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The Influence of Dyes on Thermal and Thermo-Oxidative Degradation of Dyed Polymeric Fibers

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The influence of reactive dyes and their deactivated forms on the thermal degradation of polyvinylalcohol (PVA) and polycaproamide (PCA) fibers was investigated. Complex thermographic analysis in air and inert atmosphere showed that fibers dyed by reactive dyes are more resistant to thermo-oxidative degradation than untreated PVA and PCA fibers. A possible mechanism of the stabilizing influence of the dyes on the thermooxidative degradation of the investigated polymers was proposed.

KEY WORDS Dyes, thermal degradation, thermo-oxidative degradation, polyvinylalcohol, polycaproamide.

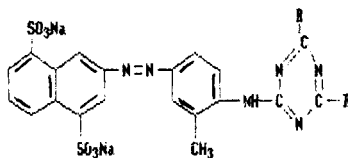
INTRODUCTION

Recent study of the effect of dyes on the thermal and thermooxidative degradation of polyvinylalcohol (PVA) and polycaproamide (PCA) has aroused considerable interest.^{1,2} It has been previously reported that the reactive dyes bonded covalently to the macromolecules of PVA, and cation dyes incorporated in the PCA bulk promote the thermal stability of these polymers.^{1,3} The aim of the present investigation is to study the effect of fiber reactive dyes and the nature of their bonding to the polymers on thermal and thermooxidative stability of the above polymers. To do this a complex thermogravimetric study of the behavior of dyed polymeric materials in comparison with undyed ones was carried out under dynamic as well as isothermic heating.

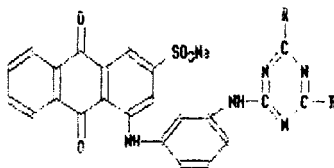
EXPERIMENTAL

Dyes. In this study fiber reactive dyes I–III and their deactivated analogues IV–VI were used.

I R = Cl
IV R = OH

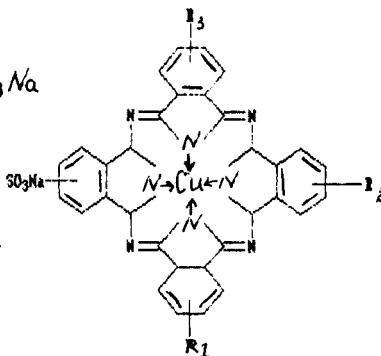


II R = Cl
V R = OH



III $R_{1,2} = \text{SO}_2\text{CH}_2\text{CH}_2\text{O}\text{SO}_3\text{Na}$
 $R_3 = \text{SO}_3\text{Na}$

VI $R_1 = \text{H}$ $R_2 = \text{SO}_3\text{Na}$
 $R_3 = \text{H}$



Deactivated forms IV and V were obtained by alkaline hydrolysis of fiber-reactive dyes I and II with 3N NaOH solution for 6 hours followed by neutralization with concentrated HNO.⁴

Dyed materials. PVA was dyed in a water solution. The samples in which the dyes were covalently bonded with macromolecules of PVA were obtained when I–III were used whereas when inactive forms IV–VI were used a solid solution of these dyes in PVA were obtained. The method is described in detail elsewhere.⁵

PCA fiber was dyed by dyes I and IV according to the method described by Kalontarov.⁶

Thermogravimetry investigations. (DTA) and (TGA) measurements were carried out on derivatograph "Paulik and Erdey" system in argon and air atmospheres at a heating rate of 5°C/min and 120 min. of exposure.

Aluminum oxide heated to 1000°C was used as the internal standard.

Isothermal investigations. The measurements of the sample mass loss were carried out on the thermobalance with continuous weighing of the samples in a thermostated cell. Thermal degradation of the initial and dyed PVA in vacuum was investigated by using a vacuum-device⁷ followed by gas-chromatographic determination of gaseous products of degradation.

RESULTS AND DISCUSSION

The DTA curves of PVA samples dyed by I and II and solid solutions of IV and V in PVA are shown in Figure 1 in comparison with the DTA curve of untreated PVA.

