

Crystallization of Poly(vinyl alcohol) During Solvent Removal: Infrared Characterization and Mathematical Modeling

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ABSTRACT: Crystallization of semicrystalline polymer films during drying has a significant effect on the rate of solvent removal. Understanding and controlling the crystallization kinetics is important in controlling residual solvent levels and drying kinetics. The degree of crystallinity of the poly(vinyl alcohol) films during multicomponent drying was investigated using Fourier transform infrared spectroscopy (FTIR). The 1141 cm^{-1} band is sensitive to the degree of crystallinity of the polymer and the growth of intensity of this band was monitored as drying progressed. The results from the FTIR studies were comparable to the results obtained from differential scanning calorimetry. Studies were conducted to test the effect of initial solvent composition (water–methanol mixture), drying temperature, and polymer molecular weight on the rate of crystallization and the final crystallinity of the films. An increase in initial methanol composition increased the crystallization rate but did not affect the final degree of crystallinity. An increase in drying temperature and decrease in polymer molecular weight increased the rate of crystallization as well as the final degree of crystallinity. Based on the experimental data, rate constants for crystallization kinetics were extracted from our previously developed model based on free volume theory. The experimental data and the simulation results showed good agreement. The ability of the free volume theory to illustrate the crystallization behavior validated the model and improved its capability. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 930–935, 2007

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INTRODUCTION

The knowledge of crystal formation and growth in semicrystalline polymers is essential in determining the optimal drying and processing techniques. In polymer–solvent systems, the crystallin-

ity and morphology of the polymer changes significantly during the drying process. These changes are accompanied by changes in solvent diffusion rates and possible rubber-to-glass transitions throughout the drying process. This presents a dynamic and complex problem in understanding the behavior of polymer–solvent systems during drying. The knowledge of polymer degree of crystallinity is essential in determining the drying kinetics as well as residual solvent levels. A multicomponent solvent system

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provides more flexibility in tailoring the polymer crystallization as well as drying kinetics.

Fourier transform infrared spectroscopy (FTIR) is a well-established method to study the conformational changes in polymer systems.^{1–9} The ability to examine the molecular structure through FTIR in a nondestructive and rapid way has a great advantage over other crystallinity measurement techniques. Poly(vinyl alcohol) (PVA) and its IR behavior has been studied extensively.^{8–16} The 1141 cm^{-1} band was determined to be crystallinity-sensitive, though the precise mode of vibration is still debated.^{8–10}

Numerous mathematical models have been developed by various researchers to study the drying behavior of amorphous and semicrystalline polymers.^{15–26} Our previous studies of the drying behavior of multicomponent semicrystalline polymers lead to the development of a new crystallization kinetics model for polymers undergoing drying processes.^{27,28} This model utilizes the Vrentas–Duda free volume theory to determine the mobility of the amorphous phase in the presence of solvents and their capability to form crystals. However, an accurate estimation of the rate constant of crystallization is important to be able to accurately predict the drying kinetics using the model.

In this study, we focus on bridging the experimental techniques and mathematical modeling to better understand the changes in degree of crystallinity of the PVA during drying. We monitored the intensity of the 1141 cm^{-1} band throughout the drying experiment under various conditions to determine which factors influence the development of crystalline structures. Data collected from the studies were used in our model to validate the crystallization kinetics model that we developed, as well as to obtain a better estimation of the kinetics rate constant in the model.

EXPERIMENTAL

Materials

PVA powders with molecular weights 17,600, 35,240 (Elvanol[®] grades, E. I. du Pont de Nemours, Wilmington, DE), and 133,000 (Poly-science, Warrington, PA) were used without further purification. The PVA sample with $\bar{M}_n = 17,600$ was partially hydrolyzed (degree of hydrolysis 88%), while PVA samples with $\bar{M}_n = 35,240$ and 133,000 were fully hydrolyzed (degree of hydrolysis > 99%).

The polydispersity indices of the polymers were 2.15.

Sample Preparation

The weight of PVA powders were measured and added into a water–methanol mixture to produce a 10% (w/v) PVA solution. The solution was heated at 75 °C for 6–8 h and stirred periodically to achieve homogenous solution. The PVA solutions were kept within a 40 °C oven until they were used in the experiments.

