

The Effect of Irradiation Conditions on Photodegradation of a Impact Resistant Polyphenylene Sulfide-Based Composite

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Abstract—In this paper, we study the effect of the spectral composition of light and temperature on the change in colorimetric characteristics during accelerated tests of the light resistance of a composite based on glass-filled polyphenylene sulfide. The activation energy of photodestruction is determined. The revealed patterns indicate the promising use of colorimetry as a nondestructive method of stability testing of polyphenylene sulfide-based materials.

Keywords: composites, polyphenylene sulfide, light resistance, accelerated tests, colorimetry

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Polyphenylene sulfide (PPS) possesses a number of important properties, among which, first of all, it is necessary to note high heat resistance; chemical resistance to acids, alkalis, and organic solvents; crack resistance; slight water absorption; low creep; and excellent electrical characteristics. Owing to these qualities, PPS-based materials are widely used in the electrical and electronic industries, as well as others [1].

The increased use of PPSs, in particular, in aerospace engineering, is stimulating the development of PPS-based composite materials. Glass and carbon fibers [2–4] and nanoparticles [5–8] are usually used as active fillers. Such composites possess enhanced physical and mechanical characteristics, though it is not possible to completely eliminate one of the main disadvantages of PPSs—fragility—in this way. To further increase the impact strength, it was proposed to use mixtures of PPSs with other polymers [9]. However, such a modification can lead to a change in both the physicomechanical and physicochemical properties of the material [10], especially the property that is relatively critical for PPSs as relatively low light fastness. This disadvantage is most clearly manifested in the rapid coloring of PPSs during irradiation [11].

This study is aimed at analyzing the effect of light and heat, as well as the sequential effect of light with a various spectral composition, on the kinetics of change in color of a composite material based on a glass-filled PPS modified with an ethylene and glycidyl methacrylate copolymer (EGMC) and designed for widespread use [9]. The promise of this approach was previously shown by the example of photodegra-

dation of composite materials based on polyvinyl chloride [12].

Samples for investigation in the form of disks with a diameter of 50 mm and a thickness of 2 mm are prepared by injection molding of glass-filled impact resistant polyphenylene sulfide (IRPPS) TERMORAN PPS SV-40UP, TU 20.16.59-001-01531596–2017. The glycidyl methacrylate content in the EGMC is 8 wt %, while the EGMC content in the composite is 10 wt % (calculated per polymer part).

Photochemical aging was performed using a SUNTEST XLS+ apparatus (ATLAS, United States) with a filter system ensuring that the spectral composition corresponded to sunlight under natural conditions (the radiation wavelength being greater than 290 nm) at a light intensity of 500 W/m² and a black panel temperature of 50 or 60°C.

The spectral composition of light was varied using additional filters: UFS5 (290 nm ≤ λ ≤ 390 nm), BS7 (λ ≥ 360 nm), BS8 (λ ≥ 380 nm), ZhS11 (λ ≥ 410 nm), or ZhS12 (λ ≥ 440 nm).

The color characteristics were determined using a ColorFlex spectrophotometer (Hunter Lab, United States) in the mode of 45°/0°, a observation angle 10°, and a D65 light source. Color difference ΔE that was used as the main criterion in the CIELAB-76 system was determined by formula (1):

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

where $\Delta L^* = L_0^* - L_i^*$, $\Delta a^* = a_0^* - a_i^*$, $\Delta b^* = b_0^* - b_i^*$. In this case, index 0 refers to the sample before testing,

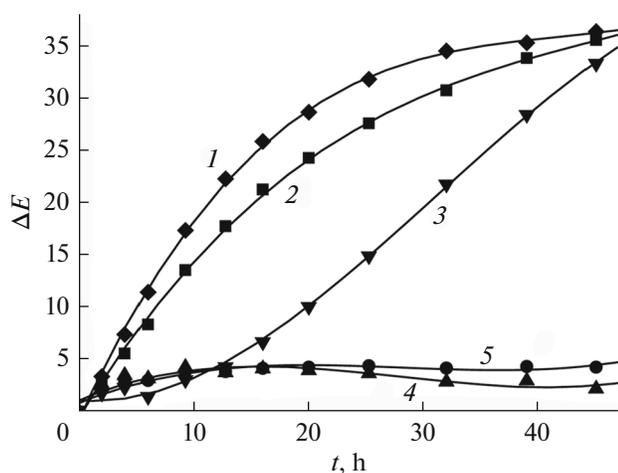


Fig. 1. Change in color difference ΔE upon irradiation of the IRPPS in the SUNTEST apparatus (1) without additional color filters or with filters: (2) UFS5, (3) BS8, (4) ZhS11, and (5) ZhS12.

while index i refers to the sample after a certain test period. The values of L^* , a^* , and b^* were determined directly as a result of measurements according to the standard procedure for processing the reflection spectra using the software of the ColorFlex instrument.