It should be noted that unlike the initial films, the dyed PVA films have no deep endo-effect at 120°C, corresponding to the loss of sorption water. Endoeffect at 220°C (initial sample of PVA) without the mass loss and corresponding to the melting of crystalline regions of the polymer has been shifted in the dyed samples to the region of 235–239°C.

The endoeffects at 280°C (curve 1), characteristic for the beginning of PVA deep dehydration, is observed in IV–V solid solution in PVA at 309–310°C and in chemical combination of I and PVA—at 358°C, and of II and PVA at 341–349°C.

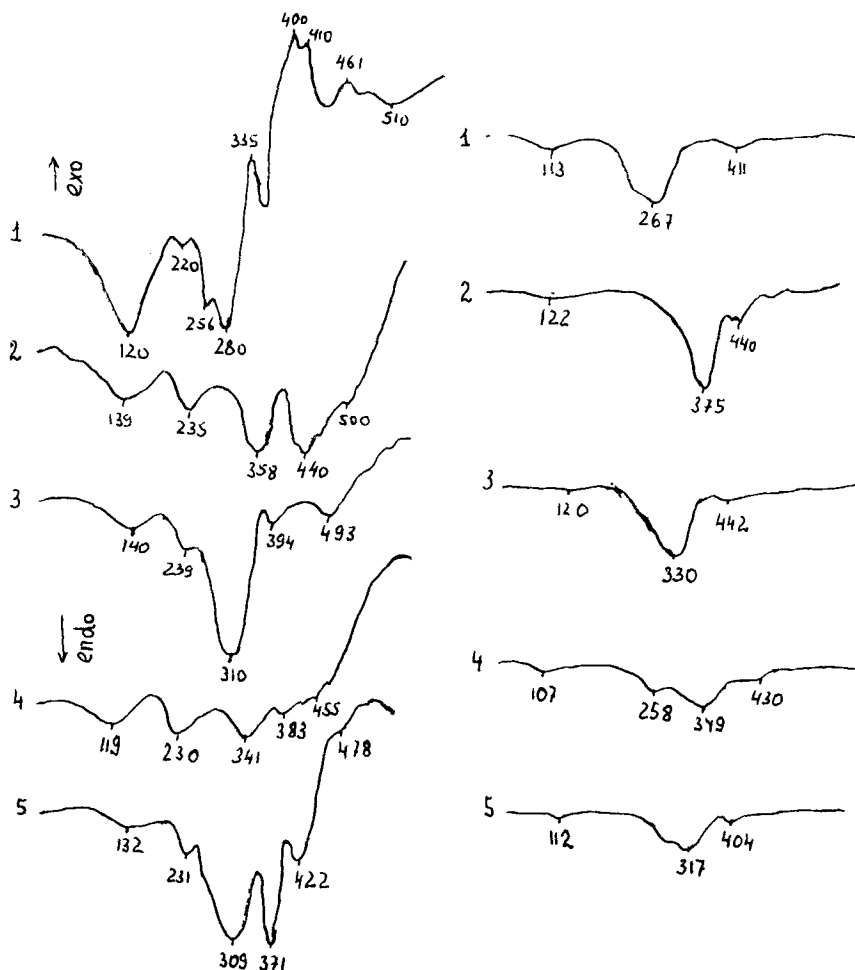


FIGURE 1 The DTA (a) and DTG (b) curves of dyed PVA-films (initial mass—500 mg) 1—initial PVA; 2–5—dyed by: 2—I; 3—IV; 4—II; 5—VI.

The differences of DTA curves are noticeable at 400–500°C. The complex processes of oxidation and decomposition of PVA take place in this region. The DTG curve confirmed that the maximum speed of mass loss of undyed PVA is observed at 267°C. The corresponding value for PVA covalently bonded with I is at 375°C, or a 100°C increase.

The data on thermostability of dyed samples compared to undyed samples obtained on the basis of TG curves are shown in Figure 2.

These curves show that PVA thermostability increases with the addition of dyes since the intensive degradation of dyed samples begins at higher temperatures and the depth of degradation at a given temperature decreases. The highest thermostabilizing action is exhibited by covalently bonded PVA-dyes, particularly with dye I.

Taking into account that polymeric materials were used for a long time in narrow temperature intervals, we investigated the kinetics of thermal degradation by isothermal heating.

