Rheological Investigation of the Effects of Introducing Diethylene Glycol on the Physical Properties of PVA Solutions and PVA Films

Myung-Hwan Chang, Byoung Chul Kim

Summary: The effects of diethyl glycol (DEG) on the rheolgical properties of polyvinyl alcohol(PVA) solutions in dimethyl sulfoxide and on the physical properties of PVA films were investigated. DEG seemed to change the state of hydrogen bonding in the solutions and in the films. In the case of 6 wt% PVA solutions, incorporating DEG abruptly reduced shear viscosity if DEG content exceeded 30 wt% to PVA whereas a little decrease of them was observed in 12 wt% PVA solutions over the DEG content observed. Further, at the same DEG content 6 wt% PVA solutions showed a more notable increase of viscosity with time at a constant shear rate than 12 wt% solutions. Dynamic mechanical thermal analysis revealed that introducing DEG broadened the peak of tan δ curve and lowered the glass transition temperature of PVA. DEG imparted toughening effects to PVA film preferably in the range of 10 to 20 wt% to PVA.

Keywords: diethylene glycol; films rheological properties; polyvinyl alcohol; solutions

Introduction

Polyvinyl alcohol (PVA) is mostly produced by hydrolysis of polyvinyl acetate because the vinyl alcohol monomer does not exist in the free state. The excellent chemical resistance and physical properties of PVA have led to their broad industrial use. Further, it can cover a wide range of applications because variation of tacticity and molecular parameters offers a wide range of properties.[1] Recently, PVA has been widely explored as water soluble polymers for numerous biomedical and pharmaceutical applications due to the advantages of nontoxic and bioadhesive properties.[2,3] It is well known that PVA solutions can form physical gel and cause phase separation from various kinds of solvents, such as water, diethylene glycol (DEG), dimethyl sulfoxide (DMSO), and the mixtures of these solvents.[4,5] PVA can produce physical and chemical crosslinking between polymer chains when it is dissolved in highly polar solvents and blended with highly polar polymers. Blending PVA with other polymers offers a useful way of designing properties by properly combining the properties of component polymers.

PVA films have good tensile strength, abrasion resistance and oxygen-barrier properties under dry conditions. PVA films have attracted much attention as polarizing films in electronic devices, which produced by solution casting or extrusion.[6] However, the problems lie in optimizing the processing conditions coming from the extremely complicated rheological properties of the multi-component solution systems. Thus they should be carefully adjusted in fabrication processes to obtain desired properties. In addition, PVA films are very stiff and brittle due to high degree of crystallization. Recently, numerous plasticizers are explored and studied to confer better impact properties to PVA films. Ethylene glycol (EG) is one of the candidates.[7] DEG is constructed by two

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EG molecules, which is a poor solvent of PVA and imparts a lubricanting effect to the PVA films. In spite of the practical importance, the rheological properties of PVA/DEG solutions in DMSO and the physical properties of PVA/DEG films have not been systematically studied.

This paper studies the effects of introducing DEG on the rheological properties of the PVA solutions in DMSO and other physical properties of PVA/DEG blends such as thermal mechanical properties.

Experimental Part

Materials

An Aldrich PVA powder was used whose weight-average molecular weight (M_w) and degree of hydrolysis were 89,000 ~ 98,000 and 99%, respectively. To obtain reproducible results, the powder was completely dried in a vacuum oven for 24 hours prior to use. DEG and DMSO, the commercial products of Aldrich, were used without further purification.

Preparation of Solutions

The rheological properties of polar polymer solutions in polar solvents are greatly affected by dissolution process and conditions. To rule out the errors resulting from these artifacts, the dissolution process was carefully adjusted. The mixture of PVA and DEG was dissolved in DMSO at 90 °C for 3 hours with stirring. Final concentration of PVA-DEG in DMSO was set to 6 and 12 wt%. DEG content was 10, 20, 30, 40 wt% based on the weight of PVA. The samples were coded as X-PVA-Y in which X is the concentration of PVA-DEG in DMSO and Y is the content of DEG. The dope of films was prepared by dissolving PVA/DEG mixture in water at 90 °C for 5 hours with stirring. The concentration of solutions was set to 15 wt% in which the mixing ratio of PVA to DEG was varied; 100/0, 90/10, 80/20, 70/30, and 60/40. The dope solutions, thus obtained, were cast on the glass plate, solidified for 12 hours at room temperature, and finally vacuum dried for 24 hours at 90 °C.

