

Studies on Laser-Induced Irreversible Surface Softening in a Thermoset Polymer of Allyl Diglycol Carbonate (CR-39)

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SYNOPSIS

It is shown that controlled irreversible surface softening can be obtained in thermoset polymer of allyl diglycol carbonate (CR-39) without degrading its bulk properties on treating it with a cw-CO₂ laser. An average value of the threshold fluence for the onset of softening is found to be about 9 J/cm², which changes slightly with the interaction time and power density of the laser beam. Beyond this threshold the hardness of the treated surface decreases on increasing the power density and/or the interaction time till the onset of volatile decomposition in this polymer, which takes place at the laser fluence of 25 J/cm². Thereafter, the hardness tends to saturate at nearly 60% of its original value for the untreated surface. Formation of a new heterogenous interlinked porous microstructure has been observed in the laser softened polymer surface. Solution of the 1-dimensional heat flow equation incorporating the temperature-dependent decomposition energy of CR-39 has shown that at 9 J/cm² the surface attains the maximum temperature of about 280°C and then cools at a rate of about 10³ °C/s. The starting value of the surface cooling rate increases with the fluence. A part of the absorbed energy goes in for the depolymerization, which is found to increase from about 0.004 to 4.5 J/cm² when the laser fluence is increased from 9 to 25 J/cm². The laser-induced depolymerization and subsequent rapid cooling of the surface explain the observed effects.

INTRODUCTION

Thermoset polymer of allyl diglycol carbonate (CR-39) is known as an excellent material for a number of industrial, medical, and optical uses.¹ This polymer has good optical clarity, structural stability, and high resistance to heat, abrasion, impact, and inertness to most of the chemicals.^{2,3} Its hardness (Rockwell, M 95–100) is an advantage in many of its applications¹ but restricts its use in certain other areas such as in making contact lenses because it causes mechanical irritation, etc. Recently, we have observed that the surface of CR-39 can be softened permanently without affecting its bulk properties when it is treated with cw-CO₂ laser under controlled conditions.⁴ This is an important phenomenon for two reasons:

(a) It offers a unique method of thermal soft-

ening of a thermoset polymer which by definition cannot be softened on heating. Till now it was understood that heating of a thermoset polymer only degrades it.^{5,6}

(b) Irreversible surface softening on a hard polymer of CR-39 will increase the usefulness of this polymer in many areas. This will be discussed at the end of this paper.

Laser surface treatment of metals has been extensively studied and used in a variety of processes.^{7–9} For example, a soft metal can be hardened by rapid heating and self-quenching resulting from interaction with short duration laser pulses. However, laser surface treatment of polymers to modify its surface properties to suit a particular requirement while retaining its bulk properties is not reported so far. To the best of the author's knowledge, this paper presents the first work on the laser surface treatment of a polymer. The increasing use of polymers for substituting other materials in a variety of applications¹⁰ necessitates tailoring of its surface

properties to meet the requirements of specific applications.

In this paper, a parametric study on the irreversible surface softening in laser treated CR-39 and investigations to understand the reasons for this phenomenon are presented. Physical form of the microstructure in the laser softened surface is discussed. Dependence of the surface hardness of the treated CR-39 on the power density and beam residence time of the laser beam are presented. Theoretical calculations have been carried out to understand the thermal evolution in the polymer sheet moving under the cw laser beam during the treatment. At the calculated temperature, thermal behavior of CR-39 has been investigated in independent experiments. The results of these investigations have been used to explain the observed effects.

EXPERIMENTAL

A 125 W cw-CO₂ laser, developed at our laboratory,¹¹ was used for treating the CR-39 sheets (1.6 mm thick, manufactured by SGL Homolite of U.S.A.). The multimode (TEM₀₀ + TEM₁₀) laser beam was focussed with an astigmatism-free arrangement of mirrors.¹² The converging laser beam progressed vertically downwards and was made to interact with the polymer sheets moving on a horizontal turntable. The spot diameter of the laser beam at the surface of the polymer sheet was adjusted to 5 mm. The speed of the turntable was changed to vary the beam residence time. For changing the power density of the interacting laser beam output power from the laser was varied in the range of 5–100 W. The surface treatment of CR-39 sheets was carried out in air.

Hardness of the CR-39 sheets was measured on a Vickers hardness tester. The pyramidal diamond tip of the hardness tester was allowed to penetrate vertically downwards into the polymer under an optimum weight of 100 g for 35 s. This resulted in the formation of a permanent indentation at the polymer surface. The diagonals of the indentations on the laser treated and untreated surfaces were measured with a microscope with least count of 1 μm. The surface hardness of the laser treated polymer sheet (H_L) relative to that of the normal untreated sheet (H_N) was calculated from the following expression:

$$\frac{H_L}{H_N} = \frac{D_N^2}{D_L^2} \quad (1)$$

where D_N and D_L are the length of the diagonals of the indentations in the normal and the laser-treated polymer samples. This expression is based on the fact that the hardness is inversely proportional to the area of the indentation which is proportional to the square of its diagonal. The hardness of the treated polymer was measured relative to that of the normal polymer because in the Vickers hardness tester a standard sample of known hardness is necessary. In this case the untreated CR-39 was found to be the most suited standard sample.

To make the indentations on the transparent CR-39 sheet clearly visible in reflected light, its surface was dyed. To ensure that the hardness being measured was that of the laser treated polymer, the depth of the indentation was kept smaller than the thickness of the softened region. Some of the samples treated at low fluences of the laser had very thin softened surface (less than 10 μm) and hence were not used for these measurements. The thickness of the laser softened surface was estimated based on the observation that the bulk etch rate of the treated polymer surface (about 50–200 μm/h depending on the fluence for the treatment) was much higher than that of the normal polymer (1.2 μm/h).¹³ The bulk etch rate of the treated polymer decreased along the depth and below the laser affected depth of the polymer it saturated at its normal constant value.¹³ The depth of the treated region was thus estimated to be in the range of 8–30 μm when the fluence of the treating laser beam was varied from 10–40 J/cm².

