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SOBRE AS PROPRIEDADES DISSIPATIVAS EFICAZES DA CAMADA WHISKERIZADA EM COMPÓSITOS DE FIBRA MODIFICADOS COM FIBRAS WHISKERIZADAS

EFFECTIVE DISSIPATIVE PROPERTIES OF A WHISKERED LAYER IN MODIFIED FIBROUS COMPOSITES WITH WHISKERED FIBRES

ОБ ЭФФЕКТИВНЫХ ДИССИПАТИВНЫХ СВОЙСТВАХ ВИСКЕРИЗОВАННОГО СЛОЯ В МОДИФИЦИРОВАННЫХ ВОЛОКНИСТЫХ КОМПОЗИТАХ С ВИСКЕРИЗОВАННЫМИ ВОЛОКНАМИ

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RESUMO

Sabe-se que as propriedades mecânicas dos compósitos fibrosos são controladas pelas condições de contato entre a fibra e a matriz. Nesse sentido, grandes esforços dos engenheiros mecânicos são direcionados para o desenvolvimento de diversas técnicas para melhorar a qualidade da interface. Os mais comuns são: modificação da superfície da fibra, melhoria das interações químicas ou adição de uma terceira fase (camada interfacial) entre a fibra e a matriz. No presente trabalho, pretendemos examinar as propriedades dinâmicas efetivas da camada whiskerizada de fibras em compósitos modificados levando em consideração as características estruturais da camada interfacial – sua espessura – comprimento de whiskers, conteúdo volumétrico de whiskers e suas propriedades mecânicas. Avaliamos o desempenho dinâmico da camada whiskerizada ao redor da fibra base em compósitos modificados. A camada whiskerizada é considerada um compósito fibroso, que é formado por whiskers nanométricos crescidos na superfície e uma determinada matriz. Um aglutinante de epóxi ou um polímero viscoelástico é considerado a matriz. Foi utilizado um modelo aproximado, segundo o qual as características efetivas da camada whiskerizada foram modeladas e determinadas como as propriedades de um sistema fibroso isotrópico transversal com o eixo de isotropia coincidindo com os nanowiskers na camada whiskerizada. Uma característica da camada whiskerizada é que a densidade dos whiskers muda com a distância a partir da superfície da fibra e, portanto, depende do comprimento dos nanowiskers (espessura da camada interfacial). Acontece, neste caso, que o volume da matriz na camada whiskerizada é muito significativo mesmo na densidade máxima de nanowhiskers crescidos na superfície da fibra e para camadas interfaciais suficientemente finas.

Palavras-chave: *compósito de fibra difusa, nanofibras, aglutinante de epóxi, propriedades de amortecimento.*

ABSTRACT

It is known that the mechanical properties of fiber-reinforced composites are controlled by the conditions of contact between the fiber and the matrix. In this regard, great efforts of mechanics are directed to developing various techniques to improve the quality of the interface. The most common are: modification of the fiber surface, improvement of chemical interactions, or the addition of a third phase (interfacial layer) between the fiber and the matrix. The most common are: modification of the fiber surface, improvement of chemical interactions, or a third phase (interfacial layer) between the fiber and the matrix. In this study, the authors aim to examine the effective dynamic properties of a whiskered layer of fibers in modified composites, taking into account the structural characteristics of the interfacial layer – its thickness – length of whiskers, volumetric content of whiskers, and their

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mechanical properties. The dynamic performance of the whiskered layer surrounding the base fiber in modified composites was estimated. The whiskered layer is considered a fibrous composite formed by nanoscale whiskers grown on the surface and a matrix. An epoxy binder or a viscoelastic polymer is considered as a matrix. An approximate model was used. The effective characteristics of the whiskered layer were modeled and determined as the properties of a transversally isotropic fibrous system with the isotropy axis coinciding with nanowhiskers in the whiskered layer. A feature of the whiskered layer is that the density of whiskers varies with distance from the fiber surface. Therefore, it depends on the length of the nanowhiskers (the thickness of the interfacial layer). In this case, it turns out that the bulk for the matrix in the whiskered layer, even at the maximum density of nanowhiskers grown on the fiber surface and for sufficiently thin interfacial layers, is very significant.

