Effect of ultraviolet and x-ray radiation on optical properties of epoxy polymers dyed with organic phosphors

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Abstract. Highly purified industrial bisphenol and cycloaliphatic epoxy oligomers of ED-24 and UP-612 brands were used to produce optically transparent products. UV radiation of a low-pressure mercury lamp with 80% of the light energy at 254 nm was used to study photodegradation. X-ray apparatus with 0.7BSV-Ag tube was used as an ionizing radiation source to investigate the effect of X-rays on the spectra of organic dyes in epoxy polymer. The threshold value of the energy generated by ruby laser which indicated the degradation in the test samples recorded by light scattering method was determined to study radiation resistance of epoxy polymers. Basically, all the dyes exhibited high resistance to UV light. The observation of the absorption spectra showed that on average, a third of the dye molecules in the matrix experienced photobleaching within 200 hour exposure. The exception was coumarin 1, which was completely decolourized after 40 hours of exposure. X-ray irradiation of the samples for two hours results in the change in the optical density equivalent to that caused by 40 hour exposure to UV irradiation. However, in the first case, the matrix optical density is proportional to the irradiation time, and in the second case, it remains stable upon further UV irradiation. The comparison of photoaging processes in dyed and undyed epoxy polymers showed that the investigated organic dyes do not have a sensitizing effect on the matrix. The stability of the optical properties of the epoxy matrices exposed to the effects of different factors was found to depend on the nature of epoxy polymer and the technique of its production. The results of these effects are significantly different in the character of the change in the optical density and mechanisms of chemical transformations in polymer.

1. Introduction

One of the promising areas for application of transparent polymeric materials is laser technology, where these materials can be used to make active elements with lasing dyes, bleaching filters for Q-switching, and others. A dye laser with a dye-doped solid matrix combines the advantages of solid-state lasers, which can generate radiation in a wide spectrum range completely overlapping the entire visible spectrum [1–3].

Practical use of laser elements largely depends on their ability to provide the operational life and to efficiently convert pump radiation of different power levels. These parameters depend on both the solid medium and the dye incorporated [4–6].

This paper presents the results obtained from the experimental study of photo- and X-ray degradation of dyed epoxy polymers.

2. Materials and methods

Epoxy oligomers are typically produced through the reaction of epichlorohydrin with phenol. The structure and properties of cross-linked epoxy polymers and the kinetics and thermodynamics of their formation are well studied [7]. The basic reactions occurring during epoxy polymer curing using amines, most commonly used curing agents, can be represented by the following scheme (Fig. 1).

The reacting system components, starting materials and reaction products, are hetero- and auto complexes that can be formed both inter- and intramolecularly. At high temperatures, the formed epoxy groups are condensed with unreacted hydroxyl and with each other that induces formation of additional lattice points.

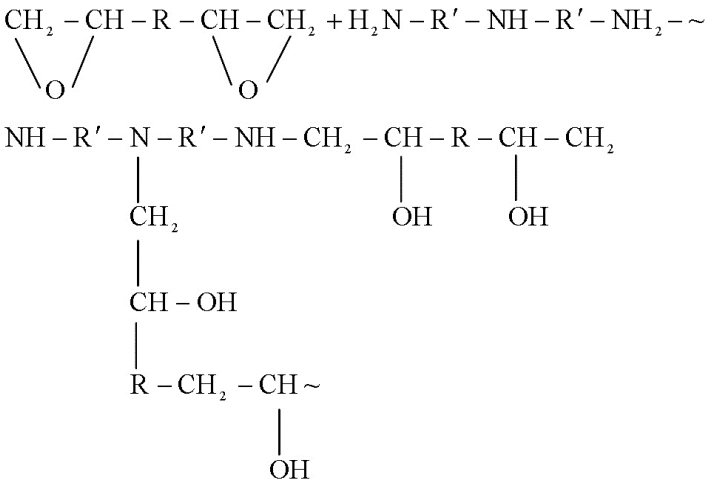

Figure 1. Scheme for producing epoxy polymers.