Experimental Details

Nicolet 7600 spectrometer (Thermo Electron, Waltham, MA) was used for all the FTIR experiments. A single zinc selenide screen was used in the experiment for its high transmission at low wavenumbers. A small amount of PVA solution (1 mL) was deposited on the screen and then positioned in transmission mode within the FTIR. The wavelength of interest ranges from 700 to 4000 cm^{-1} , with resolution of 4 cm^{-1} and 32 scans. The spectra of the polymer–solvent system were taken every minute for the first 15 min and every 5 min for the remainder of the hour. Omnic[®] and TQ Analyst[®] software (Thermo Electron, Waltham, MA) were used to collect and analyze the spectra. For the temperature studies, a TLC 50 temperature cell and its controller (Quantum Northwest, Spokane, WA) was used to regulate the temperature of the screen and its surrounding environment. A custom holder was made to fit screen to the temperature cell.

Differential scanning calorimetry (DSC) (DSC7, PerkinElmer, Boston, MA) was used as an independent method to determine the crystallinity of the PVA film. A small sample (5 mg) of the film was encapsulated in an aluminum sample pan and was heated from 25 to 250 °C at rate of 10 °C/min. The melting curves were analyzed and the required heats were compared to the literature value of a pure PVA crystal to obtain the degree of crystallinity of the film.¹²

MATHEMATICAL MODEL

The mathematical model developed previously aimed to understand the interaction among diffusion of solvents, possible glassy skin formation, and the effect of crystallinity during the drying process of semicrystalline polymer films.^{27,28} The model incorporates a new crystallization kinetics

and a multicomponent diffusion scheme, which is based on Vrentas–Duda free volume theory and Flory–Huggins thermodynamic theory as well. For the crystallization kinetics, we expanded the kinetics expression first developed by Ramesh²⁹ to be used in a ternary system. In this approach, the transformation of the amorphous phase to the crystalline phase is described by a reaction with a reaction rate constant k . In the presence of two solvents, the rate of crystallization, r_c , is given by eq 1.

$$r_c = -k \frac{v}{\widehat{V}_4} (v - v_\infty) \quad (1)$$

Here, \widehat{V}_4 is the specific volume of the crystalline phase, v is the volume fraction of the crystalline phase at time t , and v_∞ is the volume fraction at time $t \rightarrow \infty$. The originality of eq 1 comes from the definition of the reaction rate constant k . Simply, it depends on the mobility of the amorphous polymer in the amorphous phase as given by eq 2.

$$k = k_0 \exp \left(\frac{\frac{\omega_1 \widehat{V}_1^*}{\zeta_{i3}^R} + \frac{\omega_2 \widehat{V}_2^*}{\zeta_{i3}^R} + \omega_3 \widehat{V}_3^*}{\frac{\widehat{V}_{FH}}{\gamma}} \right) \quad (2)$$

In eq 2, k_0 is the pre-exponential factor, \widehat{V}_i^* is the specific critical hole free volume of component i , ζ_{i3}^R is the ratio of molar volumes for component i and polymer jumping units, while ω_i is the weight fraction of component i and $\frac{\widehat{V}_{FH}}{\gamma}$ denotes total hole free volume available for diffusion, as shown in eq 3.

$$\begin{aligned} \frac{\widehat{V}_{FH}}{\gamma} = & \omega_1 \frac{K_{11}}{\gamma} (K_{21} - T_{g1} + T) \\ & + \omega_2 \frac{K_{12}}{\gamma} (K_{22} - T_{g2} + T) \\ & + \omega_3 \frac{K_{13}}{\gamma} (K_{23} - T_{g3} + T) \quad (3) \end{aligned}$$

Subscripts used in eqs 2 and 3 denote the species in the system; subscripts 1 and 2 denote the solvents in the system, while subscripts 3 and 4 denote the amorphous and crystalline polymer in the system. In addition, $\frac{K_{ii}}{\gamma}$ and $K_{2i} - T_{gi}$ are free-volume parameters for the component i . The details of the full mathematical model can be found elsewhere.²⁸ The initial and operating conditions used in the models reflect those that were used in the FTIR experiments, as shown in Table 1. Parameters used in eqs 2 and 3 are shown in Table 2. From the experimental work, the value of k_0 in eq 2 was determined.