PHYSICAL FORM AND MICROSTRUCTURE OF THE TREATED SURFACE

To the unaided eye, CR-39 sheets treated at low fluences (up to 20 J/cm²) appeared like the normal ones with the same optical clarity. In the samples treated at higher laser fluences, very shallow non-uniformities started appearing at the surface. These nonuniformities corresponded to similar variations in the spatial intensity distribution of the laser beam used for the treatment. Beyond the fluence for the volatile decomposition in CR-39 which is found to be 25 J/cm²,¹² the transparency of the treated region started reducing and the formation of a thin yellowish translucent layer took place.

Laser treatment resulted in the formation of a heterogeneous microstructure with interlinked polymer clusters and pores. It makes the treated surface coarse compared to the untreated one. This is shown in Figure 1(a). The average size of a unit (polymer

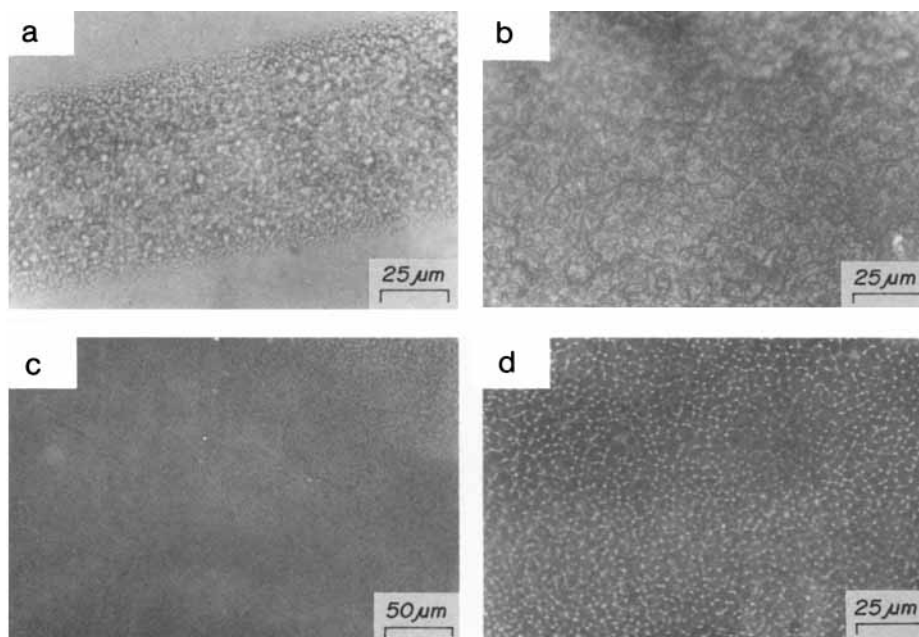


Figure 1 Optical micrographs of the laser treated surface of CR-39 sheets: (a) surface microstructure formed at the laser fluence of 15 J/cm^2 in reflected light; (b) micrograph of the surface structure at the fluence of 35 J/cm^2 in reflected light; (c) occasional formation of the closed loop wide spread boundaries on the surface beyond 25 J/cm^2 ; (d) transmission micrograph of the polymer sheet, the surface structure of which is shown in (b).

cluster or pore) in the heterogenous structure was found to depend on the power density and the beam residence time of the laser beam. In general, on increasing the laser fluence during the treatment, the size of the resulting microstructures increases as seen in Figure 1(b). Its reason has been discussed later. Near the threshold fluence for the volatile decomposition, the heterogenous structures are enclosed within the continuous boundaries of different shapes and sizes which is shown in Figure 1(c). The microstructure of the treated region in the transmitted light is shown in Figure 1(d). Inhomogenous density distribution with micro pores in the surface region of the laser treated CR-39 are clearly evident in this micrograph.

Normally, the heterogenous structure in the treated region is uniformly distributed on the surface. If there is some compositional or structural irregularity, scratch, pit, or contaminant present at some location on the surface, the local optical and thermophysical properties are modified. This results in a nonuniformity in the treated region. Structural nonuniformity due to a nonuniform absorption of the laser radiation at the surface of the polymer is shown in Figure 2(a). The density of the clusters

and pores is increased in the region of higher absorption and reduced where the absorption is relatively weak (near the top in the micrograph). These nonuniformities in the absorption were due to compositional irregularities in the polymer itself. The effect of increased local absorption in a micropit at the surface can be seen in Figure 2(b). Such nonuniformities are expected to change the local hardness at the treated surface correspondingly. Another type of surface nonuniformity can be introduced because of the release of certain decomposition products which are not volatile and are formed slightly below 25 J/cm^2 . The surface irregularity due to such products is shown in Figure 2(c). A nonuniformity which results from the combined effect of the irregularity in the absorption and deposition of the decomposition products is shown in Figure 2(d).

