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Growth Kinetics of Environmental Crazing in Polycarbonate

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A variable radius of curvature strain-bending apparatus was used to investigate the kinetics of surface craze growth in polycarbonate exposed to three different normal alkanes and a series of mixtures. The environmental craze growth was characterized by two solvent-dependent parameters, B , a characteristic strain constant independent of temperature and $A(T)$, a characteristic rate constant which varied with temperature following the Arrhenius-type of relationship, i.e., $A(T) = G_0 \times \exp(-\Delta E_G/RT)$. The constant G_0 was related to the entropy of activation, whereas the parameter ΔE_G was interpreted as an activation energy for the crazing process. It was found that within the range of temperature and strain studied the crazing process is diffusion controlled and the size of the solvent molecule is more important than the compatibility of the two materials. For the mixtures of two crazing agents, non-linear behavior appears most probable, but a linear rule of mixtures may be adequate for estimating the characteristic parameters. Inherent difficulties with the experimental technique and data analysis raise concerns about the suitability of the technique as an analytical tool. In this regard, comments about the usefulness of the strain-bending experiment are offered.

INTRODUCTION

Environmental stress crazing has long been considered as one of the most troublesome practical problems afflicting glassy polymers. The formation of crazes not only changes the physical and mechanical properties, but usually precedes crack propagation and catastrophic failure.^{1,2}

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One of the most widely used techniques in industry for characterizing environmental crazing of commercial polymers has been a constant strain test. An unnotched polymer material is flexed over an elliptical bending form (strain-bending apparatus) and held at constant strain. The specimen together with the bending form is then immersed in a solvent for a certain period of time and at a constant temperature. The minimum strain at which a craze appears after a fixed period of time is recorded and this value is defined as the critical strain required for craze growth. Iannone *et al.*³ adopted this simple constant-strain experiment to study the craze growth kinetics in polycarbonate exposed to *n*-heptane. By using the nucleation and growth rate equations proposed by Nicolais and DiBenedetto,⁴ an activated-state theory was developed to describe the kinetics of craze growth. Furthermore, rather than reporting a static or "equilibrium" value of critical strain, they defined the critical strain by setting a criterion of a maximum allowable craze growth rate. Priori *et al.*⁵ extended these studies to craze growth in polycarbonate in a homologous series of normal hydrocarbons and correlated the kinetic parameters of the model with the properties of the solvents. However, in both studies, the stress-relaxation effect was assumed to be negligible, which seemed to be an unwarranted oversimplification for a constant-strain system. The stress-relaxation effect was taken into account by Nobile,⁶ who proposed a model which appeared to fit experimental data on long term craze growth over a wide range of conditions, but gave questionable values in the limit of zero time. An objective of this investigation is to propose a realistic model that can adequately describe the craze growth kinetics in polycarbonate at constant strain and under long terms of exposure to normal hydrocarbons and their mixtures. A second objective is to determine if data collected using the strain-bending apparatus can be used to obtain fundamental information concerning the mechanism of craze growth.

EXPERIMENTAL

Experiments were conducted on a variable radius of curvature strain-bending apparatus as shown in Figure 1, based on the design

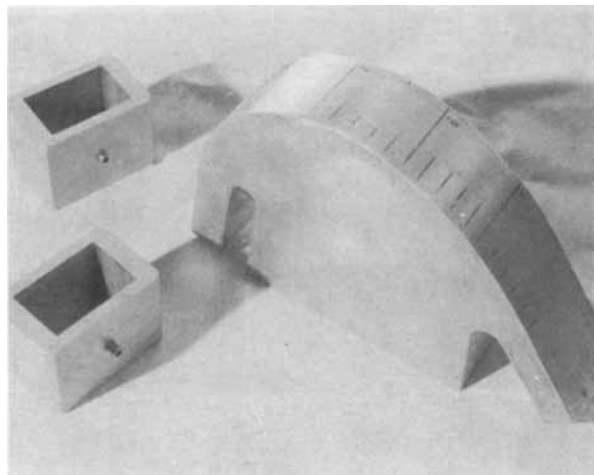


FIGURE 1 The strain-bending apparatus.

of Stolki and Haslett.⁷ The PC (Lexan, G.E. Co.) specimens were cut from an extruded sheet to the final dimensions (250 by 50 by 2.9 mm) without the introduction of a pre-crack. All the specimens were dried in an oven for 3 hours at 100°C and then annealed at 100°C under vacuum for another 3 hours. A test specimen was then flexed over the surface of the apparatus and conformed to the metal form by fixing the clamps at both edges as shown. The strain ϵ in the test specimen at any point is defined as:

$$\epsilon = d/R \quad (1)$$

where d is the half-thickness of the specimen and R is the radius of curvature at the neutral axis of the flexed sample. A millimetric scale was etched on one edge of the apparatus adjacent to the mounting surface, and the strain was measured as a function of position along the surface.⁶

