ELSEVIER

Polymer 40 (1999) 5393–5400

polymer

Quantitative analysis of crystallization and skin formation during isothermal solvent removal from semicrystalline polymers

Meo O. Ngui, Surya K. Mallapragada*

Department of Chemical Engineering, Iowa State University, Ames, IA 50011-2230, USA

Received 14 September 1998; accepted 14 October 1998

Abstract

A mathematical model was developed to predict the isothermal drying kinetics of semicrystalline polymer films. The model considers the mechanism of semicrystalline polymer drying that was proposed by us based on experimental studies. Experimental studies have indicated an increase in the degree of crystallinity of semicrystalline poly(vinyl alcohol) (PVA) during drying, which slows down the rate of diffusion of the solvent remaining in the polymer film. The model considers the crystallization kinetics and the changes in the polymer degree of crystallinity produced in semicrystalline polymers during solvent removal. The model also takes into account rubbery–glassy transition and skin formation during solvent removal and its effect on the drying kinetics. Model predictions include polymer film thickness, skin thickness, rate of solvent removal and degree of crystallinity of the polymer as functions of time. These predictions were compared with experimental results for drying of PVA films and good agreement was observed between the model predictions and the experimental data. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Drying; Semicrystalline polymers; Skin formation

1. Introduction

Drying of polymers is an important step in many cases such as solvent-cast films and for polymers synthesized by solution or suspension polymerizations. The drying mechanisms of amorphous and semicrystalline polymers have been investigated in detail using a variety of experimental techniques [1–6]. The different kinetic regimes observed during the solvent removal process were identified using thermal analysis techniques [1]. In the case of semicrystalline polymers, the degree of crystallinity of the polymer was found to increase as a function of time [1]. Therefore, solvent removal from semicrystalline polymers is hindered during the later stages of drying due to the presence of additional crystallites.

Many polymers are glassy at room temperature and become rubbery in the presence of sufficient solvent. As the solvent is removed from the polymer, there is a rubbery–glassy transition and part of the polymer turns glassy while the core remains rubbery, leading to skin formation. As the solvent removal rate is fastest at the polymer–air interface, compared with the polymer core, the rubbery–glassy transition occurs first at the surface, resulting in the formation of a glassy skin at the polymer–air interface. Solvent diffusion through this glassy skin acts as a rate limiting step for polymer drying. Therefore, it is crucial to be able to understand and predict skin formation rates to accurately predict the drying kinetics of semicrystalline polymers.

A number of mathematical models have been proposed for describing the drying of amorphous polymers. Drying of thin gel films [7], pellets [8], paper coatings [9], and shells [10] has been modeled in the past using diffusion equations. Drying of solvent-coated polymer films has been modeled [11,12] and the surface concentration effects have been considered [13]. These models have been helpful in designing industrial dryers with convective and radiant heating [14]. Drying regimes have also been predicted by models developed for coatings that react and gel [15]. Viscoelastic and relaxational effects during polymer drying have been incorporated into mathematical models to predict drying kinetics [16]. A model was recently developed to predict trapping skinning in polymers [17]. It has been shown that effective diffusion parameters can be extracted from drying experiments [18].

However, models for drying of semicrystalline polymers have received very little attention in the past. The drying

---

* Corresponding author. Tel: + 1 515 294 7407; fax: + 1 515 294 2689.
E-mail address: suryakm@iastate.edu (S.K. Mallapragada)

PII: S0032-3861(98)00737-X

rates of semicrystalline polymers differ significantly from those of amorphous polymers because the increase in the degree of crystallinity changes the drying rates during the solvent removal process [1]. Recently, a mathematical model was proposed by us to predict the drying kinetics and changes in the degree of crystallinity of semicrystalline rubbery polymers films [1]. However, this model does not take into account the rubbery–glassy transition and skin formation that usually accompanies the drying process. Since the skin formation rate can be the rate controlling step for polymer drying, especially in the later stages of drying, it is crucial to predict skin formation rates to be able to predict drying kinetics of semicrystalline polymers. Predictions of skin formation rates are also important in determining residual solvent content levels in the polymer at the end of the drying process. This paper details the development of a mathematical model that predicts skin formation as well as crystallization kinetics during the drying of semicrystalline polymer films. The model predictions are compared with experimental results obtained in our laboratory of the drying kinetics of semicrystalline poly(vinyl alcohol) films [1].

