

Analysis of the Polymeric Material Stability under Extreme Conditions by Using Colorimetry Method

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Received December 1, 2020; revised December 1, 2020; accepted January 15, 2020

Abstract—The advantages and limitations of the colorimetric method as applied to evaluation of the stability of polyvinyl chloride- and polyphenylene sulfide-based polymers and polymeric materials under high temperature and light exposure were considered. The kinetic regularities and specific features of the changes in the color difference and color characteristics during thermo-, photo-, and photothermodegradation were analyzed. The activation energies of the processes were estimated. The prospects offered by the kinetic approach for assessing the degradation characteristics and predicting the stability of the polymeric materials were shown.

Keywords: colorimetry, photodegradation, polyvinyl chloride, polyphenylene sulfide, reversible color change, thermodegradation

DOI: 10.1134/S107036322112????

1. INTRODUCTION

Colorimetry is an important tool of objective comparative analysis of materials and products, including items made of plastics, varnishes and paints, as well as of fabrics. Also, colorimetric techniques are used for quantification of changes in the appearance of materials exposed to various physicochemical impacts, including high and low temperatures, light, corrosive gases, water (moisture), as well as to a combination of two or more of these factors. Another application of colorimetry is comparative evaluation of the stability of materials and of the effectiveness of new stabilizing systems, as reported in numerous scientific and technical publications.

The colorimetric method is potentially applicable to almost all polymers and composite materials, since all of them exhibit, to a certain degree, coloration or a change in color under exposure to external factors, particularly to high temperatures and light. However, use of colorimetry seems the most promising in the case of polymers whose degradation involves the formation of polyconjugated structures (PCS). High extinction coefficients displayed by the latter in the visible region of the spectrum allow

studying the degradation processes in the initial stages, when the PCS concentrations are low and the main physicochemical characteristics of the material remain unchanged or at a level acceptable for operation. At the same time, using colorimetric method it is possible to directly analyze the reactions involving macromolecules, i.e., to detect the main potential cause of changes in the material properties.

Formation of PCS and its associated color change are most clearly manifested in the processes of thermo- and photodegradation of polyvinyl chloride (PVC) [1–3] and polyphenylene sulfide (PPS) [4, 5]. Accordingly, we considered herein the general regularities and peculiar features of the degradation of specifically these polymers in the context of the previously published [6–10] and new experimental data. These research objects have gained additional attention due to widespread use of PVC- and PPS-based materials in electrical engineering, electronic, aerospace, and other industry sectors.

The main goal of this study was to demonstrate the advantages and limitations of colorimetry as applied to

evaluation and prediction of the stability of polymeric and composite materials.

2. METHODOLOGICAL APPROACH TO ANALYSIS OF THE MATERIAL STABILITY BY THE COLORIMETRY METHOD

In the CIELAB 1976 color scale [11] each color is represented by a color point in the color space with L^* , a^* and b^* color coordinates, where L^* indicates brightness (lightness), parameter a^* , intensity of red (+) and green (–) color, and parameter b^* , that of yellow (+) and blue (–) color. The main characteristic of the color change is the color difference ΔE defined by the formula (1):

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}, \quad (1)$$

where $\Delta L^* = L^*_i - L^*_0$, $\Delta a^* = a^*_i - a^*_0$, $\Delta b^* = b^*_i - b^*_0$, index 0 generally refers to the sample before testing, and index i , to the sample after a certain test period. The L^* , a^* , and b^* parameters are determined directly via measurements using the standard procedure for processing the reflection spectra with the aid of the software provided with a spectrophotometer. In some cases it is more expedient to use Δb^* as the major characteristic because of the initial formation of PCS with relatively short conjugation chains absorbing mainly in the blue region of the spectrum. As a result, specifically parameter b^* is the measure of the PCS concentration in the surface layer.

It is noteworthy that the colorimetric characteristics are the parameters that are strictly, though conditionally, determined from the reflection spectra; their usage benefits are due to the possibility of quantifying the visually observed changes in the material that they offer.

Colorimetry is commonly employed to assess the quality or the change in characteristics of the material based on criteria for acceptable color difference or acceptable change in the color coordinates.

Recently developed relevant approaches include the analysis of the kinetic regularities of the changes in ΔE and color coordinates [6–10]. The kinetic parameters and kinetics dependences on the degradation conditions determined are used to evaluate the role played by the main external factors and material components in the color characteristics changing processes, which allows evaluation of their influence on the formation of PCS and other degradation products. For higher objectivity of assessment, the data obtained are compared with the results from studies of the same or similar materials by

some different methods, including DSC, TGA, TMA, IR spectroscopy, and physicochemical analysis methods. The revealed regularities and determined kinetic parameters provide a scientific basis for predicting the storage stability and operational stability of materials and products, in particular, under extreme operation conditions.