Keywords: *fuzzy fiber composite, nanofibers, epoxy binder, damping properties.*

АННОТАЦИЯ

Известно, что механические свойства волокнистых композитов контролируются условиями контакта между волокном и матрицей. В связи с этим большие усилия механиков направляются на разработку различных методик для повышения качества интерфейса. Наиболее распространенными являются: модификация поверхности волокна, улучшение химических взаимодействий, либо добавление третьей фазы (межфазного слоя) между волокном и матрицей. В этой работе авторами были изучены эффективные динамические свойства вискеризованного слоя волокон в модифицированных композитах с учетом структурных характеристик межфазного слоя – его толщины – длины вискерсов, объемного содержания вискерсов, их механических свойств. Авторами были оценены динамические характеристики вискеризованного слоя, окружающего базовое волокно в модифицированных композитах. Вискеризованный слой рассматривается как волокнистый композит, который образован наноразмерными вискерсами, выращенными на поверхности и некоторой матрицей. В качестве матрицы рассматривалось эпоксидное связующее или вязкоупругий полимер. Использовалась приближенная модель, согласно которой эффективные характеристики вискеризованного слоя моделировались и определялись как свойства трансверсально изотропной волокнистой системы с осью изотропии, совпадающей с нановискерсами в вискеризованном слое. Особенностью вискеризованного слоя является то, что плотность вискерсов меняется с расстоянием от поверхности волокна, и, следовательно, зависит от длины нановискерсов (толщины межфазного слоя). Оказывается, при этом, что объемная часть для матрицы в вискеризованном слое даже при максимальной плотности нановискерсов, выращенных на поверхности волокна и для достаточно тонких межфазных слоев, весьма значительна.

Ключевые слова: *Фуззи-волокнистый композит, нановолокна, эпоксидное связующее, демпфирующие свойства.*

1. INTRODUCTION:

1.1. The main features of fibrous composites

It is known that the mechanical properties of fiber composites are controlled by the conditions of contact between the fiber and the matrix. In this regard, great efforts of mechanics are directed to developing various techniques to improve the quality of the interface. The most common are: modification of the fiber surface, improvement of chemical interactions, or the addition of a third phase (interfacial layer) between the fiber and the matrix (Kim and Mai, 1998; Lin *et al.*, 2009). The ideas behind these techniques are to improve the interfacial adhesion properties and to increase the fiber surface area for more efficient transfer of loads between the fibers and the matrix, and further improve composite properties. At present, technologies for obtaining modern fiber composites are actively developed, in which special microstructures containing nanofibers (whiskers) – nanowires are grown to increase the shear properties on the fiber surface (Lin *et al.*, 2009; Galan *et al.*, 2011) and carbon nanotubes (“fuzzy” fibers) (Garcia *et al.*, 2008; Sharma and Lakkad, 2010).

Among the many types of whisker-reinforced composites, it is possible to distinguish fiber composites, including CNT- whiskered structures (carbon fiber (T-650-5, whiskers-CNT, epoxy matrix), fiber composites including nanowires as whisker-reinforced systems (carbon fiber IM7, additional phase – zinc oxide). There are fibrous composites, based on aluminum, reinforced with continuous fibers Al_2O_3, whiskered by Mullites. Nanowires of cadmium telluride (CdTe), whiskered by nanowires of silicon oxide (SiO_2), have been created (Wang *et al.*, 2004). This structure has three components (Sealy, 2004; Guz *et al.*, 2008): 1) solid CdTe nanowire; 2) SiO_2 coating, and 3) SiO_2 nanowire. Experimental

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strength analysis has shown that for composite materials with whiskered fibers, higher ultimate strength and shear stiffness are manifested in comparison with standard composites that do not have an additional microstructure on the fiber surface (Goan and Prosen, 1969; Garcia *et al.*, 2008; Galan *et al.*, 2011; Agnihotri *et al.*, 2011), as well as significantly increases the compressive strength of the composite in the direction of growing nanotubes (Sharma and Lakkad, 2010). Tests show that by varying the diameter and length of the nanowire, the shearing strength of the interface can be increased up to 228%, while the average shear modulus increases by 37.5% (Lin *et al.*, 2009).

