Moisture-Induced Effects on the Tensile Mechanical Properties and Glass-Transition Temperature of Poly(vinyl alcohol) Films

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ABSTRACT: In this study, the effect of sorbed water on the tensile mechanical properties of noncrosslinked, thermally treated poly(vinyl alcohol) (PVA) films was studied. The Young's modulus, elongation at break, and tensile strength of the PVA films equilibrated at different relative humidities (0–86%) are reported, together with the depression of the glass transition of the polymer at each equilibrating humidity, as determined by temperature-modulated differential scanning calorimetry. The results indicate that drastic changes in the tensile properties were correlated with the transition of the hydrated polymer from the glassy to the rubbery state. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3381–3386, 2011

Key words: differential scanning calorimetry (DSC); films; glass transition; hydrophilic polymers, mechanical properties

INTRODUCTION

The plasticizing effect of water on hydrophilic polymers leads to the modification of various material properties of the polymer when it is exposed to humid atmospheres, and the extent of the modification depends on the water content of the surrounding atmosphere. The importance of these water-induced effects in most applications of materials is evident when we consider the large seasonal and geographical variations of atmospheric moisture content.[1]

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer, suitable for a broad spectrum of applications, ranging from biomedical ones, such as controlled release systems and arthroplasty, to membrane separation processes. PVA is soluble in hot water because of the abundant OH groups in the polymer chain, and it is usually subjected to chemical crosslinking, heat treatment, or repeated freeze–thaw cycles to enhance its resistance to dissolution in water, to improve its mechanical properties, and to modify the equilibrium water uptake by the polymer.[2–5] The effect of these treatments[2,5] and of other structural factors, such as the molecular weight (MW)[6] and degree of hydrolysis (DH) of the polymer,[6,7] on the mechanical properties

of PVA samples conditioned at a certain humidity level have been studied in some detail. Thus, for uncrosslinked samples, a higher MW and/or higher DH result in improved tensile properties [i.e., higher modulus, tensile strength, and elongation at break $(\Delta L/L_o)$],[6] whereas crosslinking increases the tensile strength but reduces $\Delta L/L_o$.[5,8] In relation to the effect of equilibrating humidity, a comparison of available literature data on samples of similar DH, indicates that even low water uptakes have a drastic effect on the tensile properties of the polymer. Thus, PVA samples of DH > 97%, when desiccated[5,9] or equilibrated to low relative humidity (RH),[10] are characterized by tensile modulus values higher than 1 GPa, whereas when they are equilibrated to a higher RH (50%),[5,11] they exhibit a marked decrease in the modulus with a concurrent decrease in the tensile strength and an increase in $\Delta L/L_o$. Various experimental techniques, such as differential scanning calorimetry (DSC),[12,13] IR spectroscopy,[13] positron annihilation,[14] and NMR,[14] have been used to characterize the physical state of sorbed water in PVA and to elucidate the plasticization mechanism it exerts on the polymer. Studies of the glass-transition temperature (T_g) of PVA as a function of water uptake indicate that at relatively low water contents (and low external equilibrating water activities), the T_g of the system is depressed below ambient temperature[14,15] and the hydrated polymer exists in a rubbery state. The transition from the glassy to the rubbery state is expected to have a drastic effect on the mechanical properties, such as the ductility, modulus of elasticity, and

strength, of the polymer.[1] To our knowledge, literature on the tensile properties of PVA as a function of water content is rather rare[5,16] and, moreover, does not correlate the observed changes to the water-induced depression of the T_g of the polymer.

In this article, we present data on the tensile mechanical properties of PVA films equilibrated to various humidity levels. T_g versus water uptake relation was determined by temperature-modulated differential scanning calorimetry (TMDSC) and gravimetric measurements. The results show that abrupt changes in the Young's modulus (E), tensile strength, and ultimate elongation is correlated with the transition of the hydrated polymer from the glassy to the rubbery state.

