

Combined Effect of Relative Humidity and Temperature on Dynamic Viscoelastic Properties and Glass Transition of Poly(vinyl alcohol)

Hongjiu Hu,^{1,2} Xiaolong Zhang,^{1,2} Yaolong He,^{1,2} Zhan-sheng Guo,^{1,2}
Junqian Zhang,^{2,3} Yicheng Song^{2,3}

¹Shanghai Institute of Applied Mathematics and Mechanics, Shanghai University, Shanghai 200072, China

²Shanghai Key Laboratory of Mechanics in Energy Engineering, Shanghai University, Shanghai 200072, China

³Department of Mechanics, Shanghai University, Shanghai 200444, China

Correspondence to: H. Hu (E-mail: huhongjiu@shu.edu.cn)

ABSTRACT: On the basis of the experimental studies on viscoelastic properties of poly vinyl alcohol (PVA) films at various relative humidity (RH) and temperature conditions by dynamic mechanical analysis (DMA), the influence of both temperature and RH on the glass transition are discussed and an improved property model is developed to relate the dynamic modulus to RH and temperature. The results indicate that (1) with increasing the RH, the storage modulus of PVA decrease remarkably, while both loss modulus and $\tan\delta$ sharply increase to reach the peak and then markedly drops. The intensity of this variation is highly dependent upon temperature. (2) Moisture increase will cause the glass transition of PVA at isothermal condition and the transition point can be detected by glass transition relative humidity (RH_g) that obtained by isothermal RH scans. (3) Similar to the relationship between T_g and RH, the RH_g of PVA vary linearly with temperature. The state diagram of RH_g versus temperatures is nearly consistent with that of T_g versus RH. (4) The present equation based on model of Mahieux and Reifsnider (Mahieux and Reifsnider, Polymer 2001, 42, 3281) can predict well the dynamic modulus of PVA at various RHs and temperatures. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3161–3167, 2013

KEYWORDS: glass transition; hydrophilic polymers; viscosity and viscoelasticity; properties and characterization

Received 22 March 2013; accepted 14 March 2013; Published online 13 June 2013

DOI: 10.1002/app.39547

INTRODUCTION

There is a significant interest in the use of Poly(vinyl alcohol) (PVA) in sensors, food, biomedical field and paper industry. The outstanding characteristics (biocompatibility, nontoxicity, biodegradable, chemical stability, excellent film forming, adhesive ability, good mechanical strength and flexibility, as well as high oxygen and aroma barrier performances) of PVA make it one of the preferred choices for such applications. These important properties of PVA are the result of its significant cohesive energy due to its polarity from hydroxyl groups. However, the same characteristics that endow PVA with hydrophilicity make it susceptible to plasticization in humid environments.¹ Therefore, considerable efforts have been made in studying plasticizing effect caused by water on pristine PVA and PVA system by the various ways.^{1–10} López et al. reported the water content dependence of the dynamics of PVA and PVA-based composite films by means of dielectric spectroscopy (DS) and dynamic mechanical analysis (DMA).² Meanwhile, the thermal behavior and viscoelastic properties of wet PVA and PVA gels have been investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and DMA.³ Similarly, the moisture-induced effects on the tensile

mechanical properties and glass transition temperature (T_g) of PVA films were measured by using temperature modulated differential scanning calorimetry (TMDSC).⁴ It was found that increasing the water content in PVA would cause decreases in tensile strength, elastic modulus and T_g , increases in elongation properties and loss tangent ($\tan\delta$) of the polymer. To elucidate the plasticization mechanism of water molecules in PVA, the temperature of crystallization and melting of water in PVA membranes was measured at different cooling and heating rates by DSC.⁵ Moreover, the structure of water molecules absorbed in PVA was studied by DSC and Fourier transform infrared spectroscopy (FTIR).⁶ The influences of water content on free volume, chain mobility and glass transition behavior of PVA have been investigated by positron annihilation lifetime spectroscopy (PALS), solid state ¹³C-nuclear magnetic resonance (NMR) and dynamic mechanical analysis (DMA).⁷ Additionally, an aqueous PVA model has been extensively studied by using the molecular dynamics (MD) simulation method.⁸ The simulation reveals the cooperative behavior of PVA and H₂O which is responsible for the glass transition of the binary system. Recently, the plasticizing influence of water

on the molecular dynamics of PVA was revisited by DS, DMA, TGA, and X-ray diffraction (XRD).⁹

Both relative humidity and temperature are environmental factors in determining the amount of water absorbed by hydrophilic films, which may simultaneously affect the film properties. However, in above studies which have highlighted on the effect of water content on the main functional properties of PVA, testing was performed after conditioning the materials at specific temperature conditions. Additionally, the influence of temperature on the mechanical properties of PVA was well-known already, but it must be emphasized that these measurements were usually performed under an atmospheric environment, in which the precise control of humidity has been proved difficult to achieve. To our knowledge, no previous work has quantified the combined effect of relative humidity and temperature on dynamics of PVA in the published literatures.¹⁰

The present study has been undertaken in order to systematically investigate and quantify the combined influence of relative humidity and temperature on the dynamic viscoelastic properties and glass transition behaviors of PVA film. Both temperature scan and RH scan experiments were performed with DMA to provide the dynamic viscoelastic properties of PVA as function of relative humidity and temperature. Furthermore, the relative humidity and temperature dependence of glass transition was discussed in detail to construct the state diagram, which can be used to predict the glass transition behavior of polymers exposed to humid atmosphere. Finally, an improved property model was developed to describe the temperature-RH dependent storage modulus of PVA.