The kinetics data of mass loss of samples for heating in the air at 200°C are shown in Figure 3, which shows that the initial PVA (curve I) incurs the greatest mass loss. The range of mass loss over 5 hours varies from approximately 15% for undyed PVA to 1.8% for samples dyed with III.

One can see that the thermostability of samples dyed covalently is higher than for samples containing the same dyes in deactivated form. For a sample dyed by I the mass loss is 4.5% for 5 hours, and 6% with dye IV; likewise 6.7% for dye II compared to 10.5% for dye V. Figure 3 shows that dye addition increases the PVA thermostability under heating in air, and the extent depends not only on the nature of the dye-polymer bond but also on the chemical structure of the dye. Phthalocyanine dyes show the greatest effect, then azodyes, and antraquinone dyes show the least effect.

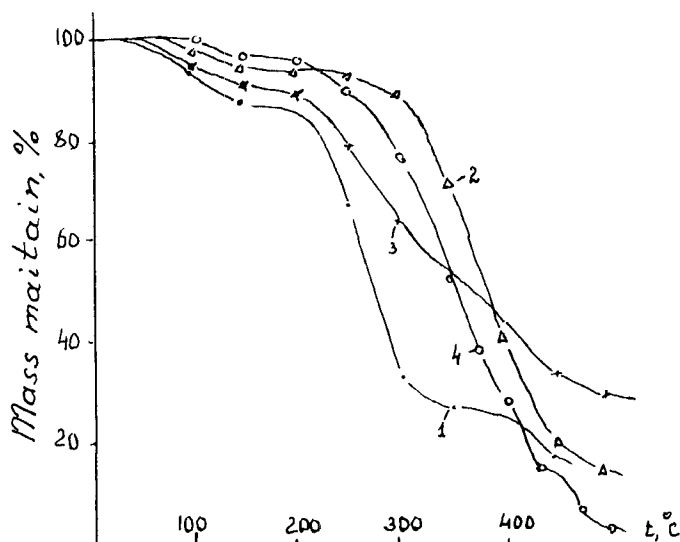


FIGURE 2 The thermostability of PVA-films: 1—initial; 2—dyed by I; 3—dyed by II; 4—dyed by III.

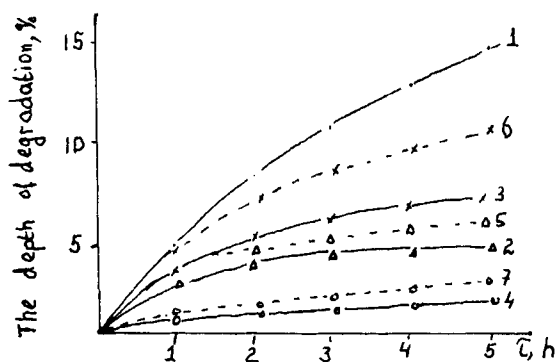


FIGURE 3 Degradation kinetics of PVA films in the air at 200°C: initial (1) and dyed (2-7): 2—I; 3—II; 4—III; 5—IV; 6—V; 7—VI.

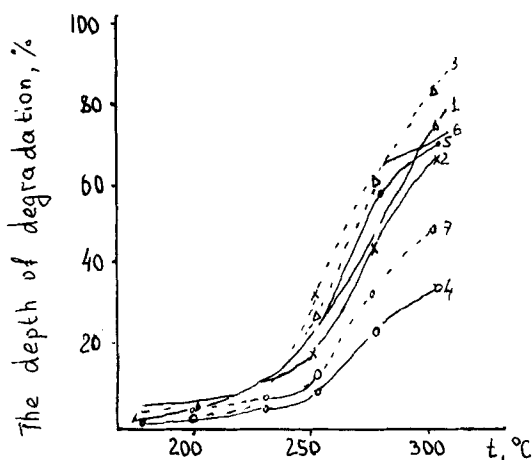


FIGURE 4 Degradation depth (weight %) PVA films under heating in air in the interval 200–300°C (designations are the same as at Figure 1).

At the same time the general tendency of samples containing covalent-bond dyes to increase resistance to thermooxidizing degradation was confirmed.