EXPERIMENTAL

Materials and film preparation

PVA in the form of powder was supplied by Sigma-Aldrich (St Louis, MO, cat. No 36313-8) with the following specifications: 98–99% hydrolyzed and MW = 31,000–50,000. PVA aqueous solutions (10 wt %) were prepared by dissolution of the polymer powder in deionized water at 90°C for 6 h under magnetic stirring. After the solutions were cooled to ambient temperature, films were prepared by transferring the solution to Petri dishes, allowing the evaporation of water under atmospheric conditions, and then drying the samples further in a desiccator. All of the films were thermally treated by heating them for 20 min at 130°C [i.e., at a temperature between T_g and the melting temperature (T_m)] and subsequently kept in a desiccator containing $CaCl_2$ until use. Films with thicknesses in the range 30–50 μm (as measured with a micrometer gauge reading ±1 μm) were used for DSC and mechanical properties testing under various humidity levels. To cover a broad range of RHs, saturated aqueous solutions of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$; Fluka, Buchs, Switzerland], ammonium nitrate (NH_4NO_3; Merck, Darmstadt, Germany), and potassium chloride (KCl; Merck, Darmstadt, Germany) were used to establish constant RH values of 42, 65, and 86%, respectively. Completely desiccated samples, as determined by the absence of a water evaporation endotherm in the DSC thermogram, were also studied.

DSC

TMDSC (model MDSC 2920, TA Instruments, New Castle, DE), under nitrogen, was used to determine the T_g, crystallinity, and T_m values of the PVA films equilibrated at different RHs. A glove box containing saturated aqueous solutions of salts was used to
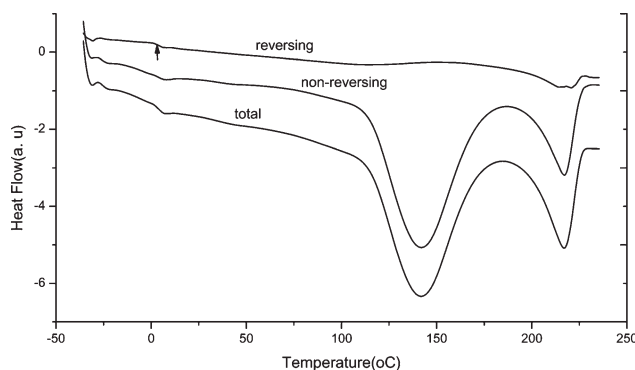
Figure 1 Representative TMDSC thermogram of a PVA sample equilibrated at 65% RH: total, reversing, and non-reversing heat-flow signals.

equilibrate samples of 5–15 mg to a constant RH. Equilibrium, determined by the constant weight gain of each sample, was reached in 5–7 days, depending on the thickness of the sample and the equilibrating RH. Subsequently, the samples were placed into nonhermetically sealed aluminum DSC pans for measurement. The TMDSC run consisted of cooling at a rate of 5°C/min to −40°C followed by heating to 250°C (with the same heating rate of 5°C/min) and a temperature modulation of ±0.80°C every 60 s. At each humidity studied, separate samples of 60–80 mg were also equilibrated in the glove box, and the water uptake was determined by weighing in stoppered bottles. In addition, desiccated (with the use of $CaCl_2$ as a desiccant) PVA samples were studied. The weight-gain measurements were performed in triplicate, and TMDSC measurements were at least duplicated.

Mechanical properties

PVA specimens with lateral dimensions of 4.0 × 0.5 cm^2 and thicknesses of 30–50 μm were equilibrated and tested at three different RHs with a tensile tester (TENSILON UTM-II-20, Toyo Baldwin Co., Ltd., Tokyo, Japan). Desiccated samples were also studied. Stress–strain tests with an initial gauge separation of 2 cm were performed at a constant rate of elongation of 10 mm/min at 23 ± 1°C.