2. Mathematical model

We recently proposed a model to predict the drying kinetics of rubbery semicrystalline [1] polymers (DRP). Though this model does take into account crystallization kinetics during drying, it does not predict skin formation during drying. Many polymers are glassy at room temperature. As the drying proceeds, the polymer gradually turns glassy and skin formation occurs. The model proposed here for drying of glassy polymers (DGP) was developed to explain the crystallization phenomena as well as the skinning effect during the drying process where the surface of the film becomes glassy but the inner layer still remains in the rubbery state. A schematic representation of polymer film drying is shown in Fig. 1. The polymer is coated onto a substrate, so the films are impermeable at $x = 0$ while the solvents are removed from the film at the other face at $x = L$. The initial diffusion rate at the outer layer of the polymer film is faster than the inner core which causes a glassy region to be formed at the air–polymer interface while the polymer's core is still rubbery. As more solvent is removed from the film, more of the polymer changes from rubbery to glassy state. This is a moving boundary problem since both air–polymer and glassy–rubbery interfaces move inward as the solvent is removed from the polymer film. The polymer in the region $0 < x < R$ is in the rubbery state, whereas the polymer in the region $R < x < L$ is in the glassy state. Initially, L coincides with R since the entire polymer film is in the rubbery state. As the solvent diffuses out of the polymer, the polymer transforms to glassy state at the air–polymer interface and this leads to skin formation at the polymer surface. This surface layer or skin becomes thicker and thicker as more of the polymer changes from rubbery to glassy state. The diffusion coefficient of solvents in glassy polymers is orders of magnitude lower than that in rubbery polymers. The glassy region acts as a diffusion barrier for further removal of solvents from the rubbery region. This model considers the movement of the glassy–rubbery interface and predicts the drying rates of glassy polymers.

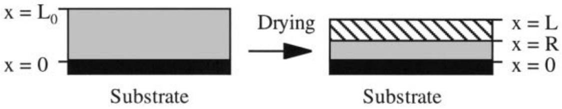

Fig. 1. Schematic representation of drying of a semicrystalline polymer film.

The model assumes isothermal drying kinetics and one-dimensional transport. Solvent removal is controlled by the diffusion of the solvent through the polymer slab. Once the solvent reaches the polymer–air interface, it is assumed to escape to the air immediately. The model also assumes uniform initial size distribution of the crystals for predicting how the degree of crystallinity of the polymer changes as a function of drying time. As shown from previous experimental studies [1], the degree of crystallinity of the polymer increases as a function of drying time. This mechanism is similar to annealing above the glass transition temperature of the polymer in order to increase its degree of crystallinity. This model considers the crystallization kinetics during solvent removal from semicrystalline polymers. The three components in the system are solvent, amorphous portion of polymer, and crystalline portion of polymer. The suffixes 1, 2a, and 2c refer to the solvent, amorphous portion of the polymer, and crystalline portion of the polymer, respectively. The rates of change of the components during drying are expressed in terms of volume fractions, υ. The sum of the three volume fractions is always equal to unity. This model is not limited to glassy polymers, but can be applied to predict drying rates of various semicrystalline polymer–solvent systems, since the drying of rubbery polymers is only a special case of this problem:

$$\upsilon_1 + \upsilon_{2a} + \upsilon_{2c} = 1 \tag{1}$$

In the rubbery region, $0 < x < R$, the rate of change of the crystalline portion of the polymer during drying is proportional to the chain folding rate, k_1. The value of k_1 was calculated [1] based on the theory developed by Lauritzen and Hoffmann [19] for crystallization kinetics:

$$k_1 = 2\frac{kT}{h}N_0 \exp\left[\frac{l(b\sigma_s - bw\Delta G)}{kT}\right] \times \exp\left(\frac{2bw\sigma_e}{kT}\right)\sinh\left[\frac{bw(l\Delta G - \sigma_e)}{2kT}\right] \tag{2}$$

The values of σ_e and σ_s, the end and side surface free energies of the crystals, were calculated from theory [20]. The free energy change, ΔG, for folding a polymer chain of length l, thickness b, and width w during crystallization was

Table 1
Values of parameters used in numerical simulations of isothermal drying of rubbery−glassy polymers

Parameter	Value
Initial v_{2c}	0.08
Initial v_1	0.65
k_1	10^{-3}–10^{-5} s^{-1}
D_0	10^{-8}–10^{-11} m^2/s
v_{1t}	0.01
n	1.0–3.0
k_2	10^{-8}–10^{-6} m/s

calculated from the following equation [20]:

$$\Delta G = \frac{\Delta h_f (T_m^0 - T)}{T_m^0} \tag{3}$$

where Δh_f is the heat of fusion per unit volume of the polymer, T_m^0 is the melting point of an infinitely thick polymer crystal, and T is the crystallization temperature.

