# DEFORMABILITY AND DURABILITY OF CFRP REBARS AND COMPONENTS UNDER MOISTURE AND TEMPERATURE ACTION

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**ABSTRACT**

The results of complex investigation of deformability and strength properties of unidirectional carbon fibber reinforced plastics (CFRP) used as a reinforcing element and its structural components under temperature and moisture action are presented. Sorption and desorption processes in the vinylester resin, used as a binder of CFRP are experimentally investigated. Some models of non-Fickian sorption are applied for description of the experimental data and improving the approximation. Effect of temperature on the resin sorption kinetics is quite significant. Structural approach and computer simulation were used for calculations of diffusion characteristics. Significant anisotropy effect of sorption process parallel and normal to the fibbers direction was observed in tests. Quasi three phase model is suggested for the description of CFRP composite sorption. The model is based on consideration of sorption process of the diffusion character for a composite consisted of two phases: resin and microplastic. Effect of sorption anisotropy is considered on an example of moisture transfer from a point source modelling a damaged zone.

Effect of temperature and moisture on mechanical properties of the resin and CFRP rebars were investigated. Strength and elastic characteristics of the resin undergo essential changes due to action of the environmental factors. Temperature increase from 20 up to 70 $^{o}$C leads to the strength decrease by 40% and ultimate strain increase by about 30%. Elastic modulus of the resin $E = 3.8$ GPa decreases by 34 and 10% due to temperature and moisture action, respectively. Essential activation of relaxation processes is observed in creep tests of the resin. Long term creep properties of the resin are most sensitive to the action of external factors. The elastic modulus and strength of the CFRP rebars were determined in tension tests and their values are $E_{11} = 130$ GPa and $\sigma > 3$ GPa. The effect of temperature and moisture on the rebars properties in direction of fibbers is not essential, but $E_{22}$ value decreases for about 20 and 5%, respectively. The obtained results could be used for the reliable prediction of long-term deformability of the material upon the action of service factors and estimation of the environmental effect.

## 1. INTRODUCTION

Unidirectional carbon fiber reinforced plastics (CFRP) rebars serve as reinforcement in civil engineering constructions. Distinguishing features of such the materials are heterogeneity and anisotropy. The anisotropy induced by anisotropy of fibbers itself and its orientation in the composite complicates determination of mechanical characteristics. Physical properties are also anisotropic. This leads to essential changes in kinetics of some processes responsible for durability of CFRP.

Main disadvantage of many polymer composites and CFRP in particular is their essential sensitivity to environmental action [1, 2]. Effect of such factors as temperature and atmosphere humidity reduces operating characteristics and durability. The investigation of moisture and temperature effect on separate structural elements of the composite (matrix and fibbers) allows to calculate and predict changes in the mechanical behaviour of the composite as a whole. Taking into account high environmental resistance of carbon fibbers moisture and temperature effect on physical and mechanical properties of CFRP rebars is substantially defined by properties of a polymer matrix. Elaboration of a structural approach allows to evaluate properties of the composite using appropriate characteristics of its components — carbon fibbers and matrix. For the prediction of the composite durability the investigation of moisture sorption kinetics is required.

The aim of the present paper is evaluation of deformability and strength properties of unidirectional CFRP and its structural components under temperature and moisture action.

## 2. EXPERIMENTAL DETAILS

The investigated materials are pultruded carbon fiber reinforced plastics (CFRP) rebars and vinylester resin HETRON 970/35 used as a matrix. The rebars were sanded and spiral wound with carbon fibbers to improve an adhesion. Nominal diameter of the rebars is 8 mm. Composite reinforcement ratio by volume is $v_f = 0.65$. Specimens of the resin had a bar or dog-bone shape and dimensions 2x10x150 mm.

The experimental investigation of the vinylester resin sorption and desorption processes were carried out in atmosphere with different relative humidity φ at room temperature. The "dry" atmosphere with φ ≈ 0% was created by a silica gel. Other atmospheres – by saturated salt solutions of KCNS, NaCl and $K_2SO_4$ which created φ = 47, 77, and 98%, respectively. For the investigation of water sorption kinetics specimens were placed in water at temperatures $T$ = 7, 20 and 40 °C. At least 6 specimens were moistened at each the conditions. The investigation of the CFRP rebars moisture sorption is carried out in an atmosphere with φ = 98% at room temperature on specimens of 25 ± 0.2 and 0.5 ± 0.1 cm length.