EXPERIMENTAL

Materials

Poval[®] PVA-224 (Kuraray, Osaka, Japan) powder with alcoholysis degree of 87–89% was adopted in this study. PVA aqueous solutions (10 wt %) were prepared by dissolving polymer powder in distilled water at 95°C for 3 h under stirring at 90 r/min. After the solutions were cooled to ambient temperature, films were prepared on Teflon-coated glass plate and dried in a desiccator for 2 days to evaporate the water. Subsequently, films with dimensions of 20 mm × 5 mm × 0.03 mm were annealed at 120°C for 30 min to erase the previous thermal history, and then kept in a desiccator with freshly dried silica gel at ambient temperature (25°C) prior to use. Thickness of 0.03 mm was selected to facilitate efficient water transfer throughout the film, and thereby making it possible for the relative humidity to attain the equilibrium state in a short time.

DMA and DMA-RH Accessory

Dynamic viscoelastic properties of PVA equilibrated at various relative humidity and temperature conditions were measured with a TA Instruments DMA Q800 and DMA-RH Accessory. Testing temperature can be kept within $\pm 0.5^\circ\text{C}$ over the temperature range 5–120°C. The relative humidity of sample chamber is controlled by mixture of N₂ and water vapor from DMA-RH Accessory cabinet, in which the maximum humidity ramp rate is 2% RH/min both linear decreasing and increasing with time. The humidity accuracy is $\pm 3\%$ at 0–90%RH and $\pm 5\%$ RH above 90%RH. Film tension clamp was selected with constant amplitude loading of frequency 1 Hz for both temperature scans and RH scans.

Temperature Scans and RH Scans

Two measurement methods used in present investigation are as follows:

1. Temperature scans under controlled relative humidity
The samples were first equilibrated at 10°C, 0% RH for 10 min, and then the relative humidity in testing chamber was adjusted to fixed values: 0, 10, 20, 30, 40, 50, and 60%, respectively. After 30 min equilibration, thermal scans were carried out at 1°C/min under these various constant RHs from 10°C (0, 10, 20%RH) or 20°C (30, 40, 50, 60%RH) to the temperatures at which the PVA films are in rubbery state at each experimental humidity.
2. RH scans under controlled temperature.
Specimens were quickly dried in measuring chamber at 0% RH, 25°C for about 30 min, and then the experimental temperature was set to 10, 20, 30, 40, 50 and 60°C, respectively. After 10 min isothermal holding, RH scans were performed isothermally at these temperatures at the rate of 0.5% RH/min. The humidity range is 0%RH to the RHs at which the PVA films are in rubbery state at each testing temperature.

RESULTS AND DISCUSSION

Relative Humidity and Temperature Dependences of Dynamic Viscoelastic Properties

The influences of relative humidity and temperature on the storage modulus (E'), the loss modulus (E'') and the loss tangent ($\tan\delta$) of PVA measured by both temperature scans and RH scans are respectively shown in Figures 1–3. It is clearly observed that there is almost no difference in measured dynamic viscoelastic properties of PVA with respect to relative humidity and temperature by temperature scans and RH scans.

Figure 1 shows the E' values of the polymer decrease remarkably with increasing relative humidity at isothermal conditions (10, 20, 30, 40, 50, and 60°C), respectively, and the intensity of this variation is highly dependent on the temperature of the sample chamber: the higher the temperature, the more rapid the decrease in storage modulus. Similarly, an increase in temperature of the measuring chamber caused a decrease in storage modulus of PVA samples kept at constant relative humidity of

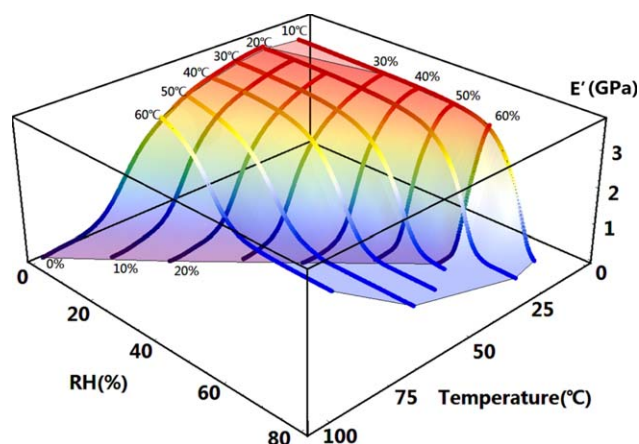


Figure 1. Effects of relative humidity and temperature on the storage modulus (E') of PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