Rheological Measurement

The dynamic rheological properties of PVA/DEG solutions in DMSO were measured using Advanced Rheometric Expansion System (ARES Rheometric Scientific, Inc.) rotational rheometer. Parallel plate geometry with a diameter of 50 mm was employed. The plate gap and strain level were 1 mm and 10%, respectively. The frequency sweep tests were carried out in an oscillatory mode range from 0.05 to 500 rad/s at 90 °C. Prior to testing, the specimens were hold for 3 min to eliminate the thermal and shear histories.

Thermal and Mechanical Analysis

The thermal properties of PVA/DEG films were investigated using differential scanning calorimeter (DSC 2010; TA instrument) in nitrogen atmosphere. The samples were held at 240 °C in the molten state for 5 minutes to erase the previous thermal history before cooling scan. The following testing procedure was adopted for all samples: heating from 40 to 240 °C at 10 °C/min (first scan), followed by cooling to 40 °C. Holding at the temperature for 1 min, then subsequent heating to 240 °C at 10 °C/min (second scan).

Dynamic mechanical thermal analysis (DMA) was conducted using DMA 2980 instrument (TA instrument) in the tensile mode at 3 Hz. The heating rate was 2 °C/min over the temperature range −70 to 130 °C. The instrument was equipped with pre-tensioning device to accommodate the changes in rigidity of the materials.

The tensile tests were carried out using Instron universal material testing system (model 4465) at room temperature with gauge length of 25 mm and crosshead speed of 10 mm/min. The quenched films were finally punched into dogbone specimens with regular size.

Results and Discussion

In the PVA/DMSO solutions, some physical structure formed through hydrogen bonding through hydroxyl groups of PVA makes the solutions heterogeneous in spite of optical transparency. Thus, the rheological properties of the solutions are mainly determined by the strength and number of hydrogen bonds in the solution systems. Figure 1(a) and (b) show the dynamic viscosity (η') of 6 wt% and 12 wt% PVA/DEG/DMSO solutions, respectively. All

