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Effects of cold climates on polymer composite material properties

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Abstract

The effects of temperature and moisture on the properties of polymer composite materials in cold climates have been considered. A review and analysis of changes in the mechanical properties of polymer composite materials under the influence of temperature and moisture are carried out with reference to foreign and Russian scientific literature. Examples are revealed that show that the deterioration of the mechanical parameters of polymeric composition materials after exposure at open stands in a moderately cold, cold, and extremely cold climate is comparable or even more significant than after staying in warm and humid regions. The mechanism of aging of polymeric composition materials in cold climates has been substantiated and the conditions under which their mechanical properties deteriorate more significantly than when exposed in dry and humid tropics and subtropics have been substantiated. Composites develop internal stresses, caused by unequal thermal expansion of reinforcement fibers and polymer matrices. The internal stresses cause an occurrence of micro-cracks, their coalescence, and the formation of macro-damages in the bulk of a binder or at the interface with fibers.

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1. Introduction

PCM based on glass, carbon, basalt, organic, and other fibers, used in various branches of mechanical engineering, have a high strength in works by Kablov and Startsev (2020, 2012), which decreases over time due to

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ageing (irreversible physical and chemical transformations in binders, fillers, and at the polymer-fiber interface) performed by Pochiraju et al. (2012), White et al. (2017) and Startsev (2018). In design of elements of equipment, information on durability of used PCM under the environmental impacts is always required, aggressiveness of which is defined by a combination of temperature, humidity, solar radiation, chemically active particles, etc. From the early days of PCM application in various branches of technology, prediction of their strength during ageing has been the focus of interest of many researchers, and remains an urgent scientific problem today.

Temperature, humidity, precipitation, oxygen, ozone, occurrence of chemically active compounds, and UV radiation are the environmental factors causing PCM ageing by Kablov (2019). Daily and seasonal fluctuations of temperature, humidity, and solar radiation intensity have been determined in typical climatic regions (hot dry deserts, humid tropics and subtropics, regions with moderate, low, and extremely low temperatures, etc.). According to the research by Dexter (1987), Hoffman and Bielawski (1990) and Baker (1994), a drop in the PCM strength rates by 20-30% and even by 40% was revealed, following prolonged exposure of PCM to various climatic effects. The effect of ageing agreed with an exposure site, PCM composition, and an indicator under measurement. As a rule, by Startsev (2018) and Kablov and Startsev (2018), the shear strength τ and the flexural strength σ_b are more sensitive to climatic impacts than the tensile strength σ_t . CFRP are more resistant to aggressive climatic impacts than organoplastics. Tests of PCM in New Zealand and Brazil showed that samples absorbed the largest amount of moisture. In Hawaii, UV radiation was the most affected. Mechanical properties of PCM tested in Frankfurt changed to a lesser extent than those of PCM exposed in the tropics. Admittedly, atmospheric aggressiveness in temperate climates was lower than that in humid tropics.

Nomenclature

k_R	relative retention rate
R_t	strength and modulus
R_0	the initial values of the corresponding rates
σ_t, E_t	tensile strength and modulus
σ_c, E_c	compressive strength and modulus
σ_b, E_b	flexural strength and modulus
τ, G	shear modulus of the interlayer, measured after different exposure terms
T	air temperature
T_0	temperature with zero stresses
φ	relative air humidity
Q	total solar radiation flux density
q	UV flux density of ultraviolet components of solar radiation,
H	rainfall
WS	wind speed
W	wind direction
β_i	material properties (composition and reinforcement pattern)
t	duration of climatic impacts
CFRP	carbon fibre reinforced polymers
PCM	polymeric composition materials
UV	solar ultraviolet
OP	organoplastics
V	Virginia (Hampton)
A	Alaska (Ft. Greely)
B	Batumi
S	Sochi
G	Gelendzhik
M	Moscow
Ya	Yakutsk

Development of the Arctic attracts attention of researchers to the problem of PCM ageing in cold climates such as Startsev (2018), Kablov et al. (2018), Kablov and Startsev (2018). There are examples works by Baker (1994), Kablov (2017), Nikolaev et al. (2016) and Startsev (2018) showing deterioration of mechanical parameters of PCM after exposure to effects of moderately cold, cold, and extremely cold climates as equal to or even more significant than that following PCM exposure in warm and humid regions.

The objective of the current study is to substantiate mechanisms of PCM ageing in cold climates and to consider conditions under which PCM mechanical parameters deteriorate more significantly, as compared with those of PCM exposed to dry and humid tropics and subtropics.

