TRANSPARENT DIELECTRICS STRUCTURE NONTERMAL CHANGES AFTER LASER TREATING

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Changes in the molecular structure of polymethyl methacrylate caused by irradiation with laser pulses of different powers were investigated by x-ray diffractometry methods. An analysis was made of the position and half-width of a halo in x-ray diffractograms. Coherent scattering regions and the distributions of the moduli of the interatomic vectors were determined. Action of laser radiation on this transparent dielectric induced molecular structure changes associated with an increase in the molecular order in the amorphous matrix and with the formation of clusters at certain specific laser radiation energies. Similar effects can be observed in glasses.

Introduction

The physical properties of substances depend on a large number of various factors, which can be divided into four groups: composition, structure, defects, external actions. The last group of factors influences all the others, i.e. external action may alter the composition, the structure, and the defect system. Among the various external factors one should mention heating and cooling, deformation, physicochemical treatments, irradiations, etc. There is much current interest to the processes that occur in condensed media under the action of high-power light pulses. Fairly detailed investigations have been made of changes in the macrostructure of irradiated samples and of the generation of shock and acoustic waves during irradiation.

Changes in the atomic and molecular structure of substances after and during laser irradiation have been studied much less. The attention of investigators has usually been concentrated on changes in the structure and phase composition and on defect formation in metals (particularly steels and iron alloys), semiconductors, and opaque dielectrics. Changes in the microstructure of transparent dielectrics under the action of powerful light fluxes have not been investigated sufficiently thoroughly and the studies have been limited mainly to local phase changes in the films of some glasses when exposed to laser radiation of fixed power.

Our aim was to investigate the dependences of the changes in the atomic and molecular structure of polymethyl methacrylate (PMMA) on the energy of millisecond laser pulses and on the thickness of a sample.

Experimental methods and results

Radiation from a free-running GOR-100M ruby laser (pulse duration $\tau \approx 1.2$ ms, $\lambda = 0.69342$ μm) passed through a focusing system and was directed to the investigated sample. The focusing spot had 2 mm in diameter. The experimentally determined size of the focal region (i.e. of the caustic) of the system did not exceed 2 mm when this laser was used. Some of the laser radiation (~ 4%) was directed by the front face of a glass wedge to an IMO-2N energy meter whose entry pupil was located in the focal plane of a lens. The energy of the laser pulses E_o was varied from 4 to 60 J. Some of the radiation (~ 4%) transmitted by the sample was directed by a second wedge and a lens to another IM0-2N energy meter. Under these conditions we could ignore the energy representing the absorption and re-emission as a result of bremsstrahlung and recombination processes [1] and the energy scattered by the absorption region [2]. The difference between the readings of the two IM0-2N meters was used to find the absorbed energy E_a.

The density and temperature fields of a sample during irradiation were determined by high-speed holographic cinematography [3]. The spatial resolution over the object field was approximately 25 μm and the temporal resolution was 1 μs. The errors in the determination of the refractive index and the associated quantities were governed by the precision in measurement of the shifts of fringes in reconstructed interference patterns, and they did not exceed 10%.

When the thickness of a sample was $l > 3$ mm, the crater profiles and the density and temperature isolines were qualitatively similar to those reported in Ref. [3], if a suitable scaling was applied. The density was calculated from the Lorentz - Lorenz formula. The refractive index needed in such calculations was obtained from interferograms by the Abel transformations. Temperatures were deduced from reference data applying standard interpolation methods.

Craters were formed on the front and rear ends of a sample when it was subjected to laser radiation. The rear end damage was fully expected since the dimensions of the focal (caustic) region of the focusing system exceeded 1 mm. A crater grew only during the first 100 us from the beginning of a laser pulse, which was not in conflict with the results reported in Ref. [3]. Subsequently ($t > 100$ μs) we found that changes in the density (and temperature) isolines of samples with $l \geq 3$ mm were three-dimensional (nearly spherical) and that these changes were much slower than during the first 100 μs. For a sample with $l = 1$ mm the density (and temperature) isolines were radial and changed only slightly in the axial direction.

The structural changes caused by laser irradiation of PMMA were studied on the basis of x-ray diffractograms obtained with a DRON-2.0 general-purpose x-ray diffractometer. We have used the K_a line generated in a tube with a copper anticathode, filtered off at the wavelength 154.050 pm.

Our investigations showed that x-ray diffractograms of PMMA samples with $l > 3$ mm or thicker were practically the same before and after the action of laser pulses. In the case of samples with $l = 1$ mm we observed changes in the position of the halo maximum θ, as well as in the intensity I, the half-

width Δ, and the asymmetry parameter A ($A = I_1/I_2$ is the ratio of the intensities of this radiation scattered through angles $\varphi + 4°$ (I_1) and φ-4° (I_2)).