Temperature and moisture effect was evaluated in tensile stress-strain and creep tests. The specimens were conditioned at a certain temperature at least 15 minutes or moistened up to an equilibrium state prior to testing. Stress-strain tests were carried out by MTS system with a constant speed of displacement of the lower traverse 5mm/min.

Short- and long-term tensile creep tests were performed according to ASTM D2990-01 under different constant temperatures and relative humidity of an atmosphere. The accuracy of the strain measuring by the extensometer in short-term and cathetometer in long-term tests was within 0.2 and 0.1%, respectively. The tests at elevated temperatures were carried out using an electrical mini oven that was attached to a specimen.


## 3. RESULTS & DISCUSSION

**Moisture and water sorption by the resin.** For many isotropic polymer materials the dominant sorption mechanism is diffusion [1, 2]. The solution of Fick's equation describing for relative moisture content of one dimensional sorption problem with stationary boundary and initial conditions for a bar shape specimen of thickness $a$ is [3]

$$\frac{w(t) - w_0}{w_\infty - w_0} = 1 - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\left[1 - (-1)^k\right]^2}{k^2} \exp\left[-\lambda_k^2 Dt\right], \tag{1}$$

where $\lambda_k = \pi k / a$, $D$ is diffusion coefficient independent of concentration, $w_0$ and $w_\infty$ are initial and equilibrium moisture contents, respectively.

Non-Fickian models are used in the case of sorption with two-stage character. Langmuir two-phase model [4] considers a free diffusion phase and a bound phase of a diffusant which does not involve diffusion. The equation for moisture content in this case can be approximated by

$$\frac{w(t) - w_0}{w_\infty - w_0} = \left[1 - \frac{\beta}{\alpha + \beta} \exp(-\alpha t) - \frac{\alpha}{\alpha + \beta} \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{\left[1 - (-1)^k\right]^2}{k^2} \exp\left[-\lambda_k^2 Dt\right]\right], \tag{2}$$

where α is the probability of a molecule of water transition from a combined state to the free phase, and β is the probability of a molecule of water transition from the free to the combined phase. It can be seen when α >> β, i.e. the contribution of the free phase to the total sorption is dominant, the two-phase model approaches the one-phase model (see Eq. 1).

The model of Jacobs and Jones [5] is based on assumption that a polymer consists of two phases: a general phase (phase 1), where the major part of water is absorbed, and a second phase (phase 2), with a different density or/and hydrophilic character than phase 1. The

diffusion proceeds in both phases by parallel Fickian processes. The model for such a polymer takes the form

$$w(t) = w_{\infty 1}\left[1 - \frac{2}{\pi^2}\sum_{k=1}^{\infty}\frac{\left[1-(-1)^k\right]^2}{k^2}\exp\left[-\lambda_k^2 D_1 t\right]\right] + w_{\infty 2}\left[1 - \frac{2}{\pi^2}\sum_{k=1}^{\infty}\frac{\left[1-(-1)^k\right]^2}{k^2}\exp\left[-\lambda_k^2 D_2 t\right]\right], (3)$$
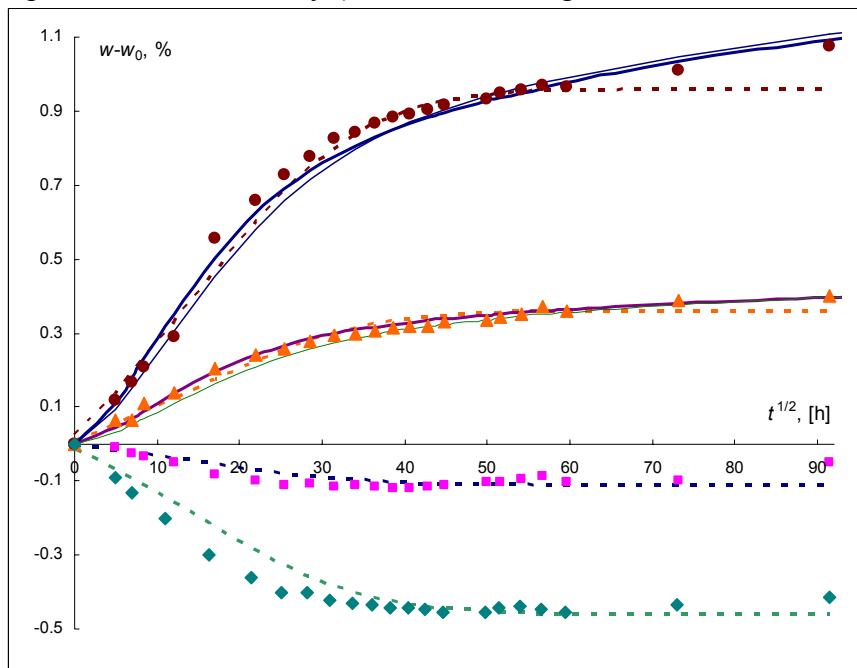
where $D_1$ and $D_2$, $w_{\infty 1}$ and $w_{\infty 2}$ are the diffusion coefficients and equilibrium moisture content in the two phases, respectively. The total moisture equilibrium is a sum of moisture equilibrium of two phases, i.e. $w_{\infty} = w_{\infty 1} + w_{\infty 2}$.