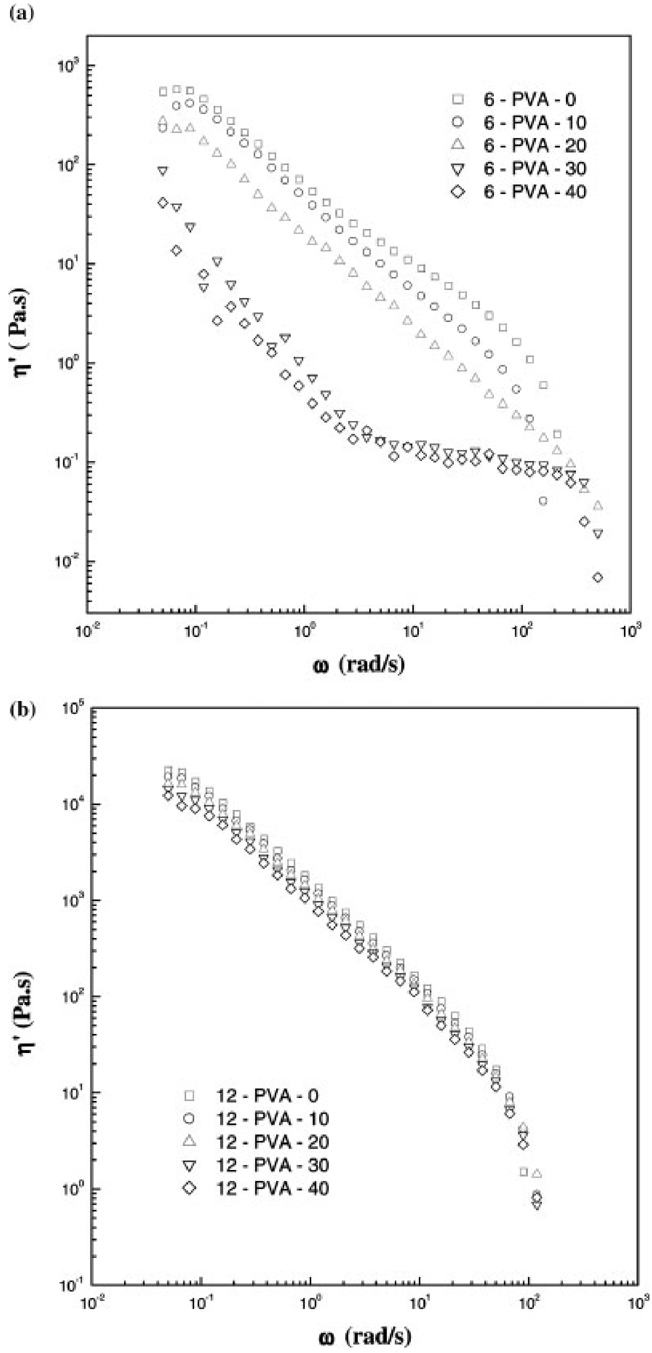

Figure 1.
η' curves of 6 (a) and 12 wt% (b) PVA/DEG/DMSO solutions at 90 °C.

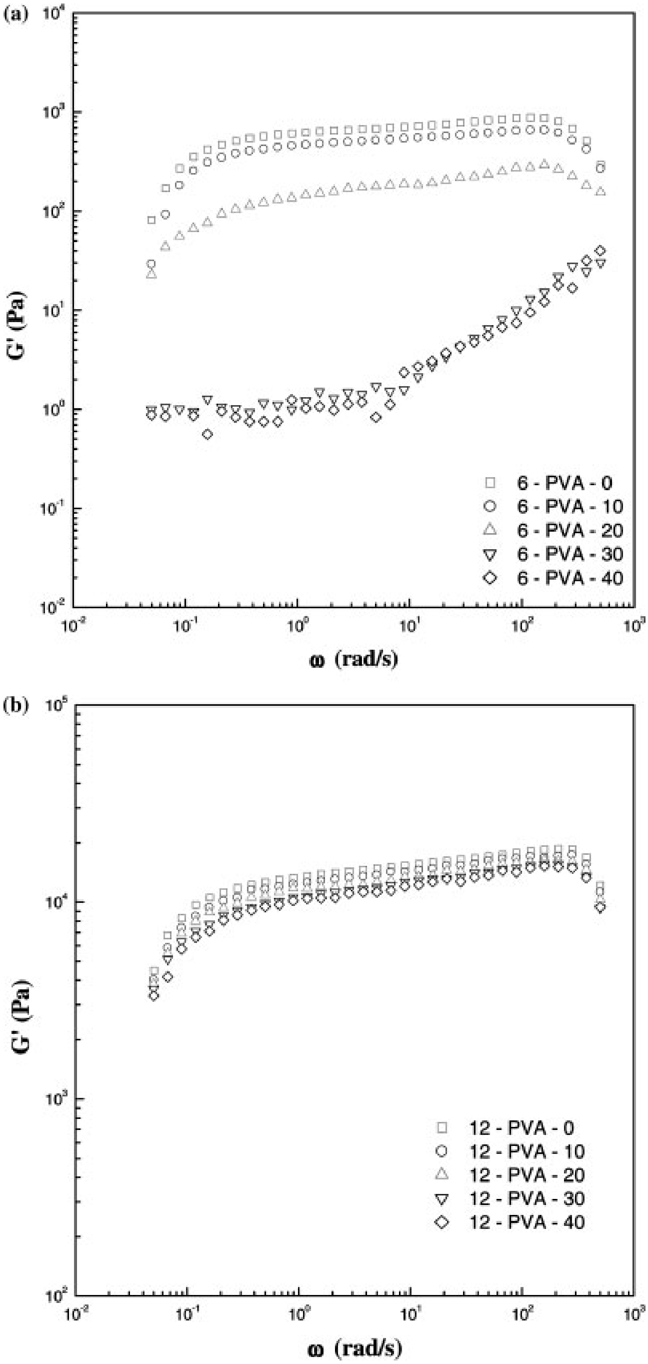

Figure 2.