The strain-bending apparatus, with test specimen mounted, was placed in an open glass vessel containing the solvent at the temperature under test. To maintain a constant temperature, a thermostatic water bath (Haake model F3) was used. Runs were made over the temperature range of 293 to 333 K. The test specimen was positioned in such a manner that the crazes forming

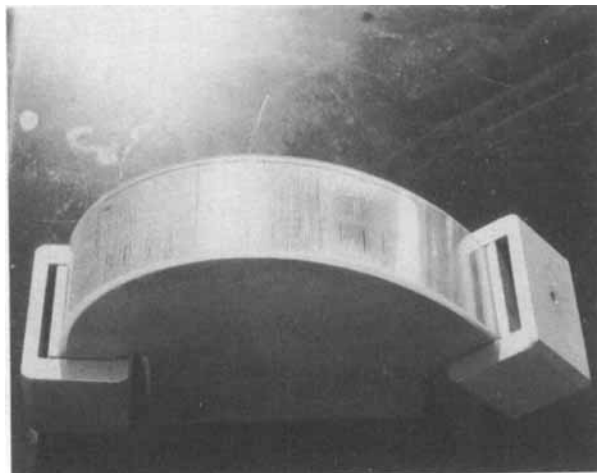


FIGURE 2 Craze growth in a polycarbonate specimen exposed to normal hydrocarbons.

on the surface could be easily seen and photographed at different times in the course of an approximately 2 hour experiment. A typical picture of craze growth in the PC specimen is shown in Figure 2. Negatives of these photographs were then mounted in slide frames and projected on a screen to a magnification of about 10 times of the real dimension of the specimen. Hence, the length of each individual craze could be measured as a function of time and strain for each solvent at a given temperature. About 10 to 25 crazes were measured for each test.

The solvents used as crazing agents were *n*-octane, *n*-decane, *n*-dodecane and a series of octane/dodecane mixtures with different volume proportions. Table I shows the solubility parameters and molecular weights of these solvents.

ANALYSIS

When a polymeric solid is flexed and mounted on the strain-bending apparatus, the outer surface of the specimen, in contact with a solvent, is subjected to maximum tensile strain. Crazes nucleate at

TABLE I
Solubility parameter and molecular weight of hydrocarbons

Environment	δ (MJ/m ³) ^{0.5}	Mol. wt. (g/mole)
<i>n</i> -octane	15.55	114.23
<i>n</i> -decane	15.75	142.29
<i>n</i> -dodecane	16.16	170.34
octane/dodecane mixtures:		
0.80 : 0.20	15.67*	—
0.50 : 0.50	15.84*	—
0.20 : 0.80	16.04*	—
Polycarbonate	20.05	

* Effective solubility parameter of mixtures: $\delta = \sum \phi_i \delta_i$, in which ϕ_i is the volume fraction of each component.¹⁶

sites of stress inhomogeneities and subsequently grow to macroscopic dimensions in a direction perpendicular to the imposed tensile load. If the distance between crazes is sufficient, the nucleation and growth of surface crazes are not affected by the presence of others. Under such conditions, it has been shown that both the nucleation and growth rate of the "non-interfering" crazes are linear^{8,9} and can be represented by a one-dimensional model.¹⁰ Following the work of Zhurhov *et al.*,⁸ Nicolais and DiBenedetto⁴ used a kinetic model to describe the craze growth rates as a linear, one-dimensional process:

$$\frac{dG}{dt} = G_0 \exp\left(\frac{-\Delta E_G}{RT}\right) \sinh\left(\frac{\delta(t)}{\sigma^*}\right) \quad (2)$$

where dG/dt is the craze growth rate, G_0 is a constant, ΔE_G is the activation energy and σ^* is a characteristic stress constant. Eq. (2) can be rationalized by comparing it to Eyring's theory of rate processes:

$$\begin{aligned} K &= P \left(\frac{kT}{h}\right) \exp\left(\frac{-\Delta G}{RT}\right) \\ &= P \left(\frac{kT}{h}\right) \exp\left(\frac{-\Delta H}{RT}\right) \exp\left(\frac{\Delta S}{R}\right) \end{aligned} \quad (3)$$

where K is the rate constant in an activated process; ΔG , ΔH and ΔS are Gibbs free energy, enthalpy and entropy of activation

respectively. The factor P represents the probability that a process occurs once the system is in the activated state, and is usually assumed to be 1. The terms h and k are Plank's constant and Boltzmann's constant respectively. When $\sigma^* \ll \sigma(t)$, the stress biased activation energy of craze growth ($\Delta E_G + \sigma(t)RT/\sigma^*$) can be interpreted as the enthalpy contribution to the process, and the pre-exponential factor G_0 as the entropy contribution.

