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THE INFLUENCE OF INTERNAL STRESSES ON THE AGING OF POLYMER COMPOSITE MATERIALS: A REVIEW

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The formation of internal stresses in polymer composite materials (PCMs) caused by different elastic moduli and thermal expansion coefficients of polymer resin and reinforcing fibers, as well as by swelling due to the moisture uptake is discussed. The influence of thermal cycles on the internal stresses and strength of the materials was studied in dry and wet atmospheres. It shown that thermal cycles cause a periodic jumps in the stresses at low-frequency mechanical loadings, during which the mechanical properties are degraded due to the formation of microscopic cracks in the polymer matrix. The relative changes in the strength, elastic modulus, glass-transition temperatures, moisture diffusion coefficient, and other PCM physical characteristics are proportional to the logarithm of the number of cycles and also depend on the form and size of specimens, amplitude, conditions, and length of thermal cycles. A prolonged action of external actions relaxes the internal stresses and reduces their influence on the aging of PCMs.

Introduction

When considering the causes for aging of polymer composite materials (PCMs) based on thermosetting binders mentioned in the foreign [1-7] and domestic [8-17] literature, the influence of temperature, humidity, solar radiation, oxygen, chemically active substances, erosion, precipitation on condition of matrices, reinforcing fillers, polymer-filler interfaces are discussed. Under the influence of these factors, destruction, hydrolysis, additional hardening, swelling, plasticization, structural relaxation and other physicochemical transformations occur in them, which accelerate or slow down the changes in their mechanical

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parameters [16]. In recent years, an in-depth analysis of significant factors affecting the properties of PCM has been carried out [5, 17-22]; however, when discussing the regularities observed, an insufficient attention is paid to such an important factor of influence as the action of internal stresses [23].

More than 20 years ago, it was shown [24] that internal stresses in various climatic conditions cause the appearance of microcracks in PCM binders or at the boundaries with fibers and a decrease in the strength of PCM. A typical example is work [25], where the mechanical properties of fiberglasses based on an epoxy matrix cured at 50°C, after a thermal cycling from –20°C to 20°C in dry air, holding in water at room temperature with cooling to –20°C, alternating UV exposure at 60°C and 100% RH are investigated. After 2000 h of cyclic tests under these conditions, the tensile strength of a fiberglass filled with chopped E-glass fibers decreased by 7, 32, and 42%, respectively, due to the formation of cracks and voids with dimensions of 50-100 μm. This experiment shows, that even simple thermal cycling in dry air under the influence of internal stresses, causes a decrease in the strength of fiberglass, which significantly increases for water-saturated samples.

In [26], the level of internal stresses in a unidirectional fiberglass based on a polyester binder cooled to –60°C reached 62 MPa. This value is commensurable with the ultimate tensile [12] or compression strength [27] of the material and should be taken into account when analyzing the reasons for the formation of microcracks during daily and seasonal temperature fluctuations in open climatic conditions [23].

The elements of aviation and space technique made of PCMs can undergo repeated thermal cyclings under operating conditions with temperature drops up to 250°C [11–13].

In this regard, the following tasks were set in this work:

• to clear up reasons for the occurrence of internal stresses in PCMs;

• to reveal the levels of changes in the mechanical properties of PCMs under the action of internal stresses;

• to determine the factors causing the increase or decrease in internal stresses;

• to show that internal stresses are a significant factor in the aging of PCMs in aggressive environments and in open climatic conditions.

Causes for internal stresses in PCMs

During curing, thermosetting matrices provide a good adhesion interaction with fibrous reinforcing fillers of PCMs and create a monolithic three-phase system (filler, matrix, and transition layer) with high mechanical characteristics. The PCMs used in the mechanical engineering [28] are often cured at elevated temperatures. After cooling, internal stresses arise in them due to differences in the coefficients α of linear thermal expansion (CLTE) of composite components, which can be determined on the basis of linear mechanics of PCM [29, 30].

