Mechanistic Investigation of Drying Regimes During Solvent Removal from Poly(vinyl alcohol) Films

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ABSTRACT: The mechanism of removal of solvents such as water and methanol from semicrystalline poly(vinyl alcohol) films was investigated using various thermal analysis techniques to obtain a mechanistic understanding of the drying process. Various drying regimes were identified, which correspond to different rate-controlling steps, and characterized by differences in drying rates and mechanisms. The kinetics of solvent removal was measured gravimetrically using thermogravimetric analysis (TGA). The drying kinetics studies yielded four distinct drying regimes hypothesized to be due to (1) removal of free solvent, (2) elimination of bound solvent, (3) solvent removal during the rubbery-glassy transition, and (4) drying when the polymer is in the glassy state. The amounts of free and bound water present in the polymer were measured using differential scanning calorimetry and compared with the TGA results, and they were found to verify the proposed hypothesis. The rubbery-glassy transition observed in TGA results was confirmed using dynamic mechanical analysis. The thickness of the films was also measured as a function of drying time using thermomechanical analysis. The drying rate plots were found to be qualitatively similar to the plots of changes in film thicknesses as functions of drying time. The results of these various techniques were analyzed to propose a comprehensive mechanism of solvent removal from poly(vinyl alcohol) films. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1913–1920, 1999

Key words: drying; semicrystalline polymers; poly(vinyl alcohol); solvent removal; thermal analysis

INTRODUCTION

The removal of solvents from amorphous polymers is important in many applications such as in solvent-cast films and has been studied in detail.¹⁻¹² Various techniques, such as gravimetry,¹⁻⁴ intramolecular rotor fluorescence,⁵ electron paramagnetic resonance,⁶ and nuclear magnetic resonance,⁷ have been used to investigate solvent removal from amorphous polymers such as poly(styrene-*co*-divinylbenzene) in the glassy, as well as rubbery, states. Studies were conducted to determine how the molecular structure of the solvent and the drying conditions affect the transitions of amorphous polymers from the rubbery states to the glassy states, as well as the population distribution of molecules trapped in the glassy state.^{11,12} The drying¹³ of solvent-cast polymers and paint coatings has also been investigated in the past. The concentration effects¹⁴ on the initial rates of solvent removal from solventcast polymer films were analyzed, and many mathematical models have been developed to predict the drying rates of amorphous polymers.^{15–19}

However, the drying kinetics of semicrystalline polymers is not well understood. The degree of

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crystallinity of semicrystalline polymers increases during drying and hinders the diffusion of solvents through these polymers,²⁰ and further complicates the problem. A model for steady state, one-dimensional, isothermal drying of rubbery semicrystalline polymer films was developed by us, but this does not take into account glassyrubbery transitions during drying.²¹ An understanding of the drying process is necessary to obtain controllable polymer microstructures, because the solvent removal rate from the polymer alters its properties. The objective of this research is to understand the mechanism of solvent (water and methanol) removal from semicrystalline poly-(vinyl alcohol) (PVA) films, and identify and delineate the different kinetic regimes during drying. These various drying regimes correspond to different mechanisms and rate-controlling steps operating during the drying process. A knowledge of drying rates and mechanisms in the various drying regimes will aid in selecting optimal drying conditions.

EXPERIMENTAL

Sample Preparation and Characterization

PVA was chosen for the drying studies because it is a semicrystalline polymer that is generally synthesized by a suspension polymerization process and is used in coatings. Therefore, solvent removal from PVA films is of industrial interest. PVA (Elvanol[®] grades, E. I. DuPont de Nemours, Wilmington, DE) with $\overline{M_n} = 17,600, 64,000, \text{ and}$ 133,000; degrees of hydrolysis > 99.0%; and with polydispersity indices of 2.15 were used for the experimental studies. PVA films were obtained by dissolving PVA powder in deionized water (10% w/v) at 90°C for 6 h and casting the solutions on siliconized glass plates. To obtain consistent sample thicknesses, 35 mL of PVA aqueous solution was poured slowly into 100×15 mm siliconized Petri dishes. Films were dried at 23°C in air with a relative humidity of 45% for at least 5 days until constant sample weights were reached. The films produced using this technique were found to have uniform thicknesses of ~ 0.40 mm. The thicknesses of these films was kept small to minimize skin formation during drying and also to ensure one-dimensional solvent transport through the polymers.

