the role of intermolecular interactions between polymer chains gets more dominant in the concentrated solution systems. Particularly with PVDF-HFP/DMAc solutions it is expected to produce

notable intermolecular interactions through polarization of pendant groups because of asymmetrical structure of PVDF-HFP molecule as shown in Fig. 2.

According to Table 1, increasing temperature would shrink the dimension of polymer coils and increase the mobility of polymer chains. Hence the polar pendant groups of polymer chains would have more chance to get closer particularly in the concentrated solutions, which

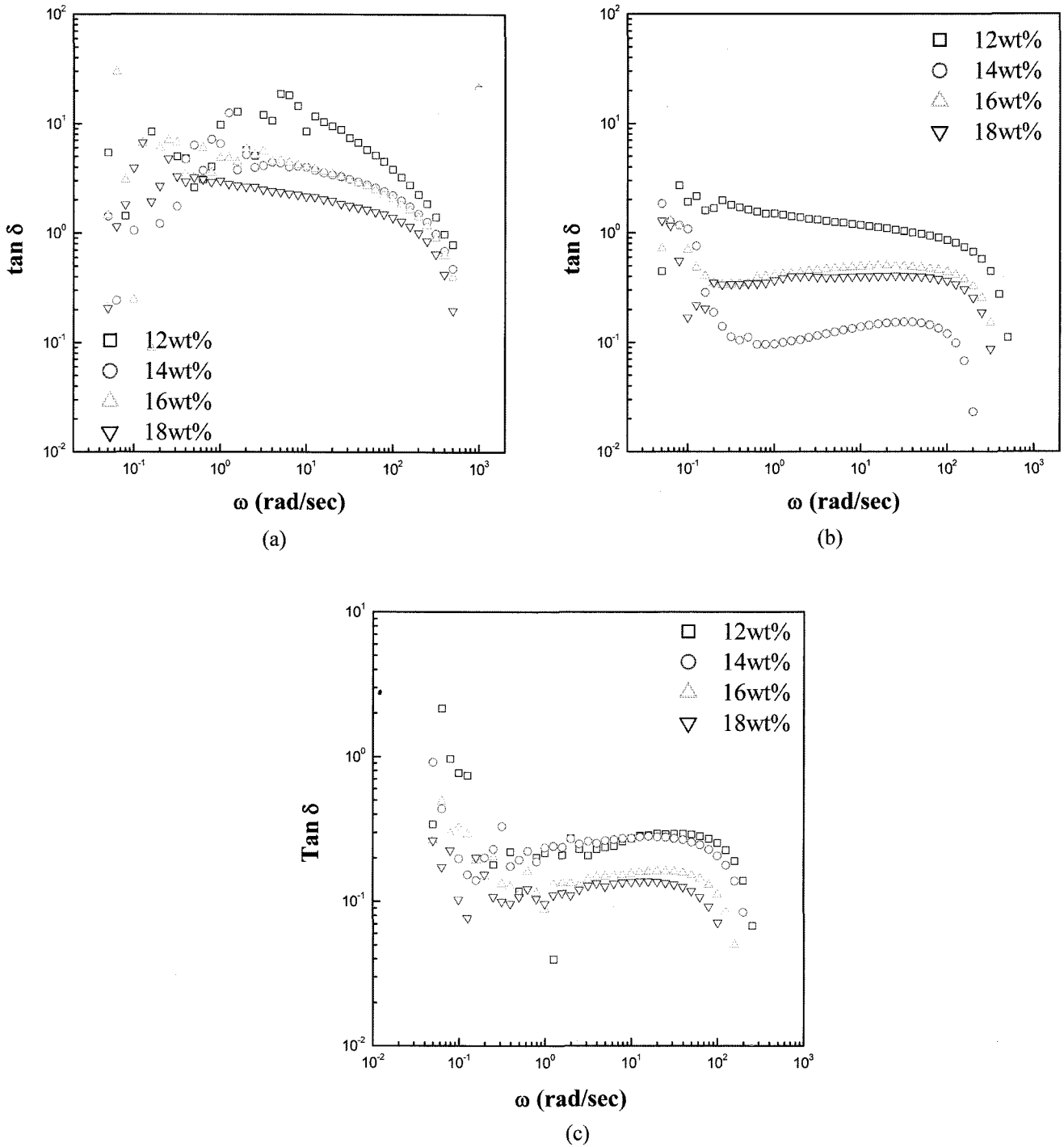


Fig. 3. Variation of  $\tan \delta$  with frequency for PVDF-HFP solutions in DMAc at; (a) 30, (b) 50, and (c) 70°C.