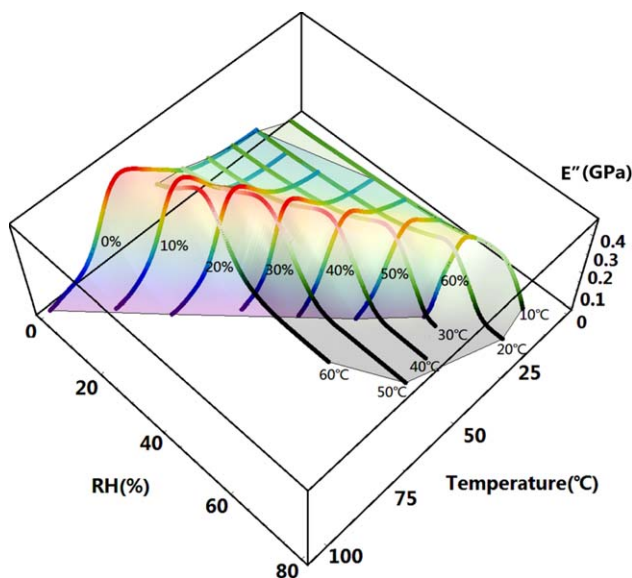


Figure 2. Effects of relative humidity and temperature on the loss modulus (E'') of PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0, 10, 20, 30, 40, 50, and 60%, respectively. Meanwhile, the reductions of E' induced by temperature increase are also getting more and more obvious with increasing RH.

The variations in E' and $\tan\delta$ of PVA films against RH at various temperatures (10, 20, 30, 40, 50, and 60°C) are presented in Figures 2 and 3, respectively. As the relative humidity increases, both E' and $\tan\delta$ sharply increase to reach the peak and then markedly drop under each isothermal condition. It can be seen that the position of these peaks obtained by RH scan shifts to the lower moisture, while the magnitude of peaks gradually declines with increasing temperature. According to DMA data from controlled RH temperature scan, the influence of temperature on the E' and $\tan\delta$ of PVA is very similar to the influence of relative humidity.

Above mentioned plasticizing effects of relative humidity and temperature on viscoelastic properties of PVA can be interpreted well on the basis of the free volume concept in the amorphous region. According to positron annihilation spectroscopy (PAS) investigation of PVA, the increment in temperature provides an increase of thermal energy in the system to overcome hydrogen bonding, the amount of free volume in the polymer would be expected to increase accordingly.¹¹ Furthermore, the absorbed water in PVA film not only disrupts hydrogen bonding, but also contributes more free volume and lubrication, where the polymer segments become readily mobile and rapidly responding to the load change.⁷ Therefore, increasing temperature and increasing humidity have a similar effect on the free volume and thus the storage modulus, the loss modulus and the loss tangent of PVA.

Influence of Relative Humidity and Temperature on Glass Transition

Glass Transition Temperature (T_g). From a DMA curve, the glass transition temperature is found from the first inflection point of the storage modulus curve (T_{gA}) or the peak of the loss modulus curve (T_{gB}) or the peak of the tan delta curve (T_{gC}).¹² However, the

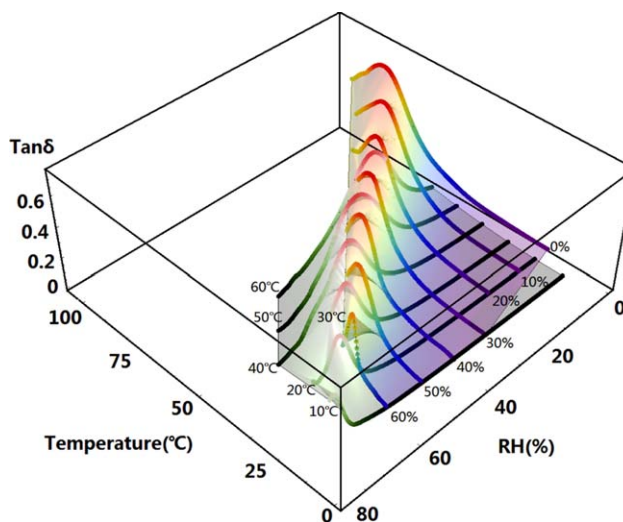


Figure 3. Effects of relative humidity and temperature on the loss tangent ($\tan\delta$) of PVA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respective peaks or points usually occur at different temperatures which result in a broad transition region for polymer.¹³ Therefore, these three criteria were applied to determine the glass transition temperature of PVA films at various relative humidity levels, and the resulting T_{gs} are plotted in Figure 4.