Because the glass transition temperature of PVA is 85°C, the films were crystallized by an-

nealing at temperatures ranging from 90°C to 130°C, and for times varying from 10 min. to 1 h. Degrees of crystallinity of the initial and final (after crystallization) samples were measured using differential scanning calorimetry (DSC) (DSC7, Perkin–Elmer, Danbury, CT). Samples were heated from 25°C to 250°C, and the heat required for melting the crystals in the sample was compared to the heat required for melting a 100% crystalline PVA sample to calculate the degree of crystallinity of the film.²⁰

The crystallized samples were placed in deionized water and allowed to equilibrate. The amount of PVA dissolved was measured using a spectrophotometric technique.²¹ PVA in the solution was complexed with iodine/potassium iodide and boric acid solutions, and the absorbance was measured using a spectrophotometer. In all cases, only a negligible amount of PVA was found to dissolve in water at room temperature. The volume fraction of solvent in each of these films was measured using a buoyancy technique described elsewhere.²¹ Briefly, the weights of the swollen and dry samples in air and in a nonsolvent (heptane) were measured. Archimedes' principle was used to calculate the volumes of the dry and swollen polymers, and thereby, the volume fraction of solvent in the swollen polymer. While comparing the effect of different variables on drying kinetics, samples with the same initial solvent volume fractions were used. The Flory-Rehner theory was used to predict the equilibrium water volume fraction in the polymers to provide an estimate of the magnitudes of solvent volume fractions involved.²¹ The same experimental procedure was used to study the drying kinetics of methanol from semicrystalline PVA films.

Drying Kinetics Measurements

The drying was assumed to be isothermal and one-dimensional, with negligible forced convection. A thermogravimetric analyzer (TGA) (TGA7, Perkin–Elmer) was used to monitor the water loss as a function of time. Nitrogen gas was allowed to flow to the furnace at ~ 40 mL min⁻¹. Air was purged into the sample holder at a considerably low flow rate of 5 mL min⁻¹ to minimize forced convection. To determine appropriate drying temperatures, PVA powder was heated from 25° to 250°C at a scanning rate of 10°C min⁻¹. Based on the TGA degradation curve for dry PVA, suitable drying temperatures, at which no significant polymer weight loss occurred, were chosen.

Temperatures lower than 70°C were chosen for the experimental studies, because no degradation was observed at these temperatures.²¹

Drying kinetics for the PVA-solvent systems were obtained using TGA. Weights of the swollen samples were measured as functions of time using TGA. Samples were dried at three different temperatures—25°C, 45°C, and 65°C—under controlled conditions. Samples were studied for 1,000 min until the changes in their weights were small. The solvent weights in the films were plotted as functions of time.

Experimental methods for studying the drying kinetics of methanol–PVA system were essentially the same as those for the water–PVA system. The only difference was that PVA films were immersed in methanol for a longer time due to the lower swellability of PVA in methanol.

Free and Bound Water Determination

The drying kinetics experiments using TGA indicated a change in the slope of the graph depicting weight of sample as a function of time after ~ 15 min of drying. This decrease in the rate of drying was attributed to a change in the mechanism of drying. PVA undergoes hydrogen bonding with water (bound water). Because bound water is more difficult to remove than free water, the sudden decrease in the drying rate after ~ 15 min of drying was attributed to the removal of bound water, as opposed to removal of free water in the polymer. DSC, a convenient and reliable technique to distinguish free water from bound water, was used to test this hypothesis. The bound water is $unfreezable^{22}$ at temperatures even as low as -40° C. The free water freezes at $\sim 0^{\circ}$ C, and the amount of free water can be determined from DSC melting peaks. Samples were prepared using the same method as in the TGA measurements. Sample weights were also similar to the weights used in TGA studies. Therefore, the amount of free water loss, determined from DSC measurements during any stage of the drying process, can be compared with the amount of water loss from TGA measurements. Samples were immersed in deionized water and dried at 25°C. DSC runs were made during various stages of drying. To start the DSC experiments, the samples were quenched to -40° C. Samples were then heated from -40°C to 10°C at a scanning rate of 10°C min⁻¹. A scanning rate of 10°C min⁻¹ was found to produce reliable results without introducing kinetic effects into the DSC measurements.