may offer more favorable conditions to produce polar-polar interactions. In consequence, the intermolecular interactions of PVDF-HFP chains are enhanced with increasing temperature, promoting the formation of 3-dimensional physical structure. The effects of concentration as well as temperature may be traced by examining the power-law index given in Table 2. The power-law index decreases with increasing concentration. In the case of 12 wt% solu-

tion, the physical structure would not so strong because of low frequency of pendant groups especially at low temperature, hence exhibits the highest value of power-law index.

The heterogeneity of a polymer solution can be further supported by the presence of the positive values of yield stress, the minimum energy required to break pseudo-structures such as gels, microstructures, and aggregation of

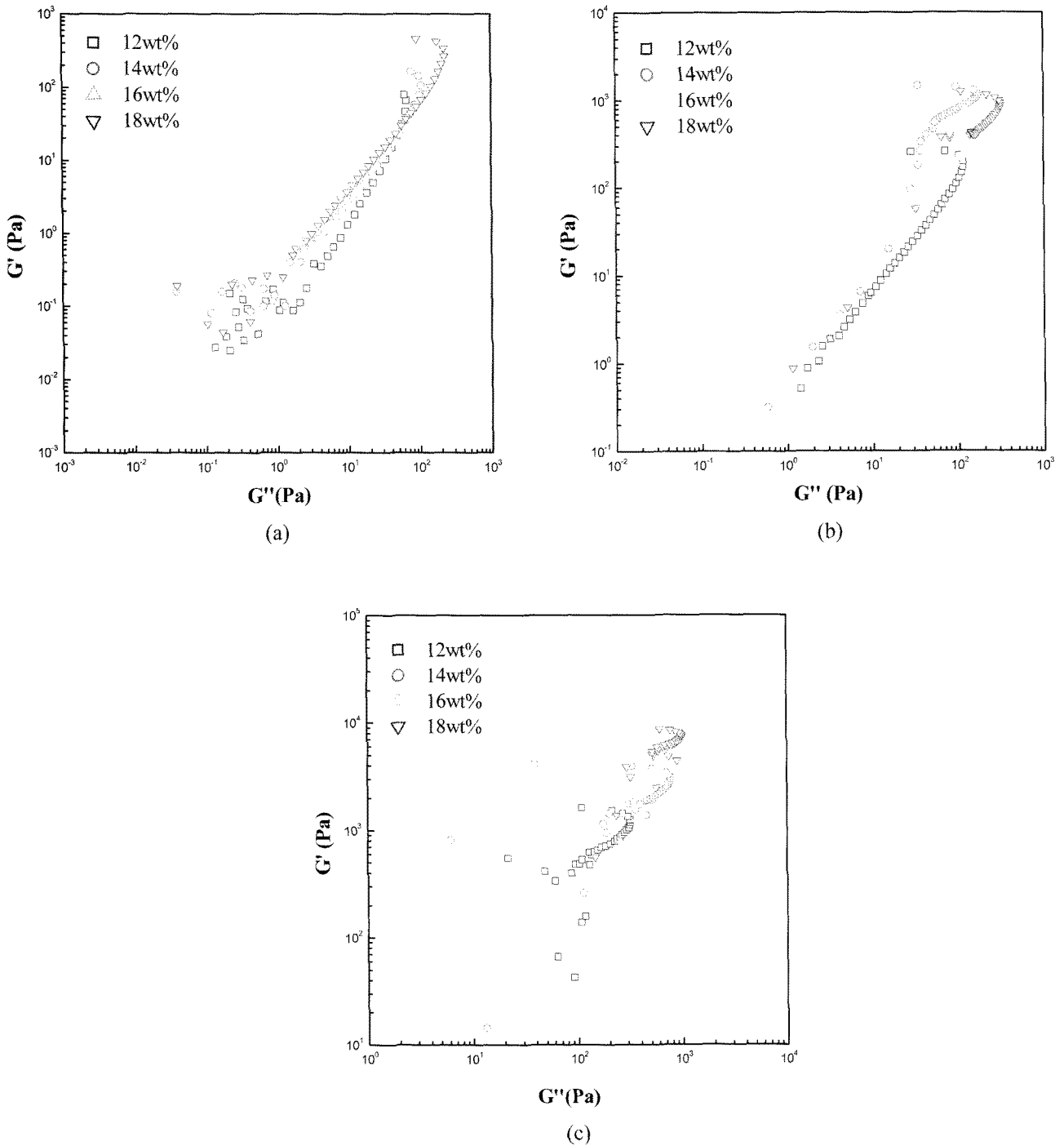


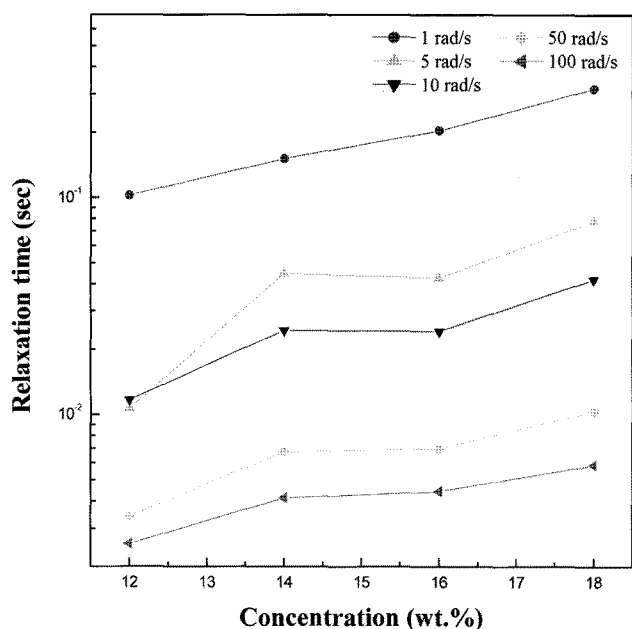
Fig. 4. Modified Cole-Cole plot of PVDF-HFP solutions in DMAc at; (a) 30, (b) 50, and (c) 70°C.

particles. The yield stress ( $G_0''$ ) can be determined from the intercept on the plot of square root of loss modulus ( $G''$ ) vs. square root of frequency ( $\omega$ ) in oscillatory shear experiment (Hong *et al.*, 1993).

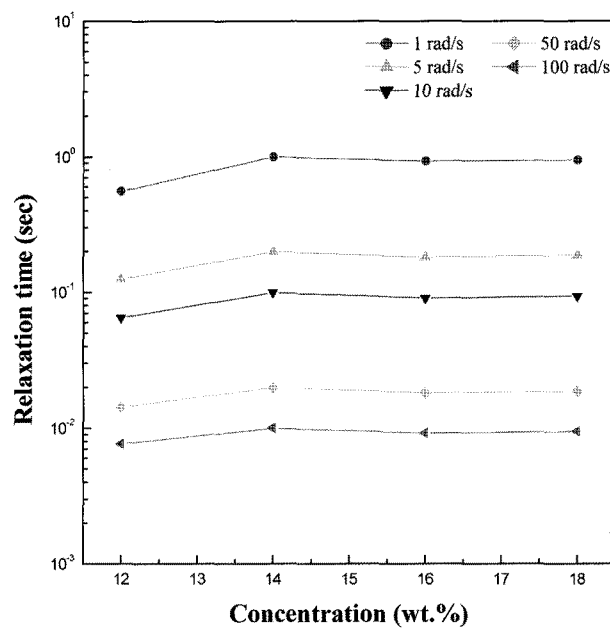
$$G''^{1/2} = G_0''^{1/2} + K' \cdot \omega^{1/2} \quad (3)$$

in which,  $K'$  is a constant. The result is given in Table 3. The higher value of yield stress indicates the existence of

