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Accelerated climatic aging of polymer composite materials based on polypropylene and aluminum oxide

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The article is devoted to the study of changes in the deformation and strength properties of polymer composite materials based on polypropylene and aluminum oxide during accelerated climatic aging and assessing the possibility of predicting the approximate terms of their operation. It has been found that the values of the thermal conductivity coefficient of polypropylene-aluminum oxide composites naturally increase with an increase in the proportion of filler from 0.10 to 0.21 W/(m·K), which indicates the feasibility of creating these materials. It was also shown that an increase in the content of aluminum oxide in the polypropylene matrix leads to an improvement in the strength characteristics (tensile strength) of the composite. Similar patterns are observed for the dependence of the tensile strength on the content of aluminum oxide. Accelerated aging of polymer composite samples is accompanied by a decrease in their strength, which indicates the ongoing processes of destruction of polypropylene macromolecules. According to the results of accelerated climatic tests, it was found that samples of polymer composites based on polypropylene and aluminum oxide are characterized by small predicted approximate service life (13–15 months) under the influence of the main environmental factors (UV radiation, humidity, temperature cycling), practically not differing from the service life of materials made of unfilled polypropylene, therefore, either these materials must be used in milder conditions, for example, as elements of products used indoors, or stabilizers must be included in the proposed compositions.

Keywords: polypropylene, aluminum oxide, strength, accelerated climatic tests.

УДК: 620.169.2

Об ускоренном климатическом старении полимерных композиционных материалов на основе полипропилена и оксида алюминия

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Статья посвящена изучению изменения деформационно-прочностных свойств полимерных композиционных материалов на основе полипропилена и оксида алюминия при проведении ускоренного климатического старения и оценке возможности прогнозирования приблизительных сроков их эксплуатации. Установлено, что значения коэффициента теплопроводности композитов полипропилен-оксид алюминия закономерно возрастают с повышением доли наполнителя от 0.10 до 0.21 Вт/(м·К), что свидетельствует о целесообразности создания данных материалов. Также показано, что повышение содержания оксида алюминия в полипропиленовой матрице приводит к улучшению прочностных характеристик (прочности на разрыв) композита. Аналогичные закономерности имеют место и для зависимости прочности на растяжение от содержания оксида алюминия. Ускоренное старение образцов полимерных композитов сопровождается уменьшением их прочности, что свидетельствует о протекающих процессах деструкции макромолекул полипропилена. По результатам ускоренных климатических испытаний установлено, что образцы полимерных композитов на основе полипропилена и оксида алюминия характеризуются небольшими прогнозируемыми приблизительными сроками эксплуатации (13–15 месяцев) в условиях воздействия основных факторов внешней среды (УФ-излучение, влажность, циклическое изменение температуры), практически не отличающимися от сроков эксплуатации материалов из ненаполненного полипропилена, следовательно, либо данные материалы должны эксплуатироваться в более мягких условиях, например, в качестве элементов изделий, применяемых внутри помещений, либо в предложенные композиции необходимо включать стабилизаторы.

Ключевые слова: полипропилен, оксид алюминия, прочность, ускоренные климатические испытания.

1. Introduction

Among the materials based on thermoplastics, polypropylene (PP) occupies the leading position [1]. Materials based on it are characterized by high dynamic resistance, resistance to mechanical stress, chemical resistance, and water resistance. The main disadvantages of PP are low resistance to low temperatures, high flammability, low thermal conductivity and low resistance to aging, i. e. to deterioration of properties during storage and operation under the influence of environmental factors. These disadvantages can be partially or completely eliminated by introducing appropriate additives. The additives that are most capable of changing the properties of the polymer binder are fillers, which are an indispensable component in the creation of polymer composite materials (PCM). PCM in the presence of certain fillers are characterized by a more perfect structure, a high complex of technological, physical-mechanical and operational properties [4 – 5].

Solid PCM fillers are divided into four groups: dispersed, fibrous, bulk and sheet. Dispersed fillers are the most widespread [6]. The introduction of a mineral dispersed phase into the composition of the composite can significantly reduce the consumption of scarce polymer resins, as well as increase the hardness, rigidity and wear resistance of the material, reduce shrinkage and tendency to cracking [7, 8].