The rate of change of crystalline volume fraction is assumed to be proportional to the chain folding rate and solvent volume fraction in region $0 < x < R$:

$$\frac{\partial v_{2c}}{\partial t} = k_1 v_1 \tag{4}$$

The expression for rate of change of amorphous volume fraction has a generalized Fickian diffusion term and a term for the decrease of amorphous portion due to the transformation of amorphous phase to crystalline phase during the chain folding process. Thus, the equation for rate of change of amorphous portion is expressed as:

$$\frac{\partial v_{2a}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial v_{2a}}{\partial x}\right) - k_1 v_1 \tag{5}$$

The diffusion coefficient, D, depends on solvent volume fraction [21], crystallinity, tortuosity, and temperature using the free volume theory:

$$D = D_0[\exp(a_D v_1)](1 - v_{2c})/\tau \tag{6}$$

The constant a_D is determined theoretically [21] or calculated from spin echo NMR studies [22]. It has been shown that the value of tortuosity τ is equal to 3 for the diffusion of small molecules through semicrystalline polymers, unless the volume fraction of the crystals is very low [23]. The value of τ was taken to be 1.0 when $v_{2c} \le 0.05$ and 3.0 when $v_{2c} > 0.05$. D_0 is dependent on temperature.

The movement of the glassy–rubbery interface can be predicted using the expression proposed by Astarita and Joshi [24]:

$$\frac{dR}{dt} = -k_2(v_{1|x=R} - v_{1t})^n \tag{7}$$

where v_{1t} is the volume fraction corresponding to the threshold activity for deswelling and k_2 and n are the fitting parameters of the kinetics model. These values can be determined from sorption experiments [25].

The expressions used in the glassy region, $R < x < L$, are very similar to those used in the rubbery region, except for a few modifications. The transformation from amorphous portion to crystalline portion is assumed to occur only in the rubbery state where $0 < x < R$. The chains do not have enough flexibility to fold in the glassy state, and the crystallinity is assumed to remain constant in the region $R < x < L$ (glassy region).

Since the degree of crystallinity remains constant in the glassy state, only one equation is required to predict the volume fractions of solvent, amorphous region, and crystalline regions during the drying. The rate of change of amorphous volume fraction in the glassy state ($R < x < L$) is calculated using the following equation:

$$\frac{\partial v_{2a}}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial v_{2a}}{\partial x}\right) \tag{8}$$

D is the diffusion coefficient of the solvent in the glassy polymer. The values of D can be determined from Eq. (6). The value of a_D corresponds to that for a glassy polymer and the degree of crystallinity in the glassy region is assumed constant.

The initial conditions for this system are known:

$$\text{at } t = 0,\quad L = R = L_0 \tag{9}$$

The boundary conditions assume that the flux of solvent is zero at $x = 0$, due to an impermeable substrate. A pseudo-equilibrium assumption, obtained by equating solvent chemical potentials on either side of the boundary, is used at the polymer−air interface:

$$\text{at } t \ge 0,\quad x = 0,\quad \frac{\partial v_{2a}}{\partial x} = 0 \tag{10}$$

$$\text{at } x = L(t),\quad t > 0,\quad \frac{v_{2a}}{1 - v_{2c}} < 1 \tag{11}$$

This is a moving boundary problem which is converted to a fixed boundary problem using a Landau transform [26]. A normalized position ξ is defined as:

$$\xi = x/L(t) \tag{12}$$

The transformed equations were solved using finite difference algorithms [27]. At each time step, R and L are calculated and for the region $0 < x < R$, the rubbery polymer equations are used, and for $R < x < L$, the glassy polymer equations are applied to yield model predictions.

3. Results and discussion

The model predictions consider the increase in polymer degree of crystallinity during drying, skin formation at the film surface as well as drying in the glassy state. The model predicts the film thickness, thickness of the glassy skin, solvent weight loss, and volume fraction of the crystalline portion of the polymer as functions of drying time. Table 1 shows representative ranges of the