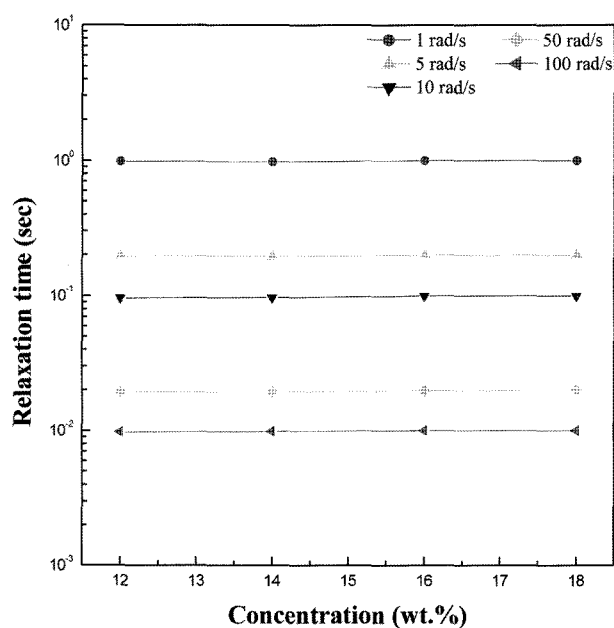
stronger pseudostructures in the solution. Thus this table also supports that stronger physical structure is generated with increasing concentration and temperature. This can be further ascertained by loss tangent ( $\tan \delta$ ) curves of PVDF-HFP solutions in Fig. 3. As known,  $\tan \delta$  is a quantitative measure of solid-like elastic or liquid-like viscous properties of a system. At a given concentration, increasing temperature makes the solution system more solid- or gel-



(a)



(b)



(c)

Fig. 5. Relaxation time vs. concentration for PVDF-HFP solutions in DMAc at; (a) 30, (b) 50, and (c) 70°C.

like and decreasing concentration makes the solution system more liquid-like at a given temperature.

The storage modulus ( $G'$ ) of PVDF-HFP solutions is plotted against the loss modulus in Fig. 4. In theory, the so-called modified Cole-Cole plot gives slope 2 irrespective of temperature or concentration only if the polymer melt or polymer solution is isotropic and homogeneous. As one may imagine, however, the slope is to be reduced when the

melt or solution contains physical structure, which dissipates energy by collapse under shear. Thus the slopes of solutions verify the existence of some physical structures and the slope is decreased as temperature and concentration is increased.

The presence of physical structure in the polymer solution also affects relaxation behavior. In the polymeric systems relaxation time ( $\lambda$ ) under dynamic shear may be