Storage modulus of 6 (a) and 12 wt%(b) PVA/DEG/DMSO solutions at 90 °C.

the solution systems show Bingham behavior, suggesting which results from the heterogeneity associated with localized gel formation. That is, the hydrogels formed at rest are so soft that to be easily destructed and deformed even by low shear.[8]

In addition, the incorporated DEG molecules weaken the physical structure in the solutions because DEG penetrates between PVA polymer chains and disturbs hydrogen bonds. Further, DEG has a large flexibility due to ether group, which imparts

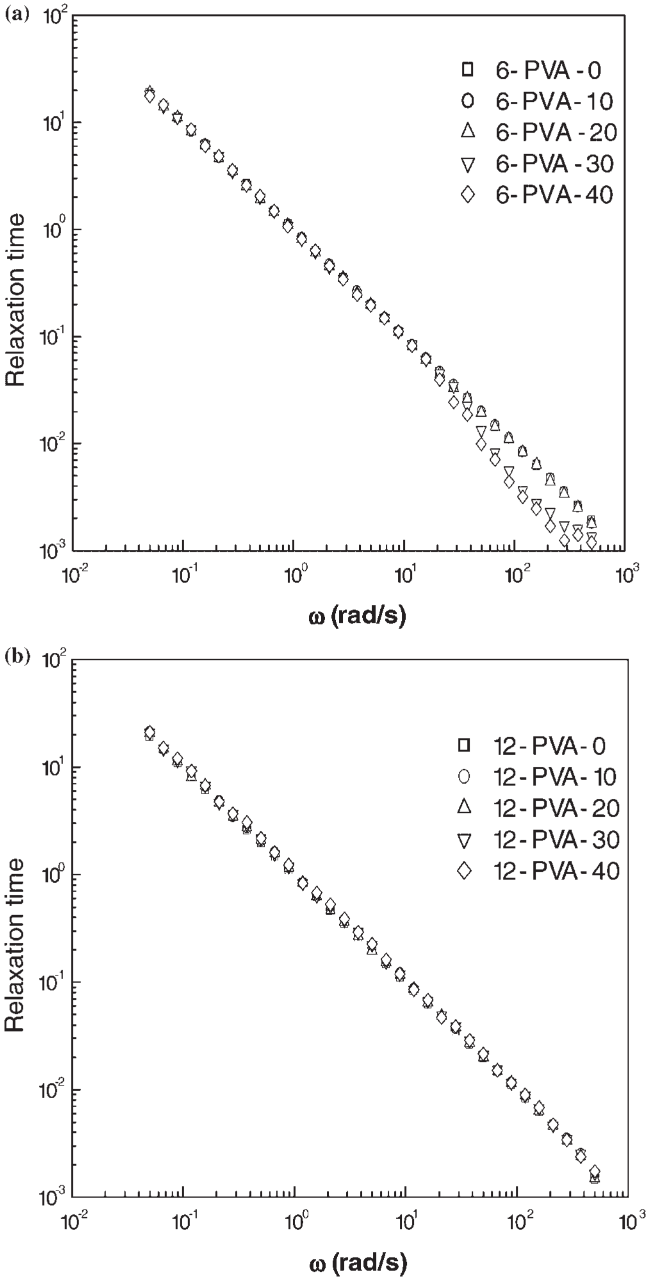

Figure 3.

Relaxation time of 6 (a) and 12 wt% (b) PVA/DEG/DMSO solutions at 90 °C.

a plasticizing effect to PVA polymers. As shown in Figure 1, the effects of DEG on the rheological properties were much more noticeable in the 6 wt% PVA solutions than in 12 wt% PVA solutions. In the case of 6 wt% solutions, an abrupt reduction of viscosity is observed from the DEG content 30 wt% whereas the 12 wt% solutions exhibit a linear diminution of viscosity with DEG content. This seems to be related with the breakdown of pseudostructure by shearing.

In 6 wt% solutions the frequency of hydrogen bonds would be much less than in 12 wt% solutions. Consequently, the pseudostructure in 6 wt%, formed through hydrogen bonding, must be weaker than that in 12 wt% solutions. So the physical structure is suddenly collapsed when DEG content exceeds 30 wt%, leading to an abrupt reduction of viscosity.