Thermoplastics, including PP, are known to be poor heat conductors [9]. They usually do not have free electrons available for the mechanisms of electronic and thermal conduction. For thermoplastics with a low degree of crystallinity at 0 – 200°C, thermal conductivity ranges from 0.125 to 0.2 W/(m·K). Higher thermal conductivity is achieved only in the presence of certain fillers [4]. From this point of view, a promising mineral dispersed filler PCM based on PP is aluminum oxide, which has a number of advantages: it has high chemical and thermal stability, has excellent thermal and electrical characteristics, good mechanical resistance, a wide raw material base and the ability to impart low combustibility to materials [10 –12].

However, the introduction of dispersed fillers into polyolefins leads to significant changes in the physicochemical and mechanical properties of the obtained polymer composite materials [13], and also has a significant effect on the processes of their thermal, thermal and photooxidative destruction, and, consequently, on the service life of plastic materials. products based on polyolefins.

The service life of products based on polyolefins (PO), including PP, depends on the operating conditions. Household and biomedical products are usually operated under environmental conditions and the change in their properties under the influence of environmental factors (ultraviolet radiation, moisture, oxygen, ozone, etc.) is called “aging”. Thermoplastics, which include many polyolefins, are especially susceptible to thermal, thermo-oxidative and, especially, light (photo-oxidative) aging [14].

Numerous publications of domestic and foreign authors, for example, works [14 –16], are devoted to the study of the processes of photooxidation of polyolefins. These works indicate that the formation of a significant number of carbonyl groups during operation in PO materials leads to an increased ability to absorb oxygen, which results in the formation of vinyl and vinylidene groups, which significantly reduce the thermal oxidative stability of the polymer during subsequent processing, initiate the process of photoaging of such materials and products. of them, reduce their service life. The presence of carbonyl groups does not determine either the mechanical properties (their introduction up to 9% into the initial PO macromolecule has no significant effect on the mechanical properties of the material), or the transmission of sunlight by the film (the absorption of light by carbonyl groups lies in the wavelength range less than 280 nm, and the light of such composition is practically not contained in the solar spectrum). However, it is the presence of carbonyl groups in PO that determines its very important property — resistance to light. The initiator of PP photoaging are hydroperoxides, which are formed during the processing of the primary material in the process of mechanochemical destruction. Their initiating action is especially effective in the early stages of aging, while carbonyl groups have a significant effect in the later stages.

Aging is accompanied by competing reactions of destruction and structuring. The result of the first is the formation of low molecular weight products, and the second is the formation of an insoluble gel fraction. The rate of formation of low molecular weight products is maximum at the beginning of aging. This period is characterized by a low gel content and a decrease in physical and mechanical parameters. Subsequently, the rate of formation of low molecular weight products decreases, a sharp increase in the gel content and a decrease in elongation are observed, which indicates the progress of the structuring process. Such phenomena lead to a decrease in physical and mechanical characteristics and a decline in optical properties.

Thus, the purpose of this work was to study the change in the deformation and strength properties of polymer composites PP-Al_2O_3 during accelerated climatic aging and to assess the possibility of predicting their service life.

2. Experimental part

In the creation of PCM, PP grade PP H120 GP/1 manufactured by LLC Tomskneftekhim (RAO Sibur) (degree of crystallinity 73%, melting point 172°C) and aluminum oxide (reagent grade) with a particle size of 10 – 20 microns.

The composites were prepared in melt at a Plastograph EC laboratory station (Plastograph EC) by Brabender at a mixing chamber temperature of 180°C and a rotor speed of 30 rpm for 5 –15 min at a load of 200 N.

The pressing was carried out on an automatic hydraulic press "AutoMH-NE" (Carver, USA) at 210°C and holding under a pressure of 7000 kgf for 3 min, followed by cooling or without cooling on the press.

Physicomechanical properties of polymer composites were determined according to GOST 11262-80 on a Shimadzu AGS-X tensile testing machine (Shimadzu, Japan) at a temperature of 20°C and a moving grip speed of a tensile testing machine 1 mm/min (Fig. 1). Samples for testing were taken in the form of blades with a thickness of 1 mm in accordance with GOST 11262-80.

Statistical processing of experimental results was carried out using the STATISTICA 10.0 software package. With a confidence level of 0.95 and a number of repeated experiments of 5, the error in determining the physical and mechanical properties does not exceed 5%.

The tensile strength (MPa) was used as a criterion for the strength of the tested polymeric materials when predicting the service life.