RESULTS AND DISCUSSION

To accurately determine the degree of crystallinity of PVA using an infrared technique, a quantitative relationship between crystallinity and intensity of the peak at 1141 cm^{-1} is needed. PVA films with various degrees of crystallinity were prepared and the intensities of its 1141 cm^{-1} band were recorded. The films were then subjected to DSC measurements to determine their degree of crystallinity. A linear relationship between the crystallinity and the intensity of the 1141 cm^{-1} peak was established and is consistent with previous studies.^{11,14} Figure 1 shows the typical increase in intensity of the 1141 cm^{-1} band during drying. Film produced using this method had an average thickness of 30 μm .

Several studies were conducted to examine crystallization of the polymer and the effect of initial solvent composition, drying temperature, and molecular weight on the initial crystal growth rate and the final degree of crystallinity. Figure 2 shows the crystallinity of PVA during drying with different initial solvent compositions by volume (water:methanol ratios of 4:1, 2:1, and 1:1). The molecular weight ($\overline{M}_n = 133,000$) and the drying temperature (25 $^\circ\text{C}$) were held con-

Table 1. Initial and Operating Conditions for the Crystallization Studies Carried Out

	Methanol Concentration Studies (Water:Methanol)			Drying Temperature Studies ($^\circ\text{C}$)	
	4:1	2:1	1:1	25	75
Initial volume fraction of Solvent 1	0.8	0.67	0.5	0.5	0.5
Initial volume fraction of Solvent 2	0.2	0.33	0.5	0.5	0.5
Operating temperature (K)	298	298	298	298	348

Table 2. Parameters Used in Eqs 2 and 3

Parameter	PVA/Water	PVA/Methanol
K_{11}/γ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$)	0.00165	—
K_{12}/γ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$)	—	0.000564
K_{13}/γ ($\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$)	0.000229	0.000229
K_{21} (K)	-141.73	—
K_{22} (K)	—	23.87
K_{23} (K)	-214.87	-214.87
T_{g1} (K)	0	—
T_{g2} (K)	—	0
T_{g3} (K)	0	0
V_1^* ($\text{cm}^3 \text{g}^{-1}$)	1.071	—
V_2^* ($\text{cm}^3 \text{g}^{-1}$)	—	0.959
V_3^* ($\text{cm}^3 \text{g}^{-1}$)	0.720	0.720
ζ_{ij}	0.45	0.99

stant. In the first 4 min, the intensity of the 1141 cm^{-1} peak was very weak and no meaningful data could be extracted. The first sign of the peak development occurred at 5 min and the crystallinity of the polymer increased rapidly until it reached a plateau around 25 min. The final degree of crystallinity of the film was measured using DSC after the drying and the degree of crystallinity found was comparable to the data from FTIR. Comparing the different initial solvent compositions, there was a slight increase in the rate of crystallization in the water:methanol 1:1 ratio sample compared to the higher water:methanol ratio samples. The differences in initial rate of crystallization between the water:methanol 2:1 ratio sample and water:methanol 4:1 ratio sample were less apparent. Further statistical

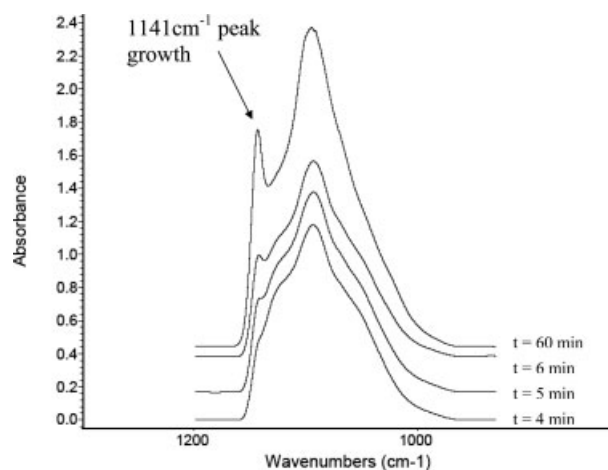


Figure 1. The FTIR spectra of poly(vinyl alcohol) during drying, showing the development of the crystalline-sensitive peak of 1141 cm^{-1} .