Figure 2(a) and (b) exhibit the plot of G′ vs. frequency for 6 wt% and 12 wt% PVA/DEG/DMSO solutions at 90 °C, respectively. On the whole the slope of the curves showing linearity is much less than 2, which is derived for the homogeneous polymer solutions. According to molecular theories, the perfectly homogeneous and isotropic melts and solutions of polymers give slope of 2 on the logarithmic plot of G′ against frequency and slope of 1 on logarithmic plot of G″ against frequency in the terminal zone.[9] Thus the fact that the slopes are less than 2 ascertains the heterogeneity of the solution systems.

In addition, G′ is generally decreased with increasing DEG content. However, 12 wt% solutions give rise to only slight increase of G′ values with frequency. This result corresponds to the viscosity behavior of the solutions.

Some pseudostructure formed by the introducing of plasticizers alters the relaxation processes of the polymer as well. The relaxation time (λ) is calculated as follows,

$$\lambda = G'/\left(|\eta*| \times \omega^2\right)$$

The η^* represents the complex viscosity. The relaxation time of 6 and 12 wt% PVA solutions with frequency at various DEG

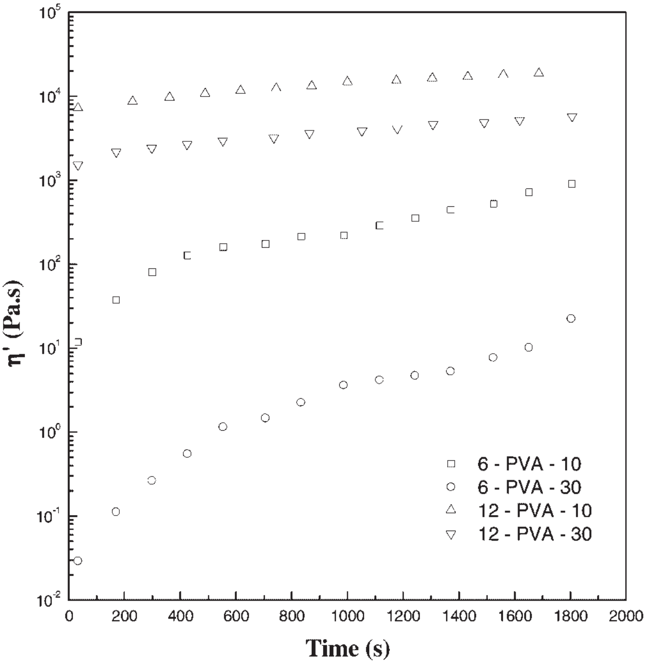

Figure 4.
η' curves of PVA/DEG/DMSO solutions in constant frequency 0.1 rad/s and at 90 °C.