The synthesis of epoxy polymers was performed using the technology developed in the Ukrainian Research Institute of Plastics (Donetsk) in the 80-ies of the last century.

To obtain optically transparent products, we used highly purified industrial bisphenol and cycloaliphatic epoxy oligomers of ED-24 and UP-612 brands. The absorption spectra of these oligomers have two maxima at 227 and 282 nm. The corresponding absorption coefficients are significantly different and equal to 112200 and 17800 for ED-24, and to 500 and 25 cm^{-1} for UP-612. The transmittance of the curing agents in the visible spectral region is also high. The hardeners include a large number of curing agents of both basic and acid series.

An important advantage of epoxy polymers is the ability to vary their properties over a wide range through the selection of epoxy oligomers and curing agents. To study photodegradation, we used UV radiation generated by low-pressure mercury lamp with 80% of the light energy at 254 nm. The samples were placed in a chamber at 0.25 m from the source. The resultant ozone was blown off. The absorption and emission spectra of the samples were measured after every 20 hours of exposure.

The X-ray effect on the organic dye spectra of epoxy polymer was studied using an X-ray apparatus URS-1.0 with 0.7BSV- tube as an ionizing radiation source. The samples were mounted close to the windows of the X-ray tube. The voltage of the X-ray tube was 45 kV, and its current was 10 mA. The samples were exposed to radiation for 8 hours, and the optical spectra were measured every 2 hours.

The threshold value of the ruby laser energy which indicated the start of the sample degradation recorded using the light-scattering method was determined to study radiation resistance of epoxy polymers. An aperture with a diameter of 3.8 mm was mounted in the path of the ruby laser radiation, and the sample was placed behind the aperture. The energy level of laser radiation was measured using the IKT-1H device and averaged over the whole spot area, $S = 0.113$ cm^2. The laser operated in a passive Q-switching mode. Phthalocyanine vanadium solution in chlorobenzene was used as a photo-optical shutter.

3. Experimental results and discussion

Fig. 2 shows the absorption and emission spectra of dyed epoxy polymers after UV irradiation. All the tested dyes largely exhibited good resistance to UV light. The observation of the absorption spectra showed that around a third of the dye molecules in the matrix were photobleached during 200 hour exposure. The exception was coumarin 1, which was completely decolorized after 40 hours of exposure. The changed luminescence intensity was proportional to the changed dye concentration in epoxy polymer.X-ray irradiation lasted for 8 hours. The absorption and luminescence spectra were measured every 2 hours.

No changes observed in the absorption spectra indicate that the tested dyes are radiation resistant. The luminescence intensity slightly decreased after exposure due to the overlapping of the dye and epoxy polymer absorption bands that leads to non-radiative losses of the absorbed radiation in the matrix.

Exposure of the samples to X-ray irradiation for 2 hours causes the changes in the optical density equivalent to those occurring during 40-hour UV irradiation. However, in the first case, the optical density of the matrix is proportional to the irradiation time, and in the second case, the density remains constant under further UV irradiation.

