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Influence of Uniaxial Deformation of Colored Polyvinyl Alcohol Films on Their Thermal-Oxidative Destruction

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Abstract—The thermal-oxidative destruction of films made of polyvinyl alcohol colored by brilliant yellow and subjected to uniaxial deformation was studied by the thermogravimetric method. The intensive dehydration of polyvinyl alcohol begins at temperatures higher than 150°C in non-deformed films and higher than 220°C in samples subjected to the uniaxial extension. The dye practically does not influence thermal-oxidative destruction of non-oriented samples. The stretching and treatment by a "cross-linking" agent during the uniaxial deformation of the film increases its thermal stability.

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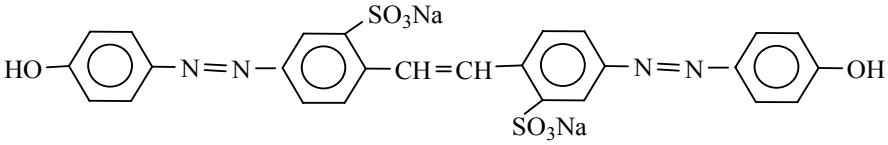
Polyvinyl alcohol films colored by molecular iodine or a dichroic organic dye and subjected to uniaxial extension are capable of polarizing light and are used in compositions of liquid-crystalline indicators. Optical properties of such films should be retained under various operating conditions, including elevated temperatures. The iodine polarizer is stable in the range from –60 up to 60°C. Replacement of iodine by a dichroic dye has allowed the upper temperature limit to be raised up to 90°C [1]. At the same time the preparation of a film material stable at temperatures above 90°C remains a topical problem.

The majority of modifiers introduced into a polymer are known to suppress or accelerate its thermal and thermal-oxidative destruction [2, 3]. Obviously, the molecules of dyes containing the substituents OH and NH_2 characteristic of inhibitors can decelerate the destruction. In fact it was found that coloring of polyvinyl alcohol films by active dyes [4] increases their thermal stability, the increase being the strongest in the case of the formation of a chemical compound of a dye with a polymer. According to [5], the decomposition temperature of a polyvinyl alcohol film increases by 35–40°C in the presence of a bisazo dye of the azobenzenenaphthalene type. The mechanism of the thermostabilizing action of a dye and interconnection between deformation changes and thermal stability of polyvinyl alcohol in a thin-film state are insufficiently studied, though it is known that the deformation affects not only its structure, but also chemical reactions proceeding in a polymeric template. For example, an increase in a stretch ratio of polyvinyl alcohol films strengthens the complex formation between a polymer and molecular iodine [6, 7].

The aim of this work was to determine quantitative parameters of thermal-oxidative destruction of polyvinyl alcohol films colored by a dichroic dye and to establish regularities of the influence of the uniaxial film deformation on its thermal stability.

As a subject of the study we have chosen polyvinyl alcohol films colored by diamond yellow, molecules of which are well compatible with the polymer. The colored uniaxially stretched films have a high polarizing power in the short-wave region of the visible spectrum (430–440 nm) [8].



Deformation of polyvinyl alcohol films on extension was studied at room temperature by a standard procedure. The shape of stress-deformation plots (Fig. 1) testifies that the deformation process depends on film moisture. Extension diagrams of dry films containing 6.5–7.5 wt % of residual water are typical for a plastic material (Fig. 1a). The linear sections of these plots correspond to the reversible elastic deformation, which obeys Hooke law. The elasticity modulus is ~1.6 MPa, and the elastic deformation limit is less than 10 MPa. Then the high-elasticity reversible deformation progresses in films, and at tensile strength higher than 19 MPa (in a film with a dye) and 23 MPa (in a film without dye) irreversible viscous-flow deformation is accumulated. The limiting deformation of films of 390 and 350% occurs at 46 and 44 MPa, respectively in the colored and uncolored films.