Some parameters of the models, such as $w_0$ and $w_{\infty}$, can be evaluated experimentally, some – by an approximation and treatment of sorption curves at small or large exposure times. According to the Fick's model the diffusion coefficient $D$ is determined from an approximation of a starting segment of moisture sorption curve. The expression for $D$ calculation is [1]

$$D = \frac{\pi a^2}{4t}\frac{(w-w_0)^2}{(w_{\infty}-w_0)^2}. \qquad (4)$$

Effect of external factors changes the diffusion characteristics and leads to an acceleration of sorption process. The temperature dependence of the diffusion coefficient can be described by the Arrhenius equation [1] $D = D_0 \exp(-U_d / R_g T)$, where $D_0$ is a constant (equal to the extrapolated value of $D$ for $1/T = 0$), $U_d$ is activation energy of diffusion, $R_g = 8.31$ J/mole·K is universal gas constant and $T$ is absolute temperature of diffusion. Analogously, the isobar of water content (i.e. equilibrium moisture content as a function of temperature at a constant relative humidity) is expressed as $w_{\infty} = w_{\infty}^0 \exp(-\Delta H / R_g T)$, where $\Delta H$ is the enthalpy of sorption.
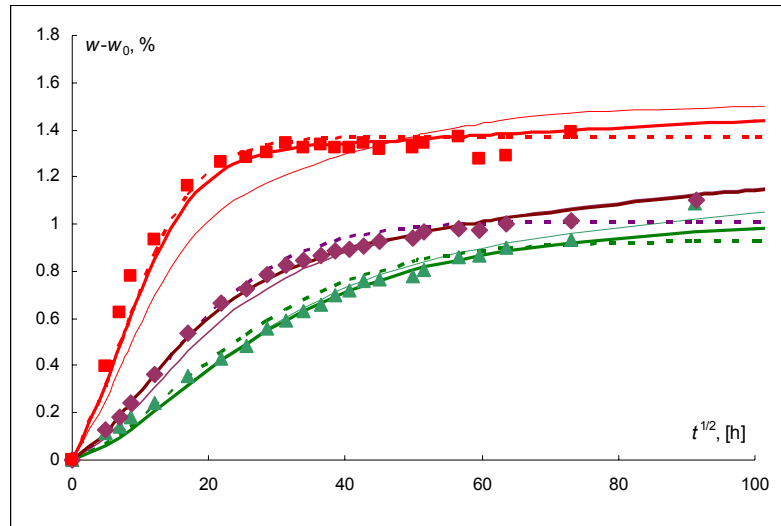
The averaged experimental and calculated sorption curves of the vinylester resin under different atmosphere relative humidity $\varphi$ are shown in Fig. 1.



"**Fig. 1.** Sorption curves of the resin at $T = 20$ °C and $\varphi = 0$ (♦), 47 (■), 77 (▲), 98% (●). Lines are approximations by Eqs. 1 (dashed), 2 (thin solid) and 3 (bold solid)."

The data are satisfactorily described by the Fick's law, since at large exposure times and high $\varphi$ approximation by the non-Fickian models gives better results.
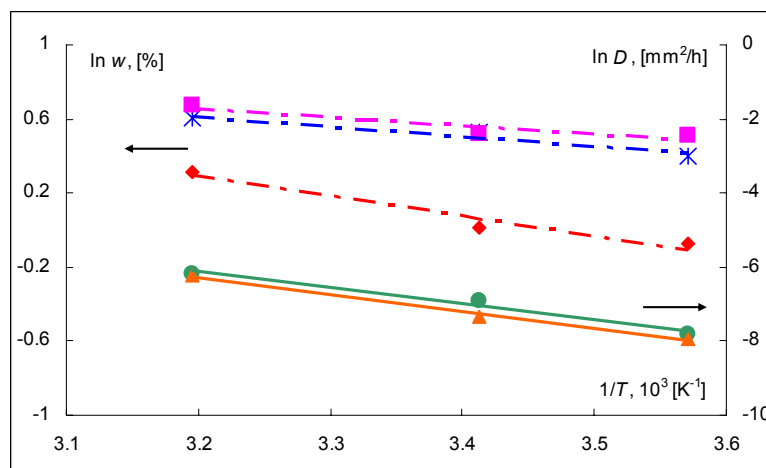
The water sorption curves at different temperatures are shown in Fig. 2. Obviously, that water sorption has a two-phase character, since at high temperatures the process becomes yet more complicated.



