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INFLUENCE OF THE FILLER TYPES ON MECHANICAL PROPERTIES OF A HETEROGENEOUS MATERIAL

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Abstract

As a subject of research was chosen the epoxy resin Primer-204 as a matrix and different types of dioxide silica nanopowder «Aerosil» with various average size and specific surface area of particles. With increase of the concentration the Young modulus of heterogeneous material increases. So at a volume concentration of 0.5% increase in Young's modulus of a mixture of powders A-200 and A-300, A-380 was 4.4%, 3.8% and 2.3% respectively. For the effect of the size epoxy filler concentrations up to 1% have been identified due to small differences in the values of variables. The mathematical model of the two-phased heterogeneous mixture was constructed and the equations expressing the Young module of a mixture from mechanical characteristics and volume concentration of components were obtained, according to hypotheses of equality of stress and strain. Prediction of the Young module of a heterogeneous material based on epoxy resin with filler is possible by means of the received mathematical model of identical stresses up to this volume concentration.

Key words: *Nanocomposite; Polymer matrix composites; mechanical properties.*

1. INTRODUCTION

When a need in a material with a new combination of properties arises, it is not always that new polymers should be synthesized and their production, launched, because this way is very long, complicated, costly, and not necessarily leading to a success. Physical modification of already available polymers with other substances, whose function is to add mechanical strength to the modified material and make it less costly and possessing a special combination of filler-defined properties, offers an alternative strategy in solving the problem. It is therefore not surprising that, in recent years, in polymer science synthesis of polymer composite materials (PCMs) has become an urgent matter. Development of scientific background for obtaining such composite materials has allowed a substantial widening of PCM application area achieved using commercially available engineering polymers.

Thus, a promising strategy in synthesis of PCMs consists in obtaining, in some process sequence, a desired combination of two dissimilar phases, a filler and a matrix. Here, a number of additional factors involved in the interaction of polymer and filler molecules need to be taken into account:

The presence of a polymer layer with a lower mobility. Part of polymer molecules gets adsorbed on the filler solid surface to become immobile. This immobility spreads to some distance over the length of macromolecule thus decreasing its mobility. The closer the adsorbed- macromolecule segment of interest lies to the point of macromolecule attachment to the filler surface, the smaller is the total number of the degrees of freedom this segment possesses.

The elastic modulus and the hardness of filler particles are usually much greater than the elastic modulus and the hardness of typical polymers; so, fillers normally cannot withstand without fracture

large deformations like those withstood by polymers. Of course, substitution of part of polymer volume with hard particles reduces the capability of the whole composition to withstand deformations.

The filler particles hamper the growth of microcracks in the composite materials at particle sizes being smaller than some critical size. During deformation of the composite material, the particles act as sources of defects and cracks generated in the polymer. The width of cracks and the size of delaminated material fragments both vary in proportion to the size of disperse particles. If the particle size is smaller than some critical value, then the material suffers no fracture. Simultaneously, polymer delamination from the filler and microcrack formation require consumption of some energy applied to the sample. As a result of the dissipation of energy in the composition volume, the mechanical strength of the composite increases. If the size of filler particles is greater than the critical size, then introduction of such a filler into the polymer leads to generation of large cracks, thus causing a material fracture at lower loads as compared to the case of a material without filler.

The purpose of the present study was to obtain an experimental and theoretical dependence of PCM mechanical properties on the characteristic size of filler particles and filler concentration.

The object of the present study was Primer-204 epoxy resin modified with Aerosil silicon dioxide nanopowders.

In preparation of structural PCMs, the main purpose of the filling procedure is normally obtaining a reinforced polymer material with improved mechanical properties. The improvement is normally achieved through introduction of an additive with a high elastic modulus and a high ultimate strength.

2. MATERIALS AND PROCESSES

As the binder in the prepared mixture, Primer-204 epoxy resin was used. The epoxy resin was chosen as a two-component compound that could be filled with filler particles; this compound is often used as a composition suitable for producing self-leveling floors. The characteristics of Primer-204 epoxy resin are listed in Table 1.