DMA results reveal a great effect of relative humidity on the glass transition temperature of PVA: the higher the relative humidity, the lower the glass transition temperatures. Moreover, the evaluated T_g values determined by above three criteria exhibit strong linear relations with RH. It is worth noting that the regression equation of T_{gB} can well describe the published glass transition temperature (TMDSC) of PVA samples equilibrated at different relative humidity (0–86%),⁴ as indicated in Figure 4. The linear dependence between RH and T_g may be interpreted in terms of the free volume change

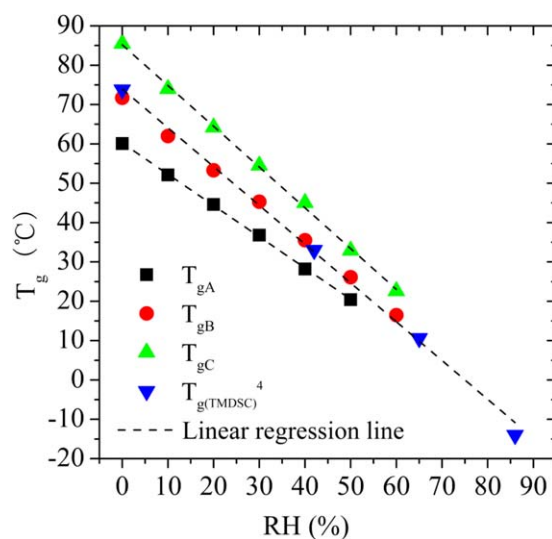


Figure 4. Relative humidity dependence of glass transition temperatures (T_g) of PVA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

induced by the absorbed water. As discussed by Zhou, Tashiro and Ii,¹⁴ the relative humidity and temperature dependence of free volume can be expressed as follows:

$$f(T, RH) = f(T, 0) + \beta(RH - RH_0) \quad (1)$$

where $f(T, RH)$ is the free volume of the water-swollen polymer at relative humidity RH and temperature T , $f(T, 0)$ is the free volume of dried polymer at temperature T , β is the proportional coefficient and RH_0 is the relative humidity of the standard state, which is usually set as 0% to simplify eq. (1) as following form:

$$f(T, RH) = f(T, 0) + \beta \cdot RH \quad (2)$$

Meanwhile, according to the discussion in the literatures,^{14,15} the free volume $f(T, RH)$ with respect to temperature is given by:

$$f(T, RH) = f(T_g^0, 0) + \alpha(T - T_g^{RH}) \quad (3)$$

where T_g^0 and T_g^{RH} are the glass transition temperature of the polymer at dry and moisture state, respectively, $f(T_g^0, 0)$ is the free volume of dry polymer at glass transition temperature, and α is the thermal expansivity.

Combining eqs. (2) and (3), the glass transition temperature of water absorbing polymers can be characterized as a linear function of relative humidity as below:

$$T_g^{RH} = \gamma \cdot RH + T_g^0 \quad (4)$$

where γ is a constant independent of RH , which is determined by the following eq. (5).

$$\gamma = -\frac{\beta}{\alpha} \quad (5)$$

Therefore the plot of T_g^{RH} versus RH is expected to be linear, and equation (4) fit fairly well to the data of RH -dependent glass transition temperature in Figure 4, the values of slopes (γ) are -79.8 , -98.6 , and -103.0 for three criteria, respectively.

Furthermore, the eq. (4) was used to correlate the data of glass transition temperature of some other hydrophilic polymers such as nylon-6,^{16,17} nylon-66,¹⁸ poly(vinylpyrrolidone) (PVP K-12),¹⁹ hydroxypropylmethyl cellulose phthalate (HPMCP),²⁰ poly(lactide-co-glycolide) (PLG)²¹ and PA 612¹⁷ at various relative humidity levels in previous literatures, as shown in Figure 5. The good regression coefficients ($R^2 \geq 0.95$) also indicate the linear dependence between RH and T_g of these polymers.

As pointed out already by Zhou, Tashiro and Ii,¹⁴ the free volume in eqs. (2) and (4) may be better expressed as a function of water content absorbed actually into the film. However, it is quite difficult to do so because the water molecules might be trapped at different region in polymer, and the role of these water molecules in affecting the mechanical performance might be various. Thus, it is more convenient to describe the moisture dependence of glass transition temperature and subsequent modulus by the RH rather than water content from a practical point of view.

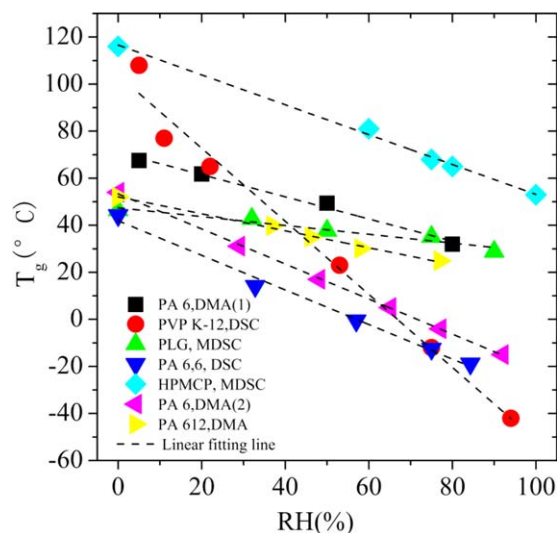


Figure 5. RH -dependent glass transition temperature of some other polymers: (■)PA 6, DMA (1),¹⁶ (◄)PA 6, DMA (2),¹⁷ (►)PA 612, DMA,¹⁷ (▼)PA 6, 6, DSC,¹⁸ (●)PVP K-12, DSC,¹⁹ (◆)HPMCP, MDSC,²⁰ (▲)PLG, TMDSC.²¹ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Glass Transition Relative Humidity (RH_g). According to the RH dependent viscoelastic properties curves of PVA films at different constant temperatures (Figures 1–3), it can be clearly found that there exists the critical relative humidity denoted as RH_{gA} , RH_{gB} , and RH_{gC} corresponding to the first inflection point of the storage modulus, the peak of loss modulus and the peak of loss tangent, respectively. That is, increased water absorption of PVA can also induce a glass transition even while temperature is held steady, and DMA can track the moisture-induced transition process as RH is scanned at a specified temperature. Therefore, it is reasonable to use the critical relative humidity, which is usually termed as the glass transition relative humidity, for detecting the glassy to rubbery transition of hydrophilic polymer in moisture surrounding.