In humidified films the high-elasticity deformation is developed practically at once under a stress action (Figs. 1b and 1c). In this case, as the amount of sorbed water increases the elasticity modulus of films decreases and differences in the deformation behavior of films are leveled. The elasticity modulus of the uncolored and colored films containing 60±2 wt % of water is ~0.04 and 0.02 MPa (Fig. 1b), respectively, and that of the films containing 75±2 wt % of water is ~0.01 MPa and does not depend on the presence of a dye (Fig. 1c). The limiting deformation of the humidified samples increases up to 520–575% in comparison with dry films and is reached at a stress of 10–15 MPa.

In the absence of enhanced environmental humidity films dried up under a load retain their length over a very long period of time after elimination of a mechanical stress. It can be explained by the formation of hydrogen bonds between polymer chains, which keep them in a drawing state in the new structure formed after deformation. The sorption of water by a film results in the destruction of these bonds and in occurrence of the relaxation processes, which result in warping the film and changing its size.

So-called "polychromatic" kinetics, which is described by a set of rate constants and activation energies [9–11], is characteristic for the thermal decomposition of polymers. The resulting rates and apparent activation energies of the process are averaged values, which characterize the decomposition of a polymer in various structural phase states.

We can distinguish several stages of the thermal-oxidative destruction of uniaxially stretched polyvinyl

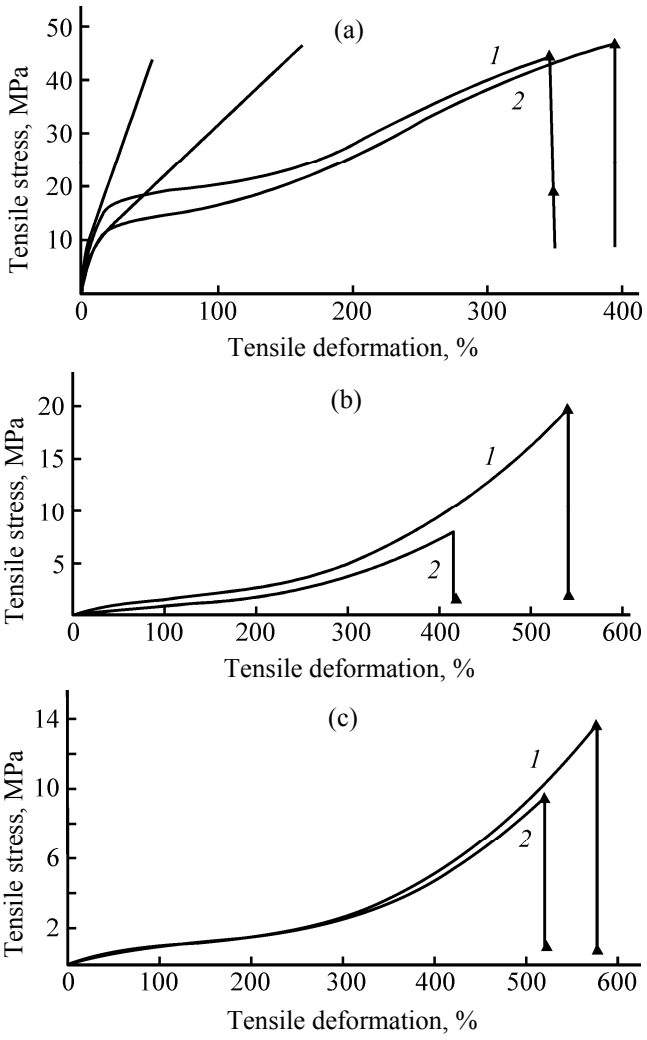


Fig. 1. Dependence of the deformation of polyvinyl alcohol films on tensile strength: (a) dry films; (b) and (c) films containing 60±2 and 75±2 wt % of water, respectively. Dye concentration in films, wt %: (*1*) 0, (*2*) 0.4.

alcohol films containing from 0 up to 1.0 wt % of dye (Fig. 2). In the temperature range from 50–60 up to 160–165°C all samples lose 9–10% of weight. As a similar weight loss (~9%) is observed during the thermogravimetric analysis of a pure dye, it is not excluded that it is connected with the removal of adsorbed water.

