(NASA-CR-173275) ENERGY ABSORPTION BY POLYMER CRAZING (Minnesota Univ.) 23 p
HC A02/MF A01 CSCL 11E
N84-16335
Unclas
H3/27 15286

D/R/A

ENERGY ABSORPTION BY POLYMER CRAZING*

S. S. Pang, Z. D. Zhang, S. S. Chern and C. C. Hsiao
Department of Aerospace Engineering and Mechanics
University of Minnesota, Minneapolis MN 55455 USA

The total energy absorbed by a craze during its development in creep is analyzed and calculated based upon a time dependent theory of crazing. Experimental measurements of the craze length have been utilized in the energy calculations. For polystyrene the initial energy absorption in the craze region is found to be several hundred times that in the uncrazed medium. This ratio reduces sharply in a short period of time to about 50 to 1 and less and remains so afterwards. For polycarbonate, a somewhat similar behavior has been found. The initial strain energy absorption by crazing is about 200 times that in the uncrazed region. The energy ratio reduces rapidly to about 55 to 1 and tends to level off thereon. However, in general, the amount of strain energy absorbed does increase as a function of time as it should.

---

*Supported in part by NASA NAG 1-278

I. Introduction

During the past thirty years, a tremendous amount of research has been done on the development of crazing in polymers [1-3]. The phenomenon of crazing has been recognized as an unusual deformation behavior associated with a process of molecular orientation in a solid to resist failure. The craze absorbs a fairly large amount of energy during the crazing process. When a craze does occur the surrounding bulk material is usually stretched to several hundred percent of its original dimension and creates a new phase.

Since the energy content in the crazing process from time to time is helpful in understanding the craze formation, an effort is made to obtain the energy absorption by a craze. This interest has stemmed from the principal role of crazing as an energy absorption process associated with micro molecular orientation in glassypolymers. This has important consequences in further studies of craze initiation and propagation. Both the deviatoric and volumetric energies during the formation of a craze affect its nucleation. The ability of the changing system to absorb energy from time to time governs the propagation behavior of the craze.

In this paper, the total energy absorbed by a craze during the crazing process in creep has been calculated analytically with the help of some experimental measurements. A comparison of the energy absorption by the new phase and that by the original bulk uncrazed medium is made in this report.

II. Energy Absorption by Crazing

The energy balance concept has been considered one of the cornerstones of fracture mechanics in application to solids [4,5,6] for many years. From the global balance of energy a conservative viscoelastic system under nonisothermal process is describable by the following rate equation:

$$\dot{W}(t) = \dot{I}_b(t) + \dot{D}_b(t) + \dot{K}_b(t) + 4\dot{H}_c(t) \qquad (1)$$

where a dot is used as a total time devivative,

$W(t)$ is the mechanical work done by external forces,

$D_b(t)$ is the dissipative energy of uncrazed bulk medium,

$I_b(t)$ is the internal energy of uncrazed bulk medium,

$K_b(t)$ is the kinetic energy of uncrazed bulk medium, and

$H_c(t)$ is the energy absorption by adrantal craze.

Due to inhomogeneities (flaws, inclusions, surface grooves, cracks etc.) the stress is not uniformly distributed throughout the medium. Crazes nucleate, in general, from regions where stress concentrations occur. Under such a critical state, the original configurational structure (parent phase) is no longer stable. A new phase (craze) consisting of highly oriented domains of fibrils and voids is created which can continue to propagate by absorbing more energy from its surroundings.

Now let us center our attention on the total absorbed energy by a single craze. Referring to a rectangular coordinate system (0-xyz), an idealized symmetrical craze of length c(t) at time t is placed in a constant simple tensile stress field $\sigma_o(t)$ as shown in Fig. 1. In the craze region, oriented molecular bundles (fibril domains) and voids are formed. We define $\sigma_c(x,t)$ as the craze envelope stress which is an average engineering stress taking fibril domains and voids together into consideration. At any section x, the half distance between the two top and bottom craze surfaces is called the craze opening displacement and denoted by w(x,t). Based upon an earlier theory [7] the energy absorption rate $\dot{H}_c(t)$ for any craze length c(t) can be obtained by performing integration of the product of the craze envelope stress $\sigma_c(x,t)$ and the craze opening velocity $\frac{\partial w(x,t)}{\partial t}$ along the envelope of the new phase boundary, i.e.

$$\dot{H}_c(t) = \int_o^{c(t)} \sigma_c(x,t) \frac{\partial w(x,t)}{\partial t} dx \qquad (2)$$

According to the previous result [7-11], in the case of creep $\sigma_o(t)=\sigma_0 u(t)$ where u(t) is a unit step function, it has been shown that the use of the two-step stress distribution results in good approximation as compared with experimental findings:

$$\left.\begin{aligned} \sigma_1(x,t) &= \alpha\sigma_o, \quad \text{for } o \le x \le a(t) \\ \sigma_2(x,t) &= \beta\sigma_o, \quad \text{for } a(t) \le x \le c(t) \end{aligned}\right\} \qquad (3)$$

where α and β are material constants, σ_o is a constant representing the external stress as shown in Fig. 1. According to experimental results for polystyrene [9] the stress $\sigma_1(t)$ is about 10% below the applied stress along the majority of its length and about 15% above the applied stress near the craze tip. That is

$\sigma_2(t)$ = 115% σ_o. It was found that a(t) must satisfy the following relationship:

$$a(t) = c(t)\cos\theta\,, \qquad \theta = \frac{\pi}{2}\,\frac{1-\alpha}{1-\beta} \tag{4}$$

The craze opening displacement field for polymers having a constant natural draw ratio λ_n is

$$w(x,t) = \frac{\lambda_n}{\lambda_n - 1}\left[C_b(0)\,\phi(x,t) + \int_0^t \dot{C}_b(t-\tau)\,\phi(x,\tau)\,d\tau\right] \,, \tag{5}$$

where

$$\phi(x,t) = \frac{2}{\pi}\int_0^{c(t)} \frac{\eta g(\eta,t)}{(\eta^2 - x^2)^{\frac{1}{2}}}\,d\eta \,, \tag{6}$$

and

$$g(\eta,t) = \int_0^{\eta} \frac{\sigma_o - \sigma_c(x,t)}{(\eta^2 - x^2)^{\frac{1}{2}}}\,dx \,. \tag{7}$$

Here $C_b(t)$ is the time dependent compliance function representing the constitutive behavior of the uncrazed bulk material. For most glassy polymers, the strain in the uncrazed portion of the polymer is usually about 1%. Hence the strain ratio or the so called Poisson's ratio ν may be assumed constant [12]. Under this situation $C_b(t)$ may be reduced to:

$$C_b(t) = 2(1-\nu^2)J(t)\,, \tag{8}$$

where J(t) is the uniaxial creep compliance function of the bulk medium.