Accelerated climatic aging of PCM based on PP and aluminum oxide in laboratory conditions was carried out using a QUV weathermeter (climate chamber) manufactured by Q-Lab (Ohio, USA) in UV radiation mode (radiation intensity 89 W/m^2 at 340 nm, temperature 25°C, 30°C) with irrigation. The hourly dose of UV radiation (Q) was about 100 W/m^2. Irradiation of the samples was carried out in a continuous mode for 2 – 6 days. Removal of samples to assess changes in deformation and strength properties was carried out at regular intervals (2, 3, 4, 6 days).

The measuring procedure of the thermal conductivity coefficient of composite materials based on PP is given in [4].

The degree of crystallinity of polymer composites was determined using the differential scanning calorimetry method under the following conditions: temperature range 40 – 200°C; dynamic mode — heating/cooling rate 10 deg/min; Wednesday — nitrogen; DSC-1 device (NETZSCH). The method allows you to determine the following thermophysical indicators: T_m, T_{cr} — melting and crystallization temperature; ΔH_{pl}, ΔH_{cr} — thermal effect of melting and crystallization. The degree of crystallinity of the polymer χ was calculated by the formula: $\chi = (\Delta H_i / \Delta H_0) \times 100\%$, where ΔH_i is the specific heat of fusion calculated on the content (i) of the polymer in the sample; $\Delta H_0 = -147$ J/g is the specific heat of fusion of fully crystalline polypropylene.

3. Results and discussion

When developing polymer composites, it is necessary to pay attention to the degree of dispersion of filler particles, since phase heterogeneity can arise in the system, which affects the processability of the polymer composition and its deformation and strength characteristics. As can be seen from the microphotograph (Fig. 2), the particles of aluminum oxide are rather uniformly dispersed in the bulk of the PP matrix, but in some places ellipse-shaped agglomerates with an average size of up to 40 μm are observed.

The expediency of introducing Al_2O_3 into PP is evidenced by the data presented in Table S1 (Supplementary material), according to which the values of the thermal conductivity coefficient of composites naturally increase with an increase in the proportion of filler.

The development of new polymeric materials is associated with the need to achieve certain strength indicators that will make it possible to use one or another polymer for various purposes. Strength is understood as the property of a polymer material to resist destruction under the action of mechanical stresses. In this case, destruction is a violation of the continuity of the material, its rupture, leading to the formation of new surfaces. To destroy a polymer body, it is necessary to destroy the bonds that unite the elements of its structure [17,18].

Ultraviolet radiation, capable of initiating photooxidative destruction, reduces the durability of polymeric materials, especially those under stress, and, accordingly, is one of the main factors affecting the service life of a polymeric product [19,20].

The most reliable method for determining the resistance of a material to climate factors is field tests, in which there is

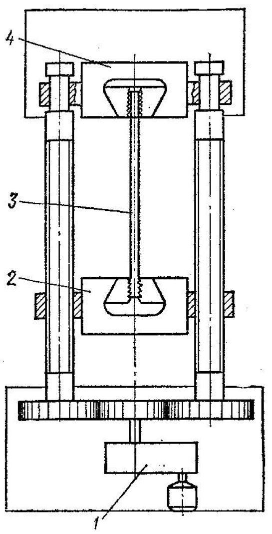

Fig. 1. Schematic of a tensile testing machine with a mechanical drive: 1 — electric drive, 2 — lower grip, 3 — sample, 4 — upper grip.

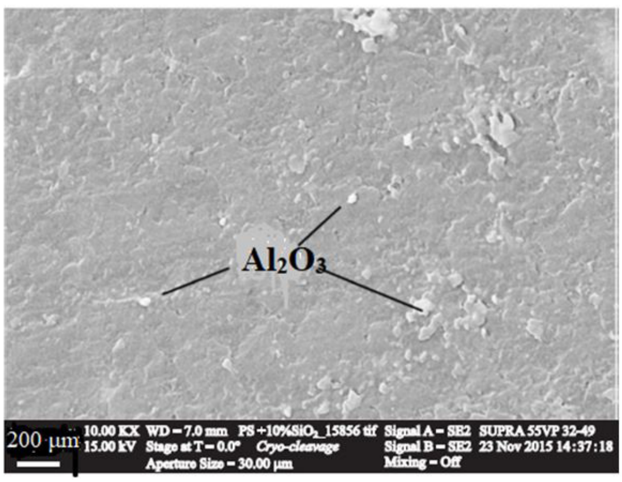

Fig. 2. Microphotograph of the surface of cryospalls of PCM PP + 10% Al_2O_3 samples.

a complex effect of climatic factors. The main normative and technical document governing testing of polymer materials in Russia is GOST 9.708-83, which defines testing at climatic stations for a given time. The main disadvantage of testing materials in natural conditions is their long duration, since the values of climatic factors can differ from year to year, therefore, the true values of changes in indicators that determine the service life of a material can be obtained only by averaging changes over a long-term period. In accordance with GOST 15150-69, the determination of the effective values of the temperature and humidity complex and the construction of a climatogram for a representative point of a geographic area is possible for a period of at least 10 years.

