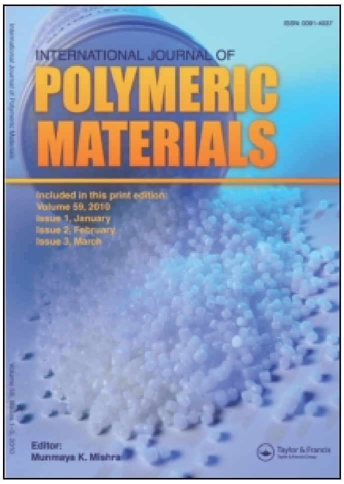

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Kalontarov, L. I. and Marupov, R.(1994) 'Degradation of Polymers Under the Action of Continuous-Wave Laser Radiation', International Journal of Polymeric Materials, 25: 1, 127 — 131

To link to this Article: DOI: 10.1080/00914039408028585

URL: http://dx.doi.org/10.1080/00914039408028585

Intern. J. Polymeric Mater., 1994, Vol. 25, pp. 127–131
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Printed in Malaysia

Degradation of Polymers Under the Action of Continuous-Wave Laser Radiation

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Degradation of polymers under the action of continuous-wave laser radiation is investigated.

KEY WORDS Polymer degradation, laser light

1. INTRODUCTION

According to the thermochemical conception, laser-induced destruction of solid polymers takes place through the development of thermochemical instability (TCI).[1,2] The formation of TCI is due to the positive feedback between the heating of the sample and absorption of the laser radiation in the degradation zone. In other words laser radiation being absorbed by the different inclusions or absorbing groups of the polymer, causes the heating of the sample and the thermodegradation of the macromolecules. Products of thermodegradation absorb laser radiation that leads to additional heating and acceleration of the thermodegradation. As a result through some period of time τ_a an avalanche like polymer destruction takes place and so called TCI is developed.

In this contribution we consider the model of TCI in a nonstationary approximation. In addition we discuss the experimental results for the degradation of poly (vinyl alcohol) (PVA) thin films under the action of continuous-wave radiation of an argon laser ($\lambda = 514.5$ nm) and an ND:YAG laser ($\lambda = 1064$ nm).

2. THEORY OF TCI IN NONSTATIONARY APPROXIMATION

Consider the equations which describe TCI in polymers[2,3]

$$\partial T/\partial t = \chi \Delta T + (\varepsilon c I/\rho c_p); \qquad \partial c/\partial t = \nu_0 \exp(-E/RT) \qquad (1)$$

where T is the temperature, t is the time, χ is the thermal diffusivity, c is the concentration of the absorbing products, ε is the molar extinction, I is the intensity of the incident laser radiation, ρ and c_p are the polymer density and specific heat respectively, and E and ν_0 are the activation energy and preexponential multiplier for the rate of thermal degradation. There are two ways to estimate the activation time of TCI τ_a: stationary and nonstationary. In the first case the stationary temperature distribution around the absorbing inclusion is determined. The activation time is defined as the time at which the initial temperature distribution is disturbed due to the effective destruction-induced increase of the size of the absorbing inclusion. This approach has been realized in References 2–4. However the formulae derived in References 2–4 for τ_a include the radius and absorption coefficient of the inclusion whose values are unknown. In the nonstationary approximation where the heat balance of the whole system is considered, the final result does not depend upon the above parameters.

Let us consider the initial stage of laster heating of a thin polymeric film, which undergoes degradation upon heating. As we consider the initial stage of destruction we do not take into account Beer's character of absorption and assume the polymer concentration to be constant. Such a problem is described by the following equations of thermal balance and chemical kinetics

$$\begin{aligned} mc_p(dT/dt) &= PA(c) - L(T), & T/_{t=0} &= T_0 \\ dc/dt &= \nu_0 \exp(-E/RT), & c/_{t=0} &= 0 \\ A(c) &= A_0 + \varepsilon cd \end{aligned} \tag{2}$$

where P is the laser power, A is the absorptivity at the laser wavelength, $L(T)$ is the power of heat losses, and d and m are the film thickness and mass, respectively. Substitution of $A(c)$ into equation of thermal balance and differentiation results in

$$d^2t/dt^2 = (I\varepsilon\nu_0/\rho c_p)\exp(-E/RT) - (1/mc_p)\, dL(T)/dt \tag{3}$$

Estimates show that changes in the heat losses can be neglected

$$d^2T/dt^2 = \gamma \exp(-E/RT) \tag{4}$$

where $\gamma = (I\varepsilon\nu_0/\rho c_p)$. The integral of Equation (4) has the following form[5]

$$t = \int \left(1\Big/\left(2\int \gamma \exp(-E/RT)\, dT\right)^{1/2}\right) dT$$

with two constants. As $T/_{t=0} = T_0$ then $(dT/dt)_{t=0}$ and constant of integration in the expression under the root sign is equal to zero. By analogy with the induction period of a thermal explosion[6] we define the activation time of TCI as

$$a = \int_{T_0}^{T'} \left(1\Big/\left(2\int \gamma \exp(-E/RT)\, dT\right)^{1/2}\right) dT \tag{5}$$

where T' is the sufficiently high temperature (e.g., the temperature of the maximum destruction rate) the exact value of which does not influence the final result,[6] $T_0 = \mu I_A + T_a$ and is the temperature of the sample in the radiation field before the development of TCI, $I_A = IA_0$ is the initial intensity of the absorbed radiation, μ is the coefficient, and T_a is the ambient temperature. As the temperature during the activation period is near the initial value T_0 we can use the following approximation[6]

$$\exp(-E/RT) \approx \exp(-E/RT_0)\exp\theta$$

where $\theta = E(T - T_0)/RT_0^2$. In this approximation the rate constant infinitely increases with temperature. Therefore:

$$\tau_a = \int_{T_0}^{\infty}\left(1\bigg/\left(2\int \gamma\exp(-E/RT)\,dT\right)^{1/2}\right)dT = (T_0/2\alpha\gamma)^{1/2}\int_0^{\infty}\exp(-\theta/2)\,d\theta$$

and the final formula for τ_a is:

$$\tau_a = (2T_0/\alpha\gamma)^{1/2}\exp(\alpha/2) \tag{6}$$

where $\alpha = E/RT_0$.

