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A STUDY OF THE TRANSPORT PROPERTIES OF SOLVENT DESORPTION FROM EXPERIMENTAL FILMS USING THERMOGRAVIMETRIC ANALYSIS

BARBARA D. BARR-HOWELL

Amoco Chemical Company, Naperville, IL (U.S.A.)

EDWARD J. GORDON

Amoco Performance Products, Inc., Amoco Research Center, Naperville, IL (U.S.A.)

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ABSTRACT

The transport properties of *N*-methyl-2-pyrrolidone (NMP) desorption from solvent-cast, polymeric films were characterized using thermogravimetric analysis. The purpose of this work was to characterize the drying process transport phenomena as an aid for large-scale process development. It was found that the amount of NMP lost during the drying process increased with the drying temperature. The mechanism by which the NMP desorbed was also found to be dependent upon the drying temperature. At temperatures above 175 °C, the drying of two solvent-cast films was characterized by super case-II transport of the NMP. Below 175 °C, the drying was characterized by Fickian, anomalous, case-II transport. Since void formation is frequently associated with Super Case-II transport, these results indicated that accurate temperature control is required during drying to prevent void formation. The results from large-scale drying studies on the experimental films were consistent with the results from this work.

INTRODUCTION

Many commercial polymeric films or polymer films on substrates are produced by a solvent casting process. Common examples of films made by this method include poly(vinyl acetals) used for coatings and adhesives, cellophane films, and plastisols and latexes. Excellent surface properties and low orientation are characteristics of solvent-cast films. In most cases, controlling the solvent removal (diffusion) is essential to producing a clear defect-free film. Hence an understanding of the transport phenomena that occur during the drying process is important in producing high quality polymeric films. Often this understanding is empirical at best.

In this work, thermogravimetric analysis (TGA) was applied to characterize solvent diffusion from a polymer film. Tong and Ouano used TGA to describe bubble formation as ethyl acetate is desorbed from a poly(methyl methacrylate) film [1]. Their work described the solvent removal process using Fickian diffusion and was concerned primarily with bubble nucleation and growth. Other authors have classified the transport behavior of solvent diffusing from polymeric films into four discrete regimes: Fickian, anomalous, case II, and super case-II diffusion [2–8].

The purpose of this work was to apply TGA to characterize the transport behavior when *N*-methyl-2-pyrrolidone (NMP) is desorbed from a polymer film. A discussion of diffusion theory, experimental conditions, and results follows below. Finally, the results from this study are related to large-scale drying experiments.

THEORY OF DIFFUSION

Dynamic diffusion studies can be used to characterize the mechanism by which solvent is released during the drying process. The loss of solvent can occur by one of several different methods: Fickian diffusion, case-II transport, anomalous transport, and super case-II transport.

The most well understood mechanism for solvent sorption is Fickian diffusion. This type of diffusion can be characterized readily by a linear relationship between the initial weight loss of solvent and the square root of time. Polymer/penetrant systems are said to be Fickian in nature if both Fick's first and second laws are obeyed [2]. The first law defines the rate of penetrant transfer through a unit area, F, as being proportional to the concentration gradient $\partial c/\partial x$ normal to the surface where D is defined as the diffusion coefficient. This is expressed mathematically as

$$F = -D\frac{\partial c}{\partial x} \tag{1}$$

Fick's second law is the partial derivative of his first law with respect to time and is expressed as

$$\frac{\partial c}{\partial t} = \frac{-\partial F}{\partial t} = \frac{\partial}{\partial t}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

If the diffusion coefficient D is independent of both concentration and time, the diffusion is said to be Fickian case-I diffusion and the integrated form of the equation becomes

$$\frac{M_t}{M_\infty} = \frac{4}{\pi}\left(\frac{Dt}{d^2}\right)^{1/2} \tag{3}$$

where M_t is the solvent loss at time t, M_∞ is the solvent loss as time approached infinity, D is the diffusion coefficient, and d is the sample thickness. Fickian diffusion can occur in both the glassy and rubbery states of a polymer system. However, Fickian diffusion is generally observed only in glassy systems where the penetrants are either simple gases or solvents with small molecular diameters [3].

Case-II transport occurs when sorption is completely controlled by stress-induced relaxation kinetics which take place at a sharp boundary separating the swollen core of a sample from its glassy boundary. Ideally, this sharp boundary moves at a constant rate and the transport process can be characterized by initial weight losses which are proportional to time. Several parameters are known to effect the relaxations necessary for this type of transport, including polymer orientation, molecular weight, molecular weight distribution, penetrant activity, and the penetrant's physiochemical properties. The mathematical model which describes case-II transport is given by [4]

$$1-\frac{M_t}{M_\infty}=1-\frac{k_0}{C_0}\frac{t^n}{d} \tag{4}$$

where n is equal to unity for thin films, d is the film thickness, c_0 is the initial concentration of the penetrant, and k_0 is the relaxation constant.