As temperature increases further (starting from 160–165°C), the weight of samples changes slightly, which is seen, for example, from the run of TG and DTG curves for the uncolored film and the film containing 0.6 wt % of diamond yellow (Fig. 2). This fact and the observed endothermic effect are connected with softening and melting of the polymer. The melting of polyvinyl alcohol in the uncolored film

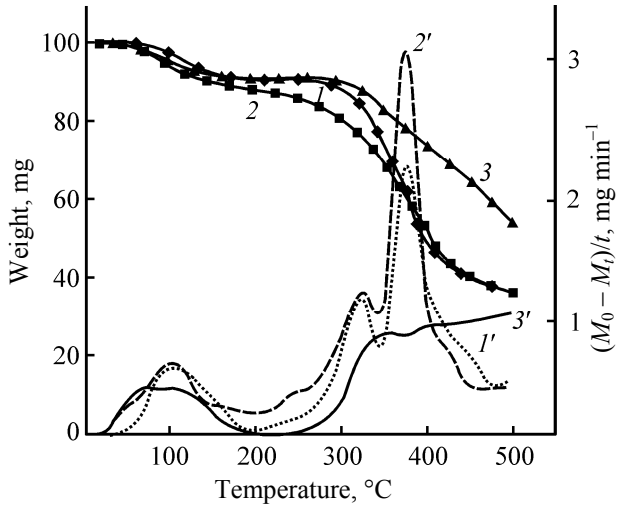


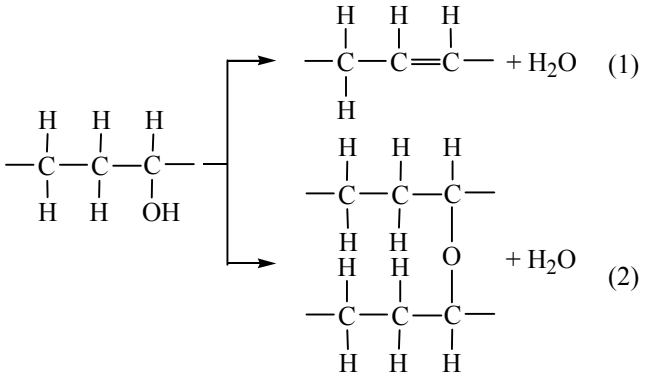
Fig. 2. Curves of (*1, 2, 3*) TG and (*1′, 2′, 3′*) DTG for (*1, 1′* and *2, 2′*) uniaxially expanded polyvinyl alcohol films and (*3, 3′*) initial dye. Diamond yellow content in a film, wt %: (*1, 1′*) 0, (*2, 2′*) 0.6.

comes to an end at 270°C and that of colored films, at a temperature ≤255°C (Table 1), then the stage of intensive dehydration of polyvinyl alcohol (stage 1) begins, which can proceed both by the intra- and intermolecular mechanisms (1), (2).

Table 1. Parameters of thermal-oxidative destruction of deformed polyvinyl alcohol films (R_s 3.5)

Parameter	Dye concentration[a] in a film, wt %						
	0	0.2	0.4	0.6	1.0	0.4[b]	0.6[b]
Stage 1 (from T_1 to T_2)							
T_1, °C	270	250	220	245	225	255	240
W_1, mg min^{-1}	1.2	1.5	1.4	1.3	1.3	0.7	0.7
T_{W_2}, °C	350	350	340	335	340	347	338
E_a^1, kJ mol^{-1}	61	55	43	35	32	40	35
Stage 2 (from T_2 to 390°C)							
T_2, °C	375	375	370	365	370	370	370
W_2, mg min^{-1}	2.4	2.3	2.9	3.0	2.4	1.6	1.4
T_{W2}, °C	385	385	380	375	380	385	385
E_a^2, kJ mol^{-1}	100	126	109	127	150	145	140
Stage 3 (from 390 to 500°C)							
E_a^3, kJ mol^{-1}	50	50	43	40	41	33	31
ΔM, mg	64	61	64	64	64	29	31

[a] Dye diamond yellow. [b] Films after irradiation by UV light within 7 h.



The probability of abstraction of a hydrogen atom of the neighboring macromolecule increases in uniaxially stretched films, which results in cross-linking of the polymer [reaction (2)]. The maximal rate of weight loss in stage 1 is reached at 340–350°C (Fig. 2).

