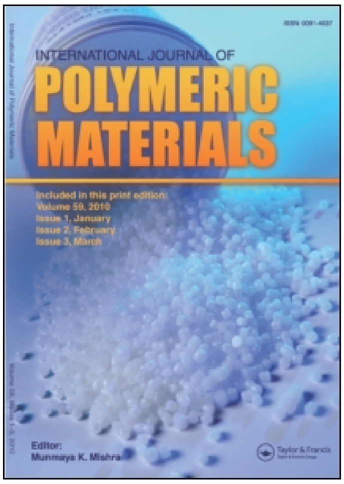

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Mathematical Model for Solvent Diffusion in Polymer-Solvent Mixtures

Mark G. Dodin[a]
[a] Energy Research Corporation, Danbury, Connecticut

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Mathematical Model for Solvent Diffusion in Polymer-Solvent Mixtures

MARK G. DODIN

Energy Research Corporation, 3 Great Pasture Road,
Danbury, Connecticut 06810

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The solvent diffusion process with a variable diffusion coefficient was examined for the case of solvent desorption from polymer films. The thermoactivation theory of diffusion in polymers served as the basis for the formulation of an integral equation in which the parameters: time, temperature and concentration of residual solvent were correlated with physical constants of the system. The equation is valid in a wide range of temperatures for binary and ternary systems. The limit of applicability, the physical meaning of the constants were examined as well as different modifications of the equation. The specific nature of the interaction between polymer and solvent is manifested in a dependence of activation energy of diffusion on the quantity of residual solvent, however the physical meaning of the integral equation remains unchanged.

The integral equation was also applied for the machine casting or plastic film from solution, and therefore can be used for guiding the production of films with specific physical and mechanical properties.

INTRODUCTION

The process of polymer film formation from solution has found application in different branches of industry. Solutions can be prepared using various solvents and solvent mixtures. Certain quantities of residual solvent are present in the film after completion of the preparation procedure and the physical and mechanical properties of films are dependent on properties and quantities of those residual solvents.[1-6] Therefore, it is desirable to propose a relationship which correlates preparation parameters with the quantity of residual solvent in the film in order to better control production processes.

The formation of polymer films from solution consists of two stages.[3] The first stage is evaporation of the solvent from the free liquid surface. During this stage, the principal movement of solvent to the evaporation surface is carried out by convection. The last stage is evaporation from the solid surface of the polymer and transference of the solvent through the polymer by molecular diffusion. There is a period between these two stages when both binds of transport occur simultaneously. We shall restrict mathematical description to the final period. Molecular diffusion is slower than evaporation and therefore its rate limits the overall process. Analytical solutions to the diffusion equation under known conditions can sometimes be used for calculating the rate of diffusion. Since solvent diffusion through a polymer involves a change of the diffusion coefficient with the quantity of the residual solvent in the film, the diffusion equation does not have a reasonable analytical solution. Although some approximate equations have been obtained.[1-3]

In this article we attempt to formulate an integral equation for the description of solvent diffusion with a variable diffusion coefficient using thermoactivation theory of diffusion in polymers as our basis. If the achievement of the definite quantity of residual solvent in a polymer is considered as a certain stage of the diffusion process, then the following correlation would seem to be valid:

$$t \sim 1/D \sim e^{Q/RT} \qquad (1)$$

where

t = time to obtain a definite quantity of residual solvent.

Q = effective activation energy of diffusion which depends on the quantity of residual solvent.

T = formation temperature, °K.

D = diffusion coefficient.

The concentration of the residual solvent in films was determined in order to examine the utility of this correlation (1).

EXPERIMENTAL PROCEDURE

Binary systems tested included:

a) Polycarbonate + methylene chloride with different molecular weights of polymer and various initial concentrations of polymer in solution.

b) Polycarbonate + 1.1.2.2 tetrachloroethane.

c) Polysulfone + methylene chloride.

d) Polyamide + ethyl alcohol (96%).