It is well known that the glass transition temperature (T_g) of the hydrophilic polymers decreases as a result of the absorption of water that causes a plasticizing effect. However, how the temperature affects the moisture-induced glass transition is still an unsolved issue.

The effects of temperature on glass transition relative humidity are also evaluated by three criteria: RH_{gA} , RH_{gB} and RH_{gC} , and the resulting values are plotted in Figure 6. As can be seen, all of RH_{gA} , RH_{gB} , and RH_{gC} of PVA decrease remarkably with increasing temperature. The chain segment mobility of the polymer increases with elevated temperature so that a lower RH is required to induce the glass transition process at higher temperatures. Moreover, the RH_g values of PVA films determined by above three criteria exhibit strong linear relations with temperature ($R^2 = 0.99$). Although a systematic explanation cannot be made for the linear dependence between RH_g and temperature of PVA film at this stage, it is worth noting that the linear dependence between RH_g and temperature have been also obtained in recent studies on RH_g values identified by DSC or dynamic vapor sorption (DVS) for some food polymers.^{22,23}

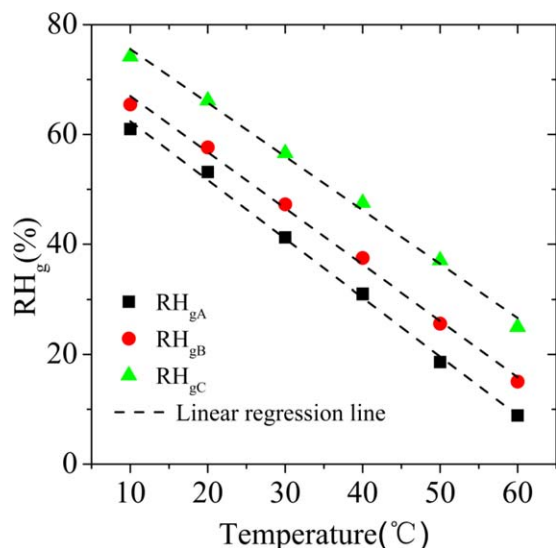


Figure 6. Temperature dependence of glass transition relative humidity (RH_g) of PVA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

State Diagram

As discussed above, whether the glass transition of amorphous glassy materials occurs or not is dependent not only on the temperature but also on the humidity of in-service condition. Thus, it is necessary to draw a polymer state diagram according to the information of temperature-RH dependent glass transition.

Since the combined effects of moisture and temperature on glass transition can be obtained by temperature scans or RH scans, one should compare the three pair dataset, “ RH_g (RH_{gA} , RH_{gB} , and RH_{gC}) versus temperature” and “ T_g (T_{gA} , T_{gB} , and T_{gC}) versus relative humidity” in Figure 7, which reveals that the values of each group are very close according to the first inflection point of the storage modulus or the peak of loss modulus or the peak of loss tangent. Therefore, the T_g of PVA at specific relative humidity may be calculated by the regression equation of RH_g versus temperature, while the RH_g values can also be obtained from the relationship of T_g and the relative humidity. Further, based only on the information obtained by RH (or temperature) scans of DMA at two different constant temperature (or RH) conditions, the slope and intercept of the straight lines of $RH_g(T) - T$ (or $T_g(RH) - RH$) can be determined to construct a polymer state diagram shown in Figure 8.

As shown in Figure 8, the state diagram can be divided into three regions by these straight lines. The first is the region of glassy state (I), the second region is the zone of transition from glassy state to rubbery state (II), and the third part is the region of rubbery state. It indicates that the state diagram can be used as an important tool for practical application to conveniently identify the glassy to rubbery transition. It is useful to determine the appropriate storage and usage conditions of relative humidity and temperature for amorphous polymer products.

