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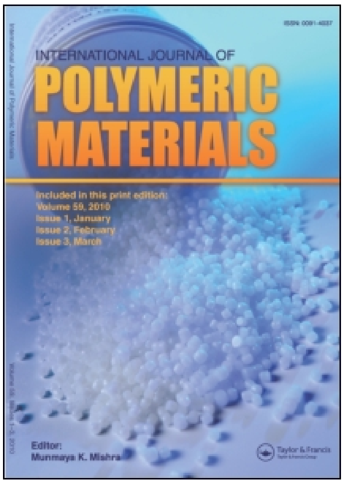

International Journal of Polymeric Materials

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 Bychkov, S. G. , Bogatyreva, N. A. and Timoshkin, A. M.(1993) 'Decrease in Epoxy Composition Combustibility After Laser Treatment', International Journal of Polymeric Materials, 20: 1, 15 — 18

To link to this Article: DOI: 10.1080/00914039308048497

URL: http://dx.doi.org/10.1080/00914039308048497

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Intern. J. Polymeric Mater., 1993, Vol. 20, pp. 15–18
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Printed in Malaysia

Decrease in Epoxy Composition Combustibility After Laser Treatment

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The influence of a preliminary CO_2-laser radiation treatment on the epoxy composition combustibility has been studied. This method of polymer surface modification is shown to provide a considerable decrease in polymer combustibility. The maximum effect is observed when an aromatic hardener is used.

KEY WORDS Epoxies, combustibility, CO_2-laser radiation.

RESULTS AND DISCUSSION

The essence of the thermal epoxy polymer treatment reported in Reference 1 is to modify only the polymer surface. However, practical use of this effective method of combustibility reduction is rather time-consuming and requires warmup of the entire bulk of the sample. At the same time, today use of laser radiation is rather significant in the chemistry of polymers for surface modification only in order to provide a material with a new set of physico-chemical properties.[2,3]

This paper deals with the influence of the preliminary laser treatment on epoxy composition combustibility. An epoxy resin (ER) (which is analogous to EDR-22) thermally hardened with aromatic (methaphenylenediamine) and aliphatic (polyethylenepolyamine) amines has been investigated. A continuous CO_2-laser with mean radiation wavelength of 10.6 mcm was chosen because the absorption bands of unreacted epoxy groups (900–1000) cm^{-1} corresponded to this spectral range.[4] In addition, the epoxy polymers have been found to effectively absorb the radiation in the given region ($1 - R = 0.95$, where R is the reflection coefficient), the absorption depth being on the order of 200–300 mcm.[5]

The diameter and the length of the cylindrical samples were 7 mm and 80 mm, respectively. The samples were irradiated in air at power densities $q = 59.8$, 69.4, 79.0 W/cm^2; the installation provided uniform irradiation of the sample surface due to the rotational-linear motion of the sample.[6] The material combustibility was evaluated by the "Oxygen index" (OI) method according to the standard technique GOST-21793-76. The material structure changes were investigated in the film samples by the ultraviolet and infrared methods.

The temperature in the irradiation region has been estimated with regard to the thermal-physical parameters of the material as well as the intensity and cyclicity of the exposure. The temperature was calculated according to the formula

$$T = \frac{(1 - R)q\mu}{\rho C}\frac{\tau_0}{U} + T_i$$

where μ is the absorption index, ρ is the density, **C** is the heat capacity, τ_0 is the beam radius, U is the linear velocity of the beam displacement along the sample surface, and T_i is the initial temperature. After the polymer was fixed in the installation, its surface area equal to the beam diameter was subjected to the sixfold quasi-pulse irradiation. The duration of one pulse was as long as 22 ms. In each subsequent turn the absorbed energy was accumulated according to the choice of the sample rotation frequency **f**, i.e. under the condition $\mathbf{f} < a/30\ \tau_0^2$, where a is the thermal diffusivity. Calculations showed that the additional temperature in the radiation zone was as high as 300 K.

It was found that the sample color changed from nearly colorless to dark brown as the absorbed energy dose increased. When the absorbed energy dose exceeded a certain critical value the surface layer loosened and separated from the main bulk of the sample. There were almost no flashes and instabilities in the process of the irradiated sample combustion.

The monotone increase in OI values was observed for all the samples of stoichiometric composition (Figure 1). It should be noted that the dependence had an extremum with a clearly marked maximum caused by the modified layer destruction at high doses of absorbed energy. For both types of composition the rate of OI change increased with the power density of the energy of radiation.

In the case of ER + PEPA composition the $\mathrm{OI_{max}}$ values increased with q, while in the case of ER + MPhDA composition the corresponding $\mathrm{OI_{max}}$ values decreased to some extent. However, the total effect in the second case was considerably greater, i.e. $\mathrm{OI_{max}}$ (q = 59.8 W/cm^2), two times that of the initial sample. The coke residue of the irradiated and initial samples of ER + MPhDA and ER + PEPA were 14.0 and 14.6; 6.1 and 6.4, respectively. The decrease in the sample combustibility cannot be explained by the increase in the total coke output only (the material is considered to be uniform at a macroscopic level). The candle-type combustion rate of the cylindrical samples is known to be determined by both the rate of a layer-to-layer burnout of the sample at its end and the rate of the flame propagation along its side. In this case it was the rate of the flame propagation along the modified surface of the material that essentially decreased. The coke residue for the film samples irradiated at q = 79.0 W/cm^2 during 80 s increased up to 20.2 and 10.6 as compared to 13.8 and 5.9 for the initial compositions of ER + MPhDA and ER + PEPA, respectively.