3. EXPERIMENTAL PART

Laser-induced destruction of PVA thin films (d = 40–60 μm) has been studied experimentally. The samples examined underwent continuous-wave radiation from argon and Nd:YAG lasers. Radiation which passed through a sample was registered by a laser powermeter connected to a recorder. The dependence of the polymer absorptivity at the laser wavelength on time was measured and followed the accumulation of absorbing products. The details of the experimental apparatus can be found elsewhere.[7,8]

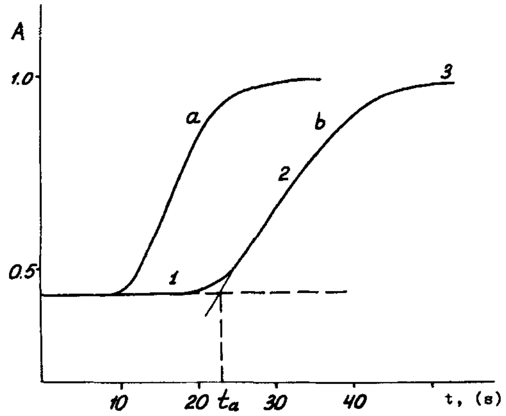

FIGURE 1 Dependence of the polymer absorptivity on time of argon laser irradiation, (a) I_A = 0.23 W/cm^2, (b) I_A = 0.20 W/cm^2.

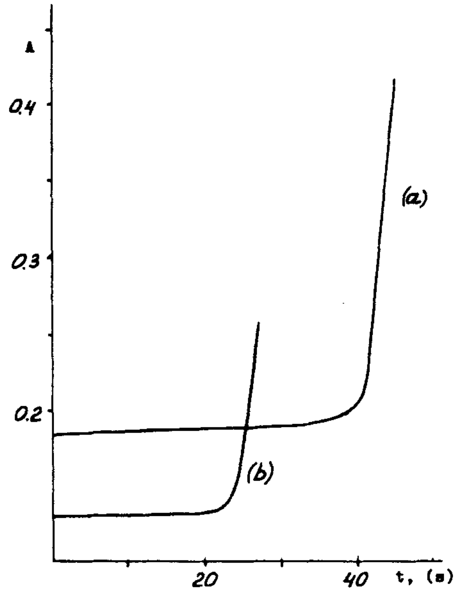

FIGURE 2 Dependence of the absorptivity of dyed PVA on the time of Nd:YAG laser irradiation. (a) PVA containing Reactive yellow 4, P_A = 1.5 W; (b) PVA containing Reactive violet 4, P_A = 0.58 W.

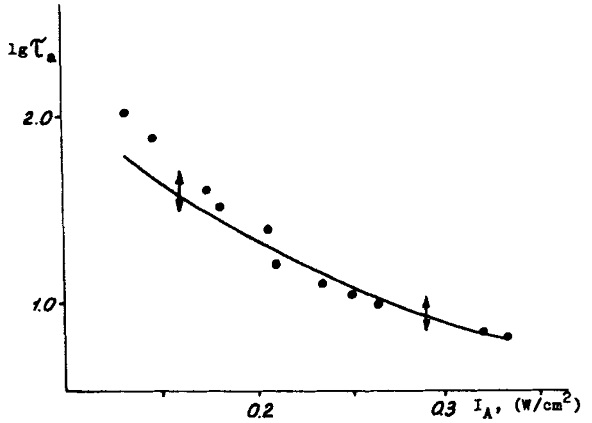

FIGURE 3 Dependence of the activation time of TCI on the absorbed laser intensity upon argon laser irradiation. Full circles denote experimental data and the solid line is calculated by means of Equation (6).

RESULTS AND DISCUSSION

Figures 1 and 2 show typical kinetic curves for the laser-induced destruction of PVA films. As follows from these figures the destruction of PVA under the action of both argon and Nd:YAG lasers comprises two stages, the first is the activation stage and the second is the avalanche like process resulting in the film perforation. Thus laser-induced polymer destruction takes place through the development of

TCI. In Figure 3 the dependence of the activation time of TCI on the absorbed laser power is presented.

The aim of our experiments is to check the theoretical formula for τ_a (6). The method for the experimental determination of τ_a is shown in Figure 1. To calculate τ_a according to Equation (6) it is necessary to know the values E and ν_0 and T_0 which is concerned with the laser intensity. To determine activation energy E and the preexponential multiplier ν_0 we measured the kinetics of the accumulation of the absorbing products at different temperatures. The dependence of the rate of accumulation on the inverse temperature gives the values $E = (47 \pm 5)$ kJ/mol, and $\nu_0/c_0 = (2700 \pm 400)\ \mathrm{s}^{-1}$. The method for the determination of temperature T_0 has previously been described in detail.[8]

Figure 3 shows the experimental and theoretical dependence of τ_a on the absorbed laser intensity. It is seen that there is good agreement between experimental and theoretical data. Thus the proposed theory of TCI in a nonstationary approximation can be used for the prognosis of the laser stability of thin solid polymeric films.

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