From previous studies,^{3,5} it has been shown that since $\sigma^* \ll \sigma(t)$, the hyperbolic sine function can be approximated by an exponential and Eq. (2) can be rewritten as:

$$\frac{dG(t)}{dt} \cong \frac{A(T)}{2} \exp\left(\frac{\sigma(t)}{\sigma^*}\right) \quad (4)$$

where

$$A(T) = G_0 \exp\left(-\frac{\Delta E_G}{RT}\right) \quad (5)$$

The quantity A has the dimensions of length per unit time, and may be interpreted as a characteristic growth-rate constant for a given polymer-crazing agent system. In the limit of $t=0$, the relation $\sigma(t) = E_0 \epsilon$ holds for a glassy polymer well below its T_g . Hence, Eq. (4) can be written as:

$$\ln\left(\frac{dG(t)}{dt}\right)_{t=0} = \ln\left(\frac{A(T)}{2}\right) + B\epsilon \quad (6)$$

where

$$B = E_0/\sigma^* \quad (7)$$

The quantity $(1/B)$ has the dimensions of a strain (i.e., dimensionless), and may be interpreted as a characteristic strain constant for a given polymer/solvent system.

From a previous study,⁶ it has been found that the bulk stress relaxation time for PC exposed to a series of normal hydrocarbons from hexane to dodecane is about 3 to 6 hours in the temperature range used in this investigation. Therefore, during a 2 hour experiment, stress-relaxation cannot be neglected. Wu and Brown¹¹ have developed a theory for stress relaxation in a polymeric solid when crazing is the only type of deformation. Their equation for the rate of change of stress with time at constant strain, $-\dot{\sigma}$, is:

$$-\dot{\sigma} = 3(\rho\gamma\alpha k_1 k_2)^{1/3} M \left(\frac{\sigma_0 - \sigma}{M} + \epsilon_0\right)^{2/3} \dot{t} \quad (8)$$

The first term in the bracket characterizes the effects of the number of crazes and their shape, and is considered to be relatively time-independent. The quantity M is a characteristic elastic modulus and is also a constant. The second bracketed quantity represents the total craze strain of the specimen, and the last term is the craze velocity. The craze velocity appears to be more strongly time-dependent than the total craze strain in a constant strain system, so, to a first approximation, Eq. (8) can be written as:

$$-\frac{d\sigma(t)}{dt} \cong Ci = C \frac{dG(t)}{dt} \quad (9)$$

where C is a constant.

By differentiating Eq. (4) and combining the result with (8) and (9), one obtains a second order non-linear differential equation:

$$\frac{d^2G(t)}{dt^2} + \frac{C}{\sigma^*} \left(\frac{dG(t)}{dt} \right)^2 = 0 \quad (10)$$

One can integrate Eq. (10) using the initial conditions $G(t) = 0$ and $dG(t)/dt = y_0$ at $t = 0$ to obtain

$$G(t) = k \ln \frac{y_0}{k} + k \ln \left(t + \frac{k}{y_0} \right) \quad (11)$$

where $k = \sigma^*/C$. A plot of $G(t)$ vs. $\ln(t + k/y_0)$ is a straight line with a slope of k and the intercept: $k \ln(y_0/k)$. Therefore, the initial rate y_0 can be calculated for a constant strain and temperature by properly choosing the value of k/y_0 . Figure 3 is a typical example of the procedure for determining the initial rate at strain $\epsilon = 0.009$ in n -octane at 40°C . The raw data are plotted on a semi-log scale with the value of $k/y_0 = 0$. By adding an increment of k/y_0 to a real time t , all data points are transposed to higher values of time. A straight line can be generated at a specific value of k/y_0 (e.g., $k/y_0 = 332.2$ in Figure 3). More formally, a linear regression analysis can be used to determine the slope $1/k$ and the intercept (k/y_0) . The initial rate of craze growth y_0 can then be calculated for a constant strain and temperature, and values of B , $\ln A(T)$, ΔE_G and G_0 can be estimated from Eq. (5) and (6).