Since the L^* value in the CIELAB-76 system determines the brightness, parameter a^* determines the intensity of red (+) and green (–) color, depending on the sign, and b^* determines that of the yellow (+) and blue (–) color. b^* was then used to evaluate the color change of the PPS in some cases directly. This is possible because yellowing occurs due to the formation of polyconjugated structures that absorb mainly in the blue region of the spectrum. Therefore, it is b^* that is a concentration measure of such structures in the composite surface layer.

In the course of the study, irradiation of the composite with full light in the SUNTEST apparatus was found to lead to its rapid coloring, initially in light yellow and then in bright yellow. At a longer light exposure, the color becomes yellow-brown. Compared to the initial color in this case, the color difference from the very beginning occurs at a high speed that then gradually decreases, while the color difference reaches a quasi-stationary level (Fig. 1, curve 1).

When exposed only to the ultraviolet component of the xenon lamp radiation of the SUNTEST apparatus that is isolated from the total radiation using a UFS5 filter ($290 \leq \lambda \leq 390$ nm), coloring also occurs at a high initial speed (see Fig. 1, curve 2), which is, however, significantly less than that during irradiation without additional filters (see Fig. 1, curve 1). It is interesting and important that almost the same quasi-stationary level is achieved in this case as when irradiated with full light (see Fig. 1, curves 1, 2). As could be expected from the published data for the unmodified PPS, this

means that the main contribution to the formation of polyconjugated structures in the composite is due to the ultraviolet component of the xenon lamp radiation.

In accordance with this statement, noticeable induction periods are observed when samples are irradiated with the use of light filters that cut off short-wavelength radiation (BS7, $\lambda \geq 360$ nm, or BS8, $\lambda \geq 380$ nm). The induction period is especially pronounced when using a BS8 filter (see Fig. 1, curve 3), and its value is ~ 10 h; i.e., a time such that a very strong sample coloring occurs when irradiated with full light. The magnitude of the induction period is much less (~ 5 h) when using a BS7 color filter. In the latter case, this is due to the fact that the shortest-wavelength part of ultraviolet light passing through the BS7 filter falls into the edge of intrinsic absorption of polyphenylene sulfide, while the light passing through the BS8 filter can affect only the chromophore groups formed during the synthesis and processing of the PPS.

It is necessary to note that the staining rate (increasing color difference ΔE) after the end of the induction period rapidly increases and becomes comparable in a certain area with the coloring rate when samples are irradiated without additional filters and even greater than the latter.

When irradiated with visible light filtered with ZhS11 ($\lambda \geq 410$ nm) or ZhS12 ($\lambda \geq 440$ nm) from total irradiation for 45 h, no noticeable coloring of the composite is observed. This is an additional confirmation of the earlier conclusion that an important contribution is made by the UV component under the effect of full light in the SUNTEST apparatus. Possible causes of very small, but clearly fixed and reproducible, changes in ΔE at the very initial stages of the process (see Fig. 1, curves 4, 5) are considered below.

The photodestruction of the IRPPS depends relatively weakly on temperature (Fig. 2). Unlike a number of other structural thermoplastics [13], kinetic curves cannot be combined by transformation along the time axis. This indicates the presence of a dependence of the activation energy on the conversion degree, which, in turn, indicates a change in the coloring mechanism over time. Using an approach widely applied in the analysis of thermal degradation of polymers by the TGA method [14, 15], it is possible to estimate the change in activation energy with increasing conversion degree α (in our case, ΔE). Assuming that the Arrhenius law holds for IRPPS, as well as other structural thermoplastics, relation (2) holds for activation energy E_α at specified conversion degree α ,

$$E_\alpha = [(RT_2T_1)/(T_2 - T_1)] \ln k_\alpha, \quad (2)$$

where T_1 and T_2 are the test temperatures, k_α is the acceleration factor at specified conversion degree α (ΔE value), and R is the universal gas constant. The

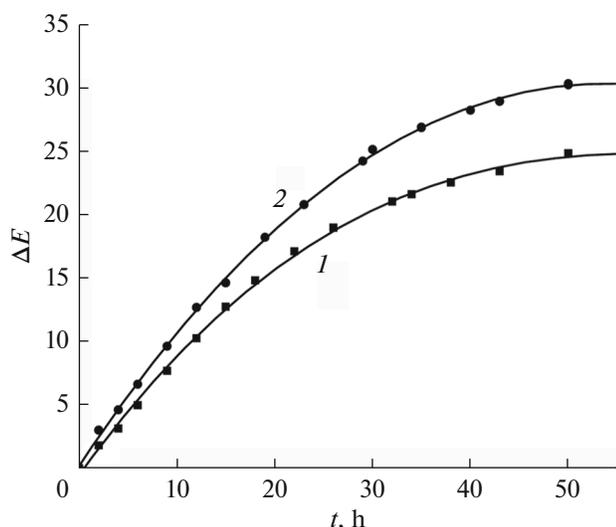


Fig. 2. Kinetic curves of the accumulation of polyconjugated structures upon irradiation of the IRPPS with full light at a black panel temperature of (1) 50 or (2) 60°C.

dependence of E_α on (ΔE calculated by formula (2) is presented in Table 1.