When considering a system of polymer matrix m and fibrous filler f adhesively bonded to each other and comparing their state at the curing temperature T_0 and operating temperature T, the mechanical stresses in it can be determined [30] from the balance of forces

$$\sigma_f S_f + \sigma_m S_m = 0 \tag{1}$$

and the equality of strains determined by the elasticity law

$$\frac{\sigma_f}{E_f} - \frac{\sigma_m}{E_m} = (\alpha_f - \alpha_m)\Delta T, \tag{2}$$

where σ and E are the tensile strength and elastic modulus, respectively; S is area; ΔT is the temperature range. A joint solution of Eqs. (1) and (2) for the case of a unidirectional PCM gives [29]

$$\sigma_{mL}^{T} = \frac{V_f E_f E_m}{V_f E_f + V_m E_m}[(\alpha_f - \alpha_m)(T - T_0)], \tag{3}$$

$$\sigma_{fL}^{T} = -\frac{V_m}{V_f}\sigma_{mL}, \tag{4}$$

where V is the volume of constituents and σ_L^T are temperature stresses along the fibers. For unidirectional PCMs, compressive stresses dominate in the fibers and tensile stresses dominate in the matrix. According to the estimates given in [31], for CFRPs with a curing temperature of 177°C, the residual tensile stress in the 3501-6 epoxy matrix at room temperature reach 29 MPa. For approximate estimates, taking into account the ratio of the elastic moduli of reinforcing fibers and polymer matrices and their volume content in typical PCMs, the stresses along fibers can be determined by the simplified relation

$$\sigma_{mL} = -E_m\alpha_m\Delta T, \tag{5}$$

giving 40-60 MPa for composites cured at 190-220°C. Such stresses in polymer matrices exceed the interlayer shear strength, equal to 20–40 MPa [12, 27]. For example, in [32], a micromechanical modeling of internal stresses causing cracking of epoxy matrices in a CFRP at temperatures from 25 to –50°C was carried out. Variants were considered in which the distance between fibers in the unit cell of the model varied from 0.05 to 5 fiber radii. Under these conditions, the stresses along the fibers reached 40-60 MPa. Similar results substantiating the formation of cracks, shrinkage, and interlayer fracture were obtained in [26, 33–37].

PCMs are sensitive to moisture [11-17]. Along with plasticization, additional curing, and hydrolysis [38] of polymer matrices, the moisture saturation of PCMs is accompanied by their swelling. It is proved that, at low concentrations of absorbed moisture, until a certain threshold value w_0 (usually $w_0 \le 0.1\%$) is reached, the sample size does not change, since water molecules fill the free volume of the polymer matrix [29, 39–41]. With a further growth in moisture saturation, the relative change in the linear dimensions of the polymer matrix is proportional to the concentration of absorbed water:

$$\left(\frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}}\right)_i = \varepsilon_i = \beta_i \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} = \beta_i w, \tag{6}$$

where l is the linear size of the polymer matrix sample; m is mass of the sample; $i = L$ along the fibers in the layer plane D across the fibers in the plane of the layer, and H perpendicularly to the layer plane; β is the moisture swelling coefficient, eqal to $3.2\cdot10^{-3}$ /% for the AS/3502 carbon-fiber-reinforced plastic [41]. In the three-phase PCM model (fiber-matrix-interface) [42], a moisture coefficient of swelling of epoxy matrices equal to $8\cdot10^{-3}$ /% of sorbed water was used.

When moisture is sorbed, polymer matrices swell in PCMs, creating the internal stresses

$$\sigma_{mL}^{w} = \frac{V_f E_f E_m}{V_f E_f + V_m E_m}(\beta_f w_f - \beta_m w_m), \tag{7}$$

$$\sigma_{fL}^{W} = -\frac{V_m}{V_f}\sigma_{mL}, \tag{8}$$

where σ_L^W are the temperature stresses along fibers due to swelling.