"**Fig. 2.** Water sorption curves of the resin at $T = 7$ (▲), 20 (♦), and 40 $^{o}$C (●). Lines are approximations by Eqs. 1 (dashed), 2 (thin solid) and 3 (bold solid)."

The parameters of the models and their temperature dependences were determined. The diffusion coefficient of the vinylester resin is independent on $\varphi$ and its value at ambient temperature determined by Eq. 4 is $D = 0.65 \pm 0.2 \cdot 10^{-3}$ mm$^2$/h. The sorption isotherm is expressed as $w_{\infty} = 0.0001\varphi^2 - 0.0002\,\varphi$. The value of the diffusion coefficient considered in Langmuir model coincide with their Fick's analogue. Values of the parameters are $\alpha = 1.625 \cdot 10^{-4}$ s$^{-1}$ and $\beta = 6.94 \cdot 10^{-5}$ s$^{-1}$. The diffusion coefficients $D_1$ and $D_2$ of the resin (see Eq. 3) were determined similarly as in the case of Fick's sorption for each the phase and their values are $D_1 = 1.0 \cdot 10^{-3}$ and $D_2 = 6.0 \cdot 10^{-5}$ mm$^2$/h. Their values do not depend on moisture concentration too.

The temperature dependences of the resin diffusion coefficients and saturation levels obtained by different models are presented in Fig. 3.



4

Values of the maximum water content and diffusion coefficients for the considered non-Fickian models are higher than those determined by the Fick's law. However, temperature dependence of the diffusion coefficients is similar. Temperature effect on the equilibrium moisture content, in turn, is appr. twice lower than for the Fick's diffusion. The activation energy of the diffusion is $U_d = 39$ kJ/mole. The enthalpy of sorption in the case of pure Fick's diffusion is $\Delta H = 8.7$ kJ/mole.

Insertion of new parameters in sorption models improves the accuracy of approximations but also complicates the calculations and requires performing of additional experiments. Therefore, for the first evaluation the Fick's model is used for the prediction of moisture sorption kinetics of the composite.

**Moisture sorption by the composite.** The solution of the Fick's equation at stationary initial and constant boundary conditions for a cylindrical shape specimen of unidirectional (i.e. monotropic composite) of radius $R$ and length $L$ for the relative moisture content is [3]

$$\frac{w(t) - w_0}{w_\infty - w_0} = 1 - \frac{8}{\pi^2} \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} \frac{\exp(-\lambda_{k,m}^2 t)\left[1 - (-1)^m\right]^2}{\gamma_k^2 m^2}, \quad \lambda_{k,m}^2 = D_r \left(\frac{\gamma_k}{R}\right)^2 + D_z \left(\frac{\pi m}{L}\right)^2 \quad (5)$$
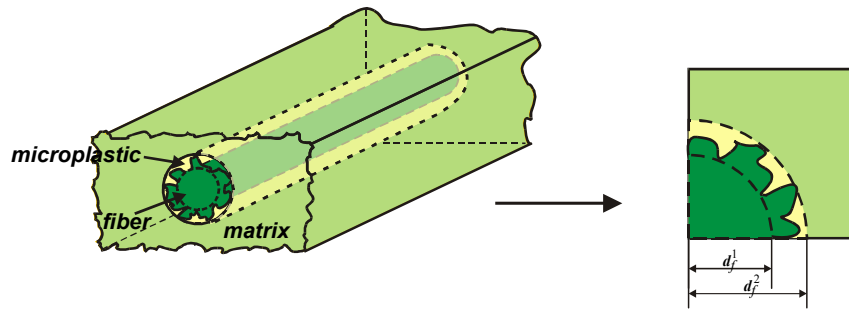
where $D_r$ and $D_z$ are components of the diffusion coefficient tensor in the general axes of symmetry ($r$ and $z$ are directed on radius and axis of a cylinder, respectively), $\gamma_k$ are roots of Bessel's functions of 0-th order.