The change in activation energy with increasing conversion degree, i.e., the number of formed polyconjugated structures responsible for coloring the composite, seems natural, given the nature of the accumulation of these structures upon irradiation. A gradual transition to the quasi-stationary level is clearly visible in Figs. 1 and 2, indicating that, at deep stages, along with the formation of polyconjugated structures, they are consumed under the effect of light. This quasi-stationary level is higher at a higher temperature (see Fig. 2).

Since the formation of polyconjugated structures is a multistage process and involves a substantial restructuring of macromolecules with energy consumption, both the initial rate and the quasi-stationary level should be lower with a lower temperature. In this case, E_α determined by formula (2) should be greater the closer the corresponding section of the kinetic curve to the quasi-stationary level, which is observed in practice (see Table 1).

In the initial sections of the kinetic curves, the formation of polyconjugated structures (destruction of the material) dominates and the activation energy calculated by formula (2) is really a measure of the temperature dependence, a strict physicochemical characteristic of this process. Therefore, the value of the activation energy in this region, which is 11 ± 1 kJ/mol, is

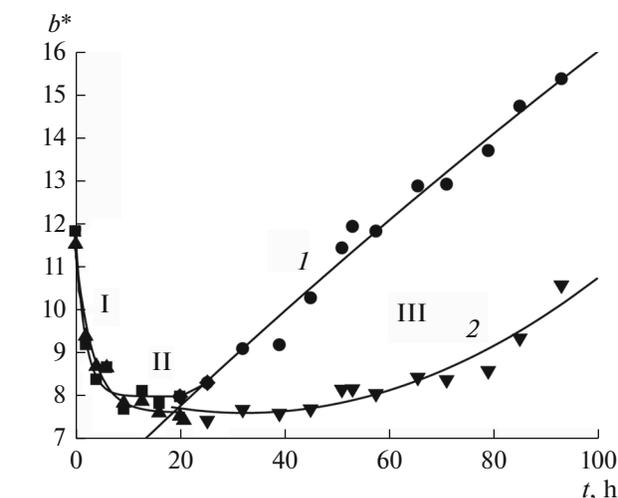


Fig. 3. Consumption and accumulation of polyconjugated structures during prolonged irradiation of samples with visible light filtered by (1) ZhS11 or (2) ZhS12.

advisable for use when predicting the composite stability when used under conditions of variable temperatures that vary due to seasonal and daily fluctuations. It is important at the same time that this value is in the same row as the activation energies of photodestruction of other structural thermoplastics [13].

A noticeable coloring of the composite also occurs when the IRPPS is irradiated with visible light, while the induction period in this case is very large and the kinetics of the process is complex (Fig. 3). At the beginning of irradiation, not coloring, but discoloration, of the samples is observed, which is recorded by a decrease in b^* that characterizes the small initial yellowness of the material. This stage ends very quickly and is satisfactorily described by an exponential function (see Fig. 3, stage I). Then, the induction period is clearly visible (see Fig. 3, stage II), the value of which when using the ZhS12 filter ($\lambda \geq 440$ nm) is significantly larger than that when using the ZhS11 filter ($\lambda \geq 410$ nm).

At the next, the third, stage, the b^* value gradually increases. However, its rate of increase remains lower than that when irradiated with full light in the apparatus (cf. Figs. 1, 3, curves 1). As noted above, similar phenomena were also observed during irradiation using filters that cut off the short-wavelength component of UV light (see Fig. 1, curve 3). However, stages I and II were less pronounced in this case, while the coloring rate at stage III was rather large. This is

Table 1. Change in activation energy E_α at an increase in color difference ΔE during sample irradiation at a black panel temperature of 50 or 60°C

ΔE	5	7.5	10	12.5	15	17.5	20	22.5	25	27.5
E_α , kJ/mol	8.5	11.8	11.7	10.9	16.3	19.9	22.1	23.9	28.8	34.9