Combining (2) - (7) one obtains: [see Appendix]

$$\int_0^{a(t)} \frac{\partial w(x,t)}{\partial t}\,dx = \frac{\lambda_n}{\lambda_n - 1}(\beta-\alpha)\,[C_b(0)(2b_1-b_2)\dot{c}(t)+\dot{C}_b(0)b_1c(t)]\,\sigma_o c(t) \quad , \qquad (9)$$

$$\int_{a(t)}^{c(t)} \frac{\partial w(x,t)}{\partial t}\,dx = \frac{\lambda_n}{\lambda_n - 1}(\beta-\alpha)\,[C_b(0)(2b_3+b_2)\dot{c}(t)+\dot{C}_b(0)b_3c(t)]\,\sigma_o c(t) \quad , (10)$$

where

$$b_1 = \frac{2}{\pi}\cos^2\theta\ [(\frac{\pi}{4}-\frac{\theta}{2})\tan\theta + \ln\sec\theta], \qquad (11)$$

$$b_2 = \frac{2}{\pi}\cos^2\theta\ \ln\sec\theta, \qquad (12)$$

$$b_3 = \frac{2}{\pi}\cos^2\theta\ (\frac{\theta}{2}\tan\theta - \ln\sec\theta). \qquad (13)$$

Substituting (3) and (4) into (2) gives

$$H_c(t) = \sigma_o\ [\ \alpha\int_0^{a(t)} \frac{\partial w(x,t)}{\partial t}\,dx + \beta\int_{a(t)}^{c(t)} \frac{\partial w(x,t)}{\partial t}\,dx] \qquad (14)$$

Now putting (9) and (10) into (14) yields:

$$\dot{H}_c(t) = \frac{\lambda_n}{\lambda_n - 1}(\beta-\alpha)\,\sigma_o^2\Big\{(\beta b_3+\alpha b_1)\dot{C}_b(0)\,c^2(t)$$

$$+\ [\beta(2b_3+b_2)+\alpha(2b_1-b_2)]\,C_b(0)\,c(t)\,\dot{c}(t)\Big\} \quad , \qquad (15)$$

Equation (15) represents the energy absorption rate by a craze at any time. Therefore the total energy absorbed by a craze is:

$$H_c(t) = \int_0^t \dot{H}_c(t)\,dt$$

$$= \frac{\lambda_n}{\lambda_n-1}(\beta-\alpha)\sigma_0^2\left\{(\beta b_3+\alpha b_1)\dot{C}_b(0)\int_0^t c^2(t)\,dt\right.$$

$$\left.+[\beta(2b_3+b_2)+\alpha(2b_1-b_2)]C_b(0)\int_0^t c(\tau)\,\dot{c}(\tau)\,dt\right\}. \quad (16)$$

In the following section, the above equation will be utilized together with experimental results of the craze length c(t) for calculating the total absorbed energy. It will be seen that the integrals in (16) have to be properly represented before programing and computing.

III. Results and Discussion

In order to obtain $c(t)$ experimentally, creep tests of polystyrene have been performed [8]. A typical curve for the changing craze length as a function of time is shown in Fig. 2. A fairly good approximation for the craze length $c(t)$ is obtainable using a function of the form

$$c(t) = c(0) + A t^n, \tag{17}$$

where $c(0)$ is associated with the initial flaw size and A and n are material constants obtainable by curve fitting techniques.

The following integrals are represented as:

$$\int_0^t c(t)\dot{c}(t)\,dt = Ac(0)t^n + 0.5\,A^2t^{2n}, \tag{18}$$

$$\int_0^t c^2(t)\,dt = c^2(0)t + \frac{2}{n+1}\,c(0)A\,t^{n+1} + \frac{1}{2n+1}\,A^2t^{2n+1} \quad . \tag{19}$$

Then (16) was calculated and the result is shown in Fig. 3.

For the unoriented medium the energy density is:

$$H(t) = \int_0^t \sigma(\tau)\dot{\varepsilon}(\tau)\,d\tau , \tag{20}$$

where

σ is the simple tensile stress,

ε is the simple tensile strain.

In the case of creep $\sigma = \sigma_0$, with σ_0 as a constant

Since the strain

$$\varepsilon(t) = \sigma_0 J(t) , \tag{21}$$

so the energy density may be written as:

$$e(t) = \sigma_0^2 J(t) , \tag{22}$$

where J(t) is the creep compliance of the unoriented material, which can be obtained through a creep test and using curve fitting technique.

Based upon crazing model (Fig. 1) the craze envelope surface initiation rate is defined as follows:

$$\dot{S}\ (t) = \int_0^{c(t)} \frac{\partial w(x,t)}{\partial t}\, dx. \qquad (23)$$

By substituting Eqs. (9) and (10) into (23), we have:

$$\dot{S}\ (t) = 4\frac{\lambda_n}{\lambda_n - 1}\ (\beta-\alpha)(b_1+b_3)[2C_b(0)\dot{c}(t)+C_b(0)\ \ c(t)]\sigma_o c(t). \qquad (24)$$

So the area of the craze region at any time is:

$$S(t) = \int_0^t \dot{S}(t)\,dt = \frac{\lambda_n}{\lambda_n - 1}\ (\beta-\alpha)(b_1+b_3)\cdot$$

$$[2C_b(0)\int_0^t c(t)\cdot\dot{c}(t)\,dt + \dot{C}_b(0)\ \int_0^t c^2(t)\,dt]\sigma_o \qquad (25)$$

Then the energy contained in a comparable volume with respect to a craze in the original polymer is as follows:

$$\begin{aligned} H_o(t) &= e(t)S(t) \\ &= \frac{\lambda_n}{\lambda_n - 1}\ (\beta-\alpha)(b_1+b_3)\sigma_0^3 J(t)[\ C_b(0)\ \int_0^t c(t)\cdot\dot{c}(t)\,dt \\ &+ \dot{C}_b(0)\ \int_0^t c^2(t)\,dt] \end{aligned} \qquad (26)$$

which is plotted in Fig. 4.

Fig. 5 shows the ratio of $H_c(t)$ and $H_o(t)$ as a function of time. It is evident that the energy absorbed by the craze is much greater than that in the original uncrazed medium. Initially several hundred folds of energy absorption took place. Later on a ratio of about 50 to 1 is maintained for the propagation of the craze.

For polycarbonate a somewhat similar behavior in energy absorption has been found. Fig. 6 shows the time dependent craze length variation obtained analytically. Figs. 7 and 8 show respectively the energy absorbed by crazed and uncrazed polycarbonate. Fig. 9 gives the ratio of the energies absorbed for comparison.

The absorbed energy has several functions in developing the craze. At first the fibril domains and possibly some voids near the craze tip are formed. During this process some energy will dissipate, parts will be stored and new surfaces are created. These energies may be calculated.

One of the important features in crazing formation is the variation of the temperature field near the neckdown region where the original polymer transfers from the original phase to a new crazed phase. This temperature field may be obtained by solving an appropriate heat equation satisfying the craze modelling. Dissipated energy may be subsequently obtained. This work is being carried out now and will be reported in the future elsewhere.

