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The Thermal Destruction and Coke Formation Intensity Influence on the Delamination and Destruction of Fiber Reinforced Plastics with a Unidirectional Filler under High Temperature Conditions

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Abstract. It is made fiber reinforced plastics (FRP) adhesion properties influence analysis on their destruction at an increase of temperature. Taking into account the thermoelastic properties of fiber reinforced plastics, it is proposed an expression for calculating the load of the composition delamination beginning, and a correlation of the destructive stress in monolayer FRP with the temperature of heating is found. It has been established that the further intensity of delamination and destruction of FRP depends on the temperature of the destruction beginning and coke formation intensity.

Introduction

During the FRP moulding on the edge of phase distribution (filler-binder), residual stresses are formed in boundary layers which have a significant influence not only on the actual strength and physical-mechanical properties of the composite, but on its flammability also [1].

When the FRP is burned, the effect of the "match" is observed (the delamination of the composite on the phase distribution edge), during which the surface of the flame heat action influence is substantially increased. This effect is also present in the initial stages of heating and ignition.

The purpose of the work is to establish the impact of the temperature of the coking onset and its intensity on the fiberglass integrity and strength characteristics loss under high temperature conditions. In this regard, in this work, we study the critical temperature limits of the delamination onset of FPR based on industrial polymers in comparison with alternative and the theoretical dependence of the delamination temperature on the composites thermoelastic properties is established.

Analysis of Recent Research and Publications

Various composite plastics differ significantly from other filled compositions by the mutual influence of phases in the boundary layers. With a developed surface of phase distribution (especially when filled with thin and shaped fibers), the volume of the interfacial zone approaches the volume of the entire binder. The mutual components influence in the interfacial zone is determined by the composition of the composite and the conditions for moulding products [2,3].

Attempts to evaluate the mutual influence of components on their mechanical properties have been carried out repeatedly. Thus, an increase in the long-term strength under cyclic loading of glass fibers after applying various binders to their surface has been studied [4]. The long-range action effect of different fillers and the nature of the interaction in the boundary layer were also investigated [5,6,7]. A number of authors also paid attention to the adhesive and strength characteristics of polymers, taking into account aging and elevated temperatures [8,9,10].

But it is very difficult to take into account the mutual influence of the components using the given dependences, without taking into account the characteristics of the materials used.

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Main Part

In determining the dependencies, the basic assumption is the adhesive strength between the plastic components. Under given loading conditions, strong adhesion of the binder to the filler is usually necessary, since the strong adhesive bond between the plastic components provides maximum design stresses are transmitted to the filler elements. In cases where the finishing increases the adhesive strength, there is a correlation between the adhesive strength and tensile breaking stress [11]. The authors of [12] showed that with a sufficiently high adhesive strength, the destruction of the composite proceeds along the filler fibers of the bonding layer. That is, it is possible to assume that the delamination of the reinforced material occurs when a stress occurs, which is equal to the breaking stress during stretching of the binder. However, the cited works do not indicate the dependence of the breaking stress on adhesion bonds when FRP is heated to temperatures typical to a fire.

In [13], a formula is given for calculating the breaking stress in tensile unidirectional plastic, which takes account the influence of physicochemical factors that determine the interaction in the boundary layers using the average coefficients (1):

$$\sigma_{xx} = \alpha_{comp} \cdot \left[K_{||} \cdot \sigma_f \cdot V_f + \sigma_b \cdot \left(1 - K_{||} \cdot V_b\right)\right], \quad (1)$$

where α_{comp} - coefficient of deviation from the ideal adhesive interaction;

$K_{||}$ - coefficient of the deviation degree of the fibers direction from the load direction;

σ_f, σ_b - breaking tensioning stresses of the fiber and the binder, respectively;

V_f, V_b - the volume of fiber and binder in the composite, respectively.

So, the coefficient α_{comp} takes account the deviation from the ideal adhesive interaction, the presence of final stresses and other factors. It has been experimentally established that for unidirectional compositions based on fiberglass $\alpha_{comp} = 0{,}7 \div 0{,}9$. The coefficient $K_{||}$ takes account the degree of deviation of the fibers from the load direction.

For a unidirectional composite, in the case of delamination (destruction) under the action of thermal deformation, the breaking stresses will be directed in the transverse direction to the filler. With this direction of load, the coefficient $K_{||} = 0$, therefore:

$$\sigma_{xx} = \alpha_{comp} \cdot \sigma_b. \quad (2)$$

Based on the above expression, it can be concluded that the breaking stresses during ignition coincide with the dependence on the breaking stress in tensile of the binder.