RESULTS AND DISCUSSION

Effect of the water uptake on the glass transition

A typical TMDSC scan obtained from a PVA sample equilibrated to 65% RH is given in Figure 1. The total heat-flow signal exhibits a broad endotherm in the range 100–180°C and a second one in the range 200–230°C. The deconvolution of the total signal showed that the former endotherm, which corresponds to the evaporation of sorbed water from the
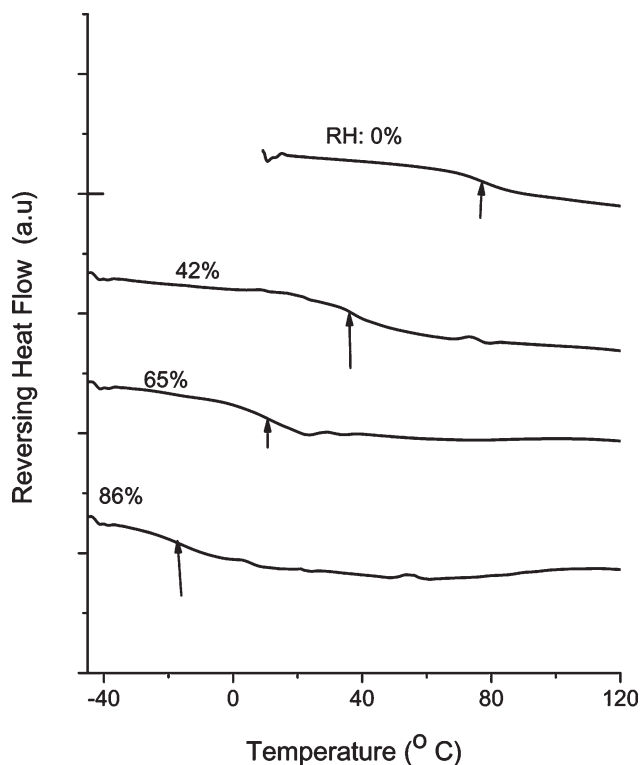
Figure 2 Reversing heat-flow signal from TMDSC runs in PVA samples equilibrated at different RHs.

sample, is exclusively present in the nonreversing heat-flow signal, whereas the latter, which corresponds to the melting of PVA crystallites after the evaporation of water, consists of both reversing and nonreversing components. The degree of crystallinity of the samples was estimated from the latent heat of melting (deduced by the integration of the 190–230°C melting area in the total TMDSC signal) in conjunction with the corresponding value of 138.6 J/g reported for 100% crystalline PVA.[17] The crystallinity of the initially desiccated samples was 45 ± 5%, and no systematic differences were found for initially hydrated samples. The inflection point in the reversing signal at 7°C in Figure 1 occurs at a temperature well below the onset of water evaporation and designates the T_g of the wet PVA sample. The small peak present in the same temperature range in the nonreversing signal is possibly indicative of enthalpy relaxation effects associated with the glass-to-rubber transition. The representative reversing heat-flow signals obtained from samples equilibrated at different RHs are shown in Figure 2. The mean values of T_g obtained from different samples at each RH level and the corresponding water weight fraction (w_1), as determined from the weight-gain measurement, are shown in Table I. The w_1 versus RH plot (not shown here) was in line with the upward curvature of the sorption isotherm (characteristic of the Flory–Huggins mode of sorption)

TABLE I
**Mean Values of T_g and w_1 Equilibrated at Different RHs**

RH (%)	T_g (°C)	w_1
0	73.8 ± 2.0	0.00 ± 0.00
42	33.0 ± 3.5	0.034 ± 0.010
65	10.6 ± 3.6	0.082 ± 0.003
86	−14.0 ± 1.5	0.141 ± 0.005

found by others for the PVA–H$_2$O system).[3,4] The T_g versus w_1 plot is shown in Figure 3. The significant drop in T_g depicted in Figure 3 is in line with studies on the state of sorbed water in PVA. Relevant studies[14,15] have shown that at the low concentration range studied here, sorbed water exists exclusively in a nonfreezable state. Nonfreezable water exerts the most efficient plasticizing action on PVA, mainly by disrupting intrachain H bonding (for water contents up to 8%) and by increasing the free volume of the matrix at higher water contents.[14]