Table 1. Description of the matrix

Composition	Modified epoxy resin, polyamine hardener, special additives
Density of mixture (at +20°C)	1.10 kg/l (according to State Standard 28513)
Viscosity of mixture	610 mPa*s (right after mixing (at +25°C)) 410 mPa*s (following 30 min (self-heating to +30°C)) 700 mPa*s (following 1 hour (strong self-heating))
Adhesive strength	not less than 2.5 N/mm2
Elasticity modulus according to State Standard 11262-80	750±50 mPa
Tensile strength according to State Standard 11262-80	25±5 mPa

Aerosil silicon dioxide powders, presenting reinforcement components, were used as fillers for the polymer material. Some characteristics of the powders are indicated in Table 2.

Table 2. Description of the filler

	A-200	A-300	A-380
Specific surface area, m2/g	200±25	300±30	380±30
Mean particle size, nm	13	9	7
SiO2 content, %	>99.8	>99.8	>99.8
Surface	hydrophilic	hydrophilic	hydrophilic

To epoxy resin, an Aerosil was added, and the resulting mixture was given an agitation treatment performed with the help of an ultrasonic disperser and lasting for five minutes. As a result, the mixture was heated to 60 °C and became homogeneous. The mass concentration of powders in the prepared mixtures was varied from 0 to 2 % at 0.2-% step. After cooling to room temperature, the epoxy resin containing a nanopowder was mixed together with amine hardener to be subsequently poured into moulds and put to tensile tests performed according to State Standard 11262-80. Following 24 hours, the samples were withdrawn from the moulds, and the top portion of each sample was removed by grinding. The specimens thus obtained were put to tensile tests performed at a fixed rate of deformation of 5 mm/min. As a result, curves of stress versus strain could be plotted, and the Young modulus and the ultimate stress of the mixture could be determined.

3. THEORETICAL TREATMENT

Equilibrium equations for the composite under uniaxial loading

To obtain the dependence of the elasticity moduli and Lame coefficients on the concentration for a multi-phase medium, we consider some volume τ occupied by a two-component heterogeneous material. Apparently, the volumes occupied by the two mixture components will sum to the volume of the whole mixture,

$\tau = \tau_1 + \tau_2$. We introduce the volume concentrations c_i:

$$c_1 = \frac{\tau_1}{\tau}; c_2 = \frac{\tau_2}{\tau}; c_1 + c_2 = 1$$

Then, for each of the materials the volume density can be represented as $\rho_1 = c_1 \cdot \rho_{11}^0; \rho_2 = c_2 \cdot \rho_{22}^0$, where ρ_{11}^0 and ρ_{22}^0 are the fixed densities of each of the components.

We express the strains in terms of displacements for the first component:

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$$\varepsilon_{xx}^{(1)}=\frac{\partial U^{(1)}}{\partial x} \qquad \varepsilon_{yz}^{(1)}=\frac{\partial W^{(1)}}{\partial y}+\frac{\partial V^{(1)}}{\partial z} \qquad 2\omega_x^{(1)}=\frac{\partial W^{(1)}}{\partial y}-\frac{\partial V^{(1)}}{\partial z}$$

$$\varepsilon_{yy}^{(1)}=\frac{\partial V^{(1)}}{\partial y} \qquad \varepsilon_{zx}^{(1)}=\frac{\partial U^{(1)}}{\partial z}+\frac{\partial W^{(1)}}{\partial x} \qquad 2\omega_y^{(1)}=\frac{\partial U^{(1)}}{\partial z}-\frac{\partial W^{(1)}}{\partial x}$$

$$\varepsilon_{zz}^{(1)}=\frac{\partial W^{(1)}}{\partial z} \qquad \varepsilon_{xy}^{(1)}=\frac{\partial V^{(1)}}{\partial x}+\frac{\partial U^{(1)}}{\partial y} \qquad 2\omega_z^{(1)}=\frac{\partial V^{(1)}}{\partial x}-\frac{\partial U^{(1)}}{\partial y}$$