Thus, it follows from relations (3), (4), (7), and (8) that the levels of internal stresses in PCMs depend on temperature, the content of sorbed moisture, elastic modulus, CTE, the volumetric content of components, and reinforcement structure. To determine the internal stresses, methods based on measuring the curvature of plates, the mechanical indicators of PCM when removing layers, drilling holes, making annular cuts, and microindentation. Nondestructive methods, such as X-ray and neutron diffraction, Raman spectroscopy, photoelasticity, etc. [43, 44], are also used.

The main result of the action of internal stresses in combination with environmental factors is the formation of additional microfaults in the form of transverse cracks in PCM layers and destruction of the interface of polymer-reinforcing filler [19]. Microcracks and delamination worsen the mechanical properties of PCMs, which has been proven by numerous studies [19, 23-26].

To achieve the goal of this work, it is necessary to clear up how the internal stresses in a PCM change under short-term and long-term continuous and cyclic actions of temperature, humidity, solar radiation, oxygen, and other aggressive environmental factors.

Effects of temperature and thermocycles

Under the action of high temperatures, the thermal aging of PCMs occurs, at which the mass of composite samples decreases, their shrinkage occurs, the surface is damaged by with the formation of microcracks, and the mechanical parameters decrease [6, 7, 11-13, 19]. These characteristic manifestations of thermal destruction become more noticeable if the materials are held in an oxygen (air) environment under an ultraviolet (UV) irradiation [45]. For example, according to the data of [46], at a temperature of 50°C and a UV irradiation for 180 days in vacuum, a CFRP losed its mass 2-3 times less than in air. Under the same conditions, the mass loss of fiberglass differred 3-6 times. If the PCM binder is not completely cured during manufacture, then elevated temperatures promote an additional curing, which is characterized by an increase in the glass-transition temperature and mechanical parameters [7, 13, 38].

Of greatest interest is the effect of variable temperatures on the properties of PCMs. Therefore, in practice, their cyclic tests are widespread, whose results have been studied in sufficient detail. Let us consider a few examples. In [47], the thermal cycling of carbon plastics was carried out. The 8-h cycle included heating to 150°C and cooling to –50°C. After 500 cycles, the aging was carried out again at a stationary temperature of 150°C for 30,000 h. It was found that thermal oxidation prevailed in the surface layers; therefore, the change in properties of the plastics depended on the thickness of plates. The compressive strength σ_c of 5-mm-thick specimens (20 layers) decreased 2.4 times faster than that of thicker specimens (26 mm, 100 layers). On thermal cycling of an epoxy basalt plastic from –40 to 120°C [48] during the initial 20 cycles, due to the additional curing of binder, its glass-transition temperature increased from 77 to 86°C, as a result of which the tensile σ_t and bending σ_b strengths increased by 10 and 15%, respectively, and the ultimate interlayer compression strength τ increased by 69%. Upon reaching 120 cycles, due to the differences in the CTEs of composite components and the action of internal stresses, the matrix peeled off from the fiber surface, and the mechanical parameters decreased. As a result of the action of thermal cycles, the density of microcracks increased [49] and the CTEC of polymer matrices decreased [50]. In similar studies [51–55], an increase in the density of microcracks with an increase in thgrowing amplitude and number of thermal cycles was confirmed, and the damage was found to be more significant in oxidizing environments [51].

Thermocycling of PCMs containing moisture

The polymer matrices of PCMs are moderately hydrophilic systems and are able to absorb up to 3-5% of water [1, 2, 8, 14, 15, 17, 38]. Therefore, to clarify the effect of internal stresses on the aging of PCMs, it is important to analyze the thermal cycling of moisture-saturated PCMs. A comparison of the research results obtained in [23, 56, 57] shows that, if the thermal cycling is carried out in the range of positive and negative temperatures, wet PCMs deteriorate their mechanical characteristics with a higher probability than dry ones. This process is facilitated by the internal stresses caused by both swelling (7), (8) and transition to the glassy state of water in the free volume of polymer matrices by the mechanism considered in [58].