Appendix

By substituting (2) into (6) and (7), one gets:

$$\phi(x,t) = \frac{1}{\pi}(\beta-\alpha)\sigma_o c(t)\left[(X+g)\cosh^{-1}\frac{1+Xg}{X+g} - (X-g)\cosh^{-1}\frac{1-Xg}{|X-g|}\right] \quad ,\text{(A1}$$

where

$$X \equiv x/c(t), \tag{A2}$$

$$g = \cos\theta \ . \tag{A3}$$

From (4) by differentiation one obtains,

$$a(t) = \dot{c}(t)\cos\theta. \tag{A4}$$

Then the following expressions can be derived

$$\phi(a,t) = \left[\frac{2}{\pi}(\beta-\alpha)\sigma_o\cos\theta\ln\sec\theta\right]c(t) \ , \tag{A5}$$

$$\int_0^{a(t)}\phi(x,t)\,dx = \frac{2}{\pi}(\beta-\alpha)\sigma_o\cos^2\theta\left(\frac{\pi}{4}\tan\theta-\frac{\theta}{2}\tan\theta-\ln\sec\theta\right)c^2(t) \ , \tag{A6}$$

$$\frac{d}{dt}\int_0^{a(t)}\phi(x,t)\,dx = \frac{2}{\pi}(\beta-\alpha)\sigma_o\cos^2\theta\left(\frac{\pi}{2}\tan\theta-\theta\tan\theta-2\ln\sec\theta\right)c(t)\dot{c}(t) \ , \tag{A7}$$

$$\int_{a(t)}^{c(t)}\phi(x,t)\,dx = \frac{2}{\pi}(\beta-\alpha)\sigma_o\cos^2\theta\left(\frac{\theta}{2}\tan\theta-\ln\sec\theta\right)c^2(t) \ , \tag{A8}$$

$$\frac{d}{dt}\int_{a(t)}^{c(t)}\phi(x,t)\,dx = \frac{2}{\pi}(\beta-\alpha)\sigma_o\cos^2\theta\left(\theta\tan\theta-2\ln\sec\theta\right)c(t)\dot{c}(t) \ . \tag{A9}$$

From (1), we have

$$\int_0^{a(t)}\dot{w}(x,t)\,dx = \frac{\lambda_n}{\lambda_n-1}C_b(0)\left\{-\dot{a}(t)\phi[a(t),t]+\frac{d}{dt}\int_0^{a(t)}\phi(x,t)\,dx\right\}$$

$$+\frac{\lambda_n}{\lambda_n-1}\left\{\dot{C}_b(0)\int_0^{a(t)}\phi(x,t)\,dx + \int_0^{a(t)}\left[\int_0^t\dot{C}_b(t-\tau)\phi(x,\tau)\,d\tau\right]dx\right\}, \tag{A10}$$

$$\int_{a(t)}^{c(t)} \dot{w}(x,t)\,dx = \frac{\lambda_n}{\lambda_n - 1} C_b(0) \left\{ a(t))\phi[a(t),t + \frac{d}{dt}\int_{a(t)}^{c(t)} \phi(x,t)\,dx \right\}$$

$$+ \frac{\lambda_n}{\lambda_n - 1} \left\{ \dot{C}_b'(0) \int_{a(t)}^{c(t)} \phi(x,t)\,dx + \int_{a(t)}^{c(t)} [\int_0^t \ddot{C}_b(t-\tau)\,\phi(x,\tau)\,d\tau]\,dx \right\} \qquad \text{(A11}$$

Since $\ddot{C}_b(t)$ is rather small at all times, it can be neglected. Now if we substitute (A4)-(A9) into (A10) and (A11) respectively, the following equations may be obtained:

$$\int_0^{a(t)} \dot{w}(x,t)\,dx = \frac{\lambda_n}{\lambda_n - 1} (\beta-\alpha)\,[C_b(0)\,(2b_1 - b_2)\,c(t) + \dot{C}_b(0)\,b_1 c(t)\,]\,\sigma_o c(t) \qquad \text{(A12}$$

$$\int_{a(t)}^{c(t)} \dot{w}(x,t)\,dx = \frac{\lambda_n}{\lambda_n - 1} (\beta-\alpha)[C_b(0)\,(2b_3 + b_2)\,\dot{c}(t) + \dot{C}_b(0)\,b_3 c(t)\,]\,\sigma_o c(t) \qquad \text{(A13}$$

where

$$b_1 = \frac{2}{\pi} \cos^2\theta\,[(\frac{\pi}{4} - \frac{\theta}{2})\tan\theta + \ln\sec\theta] \qquad \text{(A14)}$$

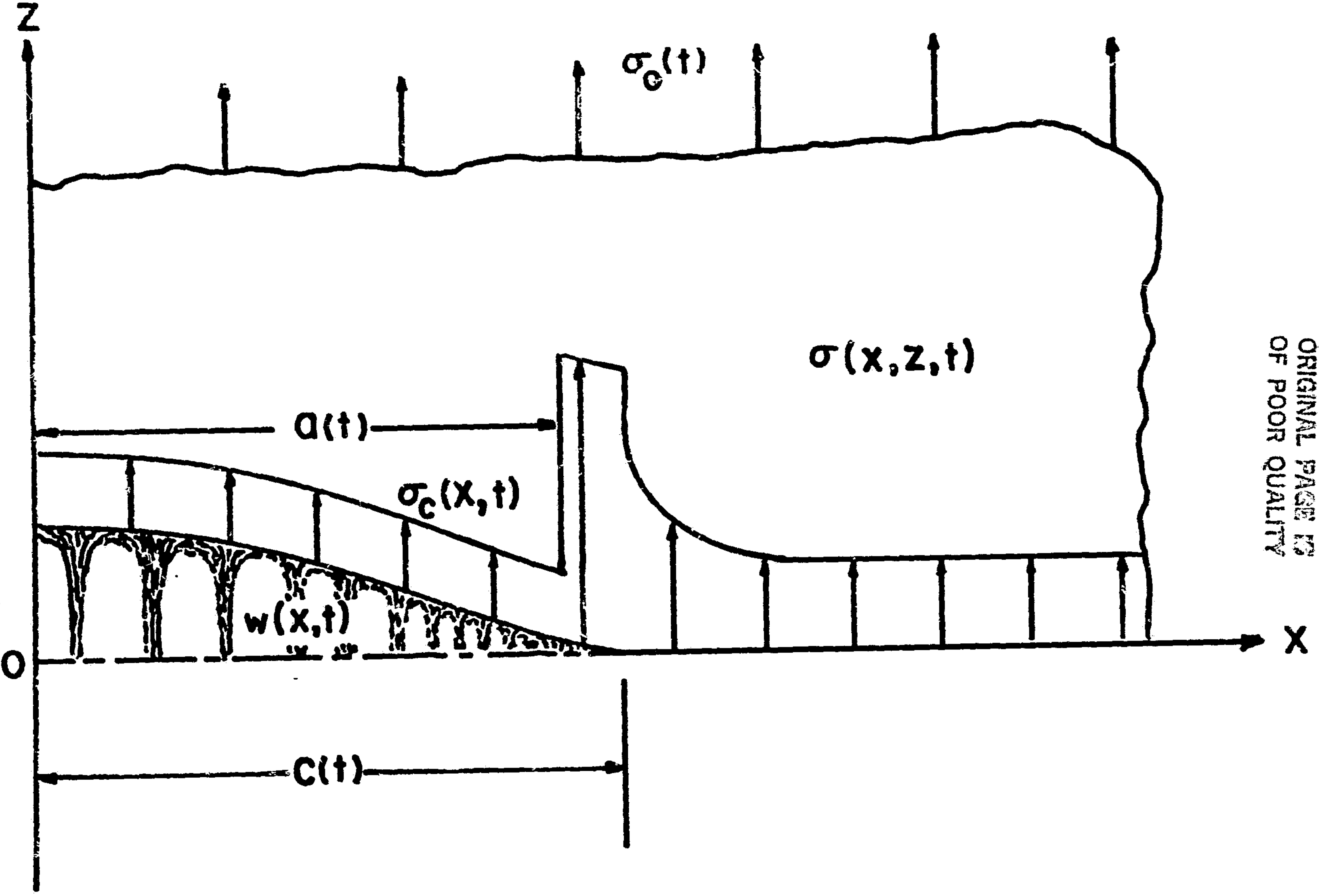
$$b_2 = \frac{2}{\pi} \cos^2\theta \ln\sec\theta \qquad \text{(A15)}$$