The sorption tests were performed on specimens of two different sizes along the axis $z$ for determination of the composite diffusion characteristics. In the first approximation, it is accepted that moisture absorption in the investigated CFRP rebars has a purely diffusive mechanism. Then the experimental sorption data were approximated by Eq. 5 assuming that the saturation level tends to a value $w_\infty = 0.52\%$ for both the specimens of different lengths $L$ (see Fig. 4). The values of the diffusion coefficients obtained by the approximation are $D_r = 1.8 \cdot 10^{-4}$ and $D_z = 70 \cdot 10^{-4}$ mm²/h. The rate of moisture diffusion in CFRP rebars along and across the fibbers differs for about 40 times that indicates to a high degree of anisotropy of the diffusive properties.

The structural approach was used for evaluation of sorption characteristics of the composite and description of its sorption kinetics. For the determination of such sorption characteristics as equilibrium moisture content and diffusion coefficient in the parallel to fibbers direction the rule of mixtures is used. There are many analytical models based on temperature and moisture transport analogy principle for the determination of transversal diffusion coefficient [1, 6, 7]. Analysis of the known models showed that the ratio of diffusion coefficients in longitudinal and transversal directions for the composite with hydrophobic fibbers does not exceed the value 4 (i.e. for an order smaller than it was obtained in the test). Applying of the computer simulation for calculation of the transversal diffusion coefficient gives the similar results. Obviously, that description of sorption kinetics of CFRP rebars using these calculated diffusion characteristics, is unsatisfactory. This requires modification of the model of composite sorption.

Let's assume that a composite consists of three phases: resin (matrix), fibbers and fibber-resin interphase. Determination of exact boundaries of the interphase and properties of each the phase are difficult tasks. Therefore, it is more rationally to turn to a consideration of a quasi three phase model consisting of the resin (which properties are the same as in macroscopic volume) and microplastic (an assembly of monofibbers glued with the resin, that is unification of two phases – fibbers and fibber-resin interphase). Here volume fraction of microplastic in a

composite is assumed equal to a composite reinforcement ratio. The scheme of the quasi three phase composite model is shown in Fig. 4.
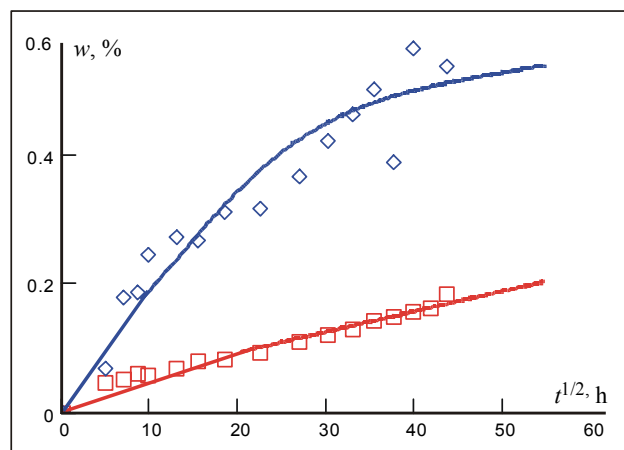


"**Fig.4.** Scheme of the quasi three phase composite model."

In the first approximation, it can be assumed that in the composite phases — resin and microplastic — the dominant mechanism of moisture sorption is the diffusion that proceeds by parallel Fickian processes. Taking into account anisotropy of cylindrical specimens analogously with the two-phase sorption model for polymer systems [5] the equation for description of moisture content growth kinetics of the quasi three phase composite is the following

$$w(t) = w_\infty^m \left[ 1 - \frac{8}{\pi^2} \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} \frac{\exp(-\lambda_{k,n}^{2}{}^{m}t)\left[1-(-1)^n\right]^2}{\gamma_k^2 n^2} \right] + w_\infty^{mp} \left[ 1 - \frac{8}{\pi^2} \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} \frac{\exp(-\lambda_{k,n}^{2}{}^{mp}t)\left[1-(-1)^n\right]^2}{\gamma_k^2 n^2} \right], \quad (6)$$