The data of Figure 3 were fitted to the Gordon–Taylor relation,[18] originally proposed for random copolymers, and treated as solutions obeying ideal volume additivity of the repeating structural units:

$$T_g = \frac{kw_1 T_{g1} + w_2 T_{g2}}{kw_1 + w_2} \quad (1)$$

where T_{g1} is the glass-transition temperature of water (138 K), T_{g2} is the glass-transition temperature of PVA (346 K, as determined in this study), and w_1 and w_2 are the weight fractions of water and pure polymer, respectively; the parameter k is defined as the ratio of the differences in the volume expansivities in the rubbery and glassy states of the two components. As discussed in ref 18, the hypothesis of volume additivity is expected to be more frequently realized in solutions of two copolymers than in solutions of one small molecule and a polymer. Stronger
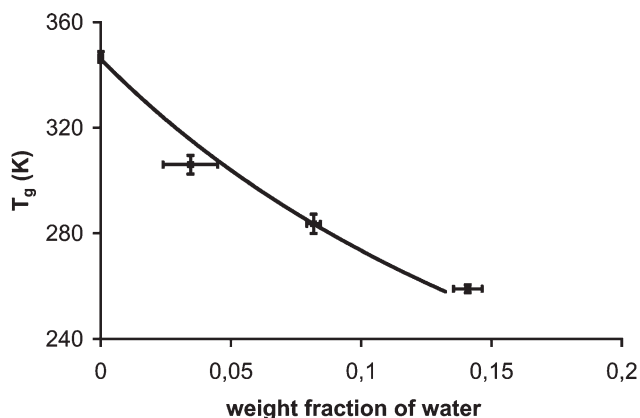
Figure 3 T_g of PVA as a function of the weight fraction of sorbed water. Points refer to the experimental data, and the solid line is the best fit of eq. (1) and yields $k = 4.8$.
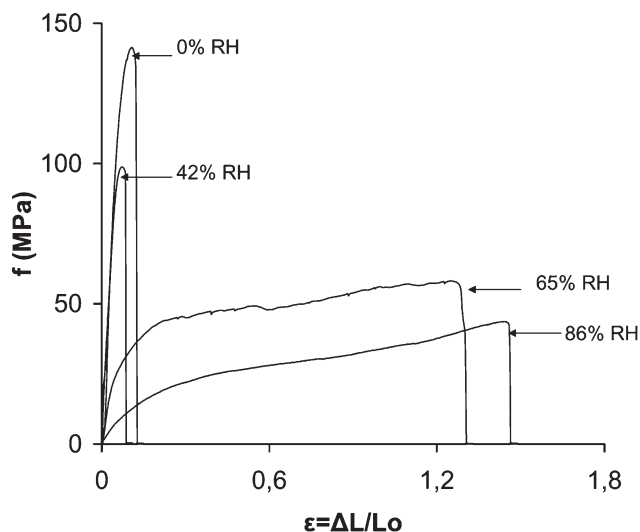
Figure 4 Representative (engineering) stress (f) - strain (ε) curves obtained at 23°C from PVA samples equilibrated and tested at different RHs (%).

deviations from ideal mixing in the latter case are attributed to stronger specific interactions between the two components and to filling of the free volume of the polymer (especially in the case of glassy polymers). Accordingly, in the case of hydrophilic polymer–water systems, the parameter k is treated as an empirical constant, indicative of the extend of plasticizing effect of water.[19] Nonlinear regression analysis was used to fit the T_g versus w_1 data to eq. (1) and to deduce a value of k. As shown in Figure 3, the experimental data were fitted reasonably well by eq. (1) with a value of $k = 4.8 \pm 0.4$. This value is very close to the value $k = 4.1$ derived from Fornasiero et al.[19] for the water-induced T_g depression of two hydrogels based on poly(2-hydroxyethyl methacrylate).

Mechanical properties

The representative stress–strain curves for a completely desiccated PVA film and for films equilibrated and tested at three different humidities are shown in Figure 4. The curve of the dry film is char-

acteristic of a glassy, brittle material failing at low elongations. The same features is also present in the stress–strain behavior of the film equilibrated at the lowest humidity (42%), whereas the two films equilibrated at higher humidities exhibit a marked ductile behavior. Because slight differences in the film preparation conditions may have affected the structure of the films, samples from different films were tested at 0 and 65% RH. The mean values of E, strain at break, and ultimate strength are shown in Table II.

