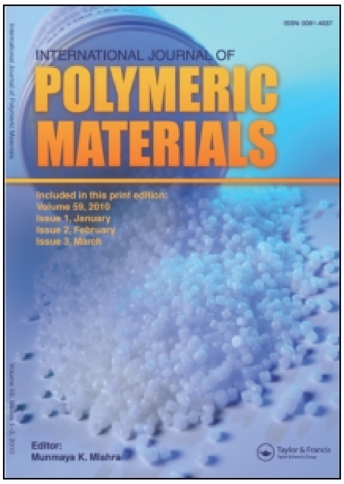

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Effect of Laser Radiation on Dyed Polymeric Films

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Destruction of the thin dyed polymeric films under the action of resonant and non-resonant laser radiation has been investigated. It is shown that laser stability of dyed polymers depends on the type of incorporated dye and it is independent of film thickness and dye concentration at the same powers of absorbed laser radiation. Moreover, laser stability of polymeric films with chemically bonded dye is higher than the polymer stability with dissolved dye. Comparative analysis showed that the polymer laser stability is determined by the kinetics of the polymer thermodegradation, which results in the appearance and accumulation of the products absorbing laser radiation. It is established that resonant irradiation of dyed polymers is considerably more efficient for polymer destruction than the nonresonant one.

KEY WORDS Laser radiation, polymer fibers, degradation.

1. INTRODUCTION

The last few years have seen a growing interest in applications of polymeric materials in laser engineering.[1] The use of polymers as matrices for active medium, e.g. in dye lasers, is one important application. The main investigations in this field were devoted to the studies of the generation characteristics of organic dyes embedded into polymeric matrix.[2–4] However this problem has another aspect. Dye being in the high power light field, the part of the absorbed radiation inevitably transforms to heat, causing the heating of the matrix and its thermodegradation and as a result the destruction of the laser element. Therefore the investigation of the regularities of the laser-induced destruction of dyed polymers and increase of their laser stability is one of the principal problems.

On the other hand application of polymers in microelectronics as a photoresistor and/or for the optical recording causes the necessity for elaboration of the methods of the polymer sensitization relative to laser radiation. From this point of view the polymeric materials with incorporated absorbing dopants, e.g. organic dyes should be considered. In particular it has been shown[5,6] that introduction of the dyes into PMMA matrix sensitizes the polymer ablation under the action of high power UV laser pulses.

A third aspect of the problem of the laser-polymer interactions is the possibility to solve the inverse problem, i.e. based on the laser experiment making a conclusion about, for example, thermal stability of polymers. We have recently[7] investigated laser-induced destruction of polyacrylnitrile and established some features of the polymer thermodegradation kinetics. Price *et al.*[8,9] used laser radiation for the modeling of the processes occurring in polymers during their combustion.

In this paper the experimental results of the study of the laser-induced destruction of the films of poly(vinyl alcohol) (PVA) containing different azodyes are discussed. We studied the influence of the type of the bond between dye and polymer on the laser stability of films. In addition, the interrelation between thermal and laser stability of dyed PVA has also been investigated.

2. EXPERIMENTAL

PVA films were obtained from a 10% water solution of the polymer. The dyes used were reactive azodyes: C.I. Reactive violet 4 (dye I) and C.I. Reactive yellow 4 (dye II). Dyeing was carried out in such a way that the dyes formed the chemical bond with polymer macromolecules. Methods of dyeing are described in detail by I. Ya. Kalontarov.[10] The thickness of the films studied were 15–50 μm.

The samples examined underwent cw radiation from an argon laser ($\lambda = 514.5$ nm) and Nd:YAG laser ($\lambda = 1064$ nm). Radiation which passed through a sample was registered by a laser powermeter connected to a recorder. The dependence of the polymer absorptivity at laser wavelength on the irradiation time was measured, thus following the accumulation of absorbing products. The time of film perforation was noted by the sharp decrease in absorptivity. Measurements were made at different laser powers P.