3. DEGRADATION AT HIGH TEMPERATURES

It was declared earlier [12] that dehydrochlorination of plasticized PVC, leading to coloration of the material, occurs at temperatures above 120°C solely.

A more detailed analysis revealed coloration at a lower temperature of 100–110°C [6, 7]. It was also shown that the recorded changes in the color difference ΔE are mainly determined by Δb^* increase characterizing the increase in the degree of yellowness of the samples. This confirms the relationship between the color change and the PCS formation, suggesting that the kinetic patterns of the color change reflect the regularities of the chemical process of PVC dehydrochlorination.

As shown in Fig. 1, both the initial accumulation rate and, more importantly, quasistationary concentration of PCS are the lower the lower the temperature. The plots presented in Fig. 1 are satisfactorily described by the first-order reaction equation (2):

$$\Delta E = \Delta E_\infty [1 - \exp(-kt)], \quad (2)$$

where ΔE_∞ is the steady-state (limiting) ΔE value, and k , rate constant of the process of reaching of this value, with both k and ΔE_∞ being dependent on the test temperature.

The activation energies E_a calculated using the data presented in Fig. 1 and the temperature dependence of the Δb^* change coincide, being 70–71 kJ/mol. This is in full agreement with $E_a = 74$ kJ/mol determined from analysis of the change in the elastic modulus during isothermal aging of plasticized PVC at 100–130°C [13].

Reaching a quasistationary PCS concentration under long-term heating in air is attributable to the competition between the processes of PCS formation and consumption via thermal oxidation. In accordance with this assumption, a jumpwise increase in temperature leads to sharp acceleration of the PCS accumulation and to a gradual transition to a new, higher quasistationary level (Fig. 2). This assumption is additionally supported by a decrease in b^* , observed for the samples that were preheated at an elevated temperature and then held at a lower temperature

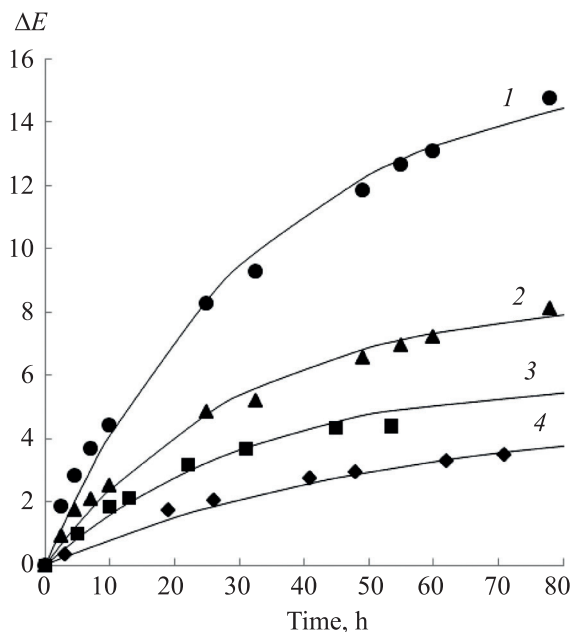


Fig. 1. Increase in the color difference ΔE during thermal aging of plasticized PVC at temperatures of 100–130°C. (Points) Experimental data and (curves) calculation according to Eq. (1) at ΔE_{∞} (k_c , h^{-1}) of (1) 3.9 (0.029), (2) 4.9 (0.046), (3) 8.3 (0.035), and (4) 14.4 (0.036).

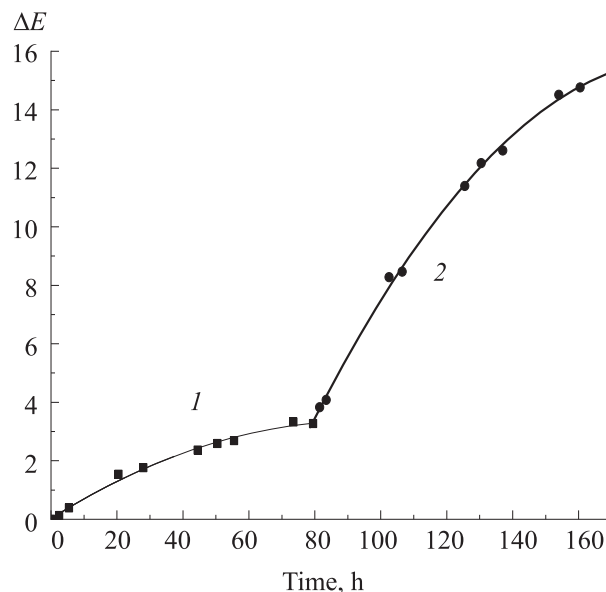


Fig. 2. Gradual reaching of the quasistationary ΔE value characteristic of the temperature of 130°C under successive heating of the plasticized PVC at (1) 100 and (2) 130°C.