where the superscripts $m$ and $mp$ designate the matrix (resin) and microplastic, respectively. The first term of Eq. 6 is related to the diffusion of moisture into the pure resin. The second term corresponds to the contribution of moisture absorption in the microplastic. The total moisture equilibrium content is $w_\infty = w_\infty^m + w_\infty^{mp}$. The equilibrium moisture content of the resin in the composite exposed from room conditions to the atmosphere with $\varphi = 98\%$ calculated using mixture rule is $w_\infty^m = 0.3\%$. The diffusion coefficient of the resin in composite remains the same as for the pure resin. Sorption characteristics of the microplastic were determined from approximation of the experimental sorption curves by Eq. 6 (Fig. 5).
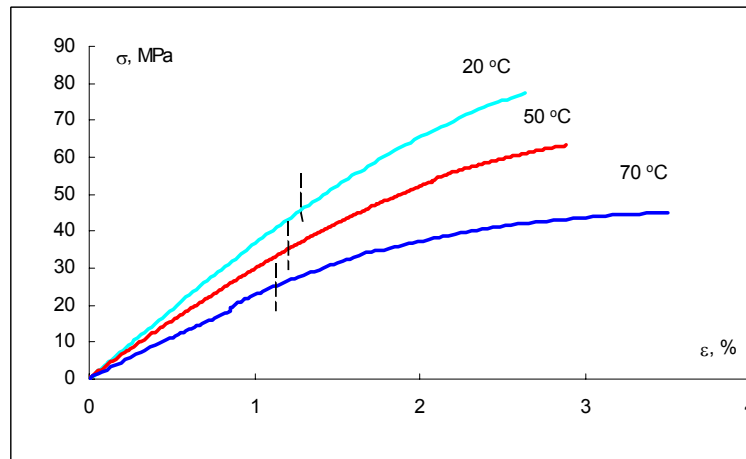


"**Fig. 5.** Moisture sorption of the CFRP rebars of 0.5 (◊) and 25 cm (□) lengths. Dots are experimental data, solid lines — approximation by Eq. 6."

The determined value of the equilibrium moisture content of the microplastic is $w_\infty^{mp} = 0.4\%$, and the diffusion coefficients are $D_r^{mp} = 1.2 \cdot 10^{-4}$ and $D_z^{mp} = 60 \cdot 10^{-4}$ mm²/h. So the calculated degree of anisotropy for the microplastic is for about 50.

The significance of anisotropy effect is considered on an example of moisture concentration front transfer in a monotropic composite from a point source. For such modelled damaged composite moistened zone along and across fibbers differs for $\sqrt{D_z / D_r}$ times, i.e. exactly depends on degree of anisotropy of diffusion characteristics.
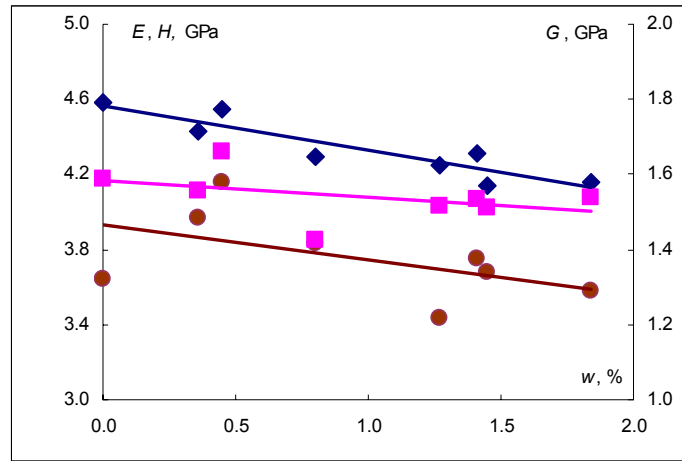
**Properties of the resin**. For evaluation of moisture and temperature effect on the composite mechanical properties, first of all, it is necessary to investigate the resin properties and their changes due to environmental influence. Average tensile stress-strain curves of the resin specimens obtained at different temperatures are shown in Fig. 6 [8]. The material behaviour is linear within large range of strain — up to half of strength. Ranges, where deviation from the linear behaviour does not exceed 2% by stress, are shown in Fig. 6 by dashed lines.



"**Fig. 6.** Stress-strain curves of the resin at tension at different temperatures."

The deformation behaviour is viscoelastic and other time-dependent effects for the specimens tested at $T = 20$ and 50 °C are not significant. Ultimate characteristics of the resin undergo essential changes due to the temperature effect. Temperature increase from 20 up to 70 °C leads to the strength decrease by 40% and ultimate strain increase by about 30%. The elastic modulus of the resin decreases by 34% relative to its value $E = 3.8$ GPa (±5%) at room temperature.