X-ray diffractograms of the irradiated samples sometimes included well-resolved selective (half-width $\Delta \approx 0.1°$) reflections, indicating the appearance of molecularly ordered regions in PMMA as a result of laser irradiation. This ordered phase (or phases) appeared only for E_a. = 10 and 30 J. At other laser radiation energies such sharp maxima did not appear in the diffractograms.

The degree of molecular ordering of noncrystalline homogeneous isotropic objects can be represented by the radius of a sphere [4] in which the length of the vector representing the deviation of the radius vector $\vec{R}$ of an atom from the corresponding lattice vector does not exceed the average interatomic distance. The average modulus of the interatomic vector $\vec{R}$ is related to the angular position of the diffraction maximum [5]: $4R \sin\theta/\lambda = 1.4303$, where λ is the x-ray wavelength and θ is the angular position of the maximum. The half-width Δ of the maximum can be used to calculate the effective size L of a locally ordered region on the basis of the Scherrer formula [4].

A more detailed investigation of the structural changes in PMMA under the action of laser radiation was made by plotting the correlation curves $W(r)$, related to the functions representing the local distribution of the atomic density $4\pi r^2\rho(r)$ by the condition which follows from the Zernike-Prins formula [4].

We have calculated correlation curves $W(r)$ for some of our samples for which corrections were made for the absorption and polarisation. The normalisation of the intensities and calculations of the errors in the structural parameters were made by a method described in Ref. [4]. The x-ray radiation intensity and the angular position of the point at which measurements were made were found with errors not exceeding 3% and 10', respectively. The function $W(r)$ was calculated for $r \leq 1.5$ nm. Since there were no changes in $W(r)$ for $r > 0.5$ nm, we analysed only the nearest and the second-nearest atomic neighbour environments, i.e. we considered the first two coordination spheres. Changes in the atomic coordinations were estimated on the basis of the relative coordination numbers (RCNs). The number of atoms in the first two coordination spheres was assumed to be 100%, i.e. the RCN of a given coordination sphere represented the percentage ratio of the number of atoms in the sphere to the number in a sphere of radius equal to the radius of the second coordination sphere. The errors in determinationof the radii of the coordination spheres were ±5 pm; the errors in the determination of the RCNs were ±3% for the first coordination sphere and ±5% for the second. The RCN maximum for $r \approx 0.26$ nm corresponded to the intramolecular C-0 bond [6]

Discussion

The results of our investigations indicated that the absorption of laser radiation by a PMMA layer 1 mm thick altered the molecular structure, as demonstrated by x-ray diffractograms. We have calculated the radii and the RCNs for the first two coordination spheres. As mentioned earlier, the radius of the first coordination sphere was $r \approx 0.26$ nm, in reasonable agreement with the macroscopic parameters of PMMA.

Let us now consider the molecular fragment CH_3—C-C-O_2-CH_3 as an element of the structure of PMMA. Its average atomic mass is $\langle m \rangle = 11.9 \cdot 10^{-27}$ kg, the volume of the 'average' atom is $V_1 = \pi d^3 / 6$, where d is the interatomic distance, and the volume per atom is $V = V_1 / k$, where k is the packing fraction.

For the closest spherical packing we have $k = 0.74$, but in the case of organic molecules the covalent binding between the atoms distorts their sphericity and the fraction k increases, but even then we have $d = \left(\frac{6 < m > k}{\pi \rho} \right)^{1/3}$ = 242 pm, which (in view of the above discussion) is in reasonable agreement with our data.

Fairly large regions with local molecular ordering can sometimes form in an amorphous matrix. This gives rise to quite clear Bragg maxima. In the majority of cases such structural changes are associated with changes in the relative positions of molecules in an amorphous phase and can be deduced reliably from the correlation functions of samples before and after laser irradiation. The main changes are observed within the first and second atomic coordination spheres. Consequently, laser irradiation not only changes the relative positions of the molecules, but it also affects their internal structure.

According to the theory of x-ray scattering by noncrystalline objects [4-5] an increase in the halo intensity and a reduction of its half-width indicates that the degree of molecular ordering increases. A change in the profile of a maximum in an x-ray diffractogram indicates that the molecular structure of an amorphous substance has ceased to be homogeneous, i.e. that regions can appear in which on the whole the degree of molecular ordering is higher than the average ordering; in other words, formation of molecular clusters begins. This is demonstrated in particular by a 7%-16% increase in the size of the locally ordered regions, and this increase is considerably greater than the experimental error.

At high laser radiation energies ($E_0 > 50$ J) a sample was burnt right through and, therefore, structural investigations cannot be made.

The nonmonotonic dependences of these experimental parameters of PMMA on the radiation energy under conditions of nearly constant and homogeneous heating of samples with $l \approx 1$ mm and the slight structural changes in thicker samples suggest, in our opinion, that the changes in the molecular structure under the action of laser pulses of ~1.2 ms duration have nonthermal nature. A similar hypothesis was put forward by us earlier [3].