3. RESULTS AND DISCUSSION

3.1 Influence of the Type of Bond Between Dye and Polymer on the Laser Stability of Polymeric Films

In this section the results of the investigation of the laser-induced destruction of PVA containing dye II under the action of argon laser radiation are discussed. Laser radiation gets into the edge of the dye absorption band, so the laser-polymer interaction is of resonant character. We studied two variants of dyeing. In first case dye was dissolved in polymer matrix (sample I) and in the second, dye was chemically bonded with polymer (sample II).

According to the thermochemical concept, laser-induced destruction of solid polymers takes place through the development of the thermochemical instability (TCI).[11,12] The formation of TCI is due to the positive feedback between the heating of the sample and absorption of the radiation in the degradation zone. In other words products of polymer thermodegradation absorb laser radiation, causing additional heating of the sample and acceleration of the thermodegradation. As a result the process of laser-induced polymer destruction is of avalanche-like character.

We have recently developed[12] the model of TCI in thin polymeric films. We have derived the relationship which concerns the activation time of TCI with laser power

$$\tau_a = (2T_0/\alpha\gamma)^{1/2} \exp(\alpha/2) \quad (1)$$

$$T_0 = \mu P_a + T_a \quad (1a)$$

where T_0 is the temperature of the polymer in the radiation field before the development of TCI, T_a is the ambient temperature, μ is the constant depending on the type of absorbing dopant and thermophysic properties of the polymer, $P_a = PA_0$ is the initial power of the absorbed radiation, P is the incident laser power, A_0 is the initial absorptivity, $\alpha = E/RT_0$, $\gamma = P\varepsilon\nu/\rho c_p S$, E and ν are the activation energy and preexponential multiplier for the rate of the accumulation of absorbing products of thermodegradation, respectively, R is the gas constant, ρ and c_p are the polymer density and specific heat, respectively, S is the irradiated area.

Laser effect on the pure PVA samples does not change the polymer absorptivity. This can be explained by the low A_0 value and as a consequence T_0. Laser irradiation of dyed PVA films initiates polymer thermodegradation, the dynamics of which is characteristic for TCI. The kinetic curves of the changes of the absorptivity have an activation interval, beyond which the sharp increase of the absorptivity occurs, i.e. TCI develops (Figure 1). The period from the beginning of the irradiation to the moment of film perforation (τ) can be divided into two intervals. The first is the activation time of TCI (τ_a) and the second is the interval of TCI development (τ_b):

$$\tau = \tau_a + \tau_b \quad (2)$$

As shown in Figure 2(a), laser stability of sample I is lower than the stability of sample II. As follows from Figures 2(b, c) this fact is caused by the larger duration of activation stage of TCI in the second variant of dyeing. According to Equation

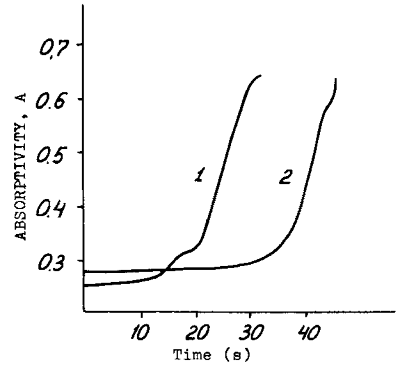

FIGURE 1 Dependence of the absorptivity of dyed PVA at the laser wavelength on the time of irradiation. P_a = 0.051 W. (1) sample I, (2) sample II.