$$b_3 = \frac{2}{\pi} \cos^2\theta\,(\frac{\theta}{2}\tan\theta - \ln\sec\theta) \qquad \text{(A16)}$$

References

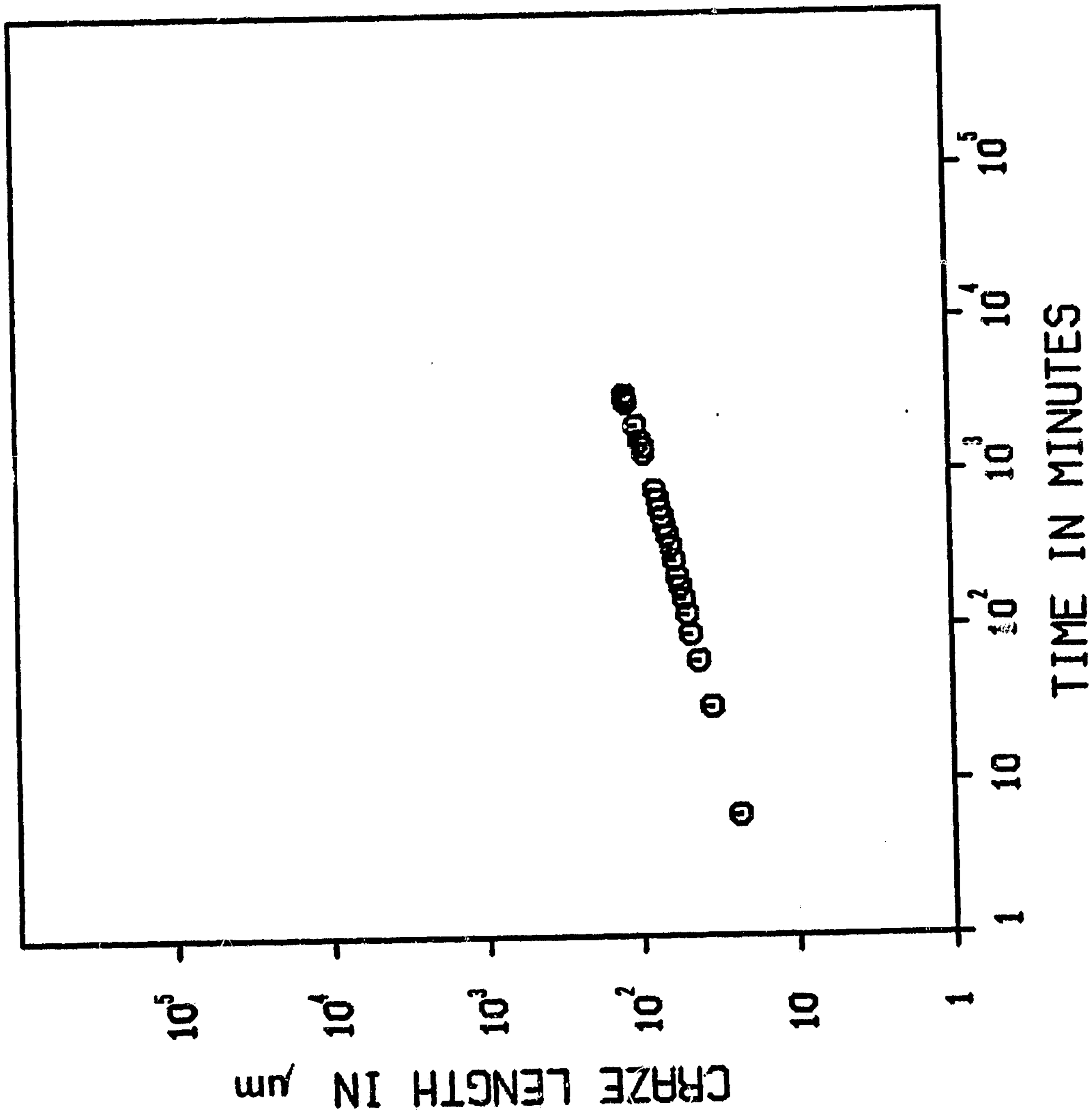
1. C. C. Hsiao and J. A. Sauer. J. Appl. Phys. 21, 1071 (1950).
2. S. Rabinowitz and P. Beardmore, Crit. Rev. Macromol. Sci. 1.1 (1972).
3. R. P. Kambour, J. Polymer Sci. D7, 1 (1973).
4. A. A. Griffith, Phil Trans. Roy Soc. (Lond). A221, 163 (1921); The Theory of Rupture, Proc. First Int. Congress Appl. Mechs. DelA. 55, (1924).
5. E. Orowan, "Fundamentals of Brittle Behavior in Metals" Proc. Symposium on Fatique and Fracture of Metals. ed. by W. M. Murray, John Wiley and Sons, 139, (1950).
6. R. S. Rivlin and A. G. Thomas, "Rupture of Rubber", J. Polymer Science, 10 (3), 291, (1953).
7. S. S. Chern and C. C. Hsiao, J. Appl. Phys. 53, 6541 (1982).
8. Z. D. Zhang, S. S. Chern and C. C. Hsiao "Propagation of Crazing in Viscoelastic Media" J. Appl. Phys. 54, (1983)
9. B. D. Lauternasser and E. J. Kramer, Phil. Mag. A. 39, 469, (1979).
10. L. Bevan, J. Polymer Sci. Polymer Phys. 19, 1759 (1981).
11. L. Bevan, J. Appl. Polymer Science, 27, 4263 (1982).
12. Z. Rigbi, J. Appl. Polymer Sci. Symp. 5, 1, (1967).