DEPENDENCE OF THE SURFACE HARDNESS ON THE LASER PARAMETERS

Variation of the hardness of the laser treated surface (H_L) relative to that of the untreated one (H_N) with respect to the laser power density at a constant beam

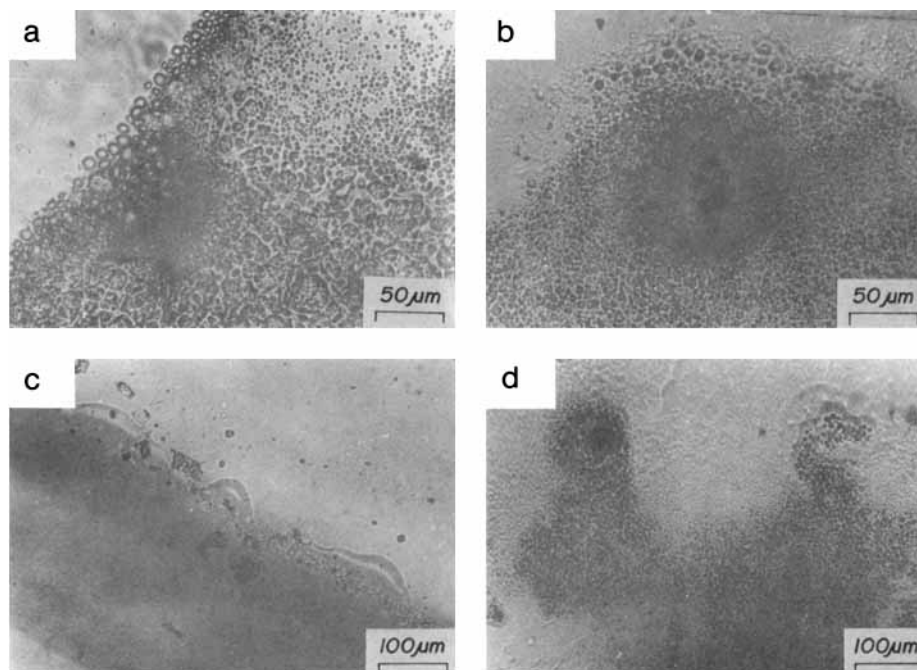


Figure 2 Different types of nonuniformities in the laser treated surface of CR-39: (a) effect of nonuniform absorption of the laser radiation due to compositional irregularities in the polymer sheet (clean region on the left side is untreated); (b) microstructure in and around a micropit on the surface which absorbed excessive energy from the laser beam during the treatment; (c) deposition of the viscous decomposition products (right side) near the boundary of the laser treated zone; (d) surface nonuniformities resulting due to irregular absorption and deposition of the viscous decomposition products. These micrographs are in reflected light.

residence time is shown in Figure 3. For power densities below the threshold for the volatile decomposition (25 J/cm^2), the hardness decreases rapidly on increasing the power density and beyond this threshold, the hardness tends to saturate. It is apparent from this figure that the surface hardness of CR-39 can be reduced to about 60% of its original value before the surface starts degrading due to the laser induced chemical decomposition beyond 25 J/cm^2 . The curve in Figure 3 has been extrapolated towards the lower power densities to a point where the hardness of the treated surface becomes equal to that of the normal one (relative hardness = 1). From this extrapolation it can be seen that the threshold power density for the onset of softening is about 250 W/cm^2 when the beam residence time is 35 ms. From these figures, the threshold fluence for the laser softening at $\lambda = 10.6 \mu\text{m}$ in CR-39 can be worked out to be about 8 J/cm^2 .

Dependence of the softening on the beam residence time for a constant power density of the laser beam is shown in Figure 4. A similar trend of sat-

uration in the softening beyond the threshold fluence for the volatile decomposition is also apparent from this figure. The value of the threshold fluence for the onset of softening as obtained from the extrapolated curve of this figure turns out to be about 10 J/cm^2 . This value is slightly higher than that obtained in the previous case. This difference can be explained from the difference in the beam residence time in the two cases. At a shorter beam residence time (as in Fig. 4) larger fluence would be required for the onset of softening which depends on the kinetics of the basic mechanism responsible for this process. This has been discussed in detail later. An average value of the threshold fluence for softening can be taken as 9 J/cm^2 . Experimental values for the hardness of the treated surface at and below the threshold fluence for the softening could not be obtained because of practical limitations. The main limitation was that at these fluences the thickness of the softened layer was found to be comparable or less than the depth of the indentation which the pyramidal tip of the hardness tester formed in the

