SOME STRUCTURAL CHANGES IN CELLULOSE UNDER
THE ACTION OF PULSED LASER RADIATION

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With the emergence of lasers, studies have been commenced actively on the effect of light pulses on the
structure and properties of highly absorbing materials such as metals, alloys, semiconductors, etc. In the
case of transparent media (glasses, crystals, polymers) studies have usually been limited to analyzing the
mechanism of their fracture [1, 2]. Virtually no studies have been made on the structures which should arise
under the action of irradiation and on the effect of the spectral characteristics of laser radiation on these
changes; also a number of procedural problems remain unsolved. However, such investigations are important
both from the point of view of acquiring a clearer understanding of the nature of the damage in such materials
and from the point of view of explaining their ability to undergo structural rearrangement under sufficiently
specific conditions (short exposure times, high temperatures and pressures, etc.).

Especially interesting are polymers which tolerate the existence of various supramolecular structures
and conformers [3]. Sometimes the damage in a polymer appears only after the action of a series of pulses,
each of which does not cause marked damage. The fracture threshold is lowered greatly here. For example,
in the case of polymethyl methacrylate it may be lowered by a factor of approximately three if the material
has been previously subjected to the action of 4–5 pulses [4]. It can be assumed that such a preliminary action
stimulates changes in the structure, facilitating the subsequent damage.

From a few studies [5–8] it is known that the physical structure of an important polymer, cellulose, is
sensitive to laser radiation. In [5] it was shown that the irradiation of cellulose triacetate (CTA) films by
monochromatic radiation from a CO2–N2–He laser favors conformational transitions which lead to the
crystallization of CTA and accelerates this process appreciably. The laser emission frequency (943.4 cm⁻¹)
[5] corresponded to the edge of the absorption band in the IR spectrum of CTA (let us call it the resonance
frequency). For such a type of selective action the spectroscopic signs of the crystallization of CTA (the new
bands 440 and 525 cm⁻¹ and the splitting of the 480-cm⁻¹ band into two at 475 and 485 cm⁻¹) appeared after
irradiation for 0.02–1 sec. For the normal temperature effect which leads to such a result this period was
varied from 0.5 min to 3 h, depending on the thickness of the film. According to the data in [6–8] the cellulose
"crystallites" melted when acted upon by a 120-W continuous CO2 laser for 1 msec.

In the present investigation we consider the spectroscopic detection of structural changes which may
take place in acetate and hydrocellulose (HC) films under pulsed laser action. The materials investigated

<table>
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<th>Power density, W·10⁶</th>
<th>Availability, %</th>
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<tr>
<td>W/cm²</td>
<td></td>
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<tr>
<td>0</td>
<td>78</td>
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<tr>
<td>2.04 (2 pulses, 1,02 each)</td>
<td>76.8</td>
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<tr>
<td>5.08 (3 pulses: 1.88; 1.27; 1.93)</td>
<td>53.4</td>
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<td>3.75</td>
<td>38.5</td>
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were industrial CTA films of different thickness, triacetate films obtained by wetting a mercury surface with a solution of the polymer in a methylene chloride/methanol (9:1) mixture, and HC films obtained by the deesterification of the CTA films. In contrast to the industrial specimens, which have always undergone some elongation, CTA films obtained on a mercury surface are completely isotropic.

The samples were irradiated by radiation from a neodymium glass laser [pulse length $\tau = (3-5) \cdot 10^{-4}$ sec, $\nu = 9434$ cm$^{-1}$], a ruby laser [$\nu = (25-30) \cdot 10^{-8}$ sec, 14403 cm$^{-1}$], and a pulsed CO$_2$ laser ($1 \cdot 10^{-7}$ sec, 943.4 cm$^{-1}$). The emission frequencies from these lasers, apparently except for the CO$_2$ laser, are nonresonance for the substances used (we did not use the CO$_2$ laser for CTA). The power density of the emission was varied either by altering the pulse energy or by altering the irradiation area (by moving the sample to a different distance from the focal plane of the focusing lens).

**Structural Changes in CTA Films**

In the investigation, CTA films of thickness $\sim 8 \mu$, whose thermal treatment at a temperature above the glass temperature did not lead to the appearance of spectroscopic signs of crystallization (Fig. 1, curve 2), were studied. However, irradiation of these films by radiation from a neodymium glass laser was accompanied under certain conditions by the appearance of absorption bands characteristic of crystallized samples (Fig. 1, curve 3). With a decrease in power density to $2.5 \cdot 10^6$ W/cm$^2$, no "crystallization" bands are revealed, only changes in the structure-sensitive region 700-800 cm$^{-1}$ taking place (Fig. 1, curve 4).

Thus, intensive action over the course of extremely small intervals of time ($\tau = 10^{-4}$ sec) may lead to profound changes in the packing of CTA macromolecules. It should also be noted that individual spectroscopic signs of three-dimensional ordering also appeared sometimes in the IR spectrum of an isotropic CTA film after the action of radiation from a ruby laser [$\tau = (28-30) \cdot 10^{-8}$ sec]. The appearance of signs of three-dimensional ordering in the polymer has not been noted previously for such short periods. The production of specific structural formations is not excluded completely here.