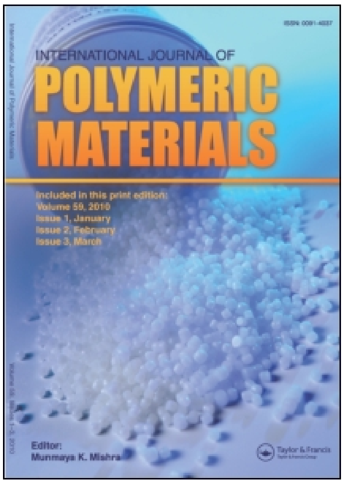
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

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

Photomechanical Degradation of Dyed Polymers

T. B. Boboev[a]; Kh Dodomatov[a]; I. Ya Kalontarov[ab]
[a] Tajik State University, Dushanbe, Tadjikistan [b] Academy of Science, Institute of Chemistry Tadjik, Dushanbe, Tadjikistan

To cite this Article Boboev, T. B. , Dodomatov, Kh and Kalontarov, I. Ya(1993) 'Photomechanical Degradation of Dyed Polymers', International Journal of Polymeric Materials, 19: 3, 223 — 230

To link to this Article: DOI: 10.1080/00914039308012035

URL: http://dx.doi.org/10.1080/00914039308012035

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1993, Vol. 19, pp. 223–230
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Photomechanical Degradation of Dyed Polymers

T. B. BOBOEV, KH. DODOMATOV and I. YA. KALONTAROV

Tajik State University, Lenin St. 17, Dushanbe, Tadjikistan and Institute of Chemistry Tadjik Academy of Science, Ayni St. 299/2, Dushanbe, Tadjikistan

A stabilizing effect of reactive dyestuffs under photodegradation is evaluated by investigating the durability and degree of the radiation damage to polycaproamide (PCA) fibers and natural silk. The character of a stretching load influence on observed stabilization effect in relation to the wavelength of the incident light was shown.

KEY WORDS Photomechanical degradation, dyed polymers, silk polycaproamide.

INTRODUCTION

Polymer degradation under the simultaneous effect of stretching load and UV-light proceeds faster than under photoaging of unloaded samples, since under photomechanical degradation breaking off the ties, due to UV-light quanta, is added to the thermofluctuational process of breaking off the ties.[1-4] Another particularity of the photomechanical degradation process is in weak air-environment influence on its rate, while oxidizing processes under photoaging play an essential part in degradation of polymer mechanical properties.[3] Hence, mechanisms of these processes and methods of stabilization of polymers under such circumstances may differ significantly.

The aim of this work is revealing the dye influence on the process rate of the photomechanical degradation of the fiber-forming polymers of the polycaproamide (PCA) and fibroin of the natural silk (FNS) in comparison with the same data for unloaded samples.

EXPERIMENTAL

The PCA and FNS were used as the polymers in the form of corresponding fibers prepared for dyeing. The reactive dyes of the dichlortriazinyl type C. I. Reactive yellow 4(I), monochlortriazinyl type–C.I, Reactive red 3(II), the vinylsulphonyl type—C.I, and Reactive violet 4(III) were used.

The PCA and FNS fibers were dyed in accordance with methods described elsewhere,[5] using the covalent chemical bond formation (method 1). The dihydroxytriazinyl derivative of the dye I, unable to form the covalent bonds, was obtained by alkali hydrolysis of I instead. The dihydroxytriazinyl derivative of I was used in dyeing the PCA fiber by the method normally used for dyeing with the acid dyes (method 2).

To investigate the PCA-fibers, photoaging, the samples were treated with the complete spectrum of the ultra-violet light of a mean pressure mercury-quartz lamp in the air with 323K temperature and intensity of irradiation $j = 700$ joule $\cdot$ $m^{-2} \cdot s^{-1}$. The natural silk samples were treated with the ultra-violet light of two wavelengths, $\lambda_1 = 254$ nm and λ_2 365 nm. The source of UV with λ_1 was the low pressure mercury lamp, with 80% emission in λ_1. The region of the spectrum near $\lambda_2 =$ 365 nm was selected from emission of the mean pressure mercury-quartz lamp with the glass filter. The photostability of the samples was evaluated by alteration of the relative tensile stability σ_p, durability τ (time from the moment of loading to sample breaking off) and the degree of radiational damaging P. This last was determined according to the formula:

$$P = 1 - \sigma/\sigma_0$$

where σ and σ_0 are correspondingly the tensile strains of irradiated and nonirradiated samples.