Ternary systems were tested with diverse thicknesses of films:

a) Polycarbonate + methylene chloride + tetrachloroethane with different correlation of components.

b) Polycarbonate + methylene chloride + toluene.

c) Polycarbonate + tetrachloroethane + toluene.

d) Methylolpolyamide + ethyl alcohol + acetone.

The films were formed either by a machine with a continuously moving belt or on a metal sheet in a drying oven.[4-6] The temperatures of film formation were varied below and above boiling point of solvents. The air temperature was taken as temperature in the machine chamber. The temperature in the drying oven was constant to ± 1°C. Reagents as received were clean and were not subjected to additional purification. The concentration of residual solvent was calculated by the equation:

$$C = \frac{P_w - P_d}{P_w} \times 100\% \tag{2}$$

where

C = concentration of residual solvent in film.

P_w = wet weight of film.

P_d = dry weight of film after drying to constant weight.

Averages for three to five specimens were used for each polymer film preparation.

RESULTS AND DISCUSSION

The experimental data (Figures 1–4) is described by the exponential equation which follows from the correlation (1)

$$t = B \exp\left[\frac{Q(c)}{R}\left(\frac{1}{T} - \frac{1}{T_p}\right)\right] \tag{3}$$

where

B = constant

T_p = the temperature corresponding to the intersection in Figure 3.

The influence of the concentration of the residual solvent for polycarbonate and polysulfone has been described by the equation:

$$Q = Q_0 - \alpha C \tag{4}$$

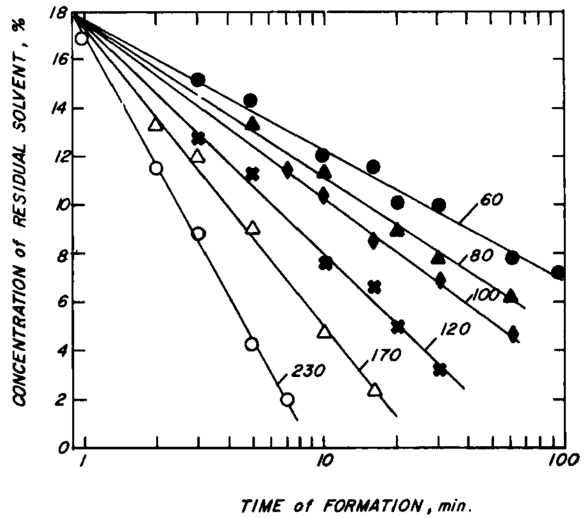

FIGURE 1 Dependence of residual solvent concentration upon time for polycarbonate +methylene chloride+toluene. Numerals near straight lines—temperatures of formation in °C.