On a quantitative basis, E of the desiccated PVA (derived from both films studied) and samples equilibrated at 42% RH are similar (2.29 ± 0.19 and 2.13 ± 0.20 GPa, respectively) and within the range of values reported for noncrosslinked PVA of similar DHs.[9,10] Similarly, the corresponding variations in $\Delta L/L_o$ and tensile strength are also small. In particular, the corresponding mean value of $\Delta L/L_o$ increases from 0.094 ± 0.027 (0% RH) to 0.16 ± 0.07 (42% RH), and the tensile strength drops from 130 ± 19 MPa (0% RH) to 98 ± 12 MPa (42% RH). These variations compare reasonably well with the results of Park et al.[5] for PVA films vacuum-dried at 100°C with DH = 99% and MW 89,000–98,000 ($\Delta L/L_o$ = 0.03 and tensile strength = 123.8 MPa) and films equilibrated at 50% RH containing 5% water ($\Delta L/L_o$ = 0.196 and tensile strength = 28.2 MPa).

At 65% RH, the polymer suffers a marked reduction in E (to 0.42 ± 0.04 GPa) and in the tensile strength (to 46 ± 6.8 MPa) and a marked increase in $\Delta L/L_o$ (to 1.61 ± 0.35). In principle, water-induced changes in the mechanical properties of a semicrystalline polymer may be due to both the plasticization of the amorphous regions and the possible partial destruction of the crystalline regions. In the case of PVA, although different research groups agree that at ambient temperatures, water molecules penetrate only the amorphous regions of the polymer,[12,14,20] their conclusions regarding the effect on the crystalline structure are contradictory. For example, a comparison of the degree of crystallinity of irradiation-crosslinked PVA samples in the dry and swollen
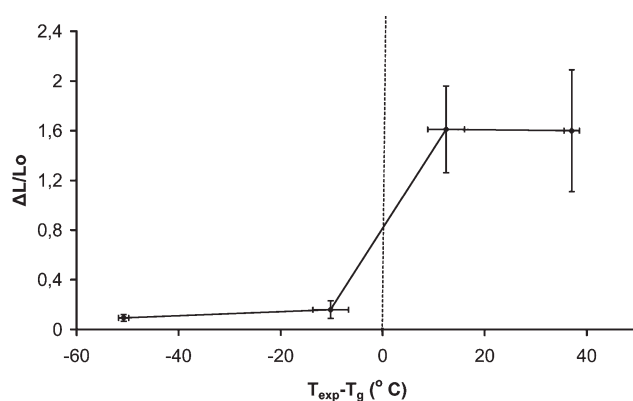
TABLE II
Mean Values of E, $\Delta L/L_o$, and Tensile Strength of the PVA Films Equilibrated at Different RHs

RH (%)	Film	E (GPa)	$\Delta L/L_o$	Tensile strength (MPa)
0	PVA-1 (seven samples)	2.26 ±0.15	0.10 ± 0.03	137 ± 22
0	PVA-2 (six samples)	2.32 ± 0.23	0.088 ± 0.026	121 ± 9.8
42	PVA-1 (five samples)	2.13 ± 0.20	0.16 ± 0.07	98 ± 12
65	PVA-3 (seven samples)	0.42 ± 0.05	1.70 ± 0.30	49 ± 8.3
65	PVA-4 (four samples)	0.42 ± 0.02	1.48 ± 0.39	43 ± 2.4
86	PVA-1 (five samples)	0.10 ± 0.01	1.64 ± 0.49	38 ± 7.3
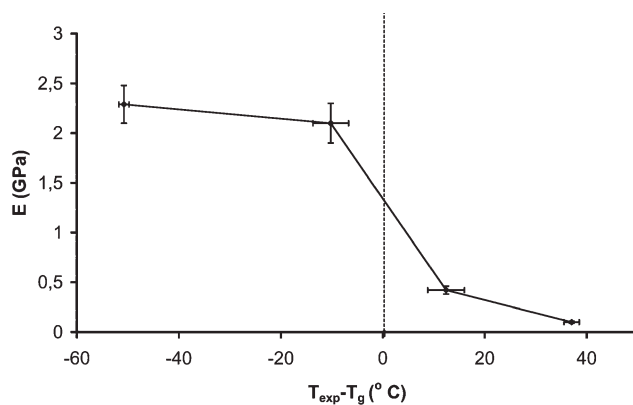
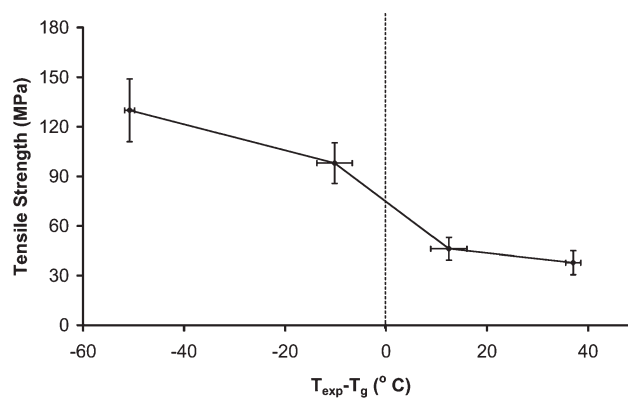**Figure 5**   E of hydrated PVA as a function of $T_{exp} - T_g$.