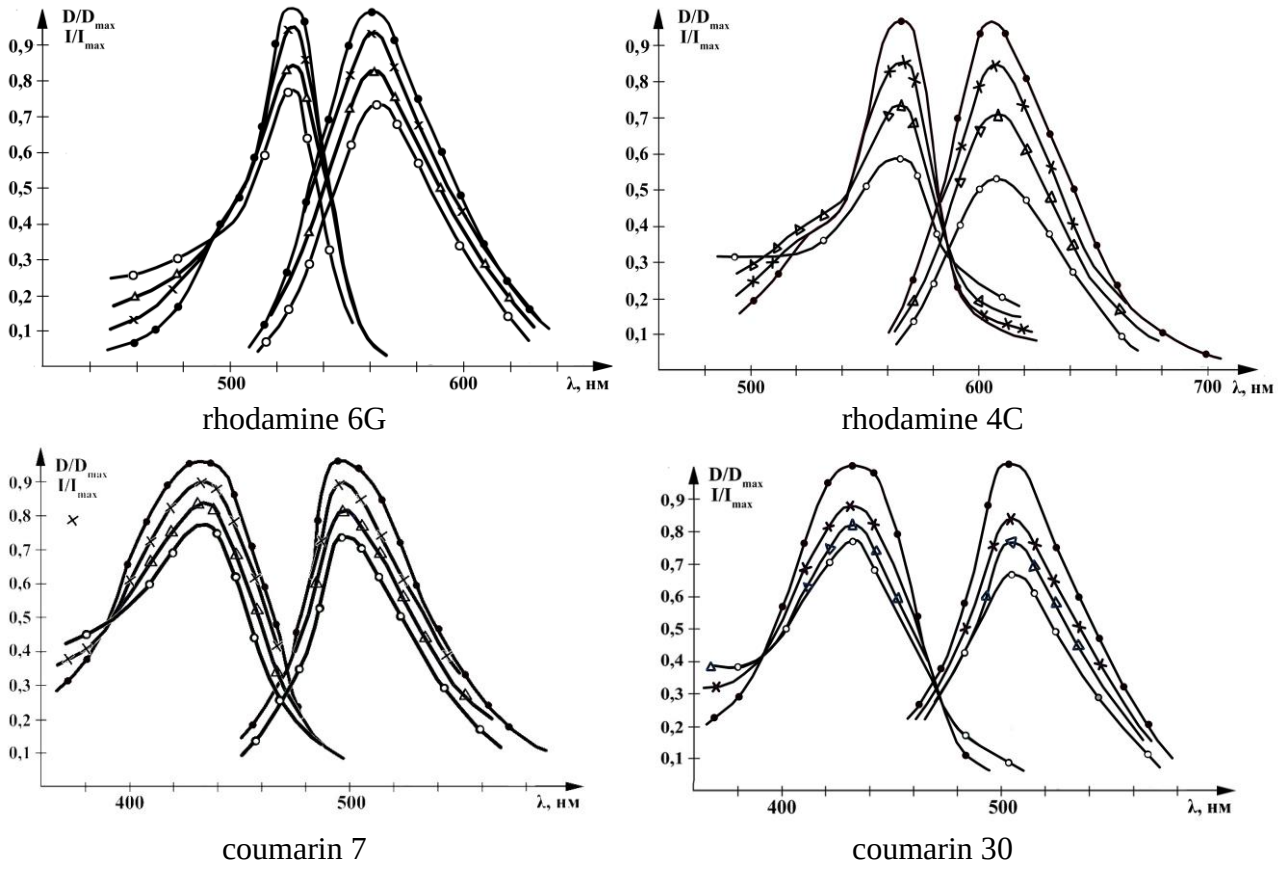

Figure 2. Effect of UV irradiation on absorption and luminescence spectra of dyed epoxy polymers.

Tables 1–2 show the position of the absorption bands after exposure to UV light and X-rays, respectively. The polymers in the tables are arranged in order of decreasing optical clarity. Sample 1919 is amine-cured epoxy polymer, and other samples are anhydride-cured epoxy polymer treated at different curing temperatures.

Table 1. Short-wavelength transmission cutoff of the epoxy polymer clarity after 200 hour UV irradiation.

Sample no.	1914	1904	1913	1901	1915	1900	1903	1919
Transmission cutoff T = 32%, λ, nm	302	325	332	316	336	346	347	370
Δλ	2	15	17	26	-28	31	35	95

As can be seen from the data presented in Tables 1–2, samples 1914, 1904 and 1901 produced at low curing temperature with different polymer-curing agent ratio exhibit the greatest stability of optical properties. In Table 1, the sign "-" before the value λΔ for sample 1915 indicates that the transmission cutoff under UV exposure shifted toward the short wavelength region. This indicates the

photopolymerization processes in epoxy polymer caused by the crosslinking agents due to photodissociation of the molecules in the hardener, which possesses a high absorption capacity in a free state in the blue spectral region.

