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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 Baimuratov, E. , Kalontarov, I. Y. and Saidov, D. S.(1993) 'The Influence of Reactive Dyes on Thermo-, γ -Radiation and Photooxidative Degradation of Stressed Polyvinyl Alcohol', International Journal of Polymeric Materials, 19: 3, 193 – 199

To link to this Article: DOI: 10.1080/00914039308012031

URL: <http://dx.doi.org/10.1080/00914039308012031>

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The Influence of Reactive Dyes on Thermo-, γ -Radiation and Photooxidative Degradation of Stressed Polyvinyl Alcohol

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Using infrared spectroscopy it has been shown that the mechanical load increases the rate of thermo- and γ -radiation of polyvinyl alcohol (PVA) and photooxidative degradation. The inclusion of reactive dye in the polymer inhibits these processes.

KEY WORDS Dyes, stress polyvinyl alcohol, degradation.

Polymeric products may be subjected to many external factors: mechanical load, different types of irradiation, temperature, etc. Using infrared spectroscopy it has been found that concurrent influence of the above mentioned factors on PVA samples together with the increase of mechanical load intensifies the processes of the thermo-, photo- and γ -radiation degradation.^{1,2} Considerable changes in the amorphous-crystalline structure, the decrease in deorientation of macromolecules and intensive formation of oxidized groups can also be observed. Different reactive dyes are used as stabilizers to inhibit the above mentioned processes. But the influence of reactive dyes on the kinetics of oxidized C=O group formation under the combined action is not sufficiently clear. That subject is the focus of this study.

EXPERIMENTAL

Uniaxially oriented PVA films at $\epsilon = 300\%$ were used as samples. The sample thickness after orientation was 6–10 micrometers. The films had been dyed by the introduction of a C.I. Reactive Yellow 4 dye to PVA solutions. The dyeing had been conducted according to a method described³ in two ways: a) a solid solution, i.e. when dye molecules are not chemically linked with a polymer and b) formation of a covalent chemical link of a dye with PVA macromolecules.

The investigation of the influence of the mechanical load on the kinetics of the formation of C=O groups during concurrent thermo-, photo- and γ -radiation degradation of loaded PVA samples was conducted according to methods described elsewhere.^{1,2} The formation of C=O groups was registered by an analysis of in-

frared spectra of PVA samples before and after tests at an absorption band of frequency 1720 cm^{-1} , relating to a valence oscillation of a $\text{C}=\text{O}$ group of a ketonic type.

THERMOMECHANICAL OXIDATION

Figure 1-a shows the dependence of relative optical density $D' = D/D_0$ at the absorption band 1720 cm^{-1} , (where D and D_0 are optical density values of tested and initial samples) from the mechanical load duration. The value of the load is σ