Rubbery-Glassy Transition Kinetics

The drying kinetics obtained using TGA indicated a drastic decrease in the rate of solvent removal where the removal rate of water decreases by a factor of 10. This was attributed to change of the amorphous portion of the polymer from the rubbery state to the glassy state during solvent removal. To test this hypothesis, dynamic mechanical analysis (DMA) (DMA 7, Perkin-Elmer) was used to study the rubbery-glassy transition during drying. The samples were cut to sizes of 0.4 \times 5 \times 8 mm and tested for the dynamic mechanical properties as functions of drying time. The measurements were made in a 3-point bending mode. Helium was used as purge gas. The drying temperature was held at 25°C, and the frequency was set at 5 Hz. The static force was set higher than that of the dynamic force to enhance the stability of the measurements. The dynamic force was controlled to achieve a 40 μ m amplitude. As the polymers changed from the rubbery state to the glassy state during drying, the static as well as dynamic forces applied to the sample increased to maintain constant amplitude. The static and dynamic forces, modulus, and compliance were measured during the drying process.

Sample Thickness Measurements

Thermomechanical analysis (TMA) (TMA7, Perkin-Elmer) was used to measure the film thickness as a function of drying time. Dry samples with initial dry weights of ~ 30 mg and sample thicknesses of ~ 0.4 mm were cut into rectangular shapes. Swollen samples were placed on the sample holder and the TMA probe was positioned on top of the film. TMA was run under expansion mode where the probe, dish-shaped with 3 mm diameter, was positioned on top of the sample. The sample was maintained at 25°C and a small fixed force, 0.5 mN, was applied to the surface of the film. This force was small enough to make accurate measurements without causing the samples to deform and large enough to prevent fluctuations during measurement. As the film thickness changed during drying, the probe position was recorded, and the sample thickness was plotted as a function of time.

RESULTS AND DISCUSSION

Drying Regimes

PVA films were found to swell to a much greater extent in water than in methanol. The volume



Figure 1 Drying of PVA ($\overline{M_n} = 17,600$) at different temperatures obtained from TGA.

fractions of water and methanol in the PVA films were ~ 0.45 and 0.03, respectively. A negligible amount of PVA was found to have dissolved in the water during the swelling process. The degree of crystallinity of the film has been shown to increase as a function of drying time.²¹ Sample weights as a function of drying time observed using TGA for the PVA-water system at three different temperatures are shown in Figure 1. Higher temperatures lead to faster rates of solvent removal from the polymers. The residual water content in the polymers is also significantly lower at higher temperatures.

As seen in the TGA thermograms, based on change of slope of the curve, there are four distinct drying kinetics regimes: A1, A2, B, and C. Initially, the drying rate is fast (regimes A1 and A2), followed by a broad transition (regime B), and finally a very slow drying rate is observed (regime C). The differences in drying rates in these different regions are attributed to differences in drying mechanisms. The duration of each regime is dependent on the drying temperature. The polymer films exhibit sharper transitions and require shorter times to reach residual solvent content levels at higher drying temperatures. The transition (regime B) is assumed to be due to the transformation of the polymer from the rubbery state to the glassy state, which will be confirmed

using DMA experiments. Polymers reach the glassy state faster at higher temperatures due to higher drying rates. The low drying rates at the final stages of drying are due to higher diffusional resistances for transport of solvents through glassy polymers.