A vast majority of polymer/penetrant systems do not follow either Fickian diffusion or case-II transport kinetics but instead are characterized by a combination of the two transport processes. For this type of diffusion, known as anomalous diffusion, the transport kinetics are often controlled by the simple superposition of Fickian diffusion and case-II transport. This is expressed mathematically as

$$M_t = M_\mathrm{I} + M_\mathrm{II} = k_1 t^{1/2} + k_2 t \tag{5}$$

where the contributions from Fickian diffusion and case-II transport to the total weight loss of a sample are given by M_I and M_II respectively [5–7]. Berens and Hopfenberg [8] developed a working model of anomalous transport which is given by

$$1-\frac{M_t}{M_\infty}=\phi_\mathrm{F}\frac{6}{\pi^2}\sum_{n=1}^{\infty} 1/n^2 \exp(-4\pi^2 n^2 Dt/d^2)+\phi_\mathrm{R}\exp(-kt) \tag{6}$$

where ϕ_F and ϕ_R are the fractions of sorption contributed by Fickian diffusion and the relaxation process respectively, D is the diffusion coefficient for the Fickian portion of the transport, d is the characteristic dimension of the sample, and k is the first-order relaxation constant.

Finally, diffusion can be classified as super case-II transport which is highly dependent on both the temperature and penetrant concentration at which diffusion occurs and also on the activity of the penetrant in the polymer. The presence of super case-II kinetics has generally been observed after a concentration profile has been established across the film. This concentration profile allows the acceleration of solvent loss within the polymer film and is frequently accompanied by a decrease in penetrant

TABLE 1

Analysis of diffusional behavior using eqn. (7)

Exponent n	Type of diffusion
0.5	Fickian diffusion
$0.5 < n < 1.0$	Anomalous diffusion
1.0	Case-II transport
>1.0	Super case-II transport

solubility. This decrease in solubility coupled with the accelerated solvent loss can result in the formation of voids during desorption [9].

The characterization of the diffusion type for polymer/penetrant systems can be achieved using a convenient method which employs fitting the sorption data to eqn. (7):

$$M_t/M_\infty = kt^n \tag{7}$$

where M_t is defined as the mass of solvent loss at time t, M_∞ is the mass of solvent loss as time approaches infinity, k is a constant dependent on the structural characteristics of the network, and n is the exponent which indicates the various types of diffusion. Equation (7) is valid only in the analysis of the first 60% of the final mass of solvent loss and cannot be used to analyze inflections or overshoots.

Once the n value for a polymer/penetrant system has been obtained, the diffusion type can be determined using the information given in Table 1.

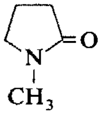
EXPERIMENTAL

Thin films, approximately 0.0035 in thick, were prepared by casting polymeric solutions onto a substrate. A proprietary polymer was dissolved in *N*-methyl-2-pyrrolidone (NMP) to a concentration of approximately 50 wt.% polymer in solvent. The physical properties of NMP are given in Table 1. This solution was cast onto Kapton® film 0.002 in thick, using a knife-over-plate filming apparatus. The case film was covered with another sheet of Kapton® film to prevent solvent loss and contamination and stored in a cold room at 0 °F until the diffusion experiments were run.

The dynamic diffusion studies were carried out isothermally using an Omnitherm TGA 1000 interfaced to an Omnitherm 35050 computer controller. The computer collected the weight loss data as a function of time on a continuous basis. The experiments were run at several different isothermal temperatures ranging from 150 to 275 °C under both nitrogen and air purges. Each test was run until no appreciable change in weight loss was observed. Uniform sample size was maintained in the diffusion studies by cutting small circles, 0.25 in in diameter, from the polymer films.

TABLE 2

Physical properties of *N*-methyl-2-pyrrolidone [a]

Chemical structure	
Empirical formula	C_5H_9NO
Molecular weight	99.1
Boiling point	202 °C (345 °F) at 760 mmHg 150 °C (302 °F) at 162 mmHg 100 °C (212 °F) at 24 mmHg
Specific gravity, D^{23C}	1.027

[a] Source: GAF Corporation, M-Pyrol® (*N*-methyl-2-pyrrolidone) Handbook.