In the temperature range from 365 up to 390°C the most intensive weight loss of films is observed. In this stage (stage 2) the thermal process is accompanied by the breaking of C–C bonds in macromolecules, the formation of volatile substances, and the carbonization as demonstrated by blackening of samples. The rate of films decomposition in stage 2 reaches maximal values (Table 1). At temperatures higher than 390°C (stage 3) the decomposition rate of films continuously decreases (Fig. 2, curves *1* and *1*').

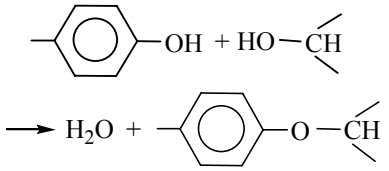
According to the dye thermogram given in Fig. 2, the dye decomposition begins at a temperature higher than 295°C. Below this temperature the dye loses 9 wt % of sorbed water (50–145°C) and melts (145–295°C), as demonstrated by a weight constancy and an endothermic effect. The maximal rate of the weight loss occurs after 340°C (Fig. 2). The presence of nitrogen in gaseous decomposition products points to the cleavage of C–N bonds in the azo dye molecule [12].

The total process of films destruction was characterized by temperatures T_1 and T_2 of the beginnings of stages 1 and 2, respectively, by maximal weight loss rates W_1 and W_2 in stages 1 and 2, temperatures T_{W1} and T_{W2} of reaching rates W_1 and W_2, values of apparent activation energy E_a^1, E_a^2, and E_a^3 of film destruction in stages 1–3, and by the total weight loss $\Delta M = (M_0 - M_e)$, where M_0 and M_e are sample weights in the beginning and in the end of an experiment. The accuracy of measuring temperature was ±2°C.

The found values of the parameters characterizing thermal-oxidative destruction of deformed films are given in Table 1, which shows that the introduction of dye in a film decreases T_1 and E_a^1, the decrease being the greater, the higher is the concentration. Most

likely, it is due to the participation of dye in the polymer dehydration reaction.

Mutual orientation of dye molecules and polymer chains promotes reaction (3). It is improbable that the effect of dye is connected with its plasticizing action, though it is known [9] that low-molecular compounds capable of such action can increase the intensity of molecular motions in polymers and, as a consequence, a chemical reaction rate. However, the accelerating action of a plasticizer is observed only at low temperatures (much lower than 100°C), when the action of heat on the molecular mobility of a polymer is less expressed. In our case the polyvinyl alcohol decomposition in stage 1 begins at T>220°C.



(3)

If diamond yellow reacts with polyvinyl alcohol to form "graft" macromolecules, the destruction of the modified polymer in stage 2 should differ from the decomposition of the initial polyvinyl alcohol. In fact, the comparison of E_a^2 values for the uncolored and colored samples (Table 1) shows that the decomposition of the film with dye is characterized by a higher apparent activation energy, and E_a^2 somewhat increases as the concentration of dye in a film increases. This regularity cannot be attributed to the influence of dye thermal destruction, as the value of E_a at the maximal rates of dye weight loss is 71 kJ mol^{-1}, which is much less than E_a^2 even for an uncolored film.

At temperatures higher than 390°C (stage 3) the thermal process of a weight loss of films is characterized by close E_a^3 values.

The influence of the chemical structure of the polymeric template on the film thermal stability is confirmed by the data obtained for samples irradiated by UV light. In comparison with non-irradiated films, the thermal destruction of these samples proceeds with lower rates (W_1 and W_2), therefore the total weight loss (ΔM) is practically reduced by one half. It is known that the irradiation of thin polymeric films by light results in cross-linking of macromolecules, i.e. in the appearance of areas with a "cross-linked" structure possessing a higher thermostability [13].