Property Model of RH-Temperature-Dependent Modulus

The variation of mechanical properties with temperature in polymer and its composites is widely discussed in previous

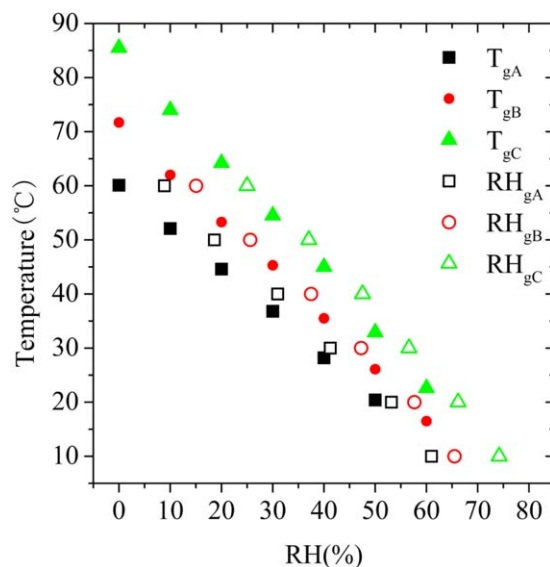


Figure 7. RH_g (0.5% RH/min) values of PVA films as a function of temperature and T_g (1°C/min) values as a function of relative humidity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

references, and some studies have fairly well-established temperature dependent modulus models for full region: from the glassy state to the rubbery state.^{24–30} Gibson et al. presented a semi-empirical model based on the hyperbolic tangent function for predicting temperature dependent mechanical properties of many polymer matrix composites.^{24,25} Mahieux and Reifsnider suggested a Weibull-type function based on bond failure to describe the modulus change over full range of transition temperatures.^{26,27} Bai et al. modeled the temperature-dependent modulus by the Arrhenius type equations.²⁸ We proposed a new

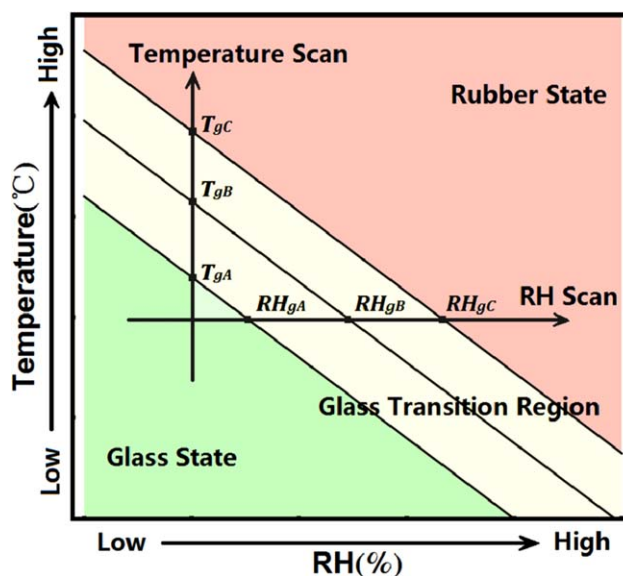


Figure 8. Schematic state diagram of amorphous glassy at different relative humidity and temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

single-parameter model in order to characterize the temperature-dependent dynamic storage modulus of the unidirectional and cross-ply epoxy/glass laminates.³⁰ However, none of these equations are able to directly describe the combined effect of relative humidity and temperature on modulus.

In current situation, it is generally not possible to implement an analytical closed-form model for coupling the mechanical behavior to the thermal and moisture response. Thus, it may be a good way to model the RH-temperature dependent modulus of PVA by developing existing equations of temperature-dependent modulus.

As compared among above methods for relating the changes in modulus of a polymer or polymer matrix composite caused by variation of temperature, it is easily found that the stiffness-temperature model proposed by Mahieux and Reifsnider has a more reliable physical basis: increasing temperature will cause the relaxation of the polymer to occur more rapidly, and the secondary bonds need to break in order to allow side group motion or the motion of a few main chains. Because of the distance variation between atoms, it is appropriate that these molecular bond strengths were assumed to follow the Weibull distribution as a function of temperature, as shown in equation (6):

$$E(T) = E_r + (E_u - E_r) \exp \left[- \left(\frac{T}{T_g} \right)^m \right] \quad (6)$$

where, T is the temperature on the Kelvin scale, $E(T)$ is the modulus at temperature T , E_u , and E_r are the “unrelaxed” (low temperature) and “relaxed” (high temperature) values of modulus, respectively. T_g is the “mechanical” glass transition temperature and m is the Weibull exponent.

As plasticizing effects of moisture on the dynamic modulus of hydrophilic polymer, the viscoelastic properties are dependent on the relative humidity and thus eq. (6) need to be rewritten as:

$$E(T, \text{RH}) = E_r(\text{RH}) + [E_u(\text{RH}) - E_r(\text{RH})] \exp \left[- \left(\frac{T}{T_g^{\text{RH}}} \right)^m \right] \quad (7)$$

Subsequently, eq. (7) was used to relate the storage modulus versus temperature data in Figure 1 for PVA films at different constant RH (0–60%), and the obtained Weibull coefficients with respect to the relative humidity are shown in Figure 9. The absorbed water in hydrophilic polymer will obviously disrupt the hydrogen bonding, and the Weibull parameters reflect the statistics of the bond breakage. Therefore, the m exponent in equation (7) is no longer a constant but a function of relative humidity for the polymer in humid surroundings. Actually, the variation in RH has greatly altered the shape of storage modulus versus temperature relationship of PVA film: the higher the relative humidity, the sharper the modulus curve (see Figure 1). That is, the increasing RH will lead to a steeper distribution of secondary bond strengths, corresponding to increasing the value of m .