Figure 7   Tensile strength of hydrated PVA as a function of $T_{exp} - T_g$.

states (estimated by IR and density measurements, respectively) indicated that during swelling, crystallites remained intact.[20] On the other hand, wide-angle X-ray diffraction studies on noncrosslinked PVA films with various water contents indicated a gradual decrease in the crystallinity with increasing water content;[12] this was attributed to water molecules sorbed in the amorphous phase attacking crystallites at the amorphous–crystalline interface. The DSC method applied in this study is not suitable for estimating the crystallinity of the hydrated samples because of unavoidable water evaporation (during the heating run) at significantly lower temperatures than T_m of PVA (see Fig. 1). Thus, although some deterioration of the crystalline regions in the hydrated state cannot be excluded, it should be of small extent at the relatively low water contents studied here. On the other hand, drastic changes in the mechanical properties of a polymer, such as those observed at 65% RH (Table II), may indicate a phase transition.[21] Accordingly, the data of Table II are plotted in Figures 5–7 as a function of $T_{exp} - T_g$, where T_{exp} is the experimental temperature (23°C). The plot of E versus ($T_{exp} - T_g$) of Figure 5 bears close similarity to that observed for the modulus of a polymer as a function of temperature.[21,22] In par-

ticular, for completely amorphous polymers, the modulus of the unplasticized polymer drops as much as three orders of magnitude as the measurement temperature increased above T_g, due to the increased mobility of the macromolecular chains. The reduction of E with increasing temperature was noticeably milder for semicrystalline polymers[21,22] and similar to that observed here. The equivalence of the temperature and water sorption effects has been pointed out for other structural properties of PVA. In particular, Hodge et al.[14] found that the mean radius of free-volume cavities (as determined by positron annihilation studies) remained practically constant for water contents lower than 8% (on an amorphous polymer base) and starts to increase markedly for water contents greater than 10%, where the polymer enters the rubbery state. The same authors call attention to similar results for variations of the mean radius of free volume cavities with temperature. On the other hand, they point out that the equivalence of water-induced and temperature-induced effects is restricted by the fact that they may influence the crystallinity of the polymer in different ways.

CONCLUSIONS

E, $\Delta L/L_o$, and tensile strength of noncrosslinked, thermally treated PVA films equilibrated at various humidities indicate that the polymer behaves as a brittle, glassy material up to 42% RH. Equilibration to 65% RH results in significantly more ductile behavior, characterized by an approximately fivefold reduction of E and a 15-fold increase in $\Delta L/L_o$. A further increase in the humidity level (86% RH) had no significant effect on the tensile properties of wet PVA. TMDSC measurements of the glass transition of the hydrated polymer indicate that the humidity region of drastic changes in the tensile properties of the polymer corresponds to the transition region from the glassy to the rubbery state. The plot of E of hydrated PVA versus ($T_{exp} - T_g$) bears close analogy

Figure 6 $\Delta L/L_o$ of hydrated PVA as a function of $T_{exp} - T_g$

to the corresponding plots of E of the semicrystalline dry polymers versus the temperature.

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