FIGURE ATTACHMENTS



ORIGINAL PAGE IS
OF POOR QUALITY

Fig. 1 Quasimental Craze and a Two-Step Craze Envelope Stress


TIME IN MINUTES
1
10
10^2
10^3
10^4
10^5
CRAZE LENGTH IN µm
1
10
10^2
10^3
10^4
10^5

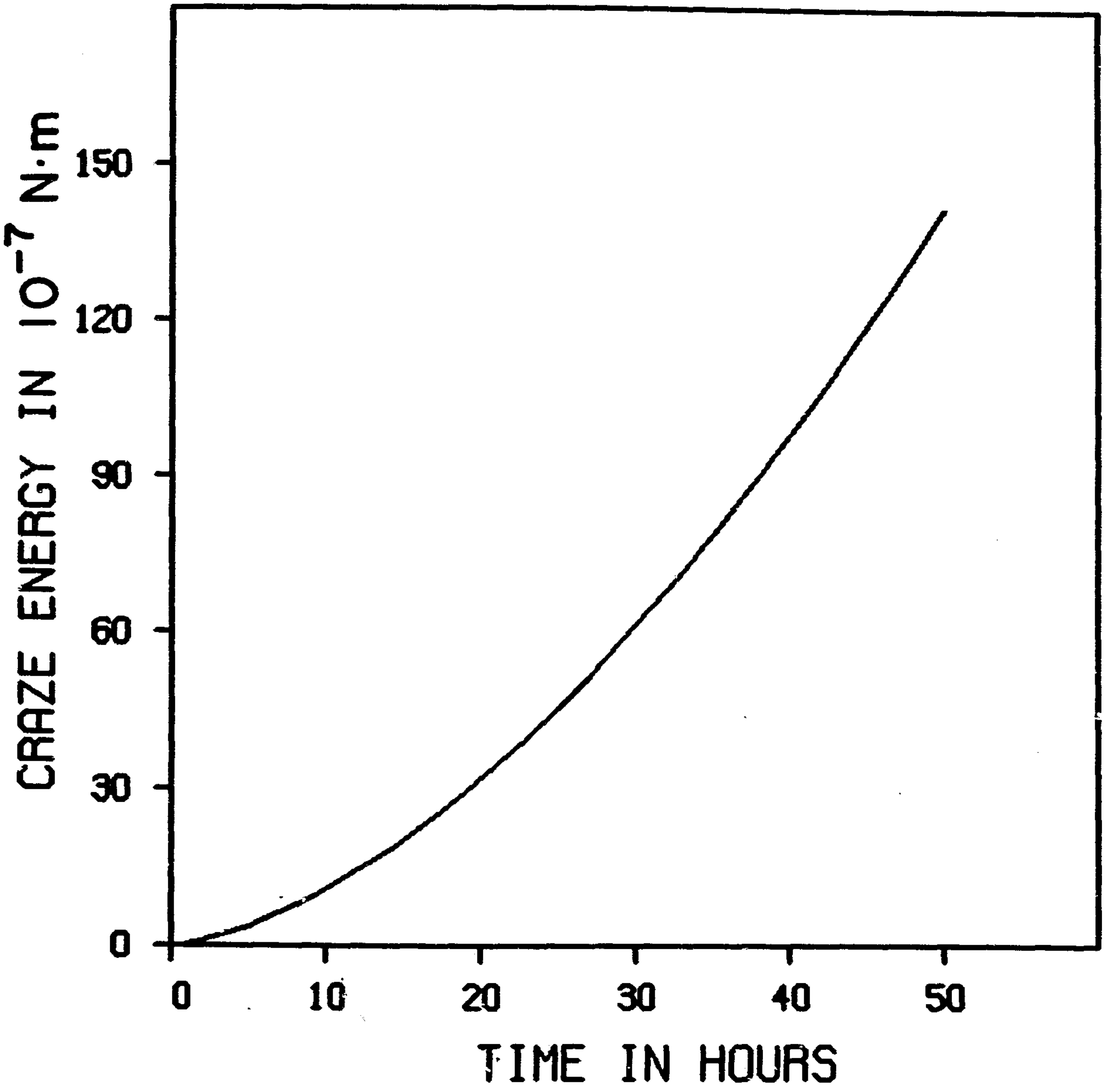