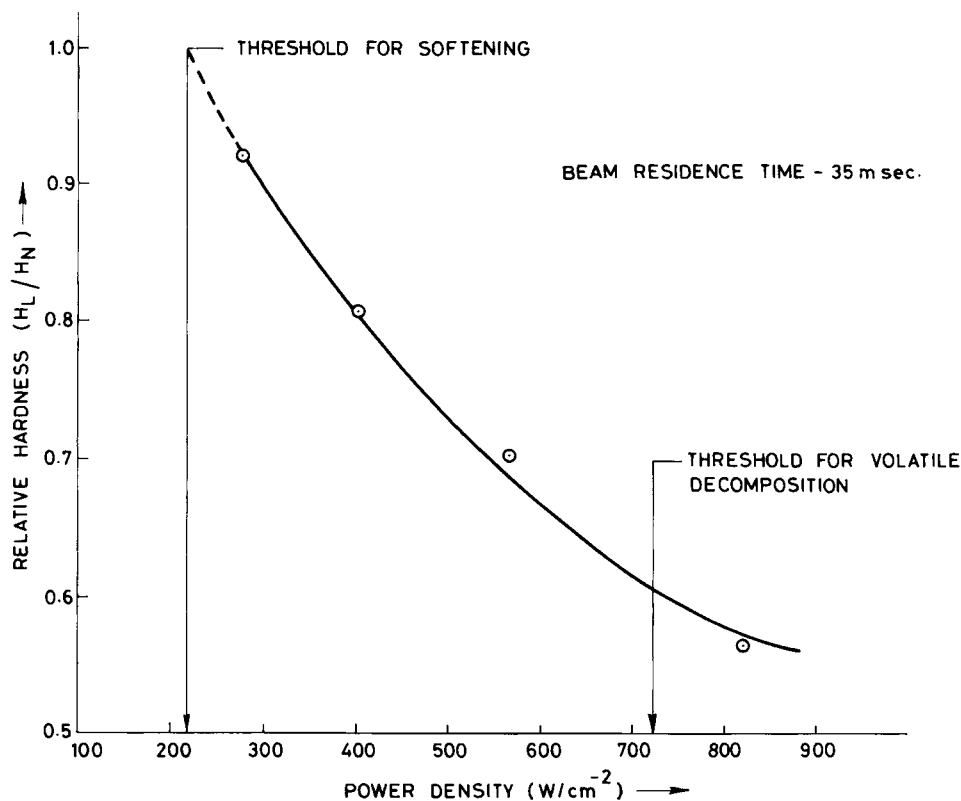


Figure 3 Hardness of the laser treated CR-39 surface (H_L) relative to that of the untreated one (H_N) at different power densities and a constant beam residence time of the CO₂ laser beam.

polymer. This rendered the measurements unreliable as stated earlier.

THERMAL EVOLUTION IN THE LASER HEATED POLYMER

A detailed knowledge of the thermal evolution in the polymer interacting with the laser beam is necessary for proper understanding of the resulting effects stated above. For studying the thermal evolution, we treat the laser as an optical source of heat and use the method of finite differences¹⁴ to solve the time-dependent heat flow equation. The temporal variation of the temperature at different depths in the polymer, distribution of the absorbed energy in various thermal processes, and the surface cooling rate have thus been calculated. From these data and the experimentally investigated thermal behaviour of the CR-39 it would be possible to understand the effects of the laser treatment on the polymer.

Let us consider a cw laser beam incident normally

on the polymer sheet moving at a constant speed. Because the diameter of the laser beam (5 mm) is much larger than the thickness of the thermally affected polymer (typically less than 30 μm), the problem of heat diffusion under these conditions may be treated as 1-dimensional and we have^{14,15}:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left[\frac{k}{\rho c} \cdot \frac{\partial T}{\partial z} \right] + \frac{\alpha}{\rho c} I(z, t) \quad (2)$$

where T , t , k , ρ , c , and α denote the temperature, time, thermal conductivity, mass density, specific heat, and linear attenuation coefficient of the polymer for the laser radiation, respectively. $I(z, t)$ is the laser intensity at depth z and time t . For a homogenous absorbing medium it is given by:

$$I(z, t) = I_0(t)(1 - R)\exp(-\alpha z) \quad (3)$$

where $I_0(t)$ is the time dependent intensity of the laser beam at the surface and R is its reflection coef-

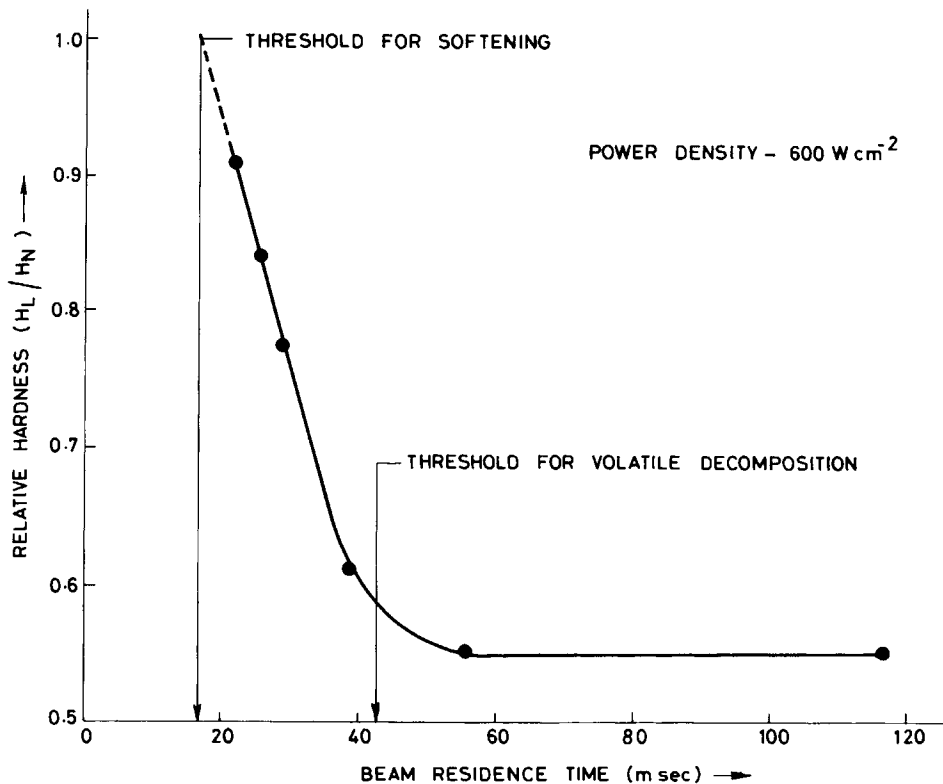


Figure 4 Hardness of the laser treated CR-39 surface (H_L) relative to that of the untreated one (H_N) at various beam residence times and a constant power density of the CO_2 laser beam.

ficient. Although the actual laser beam had a radial intensity profile of $\text{TEM}_{00} + \text{TEM}_{10}$ mode, for the present calculations the radial intensity distribution is taken to be flat. As a result, the temporal profile of the interacting laser beam will also be flat over the time equal to the beam residence time (τ_p). The functional form of $I_0(t)$ based on these considerations was taken to be:

$$I_0(t) = I_{\max} = E/\tau_p, \quad 0 \leq t \leq \tau_p \quad (4)$$

$$= 0, \quad t > \tau_p$$

Here I_{\max} is the cw intensity on the surface of the polymer and E is the fluence.