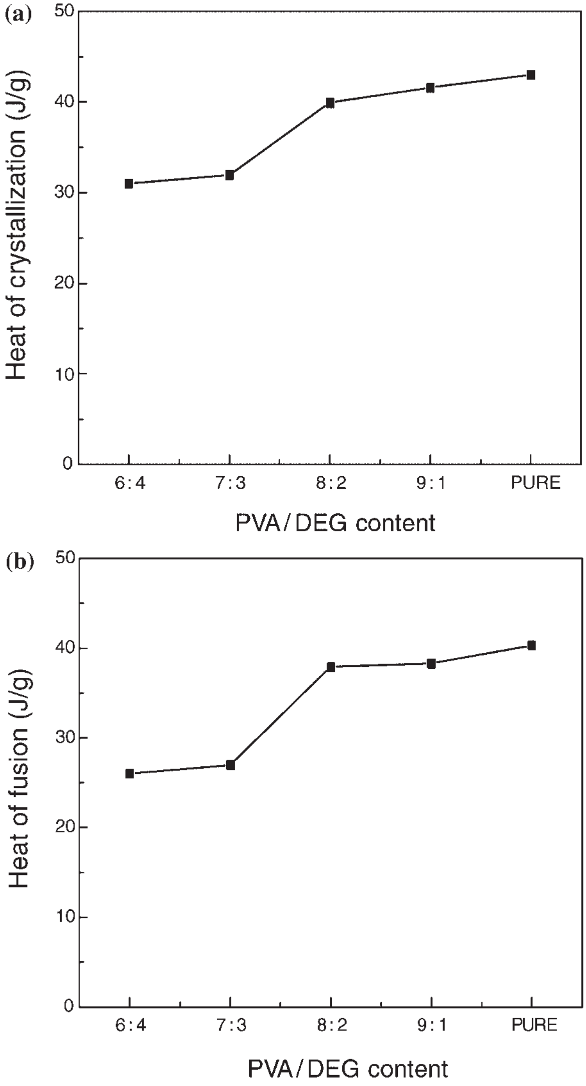

Figure 5.
Heat of crystallization (a) and heat of fusion (b) of PVA/DEG films.

contents is shown in Figure 3(a) and (b), respectively. The λ of the PVA solutions is little affected by DEG content except for DEG content of 30 and 40 wt% for 6 wt% solution. In this exceptional range some effective plasticizing facilitates the molecular slippage by breaking up the hydrogen bonds. This indicates that chain mobility of PVA polymer is affected by DEG.

Figure 4 plots the time dependence of the η′ of PVA solutions with DEG content

Table 1.
The values of T_c, T_m and T_g in curves of PVA/DEG films.

	$T_c{*}^{1}$ °C	$T_m{*}^{1}$ °C	$T_g{*}^{2}$ °C
PVA - 40	197.87	224.75	53.62
PVA - 30	198.26	224.96	54.11
PVA - 20	198.32	225.01	54.34
PVA - 10	198.85	225.18	56.72
PVA - 0	199.87	225.44	63.97

*1: measured by DSC; *2: measured by DMA.

at constant shear rate at 90 °C. The η′ of solutions decreases as the DEG content is increased. In addition, the η′ of solutions is increased with time, which is more noticeable with low concentration PVA solutions. It is suggested that some reversible structures are generated by shear induced orientation and crystallization at constant shear rate in prolonged shearing time. Particularly, the increase of the η′ is more noticeable in low shear rate. In the case of 12 wt% PVA solutions, high frequency of hydrogen bonds makes much stronger physical structure. In consequence, the DEG content has only a limited influence on the time-dependence.

The degree of crystallization has a pronounced effect on the solubility, thermal properties, tensile strength, oxygen-barrier properties, and other physical properties of polymers.[10]

Figure 5(a) and (b) show the heat of crystallization and heat of fusion of PVA/DEG films, respectively. In addition, the

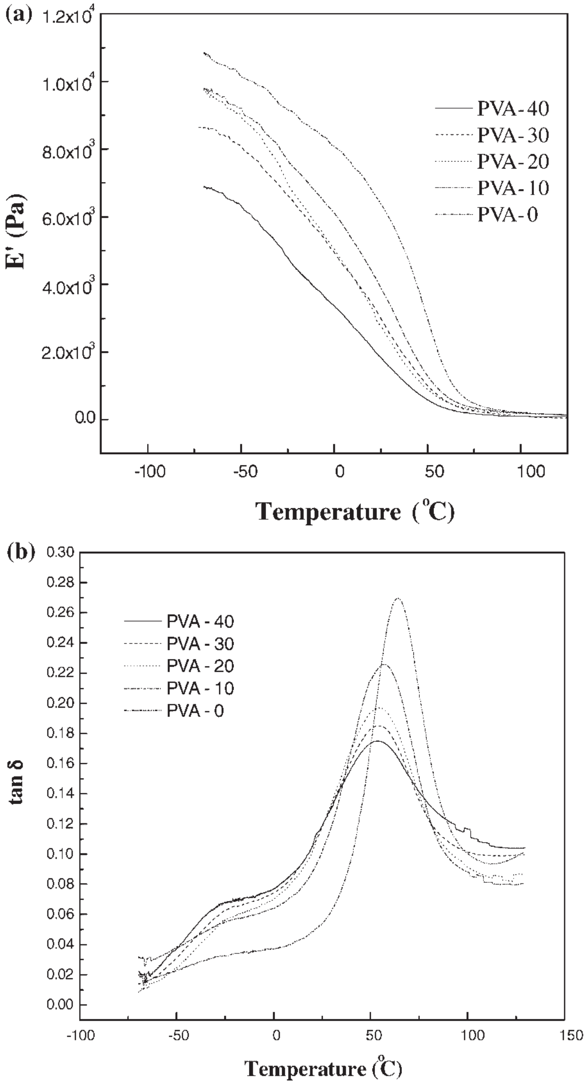

Figure 6.
(a) E′ curve and (b) tan δ curve of PVA/DEG films measured by DMTA.