Depending on the thickness of the interfacial layer, the degree of its substitution for the epoxy matrix can be very significant. As shown by preliminary studies of composites, their dynamic characteristics significantly depend on the relative stiffness characteristics of the phases. Consequently, the influence of the interfacial layer on both the mechanical and dynamic properties can be significant, especially if to take into account that the stiffness characteristics of the microstructure of the interfacial layer can vary within wide limits.

In the present work, the authors aim to examine the effective dynamic properties of a whiskered layer of fibers in modified composites considering the structural characteristics of the interfacial layer – its thickness – length of whiskers, volumetric content of whiskers, and their mechanical properties.

1.2. Theoretical overview

Composite materials based on functional fibers (Galan *et al.*, 2011) are called combined composite materials. Different properties of composites can be simultaneously improved for them: strength, stiffness, damping, fatigue, and electrical and thermal conductivity (Gibson, 2010). Initially, to simulate such composites, a modified matrix model was used (Tarnopolskij *et al.*, 1987), which did not fundamentally differ from the calculated models of elastic characteristics of materials, and did not allow taking into account (except for the volume fraction of whiskers) the geometric characteristics (length and diameter) and density of whiskers in the composite. There are currently several analytical models to consider the effect of whiskers characteristics on the effective mechanical properties of fiber composites. In papers (Guz *et al.*, 2008; Guz *et al.*, 2009; Guz *et al.*, 2013), using the complex potential method, the effect of the density of whiskers on the effective elastic properties of a carbon fiber composite with four layers – a base fiber, a coating, a whiskered interphase layer, and a matrix.

The Mori-Tanaka method was used to simulate the properties of a fuzzy fiber composite (Kundawal and Ray, 2011). The same composite system was investigated in (Chatzigeorgiou *et al.*, 2012) using methods of combining two phases and three phases. In (Lurie and Minhat, 2014), based on the three-phase method, a method was proposed for studying the effective properties of multifunctional composites, which simultaneously considers the effect of density, diameter, length, volume fraction, and properties of whiskers in the interphase layer. This method was investigated in studies where it was shown that depending on the type of loading, the strength of whisker-reinforced composites with an interfacial layer can be controlled either by the strength of the fiber or by the strength of the whisked interfacial layer (Lurie *et al.*, 2018). Later in (Lurie *et al.*, 2019), an analytical method was proposed for assessing the strength of modified whisker-reinforced composites, which, depending on the type of loading, allows taking into account the geometric and physical characteristics of all elements of the composite structure (fibers, whiskers, matrices).

It was found that the whisker-reinforced interphase layer increases not only the transverse strength and rigidity but also the damping characteristics and electrical conductivity of composites (Garcia *et al.*, 2008). However, at the moment, there are practically no theoretical studies of the damping characteristics of multifunctional fiber composites, despite the intensive study of the dissipative properties of composites (Chandra *et al.*, 1999; Gusev and Lurie, 2009; Fisher and Brinson, 2011). In the aerospace industry, the requirement for high vibrational damping and high strength/stiffness materials now seems to be mandatory since more structural parts of aircraft are being designed with reinforced polymer-matrix composite materials. Several “traditional” design optimization concepts and materials were proposed to enhance the damping properties of composites at the micromechanical or macromechanical level (Finegan and Gibson, 1999; Chandra *et al.*, 2019). With this kind of optimization, a remarkable high loss amplification effect can be observed. A hybrid concept of viscoelastic and composite material to design composites with a good combination of high damping and high stiffness properties is elaborated in (Lakes, 2003; Wei and Huang, 2004;

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Fisher and Brinson, 2011; Meaud *et al.*, 2013). Obtained results revealed that there is a trade-off between its stiffness and damping properties. Finding the optimal balance of properties in the work (Gusev and Lurie, 2009) examined the effect of thickness of the viscoelastic coating layer surrounding spherical inclusions embedded in the epoxy matrix system. It is found that at an extremely thin coating layer of lossy material, the effective shear loss modulus of the composite increases substantially. Based on the paper (Gusev and Lurie, 2009), it can be concluded that high damping and high stiffness composite structure might be attainable due to the presence of high shearing damping mechanism in lossy material (Gusev and Lurie, 2009; Meaud *et al.*, 2013).