The solution of (2) has to be carried out numerically because some of the physical properties are taken to be temperature dependent and an irreversible term for the depolymerization energy is incorporated in these calculations. We have used the method developed by Jain et al.¹⁵ with certain modifications to take care of mainly the laser induced depolymerization. In this method, the relevant portion of the polymer sheet is divided into a number of thin layers along the depth. If the temperature of

a layer (say i th) at time t is T_i^0 , we want to know its temperature T_i at time $t + \Delta t$. Here Δt is a small interval of time over which the temperature of each layer is assumed to be constant. Each layer will have a definite set of thermophysical properties depending on its temperature. The layer at the surface is numbered as i_0 . We define ΔZ_i as the thickness of the i th layer. The intensity I_{i_0} incident on the surface and I_{i+1} incident on the $(i+1)$ th layer can therefore be given by:

$$I_{i_0} = I_0(t)(1 - R) \quad (5)$$

$$I_{i+1} = I_i \exp(-\alpha \Delta Z_i), \quad i \geq i_0 \quad (6)$$

The temperature of the $(i+1)$ th layer will change because of the direct absorption of the laser energy and also due to the diffusion of heat from i th layer and to $(i+2)$ th layer. The effects of surface cooling due to the radiation losses and heat flow to the atmosphere are negligible; therefore, we have not included those in these calculations.

The energy absorbed per unit area in the i th layer

from the laser radiation in a small interval Δt is given by:

$$\Delta Q_{\text{abs}} = (I_i - I_{i+1}) \Delta t, \quad i \geq i_0 \quad (7)$$

If T_i^0 is the temperature of the i th zone at time t , the contribution from diffusion of heat over the small interval Δt will be given by:

$$\Delta Q_{\text{diff}} = [(T_{i-1}^0 - T_i^0) + (T_{i+1}^0 - T_i^0)] k \Delta t / \Delta Z_i \quad (8)$$

where k is the thermal conductivity of the polymer. Under the assumption of no heat flux at the surface only the second term in (8) is to be taken for $i = i_0$. The temperature T_i of the i th layer at time $t + \Delta t$ is then given by:

$$T_i = T_i^0 + [(\Delta Q_{\text{abs}} + \Delta Q_{\text{diff}}) / C_i \rho \Delta Z_i] \quad (9)$$

here ρ is the density of the polymer and C_i is the specific heat of the i th layer. Specific heat of the polymer has been measured using differential scanning calorimeter at different temperatures and given in Table I (as C'_i , C''_i). As can be seen in this table, C_i is constant (C'_i) up to 155°C . Beyond this temperature it increases with temperature at a rate given in Table I. To account for this an additional component (C''_i) is added to C'_i . It has also been found from thermo-mechanical and thermo-gravimetric analysis of CR-39 that depolymerization in this polymer is initiated beyond a temperature of 262°C . Therefore, for temperature greater than 262°C , an additional term of depolymerization energy (C_d) is included in C_i and the value of $C'_i + C''_i$ is taken constant. Mathematically it is expressed as follows:

$$\begin{aligned} C_i &= C'_i, & \text{for } t \leq 155^\circ\text{C} \\ C_i &= C'_i + C''_i, & \text{for } 155 < T \leq 262^\circ\text{C} \\ C_i &= C'_i + C''_i + C_d, & T > 262^\circ\text{C} \end{aligned} \quad (10)$$

The value of C_d , which is the temperature dependent depolymerization specific energy is also given in Table I. An important feature of C_d is that it is irreversible [i.e., it is included in (9) only during the heating (for $t \leq \tau_p$) and not during the cooling]. As a consequence of this, the cooling rate becomes higher than its value which would have resulted if this term was reversible.

If the absorbed laser energy (E_{abs}) raises temperature of the polymer to 262°C or more, a part of this absorbed energy is used up in the depolymer-

ization. To calculate the energy used in the depolymerization (E_{dep}), the total heat content (E_{con}) of the polymer sheet is found at the end of the laser heating. In different temperature ranges it is calculated from the following expressions:

for $T \leq 155^\circ\text{C}$,

$$\begin{aligned} E_{\text{con}} &= \sum_i \left[\int_{T_r}^{T_i} C'_i \rho \Delta Z_i dT \right] \\ &= \sum_i [C'_i \rho \Delta Z_i (T_i - T_r)] \end{aligned} \quad (11)$$

for $155 < T \leq 262^\circ\text{C}$

$$\begin{aligned} E_{\text{con}} &= \sum_i \left[\int_{T_r}^{155} C'_i \rho \Delta Z_i dT \right. \\ &\quad \left. + \int_{155}^{T_i} (C'_i + C''_i) \rho \Delta Z_i dT \right] \\ &= \sum_i \rho \Delta Z_i \left[C'_i (T_i - T_r) + \int_{155}^{T_i} C''_i dT \right] \end{aligned}$$

using $C''_i = a(T - 155)$ where $a = 6.093 \times 10^{-3}$ (from Table I), the above expression can be simplified as:

$$\begin{aligned} E_{\text{con}} &= \sum_i \rho \Delta Z_i \left[C'_i (T_i - T_r) \right. \\ &\quad \left. + a \int_{155}^{T_i} (T - 155) dT \right] \\ &= \sum_i \rho \Delta Z_i [C'_i (T_i - T_r) \\ &\quad + a/2 (T_i - 155)^2] \end{aligned} \quad (12)$$

for $T > 262^\circ\text{C}$

$$\begin{aligned} E_{\text{con}} &= \sum_i \left[\int_{T_r}^{155} C'_i \rho \Delta Z_i dT \right. \\ &\quad \left. + \int_{155}^{262} (C'_i + C''_i) \rho \Delta Z_i dT \right. \\ &\quad \left. + \int_{262}^{T_i} (C'_i + C_k) \rho \Delta Z_i dT \right] \end{aligned}$$

where C_k is the constant value of C''_i for temperatures equal to and more than 262°C . From Table I this value of C_k turns out to be 651.95×10^{-3} . Using this value of C_k , the above expression can be written as:

Table I Physical Properties of CR-39 Used in the Calculations

| Property | Value | Unit |
|---|--|--|
| Density (ρ) | 1.32 | g cm^{-3} |
| Conductivity (k) | 3.241×10^{-4} | $\text{W cm}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Attenuation coefficient (α) (for $10.6 \mu\text{m}$) | 1.1×10^{-2} | μm^{-1} |
| Reflectivity (R) (at $10.6 \mu\text{m}$) | 0.04 | — |
| Specific heat (C_i') | 2.301, $T \leq 155^\circ\text{C}$ | $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| (C_i'') | $6.093 \times 10^{-3} (T - 155)$, $155 < T \leq 262^\circ\text{C}$ | $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Specific depolymerization energy (C_d) | $5.433 \times 10^{-2} (T - 262)$, $T > 262^\circ\text{C}$ | $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$ |

$$E_{\text{con}} = \sum_i \rho \Delta Z_i [C_i'(T_i - T_r) + \alpha/2(262 - 155)^2 + C_k(T_i - 262)] \quad (13)$$

In the above expressions T_r is the room temperature at which the polymer sheet was before the laser heating. T_i is the temperature of the i th zone. The energy used up in the depolymerization E_{dep} is then calculated using eqs. (11)–(13) from the following expression:

$$E_{\text{dep}} = E_{\text{abs}} - E_{\text{con}} \quad (14)$$

Using the procedure outlined above, calculations have been carried out for the CR-39 sheets moving under a cw- CO_2 laser beam at different fluences and beam residence times. Calculations were carried out for the complete depth of 1.5 mm in the polymer sheet with a step of $\Delta Z = 2 \mu\text{m}$ for the first $100 \mu\text{m}$ and $\Delta Z = 10 \mu\text{m}$ for the remaining depth of $1400 \mu\text{m}$. The time step in these calculations was taken to be 0.1 ms , which satisfies the condition for the convergent solution¹⁶ given as:

$$k \Delta t / [\rho C_i (\Delta Z_i)^2] < 0.5 \quad (15)$$

Total time for studying the thermal evolution was taken to be 100 ms . This time was found to be sufficient because beyond this time the temperature in the polymer comes to a level where no significant thermal effect can take place.

The optical and thermophysical properties of CR-39 used in these calculations are given in Table I. Some of the physical properties like the mass density, thermal conductivity, and specific heat at room temperature were available in Ref. 3. Other prop-

erties such as reflectivity and attenuation coefficient at $\lambda = 10.6 \mu\text{m}$ were found experimentally by measuring the reflected (at an incidence angle of 5°) and transmitted powers (at normal incidence) from the CR-39 sheet of known thickness. The intensity in this experiment was kept only about 200 mW/cm^2 which is much below the threshold for any thermal change in this polymer. The temperature dependent specific heat and the depolymerization specific energy were found using a differential scanning calorimeter.

Figure 5 shows the calculated temporal profiles of the temperature at different depths in the CR-39 sheet heated with the CO_2 laser beam at the threshold fluence for softening (i.e., 9 J/cm^2 and beam residence time of 17 ms). Under these conditions, the polymer surface attains a maximum temperature of about 280°C at the end of the beam residence time. It can also be seen from this figure that the heating rate due to direct absorption of the laser beam and the resulting temperatures attained in the successively lower depths reduce. The top layer starts cooling after the direct laser heating while the layers below the depth of about $100 \mu\text{m}$ continue to heat up due to conduction of heat from the upper layers along the depth.

The rate of cooling at the surface of the heated polymer is also shown in Figure 5 by the broken curve. The initial value of the rate of cooling is about $10^3 \text{ }^\circ\text{C/s}$. The maximum surface temperature and its cooling rate are found to depend on the power density and beam residence time of the laser beam during the treatment as expected. At a fluence of 9 J/cm^2 and a beam residence time of 35 ms , the peak temperature at the surface was computed to be 272.3°C and the maximum surface cooling rate to