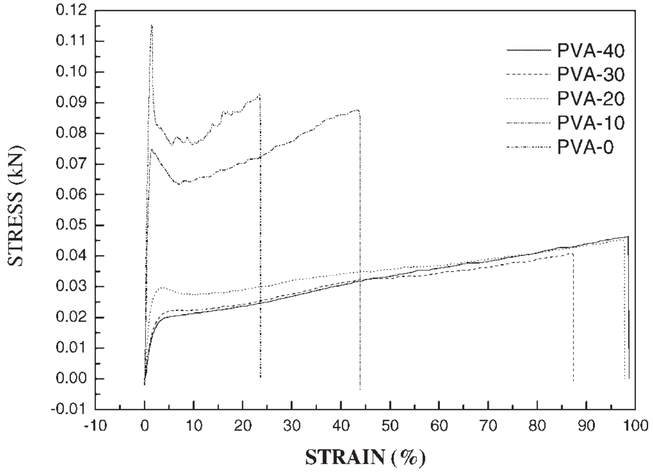

Figure 7.
The stress-strain curves of PVA/DEG films measured by Instron.

values of T_c, T_m and T_g are summarized in Table 1. The crystallization temperature is shifted to lower temperature with increasing DEG content, indicating DEG has a negative effect on crystallization. This results from disturbing the participation of the polymer chain in the crystallizable unit due to the significantly increased interfacial area. In other words, DEG interrupts the chain folding and packing of PVA. In addition, DEG prevents growth of crystals, thus the perfection of crystallinity and crystal size are reduced. It takes a more segmental mobility of PVA than neat one by plasticizing effect.

The position of the maximum value of melting temperature in heat flow shifts toward the lower temperature region with increasing DEG content. This result corresponds to T_c shifting behavior. Because DEG disturbs the crystallization, crystal has not a maximum perfection and a sufficient growth, shifting T_m to higher temperature.

The DMA technique, which yields the elastic modulus(E') and the mechanical loss factor as a function of temperature, is used in the present work to obtain information about the mechanical relaxation processes of the films.[11] The E' and $\tan\delta$ of PVA/DEG films are shown in Figure 6(a) and (b), respectively. Figure 6(a) shows that the E' is directly associated with elastic response and $\tan\delta$ is related with the molecular chain relaxation.[12] The PVA films containing DEG exhibit smaller E' than the neat PVA film. In addition, E' is decreased with increasing DEG content.

The $\tan\delta$ is another important dynamic mechanical parameter which is a measurement of damping, the relation between the elastic energy stored and the energy dissipated per cycle of vibration.[13] The $\tan\delta$ of PVA/DEG films is plotted against temperature in Figure 6(b). The T_g is decreased with increasing DEG content. This further verifies that DEG plays a role as plasticizer for PVA.

Figure 7 shows the stress-strain behavior of PVA/DEG films with DEG content. The addition of DEG decreases the initial elastic modulus and yield stress. However, DEG increases the elongation at break of the films, probably due to the plasticizing action of DEG molecules. That is, the DEG molecules disturb crystallization and regular hydrogen bonding between PVA molecules, resulting in easier sliding of PVA molecules each other. The Young's modulus, yield stress, and toughness are given in Table 2. Although introducing DEG causes decrease of mechanical prop-

Table 2.
Mechanical properties of PVA/DEG films.

PVA/DEG	Young's modulus	Yield stress	Toughness
	MPa	MPa	MPa
100/0	2026	89.82	75.60
90/10	1331	51.78	111.1
80/20	588.5	27.18	156.9
70/30	274.4	22.45	133.6
60/40	152.0	.	124.4

erties, it can gives flexibility to PVA films and improves productivity.

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