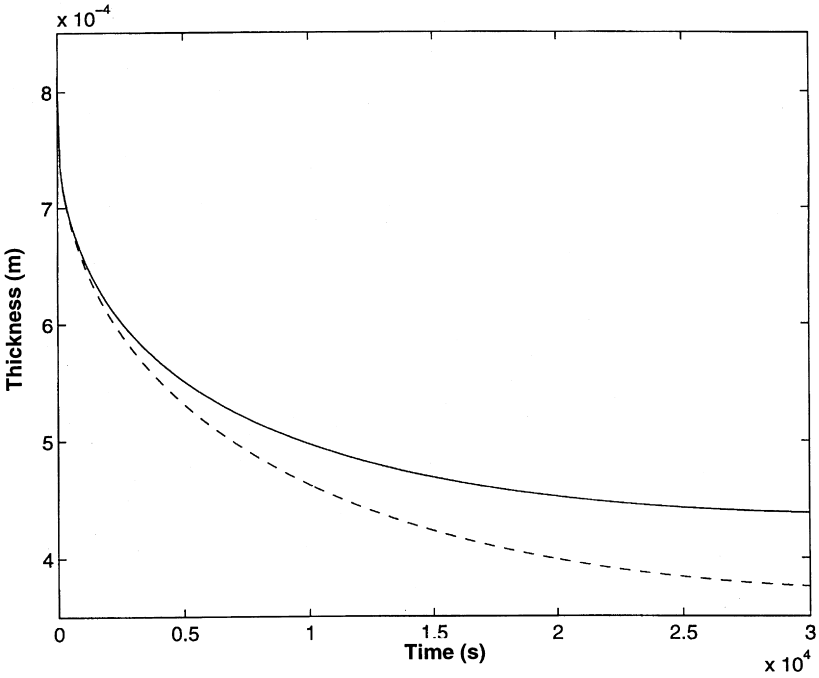

Fig. 2. Model predictions of positions of the air–polymer (—) and the rubbery–glassy (- - -) interfaces as functions of drying time ($k_2 = 10^{-8}$ m/s and $n = 1$).

model parameters used in the analysis. The values of the parameters are those calculated or measured for poly(vinyl alcohol) (PVA)–water systems to enable comparisons with the experimental results available from our laboratory for the drying kinetics of semicrystalline PVA films [1]. The values of a_D used were 7.0 and 3.0 in the rubbery and glassy states [26], respectively.

The model predicts the thicknesses of the polymer film and the rubbery portion as functions of drying time as shown in Fig. 2. As the solvent is removed from the polymer, a layer of glassy polymer is formed at the surface. Both

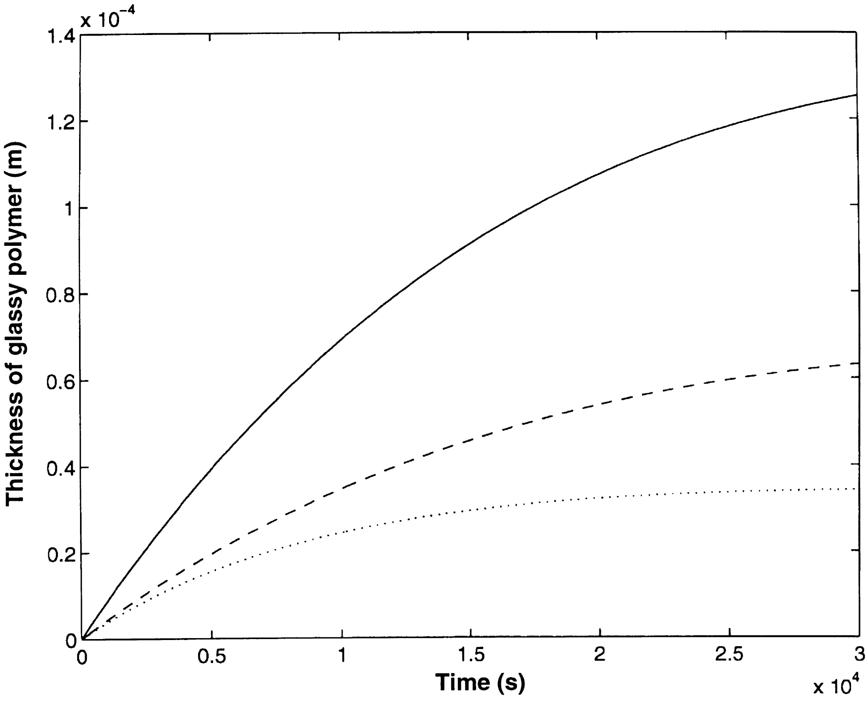

Fig. 3. Model predictions of skin thicknesses for various parameters: (—) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 1$); (- - -) ($k_2 = 1 \times 10^{-8}$ m/s, $n = 1$); and (· · ·) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 2$).