(Fig. 3). Interestingly, in this case the formally determined activation energy of the process is negative, since its rate tends to increase with decreasing temperature. It would be reasonable to attribute this phenomenon to the competition between the PCS formation and consumption processes. Under the conditions indicated, with a decrease in temperature the rate of PVC dehydrochlorination decreases more sharply, since E_a for this process is higher than that for PCS oxidation.

Polyphenylene sulfide-based composite materials also exhibit coloration when heated; they initially turn light beige and acquire a darker color upon more prolonged heating.

For a glass-filled PPS composite that does not contain impact modifiers the parameter ΔE after the initial very fast stage (“jump”) changes for a long time at a practically constant rate which naturally increases with increasing temperature. The temperature dependence of the steady-state rate in the range of 90–130°C is satisfactorily described by the Arrhenius equation (Fig. 4). The activation energy of degradation is in the range of 110–120 kJ/mol. The peculiar feature of the

initial stage (a jump in ΔE , which also increases with increasing temperature) is apparently attributable to rapid formation of PCS with long conjugation chains from precursors having short conjugation chains, that were formed in the stages of preparation of the composite and the production of samples at high temperatures.

For the composite whose impact strength was improved by adding ethylene-glycidyl methacrylate copolymer of (4–20 wt %) the run of the kinetic curves of the change in ΔE varies with temperature (Fig. 5). Specifically, at low temperatures (100–110°C) the process is described by a linear, or a near-linear, function, and at higher temperatures, by an exponential dependence, like in the case of thermal degradation of PVC [(Eq. (2))].

The initial degradation rate tends to increase with increasing temperature in accordance with the Arrhenius equation. The corresponding activation energy is 108–134 kJ/mol depending on the content of the modifier. This is in good agreement with the activation energy of the PPS/elastomer composite (119±17 kJ/mol), estimated from the thermally induced changes of luminescence [14].

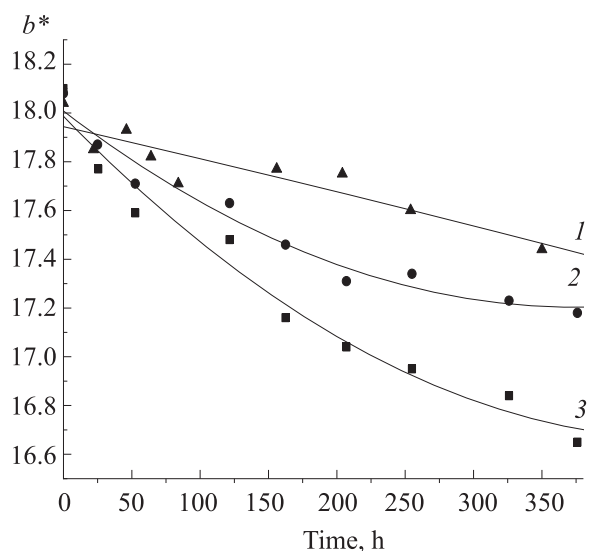


Fig. 3. Increase in the degree of yellowness of plasticized PVC after thermal pre-aging at 130°C for 43 h and subsequent holding at a temperature of (1) 80, (2) 70, and (3) 60°C.

Thus, coloration of PVC and PPS follows similar formal kinetic laws, which is indicative of a common mechanism of the phenomenon underlain by the PCS formation. Some of the features of the processes are associated with the influence of the components on the balance of the processes of PCS formation and consumption, mainly via oxidation.

The experimentally determined rates and kinetic parameters of degradation allow predicting the stability not only under conditions of long-term storage or operation under ordinary conditions but at extremely high temperatures as well.

4. DEGRADATION UNDER INTENSE LIGHT EXPOSURE

Irradiation, as well as exposure to high temperatures, leads to PCS formation and the resulting coloration of the material [2, 3]. Colored and stabilized compositions are characterized by the occurrence of induction periods whose length is determined by the effectiveness of the stabilizers used and the stability and catalytic activity of pigments and dyes involved (Fig. 6) [8]. Both the rate of dehydrochlorination after the end of the induction period and the length of the induction period itself depend on the intensity and spectral composition of light as well [2]. The main contribution, particularly in the initial stage,