RESULTS AND DISCUSSION

Reactive Dye Influence on PCA-Fiber Photodegradation Kinetics

Figure 1 shows the results of influence of beforehand irradiation by unfiltered UV light on durability of PCA-fibers. The data indicate that beforehand UV irradiation has different effects on the durability of dyed and undyed samples.

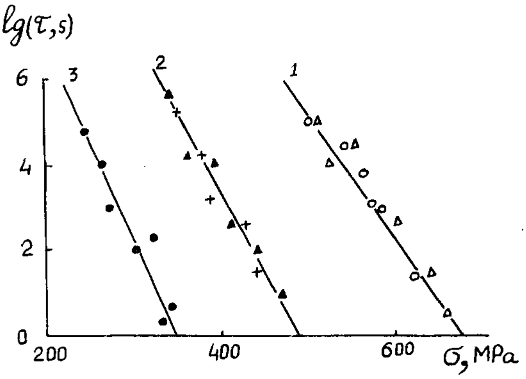


FIGURE 1 The influence of preliminary exposure to UV-light ($j = 700\, j \cdot m^{-2} \cdot s^{-1}$) on durability of PCA fibers. 1—unexposed undyed (—0—) and dyed (—∇—) samples: 2—dyed using two methods, exposed (—▼— method 1, —×— method 2); 3—undyed, exposed (—●—). Time of exposure—70 hours.

On irradiation, the decrease of dyed samples in comparison with non-irradiated control is much less than with undyed sample. In addition, the radiation damage in dyed samples does not depend on the method of sample dyeing. This is clearly seen in Figure 2, where dependence of altering of relative stability of dyed and undyed samples on irradiation time is presented.

Thus from given experimental data it follows that independent of the method of polymer dyeing the same stabilizing effect against light aging in an unloaded state will result.

Convinced of the effectiveness of this dye in resisting the photoaging process, we subsequently investigated its stabilizing effect on the durability of samples under photomechanical degradation. The results of these experiments are presented in Figure 3. These data show that under photomechanical degradation the durability of dyed samples is much greater compared to undyed ones. Moreover the degree of increase of photostability under photomechanical degradation essentially depends on the character of polymer molecule bonds with the dye. For the samples containing 3% dihydroxytriazinyl dye, dyed using the method of physical adsorption, the effect of light stabilization is less than for samples dyed using dye I(2.4%), which forms covalent chemical bonds with PCA.

The observed effect may also be due to screening of the dye, which generally deactivates the electron excitation energy, adsorbed by the polymer macromolecules, thus slowing down the degradation process. The rate of such slowing essentially depends on the probability of the electron excitation energy migration from polymer to the dye molecule.

Probability of energy migration along the chemical bonds is much more than along inter-molecular bonds. Apparently this is the reason for higher stabilizing effect with chemical covalent bonding of the polymer molecules and the dye than without it.

Moreover, probability of energy migration between molecules depends on the number of interacting groups, and the observed effect of light stabilization by the dye, impregnated into a sample by the method of physical adsorption, may be due to this factor.

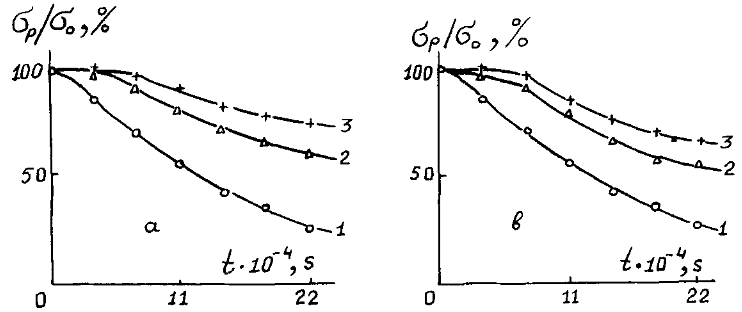


FIGURE 2 The influence of preliminary exposure to UV-light (j = 700 $j\cdot m^{-2}\cdot s^{-1}$) on altering of dyed PCA relative stability, (a) modified samples, (b) impregnated samples; dye concentration 1—0%, 2—1.5%, 3—2%.