In papers (Lurie *et al.*, 2018) for the first time, the dynamic properties of modified fiber composites containing fibers with a whiskered layer were investigated. It was assumed that the fiber microstructure of the whiskered layer is elastic, and the damping properties of the composite as a whole are related to the viscoelastic properties of the matrix. It is shown that the remarkable loss enhancement mechanism works in materials with particle morphology when the effective loss properties of the composite can exceed the loss modulus of the pure matrix by more than 20 times.

2. MATERIALS AND METHODS:

The study investigated the dissipative properties of a whiskerized layer in modified fiber composites with whiskerized fibers based on mathematical analysis, synthesis, assessment of dynamic composites, and modeling (Tarnopolskij et al., 1987).

The case of an epoxy matrix corresponds to a modified fiber composite with whiskerized fibers, in which an epoxy matrix provides the solidity. In the future, the damping properties of the whiskerised layer are investigated depending on the volumetric content of the matrix in this layer V. In this case, the volumetric content of whiskers is equal to (1-V). It was assumed that the minimum volumetric content of the matrix in the whiskerised layer, in reality, does not exceed 0.3. In this case, the epoxy binder has viscoelastic characteristics. Cases in which the viscoelastic layer and nanowhiskers form a whiskerized coating of the base fibers correspond to special modifications of the fiber composite, associated with an attempt to improve the dissipative properties of the modified composite. The idea of using a viscoelastic polymer in a whiskerized layer to increase the modulus of losses in a modified composite is based on research (Gusev and Lurie, 2009), showing that ultra-thin viscoelastic fiber coatings make it possible to obtain fiber composites with extremely high damping properties while maintaining high stiffness characteristics.

To study a composite with inclusions containing viscoelastic coatings and with high parameter b/a, b/a>>1, it is necessary to go through a number of stages:

1 To estimate the optimal thickness of the viscoelastic layer providing the maximum effective damping properties of the composite, it is enough to consider a lamellar media with the volume content of a viscoelastic polymer V and find the volume content of a viscoelastic polymer corresponding to the maximum effective shear loss modulus. The authiors consider Reuss formula discussed before for the effective complex shear modulus (Equation 1), where μ_1* and µ μ_2* are complex-valued shear moduli of the two layers respectively, and V is the volume fraction of the second layer. Suppose now that the first layer is stiff and nonlossy with a shear modulus of µ1=b while the second layer weak and lossy with Equation 2, where a, b, and η are real-valued parameters. It is easy to see that the effective shear modulus goes through a maximum, reaching values orders of magnitude larger than that of the lossy layer. By analyzing the asymptotic behavior for $a/b \to 0$, we can see that the volume fraction of the matrix which provides the optimal value of the thickness of the viscoelastic coating is given by Equation 3;

2. Direct numerical estimates indicate that this statement is also true for fibrous composites with fibers containing viscoelastic coatings (Lakes, 2003).

3. The amplitude of the effective loss modulus of the lamella composites is proportional to the value of the modulus of the elastic phase of the lamella-type two-phase composite, μ_1* = *b and* proportional to viscosity characteristics η (Equation 4). Using Equation 1, t is possible to immediately find the equation for the maximum value of shear loss modulus (Equation 4). The amplitude of the effective loss modulus of the lamella composites (Equation 4) is proportional to the value of the modulus of the elastic phase of the lamella-type two-phase composite, μ_1* = *b and* proportional to viscosity characteristics η.