A thermal cycling causes periodic jumps in internal stresses, which is a kind of low-frequency mechanical cyclic loading characterized by the empirical relationship [59, 60]

$$S = S_0(1 - k \lg N), \tag{9}$$

showing that the $S-N$ relation is linear in the coordinates of load–the logarithm of the number of cycles to failure. In formula (9), S_0 is the load causing destruction of the sample in the initial state; S is the load during N loading cycles; k is the coefficient that determines the inclination angle of the straight line.

Relation (9) can be used to identify the regularities of thermocyclic tests of PCMs if the strength indicators R ($\sigma_b, \sigma_c, \sigma_t$, and others) are considered as an indicator of S. For example, in [61], samples of pultruded glass-reinforced plastics (FRPs) based on vinyester and isophthalic polyester were kept in water and then subjected to 3-h cycles according to ASTM C-666 (cooling to –17.8°C and heating to 4°C). After 300 cycles, the stress σ_b decreased by 32% in the DP based on the isophthalic polyester and by 22% in the vinyl ester fiberglass. The relative change in the ultimate strength $\Delta R / R_0$ in

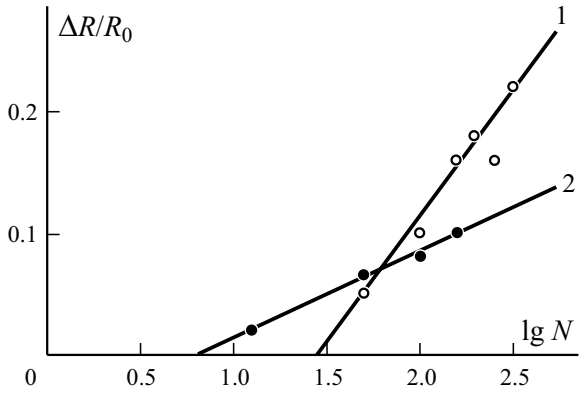

Fig. 1. Influence of the number N of thermal cycles on the relative change in the ultimate bending (1) and tensile (2) strength according to the data of [61] and [24].

bending $(\sigma_b\sigma_{b0})/\sigma_{b0}$ of the vinyl ester SP increased linearly with logarithm of the number of cycles N (curve 1 in Fig. 1). Similarly, for an epoxy DP with the [90/0] reinforcement scheme, at a thermal cycling from –60 to 60°C [24], the relative change $(\sigma_t\sigma_{t0})/\sigma_{t0}$ in the tensile strength vs. logarithm of the number of cycles was also linear (curve 2 in Fig. 1).

Usually, when conducting thermal cycling tests, the mechanical parameters of PCM are measured no more than 4-5 times for different numbers N of thermal cycles [24, 25, 48-55]. Despite the complexity and, in some cases, the conventionality of approximation of the results obtained using relation (9) with such a number of measurements, significant changes in strength indicators were found not after the first thermal cycle, but after N_0 cycles (Table 1). For the SP vinyl ester [61], $N_0 = 28$ cycles and for the SP epoxy $N_0 = 32$ cycles [24]. Depending on the material and thermal cycling conditions, units, tens and even hundreds of cycles were required, during which damage accumulated under the action of internal stresses without a significant increase in the relative strength index $\Delta R / R_0$ (see Table 1). This feature should be taken into account when conducting thermocycling tests of PCMs.

The second general rule is an increase in the coefficient k in relation (9) during thermal cycling of moisture-saturated PCMs. For example, in [25, 62], PCMs were cycled in dry air and immersed in water, and the coefficient k in the second case was found to be 3-6 greater (see Table 1).