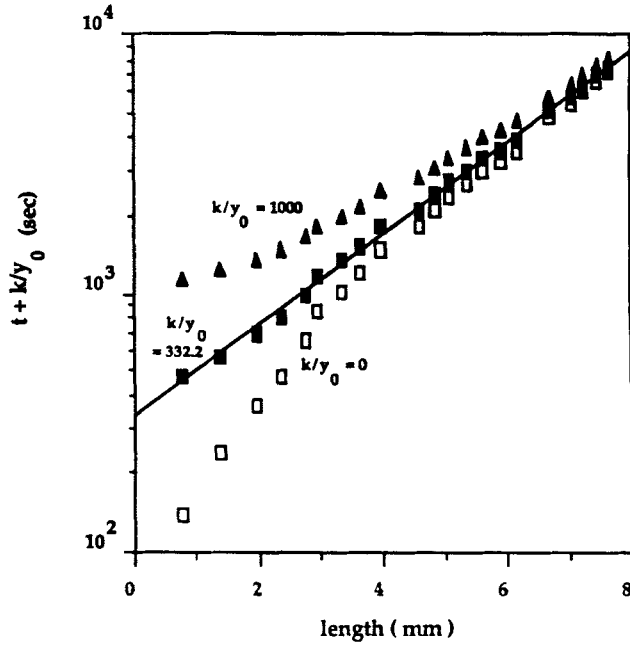


FIGURE 3 Example of initial rate determination procedures.

RESULTS AND DISCUSSION

Typical sets of experimental values for the initial rate of craze growth, $\ln(dG/dt)_{t=0}$, as a function of strain ϵ are illustrated in Figure 4 for polycarbonate in *n*-octane, and in Figure 5 for PC in 50% octane/dodecane mixture. A master curve for each solvent can also be constructed at a reference temperature by recognizing the equivalent effect of strain and temperature on the rate of craze growth.^{5,6} Figures 6 and 7 are the resultant master curves at $T_R = 313$ K for the pure-alkane/polymer and mixture/polymer systems respectively. The parameter B can be obtained from the slope of the master curve and $\ln A(T)$ can be calculated from the intercept for each solvent at the reference temperature. By shifting the master curve to other temperatures, different values of $\ln A(T)$ can be obtained. Therefore, one can use the Arrhenius plot to

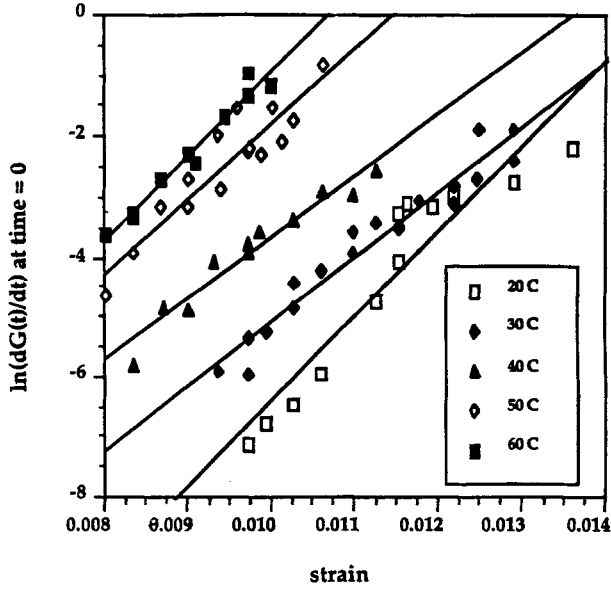


FIGURE 4 Initial rate versus strain in *n*-octane.

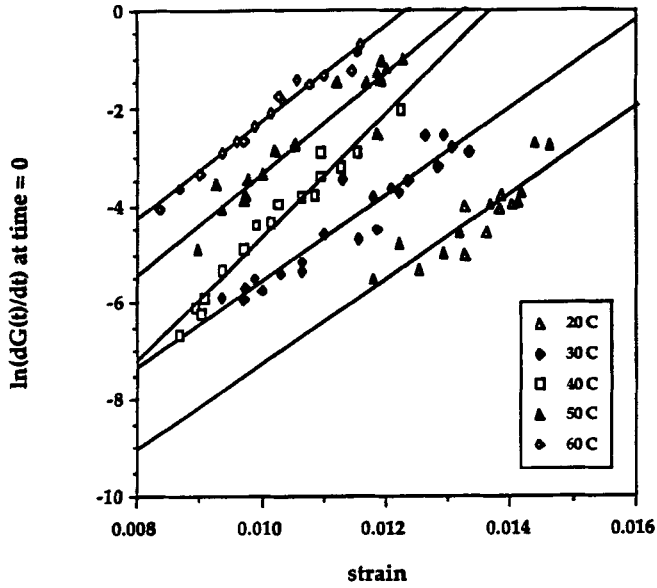


FIGURE 5 Initial rate versus strain in 50% octane/dodecane mixture.