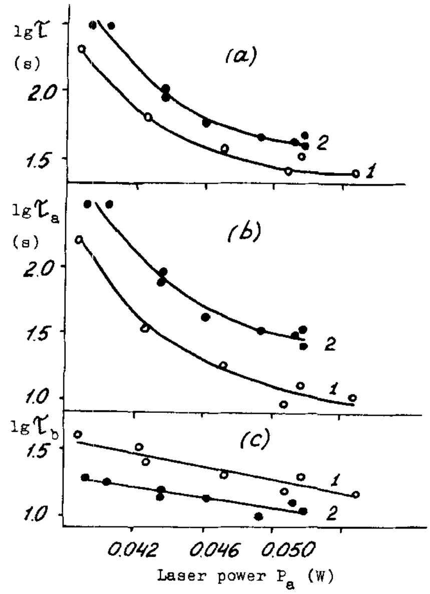

FIGURE 2 Dependences of the (a) time from the beginning of irradiation to the moment of film perforation τ, (b) activation time of TCI τ_a and (c) development time of TCI τ_b on the absorbed laser power P_a. (1) sample I, (2) sample II.

(1) the observed difference can be associated with the difference of the kinetic parameters of the thermodegradation of dyed PVA. From thermogravimetric curves of these samples[13] we have estimated the values E and ν of the destruction process (in this case it is the thermodehydration process which results in appearance of products absorbing iv visible spectral range). $E_1 = 50$ kJ/mol, $\nu_1/\beta = 11 \cdot 10^4$ mg/K are for sample I and $E_2 = 36$ kJ/mol, $\nu_2/\beta = 2 \cdot 10^3$ mg/K are for sample II, where β is the rate of heating. At the same initial power of absorbed radiation P_a and T_0 the ratio of the activation times of TCI in the different variants of dyeing is equal to:

$$\tau_{a,2}/\tau_{a,1} = (E_1\nu_1/E_2\nu_2)^{1/2} \exp((E_2 - E_1)/2RT_0) \tag{3}$$

Then

$$\ln \tau_{a,2} - \ln \tau_{a,1} = \frac{1}{2} \ln(E_1\nu_1/E_2\nu_2) + ((E_2 - E_1)/2RT_0) \tag{3a}$$

From experimental curves (Figure 2(b)) follows that at $P_a = 0.050$, 0.046 and 0.040 W, the ratio $\tau_{a,2}/\tau_{a,1}$ is equal 2.9, 2.5 and 2.2, respectively. Substitution of the values E_1, E_2, ν_1, ν_2 into Equation (3) yields that the same values $\tau_{a,2}/\tau_{a,1}$ are derived when the temperature T_0 is equal 800, 700 and 600 K, respectively. Thus Equation (3) describes accurately the dependence of $\tau_{a,2}/\tau_{a,1}$ on absorbed laser power at a wide range of temperatures T_0. The stage of development of TCI and the dependence of τ_b on P_a we have recently discussed in detail.[14]

3.2. Destruction of Dyed PVA Films under the Action of Non-Resonant Laser Radiation

In this section the results of the investigation of the destruction of the dyed PVA under the action of Nd:YAG laser radiation are presented. Neither polymer nor dyes have any absorption bands in the region of 1064 nm. Thus in this case laser-polymer interaction is of non-resonant character. The absorption occurs on the various inhomogeneities and inclusions. Dyes naturally have some coefficient of non-resonant absorption too, however they play now the role of buffer particles with effective radius R introduced into the polymeric matrix. Laser radiation being absorbed on these particles and other inclusions heats them and causes thermodegradation of the surrounding matrix. As a result of the sequence of the thermal transformations the carbonization of the polymer occurs, products of which (carbon black) efficiently absorb radiation with $\lambda = 1064$ nm. Thus the positive feedback between the absorption and heating forms in the system and above-mentioned TCI develops, resulting in film destruction.

The irradiation time dependences of the absorptivity of dyed PVA films are presented in Figure 3. These curves have a form which is characteristic for TCI: at the beginning there is activation interval and then avalanche like acceleration of the degradation which leads to the film perforation. Note that after sample fracture the carbon-black particles are observed around the hole in the film.