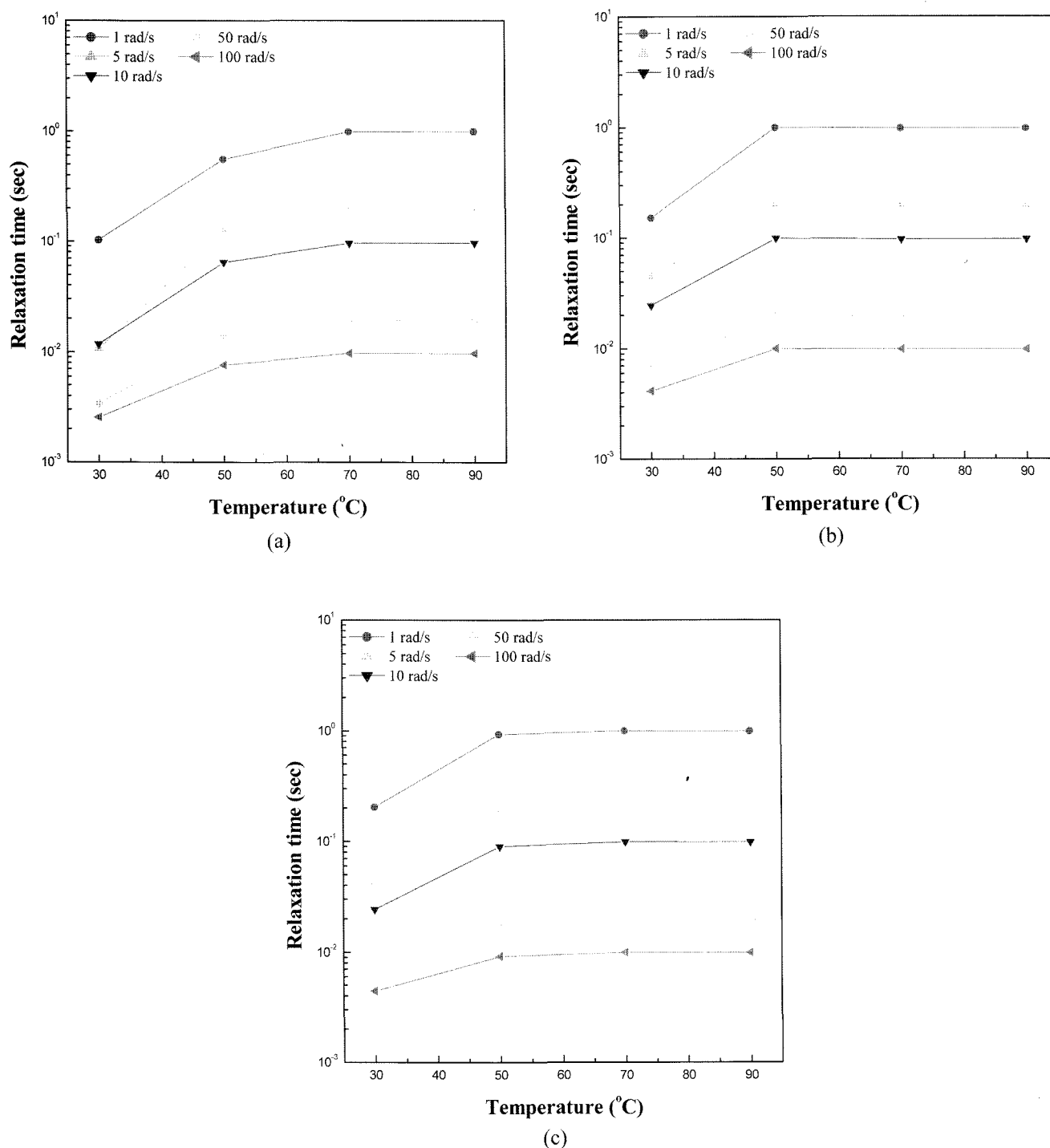


Fig. 6. Relaxation time vs. temperature for PVDF-HFP solutions in DMAc at; (a) 12, (b) 14, and (c) 16 wt%.

calculated by Eq. 4 (Wissbrun and Griffin, 1982).

$$J' = G' / ([\eta^*] \cdot \omega)^2 = \lambda / [\eta^*] \quad (4)$$

where,  $J'$  is compliance and  $\eta^*$  is complex viscosity. The relaxation time of the solutions is plotted against concentration and temperature in Figs. 5 and 6, respectively. If there is some strong molecular order or physical structure, a longer relaxation time is expected because the physical networks would interfere with the interdiffusivity of polymer chains, leading to slower relaxation process. Increasing concentration increases the relaxation time but the concentration effects disappear at high temperature and increasing temperature increases the relaxation time. This indicates that temperature is dominant factor to generate the physical structure over the range of concentrations observed.

#### 4. Conclusion

The dilute PVDF-HFP solutions in DMAc revealed that DMAc was a good solvent for PVDF-HFP but solubility was diminished with increasing temperature. The rheological properties of the concentrated PVDF-HFP solutions in DMAc suggested the existence of some physical structure in the solution systems resulting from intermolecular interactions through polar pendant groups of PVDF-HFP molecules. Both temperature and concentration influenced on the generation of the physical structure. Of the two factors temperature proved to have more dominant effects.

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