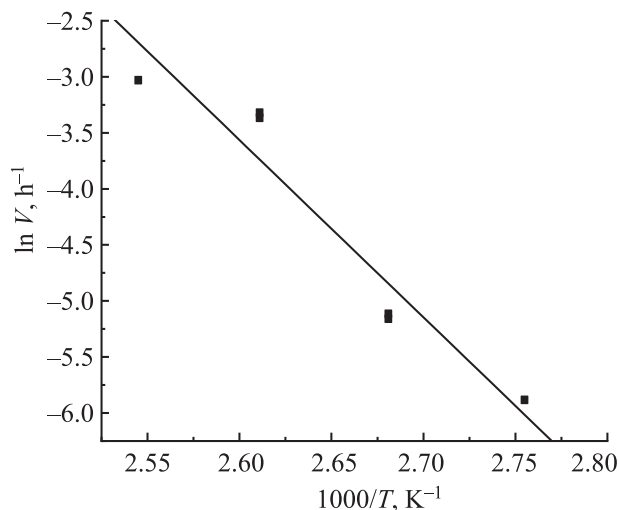


Fig. 4. Temperature dependence of the rate of increase in ΔE during thermal aging of the PPS-based glass-filled composite, plotted in the Arrhenius equation coordinates.

comes from the UV component of radiation, mainly its short-wavelength part ($\lambda \leq 320$ nm). Long-wavelength UV and visible radiation accelerate dehydrochlorination and induce the formation of PCS with longer conjugation chains [1, 2], thereby enhancing the color. However, PCS are simultaneously oxidized, which, under certain

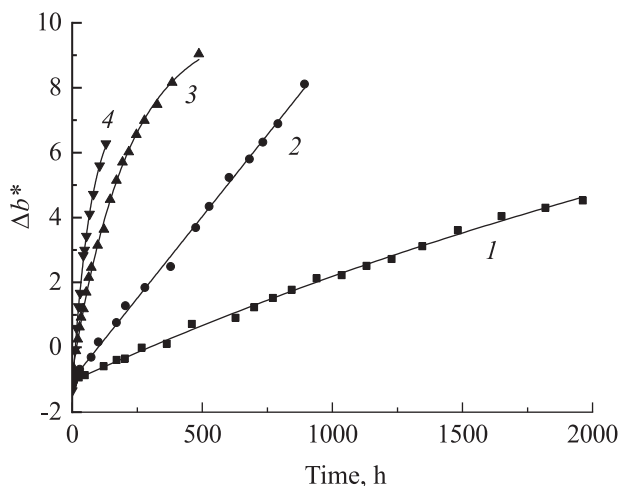


Fig. 5. Kinetic curves of accumulation of polyconjugated structures (in terms of Δb^*) during thermal degradation of PPS modified with ethylene-glycidyl methacrylate copolymer (10 wt %) at a temperature of (1) 100, (2) 110, (3) 130, and (4) 140°C.

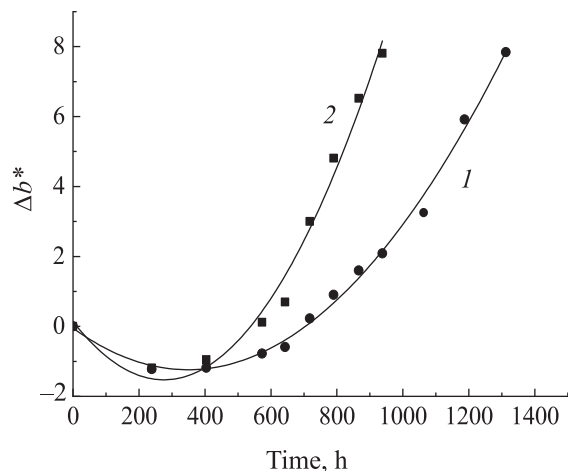


Fig. 6. Increase in the color difference ΔE under irradiation of white PVC containing titanium dioxide with (1) low and (2) high catalytic activity at the black panel temperature of (1, 3) 50 and (2, 4) 60°C.

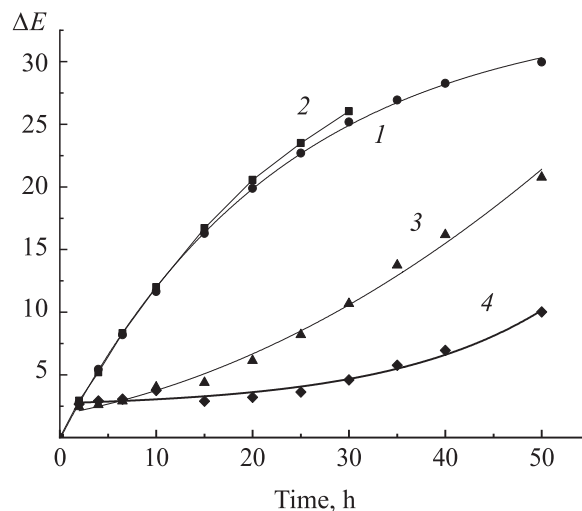


Fig. 7. Kinetic curves of the change in ΔE during irradiation of the PPS-based composite (1) without additional filters and (2) with color filters cutting off the short-wavelength radiation of (2) $\lambda < 280$, (3) $\lambda < 380$, and (4) $\lambda < 410$ nm.

conditions, causes a decrease in color intensity, most pronounced in the case of samples irradiated with visible light after preliminary exposure to total light or to its UV component only.