Figure 4 shows the dependence of the activation time of TCI on the power of absorbed radiation. As is seen the activation time depends essentially on the type of incorporated dye and at the same time the universal dependence lg $\tau_a(P_a)$ is

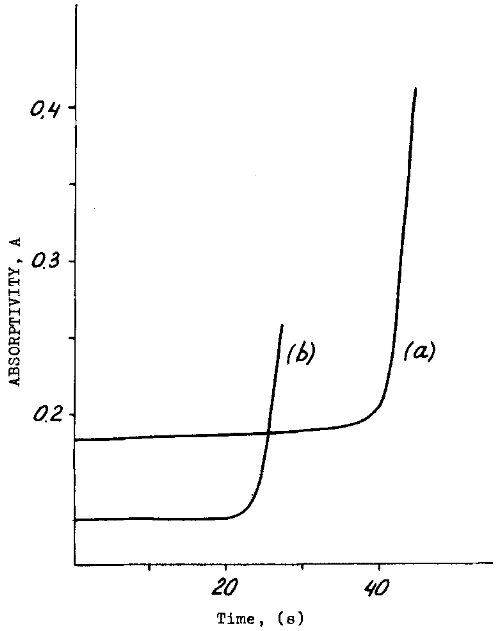

FIGURE 3 Dependence of the absorptivity of dyed PVA at the laser wavelength on the time of irradiation. (a) PVA containing dye II, $P_a = 1.5$ W and (b) PVA containing dye I, $P_a = 0.58$ W.

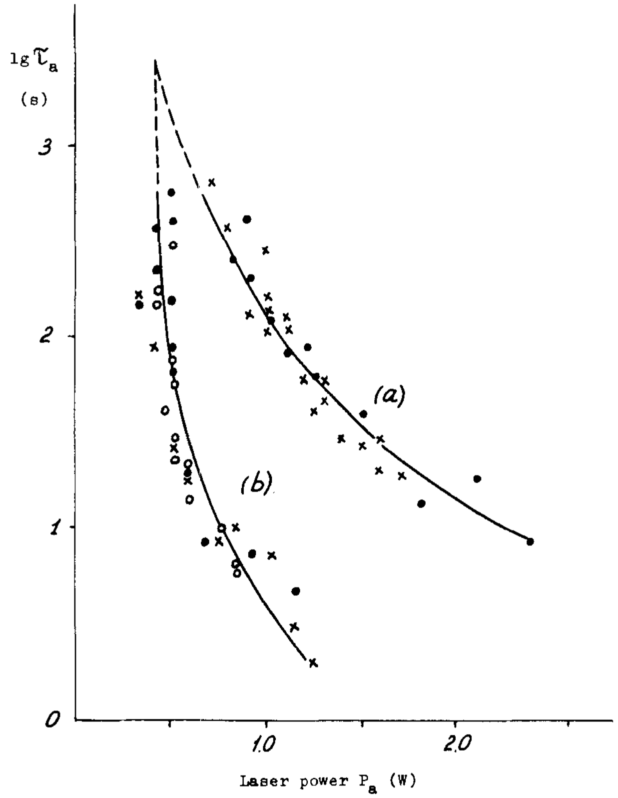

FIGURE 4 Dependence of the activation time of TCI on the absorbed laser power. (a) PVA containing dye II, (●) concentration of dye $c = 5\%$, film thickness $d = 27$ μm, (×) $c = 5\%$, $d = 17$ μm, (b) PVA containing dye I, (●) $c = 5\%$, $d = 18$ μm, (×) $c = 5\%$, $d = 48$ μm, (○) $c = 3\%$, $d = 15$ μm.

observed for films which possess different thickness and contain different concentrations of the dye. Thus the activation time of TCI is mainly determined by the type of dye and temperature of the sample in the radiation field, which is proportional to laser power (Equation 1a). Independence of laser stability on sample thickness is in good agreement with Equation (1) and indicates that films used are sufficiently thin to consider the temperature to be uniform along the thickness.

As seen in Figure 4 PVA containing dye II has a larger laser stability in the measured powers region. With the decrease of power the difference between activation times decreases and dependences $\tau_a(P_a)$ extrapolated into the region of low P_a values cross.