The investigated effect cannot be attributed to local heating of matter by the absorption in impurities and striations, since the effect would have then been observed also in 'thick' ($l \geq 3$ mm) samples. Changes in the molecular structure of PMMA under the action of powerful optical pulses are, in our opinion, the result of excitation of acoustic vibrations. Generation

of acoustic vibrations by the action of laser pulses on the surface of a solid can be described [7] in the framework of a model of a loaded region emitting waves into an elastic medium (in the case under discussion [3], the dimensions and shapes of such regions are close to the dimensions and shapes of the craters that form on the front and then rear surfaces of 'thin' samples with $l \approx 1$ mm). The wavelengths of the generated elastic waves λ_{ew} are then proportional to the radii of curvature of craters formed on the target surface: $\lambda_{ew} \approx \alpha R = \alpha d^2/h$, where h is the crater depth and d is the diameter of the crater base. The coefficient of proportionality a depends on the parameters of the medium at the temperature reached at the boundary of an inelastic strain zone and can be calculated by a method described in Ref. [7], Since, under the action of optical pulses of energies E_o = 4 - 60 J on the surface of a PMMA sample, a crater grows only during the first 100 μs, it follows that the parameters h and d at t = 100 ms can be regarded as constant. For E_a = 10 J, we have $h \approx 0.3$ mm, $d \approx 0.3$ mm, whereas for E_a = 30 J, the corresponding values are $h \approx 0.4$ mm and $d \approx 4.2$ mm.

For example, if E_a = 10 J, an elastic wave with λ_1 = 0.44 mm forms in a sample, whereas if E_a = 30 J, this wave is characterized by λ_2 = 0.56 mm. We recall that, in the experiments described above, the size of the focal region of the focusing system exceeded 1 mm, so that when radiation was focused on the exposed front surface of a sample with l = 1 mm, a crater appeared also at its rear surface. A second crater did not form on 'thick' samples (l > 3 mm). Therefore, for E_a = 10 J, the real thickness of the target in the crater zone is $l_1 = l - 2h_1$ = 0.4 mm, i.e. it is approximately equal to λ_1 , whereas for E_0 = 30 J, the target thickness is $l_2 = l - 2h_2$ = 0.3 mm, or approximately $\lambda_2 / 2$. Since in both cases an integral number of half-wavelengths of acoustic vibrations can be fitted in the distance equal to the real thickness of the target, standing elastic waves should appear in the irradiated samples and they should exist for at least 1.4 ms. The practically constant positions of the elastic wave maxima were observed by us also in the interferograms. For other values of E_a (different from 10 and 30 J) an integral number of half-wavelengths could not be fitted within the real thickness of the target and, consequently, standing waves could not form.

There is evidence that structural defects are generated by intense elastic fields at the sample. We can assume that changes in the molecular structure are also possible in amorphous substances and that these changes include clusterisation. In the irradiated zone of PMMA, such acoustic waves create stresses close to the elastic limit at the temperature induced by the laser beam, i.e. this substance is in the 'preflow' state. Nonlinear elastic effects may alter the interatomic bonds in chains.

On the other hand, the action of a wavefront may rotate monomers and, consequently, molecular clusters can form in PMMA and changes can occur in the molecular order in the amorphous matrix, as found experimentally. If E_a differs from 10 and 30 J, standing waves are not excited in a sample and, consequently, the microstructure of PMMA changes much less. In 'thick' samples (l > 3 mm), the addition of a wave generated directly by the damaged region to a wave reflected from the back side may give rise to standing waves. However, the amplitude A_r of a reflected wave is considerably less than the amplitude A_o of the initial wave both because of geometric factors (the generated wave is near-spherical) and because of surface irregularities on the reflecting face, whose typical size is 100-200 μm (i.e. it is of the same order as the wavelengths of the excited elastic waves). Consequently, the amplitude of a standing wave then produced is $A_s = 2A_r \ll A_o$.

In view of the near-spherical geometry of the fronts of A_o and A_s, the dimensions of the region where standing waves are formed are considerably less than in samples with $l \approx 1$ mm. Finally, the region of appearance of stresses close to the elastic limit at the temperatures reached, which is the only region where changes in the microstructure are possible under the action of acoustic vibrations, occupies a considerably smaller part of the volume of a 'thick' sample than the corresponding fraction of a 'thin' sample. All these factors are responsible for the fact that only slight changes in the molecular structure take place in a 'thick' sample.

Conclusions

Our investigations showed the possibilities of the changes in the molecular structure of the irradiated PMMA material. The dependence of the degree of changes in the microstructure on the absorbed energy E_a is not monotonic: the greatest changes in the ordered zones, at of molecular order degree, and in the average density of this substance are observed at very definite values of the absorbed energy (which in our case are 10 and 30 J). These effects may be associated with the excitation of standing acoustic waves in the irradiated sample.

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