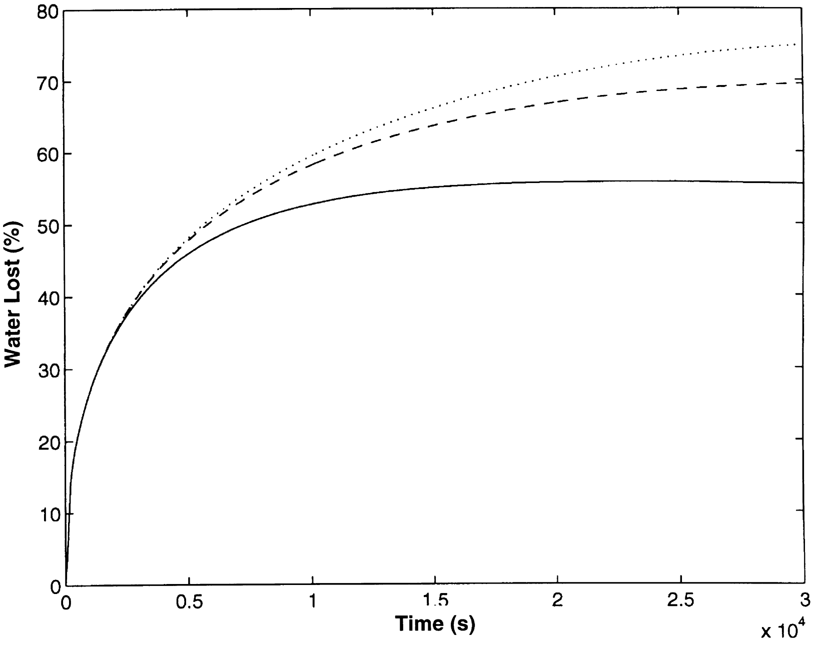

Fig. 4. The effect of skin thickness on the water lost as a function of drying time: (—) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 1$); (- - -) ($k_2 = 1 \times 10^{-8}$ m/s, $n = 1$); and (· · ·) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 2$).

polymer–air and rubbery–glassy interfaces move inward during drying, and the thickness of the skin increases. The difference between the two interface positions at any time is a measure of the skin thickness. Fig. 3 predicts the skin thicknesses as functions of drying time for various values of the parameters k_2 and n. The values of the parameters chosen here are in the range suggested by Joshi and Astarita [25] based on sorption experiments. The skin thicknesses are seen to be larger for higher values of k_2 and lower values of n. The actual values of k_2 and n can be determined for a particular polymer–solvent system from sorption experiments.

The glassy polymer formed on the surface controls the rate of solvent removal from the rubbery polymer core. Fig. 4 shows the effect of skin formation on the drying kinetics. The values of the parameters k_2 and n are the same as those

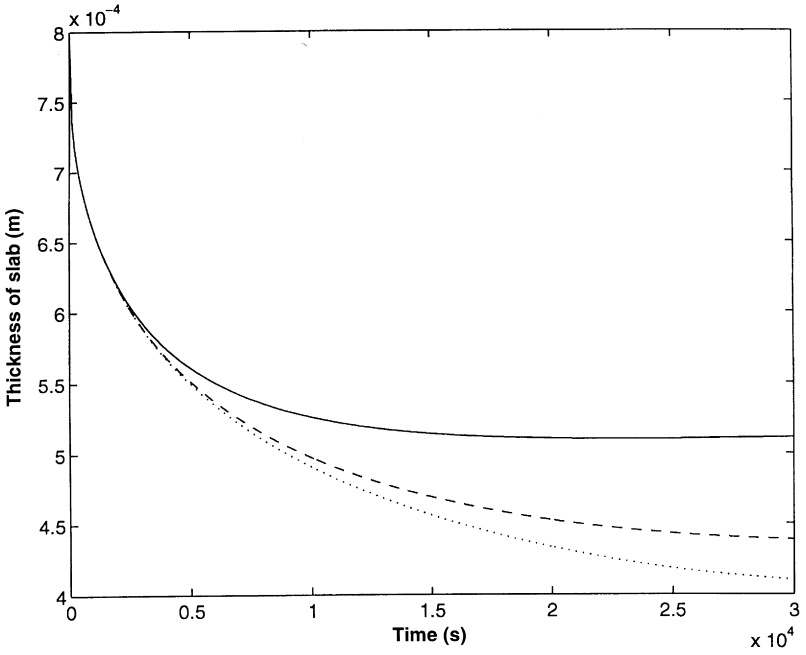

Fig. 5. The effect of skin thickness on the change in polymer film thickness as a function of drying time: (—) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 1$); (- - -) ($k_2 = 1 \times 10^{-8}$ m/s, $n = 1$); and (· · ·) ($k_2 = 2 \times 10^{-8}$ m/s, $n = 2$).