Figure 2 shows in detail, the fast drying regimes, A1 and A2, when the TGA thermogram is zoomed in to study the initial stage of the drying process. During the first 15 min of drying, the drying process is extremely fast, and more than half of the water is removed from the polymers during this stage. The extremely fast drying rates correspond to the removal of free water from the polymers, and this will be explained in the next section on DSC studies. The further drying process involves the removal of bound water. The removal rates of free water from the polymers are also very much dependent on temperature. To ensure that the change in slope found in the TGA results is due to the removal of free water, the TGA results of samples dried for 15 min prior to the TGA run were compared with those that were not. These results are shown in Figure 3. The



Figure 2 Initial drying of PVA ($\overline{M_n} = 17,600$) at three different temperatures.



Figure 3 Weight percents of PVA films as functions of drying time at 25°C for runs started at two different stages of drying: (0 min) initial swollen sample and (15 min) sample dried for 15 min.

differences in final weight percentages for the two plots correspond to the water removed during the first 15 min of drying. The samples dried for 15 min prior to the TGA run did not exhibit the change in slope found in the other samples (A1– A2). This confirmed that the change in drying rate was actually occurring in the initial stages of the drying process.

The drying kinetics for the PVA-methanol system were also studied using TGA. The drying kinetics at two temperatures, 25°C and 45°C, are shown in Figure 4. The initial drying kinetic behavior for methanol removal is similar to that of water removal and is shown in Figure 5. The drying curves are similar to those observed for the PVA-water system. However, faster removal rates of free methanol are observed in PVA-methanol system, because methanol is more volatile than water and the initial amount of methanol in PVA is less than that of water. Almost all of the free methanol is removed from the polymer within 5 min drying time.

Free and Bound Water Studies

As observed from the TGA measurements, the initial drying rates (regime A) are extremely fast,



Figure 4 Sample weight percents for the PVA-methanol system as a function of drying time for drying temperatures of 25°C and 45°C.

compared with the rates in the other three drying regimes. It is hypothesized that the drying process during this regime corresponds to the re-



Figure 5 Initial removal kinetics of methanol from PVA at drying temperatures of 25°C and 45°C.



Figure 6 DSC thermograms for PVA ($\overline{M_n} = 17,600$) samples with no drying allowed (0 min) and after 15 min drying (15 min).

moval of free solvents, and the removal of bound solvents occurs during the other three drying regimes. To verify this assumption, DSC experiments were conducted to determine the amount of free and bound solvents in the polymers at various stages of drying.

Figure 6 shows the DSC runs at two different stages of drying—the initial swollen sample and sample that was dried at 25°C for 15 min. The peaks were observed for the initial swollen sample that implies that free water exists in the polymers initially. The peaks correspond to the melting of free water. For the other samples, the peaks do not appear in the DSC thermogram at $\sim 0°C$ for the sample dried for 15 min. This indicates that there is no free water in the polymer after 15 min of drying, and the water exists in bound form.

Further drying involves the removal of bound water that requires higher energy to overcome the interactive forces between the polymer and the solvent, and thus leads to slower drying rates.

The amounts of free water present in the polymers at various stages of drying were determined using DSC by assuming that the heat of fusion²² of freezable water is equal to that of the pure water, 79.7 cal g^{-1} . The peak areas are proportional to the heat required to melt the freezable water. The ratio of the peak areas from DSC to the heat of fusion determines the amount of free water in the polymers. DSC results showed that 0.332 mg free water/mg dry sample was present in the polymers initially. After 15 min drying time, no free water was found in the samples, which meant that all of the free water was removed from the samples. The amounts of free water loss calculated from DSC was compared with the amount of water weight loss obtained from TGA measurements during the first 15 min of drying. It was found from TGA that 0.317 mg water/mg dry sample was removed during this time period, which is very similar to the value obtained from DSC studies. This supports the hypothesis that the initial drying process (regime A1) involves the removal of free water. Table I shows the comparison between the amount of water weight loss obtained from TGA and the amount of free water loss determined from DSC at two different stages of drying.