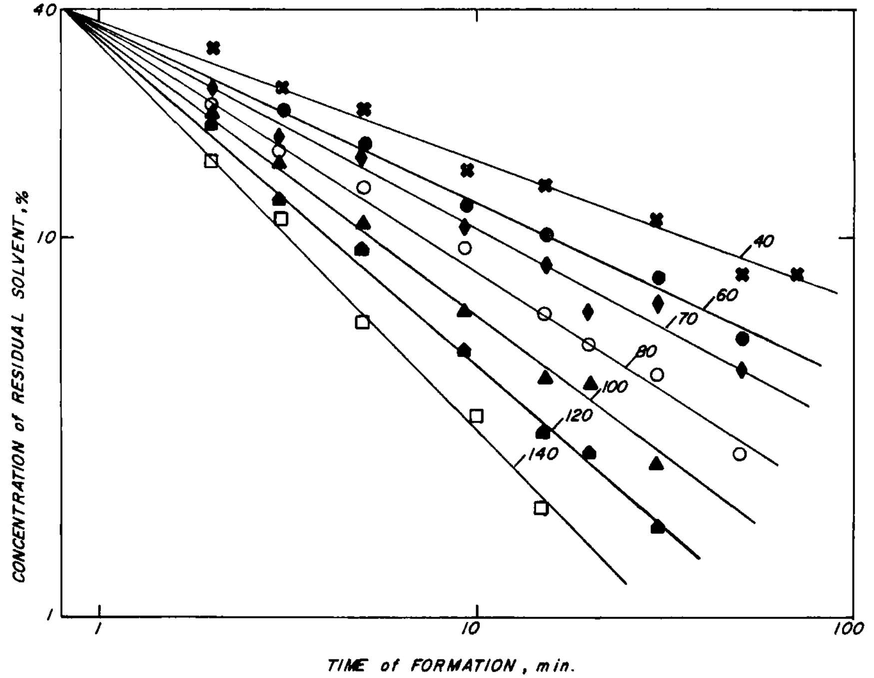

FIGURE 2 Dependence of residual solvent concentration in film upon time for polyamide 548+ethyl alcohol. Numerals near straight lines—temperatures of formation in °C.

A different variation of Eq. (4) has also been explored for polyamides.

$$Q = Q_0 - \alpha \log C \tag{5}$$

where

Q_0 = activation energy of diffusion when the quantity of the solvent is equal to zero.

α = constant of the polymer-solvent system.

C = concentration of residual solvent in film, %.

The form of Eq. (3) suggests that diffusion of the solvent through the polymer is realized by thermal fluctuations, which create the conditions for molecules to overcome a potential barrier, Q. The specific nature of interaction between polymer and solvent are manifested in a dependence of $Q(c)$.

Equation (3) is valid for all polymers tested over a wide range of temperatures which spans the normal solvent boiling point. However the constants of Eq. (3) have different values for various solvent conditions. The temperature ranges where the constants of Eq. (3) have a steady quantity are limited

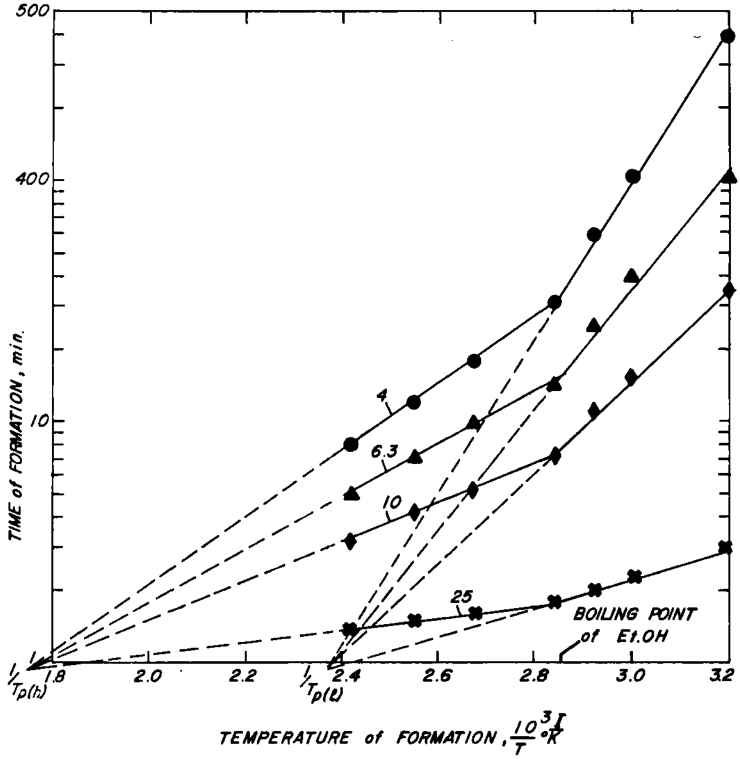

FIGURE 3 Dependence of formation time upon temperature for polyamide 548+ethyl alcohol. Numerals near straight lines—concentration of residual solvent, %.

to the boiling points of solvents in the mixture. Therefore, binary systems have two temperature ranges: high and low; ternary systems have three temperature ranges: high, middle and low. The constants of Eq. (3) for tested systems are presented in Tables I and II.