4. The dynamic performance of the whiskered layer surrounding the base fiber in modified composites was evaluated. The

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whiskered layer was considered to be a fibrous composite formed by nanoscale whiskers grown on the surface and some matrix. The properties of polymeric materials depend on the choice of the initial components and their ratio, the interaction between them, the method and technological conditions for manufacturing the product (pressure, temperature, time), additional treatment of the product, and a number of other factors. An epoxy binder or a viscoelastic polymer was considered as a matrix. An approximate model was used. The effective characteristics of the whiskered layer were modeled and determined as the properties of a transversely isotropic fibrous system with an isotropy axis coinciding with nanowhiskers in the whiskered layer.

5. The interfacial layer characteristics were investigated separately as a transversely isotropic fibrous material with an isotropic plane perpendicular to the nanofibers. The effective properties of the interfacial layer, determined from this preliminary consideration, were subsequently used to evaluate the effective properties of the modified fiber composite as a whole. In the general case, for all phases of the modified composite, a cylindrical coordinate system was used for an orthotropic material with constitutive relations connecting the stress vector (Equation 5) and the strain vector (Equation 6) through the tensor of elastic moduli of the sixth rank (Equations 7-9).

The lower indices of r θ, z in the stiffness tensors were replaced by indices 1, 2, and 3, respectively. The upper bracketed right index represents the i-th layer, for example, for fiber i = 1, for coating layer i = 2, for matrix i = 3, and for the effective medium i = 4. For isotropic layers (i = 1,2,3), the stiffness constants in Equations 7-9 have these typical relations (Sealy, 2004). The effective properties of the viscous layer were found with the use of the generalized self-consistent (GSC) method for the representative volume element (RVE) of whiskered interphase layer. To implement the GSC method, it was required to determine the pre-stress-strain state of the basic solutions system for canonical cylindrical domains in analytical form.

The statement of the boundary problems for the bases strain-stress states solutions were formulated using the constitutive Equation 3, Cauchy's relations for deformations in the cylindrical coordinates, and the equilibrium equations and the specific boundary conditions. The solution used in the generalized self-consistent method was based on the fundamental original result of Eshelby (Eshelby, 1956) where for a two-phase composite, the difference in elastic energy between medium with inclusion U^{RVE} and medium without the inclusion U^0 can be written as (Equation 10), where U' is the surface energy interaction between inclusion and matrix (Equation 11). However, this original approach was only applicable to a composite with a dilute concentration of inclusions. To solve for non-dilute solution and search for the correct estimation of transverse shear modulus that lies within the Hashin-Shtrikman bounds, the study (Christensen and Lo, 1979; Christensen, 2005) developed a self-consistent in which the initial two-phase composite was fictitiously embedded in an equivalent effective medium. As mentioned earlier, such a medium has its unknown properties the same as the unknown effective properties of the homogenized composite. This model assumed that the elastic energies of the medium with and without inclusions were identical. Mathematically this condition with the use of (Equation 10) was written as follows (Equation 12), where U' is the increment of energy in a unit cell of matrix material containing the inclusion; S is the contact surface between matrix and effective medium; σ_{ij}^1, u_i^1 are taken to be the stress tensor and displacement vector components at the contact surface that are found from the contact problem; and σ_{ij}^0, u_i^0 are the stress tensor and displacement. Eshelby's integral relation (Equation 12) always solves the problem of determining the effective modulus.

Vector components on the contact surface, which are related to the conditions of the problem at infinity. For example, to find an axial shear modulus, it was necessary to consider the fibers composite under shear homogeneous loading. For this case, at infinity, displacement $2\varepsilon_0 r\cos\theta$ was applied. It was easy to prove that the only admissible displacement field under this loading condition can be found by means of Equation 13, and admissible stress fields for every phase can be written as (Equations 14; 15). The coefficient $D_2^{(1)}$ is equal to zero to avoid singularity, while the coefficient $D_1^{(4)}$ is equal to $2\varepsilon_0$ in satisfying the boundary condition applied at infinity. All unknown coefficients and one unknown effective property $\mu_{23}^{(4)}$ in Equations 14, 15 can now be solved with the use of the displacement and stress continuity conditions at contact boundaries (Equation 16). According to the Eshelby integral equation (Equation 17): $D_2^{(4)}$ equals zero. Specifically, the axial shear modulus $\mu_{23}^{(4)} = \mu_{23}^{eff}$ was found by analyzing the stress continuity condition at R_3, which leads to Equation 18.