During ignition, as a result of the difference in the binder and the filler coefficients of thermal expansion, the effect of composite delamination occurs, which leads to a significant increase in the area of flame thermal irradiation and, as a consequence, to an increase in the rate of combustion and burnout, which was noted in [14].

The correlation between the thermoelastic properties of the composite components and the breaking stress is known [15]:

$$\sigma_{therm} = \mathrm{E}_{comp} \cdot \left(\alpha_b - \alpha_f\right)/\Delta\mathrm{T}, \quad (3)$$

where E_{comp} - the modulus of elasticity of the FRP;

α_b, α_f - coefficients of linear thermal expansion of the binder and filler, respectively;

ΔT - the temperature of the ignition source (heating), up to which effective coke formation does not begin on the composite surface.

To use formula (3), several assumptions must be made. Since the composite behavior is considered only at the stage of heating in a narrow time interval and does not takes account the processes that occur after ignition, the time can be neglected.

Analysis of the data regarding the characteristic temperatures of fires [16] and the behavior of fiberglass binders during heating [17] shows that the main thermochemical changes in a short time interval occur up to a temperature of 600 °C.

That is, in a certain temperature range, a noticeable destruction of the binder begins and a sufficient mass ratio of coke residue is released, the elastic-strength characteristics and the qualitative composition of the composite change. Based on the above, the maximum ΔT is taken equal to 600 °C.

When the considered temperature is exceeded, due to the formation of a coke layer on the composite surface, the effective heat amount acting on the surface of the non-destructed composite changes, that is, the heating mode changes and, accordingly, the process of expansion and delamination of fiberglass under thermal influence.

Equations (2) and (3) describe the dependence of the breaking stress during FRP transverse expansion, but proceed from different characteristics of the fiberglass components. Thus, we obtain the expression for the critical stress level in the composite, above which detachment of the binder from the filler is observed:

$$\sigma_{xx} = \sigma_{br} \tag{4}$$

From this expression, an equation can be obtained to determine the critical stress that leads to the delamination of the composite during heating and ignition:

$$\sigma_b^{cr} = \frac{\mathrm{E}_{comp} \cdot (\alpha_b - \alpha_f)}{\alpha_{comp} \cdot \mathrm{T}}. \tag{5}$$

Information about the determination of the elastic modulus is provided in [18], where it is noted that the structure of the filler (fiber) has almost no effect on the elastic modulus of the composite as a whole. So, considering unidirectional fiberglass based on industrial binding ED-20 and aluminoborosilicate glass fiber as a filler, as well as bromine-containing binder and epoxidized dinaphthol, it was experimentally determined that the modulus of elasticity of the composite varies in the range of 80000-82000 MPa. It was also noted that the fluctuation of this characteristic within 2% when testing composites in tension (Table 1) is due to the test procedure.

According to [11], the breaking stress during tension of ED-10 and melamine-formaldehyde polymers is in the range of 60-100 MPa, depending on the setting mode of the binder.

Table 1. Influence of the FRP composition on the modulus of elasticity of unidirectional glass fiber plastic

Bulk content, [%]			Tensile modulus of elasticity		
Filler	Binder	Pores	Plastic, [MPa]	Fiber in plastic	
				[MPa]	[%]
62.7	34.2	3.1	51300	80000	100
62.5	34.6	2.9	53100	80500	
64.0	34.2	1.8	51000	80900	
61.6	36.0	2.4	50500	80100	
62.0	36.0	2.0	50600	81000	

During the experiment, the samples of glass-filled composite based on ED-20 epoxy resin, bromine-containing resin and a binder based on epoxidized dinaphthol, considered in [17] are used. Aluminoborosilicate glass fiber with a filling degree of 62-63% was used as a filler. The thermal effect on the sample surface was carried out using a flat duralumin plate with a thickness of 1.5 mm pressed against the sample, which was gradually discretely heated in the temperature range of 20-600 °C.

At some point, the heated plate was brought into contact with the sample surface. After 15 seconds, it was withdrawn. Up to a temperature of 80-100 °C in the case of a composite based on ED-20 resin, no changes were recorded. For fiberglass based on a bromine-containing binder, the same behavior was inherent up to a temperature of 280-300 °C, and for epoxidized dinaphthol up to a temperature of 270-290 °C (Fig. 1).