Comparison of the thermogravimetry data for deformed and unstretched colored polyvinyl alcohol films (Figs. 2 and 3, Tables 1 and 2) shows that

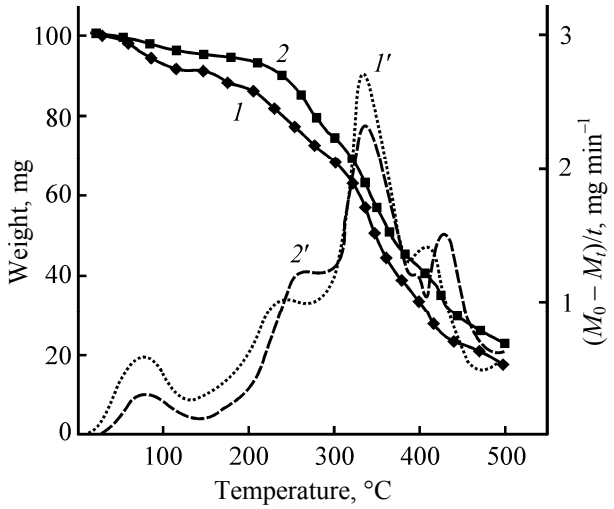


Fig. 3. Curves of (*1, 2*) TG and (*1′, 2′*) DTG of undeformed polyvinyl alcohol films. Content of dye in a film, wt %: (*1*) and (*1′*) 0, (*2*) and (*2′*) 0.6.

thermal destruction of unstretched samples proceeds easier. It is evidenced by a decrease in T_1, T_2, E_a^1, and E_a^2 values and by an increase in the total weight loss (ΔM) of unstretched films by approximately 30%. The dehydration of polyvinyl alcohol in these samples in stage 1 practically does not depend on the dye concentration (Table 2). Hence, dye, which is accumulated in amorphous areas of the non-deformed polymer, weakly reacts with polyvinyl alcohol and does not essentially affect the intra- and intermolecular interactions of macromolecules.

The dye concentration also has little or no effect on the E_a^2 value. We can assume that in these conditions reaction (3) proceeds with a low rate, and to the beginning of stage 2 a negligible amount of "graft" macromolecules of polyvinyl alcohol is accumulated in a film, which decomposes with a higher activation energy.

The influence of film deformation on the process of its destruction was studied on samples with uniaxial stretch ratios (R_s) from 0 up to 4.5. Results obtained (Fig. 4, Table 3) have confirmed the fact that polyvinyl alcohol decomposition proceeds in an unstretched sample at lower temperatures. The increase in the stretch ratio of a film has affected mainly stage 2. It is seen from Table 3 that the parameter E_a^1 was changed slightly and the activation energy E_a^2 essentially increased as R_s increased from 1.5 up to 3.5. However, it is necessary to note that at R_s 4.5 these values have decreased. The dependence of polarizing ability and thermal conductivity of anisotropic polyvinyl alcohol films on the degree of their uniaxial stretch is of an

Table 2. Parameters of thermal-oxidative destruction of undeformed polyvinyl alcohol films[a]

Dye, wt %	T_1	T_2	W_1	W_2	T_{W1}	T_{W2}	E_a^1	E_a^2	ΔM, mg
	°C		mg min^{-1}		°C		kJ mol^{-1}		
0	170	310	1.0	2.7	240	345	24	46	84
0_{tf}[b]	210	325	0.3	2.9	290	355	26	51	87
0.1	165	310	0.9	2.5	245	340	31	44	75
0.2	165	275	1.2	2.5	240	345	36	42	81
0.4	175	320	1.0	2.8	245	350	31	52	82
0.6	170	305	1.2	2.3	255	335	31	40	80
1.0	150	320	1.2	2.3	237	335	28	39	81

[a] All samples were dried at room temperature. [b] Sample 0_{tf} was additionally heated up at 60±2°C for 60 min.

analogous extreme character. The variation of polarizing ability with increasing R_s is given in Fig. 5, which shows that the maximal degree of polarization is reached at R_s 3.5–4. It was shown earlier [5] that the maximal thermal conductivity of a film along an axis of its stretch and the minimal conductivity along a perpendicular direction are observed for samples ~3.5-fold stretched. Apparently it is connected with increasing irregularity of a polymer supramolecular structure along an axis of orientation, which can be caused by the uniaxial stretching of polyvinyl alcohol films and fibers [14].