Fig. 3 Energy Absorbed by a Craze in Polystyrene

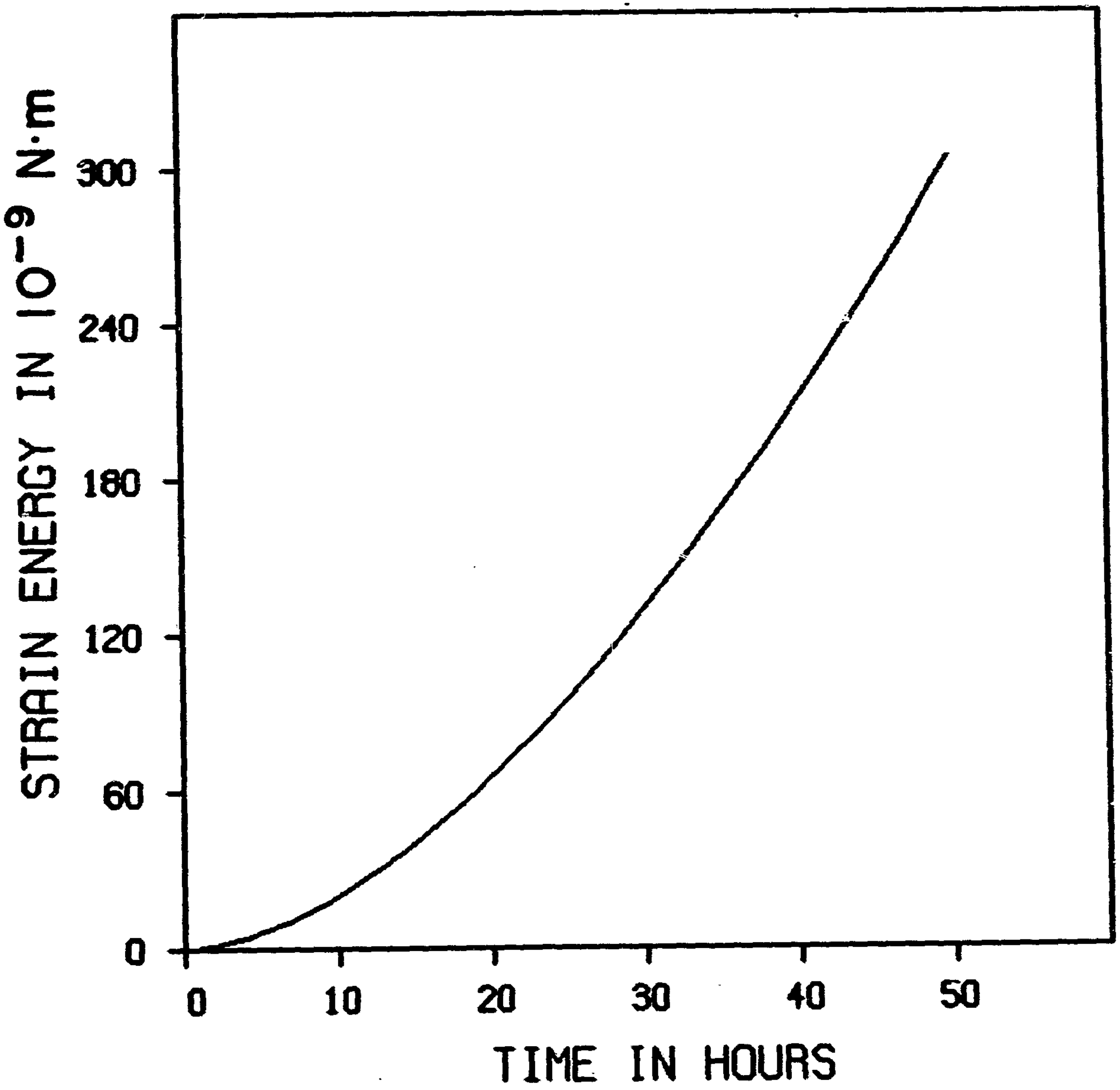


Fig. 4 Energy Absorbed in a Craze Volume in Uncrazed Polystyrene

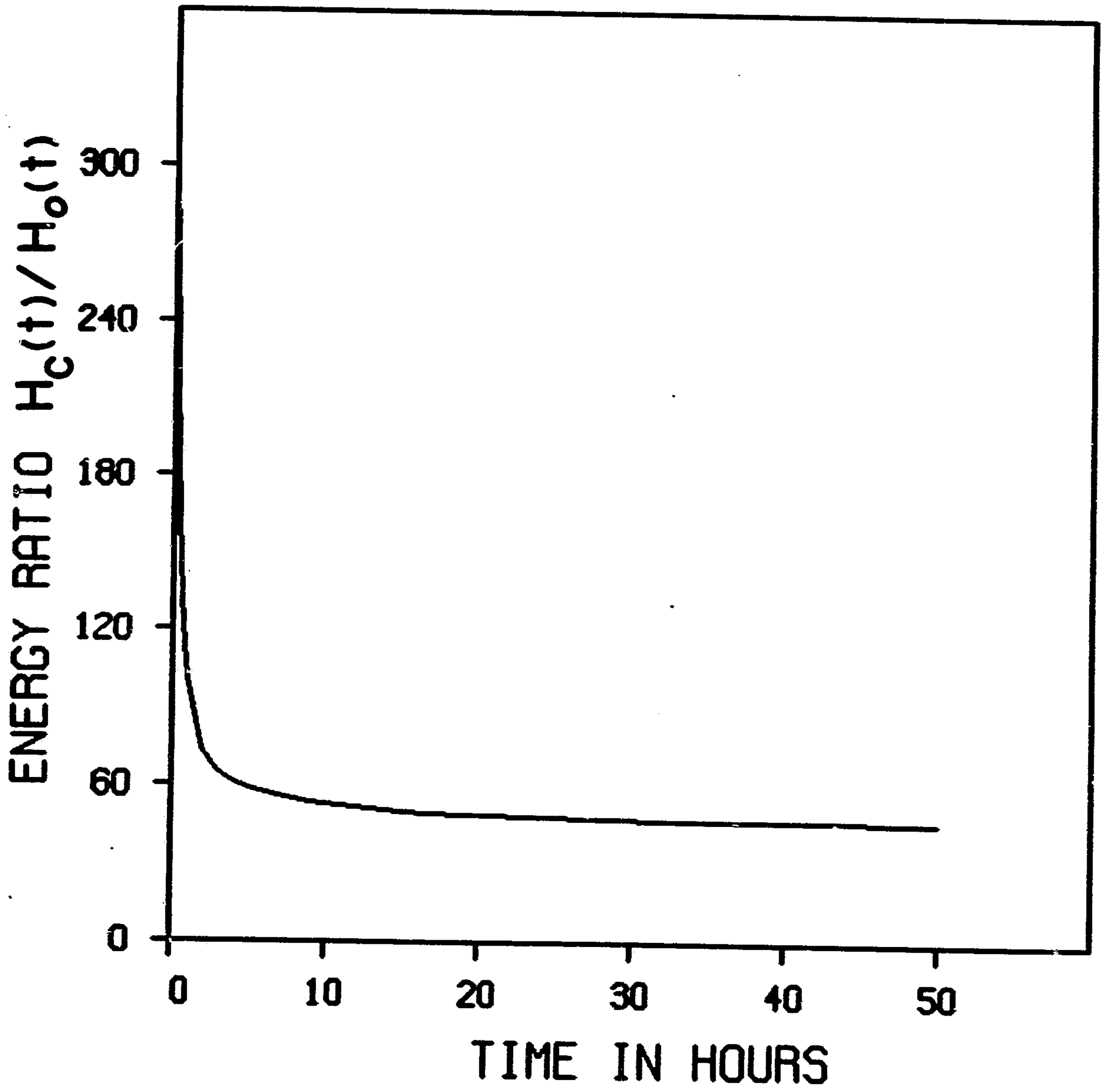