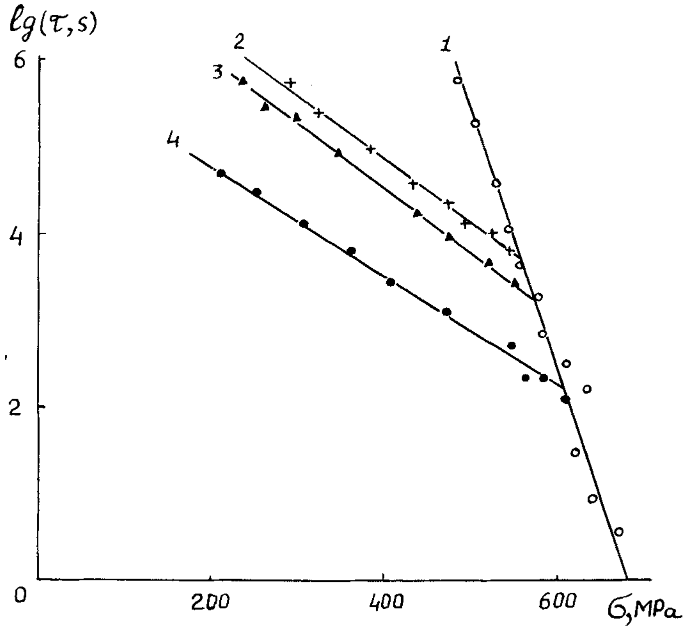


FIGURE 3 The influence of reactive dye (I) on the durability of PCA fibers under photomechanical degradation ($j = 700\, j \cdot m^{-2} \cdot s^{-1}$). 1—initial undyed sample without irradiation, 2—modified samples (dye concentation 2.4%) with irradiation, 3—impregnated exposed samples (dye concentration 3%), 4—undyed exposed samples.

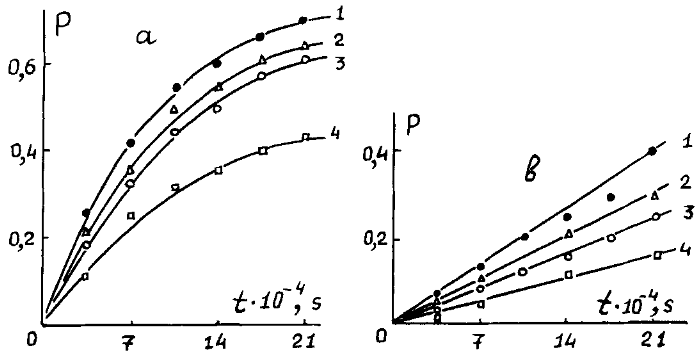


FIGURE 4 The dependence of the radiational damaging degree of natural silk (NS) samples on exposure time ($j_{absorbed} = 22 j \cdot m^{-2} \cdot s^{-1}$). (a) $\lambda_1 = 254$ um, (b) $\lambda_2 = 365$ nm; 1—initial NS, 2—NS + II, 3—NS + III, 4—NS + I.

Influence of Reactive Dyes on Kinetics of Photodegradation of the Natural Silk

The evaluation of photostabilizing effect of dyes was made by comparing of properties of dyed and undyed samples. To eliminate changes due to chemical treatment, undyed samples were treated in the "white" dye-bath, containing all chemicals except the dye.

In Figure 4, the infuence of dyes on the rate of radiational degradation (P) under constant irradiation intensity is given in dependence on the time of exposure to

UV-light of various wavelength λ. There are the same dependences for other irradiation intensities. One can see that when light is used with $\lambda_1 = 254$ nm and with $\lambda_2 = 365$ nm the rate of degradation of dyed sampes is essentially less than that of undyed ones. In addition the effect depends on the dye type.