The problem of determining the entire system of effective elastic moduli was solved similarly. The two-phase method based on the

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polydisperse model (Christensen, 2005; Chatzigeorgiou *et al.*, 2012) provided virtually the same results as the self-consistent three-phase method developed in this study to determine the effective longitudinal Young's modulus, longitudinal shear modulus, bulk modulus of compression, and Poisson's ratio. Such a coincidence of the results in the methods of two and three phases was already noted earlier in (Hashin, 1990). On the other hand, the two-phase method provides only upper and lower limits for the effective transverse shear modulus. It is not suitable for obtaining refined estimates of this elastic modulus. Therefore, the three-phase method was used to solve the problem of determining the transverse shear modulus. Moreover, as demonstrated in (Lurie and Minhat, 2014), the self-consistent three-phase method estimates all elastic moduli of the considered systems for modified composites.

4. RESULTS AND DISCUSSION:

4.1. Approximate estimation of the effective damping properties of composites with interlayers of viscoelastic polymers

Christensen and Lo (1979) provide a detailed general procedure for the self-consistent method of many Eshelby phases in determining the effective properties of a multiphase composite – a whisker-reinforced fiber composite (N ≥ 3), which has orthotropic phases corresponding to the base fiber, a whiskered interphase layer, an epoxy matrix. To estimate the five effective moduli of fiber composites in a cylindrical coordinate system, two statements are considered – in the isotropy plane (orthogonal to the fiber axis) and the plane perpendicular to it, i.e., in the direction of the fiber axis. The effective compression modulus and transverse shear modulus are determined, respectively, from solving uniform tension-compression problems across the fibers and pure shear in the transverse plane. The effective longitudinal modulus is determined by solving the problem of pure shear along the fibers. The effective longitudinal Young's modulus and Poisson's ratio in the direction of the fibers are determined by solving the problem of uniaxial tension.

In this work, the simple problem of the lamella-type composite was considered, where two types of loads can be implemented separately by shear stresses and normal transversal stresses. The effective complex shear and transverse Young's moduli can be determined using Reuss estimation with the viscoelastic correspondence principle. Thus, their effective complex moduli can be written as follows (Equations 19; 20). Where *V* is the volume fraction of the second phase; μ_1^* and μ_2^* are the complex shear moduli of the first and second phase, respectively, and E_1^* and E_2^* are their transverse Young's moduli, respectively. For the shear case, the first phase is considered as an elastic material with $\mu_1^* = b$, and the second phase is a polymeric material with Equation 21. In what follows, composites containing thin layers of viscoelastic polymers will be considered, one of the features of which is greater than the value of the parameter b/a. The behavior of the considered composite material under external harmonic strain (Equation 22) is studied: in the infinity with a given angular frequency ω, ε_0 is the amplitude of harmonic strain applied to a viscoelastic continuum.

Then in the steady-state, the system stress is also harmonic (Equation 23). At specified cyclic frequency, the typical complex modulus is defined by the real part μ' representing the storage modulus and the imaginary part representing the loss modulus of the material. The effective complex modulus is defined as Equation 24 and the effective loss factor as Equation 25, related to the dampening of a material. The following statement has a place (Gusev and Lurie, 2009). The following features of the considered composites can be formulated (Gusev and Lurie, 2009). First, the shear and bulk moduli are a similar dependence, but with a different magnification factor at the maximum. Second, it is important that for the materials under consideration, the bulk modulus magnification factor is significantly lower than the shear modulus, and the maximum is implemented at higher than for shear volumetric contents of a viscous polymer. Third, it can be concluded that the abnormally high effective damping properties of a composite with simultaneously high effective mechanical properties are realized for the second peak corresponding to the shear mode.