As the deformation action on the film was executed in a solution of boric acid, which changes the physical structure of polyvinyl alcohol [15], we have carried out a thermogravimetric analysis of a undeformed colored sample treated by a solution of boric acid (sample 0*). Parameters of its thermochemical destruction given in Table 3 point to the fact that the treatment by boric acid increases the thermal stability of the film.

Earlier it was shown by the XRD analysis that polyvinyl alcohol in films colored by a dichroic dye is in the X-ray amorphous state [15], and the orientation and thermal treatment of the film increase a crystal phase fraction in the polymeric template. As a rule, the thermochemical destruction of a polymer proceeds easier in weakly ordered amorphous areas, in which the formation of intermolecular hydrogen bonds is difficult and polymer chains are more mobile. This can be responsible for the fact that the destruction of unstretched films occurs easier than that of deformed films, and the "thermofixation" of a film consisting in

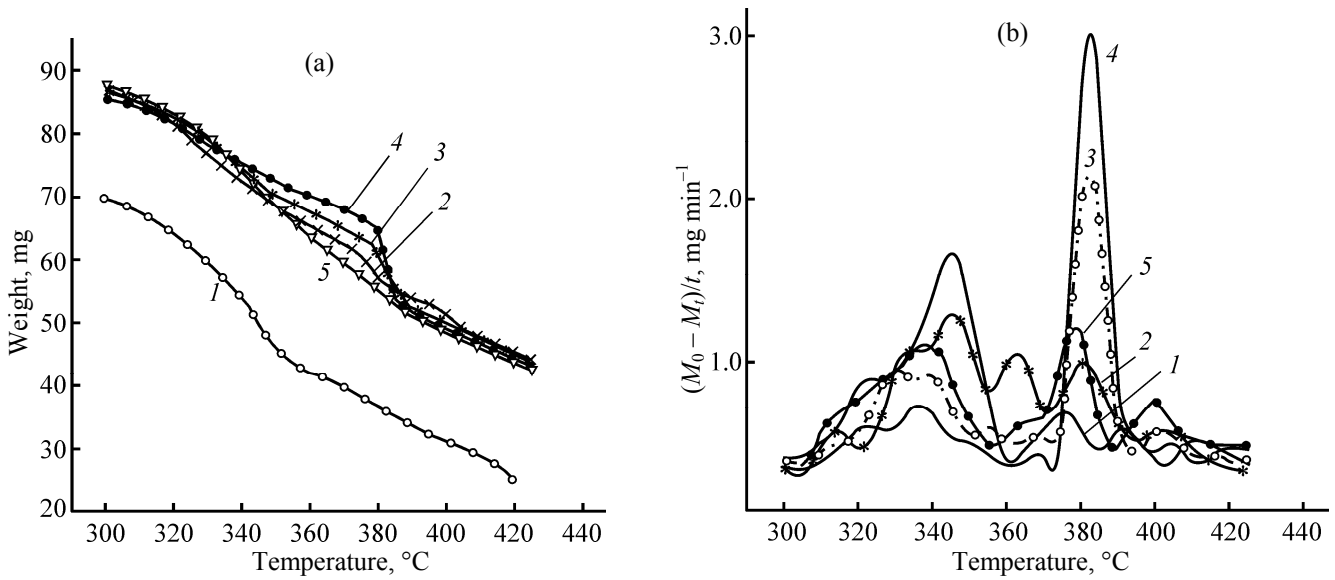


Fig. 4. Curves of (a) TG and (b) DTG of polyvinyl alcohol films. Stretch ratio R_s: (*1*) 0, (*2*) 1.5, (*3*) 3.0, (*4*) 3.5, (*5*) 4.5. Dye content in the film 0.4 wt %.

its long-term drying at 60±2°C increases its thermal stability (Table 2, 0 and 0_{tf} rows).

Supramolecular structure of polyvinyl alcohol in a film depends on the procedure of its preparation [16–18]. The treatment by boric acid during the uniaxial stretching of a film results in the formation of a homogeneous quasi-crystalline polymer structure in the form of a three-dimensional net resulting from cross-linking polymer chains by ether bridges, whereas when a polyvinyl alcohol film is drawn in water a layered structure with amorphous and crystalline regions [15] is formed. The size of crystal grains in such films is 42–48 Å (drawn in H_2O) and 18–28 Å (in a H_3BO_3 solution).