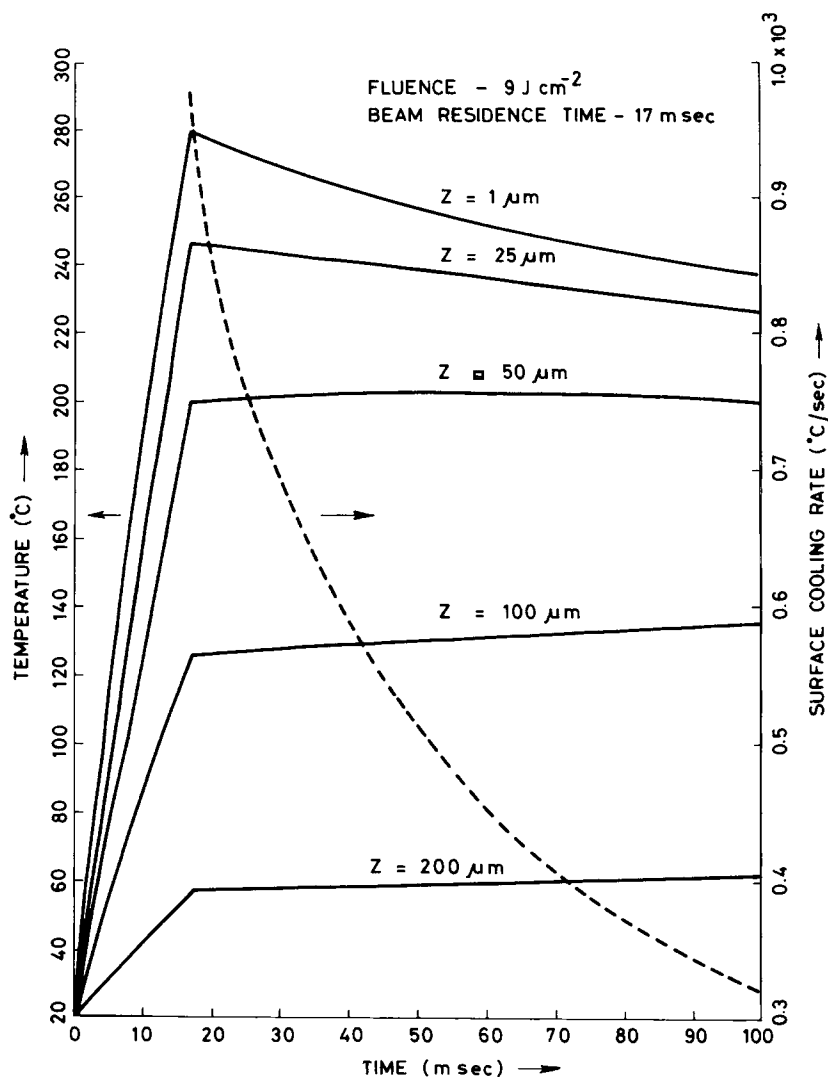


Figure 5 Calculated temporal profiles of the temperature at different depths (values of Z given on the curves) in the CR-39 sheet moving at a constant speed under the cw- CO_2 laser beam. The broken curve shows the rate of cooling at the surface.

be $0.969 \times 10^3 \text{ }^{\circ}\text{C}/\text{s}$. At the threshold fluence for the volatile decomposition (i.e., $25 \text{ J}/\text{cm}^2$) the maximum surface temperature and the cooling rate were found to be 428.3°C and $1.33 \times 10^3 \text{ }^{\circ}\text{C}/\text{s}$, respectively for the beam residence time of 35 ms. For a slightly longer beam residence time of about 42 ms these values were 426.9°C and $1.24 \times 10^3 \text{ }^{\circ}\text{C}/\text{s}$, respectively. These power densities and beam residence times were chosen so as to analyze the results at the onset of depolymerization and volatile decomposition as discussed earlier.

The portion of the absorbed laser fluence which is consumed for the depolymerization was calculated using expressions (11)–(14) given earlier. It was found that at the incident fluence of $9 \text{ J}/\text{cm}^2$ only

0.007 and $0.001 \text{ J}/\text{cm}^2$ are used up for the depolymerization for the beam residence time of 17 and 35 ms, respectively. At $25 \text{ J}/\text{cm}^2$, 4.480 and $4.462 \text{ J}/\text{cm}^2$ go in for the depolymerization at the beam residence times of 35 and 42 ms, respectively.

The calculations discussed above have been carried out under certain simplifying assumptions. These assumptions are as follows:

- All the physical properties except the specific heat and the depolymerization energy are taken to be independent of the temperature.
- The optical properties of the polymer are taken to be independent of its temperature and the intensity of the laser beam.

- (c) Spatial intensity distribution and hence the temporal intensity profile of the laser beam are taken to be flat.

DISCUSSION

In the preceding section, it is seen from the calculated temperature profiles that at the threshold fluence for the onset of softening (i.e., 9 J/cm^2), the polymer surface attains a maximum temperature of about 280°C . At the threshold fluence for the volatile decomposition (i.e., 25 J/cm^2) peak temperature at the surface turns out to be about 428°C . On the basis of the thermo-mechanical and thermo-gravimetric analysis of CR-39, it has been found that the polymer chain scission or depolymerization initiates at 262°C and the volatile decomposition sets in at about 310°C . From these observations it is apparent that the softening in CR-39 is because of the laser-induced depolymerization.

According to the theoretical calculations the softening initiates at a laser fluence for which the polymer surface attains a temperature of about 280°C while the experimentally known temperature for the onset of depolymerization is about 260°C . This difference could be explained as follows.

Some minimum level of depolymerization would be necessary for obtaining an observable softening at the polymer surface. The total amount of the depolymerized material depends on the rate of depolymerization and the time for which the process continues. The rate of depolymerization depends on the temperature of the polymer. During the laser treatment the heating is transient (over a few milliseconds). Therefore, a higher rate of depolymerization would be necessary to obtain sufficient depolymerization for observing the softening. As a result, a higher temperature for the onset of softening would be required in the case of laser heating. On the other hand, the experimentally measured temperature for the onset of depolymerization was under the steady state conditions (rate of heating about $5\text{--}10^\circ\text{C/min}$). From these considerations the difference in the temperatures for the onset of laser softening and the onset of depolymerization in steady state conditions is expected.

A similar reason is also valid for explaining the difference between the calculated and experimentally found temperatures for the onset of volatile decomposition in CR-39. The calculations have also shown that when the laser fluence is increased from 9 to 25 J/cm^2 the portion of the input fluence which goes in for the depolymerization increases from av-

erage value of about $0.004\text{--}4.5 \text{ J/cm}^2$. This portion would increase the extent of polymer chain scission which in turn appears to be responsible for the increasing softness on increasing the fluence (Fig. 3 and 4). After the threshold fluence for the volatile decomposition is reached, most of the subsequent excess fluence is used up in the volatile decomposition. As a result further increase in the depolymerization becomes insignificant. This explains the tendency of saturation in the softness at the surface of the treated CR-39 beyond the threshold fluence for the volatile decomposition as seen in Figures 3 and 4. It was seen in Figure 1 that the size of microstructure increases with the fluence of the treating laser beam. This could be explained as follows.