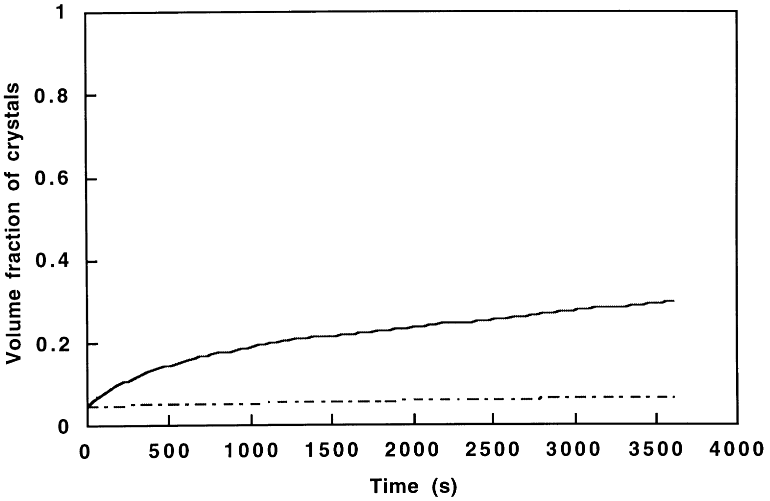

Fig. 6. The effect of crystal folding rate on the volume fraction of crystals as a function of drying time: $D_0 = 5 \times 10^{-11}$ m^2/s; (—) $k_1 = 10^{-4}$ s^{-1}; and (- - -) $k_1 = 10^{-5}$ s^{-1}.

in Fig. 3. Of the three lines, the bold line depicts the sample with the largest skin thickness, while the dotted line depicts that with the smallest skin thickness. Initially, the formation of glassy polymer does not affect the drying rate significantly while the glassy layer is still thin and the solvent volume fraction is high. However, skin formation on the surface of the polymer hinders the removal of solvents from the polymer during the later stages of drying. Drying is faster for smaller skin thicknesses. Greater skin thicknesses decrease the drying rate since the diffusional resistance to solvent transport in the glassy state is much higher than in the rubbery state. The model predicts that large values of skin thicknesses lower the drying rates and raise the residual solvent levels in the polymer. The skin formation causes the solvents to be trapped in the polymer core and makes the solvent diffusion through the glassy portion very difficult. Thus, the residual solvent content in the polymer increases when the thickness of the glassy polymer increases. The bold line represents the case where the skin thickness is higher than in the other two cases, and about 50% of the residual water is still trapped within the polymer film.

The model also predicts polymer film thicknesses during drying and explains the effect of skin formation on the movement of the polymer–air interface. Fig. 5 shows the thicknesses of polymer films as functions of drying times at

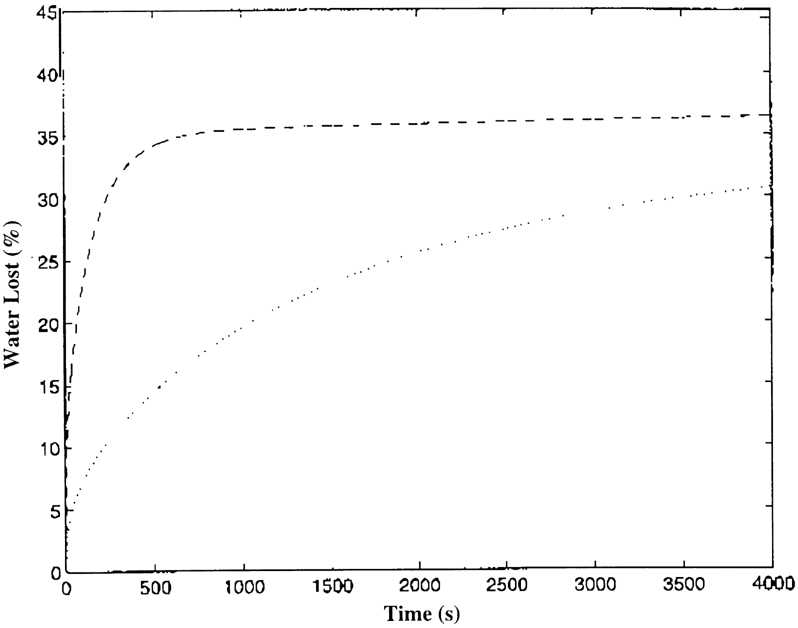

Fig. 7. The effect of crystal folding rate on the water lost as a function of drying time: $D_0 = 10^{-9}$ m^2/s; (- - -) $k_1 = 10^{-5}$ s^{-1}; and (· · ·)$k_1 = 10^{-4}$ s^{-1}.