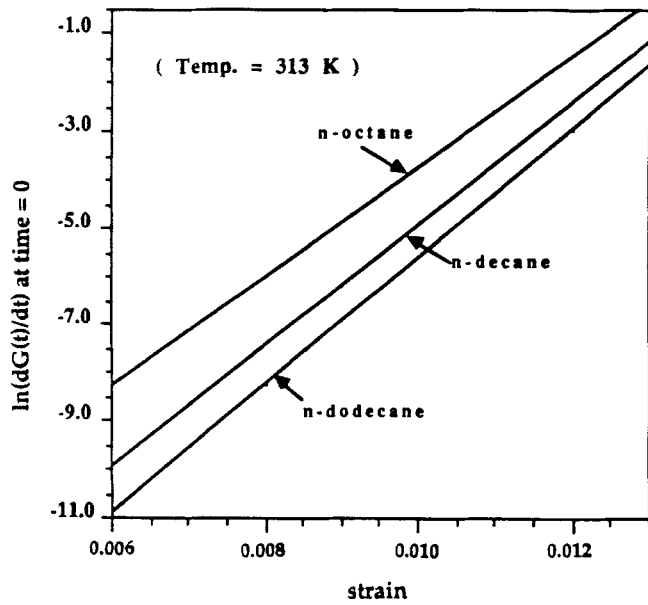


FIGURE 6 Master curves of the pure alkanes.

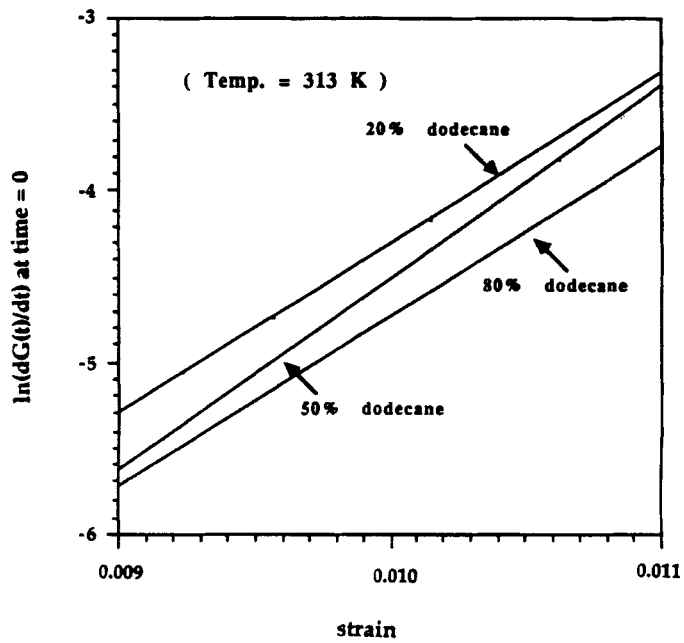


FIGURE 7 Master curves of the octane/dodecane mixtures.

TABLE II
Estimated values of the parameters

Environment	B	ΔE_G (kJ/mole)	$\ln G_0$ (mm/sec)
<i>n</i> -octane	1137	108	27.39
<i>n</i> -decane	1253	91	18.62
<i>n</i> -dodecane	1321	87	15.57
octane/dodecane mixtures:			
0.80 : 0.20	984	102	25.76
0.50 : 0.50	1134	112	27.74
0.20 : 0.80	992	105	26.48

estimate the activation energy ΔE_G as well as the rate constant G_0 . The estimated values of the parameters B , ΔE_G and $\ln G_0$ for each solvent are shown in Table II.

It appears that the parameter B increases slightly with increasing molecular weight of the pure alkane solvents. Also, it is slightly different for the mixture/polymer systems. As can be seen from Eq. (7), the parameter B is a material constant that represents the ratio of elastic modulus of the specimen E_0 to the characteristic stress σ^* . For a glassy polymer well below its glass transition temperature ($T_g = 159^\circ\text{C}$ for polycarbonate), the elastic modulus is almost independent of temperature. The characteristic stress σ^* , on the other hand, is a measure of the sensitivity of the craze growth rate to the applied stress for a given polymer/solvent system. Therefore, the parameter B should be relatively independent of temperature and dependent on the specific crazing solvent studied. The slight variation of B with solvent as shown in Table II can be attributed to a small solvent effect or, as will be discussed later, uncertainty in the calculated value caused by scatter of the experimental data.