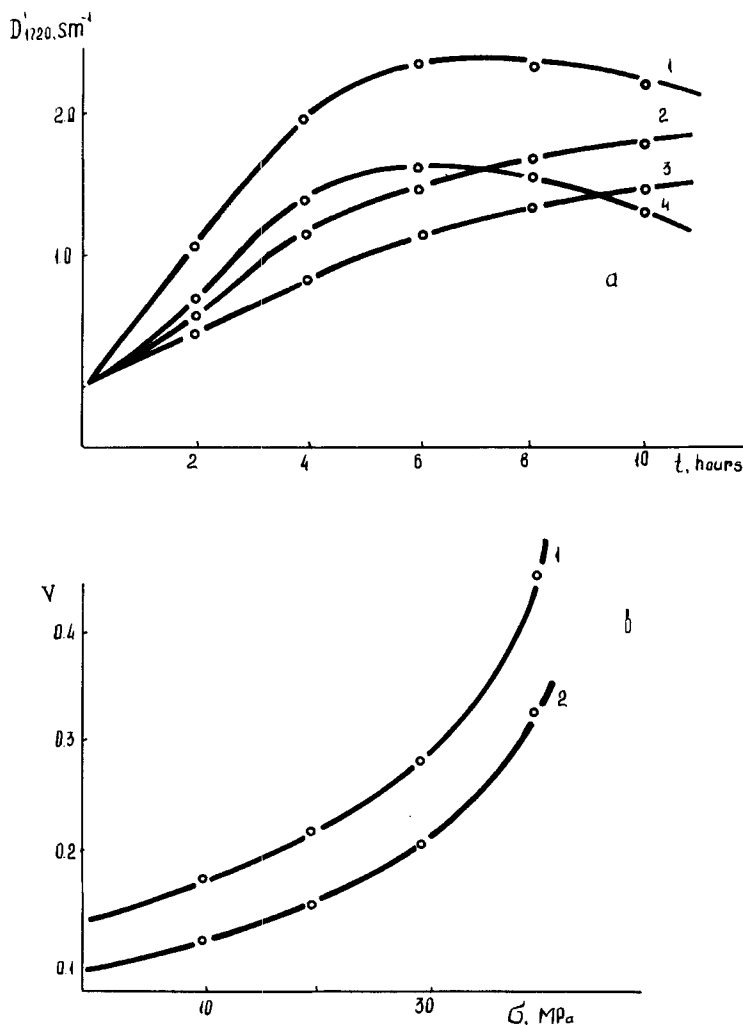


FIGURE 1 (a) Dependence of the absorption band 1720 cm^{-1} relative optical density on the heating duration at temperature 453 K . 1 and 2— $\sigma = 20\text{ MPa}$, 3 and 4— $\sigma = 0$; 1 and 4—undyed samples ($C = 0\%$), 2 and 3—dyed samples ($C = 2.2\%$). (b) Dependence of oxidized groups formation speed (V) on mechanical load at temperature 453 K , 1—undyed sample, 2—dyed sample ($C = 2.2\%$).

= 20 MPa for undyed (curves 1 and 2) and dyed samples (curves 3 and 4). There is an increase in C=O group content with an increase of heating duration. The curves show that the increase in load and heating duration up to 6 hours results in the increase of C=O group content, and then D' decreases, indicating the decreased speed of C=O group formation. It should be noted that an oxidation process is influenced by a PVA dehydration with the formation of >C=C< links and the number of forming C=O groups decreases. The speed of C=O group formation in a dyed polymer decreases in both loaded and unloaded schemes. With other test conditions being equal the value of D' for undyed PVA is twice the value for dyed PVA.

The kinetics of C=O group accumulation under different loads is shown in Figure 1-b, from which it is seen, that the speed of formation of oxidized groups increases parabolically with the load (curve 1), though for dyed samples this increase is somewhat inhibited (curve 2).

That is, the interaction of PVA with an reactive dye significantly inhibits the thermo- and thermomechanical PVA degradation. Therefore, dichlorotriazine active dyes such as C.I. Reactive Yellow 4 can be recommended as thermostabilizers for PVA and PVA-based products subjected to the concurrent influence of mechanical load and temperature.

OXIDATION UNDER CONCURRENT INFLUENCE OF RADIATION AND MECHANICAL FORCE

Figure 2-a contains curves displaying the relations of the relative optical density of initial and dyed (with C.I. Reactive Yellow 4) PVA films at a frequency 1720 cm^{-1} and γ -radiation level at irradiation with and without load.

The γ -irradiation increase to $\lg D = 3.4$ for undyed PVA irradiated in a free state leads to a slight increase of D'_{1720} , whereas further increasing $\lg D$ up to 3.8 leads to a sharp increase of D'_{1720} , indicating an intensive radiation degradation. The investigated reactive dye retards the speed of the radiation degradation, since the D'_{1720} for undyed PVA is lower than for the initial sample. At the same time, if a concurrent load is present ($\sigma = 100\text{ MPa}$), the speed of C=O group accumulation visibly increases (Figure 2-b, curve 1).

A small quantity of the reactive dye in the polymer retards its radiation degradation (Figure 2-a, curves 1, 3, 5). The irradiated PVA containing 2.2% by mass of the chemically linked reactive dye has a low C=O group accumulation rate (Figure 2-b, curve 2), though an increase in the mechanical load speeds the formation of oxidized C=O groups (the same is observed for undyed PVA). Analyzing Figures 2-a and 2-b one can conclude that C.I. Reactive Yellow 4 acts as stabilizer during concurrent γ -radiation and mechanical degradation.