For polyphenylene sulfide-based polymers the kinetic regularities of the PCS formation under light exposure are similar to those revealed for PVC photodegradation. The main contribution to the increase in the color difference ΔE for the irradiated PPS-based composite comes from the UV component of radiation, since the kinetic curves recorded for the composite exposed to total light (Fig. 7, curve 1) and to its UV component only (Fig. 7, curve 2) practically coincide. Long-wavelength ultraviolet or visible radiation can induce coloration of the composite as well (Fig. 7, curves 3 and 4). In this case, however, a high rate of the process is observed only after the end of the induction periods. The increase in ΔE is mainly driven by the change in b^* , indicating a direct connection between the coloration and PCS formation.

The color difference ΔE gradually reaches a quasi-stationary level because of the occurrence, along with dehydrochlorination, of the competing PCS consumption process, also induced by light exposure. This second function of light is manifested most clearly as a decrease in the color intensity under irradiation with visible light of the PPS samples pre-exposed to total light. The effect from exposure to visible light can be visually

and quantitatively assessed by analyzing the reflection spectra (Fig. 8). After total light exposure the reflection coefficient R decreases in the entire visible region of the spectrum (Fig. 8, curve 2). Upon subsequent exposure to visible light R increases (the sample becomes lighter), more noticeably in the long-wavelength region (Fig. 8, curve 3). This evidences a predominant decrease in the content of PCS with relatively long conjugation chains, also attributable to the dual function of light.

The major consumption path for PCS in the material exposed to visible light is oxidation, like in the case of total light exposure. This is evidenced by an increase in the content of oxygen-containing groups, mainly hydroxy ($-O-H$) and ether ($-C-O-$), recorded in the surface layer by the ATR method.

In the case of irradiation of the impact-resistant composites based on PPS blends with ethylene-glycidyl methacrylate copolymer, not only PCS but also the elastomer are involved in oxidation, since the rate of formation of the ether groups in its presence sharply increases, being the greater the higher the content of this component. It was found that the elastomer in the composite is also oxidized under exposure to visible light which is absorbed by neither the copolymer itself nor its oxidation and degradation products. This means that PCS oxidation in the PPS macromolecules may initiate the copolymer oxidation, which suggests

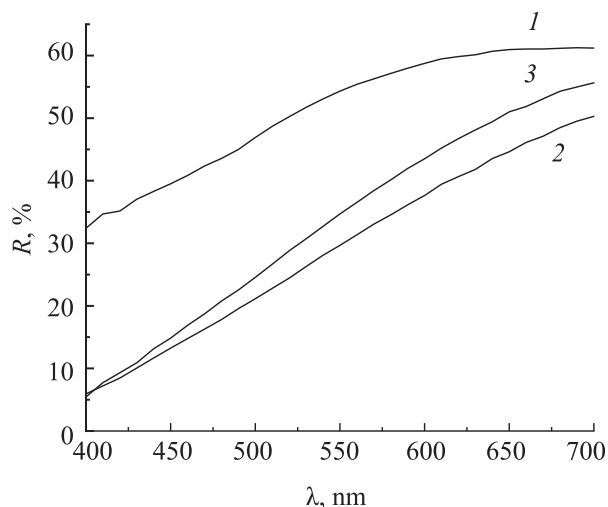


Fig. 8. Reflection spectra of the PPS-based composite (1) before and (2) after total light exposure for 30 h and (3) after additional irradiation with light of $\lambda > 410$ nm for 20 h.