Accelerated climatic tests in laboratory conditions are used to shorten the test time and compare data on the resistance of various materials, including polymeric ones, to climatic factors. Modern testing equipment makes it possible to artificially create both conditions for the forced impact of certain climatic or operational factors, and exposure conditions that will be as close as possible to the real conditions of operation, storage and transportation [21–24].

In this work, accelerated aging in a solar radiation chamber was carried out under conditions close to natural ones, that is, along with UV irradiation, PCM samples based on PP and aluminum oxide were exposed to increased humidity.

To compare the degree of aging, IR spectroscopy and modified iodometric analysis were used, the results of which are presented in Table S2 (Supplementary material). It is shown that the content of peroxide groups in the samples of PP-Al_2O_3 composites is practically independent of the filler content and increases with an increase in the duration of accelerated aging.

In connection with the above, the deformation and strength properties of PCM based on PP and aluminum oxide have been determined, including after accelerated aging in a climatic chamber.

As follows from the data shown in Fig. 4, an increase in the content of aluminum oxide in the polypropylene matrix leads to an improvement in the strength characteristics (tensile strength) of the composite, which indicates the advisability of introducing this filler into PCM based on PP, which requires increased strength. Such a change in strength can be explained both by the interaction between individual macromolecules and the particle surface, and by the influence of supramolecular structural formations, the properties of which change under the action of the filler. In fact, it can be considered that the alumina particles are the nodes of the polymer network.

Accelerated aging of samples of polymer composites based on PP and aluminum oxide is accompanied by a decrease in their strength (Fig. 3, curves 2–5), which indicates the ongoing processes of destruction of PP macromolecules. Also, the occurrence of destruction is confirmed by a decrease in elongation at break (Fig. 4).

The results on the change in the strength properties of PCM PP-Al_2O_3 after accelerated aging may indicate structural transformations in the samples. As follows from the data given in Table S3 (Supplementary material), a slight increase in the degree of crystallinity is observed both with an increase in the Al_2O_3 content and with an increase in the duration of exposure in the climatic chamber, which is consistent with the literature data [15, 16].

Based on the studies carried out, the main criterion for determining the approximate service life of PCM based on PP and aluminum oxide under specified conditions is the strength at break.

The determination of the service life is carried out as follows. The dependence of the residual strength at rupture as a percentage of the initial value σ_0 on the exposure time in the climatic chamber is plotted. After mathematical processing of the obtained data using the least squares method, the obtained experimental results were generalized by a linear relationship in the coordinates "residual strength at break (in %) - logarithm of exposure time" and the slope A of the obtained straight line was determined.

The results of mathematical processing of Eq. (1) allow extrapolating the obtained data for a longer test period:

$$\sigma_{res} = \sigma_0 - A \cdot \lg \tau, \tag{1}$$

where σ_{res} is the residual strength at rupture (in %) after exposure in the tester; σ_0 — initial value of tensile strength (in %), equal to 100; A is a value numerically equal to the tangent of the slope of the dependence in the residual strength at rupture (in %) from the logarithm of the exposure time; τ is the exposure time in the tester.

The calculation of the approximate service life of PCM based on PP and aluminum oxide was made based on the

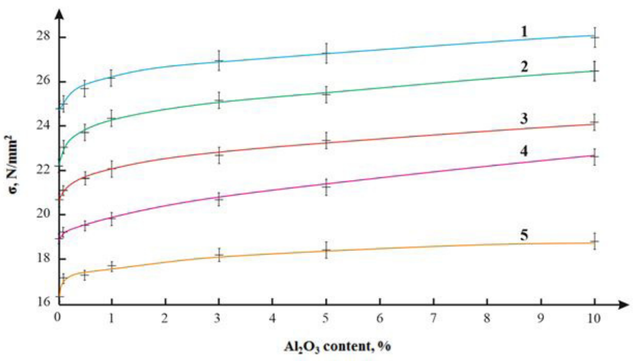

Fig. 3. (Color online) Dependence of the tensile strength of composites based on PP on the content of aluminum oxide: 1 — before accelerated aging, 2 — after 2 days of accelerated aging, 3 — after 3 days of accelerated aging, 4 — after 4 days of accelerated aging aging, 5 — after 6 days of accelerated aging.