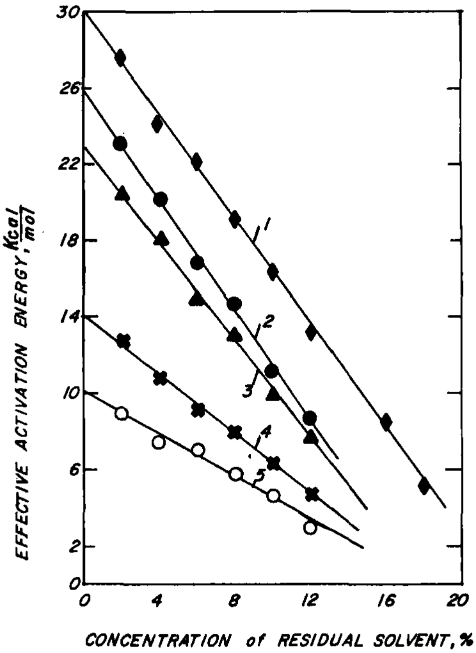

FIGURE 4 Dependence of effective activation energy upon concentration of residual solvent:

1. Polycarbonate + tetrachloroethane (T < 145°C)
2. Polysulfone + methylene chloride (T < 40°C)
3. Polycarbonate + methylene chloride (T < 40°C)
4. Polysulfone + methylene chloride (T > 40°C)
5. Polycarbonate + methylene chloride (T > 40°C)

The constant Q_0 does not depend on the initial concentration of the polymer in solution, its molecular weight, the thickness of the film, or the design of the machine, but it does change with the composition of the system. The activation energy of diffusion of methylene chloride through polysulfone is greater than through polycarbonate whose intermolecular interaction is weaker than that of polysulfone. A solvent which has a higher molecular weight and greater polarity has a greater activation energy of diffusion ($Q_0 = 20$ kcal/mol, for tetrachloroethane and $Q_0 = 10$ kcal/mol, for methylene chloride), if they diffuse through the same polymer.

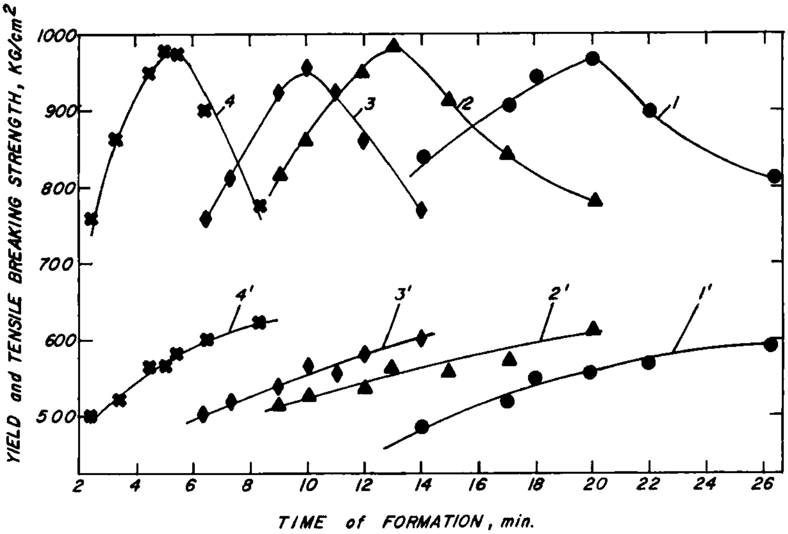

FIGURE 5 Dependence of tensile breaking strength (1–4) and yield strength (1′–4′) upon time of formation under 50 (1; 1′) 60 (2; 2′), 70 (3; 3′) and 100°C (4; 4′).