IR spectral investigation was carried out with 20–25-mcm thick film samples subjected to 10 s step irradiation (i.e., in 10 s) at q = 60 W/cm^2. The results obtained are shown in Figure 2. Figure 2 shows that the number of unreacted epoxy groups decreased as the irradiation time increased (curves 1, 2, 920 cm^{-1}). Greater relative change of the epoxy groups corresponds to ER + PEPA composition. This

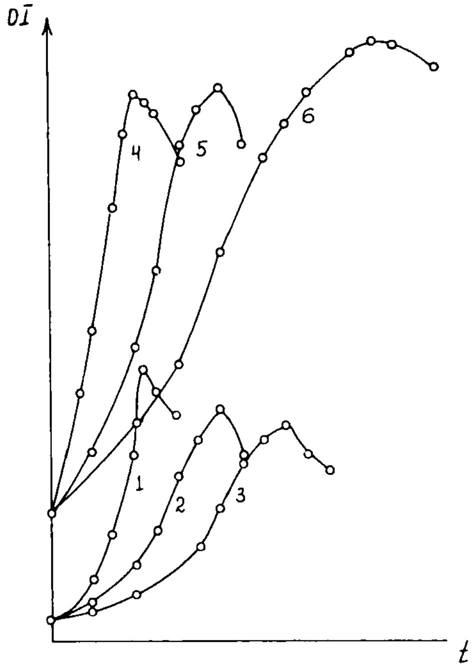

FIGURE 1 OI as the function of t (t is the irradiation time) for the stoichiometric epoxyamine compositions of ER + PEPA (1–3) and ER + MPhDA (4–6) at q = 79.1 (1, 4), 69.4 (2, 5), 59.8 (3, 6) W/cm^2.

may be caused by the greater amount of free groups in the initial ER + PEPA composition. This has been confirmed by the fact that the conversion degree values are 75% and 95% for ER + PEPA and ER + MPhDA compositions, respectively. In other words, during the laser treatment, first of all, the composition rehardening takes place which leads to a decrease in combustibility. In addition, it has already been shown by Neiman *et al.*[4] that at the initial stage of the thermal destruction process of the epoxy compositions both composition and output of gaseous products are determined by the amount of free epoxy groups. In addition, at the initial stages of ER + PEPA composition treatment the relative intensity of the absorption band increases in the region of 1580 cm^{-1} which is caused by the oscillations of the C═C aromatic ring bounds. In the course of further irradiation the absorption band intensity decreases due to the aromatic fragment oxidation as well as the formation of the conjugated structures as it takes place in the case of thermal treatment. This fact is confirmed by the absorption change in the region of 1730 cm^{-1} (C═O, curves 3, 5) as well as in the region of 1620 cm^{-1} (C═C, curves 4, 6). The relative absorption change caused by the C═C bound oscillations in both aromatic and aliphatic fragments for ER + PEPA composition is much greater due to the structure of the hardener.

Additional information has been provided by UV spectrum analysis. The surface laser treatment results in the appearance of the absorption band in the region of 460–480 nm. The intensity of the band increases with the time of irradiation, the absorption boundary shifting into the long-wave region as a result of the increase

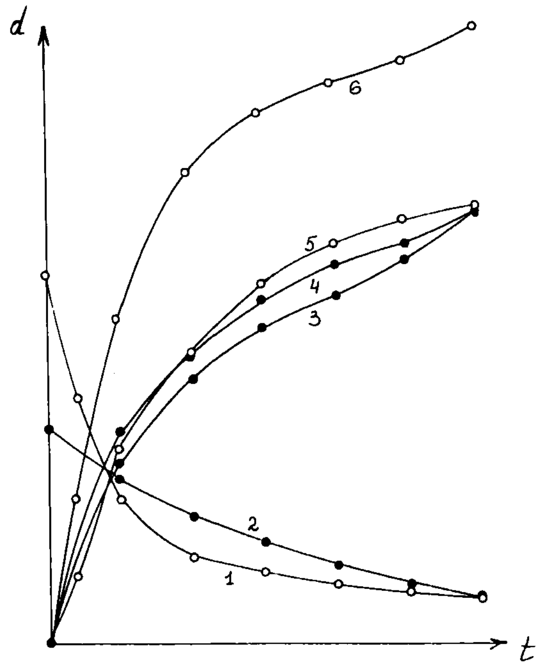

FIGURE 2 The relative intensity change of the absorption signals as the function of the irradiation time (t) for the epoxy (1, 2) and the carbonyl (3, 5) groups, C═C bounds (4, 6) at $q = 60$ W/cm^2.

in the number of condensed aromatic formations. In the case of ER + MPhDA, during further irradiation the absorption spectrum becomes structureless due to the further agglomeration of the formations above.

Thus, it has been found that the CO_2-laser radiation, first of all, stimulates the conversion of unreacted epoxy groups. In addition, the processes of oxidation and conjugation lead to the formation of the aromatic structures which appear to be the coke formation centers, thus providing a greater efficiency of the aromatic hardener. In contrast to the thermal treatment method, this method gives the positive effect for ER + PEPA composition.

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