Table 2. Short-wavelength transmission cutoff of the epoxy polymer clarity after 6 hour X-ray ageing.

Sample no.	1914	1904	1913	1901	1903	1900	1915	1919
Transmission cutoff T = 32%, λ, nm	340	358	365	360	370	385	405	completely blackens after 1 hour exposure
Δλ	40	48	50	70	58	70	30	

The study of the effect of UV radiation on optical clarity of the epoxy polymer revealed cavities on the sample surface visible to the naked eye. These cavities are attributed to the impact of ozone. The size and number of defects indicated the polymer resistance to ozone. The surface of sample 1904 remained virtually clean throughout the irradiation time. Thus, epoxy polymer 1904 exhibited the most complete set of performance characteristics required for creation of active laser media for extreme conditions.

The comparison of photoaging of dyed and decolorized epoxy polymers revealed that the investigated organic dyes do not have a sensitizing effect on the matrix. Under X-ray irradiation, the optical density of the samples was proportional to the exposure time. The comparison of the data in Tables 1 and 2 revealed a complete correlation between the resistance of epoxy polymers to UV and X-ray irradiation. However, the effects of UV and X-ray irradiation on the samples are significantly different. The radiation-induced absorption occurs in the absorption spectra of epoxy polymers in the region of 400 to 440 nm: in samples 1901–1914, it occurs after 6 hours of X-ray irradiation, in sample 1915, it can be observed after 4 hour irradiation, and in sample 1919, it is recorded after 10 minute irradiation.

The studies showed that the resistance of the epoxy matrix optical properties to the effects of various factors depends on the nature of epoxy polymer and the technique of its production. The results of these effects are significantly different in the character of the optical density changes and mechanisms of chemical transformations in polymer.

We determined the threshold value of the ruby laser irradiation energy density which indicated the sample degradation visually observed in the diffused light of the helium-neon laser.

Epoxy samples of different chemical composition were studied:

- Sample 1924 dyed with rhodamine 6G ($c=4.68\cdot10^{-5}$ g/g);
- Sample 1925 dyed with rhodamine C ($c=4.68\cdot10^{-5}$ g/g);
- Samples 1924 and 1927 bleached and modified with diaplast;
- Sample 1929 dyed with rhodamine 6G ($c=10^{-4}$ mol/l) unmodified;
- Sample 1927, polymethylmethacrylate dyed with rhodamine 6G.

The data on the damage threshold are presented in Table 3.

Table 3. Radiation strength of the polymer samples.

Sample no.	PMMA	1927	1929	1924	1925
E, J/cm^2	6.5	5.3	4.8	4.4	3.5

The results of the study show that the damage threshold of the modified polymethyl methacrylate is higher than that of epoxy polymers.

Incorporation of diaplast in the epoxy polymer matrix improved its viscoelastic properties and increased the damage threshold. This fact is in full accordance with the data reported in numerous studies that established the dependence of the polymer damage threshold on its viscoelastic properties.

Thus, the damage threshold of both epoxy polymers and PMMA can be increased through matrix modification. Moreover, the above stated results show that low-molecular plasticizers are more suitable for this purpose.

4. Conclusion

Several tens of polymers and their compositions have been used as active laser media for more than 50 years of the laser technology development. These studies identified the materials, which are most promising from a practical standpoint. It was shown that with respect to the requirements for thermal stability, mechanical hardness, solvent resistance and optical clarity over a wide wavelength range, 17 polymers are found to be suitable for their use in high power lasers.

However, 5–6 polymers (PMMA, PS, PU, PC, and epoxy polymers and their modifications) have been commonly used as active laser media so far. Epoxy polymers exhibit a wide range of differences in their properties depending on the dye, modifier and production technologies. This is the aspect we aimed to consider in the current paper.

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