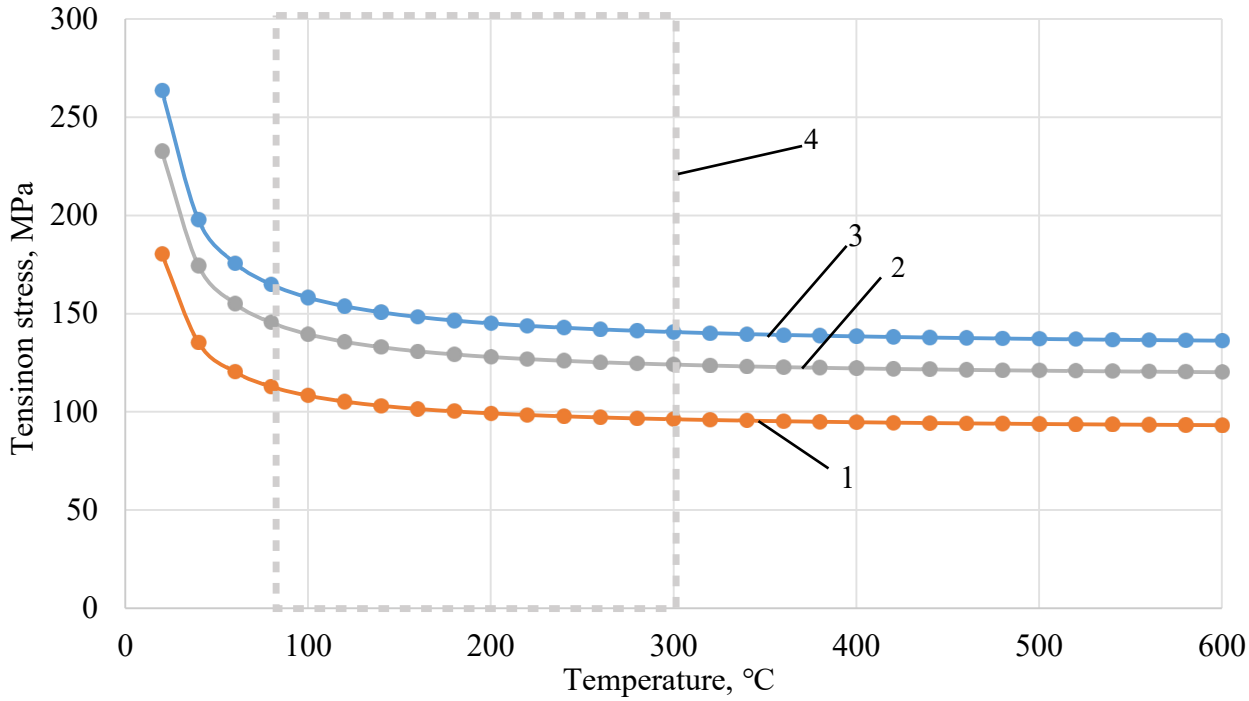

Fig. 1. Calculated tension stress values on short-term heating temperature for composites based on: 1 – ED-20; 2 – bromine-containing binder; 3 – epoxidized dinaphthol; 4 – area of the beginning of binder intensive decomposing

When the above-mentioned temperatures were exceeded, on the lateral surface of the samples, expansion of the material and detachment of the binder from the fibrous filler were visually observed, which well confirms the calculated data.

However, when the composite samples were heated to a temperature of 200-350 °C, the effect of the coke residue formation on the surface and the loss of the regularity of material delamination were observed (Fig. 2). As can be seen from the data provided, the regularity of the stress change in fiberglass changes. The change in the strength of monolayer plastic is clearly divided into two stages: with a high rate of strength fall and an established regularity. The regularities of strength decreasing are approximated by lines with a standard deviation not lower than R=0.942.