In tensor notation, we have:

$$\varepsilon_{ij}^{(1)}=\frac{1}{2}\left(\frac{\partial U_i^{(1)}}{\partial x_j}-\frac{\partial U_j^{(1)}}{\partial x_i}\right)$$

Similarly, for the other component we obtain

$$\varepsilon_{ij}^{(2)}=\frac{1}{2}\left(\frac{\partial U_i^{(2)}}{\partial x_j}-\frac{\partial U_j^{(2)}}{\partial x_i}\right);\ \sigma_{ij}^{(2)}=\lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij}+2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)};\ \Delta^{(2)}=\varepsilon_{xx}^{(2)}+\varepsilon_{yy}^{(2)}+\varepsilon_{zz}^{(2)}$$

If all components in the material are isotropic, then the Hooke law can be written for each component as $\sigma_{ij}^{(1)}=\lambda_1\cdot\Delta^{(1)}\cdot\delta_{ij}+2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)};\ \Delta^{(1)}=\varepsilon_{xx}^{(1)}+\varepsilon_{yy}^{(1)}+\varepsilon_{zz}^{(1)}$, where μ is the shear modulus, and λ is the Lame constant.

We assume that the strains in each component are identical:

$$\varepsilon_{ij}^{(1)}=\varepsilon_{ij}^{(2)}$$

Then, we obtain an equation system

$$\begin{cases}\rho=c_1\rho_{11}^0+c_2\rho_{22}^0\\ \sigma_{ij}=c_1\sigma_{ij}^{(1)}+c_2\sigma_{ij}^{(2)}\\ \varepsilon_{ij}^{(1)}=\varepsilon_{ij}^{(2)}\\ \Delta=\varepsilon_{xx}+\varepsilon_{yy}+\varepsilon_{zz}\\ \sigma_{ij}^{(1)}=\lambda_1\cdot\Delta^{(1)}\cdot\delta_{ij}+2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)}\\ \sigma_{ij}^{(2)}=\lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij}+2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)}\end{cases}$$

We substitute the last two equations into the second equation:

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$$\begin{cases} \rho = c_1\rho_{11}^0 + c_2\rho_{22}^0 + c_3\rho_{33}^0 \\ \sigma_{ij} = c_1\lambda\left\langle {}_1\cdot\Delta^{(1)}\cdot\delta_{ij} + 2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)}\right\rangle + c_2\left\langle \lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij} + 2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)}\right\rangle \\ \varepsilon_{ij}^{(1)} = \varepsilon_{ij}^{(2)} \\ \Delta = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \\ \sigma_{ij}^{(1)} = \lambda_1\cdot\Delta^{(1)}\cdot\delta_{ij} + 2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)} \\ \sigma_{ij}^{(2)} = \lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij} + 2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)} \end{cases}$$

The resultant multi-component mixture should be isotropic and, hence, the Hooke law, i.e. the dependence of stress on strain, should have the form

$$\sigma_{ij} = \lambda\cdot\Delta\cdot\delta_{ij} + 2\cdot\mu\cdot\varepsilon_{ij}; \Delta = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$$

$$\begin{cases} \rho = c_1\rho_{11}^0 + c_2\rho_{22}^0 \\ \lambda\cdot\Delta\cdot\delta_{ij} + 2\cdot\mu\cdot\varepsilon_{ij} = c_1\lambda\left\langle {}_1\cdot\Delta^{(1)}\cdot\delta_{ij} + 2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)}\right\rangle + \\ + c_2\left\langle \lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij} + 2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)}\right\rangle \\ \varepsilon_{ij}^{(1)} = \varepsilon_{ij}^{(2)} \\ \Delta = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \\ \sigma_{ij}^{(1)} = \lambda_1\cdot\Delta^{(1)}\cdot\delta_{ij} + 2\cdot\mu_1\cdot\varepsilon_{ij}^{(1)} \\ \sigma_{ij}^{(2)} = \lambda_2\cdot\Delta^{(2)}\cdot\delta_{ij} + 2\cdot\mu_2\cdot\varepsilon_{ij}^{(2)} \end{cases}$$