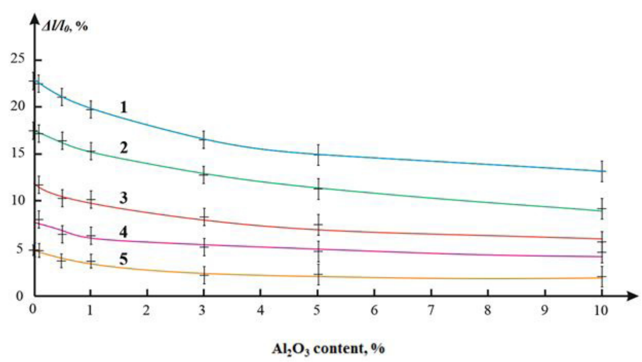

Fig. 4. (Color online) Dependence of the elongation at break of composites based on PP on the content of aluminum oxide; 1 — before accelerated aging. 2 — after 2 days of accelerated aging, 3 — after 3 days of accelerated aging, 4 — after 4 days of accelerated aging, 5 — after 6 days of accelerated aging.

Table 1. Results of calculating the approximate service life of PCM PP-aluminum oxide.

№	Indicator name	Value						
		PP	PCM with Al_2O_3 content 0.1 %	PCM with Al_2O_3 content 0.5 %	PCM with Al_2O_3 content 1 %	PCM with Al_2O_3 content 3 %	PCM with Al_2O_3 content 5 %	PCM with Al_2O_3 content 10 %
1	Tensile strength before exposure in a tester, MPa	25.4±1.3	25.9±1.3	26.1±1.3	26.7±1.2	26.9±1.3	27.9±1.3	28.1±1.3
2	Loss of strength corresponding to the influence of environmental factors within 1 year, %	57±3	56±3	56±3	51±3	56±3	57±3	53±3
3	The period during which the value of the residual strength reaches 40% of the original (service life), years	1.04±0.05	1.08±0.05	1.07±0.05	1.18±0.06	1.07±0.05	1.06±0.05	1.14±0.05

value of the loss of strength for 1 year with the subsequent determination of the period during which, at a given value of the loss of strength for 1 year, the residual strength will reach 40% of the original. The calculation results are shown in Table 1.

As follows from the data shown in Table 1, the tested samples of PP-aluminum oxide polymer composites are characterized by small predicted service life under the influence of the main environmental factors (UV radiation, humidity), which practically do not differ from the service life of materials from unfilled PP, therefore, or these PCMs must be operated in milder conditions, for example, as elements of products used indoors, or stabilizers must be included in the proposed compositions.

Thus, accelerated climatic aging can be used as a method for rapid assessment of changes in the operational and technological properties of polymeric composite materials based on polypropylene under the influence of environmental factors, including depending on the degree of filling.

4. Conclusions

1. It has been established that the values of the thermal conductivity coefficient of PP-aluminum oxide composites naturally increase with an increase in the proportion of filler from 0.10 to 0.21 W/(m·K), which indicates the expediency of creating PCM data.

2. It has been shown that an increase in the content of aluminum oxide in the polypropylene matrix leads to an improvement in the strength characteristics (tensile strength) of the composite. Similar patterns are observed for the dependence of the tensile strength on the content of aluminum oxide. Accelerated aging of samples of polymer composites based on is accompanied by a decrease in their strength, which indicates the ongoing processes of destruction of polypropylene macromolecules.

3. It was determined that the filling of PP with aluminum oxide practically does not affect the intensity of photooxidative transformations during accelerated aging under conditions close to natural ones.

4. When conducting accelerated climatic tests, it was found that samples of polymer composites based on polypropylene and aluminum oxide are characterized by small predicted approximate service life (13–15 months) under the influence of the main environmental factors (UV radiation, humidity), which practically do not differ from the terms use of materials made of unfilled polypropylene, therefore, either these materials should be used in milder conditions, for example, as elements of products used indoors, or stabilizers must be included in the proposed compositions.

Supplementary material. *The online version of this paper contains supplementary material available free of charge at the journal's Web site (lettersonmaterials.com).*

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