When analyzing the results obtained, a third regularity was also revealed: the relative change in strength and the parameters of relation (9) depended on the shape and size of thermocycled PCMs as well as on the measured indicator R. According to [66], the most significant decreases in the tensile strength (–0.29) after 2100 cycles were found for unidirectional CFRP specimens cut across the reinforcement, while in the reinforcement direction, a similar decrease was –0.08. In this case, the parameters k of these samples differed by a factor of 11 and N_0 by a factor of 5 (see Table 1). In another example [55] (Table 2), polyester-based SP pultruded profiles were tested for thermal cycling with daily cycles from –20 to 20°C. After 42, 63, 83, and 125 cycles, the mechanical properties of the profiles in bending, compression and tension were measured. Depending on the shape of a profile, the application direction of the load, and the measured index, the relative bending, compression, and tension strength decreased from –0.01 to –0.26, but the parameters k and N_0 differed 2-4 times.

Relaxation of internal stresses during thermocycling of PCMs

An important regularity of internal stresses is their relaxation with increasing duration of external actions. According to [68], the internal stresses measured by the curvature of CFRP plates with reinforcement schemes $[90_m/0_n]$ decreased by 25% during 208 days of exposure to room temperature. This effect was caused by the decreasing elastic modulus of the polymer matrix in the direction perpendicular to fibers and was determined by formula (5). The relaxation of internal stresses

TABLE 1. Parameters Of Relation (9) in Approximating the Results of Changing Strength of PCM vs. the Number of Thermal Cycles

Material		Test conditions	Thermocycles		Results			Source
Composite	Matrix		Quantity	Temperature range. °C	Indicator*	Coefficient k in relation (9)	Number N_0 of cycles	
1	2	3	4	5	6	7	8	9
SP mats	Vinylether	Preexposure in water at room temperature	300	–17.8-4	σ_b	0.31	28	[61]
	Polyester					0.22	32	
SP $[90_2/0]_6$	Epoxy	Dry air	150	–60-60	σ_t	0.11	10	[24]
UP	Vinylether	Dry air	100	–23-20	σ_b	0.089	25	[62]
		Exposure in water for 1272 h				0.24	16	
SP (E-glass) unidirectional	Epoxy	Dry air	83	–20-20	σ_t	0.016	25	[25]
		Immersion in water when heated				0.093	5	
SP (E-glass) fabric		Dry air				0.14	25	
		Immersion in water when heated				0.32	13	
SP (E-glass) mats		Dry air				0.15	28	
		Immersion in water when heated				0.41	13	
UP $[0]_3$	Vinylether	Water content 1.3%. immersion in water at heating	450	–18-20	σ_t	0.38	20	[63]
UE fabric Torayca	Epoxy	Water content 0.3%. immersion in water at heating	1000	–196-20	σ_b	0.046	3	[64]
SP	Epoxy	Immersion in water when heated	300	–17-8	σ_t	0.13	16	[65]
		Immersion in water when heated under 30% load				0.18	16	
UP fabric	Epoxy	Dry air	200	–196-140	ILSS	0.12	25	[54]
					ILSS	0.13	250	
UE unidirectional	Epoxy	Dry air	2000	–175-120	σ_t	0.15	200	[53]
					σ_c	0.16	400	
UP $[0]_4$	Epoxy	Predrying in vacuum at 50°C. dry air during heating	2100	–55 -70	σ_t	0.045	63	[66]
UP $[90]_{16}$					σ_t	0.50	320	
UP $[0]_8$					σ_c	0.12	126	
UP $[90]_8$					σ_c	0.16	120	
UP $[0]_{12}$					σ_b	0.19	440	
UP $[\pm 45]_8$					T	0.076	60	
UP $[0]_{32}$					ILSS	0.10	250	
UP unidirectional	Epoxyphenol	Dry samples	960	–25 -25	σ_c	0.12	170	[67]
		Water content 1.45%				0.14	30	

*Ultimate tensile σ_t . compressive σ_c . bending σ_b . shear τ . interlamellar shear ILSS. measured at room temperature. UP - carbon fiber. SP - fiberglass.