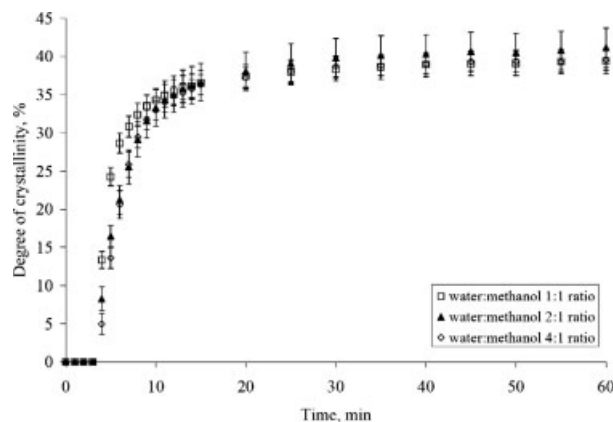


Figure 2. Comparison of the degree of crystallinity with different initial solvent composition from FTIR experiment. (\diamond) represents the initial water:methanol ratio of 4:1 by volume, while (\blacktriangle) represents water:methanol ratio of 2:1 and (\square) represents water:methanol ratio of 1:1.

analysis of the data showed that there was a significant difference between the results from water:methanol 1:1 ratio samples and the others samples from 4 min, when crystallization was detected, to 8 min, when the rate of crystallization slowed down considerably. For the comparison between water:methanol 2:1 and 4:1 ratio samples, we found no significant difference between the degree of crystallinity of the samples. Overall there were no significant differences among all three samples for the final degree of crystallinity. Using these data, simulations were performed and the results are shown in Figure 3. Similar

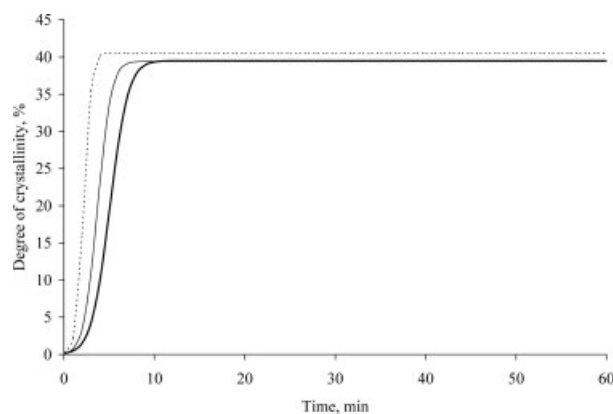


Figure 3. Comparison of the degree of crystallinity with different initial solvent composition from simulations with $k_0 = 650$. (\cdots) represents the water:methanol ratio of 4:1, while (—) represents water:methanol ratio of 2:1 and (- - -) represents water:methanol ratio of 1:1.

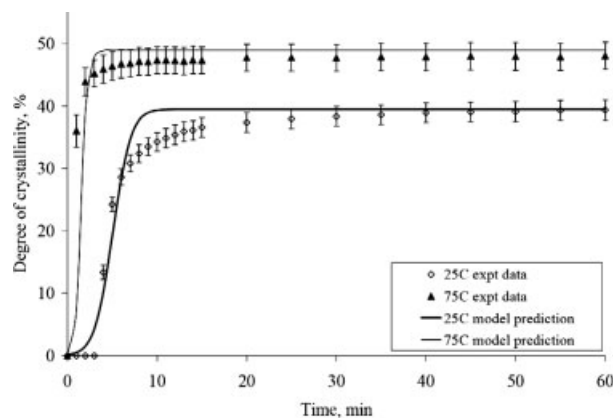


Figure 4. Comparison of the degree of crystallinity with different drying temperature from FTIR experiment and simulation. (\diamond) and (—) represent the drying temperature of 25 °C from FTIR experiment and its simulation counterpart, while (\blacktriangle) and (—) represent the drying temperature of 75 °C from FTIR experiment and its simulation counterpart.

trends were found to exist in the simulation results, where the increase in initial methanol composition has a slight positive effect on the rate of crystallization. This is consistent with the experimental results. Nevertheless, from the experimental data, the differences in initial rates of crystallization of water:methanol 2:1 and 4:1 samples are small and within experimental error. The k_0 value of 650 was found to fit the experimental data well. In eq 1, the knowledge of the value of v_∞ was required before the simulation, and the data obtained through the DSC experiments were used. Simulation results have shown that the rate of drying of water is higher than that of methanol, thus, at any time during the drying the concentration of water in the film is lower. The increase in initial methanol composition with the decrease in water composition dominates the contribution of methanol to the total hole free volume of the system. In other words, with increased methanol concentration in the solution, total hole free volume of the system, thus, mobility of amorphous polymer in the amorphous phase and its ability to form crystals increases.

