Irreversible Softening in a Thermoset Polymer–Allyl Diglycol Carbonate® due to Laser Treatment

It is understood that a thermoset polymer degrades on heating. With the advent of lasers for industrial applications, it has become possible to carry out a clean thermal treatment of the materials with fine spatial and temporal controls. Using lasers unusually large heating and cooling rates have also been achieved.[1] As a result many new surface effects have been observed mainly on metals and semiconductors.[1,2] Laser processing of polymers is well known,[3] particularly for commercial production, but very little has been reported on the laser surface treatment of polymers and laser–polymer interactions in general. At our laboratory, laser processing of a hard and brittle thermoset polymer of Allyl Diglycol Carbonate (ADC) has been investigated.[4] In subsequent experiments on controlled treatment of the ADC polymer using a continuous wave (cw) CO_2 laser, it has been found that the surface hardness of this polymer (Rockwell M95-100) can be reduced significantly and permanently without affecting its bulk properties. This phenomenon is being reported in this communication.

A 125 W cw CO_2 laser developed at our laboratory was used for the treatment of the ADC polymer sheets (1.6 mm thick; manufactured by SGL Homalite, USA). The laser beam of 10.6 μm wavelength was focussed with an astigmatism-free arrangement of mirrors.[4] The spot diameter of the laser beam on the polymer surface was kept 5 mm. The polymer sheets were held on a turntable and moved at a constant speed of 14.3 cm/s while interacting with the laser beam. The interaction time (= laser spot diameter/speed of the polymer sheet) was thus kept constant at about 35 ms. The fluence of the interacting laser beam on different pieces of the polymer sheet, was varied by changing power of the laser between 5 and 125 W.

The hardness of the treated surface (H_L) and that of the untreated one (H_N) were measured using a Vickers Hardness Tester. The relative hardness (H_L/H_N) of the polymer surface in separate pieces treated at different laser fluences is shown in Figure 1. Clearly, the hardness reduces on increasing the fluence and tends to saturate beyond a fluence of about 25 J cm^{-2}. At this fluence, volatile decomposition is initiated[4] in ADC and its optical clarity starts diminishing. It is apparent from Figure 1 that under the present conditions of the treatment in respect of the interaction-time, power density, sample thickness and wavelength of the laser, surface hardness of the ADC sheets can be decreased to about 60% of its original value before the onset of optical degradation. It can also be seen from the extrapolated curve of this figure that the threshold fluence for the softening is about 8 J cm^{-2}. The thickness of the softened layer is found to increase with the fluence. It has been estimated that when the laser fluence is increased from 10 to 25 J cm^{-2} the softened layer thickness increases from about 15 to 40 μm. This estimation of the thickness is based on the experimental observation of increase in the chemical etch rate of the laser treated region on the ADC sheets in 6N KOH solution at 60°C in the present case. The thickness of the softened layer was taken to be the depth at which the chemical etch rate attains its normal value for the untreated polymer.