The calculated surface cooling rate at 9 J/cm^2 is about 10^3°C/s while it increases to about $1.3 \times 10^3^\circ\text{C/s}$ at 25 J/cm^2 . From the temporal temperature profiles at the surface of the polymer it is also noticed that the surface remains at a temperature more than that for the depolymerization for a longer time at 25 J/cm^2 than that at 9 J/cm^2 . Although in the absence of information on the kinetics of the depolymerization and that of the clustering of the depolymerized units (oligomers) it is difficult to state a precise reason for the dependence of the size of the microstructure on the laser fluence. One possible reason could be that the time for which the surface of the polymer is at a temperature more than that for the depolymerization turns out to be longer at the higher fluence, and therefore the oligomer clusters grow to a larger size. Further, the large surface cooling rates (in excess of 10^3°C/s) following the laser-induced depolymerization could also play a significant role in the formation of the heterogeneous porous microstructure in the treated surface of this polymer as discussed in section 2. The oligomers formed due to the interaction of the laser with the polymer, when frozen at a rapid cooling rate, result in the formation of a metastable structure. This is because the oligomers do not get time to settle in the most stable state. A possible reason for the formation of the voids in the surface microstructure could be that the gases released during the laser heating are trapped in the rapidly cooling polymer surface. These gases could be either those released because of the photodecomposition of the polymer itself or the occluded gases and moisture, etc., released on heating the polymer.

Finally, from the preceding results and discussion it is established that the controlled laser treatment of CR-39 sheets in the fluence range of $9\text{--}25 \text{ J/cm}^2$ results in an irreversible softening at its surface without chemical decomposition in the polymer.

The oligomers formed due to the laser induced depolymerization cool rapidly resulting in a heterogeneous porous microstructure. This microstructure and the basic fact that the strong covalent bonds between the monomers are broken during the laser induced depolymerization explain the softening. Once the volatile decomposition initiates at 25 J/cm² the softening tends to saturate and also the optical clarity of the surface begins to degrade. Therefore in the range of 9–25 J/cm² a useful surface modification of CR-39 can be done with a CO₂ laser.

APPLICATIONS

The laser induced irreversible surface softening in the thermoset polymer of CR-39 may have many practical uses. Some of them are thought to be the following ones:

1. The surface softened CR-39 could also prove superior in making eye implants like contact lenses¹⁷ and artificial cornea, etc. The soft surface would help in reducing the mechanical irritation with the eye tissues and porous microstructure will possibly help in the diffusion of the oxygen and the metabolites produced at the polymer–tissue interface.¹⁸
2. The microporosity in the treated polymer could be useful for grafting over biological organs where the surface diffusion of oxygen is desired (e.g., for grafting over burnt skin).
3. It may improve printing on this polymer because of formation of the free bonds of the oligomers and resulting softness of the surface.
4. It may improve the binding of this polymer with adhesives due to the coarse microstructure and the free bonds of the oligomers.
5. This process could also possibly help in making a semi-permeable membrane on CR-39.
6. Because of the observed increase in the chemical etch rate of the laser treated CR-39, fine engraving can be done in the polymer in a spatially selective manner.

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REFERENCES

1. Modern Plastics Encyclopaedia, **56**, McGraw-Hill, London, 1979–80, p. 11.
2. Modern Plastics Encyclopaedia, **56**, McGraw-Hill, London, 1979–80, p. 501.
3. H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds. *Encyclopaedia of Polymer Science and Technology*, Vol. 1, Wiley-Interscience, New York, 1964, p. 799.
4. L. M. Kukreja, *J. Appl. Polym. Sci.*, **33**, 985 (1987).
5. G. F. Kinney, *Engineering Properties and Applications of Plastics*, Wiley, New York, 1975, pp. 3–4.
6. H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds. *Encyclopaedia of Polymer Science and Technology*, Vol. 4, Wiley-Interscience, New York, 1966, p. 651.
7. E. V. Locke, *Opt. Eng.*, **17**, 192 (1978).
8. R. A. Hella, *Opt. Eng.*, **17**, 198 (1978).
9. E. M. Breinan, B. H. Kear, and C. M. Banas, *Phys. Today*, **29**, 44 (1976).
10. H. R. Simonds, A. J. Weith, and M. H. Bigelow, *Handbook of Plastics*, Van Nostrand, New York, 1943, pp. 1114–1174.
11. L. M. Kukreja, S. K. Sehgal, U. K. Chatterjee, and D. D. Bhawalkar, *J. Phys. D.*, **19**, 417 (1986).
12. L. M. Kukreja, D. D. Bhawalkar, U. K. Chatterjee, and B. L. Gupta, *Appl. Phys. A*, **36**, 19 (1985).
13. L. M. Kukreja, V. B. Joshi, A. M. Bhagawat, U. K. Chatterjee, and D. D. Bhawalkar, *Nucl. Instrum. Meth., B.*, **28**, 369 (1987).
14. P. Baeri, S. U. Campisano, G. Foti, and E. Rimini, *J. Appl. Phys.*, **50**, 788 (1979).
15. A. K. Jain, V. N. Kulkarni, and D. K. Sood, *Appl. Phys.*, **25**, 127 (1981).
16. V. W. Arden and K. N. Astill, *Numerical Algorithms: Origins and Applications*, Addison-Wesley, London, 1970, p. 280.
17. Y. Mizutani and K. Eguchi, *Nippon Ganka Gakki Zosshi*, **66**, 379 (1962).
18. H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds. *Encyclopaedia of Polymer Science and Technology*, Vol. 1, Wiley-Interscience, New York, 1964, p. 195.

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