2. Examples of abnormally active effects of cold climates on PCM properties

The highest relative retention rates were found after exposure to effects of cold climates in the testing of PCM samples for exposure to effects of various climatic conditions. A relative retention rate is defined as

$$k_R = R_t / R_0. \quad (1)$$

For example, the values σ_t and τ were compared for three pultruded vinyl-ester CFRP after 11- year exposure to effects of subarctic, temperate, subtropical, and mountainous climates by Nishizaki et al. (2012). The parameter τ decreased by 14% in temperate climates and by 32% in subtropical climates. Similarly, σ_t decreased, respectively, by 15 and 28%. According to the data by Nikolaev et al. (2016), k_R of the fiberglass VPS-48/7781 after one- year exposure in Sochi (warm and humid climate) was 3–10% lower than that after testing in Yakutsk (extremely cold climate). A comparison of alterations of mechanical properties of the fiberglass VPS-47/7781 based on the melt cyanogen-ester binder VST-1208 following one-three-year exposure at 9 stations in various climatic zones performed by Andreeva (2019) showed the greatest decrease of σ_b and τ in the samples exposed to humid tropical climate. Exposure of fiberglass samples to effects of temperate and cold climates resulted in an insignificant decrease of the indicators.

However, in some cases, this pattern was violated. Table 1 gives examples of abnormally strong effects of cold climates, showing that post-exposure rates of R_t in Yakutsk and Aldan decreased more significantly (by 10-15% and more), as compared with those after the similar exposure in warmer regions. The influence of the place and duration of tests on the change of mechanical parameters of the PCM is shown according to the data presented by Baker (1994) - №1-4, Kablov (2015) - №5-12, Nikolaev et al. (2016) - №13, Startsev et al. (2019) - №14 (see Table 1).

Table 1. Examples of an abnormal decrease of mechanical parameters of exposed PCM.

№	PCM	Test site	Ageing time, yrs.	Index, MPa		
				Symbols, R in (1)	Initial value in (1)	R_t / k_R in (1) after ageing
1	Painted OFRP Kevlar-49/F-185	V	1	σ_c	139	136/0.97
		A	1	σ_c	139	125/0.90
		V	1	τ	41,5	42.3/1.02
		A	1	τ	41,5	38.4/0.92
2	Painted OFRP Kevlar-49/LRF-277	V	1	σ_c	154	137/0.89
		A	1	σ_c	154	130/0.84
		V	1	τ	26.7	25.9/0.97
		A	1	τ	26.7	23.4/0.88
3	OP Kevlar-49/CE-306	V	1	σ_c	126	132/1.05
		A	1	σ_c	126	119/0.94
		V	1	τ	36.4	37.1/1.02
		A	1	τ	36.4	33.8/0.93

Table 1 (continued). Examples of an abnormal decrease of mechanical parameters of exposed PCM.

№	PCM	Test site	Ageing time, yrs.	Index, MPa		
				Symbols, R in (1)	Initial value in (1)	R_i/k_R in (1) after ageing
4	CFRP T-300/E-788	V	1	σ_c	872	883/1.01
		A	1	σ_c	872	837/0.96
		V	1	τ	77.4	78.7/1.02
		A	1	τ	77.4	71.7/0.93
5	CFRP KMU-3	B	5	σ_c	410	410 / 1.0
		Ya	5	σ_c	410	365 / 0.89
6	CFRP KMU-4e	S	1	σ_t	1300	1200 / 0.92
		Ya	1	σ_t	1300	1060 / 0.82
7	CFRP VKU-39	G	1	σ_b	1000	930 / 0.93
		Ya	1	σ_b	1000	850 / 0.85
8	Fiberglass VPS-31	S	5	σ_b	1600	1700 / 1.06
		Ya	5	σ_b	1600	1470 / 0.92
9	Fiberglass VPS-31K60	S	1	σ_b	1400	1294 / 0.92
		Ya	1	σ_b	1400	1170 / 0.4
10	OP Organite 16T-Rus	S	5	σ_c	250	200 / 0.80
		Ya	5	σ_c	250	190 / 0.76
		S	5	$\sigma_c(150^\circ\text{C})$	170	120 / 0.71
		Ya	5	$\sigma_c(150^\circ\text{C})$	170	110 / 0.65
11	Hybrid composite GKM-1(m)	S	5	σ_b	800	720 / 0.90
		Ya	5	σ_b	800	710 / 0.88
12	CFRP KMKU-2m.120.	G	3	$\sigma_b(120^\circ\text{C})$	610	480 / 0.79
		S	3	$\sigma_b(120^\circ\text{C})$	610	455 / 0.75
		M	3	$\sigma_b(120^\circ\text{C})$	610	275 / 0.45
		Ya	3	$\sigma_b(120^\circ\text{C})$	610	255 / 0.42
		S	3	σ_c	560	500 / 0.89
		Ya	3	σ_c	560	400 / 0.71
13	Fiberglass VKU-39	G	1	σ_b	1000	930/0.93
		Ya	1	σ_b	1000	850/0.85
14	Basalt Plastic ED-22	G	2,5	σ_b	1210	1090/0.90
		Ya	2,5	σ_b	1210	780/0.65