It is seen more evidently in dependence (given in Figure 5) of initial rate of radiational degradation $\dot{P}$ on intensity of irradiation; $\dot{P} = dP/dt$ ($t \sim 0$) is the slope of the initial part of the $P(j)$ curve. The values of quantum yield (μ_j) were determined from the slope of $P(j)$ dependence (see Table I)

Comparison of these values shows that dyeing reduces quantum yield of photodegradation of unloaded samples for λ_1 and for λ_2, and that means that the analyzed dyes have good light stabilizing effect. Samples treated with dye I, are more light stable, than initial. This difference, according to Vershinina *et al.*[9] may be interpreted as follows: dye I is bifunctional and characterized by simultaneously forming two dye-fiber chemical bonds, which may result in cross-linking the fiber. This has been confirmed by a sharp reduction of solubility for dyed NS in 60% $ZnCl_2$ solution.

Presence of such "cross-links" increases the probability of transferring the electron excitation energy from the polymer molecules to dye molecues, which increases the light stability of samples. Dyes II and III are monofunctional, and the number of bonds formed between the dye and the polymer is considerably less than for dye I. In this case the probability of transferral of energy from the polymer to the dye will be less than in the first case, and as a result the effect of light stability will be less.

The process of the photomechanical degradation of dyed and undyed natural silk was investigated in order to clarify the influence of stretching load on observed effect of light stabilization. For this purpose the samples were tested for durability

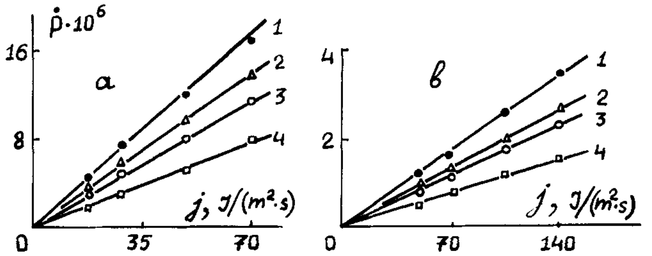


FIGURE 5 The dependence of the NS radiational damaging rate on irradiation intensity. (a) $\lambda_1 = 254$ nm, (b) $\lambda_2 = 365$ nm; 1—initial NS, 2—NS + II, 3—NS + III, 4—NS + I.

TABLE I

Quantum yield μ_j values for the photodegradation process of unloaded natural silk (NS) samples

	$\mu_j \cdot 10^4$			
λ, nm	NS undyed	NS + I	NS + II	NS + III
254	100	47	70	82
365	32	4.8	7.2	9

under the simultaneous action of a load and UV-light treatment. The results of experiments for UV-light of λ_1 and λ_2 are given in Figure 6. The nature of the dependence of radiation-mechanical durability τ_j upon strain σ independent of light wavelength for dyed and undyed samples is represented by the two linear parts of the plots.

Below we shall consider only that part of the plot where UV-light influence on τ_j becomes manifest. The τ_j dependence on σ in this part of plot may be described by the formula[1-3]

$$\tau_j = A_j e^{-\alpha_j \sigma}, \tag{1}$$

where A_j and α_j are parameters characterizing the material's light stability at the condition of photomechanical degradation. The results obtained show that dyed samples are more durable than undyed, meaning that dyeing leads to increased light stability of samples under the condition of photomechanical degradation also. This additional stabilizing effect of dyes is observed for λ_1 as well as for λ_2. Dyeing leads to increasing A_j and reducing the quantum yield of photodegradation (Table II).

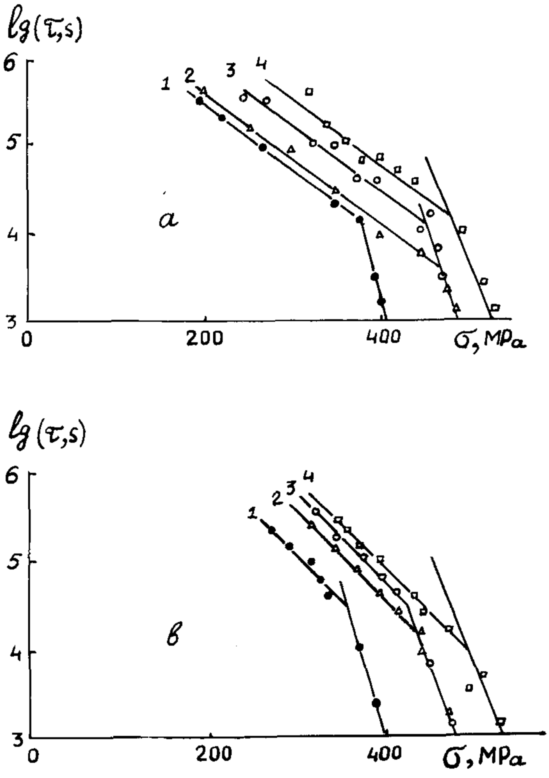


FIGURE 6 The dependence of the radiational durability of starting and dyed NS samples ($j$absorbed $= 22 j \cdot m^{-2} \cdot s^{-1}$). (a) $\lambda_1 = 254$ nm, (b) $\lambda_2 = 365$ nm; 1—initial NS, 2—NS + II, 3—NS + III, 4—NS + I.