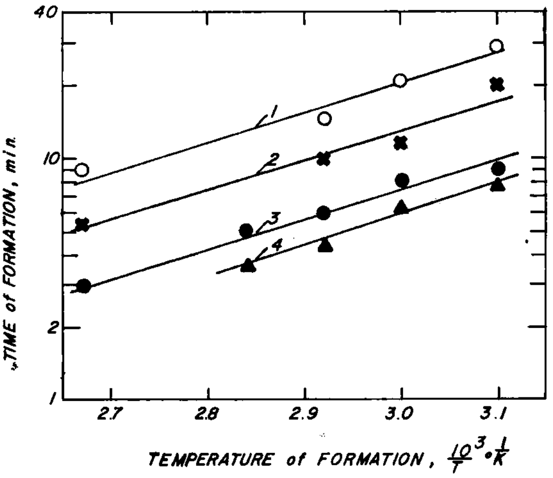

FIGURE 6 Dependence of formation time upon temperature (corresponding to maximum breaking strength) for polycarbonate+methylene chloride.

1. δ = 30 mic; 2–20 mic; 3–15 mic; 4–10 mic.

TABLE I

Constants of Eq. (3) for temperatures of experiment above the boiling points of the solvents

Composition of the solution	Initial concentration of the polymer in solution, %	Q_0, kcal/mol.	α kcal/mol.%	B sec.	T_p °C	C_p %
1. Polycarbonate+methylene chloride (M.W. = 55,000)	11.5	9.5	0.55	70	215	18
2. Polycarbonate+methylene chloride (M.W. = 55,000)	15	10.5	0.56	27	240	18
3. Polycarbonate+methylene chloride (M.W. = 55,000)	18	10	0.55	24	254	18
4. Polycarbonate+methylene chloride (M.W. = 126,000)	8	10	0.55	30	237	18
5. Polycarbonate+tetrachloroethane (M.W. = 126,000)	8	20	0.91	200	232	22
6. Polysulfone+methylene chloride	15	14	0.78	46	228	18
7. Polycarbonate+tetrachloroethane+methylene chloride (70 : 30 w.p.)	8	17	0.77	357	233	22
8. Polycarbonate+tetrachloroethane+methylene chloride (50 : 50 w.p.)	8	14	0.61	476	227	23
9. Polycarbonate+tetrachloroethane+methylene chloride (25 : 75 w.p.)	8	13	0.56	366	240	23
10. Polycarbonate+toluene+methylene chloride (30 : 70 w.p.)	8	9	0.5	43	403	18
11. Polycarbonate+toluene+tetrachloroethane (25 : 75 w.p.)	8	15	0.67	240	237	22
12. Polyamide 548+ethyl alcohol[a]	21	11	6.88	50	292	40
13. Methylolpolyamide+ethyl alcohol+acetone (50 : 50 w.p.; δ = 35 mic)[a]	25	11	11	200	170	10
14. Methylolpolyamide+ethyl alcohol+acetone (50 : 50 w.p.; δ = 100 mic)[a]	25	11	11	755	170	10

[a] Eq. (5) is valid for these systems.

TABLE II

Constants of Eq. (3) for temperatures of experiment below the boiling point of one of the solvents

Composition of the solution	Q_0 kcal/mol.	α kcal/mol.%	B sec.	T_p °C	Temperature range °C
1. Polycarbonate+methylene chloride	23	1.28	27	105	<40
2. Polycarbonate+tetrachloroethane	30	1.33	200	205	<145
3. Polysulfone+methylene chloride	26	1.44	46	100	<40
4. Polyamide 548+ethyl alcohol	25	15.6	50	150	<78
5. Polycarbonate+tetrachloroethane+methylene chloride (70 : 30)	26	1.18	357	195	$145 > t > 40$
6. Polycarbonate+tetrachloroethane+methylene chloride (50 : 50)	23	1.0	476	190	$145 > t > 40$
7. Polycarbonate+tetrachloroethane+methylene chloride (25 : 75)	20	0.87	366	205	$145 > t > 40$
8. Polycarbonate+methylene chloride+toluene	16	0.89	43	235	$110 > t > 40$
9. Methylolpolyamide+ethyl alcohol+acetone ($\delta = 35$ mic)	21	21	200	120	$78 > t > 56$
10. Methylolpolyamide+ethyl alcohol+acetone ($\delta = 100$ mic)	21	21	755	120	$78 > t > 56$

Q_0 changes if the composition of solvents in the system varies. It is proportional to the concentration of components in the mixture of solvents multiplied by the activation energy of diffusion of each solvent; at high temperatures, Eq. (3) becomes

$$t = B\exp\left[\frac{(Q_1P_1+Q_2P_2)-\alpha C}{R}\left(\frac{1}{T}-\frac{1}{T_p}\right)\right] \tag{6}$$

where

Q_1 and Q_2 = activation energies of diffusion of pure solvents which make up the mixture.