The activation energies ΔE_G and the pre-exponential constant $\ln G_0$ for the craze growth also appear to be dependent on the solvents studied. Following the lead of previous research,⁵ we chose to correlate these variables with the square of the differences between the solubility parameters of the polymer and crazing solvent, $(\delta_p - \delta_s)^2$. As shown in Figure 8, ΔE_G decreases as $(\delta_p - \delta_s)^2$ decreases, indicating that as the polymer and crazing solvent become more compatible and closer in size and shape, the activation energy decreases. This suggests that the rate-controlling

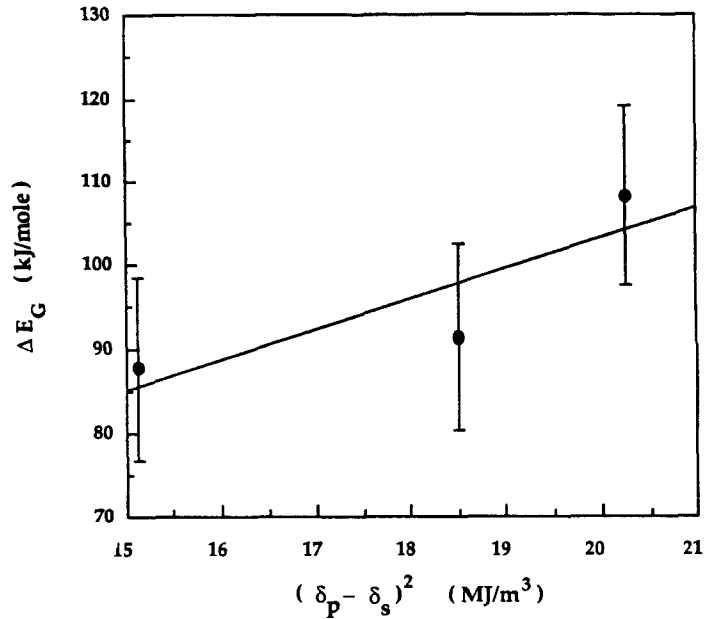


FIGURE 8 Activation energy vs. the difference of the solubility parameters between the polymer and solvent.

process for craze growth is most probably related to the plasticizing ability of the crazing solvents. Similar results have been reported for the activation energy of craze growth in polycarbonate by Priori *et al.*⁵ who used a spectrum of hydrocarbons from *n*-hexane to *n*-dodecane, and by Kirloskar and Donovan¹² who studied craze growth in a series of alcohols from methanol to *n*-pentanol as the crazing solvents.

Figure 9 demonstrates the variation of the pre-exponential constant $\ln G_0$ with the square of the differences between the solubility parameter of the polymer and the pure crazing agent, $(\delta_p - \delta_s)^2$. It can be seen that as the polymer and crazing agent become more compatible and closer in size and shape, $\ln G_0$ also decreases. In other words, the activation entropy decreases with the increasing compatibility of the polymer and crazing agent.

From Eqs. (3) and (5), one can see that the rate parameter $A(T)$ is controlled by both the energy and entropy of activation.

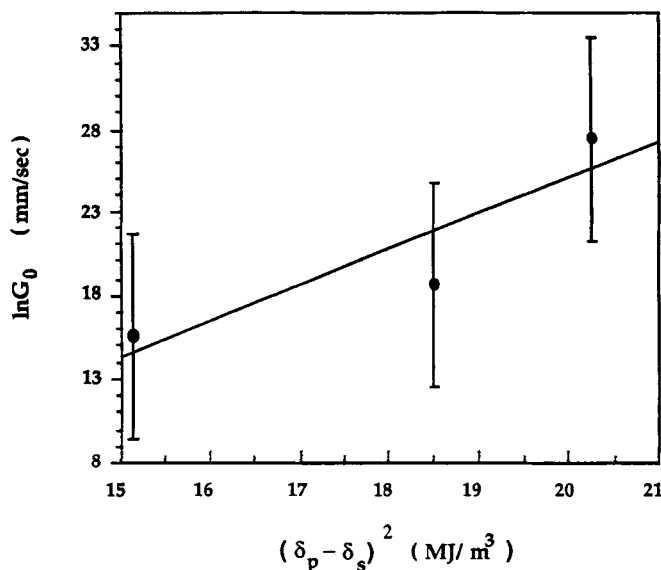


FIGURE 9 Pre-exponential constant vs. the difference of the solubility parameters between the polymer and solvent.