So far as in this case the absorption of laser radiation is of non-resonant character and dyes studied have a similar structure. We can then consider coefficient μ in Equation (1a) to be independent of the type of incorporated dye. Then according to Equation (1) the difference between laser stability of PVA films is caused by the dependence of activation energy and preexponential multiplier of the process of the accumulation of absorbing products on the type of the introduced dye. The ratio of activation times of different PVA films is given by Equations (3 and 3a), where the indeces 1 and 2 denote PVA containing dye I and dye II, respectively. As the difference ($\lg \tau_{a,2} - \lg \tau_{a,1}$) increases with the raise of the absorbed laser power, then according to Equation (3a) $E_2 < E_1$ and $\nu_2 < \nu_1$. From Equation (3a) it is easy to determine the temperature T_0^* which corresponds to the equality of the activation times $\tau_{a,2} = \tau_{a,1}$

$$T_0^* = (E_2 - E_1)(R \ln(E_2\nu_2/E_1\nu_1))^{-1} \tag{5}$$

Independence of the τ_a on the concentration of the dye indicates that the parameters E and ν do not depend on the dye concentration in the investigated range.

To establish the interrelation between laser and thermal stability of polymers we have investigated the kinetics of the thermodegradation which results in the accumulation of the absorbing products in dyed PVA films. The rate of the absorbing products accumulation at the different temperatures was measured by spectrophotometer at $\lambda = 650$ nm. The absorption at this wavelength is of non-resonant character not only for the original polymer but for the initial products of the thermodegradation as well. So, the red boundary of the polyenes absorption (which are the main products of PDA thermodecomposition) is in the region 630 nm.

Figure 5 shows Arrhenius plots for the rate constant of the accumulation of absorbing products forming as a result of PVA thermodegradation. These dependences are of linear character and their slope depends on the type of incorporated dye and is independent of the concentration. In the temperature range studied the rate of the accumulation of the absorbing products for PVA containing dye I is lower than for PVA with dye II. At increased temperatures the difference

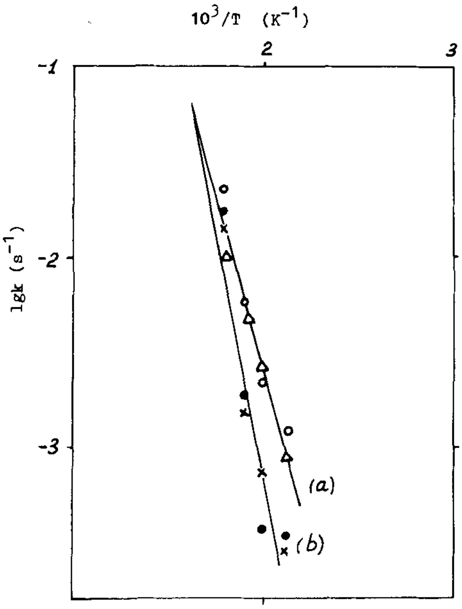

FIGURE 5 Arrhenius plots for the rate constant for the accumulation of the absorbing products. (a) PVA containing dye II, (b) PVA containing dye I.

between rates decreases and from some temperature T^* PVA containing dye II starts to destruct faster. Temperature T^* is determined by the equality of the rate constants.