P_1 and P_2 = volume fractions in the mixed solvent.

The activation energy of diffusion is greater at a lower temperature range and, in addition, Q_0 increases by an amount approximately equal to the heat of evaporation of the solvent whose boiling-point lies between the two temperature ranges. Therefore the value of the energy jump is related to the nature of the solvent. Q_0 is determined by polymer-solvent system.

α, as is Q_0, is defined by the polymer-solvent system and their values change similarly by the variation of components in the system.

T_p does not depend on the conditions of film production, the nature of the solvent, or the composition of the mixture for dissolution. For some systems at higher temperature ranges, the value of T_p is about the same as melting point of the polymer used in the solution. For other systems which form stable complexes between polymer and solvent, the value T_p is displaced at higher temperatures (near the polymer's temperature of decomposition), e.g. (a) all polyamides, (b) polycarbonate + methylene chloride + toluene.

Constant T_p at middle and low temperature ranges does not depend on the composition of the solution and is practically the same for solutions of different polymers in methylene chlorides. T_p is probably near the temperature of decomposition of a solvent whose boiling point is at the upper end of the temperature range.

For systems which form stable complexes, the constant T_p in middle and low temperature ranges (for three and binary systems accordingly) is near the melting point of polymers in the system.

In this way the melting point and decomposition temperature of polymers are at the upper temperature extreme of Eq. (3). The constant T_p depends only on the nature of the polymer (for a given type of polymer-solvent system) and can be determined in independent experiments.

B depends on certain factors such as the nature and initial concentration of the polymer in solution, the thickness of the films, the nature of the solvent, the mixtures, and the design of the casting machine. However, B is one constant which does not vary during transition between the high temperature range and middle temperature range of three-component system and between high and low temperature ranges for binary systems.

The straight lines in Figure 1 intersected at the concentration of a residual solvent approximately equal to 20% (18–23%) for all systems which are described by Eq. (4). The relative constancy of the solvent concentration at the point of an intersection explains the analogous change of constants Q_0 and α according to variation in the composition of the polymer-solvent system. These constants are correlated by Eq. (7) which follows from Eqs. (4) and (5):

$$\text{(a)}\quad Q = Q_0 - \alpha C_{\text{lim}} = 0; \qquad \text{(b)}\quad Q = Q_0 - \alpha \log C_{\text{lim}} = 0 \tag{7}$$

where

C_{lim} = concentration of residual solvent in film at the point of straight lines intersection in Figure 1(a) and Figure 2(b).

Thus, the concentration of solvent in a polymer at the point of intersection (C_{lim}) marks a limit for the use of Eq. (3). Also, Eq. (3) cannot be applied for the time of film formation less than the time at the intersection point, that is, *B*. However, if Eq. (3) can be employed, the time calculated is the whole time of film formation. All time previous to diffusion period of film formation are counted in values of *B*.

Existence of the concentration limit in applicability of Eq. (3) probably relates to a change of the diffusion mechanism at the region of about 20% of residual solvent in a polymer. It is possible to assume that Eq. (3) is valid at the last stage of film formation when solvent bonded with the polymer takes part in the diffusion process. Approximately 20% of the solvent is necessary in order to localize intermolecular interaction in a polymer.[7] Therefore, if the concentration of the solvent in the polymer is higher than 20%, transference of the solvent to the evaporation surface is carried out by self-diffusion of the solvent. The process of self-diffusion proceeds with activation energy which is essentially lower than the value of Q_0 in Eq. (4) or (5) and does not depend on concentration of the solvent in the polymer.[8] Obviously, a change of the diffusion mechanism take place not at the point of C_{lim} but at the region of concentrations near this point and real limit of applicability of Eq. (3) is lower than C_{lim} by 2–3%.