Moisture effect on the resin behaviour was investigated in the tensile tests of moistened specimens at room temperature. Character of the stress-strain curves had not essential changes with the growth of moisture content. The determined average values of the strength and ultimate strain are $\sigma^* = 50 \pm 10$ MPa (20%) and $\varepsilon^* = 1.6 \pm 0.3\%$ (20%), respectively. Moisture effect on elastic characteristics of the resin is more significant. The secant elastic modulus $E$ determined from the stress-strain tests and dynamical modulii of elasticity $H$ and shear $G$ [9] as functions of the specimens moisture content are presented in Fig. 7.
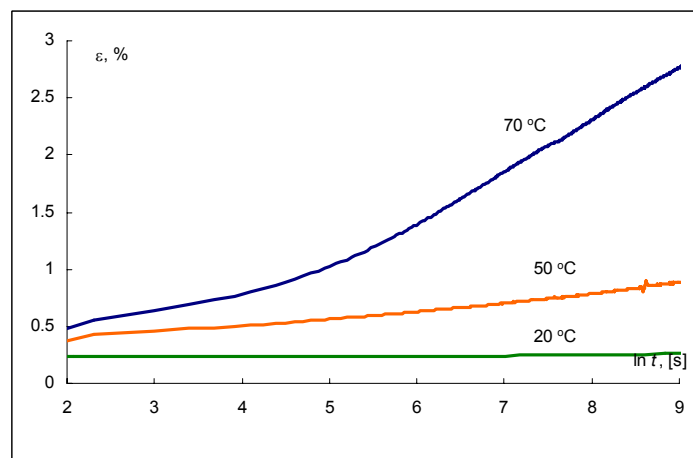
"**Fig. 7.** Elastic modulus $E$ (•) and dynamical modulii of elasticity $H$ (♦) and shear $G$ (■) as functions of the resin moisture content."

The elastic modulus decreases by about 10% with the growth of moisture content from 0 up to 1.86%. Note, that regardless of the investigation methods and differences in absolute values of the elastic modulii the effect of moisture is the same.

From series of short-term tensile creep and recovery tests it was determined that the resin elastic response is nonlinear, since the viscoelastic response is linear. The equation of Boltzmann—Volterra was used for the experimental data description. Nonlinear effects were taken into account as stress dependence of the instantaneous compliance.
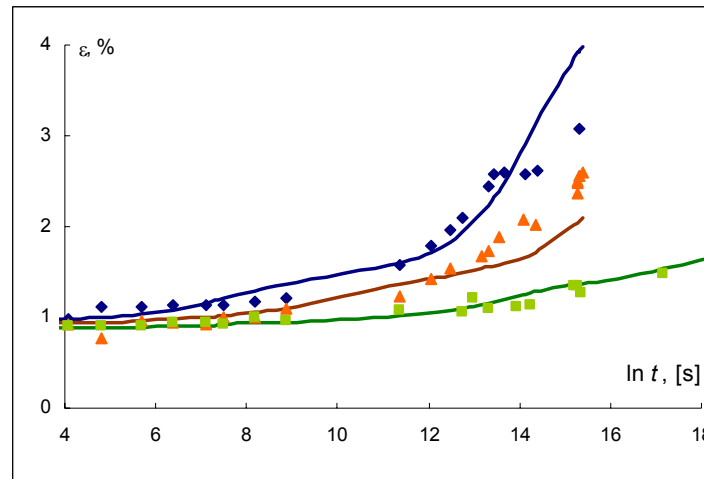
The significant effect of temperature on viscoelastic properties of the resin is shown in Fig. 8. Temperature growth on 20 $^{\circ}$C (from 50 up to 70 $^{\circ}$C) after 3 h loading leads to an increase of the creep strain value by appr. 22% ($\varepsilon_{cr} = 0.48$ and 2.3% for $T = 50$ and 70 $^{\circ}$C, respectively).

The method of time-temperature equivalencies (TTE) [10] is used for the description of the resin creep. The temperature effect on the creep strain is taken into account by the temperature reduction function upon passing to the reduced time. The time-temperature reduction function of the resin was obtained by shifting the experimental creep curves for elevated temperatures along the ln $t$ axis towards the basic curve for room temperature $T_0$. The obtained function can be described by the empirical expression $\ln a_T = 0.24(T\text{-}T_0)$ with an error of $\pm$ 3%.



"**Fig. 8.** Creep curves of the resin at different temperatures at $\sigma = 10$ MPa."