Using the hypothesis of identical strains (the third equation in the system), we obtain:

$$\begin{aligned} \lambda &= c_1\lambda_1 + c_2\lambda_2 \\ \mu &= c_1\mu_1 + c_2\mu_2 \end{aligned}.$$

In terms of Lame constants, the Young modulus of an isotropic material can be written as $E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$.

Then, for the heterogeneous mixture formed by three components we have:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} = \frac{(\mu_1 c_1 + \mu_2 c_2)\left(3\left\langle c_1\lambda_1 + c_2\lambda_2\right\rangle + 2\left\langle c_1\mu_1 + c_2\mu_2\right\rangle\right)}{c_1\lambda_1 + c_2\lambda_2 + c_1\mu_1 + c_2\mu_2} =$$

$$= \frac{(\mu_1 c_1 + \mu_2 c_2)\left(3\left\langle c_1\lambda_1 + c_2\lambda_2\right\rangle + 2\left\langle c_1\mu_1 + c_2\mu_2\right\rangle\right)}{c_1(\lambda_1 + \mu_1) + c_2(\lambda_2 + \mu_2)}$$

The obtained formula can be used to represent the Young modulus as a function of volume concentrations involving Lame coefficients. The system of equilibrium equations can be solved using

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the hypothesis of identical stresses, $\sigma_{ij}^{(1)} = \sigma_{ij}^{(2)}$. The strains will be different in the three materials; yet, on introduction of the mean value, we obtain:

$$\rho = c_1\rho_{11}^0 + c_2\rho_{22}^0$$
$$\varepsilon_{ij} = c_1\varepsilon_{ij}^{(1)} + c_2\varepsilon_{ij}^{(2)}$$

The system can be conveniently solved using the converse Hooke law (dependence of stain on stress) for each of the components:

$$\varepsilon_{ij}^{(1)} = \frac{\sigma_{ij}^{(1)}}{2\mu_1} - \frac{\lambda_1\sigma_{ll}^{(1)}\delta_{ij}}{2\mu_1}$$
$$\varepsilon_{ij}^{(2)} = \frac{\sigma_{ij}^{(2)}}{2\mu_2} - \frac{\lambda_2\sigma_{ll}^{(2)}\delta_{ij}}{2\mu_2}$$

Then, the system with identical stresses will look as

$$\begin{cases} \sigma_{ij}^{(1)} = \sigma_{ij}^{(2)} \\ \varepsilon_{ij} = c_1\varepsilon_{ij}^{(1)} + c_2\varepsilon_{ij}^{(2)} \\ \varepsilon_{ij}^{(1)} = \dfrac{\sigma_{ij}^{(1)}}{2\mu_1} - \dfrac{\lambda_1\sigma_{ll}^{(1)}\delta_{ij}}{2\mu_1} \\ \varepsilon_{ij}^{(2)} = \dfrac{\sigma_{ij}^{(2)}}{2\mu_2} - \dfrac{\lambda_2\sigma_{ll}^{(2)}\delta_{ij}}{2\mu_2} \\ \rho = c_1\rho_{11}^0 + c_2\rho_{22}^0 \end{cases}$$

As the result of these equations, the Young modulus can be written as

$$E = \frac{\dfrac{\mu_1\mu_2}{c_1\mu_2 + c_2\mu_1}\left(3\left(c_1\lambda_1 + c_2\lambda_2\right) + 2\dfrac{\mu_1\mu_2}{c_1\mu_2 + c_2\mu_1}\right)}{c_1\lambda_1 + c_2\lambda_2 + \dfrac{\mu_1\mu_2}{c_1\mu_2 + c_2\mu_1}}$$

The derived formulas reproduce the Voigt and Reuss dependences. It is not surprising since the adopted assumptions of identical strains or displacements reproduced respectively the Voigt and Reuss hypotheses. In fact, here we have another derivation of the expression for the mechanical characteristics of mixture in terms of filler volume concentration. Plots of derived dependences are shown in fig. 1.