The mass loss curve for dye PVA samples under heating in air for one hour versus heating temperature are shown in Figure 4. As shown, the samples' mass loss is below 10% up to a heating temperature of 225°C, but increases dramatically with subsequent temperature increase.

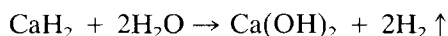
The formation of covalent-bond PVA with dyes I, II, and III diminishes sample mass loss, with the greatest effect observed for phtalocyanine dye III, then for I, while anthraquinone dye II barely influences the depth of polymer degradation. Deactivated dyes IV and V show some increasing of the degradation depth; phtalocyanine dye VI is an exception which shows stabilizing effect, but not relative to the covalently bound dye III. For example, at 300°C the degradation depth of undyed PVA is 74%; introduction of VI into PVA reduces it to 51%, and covalently bonded III brings it down to 35%.

The oxidation process of PVA undyed and dyed by fiber reactive and deactivated

dyes is characterized by complex reactions, distorting the real nature of degradation. Therefore, it was expedient to study the degradation of PVA and its dyed forms in a vacuum. It turned out that heating the samples in a vacuum over the same temperature interval produces a slightly different picture. The mass loss curves of the samples heated in a vacuum for an hour versus temperature are shown in Figure 5. As shown, the mass loss of undyed samples increases almost linearly up to 250°C, and one can observe the inhibiting effect of dyed samples up to 200–215°C.

The degradation depth of dyed samples increases sharply at even higher temperatures, and degradation depth is least for PVA dyes by I and III.

Analyses of the gaseous degradation products of PVA in vacuum establish that the basic volatiles are water and different aldehydes. Other gaseous products are not measured. The water content was determined quantitatively according to reaction with CaH_2 :



and gas chromatographic determination of hydrogen being released (Table I). The data in Table I that water quantity isolated at thermal degradation of PVA dyed

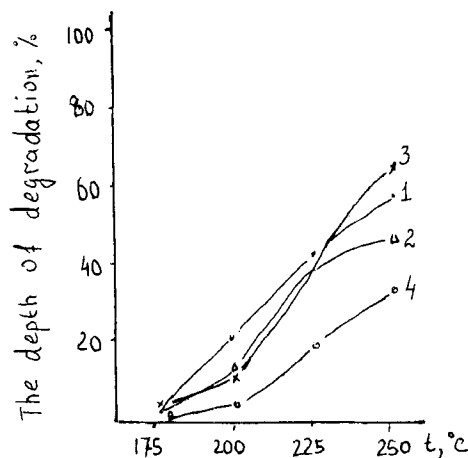


FIGURE 5 The thermal degradation of PVA films in vacuum: initial (1) and dyed (2–4) 2—I; 3—II; 4—III, at 175–250°C.

TABLE I

Quantity of water in weight %, dyed PVA sample isolated under heat in vacuum for an hour

Temperature, °C	Undyed PVA	PVA dyed by					
		I	IV	II	V	III	VI
175	0.3	0	0.4	0	0	0	0
200	2.4	2.3	2.4	1.9	2.1	0	0.8
225	5.8	7.2	6.5	8.5	9.1	1.9	2.9
250	12.7	7.6	12.3	9.7	11.5	4.1	5.1
300	—	—	—	—	—	8.2	—

by IV and V, in the chosen temperature interval are very similar. This is to be expected, since oxychlorotriazine dyes IV and V are not capable of chemical reaction with OH-groups of PVA. In PVA samples covalently-bonded with dyes I, II, and III, the quantity of isolated water at 250°C is considerably lower than for undyed PVA, and least for samples dyed with phthalocyanine (III type). Phthalocyanine dye VI in combination with PVA acts somewhat differently than the deactivated forms of dyes I and II, which could owe to the potential partial blocking of OH groups on PVA through complexation, as shown for PVA combined with direct dyes.⁸

POLYCAPROAMIDE

The DTA curves for initial and dyed PCA samples in air and in argon are shown in Figures 6 and 7. The first great endoeffect, accompanied by small mass loss in the temperature interval 80–90°C, is connected with loss of sorbed moisture. The endoeffect at 203–218°C without mass loss corresponds to melting at crystalline regions of PCA. The subsequent thermal effects are connected with oxidizing polymer degradation. Figure 6 shows that abrupt differences in thermal effects for undyed and dyed PCA are not observed. Quite a different picture is observed for DTA curves obtained in inert atmosphere (Figure 7).