The effect of moisture was investigated in long-term creep tests on the resin specimens with different relative moisture contents at room temperature and stress $\sigma = 30$ MPa. The experimental creep data are presented in Fig. 9. Creep strain after 20 days for the maximal moistened material is about 2.28% while for a dry one only 0.43% i.e. 5.3 times less. This testifies to an essential activation of the relaxation processes in the moistened material. For description of the creep process in this case, principle of time-moisture equivalence (TME) [10] is used. The time-moisture reduction function determined by approximation can be described by empirical formula: $\ln a_w = 4.7(w-w_0)$ with an error of $\pm 1\%$.



"**Fig. 9.** Creep of the resin with moisture content: 0 (■), 0.82 (▲), and 1.42% (♦), $T = 20\ ^oC$, $\sigma = 30$ MPa."

The master curve was obtained by shifting of the experimental creep curves to a basic curve for the dry specimen with $w_0 = 0\%$. The preliminary forecast corresponds to a period, that is many times longer than duration of tests.

**Properties of the CFRP rebars**. The stiffness and strength of CFRP composites are mainly determined by properties of the fibbers. Carbon fibers have high longitudinal strength characteristics and, in turn, quite low characteristics in transversal direction [11]. This leads to some problems in performing the tension tests [8]. Quite linear stress-strain curves were obtained in tension tests, that confirms to the main contribution of the fibbers properties into the total deformation of the rebars and testifies to nonessential scattering in the strength characteristics of monofibbers and their possible avalanche breaking type. The evaluated strength exceeds the value 3 GPa. Average value of the rebars secant elastic modulus is $E_{11} = 130 \pm 16$ GPa (12%). The dynamical elasticity modulus [9] is $H_{11} = 138 \pm 3$ GPa.

Experimental evaluation of temperature effect on the rebars mechanical properties is considered in [8]. The obtained experimental results showed that temperature changes practically have no effect on character of stress-strain curves of the rebars in quite wide temperature range from 25 up to 120 $^oC$.

The effect of moisture was evaluated using the structural approach. The rule of mixture and compliances composition were applied for estimation of the rebars longitudinal and transversal elastic modulus, respectively. Taking into account characteristics of the carbon fibbers and resin the obtained values are $E_{11} = 130 \pm 32$ GPa and $E_{22} = 5.4 \pm 0.6$ GPa. It was shown above that the elastic modulus of the resin decreases by about 34 and 10% due to temperature and sorbed moisture action, respectively. Assuming that carbon fibers have a high resistance to the effect of environment, one can evaluate that $E_{11}$ is not sensitive to changes of the resin properties. $E_{22}$ value decreases for about 20 and 5% due to temperature

9

and moisture action, respectively. This reduction of elastic characteristic is quite essential and has to be taken into account for the prediction improving of deformational behaviour in service conditions.

Creep properties of the rebars in the longitudinal direction are feebly marked due to high stiffness and negligible contribution of the resin viscoelastic properties to the total deformability. Since taking into account high creep of the vinylester resin, it can be assumed that viscoelastic properties of the rebars also could play an essential role at another deformation types (bending or torsion, for example).

## 3. CONCLUSIONS

The results of experimental investigation of the vinylester resin sorption processes show that the dominant mechanism of moisture sorption is diffusion. Temperature dependencies of the resin diffusion coefficient and equilibrium moisture content are satisfactorily described by Arrhenius relationships. Non-Fickian sorption models were applied for improving the approximation of two-stage sorption. Structural approach was used for evaluation of the diffusive properties of the CFRP rebars. The ratio of diffusion coefficients in longitudinal and transversal directions determined experimentally and analytically differs for an order. Quasi three phase model is applied for description of the CFRP sorption. The model considers a composite consisted of two phases: resin and microplastic consisted of fibbers and fibber-resin interphase. Strength and elastic characteristics of the resin undergo considerable changes due to the action of the environmental factors. Temperature increase from 20 up to 70 $^\mathrm{o}$C leads to the strength decrease by 40% and ultimate strain increase by about 30%. Elastic modulus of the resin $E = 3.8$ GPa ($\pm 5\%$) decreases by 34% and 10% due to temperature and moisture action. Essential activation of relaxation processes is observed in creep tests of the resin. The effect of moisture and temperature on the CFRP rebars properties in direction of fibbers is not essential. Noticeable effect of environmental factors was evaluated for the transversal elastic modulus applying the structural approach. Temperature and moisture action leads to its value decrease for about 20 and 5%, respectively.

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