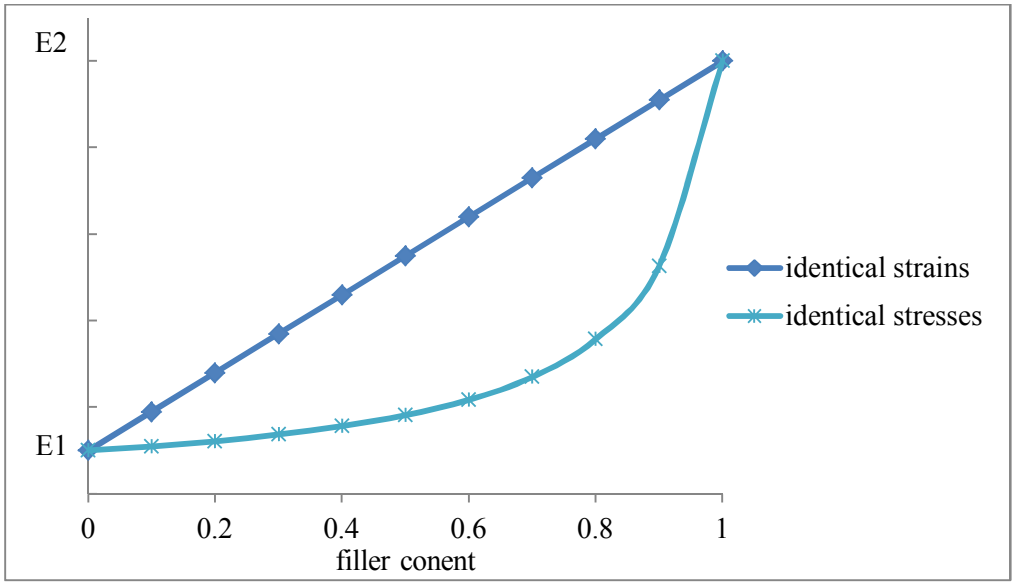

Fig. 1. Young's modulus of the filler concentration

Dependences are lines describing the change in Young's modulus of the mixture when the concentration of the components. If the modulus of elasticity E2 >> E1, change is a monotonic increase of mixture modulus from E1 to E2 from 0 to 100%. It can be seen that the hypothesis of equality of deformation gives higher estimates of the Young's modulus of the mixture.

4. COMPARISON OF THE RESULTS OF THEORETICAL AND EXPERIMENTAL APPROACHES

The experimental values of Young's modulus for different silica powders with different concentrations are presented in Table 3

Table 3. Experimental data of uniaxial tension

mass concentration	Young's modulus, MPa		
	Aerosil A-200	Aerosil A-300	Aerosil A-380
0	664±25	660±16	660±23
0,002	669±38	665±67	661±47
0,004	672±42	670±52	665±19
0,006	681±36	675±42	669±67
0,008	689±54	680±28	671±53
0,01	694±73	685±42	675±89
0,012	701±68	691±61	-
0,014	709±75	702±38	-
0,016	719±56	715±68	693±67
0,018		727±85	-
0,02		738±75	-

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Table 2 shows, the increase in Young's modulus of a mixture of all kinds of powders occurs with increasing concentration of filler. So at a volume concentration of 0.5% increase in Young's modulus of a mixture of powders A-200 and A-300, A-380 was 4.4%, 3.8% and 2.3% respectively. A further increase in the filler concentration is difficult because of a sharp increase in the viscosity of the mixture is not cured, difficulties with uniform dispersion of the particles and curing. Adding more filler is only possible when using solvents.