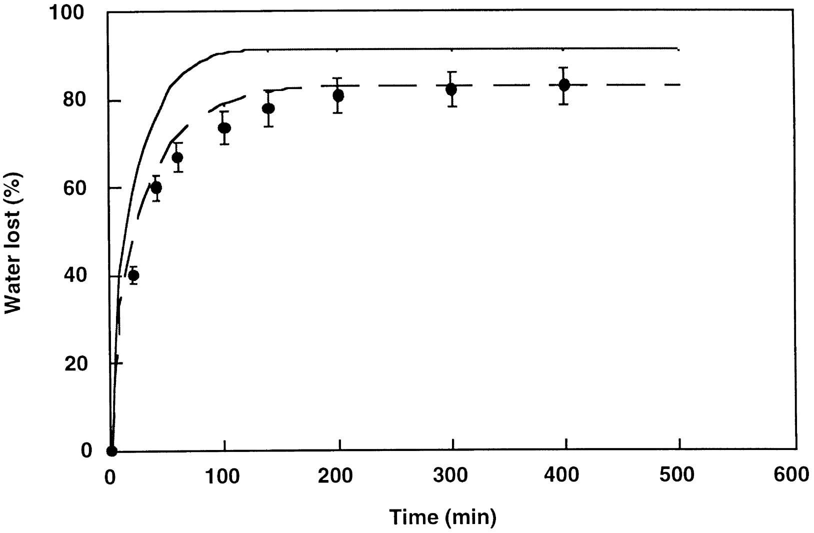

Fig. 8. A comparison of experimental data (●) for poly(vinyl alcohol) films with the DRP model predictions (—) ($k_1 = 10^{-3}\ \mathrm{s}^{-1}$, $D_0 = 10^{-8}\ \mathrm{m}^2/\mathrm{s}$) and the DGP model predictions (- - -) ($k_1 = 10^{-3}\ \mathrm{s}^{-1}$, $D_0 = 10^{-8}\ \mathrm{m}^2/\mathrm{s}$, $k_2 = 10^{-6}$ m/s, $n = 2.5$).

different values of k_2 and n. The model predicts slower changes of sample thicknesses at higher k_2 and lower n where the thickness of skin formed is greater. In addition, skin formation also causes a slowing down of the rate of change of film thicknesses during drying. Clearly, samples with thicker skins exhibit slower rates of change of film thicknesses.

Model predictions of changes in the polymer degree of crystallinity as a function of drying time are presented in Fig. 6. As the crystal folding rate increases, the volume fraction of the crystals in the polymer increases as a function of drying time. The value of the crystal folding rate can be calculated for any polymer–solvent system using the equations provided above. Past work has not accounted for this increase in the degree of crystallinity during drying, which has a significant effect on the drying kinetics. This influence of the polymer degree of crystallinity on polymer drying kinetics is shown in Fig. 7. As the rate of increase of the degree of crystallinity of the polymer increases, the drying rate is found to decrease. This is because the presence of the additional crystallites acts as a diffusional barrier to the transport of solvent molecules. The tortuosity of the polymer increases with increase in the degree of crystallinity. Samples with higher degrees of crystallinity and higher chain folding rates have larger amounts of residual solvent left behind in the polymer, as seen from the figure. Therefore, it is important to be able to predict the crystal folding rates in order to predict the drying kinetics of semicrystalline polymers.

Fig. 8 shows the comparisons of the experimental results with the predictions of the DRP [1] and DGP models for a PVA–water system. The DRP model assumes that the polymer is entirely rubbery, while the DGP model presented in this paper takes into account the rubbery–glassy transition during drying. The experimental results shown here are for a PVA–water system dried in air at room temperature. The drying kinetics were obtained using thermogravimetric analysis (TGA 7, Perkin Elmer, Danbury, CT). Since PVA is a glassy polymer at room temperature (glass transition temperature, $T_g = 85°\mathrm{C}$), it undergoes a rubbery–glassy transition in all cases where the drying temperature is less than 85°C. Therefore, in this case, the predictions of the DGP model agree better with the experimental results. The DRP model predictions of solvent lost are higher than the experimental values because this model does not consider the decrease in diffusion rate in the glassy region that occurs due to skin formation. The model predictions of sample thicknesses and drying rates for the DGP model agree reasonably well with the experimental results. However, the influence of hydrogen bonding has not been taken into account explicitly in the model, which could account for the slight discrepancy between model predictions and experimental results. The model predictions further verify that the drying of the water–PVA system is actually diffusion controlled, which has been proven experimentally [1].