The fact that the conditions of the film chemical treatment affect its thermal stability is supported by the DTA data for the samples subjected to deformation in different media. The temperature of reaching the maximal weight loss rates of the films stretched in H_2O and H_3BO_3 increases, respectively, from 273 up to 328°C (for W_1) and from 335 up to 375°C (for W_2) (Fig. 6, curves *2* and *3*). The production of the iodine-containing polarizing polyvinyl alcohol films includes triple treatment by aqueous solutions, in which the film is colored and hardens: (1) $NH_4S_2O_8$ + $CuSO_4$ + KI + KCl + H_2SO_4), (2) H_3BO_3, and (3) H_3BO_3, KI, CdI_2, $ZnCl_2$, and HCl [19]. For such film, in contrast to the film treated only by boric acid, a decrease in the rate W_2 and shift of the temperature of reaching the rate W_2 up to 430°C (Fig. 6, curve *1*) are characteristic. Salts of alkali and alkaline-earth metals catalyze the reaction of boric acid with polyvinyl alcohol [20], which results in the increase in the extent of cross-linked polymer chains in the iodine-containing film. The first peak in the DTG curve of the "iodine" film (Fig. 6, curve *1*) characterizes the decomposition of the dichroic complex {PVC–H_3BO_3–I_2} unstable at temperatures higher than 60–70°C, with evolution of molecular iodine. Obviously, iodine as a dichroic ingredient does not possess the thermal stability of azo dyes.

Table 3. Parameters of thermal-oxidative destruction of polyvinyl alcohol films with various deformation ratios[a]

R_s	T_1	T_2	T_{W_1}	T_{W_2}	E_a^1	E_a^2	E_a^3	ΔM, mg
	°C			°C		kJ mol^{-1}		
0	140	290	235	345	50	73	55	84.4
0*[b]	230	360	327	377	59	41	69	75.0
1.5	225	365	347	382	70	60	56	69.3
3.0	210	365	333	382	56	102	58	67.2
3.5	235	370	333	380	49	140	52	65.2
4.5	210	365	332	380	62	67	58	67.3

[a] Dye concentration in a film 0.4 wt %. [b] (0*) undeformed film treated by boric acid and dried within 25–30 min at room temperature and then 60 min at 60±2°C.

The activity of a dye as an inhibitor of the thermal oxidative process can appear only in stage 1, as the efficiency of ordinary stabilizers of polymers (amines, phenols, and phosphorus- and sulfur-containing compounds) irrespective of the mechanism of their action decreases as the reaction temperature increases and completely disappears at T > 270–300°C [21]. The observed dependences of T_1, W_1, and E_a^1 on the concentration of diamond yellow and differences in these values for deformed and non-deformed films point to the fact that inhibiting properties of a dye do not play a decisive role in destruction of films.

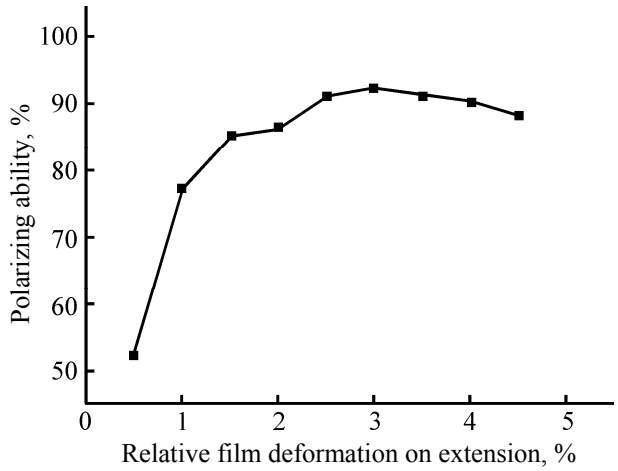


Fig. 5. Dependence of the film polarizing ability on the degree of its uniaxial stretch. Dye strength in the film 0.4 wt %.