The process of the production of plastic films from solution for industrial production, is often divided into two stages:

1) Film formation with machine drying of 20% of the residual solvent.

2) Additional solvent removal outside of the machine to a definite residual humidity.

The formulas, which follow from Eq. (3) can be applied for the process of additional drying (stage 2), for surface controlled evaporation:

$$t_{a,d,} = B \exp\left[\frac{\alpha(c_b - c)}{R}\left(\frac{1}{T} - \frac{1}{T_p}\right)\right], \quad (B = 1) \qquad (8)$$

This formula is valid, if Eq. (4) is correct for the system,

$$t_{a,d,} = B \exp\left[\frac{\alpha(\log c_b - \log c)}{R}\left(\frac{1}{T} - \frac{1}{T_p}\right)\right], \quad (B = 1) \qquad (8a)$$

This formula is valid, if Eq. (5) is correct for the system, where

$t_{a \cdot d \cdot}$ = time of additional drying.

c_b = concentration of the solvent, when additional drying was begun.

The derived Eq. (3) allows calculation of the quantity of residual solvent in the film, as a function of temperature and time of formation. But another goal of work was to demonstrate that the residual solvent determines the mechanical properties of cast films and Eq. (3) can be used for calculation of the production behavior of films with definite physical and mechanical properties. Therefore, another aspect in applying the integral equation and its modification is discussed below in the example of polycarbonate cast films which were utilized in capacitors.

Polycarbonate films were produced from solution in methylene chloride over a wide range of temperatures and time on a casting machine with a continuously moving belt (6). The results of the determination of the films strength are plotted on the graph in Figure 5 (polycarbonate + methylene chloride, mol. wt. of polycarbonate = 55,000, initial conc. of polymer in sol. = 16.6%, thickness of the film δ = 20 mic). A maximum was observed on the dependence of the ultimate tensile strength with time of the film production at a constant temperature. If the temperature of film production increases, the maximum tensile strength will be reached in less time. The dependence of the relative breaking extension on the time of the film production has the same form as the dependence of the tensile strength. The limit of forced elasticity increases monotonically when the time of the film production increases (Figure 5). The maximum film strength is probably related to the two competing processes given below:

1) The strength of the film increases because of increasing the elasticity of the polymer which results in a rise of molecular orientation and strengthening under stress;

2) The strength of the film decreases as a consequence of an increasing concentration of residual solvent.[7]

Therefore, the maximum strength should correspond to a definite quantity of residual solvent in the cast film. This is confirmed by the data of Table III which contains the results obtained for the quantity of residual solvent in films produced at various temperatures and times of formation which are related to the maximum film strength.

TABLE III

Concentration of the residual solvent in films which were produced under different conditions

Technology		Concentration of the residual solvent, %		
Temperature, °C	Time, sec.	Initial concentration of the polycarbonate in solution, %		
		11.5	15.5	18
60	1080 1110[a]	7.6	—	—
	540 565[a]	—	7.55	—
	540 575[a]	—	—	7.85
	675 700[a]	7.4	—	—
80	380 350[a]	—	7.5	—
	340 360[a]	—	—	7.6
100	240 225[a]	—	7.45	—
	220 250[a]	—	—	7.8
120	270 295[a]	7.75	—	—
	154 150[a]	—	7.8	—

[a] Time of formation which was calculated by employing eqs. (3) and (4).

Table III illustrates that in spite of changing the time and temperature of formation a maximum of film strength was achieved when the quantity of the residual solvent in film was the same (7.63 ± 0.23 %), that is below 18 %. Consequently, Eq. (3) can be employed for calculating temperature and time parameters of the casting process to determine the maximum film strength. For results of such calculations, see also Table III. The experimental data and numbers which were counted up by using Eq. (3) are in agreement.