Fig. 5 Ratio of Absorbed Energies by Crazed and Uncrazed Polystyrene

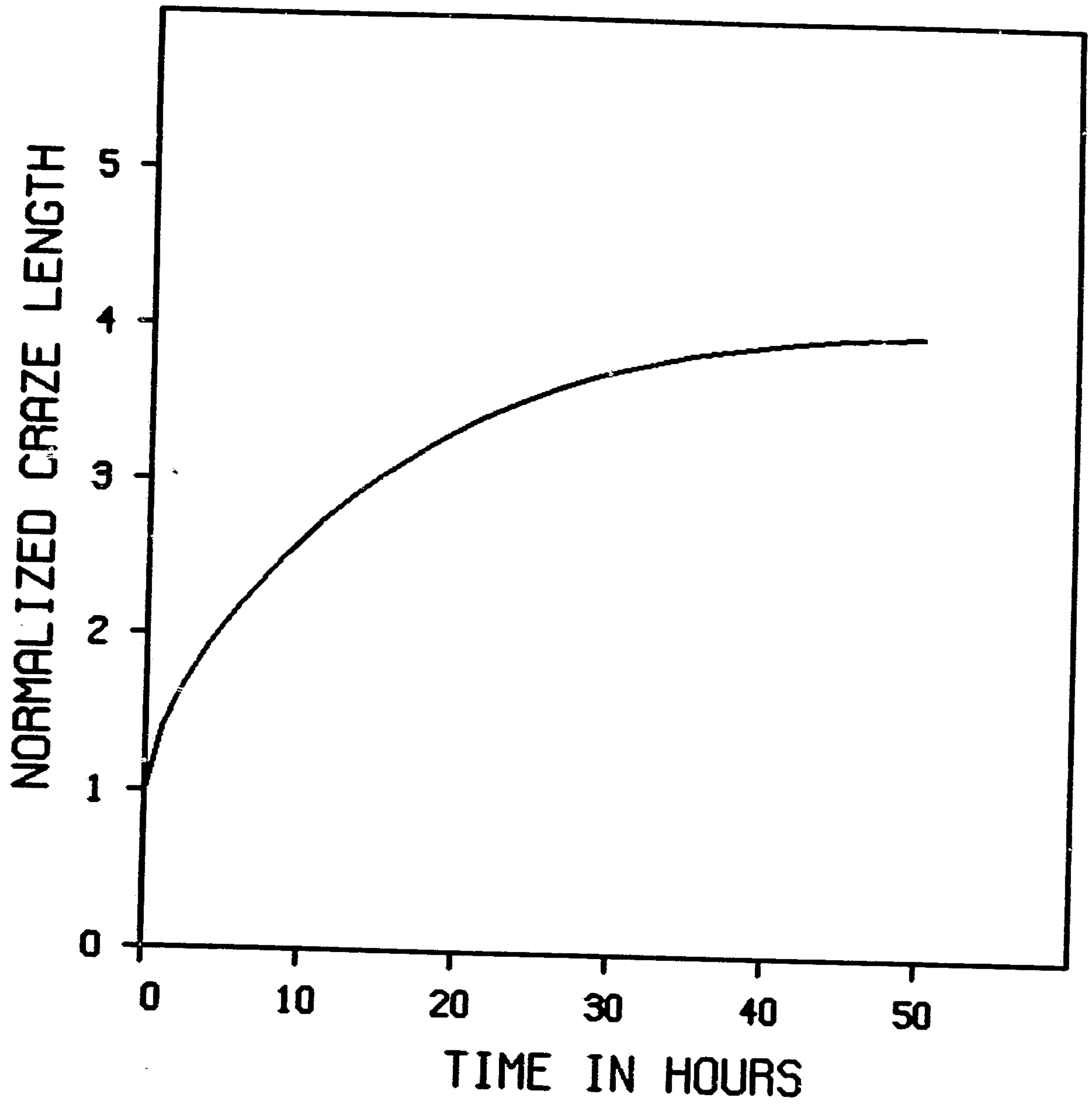


Fig. 6 Time Dependent Craze Propagation in Polycarbonate

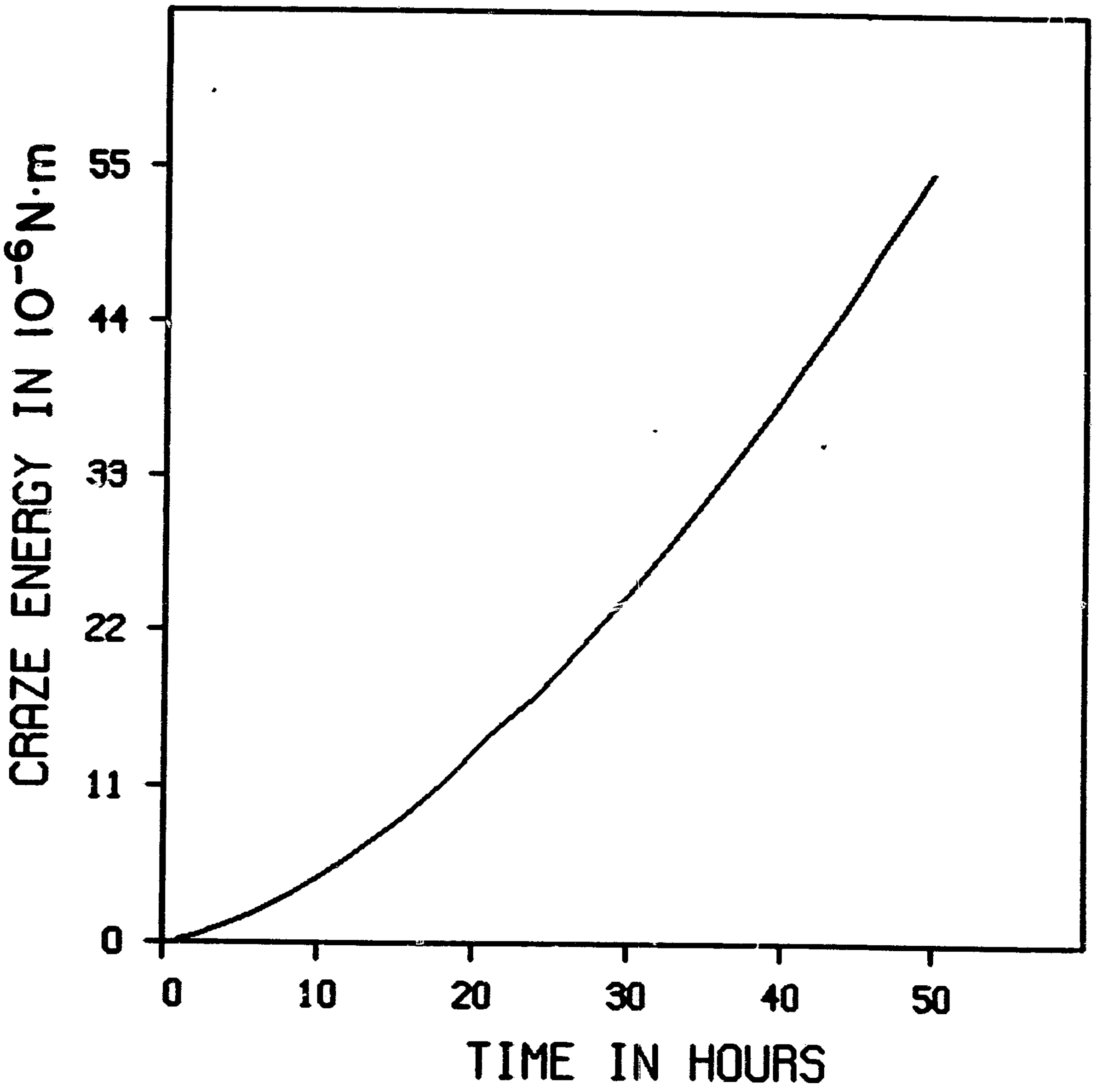


Fig. 7 Energy Absorbed by a Craze in Polycarbonate