$$T^* = (E_2 - E_1)(R \ln(\nu_2/\nu_1))^{-1} \tag{6}$$

The treatment of the lines (Figure 5) by means of the least-squares method shows that $E_1 = 20$ kJ/mol, $E_2 = 76$ kJ/mol, $\nu_1 = 2.1 \cdot 10^9\ \mathrm{s}^{-1}$, $\nu_2 = 3.2 \cdot 10^5\ \mathrm{s}^{-1}$, i.e. $E_2 < E_1$ and $\nu_2 < \nu_1$. In comparing Equation (5) with Equation (6) one can see that temperatures T_0^* and T^* are practically the same ($T_0^* \simeq T^* \simeq 600$ K). Consequently the temperature of the laser heating T_0 in the experiments presented in Figure 4 is higher than 600 K. Thus the thermal stability data are in good agreement with the results on the laser stability of polymers. When the rate of thermodegradation is higher, then laser stability of films is lower. That is the results of laser experiments can be used for the analysis of the thermal stability of polymeric materials. We have earlier shown by mass-spectroscopy[15] that the thermal and laser-induced destruction of polymers studied are characterized by the similar complex of physicochemical transformations, although the dynamics of the laser-induced thermal reactions differ greatly from the dynamics of usual thermodegradation.

It was interesting to compare the results of the destruction of PVA containing dye II under the action of resonant and non-resonant radiation. It should first be noted that upon resonant irradiation the considerably lower values of the absorbed laser power are necessary for polymer destruction (Figure 2(b) and Figure 4). So far as the temperature of the laser heating is determined by the intensity of the laser radiation (coefficient μ in Equation (1a) is proportional to S^{-1}) then note that the diameter of the hole in the film after its destruction was practically the same for both types of irradiation, i.e. the irradiated area S was equal. Let us estimate the temperature of the samples in the laser radiation field T_0. In the previous section we indicated that upon resonant influence temperature $T_0 = 800$ K corresponds to the absorbed laser power $P_a = 0.050$ W. In accordance with Equation (1a) and assuming $T_a = 300$ K we obtain a coefficient value $\mu = 10^4$ KW^{-1}. The activation time corresponding to $P_a = 0.050$ W and $T_0 = 800$ K is τ_a = antilog (1.5) (Figure 2(b)).

We have above noted that upon non-resonant irradiation the point of crossing of the curves lg $\tau_a(P_a)$ (Figure 4) corresponds to the temperature $T_0^* = T^* = 600$ K. This point of crossing occurs at the power of absorbed radiation $P_a = 0.4$ W. Consequently in this case coefficient value $\mu = 750$ KW^{-1}. Temperature $T_0 = 800$ K corresponds to the power $P_a = 0.67$ W which in turn corresponds to the activation time of TCI τ_a = antilog (2.8) (Figure 4(a)).

Difference between activation times of TCI for resonant and non-resonant irradiation at the same temperature T_0 is caused by the difference between kinetic parameters of the accumulation of the absorbing products. Indeed the activation energy of the thermodehydration leading to the absorption in the visible spectral range $E = 36$ kJ/mol (see section 3.1.) is considerably less than the activation energy of the accumulation of the non-resonantly absorbing products of the thermodegradation $E = 76$ kJ/mol. Therefore in accordance with Equation (1) the activation time of TCI for resonant absorption is less than for non-resonant absorption at the same T_0.

The other interesting feature is the great difference of the values of the coefficient μ which characterizes to some extent the efficiency of the transformation of the energy of the absorbed light to the heat. In the case of non-resonant absorption this coefficient is considerably higher. This observation can be explained in several ways, both physical and technical. In particular Figure 1 and Figure 3 show that the initial absorptivity A_0 differs little for both types of irradiation. One can suppose that in the case of non-resonant action the value A_0 is essentially exceeded, because our technique of the registration of the absorptivity does not take into account light scattering, the intensity of which can be sufficiently high upon non-resonant irradiation. Thus the difference between coefficients μ can be caused by the exceeded value A_0 upon non-resonant action. However this problem requires special investigation. On the whole the results presented show resonant irradiation to be more efficient for the destruction of the dyed polymeric materials.

4. CONCLUSION

The destruction of dyed polymeric films under the action of resonant as well as non-resonant laser radiation has a thermal nature. Laser stability of polymeric films depends both on the type of incorporated dye and the type of the bond between dye and polymer. The data on the polymer laser stability are in good agreement with results of the study of their thermodecomposition which leads to the appearance of the products absorbing laser radiation. The resonant irradiation is considerably more efficient for the stimulation of the destruction processes in the dyed polymeric films.

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