PHOTOMECHANICAL OXIDATION

The accelerating effect of the load on the PVA photooxidation process is observed in the irradiation of the polymer dyed with the reactive dye in both forms—covalence links formation and a solid solution.

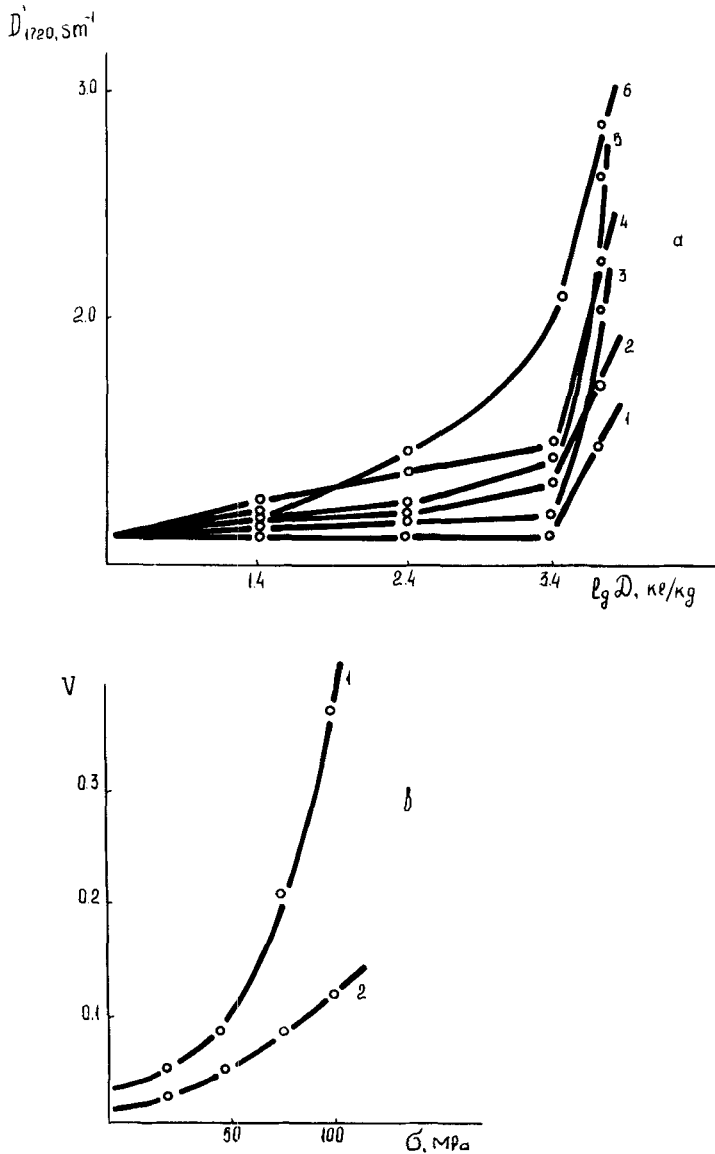


FIGURE 2 (a) Dependence of absorption band 1720 cm^{-1} relative optical density of undyed and dyed samples on irradiation dose; 1— $\sigma = 0$, 3— $\sigma = 50\text{ MPa}$, 5— $\sigma = 100\text{ MPa}$ —for dyed samples with dye concentration $C = 2.2\%$; 2— $\sigma = 0$, 4— $\sigma = 50\text{ MPa}$, 6— $\sigma = 100\text{ MPa}$ —for undyed samples. (b) Dependence of oxidized groups formation speed under concurrent radiation and mechanical destruction from mechanical load (V); 1—undyed samples, 2—dyed samples with dye concentration $C = 2.2\%$.