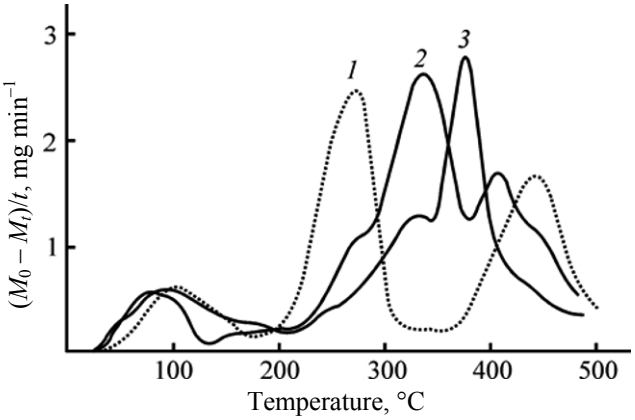


Fig. 6. Temperature dependence of weight loss rate of polyvinyl alcohol films colored by (*1*) iodine and (*2, 3*) diamond yellow. Uniaxial stretch in (*2*) water and (*3*) a H_3BO_3 solution. Diamond yellow content in a film 0.6 wt %.

Thus, it has been established that the uniaxial deformation and the concentration of dichroic dye noticeably affect thermal and energy parameters of thermal-oxidative destruction of colored polyvinyl alcohol films. An increase in the degree of the film deformation affects only slightly the hydration of polyvinyl alcohol macromolecules (stage 1) and gives rise to an increase in the rate and activation energy of the thermal process involving breaking C–C bonds in a polymer (stage 2). The character of the dye effect is defined by the film state. In unstretched colored films the intensive dehydration of polyvinyl alcohol begins at temperatures higher than 150°C, and the dye concentration practically does not influence the rate and the activation energy of the processes proceeding in both stages. In the colored films deformed in a boric acid solution (R_s 3–4) the dehydration of polyvinyl alcohol begins at temperatures higher than 220°C, and the introduction of dye reduces the activation energy of dehydration of polymer macromolecules and increases the activation energy of its decomposition in stage 2. The uniaxial deformation of a film and its treatment by a cross-linking agent increase the thermal stability of the film material. One of methods of increasing thermal stability of a film material based on polyvinyl alcohol consists in the optimization of the chemical treatment of polyvinyl alcohol films by new cross-linking agents and in the optimization of the mode of their action on a film (addition of a polymer to the initial solution or treatment of films by them). Hence, polyvinyl alcohol can be used for obtaining polarization films with operating temperature higher than 90°C.

EXPERIMENTAL

Films cast from a 10% "Moviol 28-99" solution (Höchst, Germany, M_w 150000) containing a dye, a gelatinizing agent boric acid (0.04 wt % of H_3BO_3), and a plasticizer glycerol (2.8 wt %) were dried on polished glasses in a drying chamber first at 32–34°C and then at 22–24°C. The uniaxial stretching was carried out in water or in a 4% H_3BO_3 solution at 45±2°C, then the films were washed by distilled water and dried in the stretched state for 25-30 min at room temperature, and then for 60 min at 60±2°C [5, 15, 22]. The stretch ratio (R_s) was determined as a ratio of the film length after deformation to its initial length.

The deformation at stretching films was measured by a standard procedure on a Tensometer 2020 universal testing machine at room temperature at a rate of film extension of 50 mm min^{-1}.

Diamond yellow (analytical grade, Chemapol, Czechia) was used without additional purification.

Differential thermal analysis of films was carried out in air in the range of 20–500°C at a heating rate of 5 deg min^{-1} on a Paulik-Paulik-Erdei derivatograph (MOM, Hungary). The activation energy (E_a) of polyvinyl alcohol thermal destruction was calculated by the Broido method [23].

$$E_a = R\tan\alpha.$$

Here R is the universal gas constant; tgα is the slope of straight lines in the coordinates ln {ln $[(M_0 - M_\infty)/(M_t - M_\infty)]$} – $(1/T)$; M_0 is the weight of an initial sample equal to 100 mg, M_t and M_∞ are sample weights measured in the course and in the end of the polymer destruction, respectively.

To irradiate film by UV light, we used a DRSh-1000 high-pressure mercury lamp. The intensity of the light falling perpendicularly to a sample surface was 0.12 W cm^{-2}.

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