Generally, alterations of k_R should be extrapolated by the function in agreement with environmental factors and material properties:

$$k_R = f[T(t), \varphi(t), Q(t), q(t), H(t), WS(t), W(t), \beta_i(t)]. \quad (2)$$

Effects of each factor indicated in the function $f(2)$ depend both on the type of a climate by Urzhumtsev (1986), and on individual characteristics of PCM by Kablov (2018). They contribute to the overall balance of physical and chemical transformations (plasticization, swelling, hydrolysis, post-hardening of polymer matrices activated by moisture, destruction under effects of ultraviolet radiation and oxygen, structural relaxation of the filler, binder, and their interfaces, formation of pores, microcracks on the surface and in the volume of samples, etc.) that determine k_R .

The role of environmental factors in function (2) for cold climates should be considered to substantiate abnormal alterations of the indicators in Table. 1.

3. Effects of low temperature cycling on PCM properties

The major reason for deterioration of PCM mechanical properties in cold climates is the effect of low temperatures. Thus, during the winter months in Yakutsk, the temperature drops to $-40\text{ }^{\circ}\text{C}$ and even reaches $-64\text{ }^{\circ}\text{C}$, with an average annual temperature of $-10.6\text{ }^{\circ}\text{C}$ that pointed by Nikolaev et al. (2016). Internal stresses occur at low temperatures, and their values could be estimated by differences in the coefficients of linear thermal expansion of polymer matrices and reinforcing fibers as shown by Lord and Dutta (1988), Dutta (1988, 1996, 2001):

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

where V is a volume, α is a the coefficient of linear thermal expansion, σ_L is a stresses along fibers, the indices m and f refer, correspondingly, to the polymer matrix and fiber. The simplified ratio could be applied for approximate estimates, considering the elastic moduli ratio of reinforcing fibers and polymer matrices, their volumetric content in typical PCM, and the value of stresses along fibers $\sigma_{mL} = -E_m \alpha_m \Delta T$, giving 40-60 MPa for the composites, hardened at $190\text{ }^{\circ}\text{C}$ as found by Lord and Dutta (1988). Such stresses developing in polymer matrices exceed the interlayer shear strength equal to 20-40MPa as shown by Startsev et al. (1999).

Seasonal and daily climatic thermal cycling alters the amplitude of internal stresses and accelerates an occurrence of micro-cracks, their fusion and macro-damage formation in the binder volume or the binder-fiber interface. Modelling tests showed that for F with the reinforcement pattern of $[0. 90]$, following 150 thermal cycles from -60 to $+60\text{ }^{\circ}\text{C}$, σ_t decreased by 11%. After 10 thermal cycles, a decrease of the tensile strength by 6% was identified in CFRP upon extension across the direction of reinforcement. An increase of the acoustic emission (notably, rapid intensification below $-40\text{ }^{\circ}\text{C}$) was identified at lower temperatures by Dutta (1988).

Effects of thermal cycling were studied in unidirectional FG, CFRP and BP based on the epoxy matrix Tyfo S by Li et al. (2012). Control over internal stresses along and across the direction of reinforcement was performed applying fiber sensors based on the Bragg grating. The samples were subject to 12-hour cycling at -27 and $33\text{ }^{\circ}\text{C}$. Stresses along the fiber direction in CFRP made 4 MPa (extension) at $30\text{ }^{\circ}\text{C}$ and 10 MPa (compression) at -27°C . Following 90 thermal cycles, the tensile strength of CFRP decreased by 16%, while the Young modulus dropped by 18%. Unidirectional rods made of glass and carbon fiber based on the vinyl-ester matrix were subject to effects of 250 thermal cycles (cooling to $-29\text{ }^{\circ}\text{C}$ and heating to $20\text{ }^{\circ}\text{C}$ in 12 hours) by Cusson and Xi (2002). The tensile strength decreased by 8%.

4. Conclusions

A review of modern research results on climatic aging of polymer composite materials shows that the processes of swelling, hydrolysis, additional curing and destruction of polymer matrices under the influence of temperature, humidity, and solar radiation when these materials are exposed by a cold climate are weaker than when they are exposed by a tropics and subtropics climate. The main factor affecting the deterioration of the properties of polymer composite materials is low temperature. By prolonged low-temperature seasonal and daily cycling exposure on the samples, internal stresses arise because of an accumulation of moisture in the pores and difference between the coefficients of linear thermal expansion of reinforcing fibers and polymer matrices. These internal stresses contribute to the growth of microcracks, their coalescence, the formation of macrodamages and the resulting decrease in the strength of polymer composite materials.

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