In the case of covalence links with macromolecules of dyed PVA, the photo-mechanical degradation is much slower (Figure 3-a, curves 8–10) than in case of the undyed PVA (curves 1–4) and the PVA dyed in the form of the solid solution (curves 5–7). This is apparently caused when the UV-radiation energy, influencing

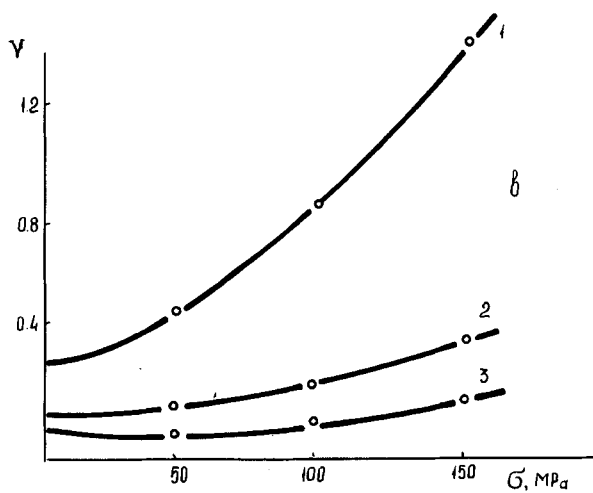
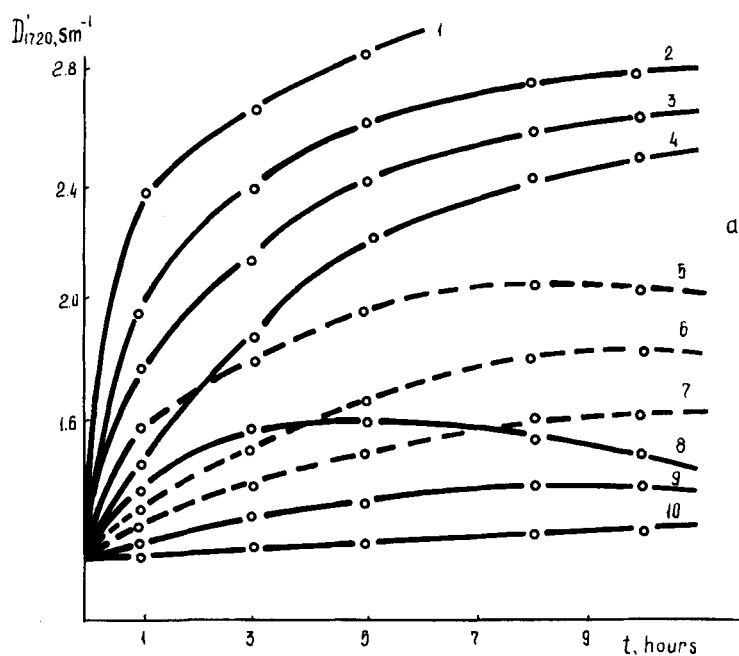


FIGURE 3 (a) Dependence of absorption band 1720 cm^{-1} relative optical density on UV-irradiation duration; 1 and 4—undyed samples; 5, 7—dyed without covalence links formation; 8, 10—dyed with chemical links formation between dye and PVA. 1, 5, 8— $\sigma = 150\text{ MPa}$, 2, 6, 9— $\sigma = 100\text{ MPa}$, 3— $\sigma = 50\text{ MPa}$, 4, 7, 10— $\sigma = 0$. (b) Dependence of oxidized groups formation speed (V) on mechanical load; 1—undyed sample, 2—dyed sample with $C = 2.2\%$, without chemical links; 3—dyed samples with $C = 2.2\%$, with chemical links.

the dyed polymer and migrating along oscillation levels, is transferred to the dye molecule by means of the covalence links. The UV-radiation energy is evidently absorbed by the aromatic rings and easily dissipated in the system of π -electrons, preventing its localization on a particular link with the following link dissociation. That is why reactive dyes (C.I. Reactive Yellow 4) ensure partial stabilization of the PVA structure under photomechanical degradation conditions.