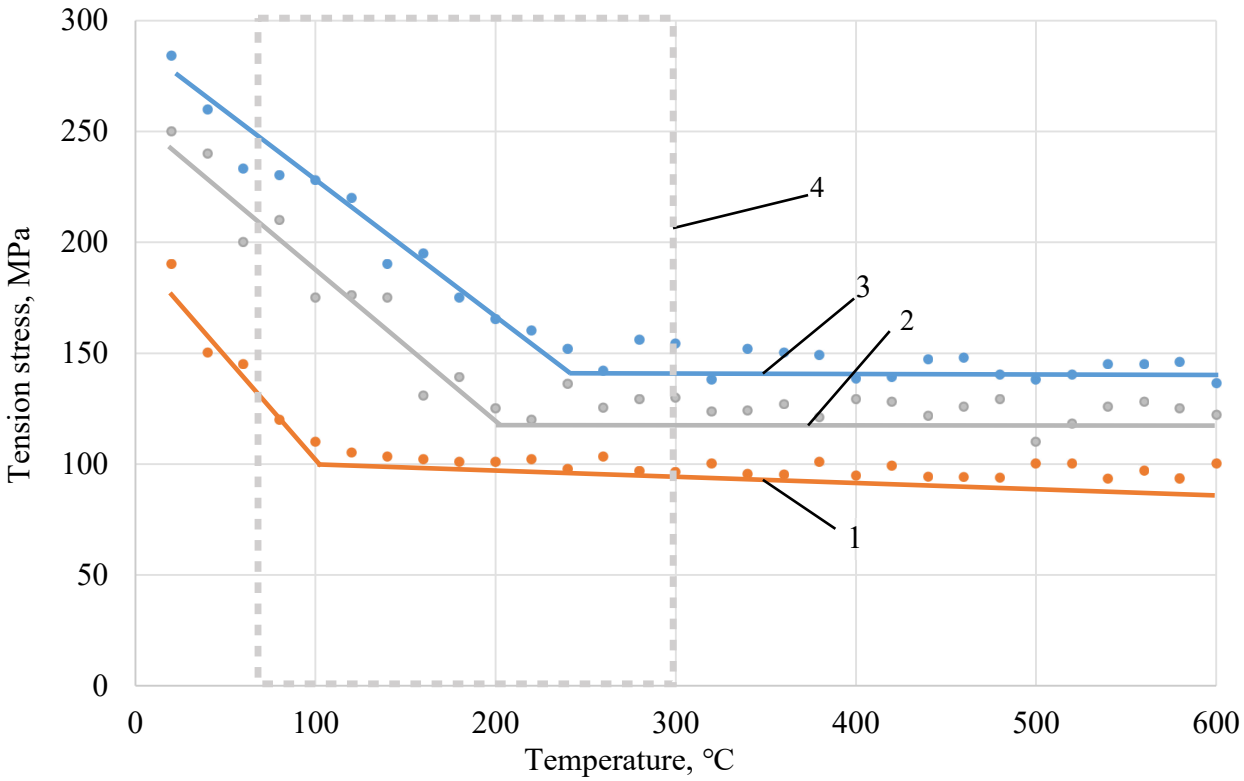

Fig. 2. Experimental tension stress values on short-term heating temperature for composites based on: 1 – ED-20; 2 – bromine-containing binder; 3 – epoxidized dinaphthol; 4 – area of the beginning of binder intensive decomposing

At the same time, at the first stage, the difference in the calculated and the experiment data reaches 24.4%. However, at the second stage, they decrease to 8.4%.

Moreover, in composites based on a bromine-containing binder, as well as epoxidized dinaphthol, the nature of the change is more pronounced. The authors associate this behavior of fiberglass with different temperatures of the thermal destruction onset, the coke formation in binders (Table 2), the transition of the polymer binder to a high-elasticity state and, accordingly, a decrease in the breaking stress for FRP. At the same time, the bromine-containing binder and dinaphthol have a higher coke residue value, which, most likely, allows the binder residues to take on part of the load.

Table 2. Characteristics of the thermal destruction process of polyepoxy binders [19]

Polyepoxide	Characteristic temperatures (data from TG and DTG), [°C*]			The amount of coke residue, [%]
	$T_{d.}$	$T_{c.f.}$	$T_{i.c.f.}$	
ED-20	80	120	240	14
Bromine-containing binder	220	480	540	19
Epoxidized dinaphthol	270	440	520	22

Note.

*1. $T_{d.}$ – temperature of the intensive decomposing beginning (with 10% of a binder mass loss). 2. $T_{c.f.}$ – temperature of the coke formation onset. 3. $T_{i.c.f.}$ – temperature of the intensive coke formation beginning.

Conclusions

The paper establishes the dependence of the appearance of the material delamination effect depending on the thermoelastic characteristics of the FRP elements up to the temperatures of the beginning of the intensive destruction of the material. Experimental data have confirmed that with

the onset of intense coke formation, the regularity of material destruction changes, while there is a dependence on the intensity of coke formation.

Comparative analysis showed that the composite based on epoxidized dinaphthol retains its integrity in a wider temperature range as compared to the given industrial analogs.

It is shown that the change in the strength of monolayer plastic is clearly divided into two stages: with a high rate of strength fall and an established regularity. At the same time, at the first stage, the difference from the calculated data in the experiment carried out reaches 24.4%. However, already at the second stage, they decrease to 8.4%.