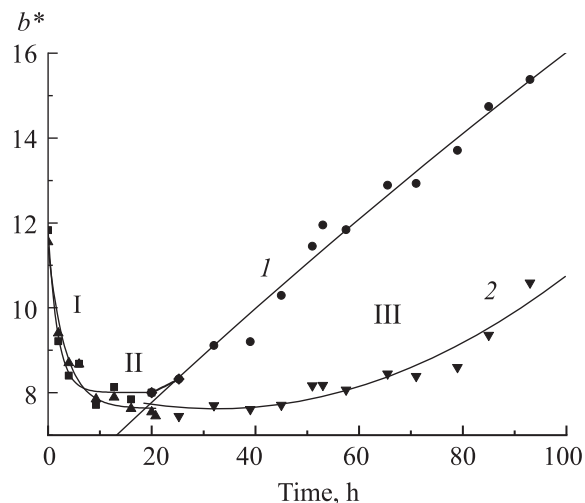


Fig. 9. Consumption and accumulation of polyconjugated structures during long-term irradiation of plasticized PVC with visible light selected by light filter: (1) ZhS11, $\lambda \geq 410$ nm, and (2) ZhS12, $\lambda \geq 440$ nm.

conjugated oxidation. Therefore, for such materials, non-light-absorbing antioxidants from the class of hindered amines [15] and synergistic blends of antioxidants and UV-absorbers [16] will be especially effective.

The short-wavelength part of visible light exerts more pronounced initiating effect than the long-wavelength part, since the length of the induction period in the change of the colorimetric characteristics is the greater, and the PCS accumulation rate is the lower, the higher the lower limit of the bandwidth of the filter (Fig. 9, curves 1 and 2). In the kinetic curves demonstrating the change in parameter b^* there are three clearly distinguishable sections: initial decrease in b^* (stage I), near-constant b^* (stage II), and increase in b^* under long-term irradiation (stage III). There seems to be nothing special in stages II and III, which are characteristic of all autocatalytic processes. At the same time, stage I, in which a decrease in b^* was recorded, seems unusual. A probable cause of this phenomenon will be discussed below.

5. COMBINED ACTION OF HIGH TEMPERATURES AND LIGHT

5.1. Successive Exposure to Heat and Light

The features of photodegradation of thermally pre-aged PPS samples are manifested most clearly under subsequent irradiation with visible light. As seen in

Fig. 10, the reflection coefficient R exhibits an increase in the short-wavelength region and a less pronounced decrease in the long-wavelength region (Fig. 10, curve 2). This indicates the predominant consumption of PCS with short conjugation chains under irradiation, which is also expressed as a more substantial change in b^* compared to other color coordinates. On the whole, the sample becomes lighter during irradiation, and ΔE decreases in

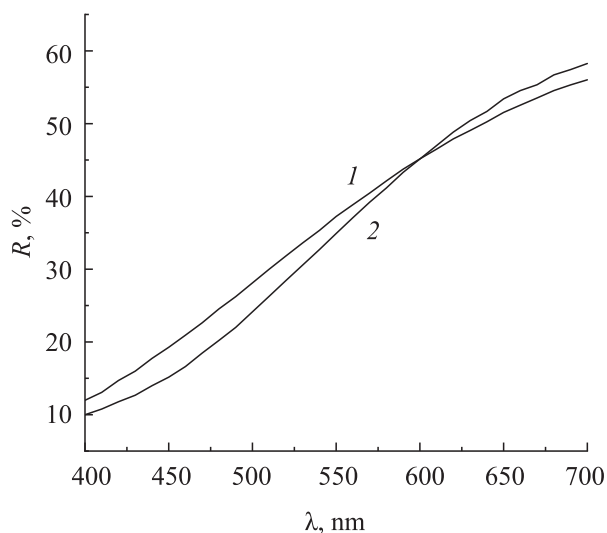


Fig. 10. Reflection spectrum of the PPS-based composite after (1) heating at 120°C for 500 h and (2) subsequent irradiation with light at $\lambda > 410$ nm for 12 h.

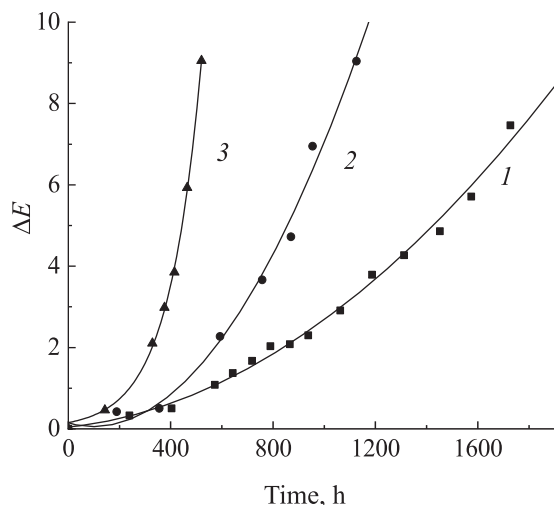


Fig. 11. Increase in the color difference under irradiation of gray-blue PVC at the black panel temperature of (1) 50, (2) 55, and (3) 60°C.

comparison with the thermally aged sample. This finding provides insight into the nature of the sharp decrease in b^* and, consequently, of the jump in ΔE under exposure of the initial PPS samples to long-wavelength radiation (see Fig. 7, curves 3 and 4; Fig. 9, stage I). The observed effects are attributed to the high-temperature exposure of PPS in the initial samples in the stages of preparation of the composite and production of the samples.