Rubbery-Glassy Transition

The complex compliance is expected to decrease when the polymers undergo a rubbery-glassy transition. The complex compliance of the polymers during the drying, obtained from the DMA studies, is shown in Figure 7. The drying time at which the transition is observed herein coincides with that obtained from TGA drying curves. Therefore, DMA studies verify that the transition (regime B) is a rubbery-glassy transition, which slows down the drying rates.

Table IComparison of Water Weight Loss Determined from TGA and FreeWater Weight Loss Obtained from DSC

Drying	Water Weight Loss	Free Water Weight
Time	(TGA)	Loss (DSC)
(min)	(mg water/mg polymer)	(mg water/mg polymer)
5 15	$\begin{array}{c} 0.254 \\ 0.317 \end{array}$	$\begin{array}{c} 0.275 \pm 0.012 \\ 0.332 \pm 0.008 \end{array}$



Figure 7 Compliance of the PVA ($\overline{M_n} = 17,600$) (obtained from DMA) as a function of drying time for a film dried at 25°C.

The physical changes occurring during drying and the mechanism for drying of semicrystalline PVA films proposed herein are qualitatively very similar to the hypothesis postulated to explain the removal of organic solvents from crosslinked poly(styrene-co-divinylbenzene) systems.¹¹ It was found that the physical changes occurring during the transition interval determine the macromolecular structure of the completely amorphous polymer obtained.¹¹ By monitoring the kinetics for elimination of residual-entrapped solvent molecules having characteristic molecular environments in the glassy state, information about this structure can be obtained.¹² The results presented in this article show that this sequence of physical changes induced by elimination of the solvent from the swollen polymer occurs even in semicrystalline polymer systems, indicating that the phenomenon may be general for all polymerliquid systems.

Changes in Film Thickness

The changes in film thickness during drying were monitored using TMA. Figure 8 shows the changes in film thickness during drying for the PVA–water system. The films shrink dramatically in the rubbery state. As the solvents are removed from the polymers, the films shrink to fill the voids that are left by solvents. In addition, chain folding—which occurs during drying causes amorphous regions to transform into crystalline regions.²¹ The shape of the curve is similar to that of the drying kinetics curve obtained using TGA. Thus, the movement of air-polymer interface can actually be used to predict the drying kinetics of the system.

CONCLUSIONS

This work focused on obtaining a mechanistic understanding of the drying mechanism of semicrystalline PVA films by delineating the various ratecontrolling steps during solvent removal at various stages of drying. The studies show that the PVA films exhibit faster drying at higher temperatures. Four distinct drying regimes were identified from the experiments. These drying regimes correspond to different mechanisms of solvent removal from PVA films. In regime A1, the drying rate was found to be much faster than in other regimes, which was found to correspond to the removal of free solvent. Further drying involves the elimination of bound solvents as seen in re-



Figure 8 Thickness of a PVA ($\overline{M_n} = 64,000$) film as a function of drying time (obtained from TMA) for a sample dried at 25°C.

gime A2. As more of the solvent molecules were removed from the films, the polymer was found to undergo a transformation from the rubbery state to the glassy state. This broad transition region (regime B) is characterized by a significant decrease in the drying rate due to gradual transformation of the polymer from the rubbery state to the glassy state. Regime C, the final stage of drying process, involves solvent removal from the polymer in the glassy state, as a result of which the drying rates are extremely slow. By changing conditions such as drying temperature and polymer molecular weight, the relative durations of the different regimes can be altered to obtain optimum solvent removal rates. The rates of change of film thicknesses are similar to the rates of drying of semicrystalline polymer-solvent systems, and thus can be used to predict qualitatively the drying kinetics in the absence of drying rate data. Similar trends were obtained for both for methanol as well as water removal from semicrystalline PVA films.

An understanding of drying kinetics of semicrystalline polymers is important in determining suitable drying conditions that can maximize drying rates and achieve controllable polymer microstructures during the drying process.

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