TABLE II

The values of α_j(mm^2/k), lg(A_j, c) and μ_j for initial and dyed NS samples

	NS initial					
	254 nm			365 nm		
T, °C	α_j	lg A_j	$\mu_j \cdot 10^4$	α_j	lg A_j	$\mu_j \cdot 10^4$
40	0.18	7.3	94	0.29	8.9	30
100	0.18	6.4	594	0.24	6.9	818
150	0.18	5.55	4000	0.19	5.7	4000

	NS + I					
	254 nm			365 nm		
T, °C	α_j	lg A_j	$\mu_j \cdot 10^4$	α_j	lg A_j	$\mu_j \cdot 10^4$
40	0.16	7.6	31	0.25	9.3	2
100	0.16	6.8	188	0.20	7.5	53
150	0.16	6.0	1062	0.16	5.8	530

The Table II shows, that observed effect of stabilization also occurs for experiments at higher temperatures. Comparison of the ratio for quantum yield for undyed and dyed samples under photoaging and photomechanical degradation distinguishes the effectiveness of dyes under these conditions. This ratio for dye I under photoaging is equal to 2.1 and 6.6 for λ_1 and λ_2, respectively, and for photomechanical degradation is equal to 3 and 15, that is to say that effectiveness of dyes under mechanical strain is larger than without it. It is possible that tensile strains block some stage of the degradation process. Vershinina *et al.*[9] proposed that stretching stains, acting along the oriented molecules, decrease transverse intramolecular distances and this increases the possibility of deactivation of electron-excited states. We tried to detect the deactivation process using photoluminescent methods. In these experiments we assumed that the more the dye quenches the polymer luminescence the better it acts as a deactivator of electron excitation energy. Undyed natural silk has a broad band of luminescence in region of 300–400 nm. Adding dye I to 3% concentration reduces the luminescence intensity 5 times; the dye acts very effectively as a quencher of electron excitation energy, and this may essentially cause its photostabilizing function in loaded natural silk samples.

In conclusion, the experiments conducted show that incorporating into the polymer matrix dyes of various reactive abilities and degree of interaction, polymer molecules may lead to change of the photostability of fabric under conditions of photomechanical degradation.

References

1. V. R. Regel and N. N. Cherny, *Vysokomolekulyarnye Soedinenya*, N6, 925 (1963).
2. V. R. Regel, T. B. Boboev and N. N. Cherny, *Mekhanika Polimerov*, N3, 442 (1969).
3. T. B. Boboev, V. R. Regel and N. N. Cherny, *Mekhanika Polimerov*, N5, 929 (1969).
4. G. G. Samoylov and E. E. Tomashevsky, *Fisica Tverdogo Tela*, **v10**, N4, 1094 (1968).

5. I. Ya. Kalontarov, *Properties and Methods of Reactive Dye Using* (in Russian), Dushanbe: Donish, 75 (1970).
6. B. N. Melnikov and G. I. Vinogradova, *Dye Usage* (in Russian), Moscow: Khimia, 83, (1986).
7. B. Ranby and Ya. Rabek, *Photodegradation, Photooxidation, Photostabilization of Polymers* (translation in Russian). Moscow: Mir, 274 (1979).
8. M. S. Umarova, I. Ya. Kalontarov, S. N. Karimov, D. Saidov and A. V. Zakharchuk, *Tesisy Dokladov Pervoy Vsesojuznoy Nauchnoy Konferentsii "Lightstabilization of Dyed Fibers and Films,"* Moscow, 92 (1979).
9. M. R. Vershinina, N. G. Kvachadze and E. E. Tomashevsky, *Fizika Tverdogo Tela*, **v19**, N8, 1356 (1977).