Exposure of the PPS-based composite to external factors in a different sequence, specifically, high-temperature exposure of the pre-irradiated sample, causes the opposite effect consisting in a sharp increase in the color difference ΔE . However, this effect is also most pronounced only upon irradiation with visible light, and only at the very beginning of thermal degradation. Thereupon the process proceeds at a rate characteristic of “ordinary” thermal degradation at a certain temperature. This phenomenon is apparently due to the fact that irradiation with visible light causes a significant decrease in the content of PCS with relatively long conjugation chains, absorbing in the visible region, while leaving unaffected short PCS absorbing in the UV region. Subsequent thermal exposure induces the transformation of these short PCS into longer ones, which is specifically responsible for enhancement of the visible light absorption and of the color.

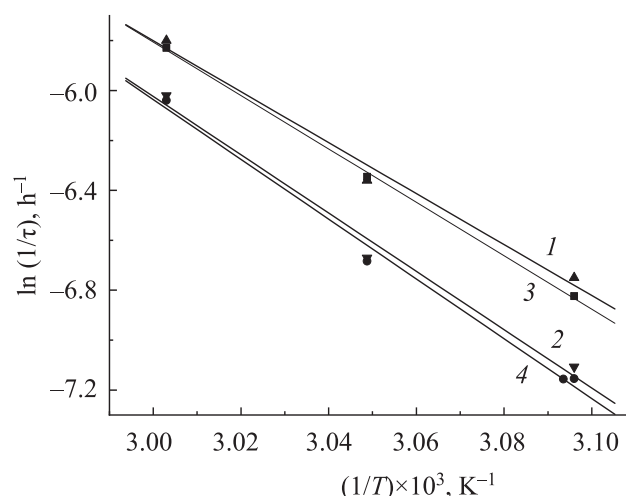


Fig. 12. Time dependences of the irradiation time until (1, 3) color difference and (2, 4) color coordinate b^* change reaches (1, 2) 2 and (3, 4) 4, plotted in the coordinates of Eq. (3) for the colored PVC irradiated with the light simulating solar radiation.

5.2. Simultaneous Exposure to Heat and Light

The discussion above evidences much faster coloration or color change for the polymeric materials under light exposure than under heating, even at sufficiently high temperatures (100–140°C). However, under the combined action of heat and light the contribution from thermal processes occurring in polymeric materials may be significant. The corresponding activation energy E_a may be relatively large, exceeding manyfold that for the photochemical reactions of organic compounds in liquid and solid solutions.

Formation of PCS requires significant rearrangement of several macromolecular units and of their immediate surrounding; therefore, specifically for this process, strong temperature dependence can be expected even under photochemical initiation. Indeed, as shown in Fig. 11, irradiation of PVC that additionally contains a dye and titanium dioxide causes significant shortening of the induction period of the change in ΔE with increasing temperature and a noticeable increase in the rate of the process. In this case it is advisable to estimate the activation energy using the approach based on analysis of the temperature dependence of the irradiation time until a certain degree of conversion (in our case, ΔE change) is reached [8, 17, 18].

Figure 12 shows the plot of $1/\tau$ vs. reciprocal temperature $1/T$ in the coordinates of the Arrhenius equation (3):

$$\ln(1/\tau) = A \exp(-E_a/RT), \quad (3)$$

where τ is the time of irradiation, h, until the color difference of 2 or 4 is reached; T , black panel temperature, K; A , pre-exponential factor; and R , universal gas constant.

The activation energy was estimated at 102 and 118 kJ/mol (for $\Delta E = 2$ and 4, respectively). Since the change in ΔE is mainly driven by the increase in b^* , the color change kinetics in this case also really reflects specifically the process of PCS formation during PVC dehydrochlorination rather than the dye transformation. Noteworthy, high activation energies E_a for radiation-initiated processes are typically associated with the contribution from the reactions proceeding without direct participation of light quanta and having a relatively high activation energy characteristic of thermal processes. One of such reactions is PVC dehydrochlorination. Therefore, the kinetics of PVC coloration during irradiation is strongly temperature-dependent.

In the PPS-based composites the rate of PCS accumulation under irradiation also tends to increase with increasing temperature, but the activation energy as defined by Eq. (1) is much lower, only 34 kJ/mol (for $\Delta E = 2$ and 4). This is probably due to the fact that PPS is a semi-crystalline polymer having a higher glass transition temperature (90–105°C, depending on the microstructure of the polymer).