TABLE 2. Influence of Measured Strength Parameters and the Load Application Direction of a Pultruded SP [55] on the Parameters of Relation (9) After 125 Thermal cycles

Indicator	Profile shape	Direction of load application	$\Delta R/R_0$	Parameters of relation (9)	
				k	N_0
σ_b	I-beam 38.3×15×4 mm	Along the main axis	–0.17	0.21	20
		Across the main axis	–0.01	0.10	25
	I-beam 25.5×15×4 mm	Along the main axis	–0.17	0.21	20
		Across the main axis	–0.08	0.14	32
	Channel 50×30×5 mm	Along the main axis	–0.16	0.36	40
		Across the main axis	–0.09	0.20	40
	Channel 50×30×3 mm	Along the main axis	–0.19	0.32	32
		Across the main axis	–0.14	0.27	35
σ_c	Pipe 30×30×3 mm	Along the axis of the square pipe	–0.13	0.23	39
	Pipe 25×25×3 mm		–0.26	0.46	39
σ_t	Thickness 4 mm	Along the direction of reinforcement	–0.09	0.10	35
	Thickness 2.5 mm		–0.14	0.30	34

TABLE 3. Parameters of Relation (9) in Approximating the Results of Changing Physical Parameters of PCM vs. the Number of Thermal Cycles

Material		Test conditions	Thermocycles		Results			Source
Composite	Matrix		Quantity	Temperature range. °C	Index*	Coefficient k in equation (9)	Number N_0 of cycles	
UP $[0_2/90_2]_s$	Epoxy	Thermocycles in air	500	–157-121	ρ	–12	35	[49]
UP $[90_2/0_2]_s$						–10	25	
UP $[0_3/90_3]_s$	Epoxy	Thermocycles in oxygen	500	–50-80	ρ	–8.9	50	[51]
		Thermocycles in air				–6.7	40	
UP $[0]_8$	Polyimide	Simulation of flight cycle	1 500	–54-87 + 163	ρ	–29	200	[73]
UP $[0/90]_9$	Epoxy	Thermocycles in vacuum	200	–159-158	E'	0.45	10	[74]
					D	–1.0	11	
UP 1 $[0/90]_9$	Epoxy	Thermocycles in space in near-earth orbit	24 000	–83-127	T_g	–36	630	[72]
					G'	0.17	550	

*ρ — density of cracks. cm^{-1}; E' — dynamic Young's modulus. GPa; G' — dynamic shear modulus. GPa; D is the coefficient of diffusion of moisture. cm^2/s; T_g is the glass-transition temperature of the polymer matrix.°C.

is facilitated by moisture, which, in addition to swelling, plasticizes polymer matrices and decreases their elastic moduli [11-13, 21, 23, 38, 40, 69].

It was determined experimentally that, during the thermal cycling of PCMs, microcracks are formed, which reduce the elastic moduli of polymer matrices and their CTE [49-51, 54, 66, 70-72]. Therefore, in accordance with formulas (3)-(5), thermal cycles also promote the relaxation of internal stresses.

Relation (9) makes it possible to evaluate the effect of thermal cycles not only on the strength, but also on other parameters of PCM. This was confirmed by an analysis of the results of some works (see, for example, [49, 51, 72-74]). Table 3 shows the parameters k and N_0 determined for the density of microcracks ρ, dynamic Young's modulus E', dynamic shear modulus G', moisture diffusion coefficient D, glass-transition temperature T_g of the polymer matrix as