To study the influence of covalence links of the dye with the polymer on the photomechanical oxidation of the dyed PVA, the influence of the UV-radiation on dye fading in PVA films (both chemically linked and in the form of the solid solution) was investigated (Figures 4-a and 4-b). Figure 4-a shows that the load leads to an increase in the dye fading speed at photooxidation; the more the load,

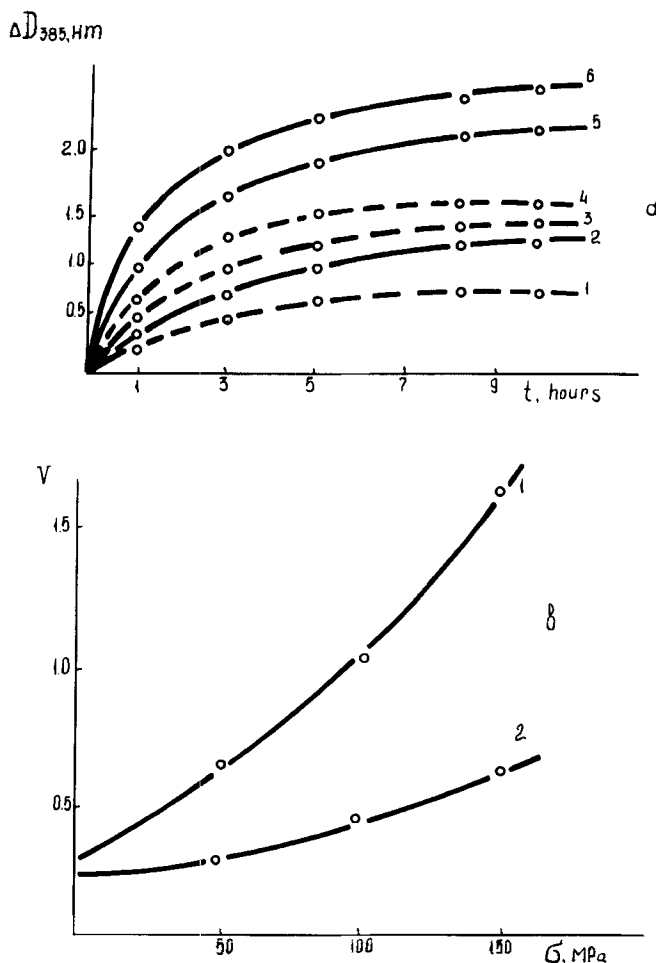


FIGURE 4 (a) Dependence of C.I. Reactive Yellow 4 fading on UV-irradiation duration in dyed PVA under different stretching loads: 1— $\sigma = 0$, 2— $\sigma = 100$ MPa, 3— $\sigma = 150$ MPa, $C = 2.2\%$ —dye is not chemically linked; 4—0, 5— $\sigma = 100$ MPa, 6— $\sigma = 150$ MPa, $C = 2.2\%$ —dye chemically linked. (b) Dependence of C.I. Reactive Yellow 4 light fading speed (V) on mechanical load, 1—dye is chemically linked; 2—dye is not chemically linked.

the more the fading speed. Nevertheless, when the reactive dye molecules are covalently linked with the polymer, its fading speed is significantly higher than in the case of the solid solution (Figures 4-a and 4-b). It can be concluded that the UV-irradiation leads to the accumulation of oxidized groups in the loaded polymer, accompanied by the increase in the reaction products, hydroperoxide groups in particular. They decompose with the free radicals' formation, leading to the decomposition of the dye molecules (Figure 4-a). I.e., in the case of covalence fixation of the dye there is an increase of the dye fading speed under the load with concurrent decrease of the polymer photooxidation speed (Figure 4-b). Comparing the C=O group accumulation speed data (Figure 3-b) and the reactive dye fading data (Figure 4-b), one notes that in both cases (covalence links of the dye and its solid solution in the PVA) active dye can stabilize the PVA by shielding, though in the first case the energy is transferred from the polymer to the dye molecule. It is also possible that the dye photoconversion products in the polymer matrix may also produce the stabilizing effect. This proves the proposed assumption of the C.I. Reactive Yellow 4 stabilizing effect under the concurrent influence of the UV-irradiation and the mechanical load. An active dye with covalence links with the PVA, fading itself, protects the polymer under combined effects of UV-radiation and the mechanical load.

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