CONCLUSIONS

Colorimetry offers a tool for nondestructive, highly sensitive evaluation of the stability of PVC- and PPS-based materials, suitable for assessing the degree of degradation of the material in the very early stages of the process.

The color change observed for uncolored and light-colored compositions is due to the formation of PCS absorbing mainly in the short-wavelength part of the visible region. Therefore, correct analysis should include, along with the data on the change of the color difference ΔE , those on the kinetics of the change of the color coordinate b^* characterizing the yellow coloration of the material, as well as the estimated changes in the reflection spectrum.

Limitations of colorimetry are associated with the dual function of heat and light, which are capable of inducing not only the formation but also the consumption of PCS via oxidation by atmospheric oxygen.

The competition between the PCS formation and consumption processes limits the experimentally determined accumulation rate and quasistationary concentration of PCS, which may cause a decrease in sensitivity of the method.

Studies of photochemical and photothermal aging should also take into account possible photochromism which manifests itself as a decrease in color intensity under exposure to visible light and its recovery under heating or UV light irradiation.

FUNDING

This study was carried out within the framework of state assignment no. 0082-18-006 (state registration no. AAAA-A18-118020890097-1).

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFEERNCES

1. Gumargalieva, K.Z., Ivanov, V.B., Zaikov, G.E., Moiseev, Ju.V., and Pokholok, T.V., *Polym. Degrad. Stab.*, 1996, vol. 52, no 1, pp. 73–79.
2. Zuravlev, M.A. and Ivanov, V.B., *Eur. Polym. J.*, 1989, vol. 25, no 4, pp. 391–394.
3. Ivanov, V.B. and Zuravlev, M.A., *Polym. Photochem.*, 1986, vol. 7, no 1, pp. 55–64.
4. Das, P.K., DesLauriers, P.J., and Fahey, D.R., *Polym. Degrad. Stab.*, 1995, vol. 48, pp. 11–23.
5. DesLauriers, P.J., Gelbel, J.F., and Das, P.K., *Angew. Makromol. Chem.*, 1997, vol. 247, pp. 45–59.
6. Ivanov, V.B., Solina, E.V., Staroverova, O.V., Popova, E.I., Lazareva, O.L., and Belova, O.A., *Russ. J. Phys. Chem. B*, 2017, vol. 11, no. 6, pp. 978–984.
7. Ivanov, V.B., Popova, E.I., and Solina, E.V., *Polym. Sci., Ser. B*, 2017, vol. 59, no. 3, pp. 348–351.
8. Ivanov, V.B. and Solina, E.V., *Polym. Sci., Ser. D*, 2019, vol. 12, no. 1, pp. 100–104.
9. Ivanov, V.B., Bitt, V.V., Solina, E.V., and Samoryadov, A.V., *Polymers*, 2019, p. 1579.

10. Ivanov, V.B., Solina, E.V., and Samoryadov, A.V., *Polym. Sci., Ser. D*, 2020, vol. 13, no. 3, pp. 353–357.
11. *Colorimetry, 3rd ed.: CIE Technical report CIE 15.3:2004*, 2004.
12. Linde, E. and Gedde, U.W., *Polym. Degrad. Stab.*, 2014, vol. 101, no. 1, pp. 24–31.
13. Padmasiri, K., Gamage, P.K., Farid, A.S., and Karunanyake, L., *J. Appl. Polym. Sci.*, 2009, vol. 112, no. 4, pp. 2151–2165.
14. Steffen, R., Meir, M., Rekstad, J., and Röder, B., *Polymer*, 2018, vol. 136, pp. 71–83.
15. Rozantsev, E.G., Kagan, E.S., Sholle, V.D., Ivanov, V.B., and Smirnov, V.A., *ACS Symp. Ser.*, 1985, vol. 280, pp. 11–35.
16. Ivanov, V.B., Rozenboim, N.A., Angert, L.G., and Shlyapintokh, V.Ya., *Dokl. Akad. Nauk SSSR*, 1978, vol. 241, no. 3, pp. 609–612.
17. Ivanov, V.B., Zavodchikova, A.A., Popova, E.I., Lazareva, O.L., Belova, O.A., Kryuchkov, I.A., and Bykov, E.V., *Thermochim. Acta*, 2014, vol. 589, pp. 70–75.
18. Vyazovkin, S., Burnham, A.K., Criado, J.M., Perez-Maqueda, L.A., Popescu, C., and Sbirrazzuoli, N., *Thermochim. Acta*, 2011, vol. 520, pp. 1–19.