As stated above, the absorbed water in PVA film contributes more free volume and lubrication, where the polymer segments become readily mobile and Weibull moduli is dependent upon the relative position of the side group to the other molecular chain. Consequently, it can be seen clearly from Figure 9 that the m values of PVA films increase nonlinearly with increasing RH from 0 to 60%.

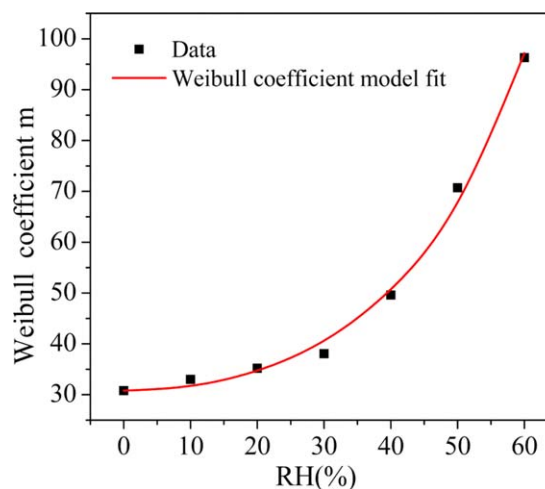


Figure 9. Relative humidity dependence of Weibull coefficient for PVA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Considering the similar effect of moisture and temperature on the free volume and thus on the molecular motions of the glassy polymer, the RH-dependent Weibull coefficient can also be expressed by the similar power functional form as:

$$m(\text{RH}) = m_0 \exp \left[\left(\frac{\text{RH}}{c_1} \right)^{c_2} \right] \quad (8)$$

where c_1 and c_2 are constants, and m_0 is the Weibull parameter of the dried polymer. A least squares fit of the data in Figure 9 yields the constant $c_1 = 0.56$ and $c_2 = 2.0$, and an excellent correlation ($R^2 = 0.99$) is obtained over the experimental range of relative humidity.

According to the linear dependence between glass transition temperature (T_g^{RH}) of PVA films and the relative humidity, the RH-temperature dependent storage modulus was thus modeled by substituting eq. (4) into eq. (7), as shown in eq. (9).

$$E(T, \text{RH}) = E_r(\text{RH}) + [E_u(\text{RH}) - E_r(\text{RH})] \times \exp \left[- \left(\frac{T}{\gamma \cdot \text{RH} + T_g^0} \right)^{m(\text{RH})} \right] \quad (9)$$

Moreover, it is clearly observed from Figure 1 that the unrelaxed modulus (low temperature) and relaxed modulus (high temperature) are almost independent upon the relative humidity. Therefore, eq. (9) can be further simplified as:

$$E(T, \text{RH}) = E_r + (E_u - E_r) \exp \left[- \left(\frac{T}{\gamma \cdot \text{RH} + T_g^0} \right)^{m(\text{RH})} \right] \quad (10)$$

Now the storage modulus of PVA film at various relative humidities and temperatures can be modeled using eqs. (8) and (10), where the value of γ is determined by T_{gB} , which is more close to the published DSC T_g of PVA at different relative humidity. The model predictions of storage modulus and experimental data are shown in Figure 10. It can be seen from Figure 10 that the measured storage modulus of PVA films at various relative humidities and temperatures can be well modeled with the modified equation based on the property model of Mahieux and Reifsnider.

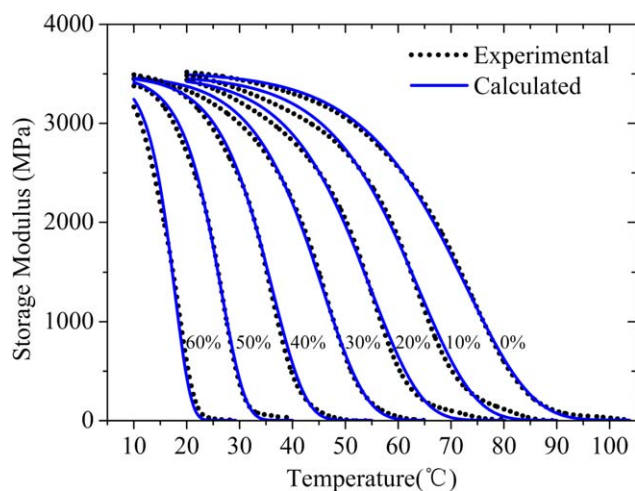


Figure 10. Comparison of the predicted RH-temperature dependent modulus with the experimental data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

From the data analysis presented above the following conclusions can be drawn.

1. As the relative humidity of sample chamber increases, the storage modulus of PVA samples decrease at different constant temperatures, while both loss modulus and loss tangent increase steeply to the maximum value and thereafter a rapid decrease. The intensity of these variations is also increased with increasing testing temperature.
2. DMA can track the moisture-induced glass transition process as RH is scanned at a specified temperature, and it is reasonable to use the glass transition relative humidity (RH_g) to identify the glass transition of hydrophilic polymer in moisture surrounding.
3. Similar to the linear relationship between glass transition temperature (T_g) and RH, the RH_g values of PVA films decrease linearly with increasing temperature, and the state diagram of RH_g values at different temperatures is nearly consistent with that of T_g versus RH.
4. The improved property model can well describe the experimental storage modulus of PVA films at various relative humidities and temperatures.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation of China (No. 10672095 and No. 11072137) and Shanghai Leading Academic Discipline Project (Grant No. S30106).