Both models predict the drying rates reasonably well. In some cases, the DRP model might work better if the skin formation is not observed for those solvent–polymer systems. On the other hand, the DGP model for the drying of polymers undergoing rubbery–glassy transitions provides excellent explanations of skin formation during drying and predicts the drying rates more accurately than the other model. The models can be utilized to predict drying rates of various semicrystalline polymer–solvent systems by choosing appropriate parameters depending on the drying characteristics of that system.

4. Conclusions

A mathematical model was developed to predict the skin formation and the isothermal solvent removal rates from semicrystalline polymer films. The model considers the mechanism for solvent removal that was proposed based on experimental studies [1]. The model also takes into account the crystallization kinetics accompanying solvent removal from semicrystalline polymers that was observed experimentally. It is a general model that also takes into account any rubbery–glassy state changes occurring in the polymer film during drying in order to predict rates of skin formation. Crystallization kinetics theories were coupled with free volume diffusion theories in a moving boundary problem to yield predictions of polymer film thickness, skin thickness, degree of crystallinity of the polymer and weight of solvent lost as functions of drying time. The increase in the degree of crystallinity of the polymer during drying was found to significantly decrease the drying rate. The skin thickness was found to increase as a function of time and act as the rate controlling step for solvent removal. The effect of various parameters on the rate of skin formation was investigated. An increase in the skin thickness was found to significantly decrease the rate of solvent removal and rate of change of thickness of the polymer film. The model predictions were compared with experimental results for drying of semicrystalline poly(vinyl alcohol) films, and the model predictions were found to agree well with the experimental results.

Acknowledgements

The authors would like to thank Dow Chemical Company for partial financial support, and Professor Steve Martin of the Department of Materials Science and Engineering at Iowa State University for allowing them to use his thermal analysis equipment. The authors would like to dedicate this paper to the memory of Professor Gianni Astarita.

References

[1] Ngui MO, Mallapragada SK. J Polym Sci, Polym Phys 1998;36:2771.
[2] Errede LA, Tiers GVD, Trend JE, Wright BB. J Polym Sci, Polym Chem 1992;30:1129.
[3] Errede LA, Aus EB, Duerst RW. J Polym Sci, Polym Chem 1992;30:1145.
[4] Errede LA, Newmark RA. J Polym Sci, Polym Chem 1992;30:1155.
[5] Incavo JA, Jain V, Qi JS, Krishnan C. Chromatographia 1996;43:31.
[6] Ngui MO, Mallapragada SK. Polym Prep 1997;38(2):377.
[7] Shah YT, Porter JH. J Appl Polym Sci 1973;17:606.
[8] Yoon JS. Korean J Chem Eng 1995;12:387.
[9] Pan SX, Davis HT, Scriven LB. Tappi J 1995;78:127.
[10] Wilemski G, Boone T, Cheung L, Nelson D, Cook R. Fusion Technol 1995;28:1773.
[11] Vrentas JS, Vrentas CM. J Polym Sci, Polym Phys 1994;32:18.
[12] Cairncross RA, Francis LF, Scriven LB. Drying Tech J 1992;10:893.
[13] Vrentas JS, Vrentas CM. J Appl Polym Sci 1996;60:1049.
[14] Cairncross RA, Jeyadev S, Dunham RF, Evans K, Francis LF, Scriven LB. J Appl Polym Sci 1995;58:1279.
[15] Cairncross RA, Francis LF, Scriven LB. AIChE J 1996;42:55.
[16] Cairncross RA, Durning CJ. AIChE J 1996;42:2415.
[17] Edwards DA. Stud Appl Math 1997;99:49.
[18] Price PB, Wong S, Romdhane IH. AIChE J 1925;1997:43.
[19] Lauritzen JI, Hoffman JD. J Res Nat Bur Stand A: Phys Chem 1960;64:73.
[20] Schultz JM. Polymer Materials Science. Englewood Cliffs, NJ: Prentice Hall.
[21] Fujita H. Fortschr Hochpolym-Forsch 1961;3:1.
[22] Peppas NA, Wu JC, von Meerwall ED. Macromolecules 1994;27:626.
[23] Harland RS, Peppas NA. Colloid Polym Sci 1989;267:219.
[24] Astarita G, Joshi S. J Membr Sci 1978;4:165.
[25] Joshi S, Astarita O. Polymer 1979;20:455.
[26] Mallapragada SK, Peppas NA. AIChE J 1997;43:870.
[27] Narasimhan B, Peppas NA. J Polym Sci, Polym Phys 1996;34:947.