The increase of drying temperature (25, 75 °C) increased the rate of crystallization as well as the final crystallinity of the film, as shown in Figure 4. The molecular weight ($\bar{M}_n = 133,000$) and the initial solvent composition (50% methanol) were held constant. Using the same rate constant, the close fit of the simulation results demonstrated that the relationship between drying temperature and crystallinity can be explained by free

volume-based new rate equation for crystallization. The increase in drying temperature increased the free volume within the sample. Consequently, the mobility of the polymer and hence its ability to align itself to form crystals significantly increased. To study the effect of molecular weight on the development of crystals, three PVA samples with different molecular weights ($\bar{M}_n = 17,600$, 35,240, and 133,000) were used. The drying temperature (25 °C) and the initial solvent composition (50% methanol) were held constant. The results were shown in Figure 5. As expected, the higher molecular weight sample ($\bar{M}_n = 133,000$) had the lowest crystallization rate and final crystallinity, which shows length of the polymer chains has a profound effect in the ability of the chain to align itself to form crystals. However, the crystallization kinetics of the $\bar{M}_n = 17,600$ and 35,240 samples did not show any significant differences. A possible reason for this is the difference in degree of hydrolysis of the samples used. For samples made with PVA of $\bar{M}_n = 17,600$, the degree of hydrolysis was $\sim 88\%$, while the sample with PVA of $\bar{M}_n = 35,240$ had a degree of hydrolysis $>99\%$. Since PVA is made by hydrolyzing poly(vinyl acetate), the degree of hydrolysis show the completeness of that reaction. A lower degree of hydrolysis in the samples means that the samples still contained a substantial amount of acetate groups in the polymer chain. The acetate groups in the polymer chain are bulkier and change the size and shape of the molecule, thus making it harder to align

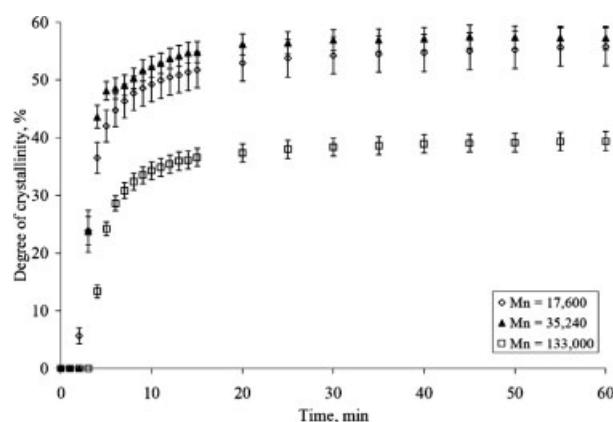


Figure 5. Comparison of the degree of crystallinity with different polymer molecular weights from FTIR experiments. (\diamond) represents $\bar{M}_n = 17,600$, while (\blacktriangle) represents $\bar{M}_n = 35,240$ and (\square) represents $\bar{M}_n = 133,000$.

and form crystals. There were no simulation results accompanying the experimental data in this study because our mathematical model does not take into account the molecular weight of the sample. Furthermore, the relationship between the crystallinity of a semicrystalline polymer and its molecular weight varies depending on the material chosen.

CONCLUSIONS

We have examined the use of FTIR as a tool to determine the degree of crystallinity of PVA in the presence of solvents as it is subjected to drying conditions. With the results obtained from the experiments, we were able to extract the crystallization rate constant from our simulations, which were found to fit the experimental data well. We performed three studies to investigate the effect of initial solvent composition, drying temperature, and molecular weight on the rate of crystallization as well as the final crystallinity of the film. Our studies showed that the increase in initial methanol composition had a slightly positive effect on the crystallization rate, yet it did not have a significant effect on the final crystallinity of the film. The increase in drying temperature and the decrease in PVA molecular weight showed significant increases in the rate of crystallization as well as the final degree of crystallinity. The simulation results agreed well with the experimental data and showed the ability of Vrentas–Duda free volume base rate expression to explain the crystallization behavior of PVA during drying. This validated and further improved the predictive capability of our previously developed mathematical model.

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