A novel approach was used to verify the possibility of applying Eq. (3) for determining mechanical properties of cast films. If the development of the maximum film strength is associated with one of the stages of the diffusion process, then the following equation is valid:

$$t = A \exp\left(\frac{Q}{RT}\right) \tag{9}$$

where

t = time to achieve maximum film strength.

A = constant which has a dimension of time.

The temperatures and times which correspond to maximum film strength were taken from Figure 5. In Figure 6, log t is plotted against $1/T$; the points fall on parallel straight lines. The data illustrate the validity of Eq. (9) as well as the independence of Q with the conditions of production. Eq. (9) describes the same diffusion process as that of Eq. (3), and consequently, Q in Eq. (9) must be the same as Q in Eq. (3). The last constant can be calculated by formula (4) for the quantity of the residual solvent corresponding to maximum film strength ($c = 7.63\%$). The comparison of the quantity Q from Eq. (9) and the quantity $Q_0 - \alpha c$ from Eq. (4) shows coincidence with sufficient precision ($Q_0 - \alpha 7.63 = 5.76$ kcal/mol, $Q = 5.55 + 5.71$ kcal/mol). These data also confirm the assertion that the maximum film strength is related to a definite quantity of residual solvent in the film and that Eq. (9) is a special case of Eq. (3). If other characteristic points of strength are taken on the curve in coordinates σ vs. t and are examined for their variability with the temperature of film production, a group of straight lines with different values of Q is obtained which correspond to various amounts of residual solvent in the film. Therefore, in the ideal case it is possible to obtain Eq. (3) from the data on film strength. However, the data which were obtained from film drying results were more precise and reliable. When the quantity of residual solvent does not determine the change of the film strength, Eq. (3) will not be valid. This is true of films which crystallize very slowly. The formulas which were derived above allow determination of the constants of polymer-solvent systems that have well defined properties and calculation of production parameters for cast film with distinct mechanical quality.

This work demonstrates that the coefficients of Eq. (3) (Q_0, α and T_p) do not depend on conditions of production. Only the coefficient B is a function of production conditions (the speed of air flow, the design of the casting machine, initial concentration of polymer in solution and thickness of film). If the constants of a polymer-solvent system are known, the simplest method to find the quantity B is determination of residual solvent concentration in the film at a definite time and temperature of production. One measurement is sufficient to estimate B for use in Eq. (3). Then the equation may be used over a wide range of times, temperatures, and concentrations of residual solvent for the particular system and stated conditions of production.

The equation obtained allows calculation of any component i.e. (t, T, c) if two others are given. It is possible to find the optimum temperature in the chamber of a machine if the casting rate of the machine and film properties are given. Determination of film properties is possible if the parameters of film production are known. It is also possible to calculate the residual solvent concentration in the film which was subjected to step drying.

CONCLUSIONS

- An integral equation was obtained for description of the solvent diffusion with a variable diffusion coefficient in case of film formation from solution.

$$t = B \exp\left[\frac{Q(c)}{R}\left(\frac{1}{T}-\frac{1}{T_p}\right)\right]$$

- Dependence of the activation energy of diffusion on the concentration of solvent in polymer has various form for different classes of polymers: (a) for polycarbonate and polysulfone:

$$Q = Q_0 - \alpha C$$

(b) for polyamides:

$$Q = Q_0 - \alpha \log C$$

- The equation is valid for binary and ternary systems in a wide range of temperatures which include the normal solvents boiling point.
- The temperature ranges where the constants of the integral equation have a steady value are limited to the boiling points of solvents in the polymer-solvent system.
- The limits of application and the physical meaning of the constants in the equation were determined.
- Various modifications of the equation and ways of their utilization were shown.
- Dependence of constants in the equation upon composition of the polymer-solvent system was examined.
- The integral equation was also applied for the machine casting of plastic films from solution and therefore, can be used for guiding the production of films with specific physical and mechanical properties.

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