References

[1] P.A. Bilym, A.P. Mihajlyuk, V.S. Nekhaev, K.A. Afanasenko, Izmenenie sostoyaniya epoksifenol'nogo svyazuyushchego v kompozicionnom materiale pod dejstviem kontaktnoj polyarizacii. Vestnik NTU «HPI». Sb. nauch. tr. Tematicheskij vypusk «Himiya, himicheskaya tekhnologiya i ekologiya», Har'kov: NTU «HPI». 14 (2005) 155-159.

[2] A. Rohumaa, A Yamamoto, C.G. Hunt, C.R. Frihart, M. Hughes, J. Kers, Effect of log soaking and the temperature of peeling on the properties of Rotary-cut birch (Betula pendula Roth) veneer bonded with phenol-formaldehyde adhesive. BioResources. 3 (11) (2016) 5829-5838.

[3] I.A. Shabanova, O.V. Mirgorod, V.V. Taranenkova, A.N. Korogodskaya, V.V. Dejneka (2005). Thermodynamic properties of binary and ternary compounds of CaO-BaO-Al_2O_3 system. Ogneupory i Tekhnicheskaya Keramika Issue, 1, (2005) 2-6.

[4] G.S. Holister, K. Tomas, Materialy, uprochnennye voloknami. Per. s angl. Pod red. V.S. Ivanovoj. M.: Metallurgiya. (1969) 149.

[5] T.I. Sogolova, Uspekhi himii i fiziki polimerov. M.: Himiya. (1970) 232-251.

[6] V.P. Solomko, Vyazkouprugie svojstva polimerov. Mekhanika polimerov. 6 (1970) 1031-1041.

[7] Awaja, Firas & Gilbert, Michael & Kelly, Georgina & Fox, Bronwyn & Pigram, Paul. Adhesion of polymers. Progress in Polymer Science. 34 (2009). 948-968. 10.1016/j.progpolymsci.2009.04.007.

[8] Yuxiang Zhang, Jianli Ma, Chengwei Wu, Xiao Han, Wei Zhang, Effects of moisture ingress on the mesoscale mechanical properties of epoxy adhesives under elevated temperature, Polymer Testing, 94 (2021) 107049.

[9] M. Eftekhari, A. Fatemi, Tensile behavior of thermoplastic composites including temperature, moisture, and hygrothermal effects, Polymer Testing. 51 (2016) 151–164.

[10] A. Chernukha, A. Teslenko, P. Kovaliov, O. Bezuglov (2020), Mathematical Modeling of Fire-Proof Efficiency of Coatings Based on Silicate Composition. Materials Science Forum, 1006, 70–75. DOI: 10.4028/www.scientific.net/MSF.1006.70

[11] G.D. Andreevskaya, Vysokoprochnye orientirovannye stekloplastiki. M.: Nauka, (1966) 370.

[12] D. Shuster, E. Skala, Monokristal'nye volokna i armirovannye imi materialy. Per. s angl. Pod red. A.T. Tumanova. M.: Mir. (1973) 379-411.

[13] P. G. Babaevskij, Plastiki konstrukcionnogo naznacheniya (reaktoplasty). Pod red. E. B. Trostyanskoj. M.: Himiya. (1974) 303.

[14] G.P. Zajcev, V.S. Strelyaev, Raschet na prochnost' konstruktivnyh elementov iz stekloplastikov. M.: Mashinostroenie. (1970) 117.

[15] N.A. Halturinskij, V.M. Lalayan, A.A. Berlin, Osobennosti goreniya polimernyh kompozicionnyh materialov. Zhurnal Vsesoyuznogo himicheskogo obshchestva im. D.I. Mendeleeva. 5 (34). (1989) 560-566.

[16] Dubinin et al., Investigation of the effect of carbon monoxide on people in case of fire in a building. Ispitivanje djelovanja ugljičnog monoksida na ljude u slučaju požara u zgradi, Sigurnost, 62 (4), (2020) 347– 357.

[17] K.A. Afanasenko, P.A. Bilim, O.P. Mihajlyuk, Do pitannya pro karbonizaciyu ta vtratu masi sitchastih polimeriv pri linijnomu nagrivi. Problemyi pozharnoy bezopasnosti: Sb. nauch. tr. Harkov: NUGZU. 33 (2013) 13-16.

[18] V.V. Vasil'ev, V.D. Protasov, V.V. Bolotin i dr, Kompozicionnye materialy: Spravochnik. M.: Mashinostroenie. (1990) 512.

[19] K. Afanasenko, A. Romin, Y. Klyuchka, V. Lypovyi & K. Hasanov (2020), Epoxidized Dinaphthol Application as the Basis for Binder with Advanced Carbonation Level to Reducing its Flammability. Materials Science Forum, 1006, 41–46.