Furthermore, since the same trend has been found for both factors they tend to be counter-balancing effects. The relative importance of these two factors can be examined from the values of rate parameter $A(T)$ and the initial rate data. From Figures 10 and 6 one can see that within the temperature range studied both the rate parameter and the initial rate data follow the order of n -octane $>$ n -decane $>$ n -dodecane. Although both the energy and entropy of activation are important in determining the rate of environmental crazing in polycarbonate exposed to pure normal alkanes, it seems that within the temperature and strain ranges studied the entropic term dominates. Based on the flow-model proposed by Marshall *et al.*,¹³ the rate of environmental crazing depends on both the rate of flow of the solvent through the crazed area as well as the rate of diffusion of the solvent into the polymer. As the solvent molecules become smaller the viscosity of the solvent decreases which enhances both the rate of flow and the diffusivity of the solvent into the polymer. Hence, the rate of craze growth increases.

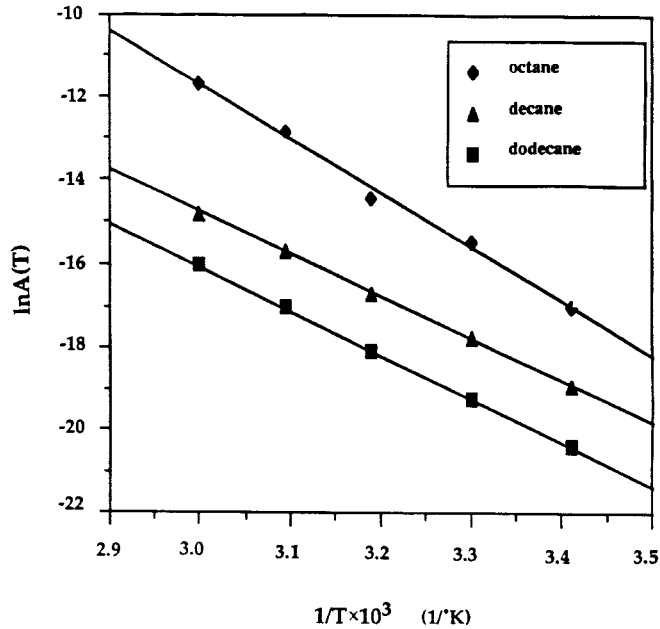


FIGURE 10 Arrhenius plot of the pure alkanes.

Although diffusion data for these pure alkanes in polycarbonate are not available to support the argument above, some experimental results for the self-diffusion coefficient of these solvents have been reported and can at least provide us some idea of the relative diffusion ability of these crazing agents. It is reported that¹⁴ the diffusion coefficient for *n*-octane is about 2.4×10^{-5} cm²/sec at 25°C while that of *n*-dodecane is about 1.1×10^{-5} cm²/sec at the same temperature. Therefore, we conclude that the smaller the size of solvent molecules, the higher the flow and diffusivity of the crazing agents, and, therefore, the higher the rate of craze growth.

Figures 11 and 12 illustrate the variations of both the activation energy ΔE_G and the pre-exponential constant $\ln G_0$ with the volume fraction of *n*-dodecane in three octane/dodecane mixtures. The most probable trends appear to be non-linear, but the error bands are such that linear decreases with volume fraction are also possible. Intuitively, one would suspect that this trend in ΔE_G is related to the heat of mixing, however, the estimated heat of mixing

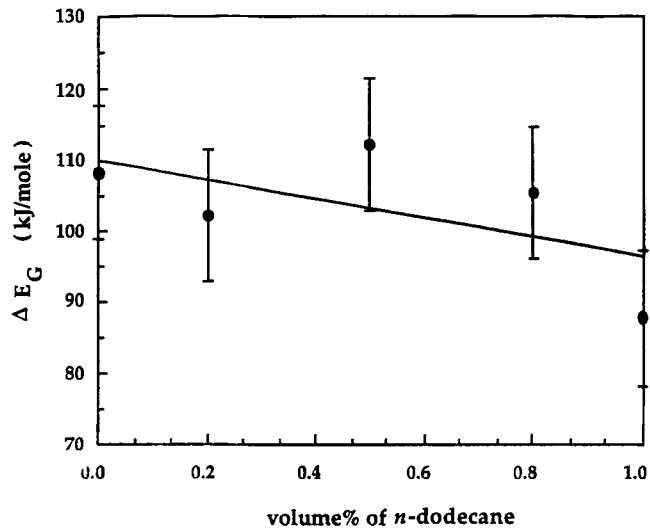


FIGURE 11 Variation of the activation energy with the volume content of *n*-dodecane in the mixtures.