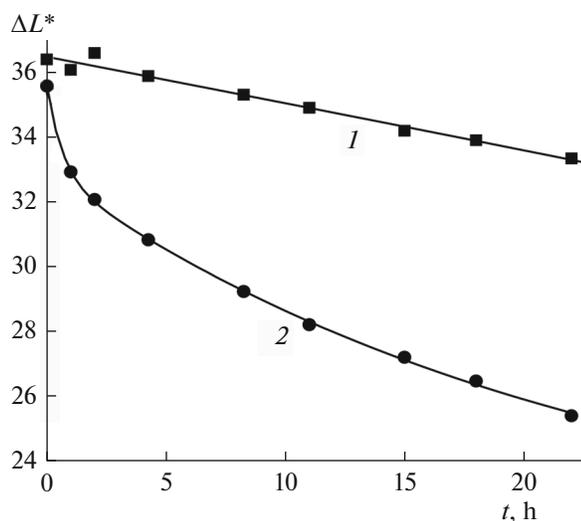


Fig. 4. A decrease in ΔL when the samples are irradiated with visible light (ZhS11 filter) after preliminary exposure to (1) full radiation in the SUNTEST apparatus or (2) only its ultraviolet component (UFS5 filter).

due to the fact that it is the UV component of light that makes the main contribution to the formation of polyconjugated structures. Therefore, when irradiated with the use of BS7 and BS8 filters, all processes proceed faster than when irradiated with visible light—stages I and II are “compressed” in time, and stage I is additionally “compressed” in terms of the scale of variation of b^* .

Color change (“bleaching”) when exposed to visible light is more pronounced for previously photochemically aged samples (Fig. 4). In this case, there is a significant difference in the kinetics of the processes for the composite irradiated for 45 h with full light in the SUNTEST apparatus (see Fig. 4, curve 1) or only with its UV component (see Fig. 4, curve 2). This feature seems unexpected, given that the samples have the same color and almost identical colorimetric characteristics since a quasi-stationary level is reached during this time of irradiation when the rates of formation and consumption of polyconjugate structures are close in magnitude.

For a sample irradiated with full light (in brackets, only with UV light), $L^* = 63.00$ (63.29), $a^* = 10.04$ (10.35), and $b^* = 36.55$ (35.60). However, the bleaching rates for these samples, especially at the initial stages, are fundamentally different. Thus, the ΔE value decreases by 2.66 (3.51) when a sample preirradiated with UV light for 1 h (in brackets, for 2 h) is irradiated with visible light and only by 0.32 (an increase by 0.2) for a sample previously irradiated with full light; i.e., the difference is almost an order of magnitude. At further irradiation, the difference in rates gradually decreases. This may be due to the increasing contribution of the above-considered processes of formation of

polyconjugated structures under the effect of visible light (see Fig. 3).

The obtained data confirm the above conclusion that light has a double effect on the IRPPS: both the initiation of the formation of polyconjugated structures leading to coloring of the composite and their consumption, which causes partial discoloration under certain conditions.

The formation of polyconjugated structures occurs mainly under the effect of UV light. This seems quite natural, given that the $-S-Ph-S$ groups of the polymer chain are absorbed only in the UV region. Polyconjugated structures with a short conjugation length that are formed during the synthesis and processing of the polymer also make a certain contribution. This explains the high sensitivity of the composite to long-wave UV light that cannot affect the absorption spectrum of the $-S-Ph-S$ groups.

The consumption of polyconjugate structures occurs under the effect of visible and UV light. This is due to the fact that visible light is $\sim 56\%$ and UV light is only $\sim 6.6\%$ of the total radiation of a SUNTEST xenon lamp simulating sunlight. However, UV light is completely absorbed, while visible light is only partially absorbed in the blue spectral region. By analogy with the consumption of polyconjugated structures during photo- and thermal degradation of PVC [15], we may suppose that this process in the IRPPS is also caused by their oxidation, which occurs both directly under the effect of light absorbed by them and with the participation of free radicals formed during the photolysis of hydroperoxides and other photochemically active products. Certainly, this should lead to the formation of hydrophilic oxygen-containing groups on the material surface.

In accordance with this hypothesis, unlike the hydrophobic surface of the original samples, the surface of irradiated samples, especially when irradiated with full light or successively UV and visible light, was found to be well wetted by water.

CONCLUSIONS

As does the unmodified PPS, the IRPPS is quickly colored when exposed to light. When irradiated with long-wave UV light and, especially, visible light, an induction period, the magnitude of which varies directly with the value of the short-wave boundary of light, is observed.

The activation energy of IRPPS photodegradation that is estimated by the colorimetric method increases as the destruction depth increases. To predict the material stability under the effect of light and variable temperatures, it is advisable to use the activation energy value of 11 ± 1 kJ/mol specific to the initial stages of destruction.

The color change during IRPPS photodegradation is partially reversible. The intensity of the color result-

ing from the full radiation of a xenon lamp or its UV component can be significantly reduced by the effect of visible light.

The effect of the spectral composition of light on the degradation rate and the ratio of formation and consumption rates of polyconjugated structures should be taken into account when choosing IRPPS test conditions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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