REFERENCES

1. Peresin, M. S.; Habibi, Y.; Vesterinen. *Biomacromolecules* **2010**, *11*, 2471.
2. Cendoya, I.; López, D.; Alegría, A.; Mijangos, C. *J. Polym. Sci. Pol. Phys.* **2001**, *39*, 1968.
3. Park, J. S.; Park, J. W.; Ruckenstein, E. *J. Appl. Polym. Sci.* **2001**, *82*, 1816.

4. Konidari, M. V.; Papadokostaki, K. G.; Sanopoulou, M. *J. Appl. Polym. Sci.* **2011**, *120*, 3381.
5. Rault, J.; Gref, R.; Ping, Z. H.; Nguyen, Q. T.; Néel, J. *Polymer* **1995**, *36*, 1655.
6. Ping, Z. H.; Nguyen, Q. T.; Chen, S. M.; Zhou, J. Q.; Ding, Y. D. *Polymer* **2001**, *42*, 8461.
7. Hodge, R. M.; Bastow, T. J.; Edward, G. H.; Simon, G. P.; Hill, A. J. *Macromolecules* **1996**, *29*, 8137.
8. Wu, C. F. *Polymer* **2010**, *51*, 4452.
9. Gonzalez-Campos, J. B.; Garcia-Carvajal, Z. Y.; Prokhorov, E.; Luna-Barcenas, J. G.; Mendoza-Duarte, M. E.; Lara-Romero, J.; Del Rio, R. E.; Sanchez, I. C. *J. Appl. Polym. Sci.* **2012**, *125*, 4082.
10. Zhou, S. M.; Tashiro, K.; Ii, T. *J. Polym. Sci. Pol. Phys.* **2001**, *39*, 1638.
11. El-Samahy, A. E.; Abdel-Rehim, N.; El-Sayed, A. M. A. *Polymer* **1996**, *37*, 4413.
12. Gabbott, P. *Principles and Applications of Thermal Analysis*; Wiley-Blackwell: Oxford, **2007**; Chapter 4, p 150.
13. Li, G.; Lee-Sullivan, P.; Thring, R. *J. Therm. Anal. Calorim.* **2000**, *60*, 377.
14. Zhou, S. M.; Tashiro, K.; Ii, T. *Polym. J.* **2001**, *33*, 344.
15. Fujita, H.; Kishimoto, A. *J. Polym. Sci.* **1958**, *28*, 547.
16. Aubuchon, S. R. *Am. Lab.* **2009**. Available at: <http://www.americanlaboratory.com/913-Technical-Articles/547-Dynamic-Mechanical-Analysis-Under-Controlled-Conditions-of-Temperature-and-Relative-Humidity/?adpi=2>.
17. Hatzigrigoriou, N. B.; Papaspyrides, C. D.; Joly, C.; Pinte, J.; Dole, P. *Polym. Eng. Sci.* **2011**, *51*, 532.
18. Lim, L. T.; Britt, I. J.; Tung, M. A. *J. Appl. Polym. Sci.* **1999**, *71*, 197.
19. Teng, J.; Bates, S.; Engers, D. A.; Leach, K.; Schields, P.; Yang, Y. *J. Pharm. Sci-US.* **2010**, *99*, 3815.
20. Greco, S.; Authelin, J. R.; Leveder, C.; Segalini, A. *Pharm. Res.* **2012**, *29*, 2792.
21. Blasi, P.; D'Souza, S. S.; Selmin, F.; DeLuca, P. P. *J. Control. Release.* **2005**, *108*, 1.
22. Shrestha, A. K.; Howes, T.; Adhikari, B. P.; Bhandari, B. R. *LWT-Food. Sci. Technol.* **2007**, *40*, 1593.
23. Yuan, X. D.; Carter, B. P.; Schmidt, S. J. *J. Food. Sci.* **2011**, *76*, 78.
24. Gibson, A. G.; Wu, Y. S.; Evans, J. T.; Mouritz, A. P. *J. Compos. Mater.* **2006**, *40*, 639.
25. Feih, S.; Mathys, Z.; Gibson, A. G.; Mouritz, A. P. *Compos. Sci. Technol.* **2007**, *67*, 551.
26. Mahieux, C. A.; Reifsnider, K. L. *Polymer* **2001**, *42*, 3281.
27. Reifsnider, K. L.; Mahieux, C. A. *J. Elastom. Plast.* **2002**, *34*, 79.
28. Bai, Y.; Keller, T.; Vallee, T. *Compos. Sci. Technol.* **2008**, *68*, 3099.
29. Richetona, J.; Schlatterb, G.; Vecchioc, K. S.; Rémonda, Y.; Ahzia, S. *Polymer* **2005**, *46*, 8194.
30. Guo, Z. S.; Feng, J. M.; Wang, H.; Hu, H. J.; Zhang, J. Q. *J. Compos. Mater.* **2012**, DOI: 10.1177/0021998312464080.