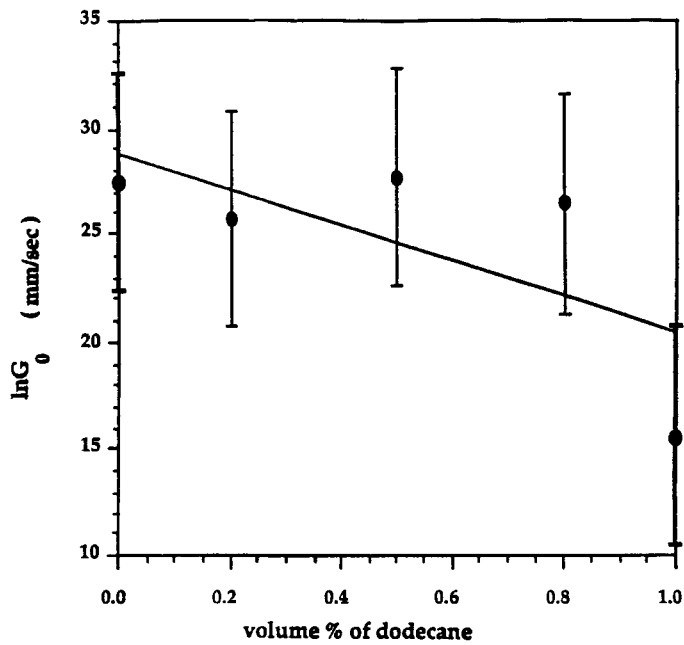


FIGURE 12 Variation of the pre-exponential constant with the volume content of *n*-dodecane in the mixtures.

for this series of alkanes is of the order of 10 cal/g-mole,¹⁵ which obviously cannot account for the experimental changes of activation energy. No conclusions are warranted in light of the uncertainty of the calculated values for ΔE_G and G_0 .

Comparing the estimated values of the kinetic parameters shown in Table II with those obtained from previous studies,^{5,6} we have found substantial differences from one investigator to another, even though similar experiments were conducted. This is probably due in large measure to the differences in measuring technique and data analysis from one investigator to another. In other words, the experimental results are not highly reproducible when interpreted by different investigators. In addition to the difficulties of measurement and data analysis, there are two other problems inherent in the experiment itself. One is the possible effect of different rates of straining when placing the specimen onto the strain-bending apparatus, which may produce a different internal stress state that results in different initial craze growth rates. Another, and probably more important, is the effect of craze interactions. Since the experiment was designed to produce multiple crazes that start growing from the edges of the specimen, the crazes in the neighborhood of the specific craze being followed will likely affect the craze growth. The extent of interaction is not understood and may be difficult to quantify. To reduce the complication caused by craze interaction, a pre-notched specimen is recommended for further investigations.

CONCLUSIONS

A variable radius of curvature strain-bending apparatus has been used to investigate the propagation of surface craze growth in polycarbonate exposed to three different normal alkanes and a series of octane/dodecane mixtures. A theoretical model, combining both the activated-state theory and the stress relaxation phenomenon, is developed to describe the environmental craze growth kinetics in terms of two parameters, B and $A(T)$. The parameter B is a characteristic strain constant independent of temperature and dependent upon the crazing solvent used. The parameter $A(T)$, on the other hand, is a characteristic rate constant which varies with

the temperature following the Arrhenius-type relationship, i.e., $A(T) = G_0 \exp(-\Delta E_G/RT)$, and is also dependent upon the crazing solvent studied. While fairly consistent values of craze rate as a function of time and temperature can be obtained quickly and simply, attempts to use initial rate data to extract energies and entropies of activation for the process are susceptible to errors of data analysis, and are not consistent from one investigator to another.

The primary advantage in using the strain-bending technique is that it is so simple that it can be used to obtain a considerable amount of data for describing the craze growth kinetics. However, the experiment, although reproducible, cannot be analyzed unambiguously to obtain reliable values of activation energies. The most probable cause is the effect of craze interactions. It seems necessary to make modifications of the experiment itself, such as using pre-notched specimens to reduce the interaction of multiple crazes. Within these acknowledged limits, however, it appears that both the constant $\ln G_0$ and the activation energy ΔE_G increase linearly with an increase in the square of the difference between the solubility parameters of the polymer and crazing agent, $(\delta_p - \delta_s)^2$. That is, when the polymer becomes less compatible with the crazing agent, both the $\ln G_0$ and ΔE_G increase, and more importantly, the characteristic rate constant $A(T)$ increases for the range of temperature studied. It appears that both plasticization of the polymer and diffusion of the solvent are important factors in controlling the rate of crazing, but that over the range of conditions studied, the diffusion ability of the crazing agent into the polymer seems to be the dominant factor. For the mixtures of two crazing agents, it is most probable that neither the pre-exponential factor $\ln G_0$ nor the activation energy ΔE_G follows a linear rule of mixtures, which suggests non-ideal solution behavior, but the data cannot be analyzed well enough to establish this with very much certainty.

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