Thermal effects of moisture loss and melting occur at 80°C and 210°C. If in air over the temperature interval 430–445°C deep exoeffects associated with mass loss is observed, then a number of endoeffects also connected with mass in the interval 420–480°C is observed in argon. While comparing DTA curves (Figures 6 and 7), it should be noted that thermodecay of PCA (endothermic reactions) takes place

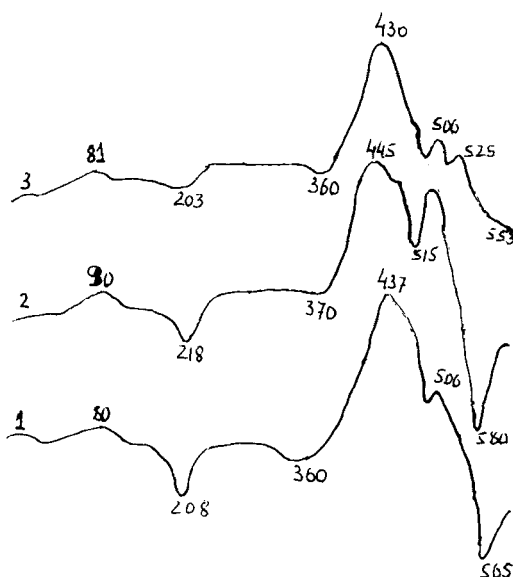


FIGURE 6 DTA curves in the air: 1—undyed PCA-fiber; 2—PCA-fiber covalently bonded with I; 3—PCA-fiber dyed IV.

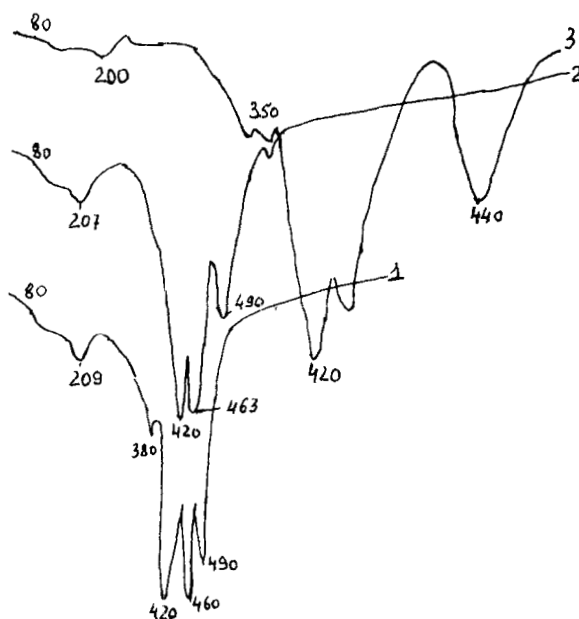


FIGURE 7 DTA curves in the argon: 1—undyed PCA-fiber; 2—PCA-fiber covalently bonded with I; 3—PCA-fiber dyed IV.