RESULTS AND DISCUSSION

Table 2 shows that the equilibrium weight loss of solvent increased with temperature. The equilibrium weight loss is defined as the weight loss at a given temperature as the drying time approaches infinity. The majority of the weight loss was attributed to solvent desorption and was not affected by the test atmosphere (nitrogen vs. air). Equilibrium weight losses were also found to increase with temperature when the films were dried in large hot-air ovens.

As explained earlier in this paper, the characterization of the diffusion type can be achieved by fitting the sorption data to eqn. (7), $M_t/M_\infty = kt^n$. Since M_∞ was found to increase with temperature, the M_∞ from the highest temperature studied for each set was selected to normalize each set of data. This allowed all data to be analyzed in a uniform manner. Figures 1 and 2 give the normalized weight loss curves for the film run under nitrogen and air. In general, these results showed that the initial weight losses occurred

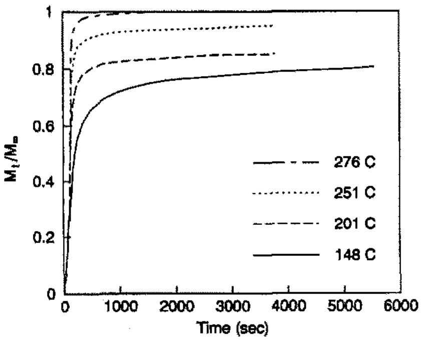


Fig. 1. Isothermal weight loss in nitrogen.

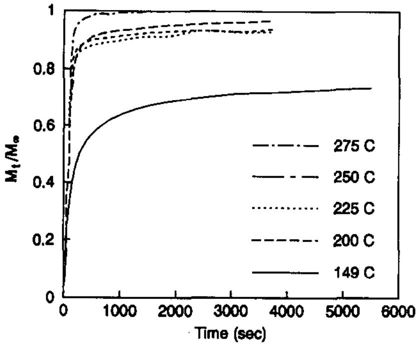


Fig. 2. Isothermal weight loss in air.

TABLE 3

Equilibrium weight losses for samples run under nitrogen

Temperature (°C)	Equilibrium weight loss (%)
148	22.6
201	23.9
251	26.7
276	28.2

TABLE 4

Equilibrium weight loss for samples run under air

Temperature (°C)	Equilibrium weight loss (%)
149	20.2
200	26.4
225	25.3
250	25.6
275	27.4

TABLE 5

Diffusion types for samples run under nitrogen

Temperature (°C)	n	k (s^{-1})	Diffusion type
148	0.87	5.16×10^{-3}	Anomalous
201	1.36	6.94×10^{-4}	Super case-II transport
251	1.36	6.4×10^{-4}	Super case-II transport
276	1.43	4.99×10^{-4}	Super case-II transport

TABLE 6

Diffusion types for samples run under air

Temperature (°C)	(n)	k (s^{-1})	Diffusion type
149	0.54	2.09×10^{-2}	Fickian
200	1.32	8.43×10^{-4}	Super case-II transport
225	1.60	2.14×10^{-4}	Super case-II transport
250	1.61	2.06×10^{-4}	Super case-II transport
275	1.49	3.27×10^{-4}	Super case-II transport

quickly, within the first 10 min, followed by a leveling off of the solvent loss after approximately 1 h.

The initial 60% of the weight loss data from each of the diffusion studies were analyzed using eqn. (7) and the results are given in Tables 3 and 4. These results show a change in the diffusion kinetics as the temperature of the diffusion studies was increased. Under both nitrogen and air, super case-II transport was observed at temperatures of 175 °C and above (see Tables 5 and 6).

Since void formation is frequently associated with super case-II transport, the results indicated that the initial drying temperatures could be responsible for the void formation during the drying process. Voids are formed by rapid volatilization of the solvent within the films. These expanded pockets or voids increase the film surface area and serve as a pathway for the solvent to diffuse through the film. Both effects increase the rate of solvent desorption from the film. Unfortunately, the use of thermogravimetric analysis to study diffusion does not allow for the direct detection of void formation.

These results were consistent with drying studies conducted on samples dried in hot-air ovens. When the initial drying temperature exceeded 190 °C, voids formed in the samples. The large-scale drying studies also supported the concept that void formation during drying could be avoided if lower initial drying temperatures were used.

CONCLUSIONS

This study found that the technique of thermogravimetric analysis could be applied to the study of solvent desorption from experimental films. The diffusion results from TGA suggested that void formation during drying was due to super case-II transport at high temperatures and that void formation could be avoided by using lower initial drying temperatures. Results from large-scale drying studies supported these findings.

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