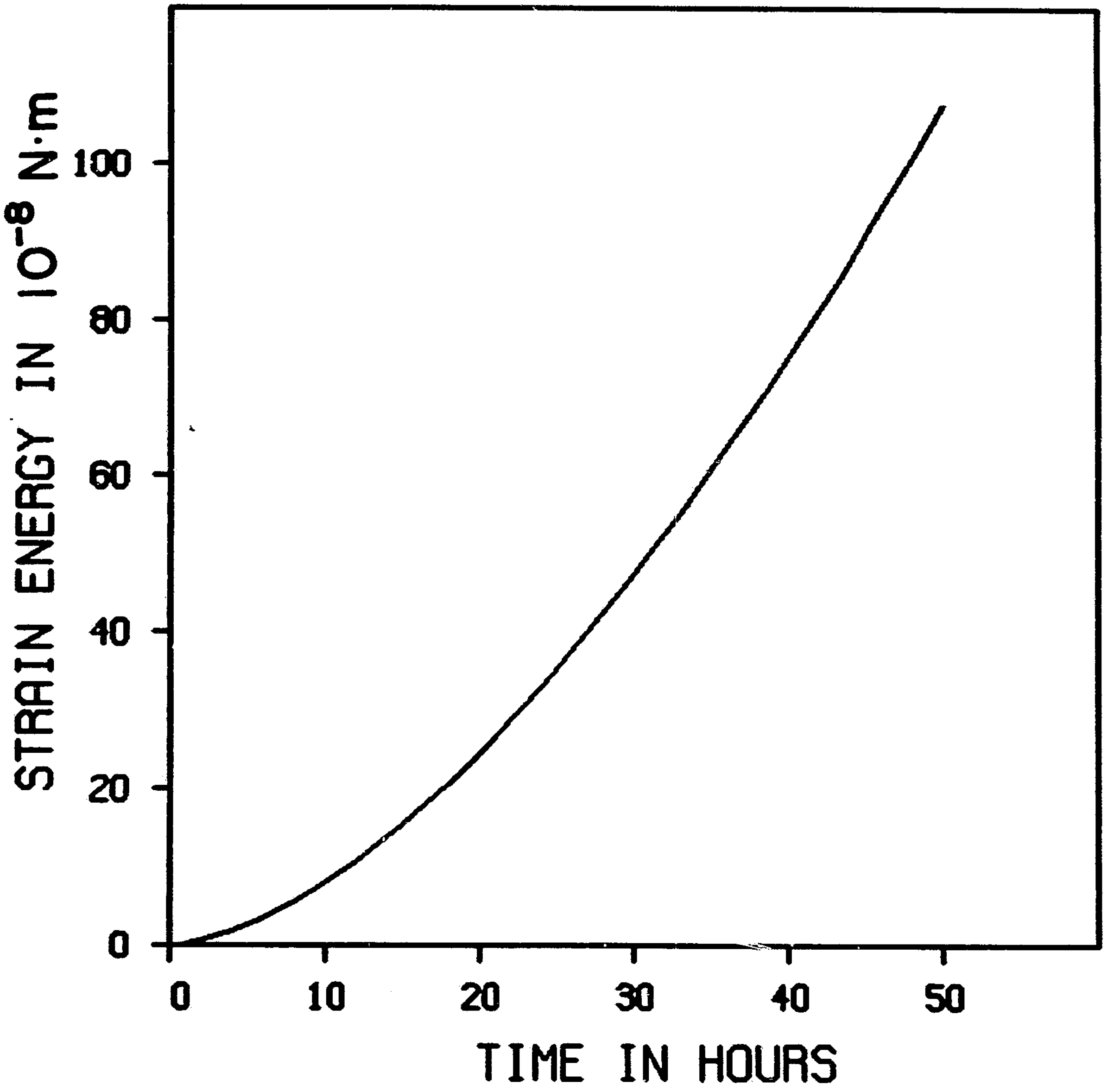


Fig. 8 Energy Absorbed in a Craze Volume in Uncrazed Polycarbonate

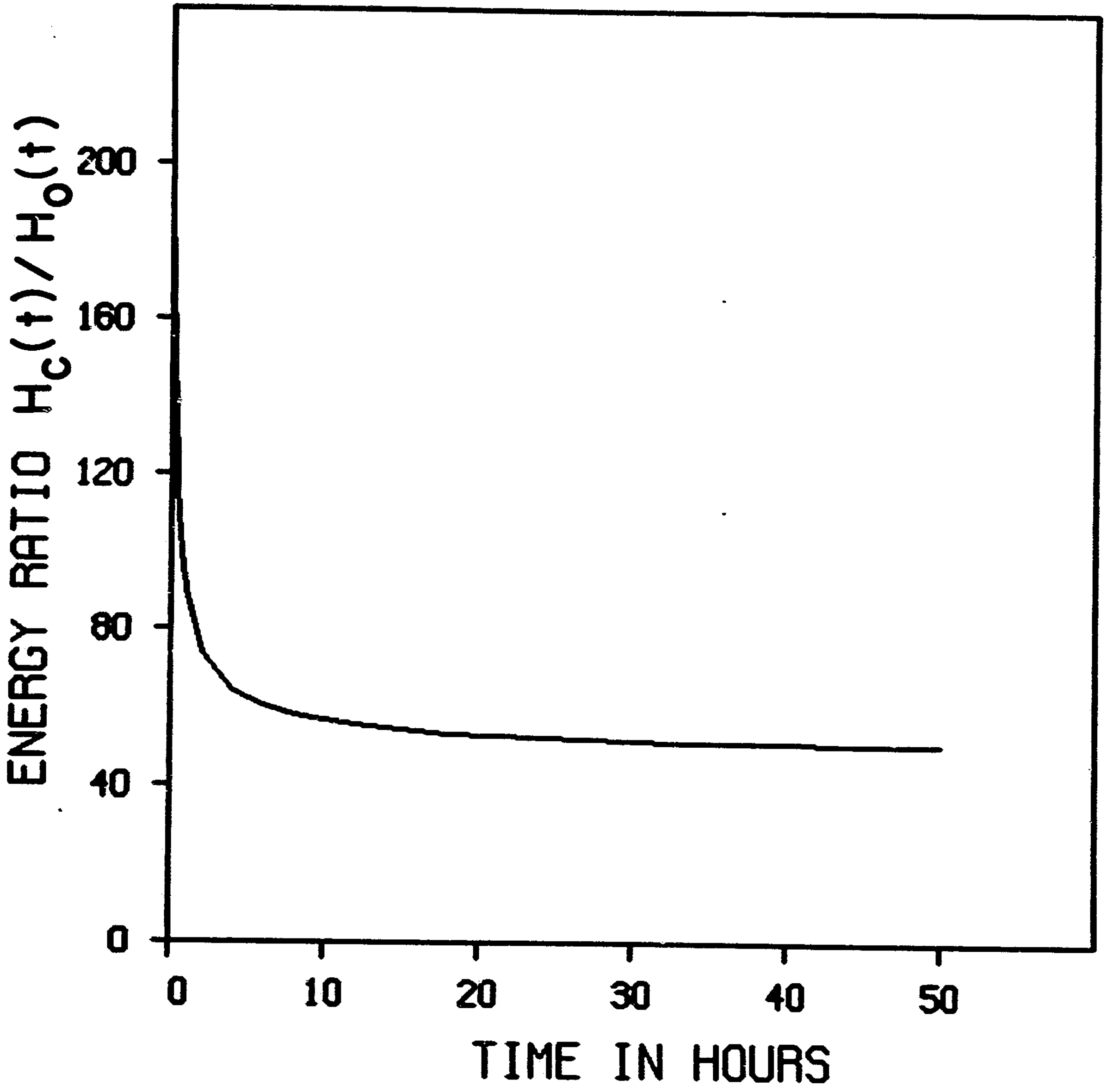


Fig. 9 Ratio of Absorbed Energies by Crazed and Uncrazed Polycarbonate