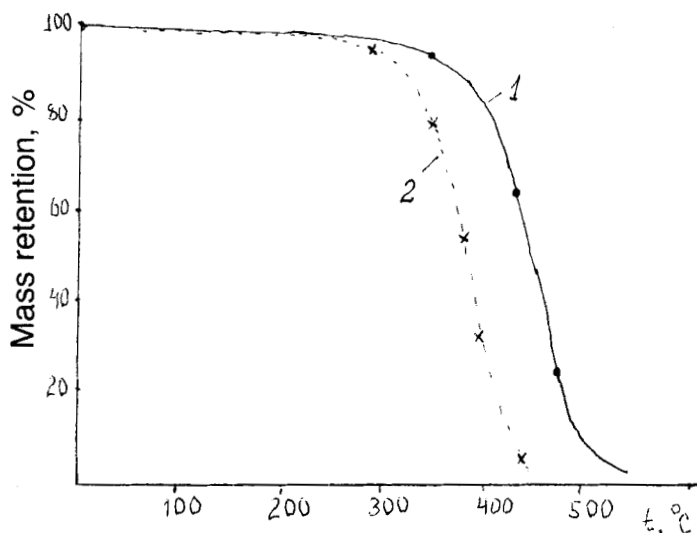


FIGURE 8 Dependence of mass retention on temperature: 1—PCA dyed in air; 2—initial PCA in air, original mass and dyed samples only 18%. It should be noted that PCA dyed by reactive dye is more stable to thermooxidation than PCA dyed by the same dye in the absence of covalent bonding.

under inert atmosphere whereas in the presence of air the oxidation of PCA (exothermic reactions) occurs according to a mechanism proposed by Rafikov.⁹ The curves of mass retention over temperature (Figure 8) indicate that undyed PCA (curve 4) is more steady under inert atmosphere than in air (curve 2). The picture

TABLE II

The dependence of the strength of PCA-fibers on thermal oxidation

PCA-fiber	Initial PCA		Thermal treated PCA		The loss of		Specific viscosity		The loss of specific viscosity, %
	Breaking tension σ , kg/mm ²	Breaking elongation σ , %	σ , kg/mm ²	ϵ , %	σ , %	ϵ , %	Thermal		
							Initial	Treated	
Initial	19.26	37.20	1.87	15.03	90.29	59.6	1.16	0.47	59.5
Covalently bonded with I	18.84	48.53	9.70	25.62	48.5	47.0	1.28	1.17	8.60
Dyed by deactivated IV	16.27	49.52	10.54	25.08	35.2	49.9	0.74	0.70	5.41

is slightly different for dyed samples. Here the greatest effect of PCA stabilization is shown at heating in air. At 400°C undyed PCA loses 60%.

These results are also confirmed while studying the change of strength and specific viscosity of PCA fibers in 200°C air for one hour (Table II). Covalent-bonding dyes protect PCA from thermodecay in inert atmosphere, though to a smaller extent than for thermooxidation. For example, at 400°C mass loss in argon atmosphere is 52% for undyed PCA and 27% for dyed PCA.

Dye stabilizing action can be explained by the presence of a conjugated system and also replacement of mobile hydrogen atoms of PCA aminogroups: it is believed that polyamides' thermostability diminishes in the presence of mobile hydrogen atoms.

CONCLUSION

Dyes covalently bonded with PVA and PCA provide increased stability with regard to thermal and thermooxidizing degradation. This effect is connected with blockage of mobile hydrogen atoms from —OH and —NH groups for PVA and PCA, respectively, and also with the presence of conjugated systems in the molecules of dyes. The degree of the influence of dyes on thermodegradation of polymer substrates depends on the chemical structure of the dye and the type of "dye-polymer" bond. The opportunity exists to select corresponding chromophores and reaction systems of dyes to obtain colored fibrous materials possessing properties resistant to higher thermal degradation.

References

1. L. N. Mizerovsky *et al.*, *Izvestija vuzov, Chimija i chim. tehnologija.*, N11, 463 (1968).
2. I. Ya. Kalontarov, *The Stability of Textile Materials Dyeing on Physico-Chemical Effects*, Legprombytizdat, Moscow, 1985, 200 p. (in Russian).
3. I. Ya. Kalontarov *et al.*, *Izvestija vuzov. Chimija i chim. tehnologiya*, N13, 1802 (1970).
4. V. I. Moor and N. P. Vorozhtsov, *J. Organ. Chimii*, **30**, 1980 (1960).

5. I. Ya. Kalontarov *et al.*, *Doklady AN Tadzhikistana*, **13**, 6, (1970).
6. I. Ya. Kalontarov, Proceeding Kohf. on Synthesis and Application of Organic Dyes, IHTI. Ivanovo, 1962, p. 198 (in Russian).
7. I. V. Zhuravdyova, Dissertation, Moscow, 1965.
8. V. E. Nepomnyaschy, Dissertation, Leningrad, 1968.
9. S. R. Rafikov, *Ageing and Stabilization of Polymers*, Moscow, 1964, p. 197 (in Russian).