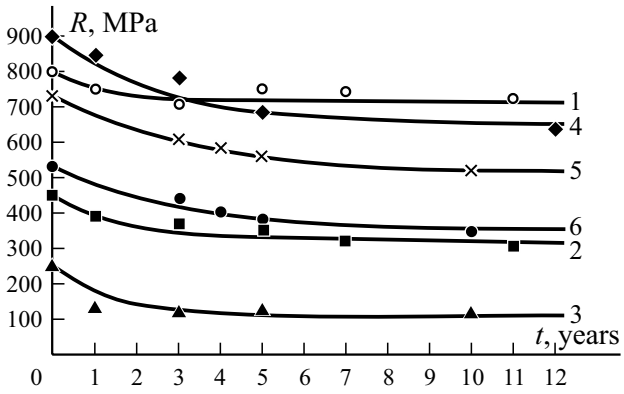

Fig. 2. Strength indicators R of PCM vs. exposure time t in the open climatic conditions of Batumi (1, 2, 3), Sochi (4), and Moscow (5, 6): carbon fiber reinforced plastic KMU-1, indicator σ_t measured at 20 (1) and 200°C (2) [76]; SK-9FA fiberglass, indicator σ_b measured at 20°C (3) [77]; fiberglass ST-69N, indicator σ_b measured at 20°C (4) [77]; ST-2227M fiberglass, the indicator σ_b measured at 20 (5) and 150°C (6) [78].

functions of the number of cycles in air [49, 51], oxygen [51], vacuum [74] in space in a near-earth orbit [72] and in the flight mode of aircraft [73].

The examples considered illustrate the noticeable effect of internal stresses on changes in the mechanical parameters of PCMs at the initial stages of aging (thermal [24, 25, 53-55, 66, 74], thermal and humid [25, 61-65, 67], climatic [8-17], [23, 27], and in open space [72]), when the threshold number N_0 of thermal cycles was exceeded. However, due to relaxation of internal stresses at later stages, a certain limiting state of physicochemical transformations and microfaults is reached [49], and then the change in the indices of material characteristics is significantly reduced. According to [72], upon exposure of a KMU-4L CFRP to open space during the initial 102 days, the glass-transition temperature T_g of the ENFB matrix increased by 14°C, but over a period from 1 to 4 years — only by 4°C. At a continued exposure for up to 12 years, this value of T_g was retained with an accuracy of ±1°C [75].

A similar tendency towards the stabilization of mechanical parameters is observed studying the long-term climatic aging of PCM in [76-78] (Fig. 2). The data in the figure indicate that, when the materials were exposed to different climatic zones from 5 to 10-12 years, the indicators σ_t and σ_b changed less than at the initial stage.

The indicators R, as functions of exposure time (see Fig. 2), can be approximated by the relation [9]

$$R = \eta(1 - e^{-\lambda t}) - \beta \ln(1 + \chi t) + R_\infty, \tag{10}$$

where η and β are material parameters; λ and χ are characteristics of the material and environmental, respectively.

With growing duration of exposure, i.e., at $t \to \infty$, the exponent R in Eq. (10) tends to its limit value R_∞. A possible reason for this is the relaxation of internal stresses under the action of daily and seasonal cyclings of temperature, humidity, solar radiation, and other factors in open climatic conditions.

Conclusions

Results of the analysis performed allow us to draw the following conclusions.

1. Owing to differences in the elastic moduli and thermal expansion coefficients of polymer matrices and reinforcing fillers, as well as due to their swelling during water sorption, internal stresses are formed in PCMs.

2. Thermal cyclings create periodic jumps in the internal stresses, which cause aging of PCMs due to the formation of microcracks in the polymer matrix.

3. In the process of thermal cycling, the relaxation of internal stresses occurs, as a result of which the aging of PCMs slows down.

4. When modeling the aging of PCMs, it is advisable to determine the parameters of Eq. (10) by the methods of thermal cycling tests.

5. To increase the reliability of predicting the strength of PCMs for long periods of operation, it is necessary to know the initial level of internal stresses and the nature of their relaxation in order to use this information to find the parameters in Eq. (10).

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