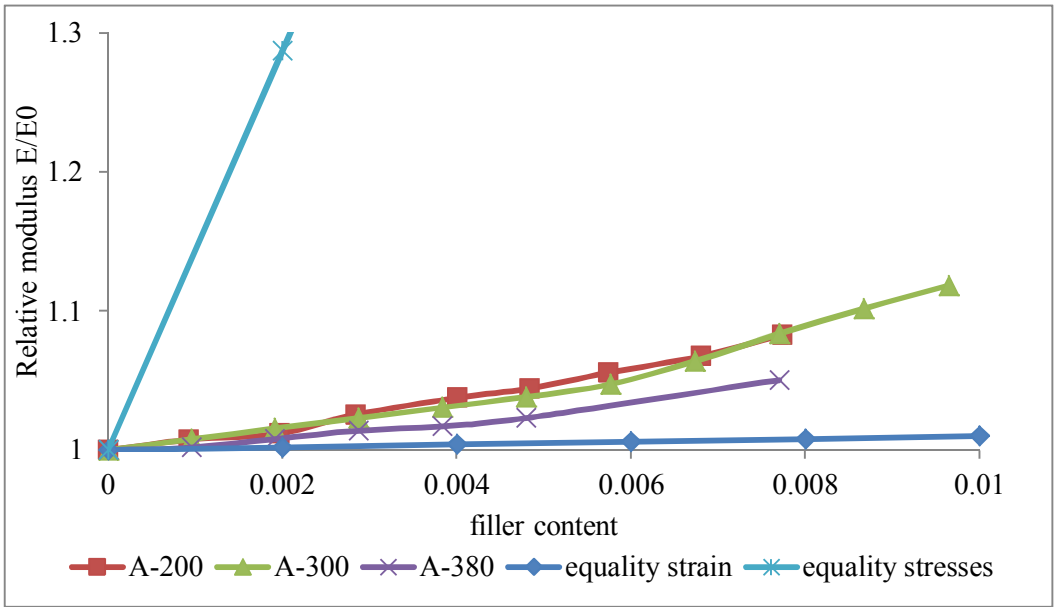

Fig.2 Relative Young's modulus of the volume filler concentration

For different types of filler observed the same dependence of Young's modulus. For the effect of the size epoxy filler concentrations up to 1% have been identified due to small differences in the values of variables. Thus, under the given concentrations for the amplification effect of the matrix and filler were found

To construct a theoretical one and comparing data requires information about the density of the powder and its mechanical properties (Young's modulus, Lame coefficients). Powder density equated to the density of quartz 2200 kg/m3, Young's modulus E = 100 GPa, Poisson's ratio ν = 0,3. Volume concentration converted through mass as follows:

$$c_1 = \frac{k_1 \rho_2}{\rho_1 + k_1 (\rho_2 - \rho_1)}$$

Experimental data showed that the model of stresses equality may be used to predict the modulus, E, of a material containing silica nanoparticles as a function of the modulus,E1, of the particles, and of the modulus, E2, of the polymer containing no silica particles.

5. CONCLUSIONS

As a result of the performed study, we have developed a process for obtaining a heterogeneous material based on disperse-filled epoxy-resin binders. Parameters of the processes enabling the obtaining of composite materials with a nanopowder uniformly distributed throughout the matrix have been identified. A comprehensive analysis of the effect due to nano-additives has allowed us to substantially improve the elastic-strength characteristics of the epoxy-resin composites. In terms of examined parameters, composites containing Aerosil-200 nanopowder were found to be the best ones. It was also found that, with decreasing the filler specific surface area, the Young modulus of the disperse-filled material increases in magnitude.

Further decrease in the filler specific surface area leads to a decreased rate of growth of elasticity modulus.

The proposed mathematical model for heterogeneous medium, yielding an expression for the Young modulus of mixture versus mechanical characteristics and volume concentrations of mixture components under an assumption of identical strains and stresses, proved to be in a qualitative agreement with the behavior exhibited by the filled polymer in the examined range of component concentrations.

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