Detailed studies have yet to be carried out to understand this phenomenon, its reason and related physico-chemical effects. Preliminary investigations on the treated samples show that the laser-induced softening is due to a structural transformation in the polymer. It is observed that a heterogeneous porous microstructure is formed in the laser-treated surface. An optical reflection micrograph of the laser treated surface is shown in Figure 2. Using differential scanning calorimetric, thermomechanical and thermogravimetric techniques it has been found that thermal depolymerization or structural decomposition in the polymer of ADC begins at about 270°C. Theoretical solution of the one-dimensional heat diffusion equation[5] under the practical conditions of the laser treatment of ADC polymer has shown that at the laser fluence of 9 J cm^{-2}, which is slightly more than the threshold fluence for softening, the polymer surface attains the
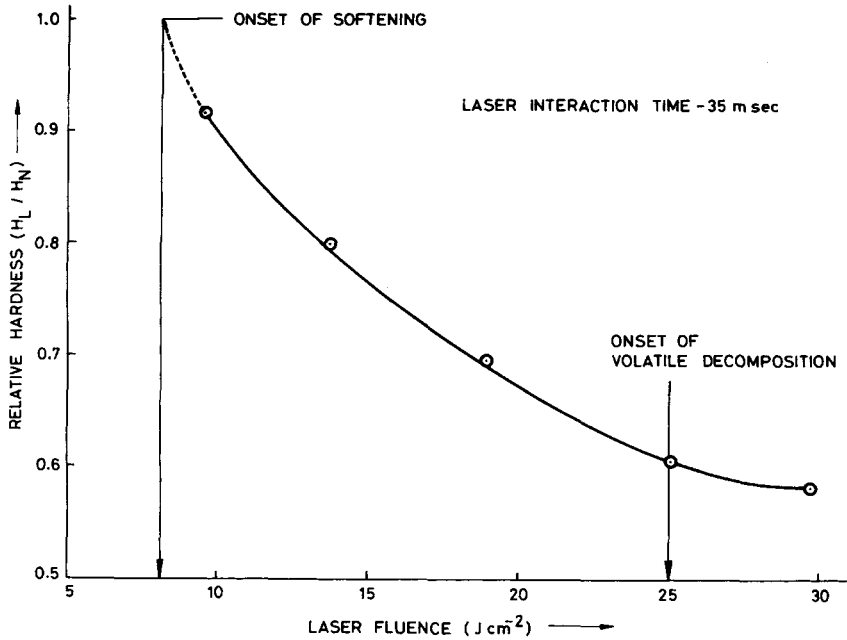
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Fig. 1.   Hardness of the laser treated CR-39® surface (H_L) relative to that of the untreated one (H_N) at various fluences of the CO_2 laser beam, used for the treatment.
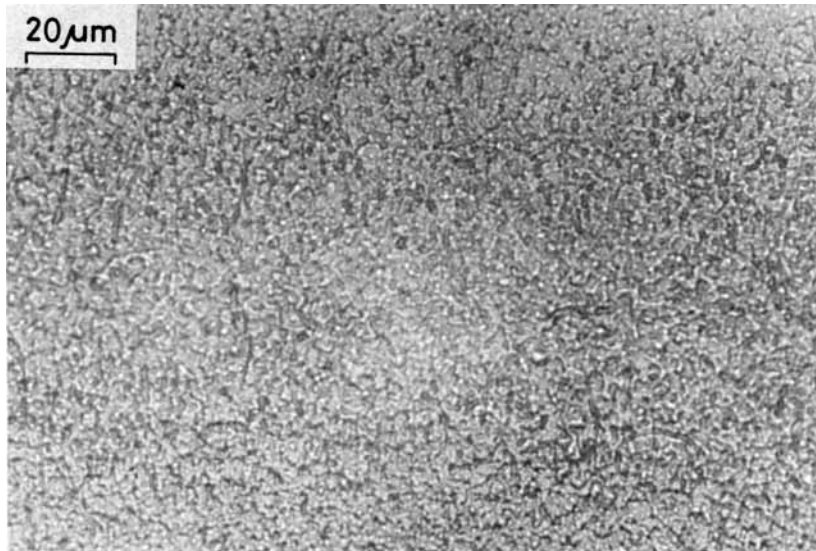

Fig. 2.   Optical reflection micrograph of the laser treated CR-39® surface. This surface structure is formed at the CO_2 laser fluence of about 17.5 J cm^{-2}.

maximum temperature of about 280°C. From these experimental data and the theoretical results which are matching within the acceptable limits, it is obvious that the laser softening is basically due to the depolymerization or structural decomposition in the polymer. Possibly, the rapid cooling, which is estimated to progress at a rate of the order of 10^3°C/s immediately after the laser heating, also plays an important role in the formation of the porous heterogeneous microstructure in the treated polymer. Further, it has also been calculated using the experimentally measured temperature dependent structural decomposition energy of the ADC polymer that at the incident laser fluence of 9 J cm^{-2}, about 0.001 J cm^{-2} is used up for the structural decomposition and the remaining fluence raises the temperature of the polymer sheet. At the incident fluence of 25 J cm^{-2}, the portion of the absorbed energy which goes in for the decomposition increases to about 4 J cm^{-2}. As the fraction of the incident energy consumed for the decomposition increases, a corresponding increase in the magnitude of the structural decomposition is expected which in turn would result in enhanced softness. This explains the experimentally observed decrease in the hardness on increasing the fluence (Fig. 1). Beyond the threshold fluence for the volatile decomposition, most of the excess energy is consumed in the chemical decomposition resulting in the formation of volatile products and further increase in the extent of depolymerization becomes insignificant. This leads to the tendency of saturation in the hardness of the laser treated polymer at the fluences beyond 25 J cm^{-2}.

Surface softening of the hard polymer ADC with its bulk properties unchanged, may have many practical uses. For example, it will possibly improve printing on this polymer, strengthen adhesion with resins and make it more suitable for eye implants like contact lenses and artificial cornea. Currently a detailed parametric investigation is being carried out on this phenomenon.

References

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