Figure 1, demonstrates the benefit of viscoelastic polymers at T_g (viscous polymer (at T_g), a_v = 0.01 GPa and η_v = 1) when compared to solid polymer below T_g (solid polymer (below T_g), a_m = 1 GPa and η_m = 0.02) for the following parameters of elastic phases: the shear modulus of elastic phase, *b* = 30 GPa, on the figures (a), (b) and the shear modulus of elastic phase, *b* = 51.85 GPa, on the figures (c) and (d). It is easy to see that the curves are shown in Figures 1 (a), and 1 (c) fully correspond to the stated statement. The use of an epoxy matrix instead of a viscoelastic polymer leads to such low effective dissipative

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properties of the system under consideration in the given figures 1 (a), 1 (c), on the accepted scales, the curves corresponding to them coincided with the abscissa axis.

It can be seen that the effective shear loss modulus at a very thin layer of viscoelastic material significantly exceeds the effective shear loss modulus of solid polymer-matrix (η_m = 0.02) almost by 300 times and its solid polymer composite by 30 times. For the composite with the epoxy matrix and with very small damping properties η =0.005, the maximum of the effective shear loss modulus of composite realizes for thin enough layer of epoxy matrix V=0.1 and exceeds the effective shear loss modulus of an epoxy matrix (η_m = 0.005) almost by 5 times. On the other hand, using the solid polymer (below T_g) and the epoxy matrix leads to composites with higher effective storage modulus (Figure 1 (b)).

4.2. Modelling the effective dissipative properties of layered systems and fiber modified composites

The author consider two examples of fiber composites for which the effective properties were calculated using the self-consistent four-phase method (fiber, viscoelastic polymer coating, matrix, and effective medium). In the first case, a unidirectional lamina was considered, which consists of a typical epoxy matrix reinforced with glass fibers coated with a viscous polymer coating (Table 1). The results of the computations on the imaginary part of the effective axial (a) and transversal shear (b) moduli are given in Figure 2.

The curves presented in Figure 2 show that the maximum values corresponding to the maximum values of the loss moduli correspond to the approximate estimates given by Equations 3, and 4. For very thin viscoelastic coatings, a second peak is observed in the shear loss modulus, which is extremely attractive for obtaining composites with high mechanical and, at the same time, abnormally high damping properties. It was shown that this property is also transferred to layered composites obtained from monolayers of a fiber composite with viscoelastic coatings. In the second case, a unidirectional composite lamina of whiskered fiber was investigated that consists of IM7 carbon fibers coated with ZnO NWs embedded in typical epoxy polymer-matrix material. The properties of these materials are summarised in Table 2.

Here, first, the general dynamic behaviors of whiskered fiber composite based on a specific configuration of whiskered interphase layer were investigated. In this numerical example, the base fiber of IM7 carbon fiber has a diameter of 5.2 μm, and the diameter and length of ZnO NW is 50 nm and 500 nm, respectively. The surface of the fiber is fully coated with NWs (100% density), and the volume fraction of NWs in whiskered interphase coating is 0.72. The authors investigated the effect of nanofiber's length on the effective dynamic properties of whiskered fiber composite with four values of fiber volume fraction Vf, which are 10%, 25%, 40%, and 50%. The diameter of base fiber and nanowires are 5.2 μm and 20 nm, respectively. The surfaces of fibers are fully coated with nanowires (100% density). The results of investigations of the axial and transversal shear moduli are illustrated in Figure 3. Curves in Figure 3 demonstrate the possibility of obtaining modified composites with sufficiently high damping properties. However, these properties are not so great in comparison with the case of viscoelastic polymer coatings. This result is quite understandable since the damping properties are associated exclusively with the viscous properties of the epoxy matrix. Even approximate estimates based on Equations 3, and 4 show that in the case of an epoxy matrix, the amplitude coefficient in Equation 4 is approximately two orders of magnitude lower than for the case of a viscoelastic polymer.

Note also that the properties of the second peak in the loss modulus for the effective transverse shear modulus are lost. Nevertheless, the curves shown in Figure 3 show that the effective damping properties of modified composites associated with longitudinal and transverse shears in the fiber system can be significant even if they are associated only with the viscous properties of the epoxy matrix. Figure 3 that all loss moduli are enhanced with increasing the length of the interphase layer for damping characteristics of whiskered fiber composite material. It is easy to see that the modified composite increases the loss moduli compared to the classical fiber composite. So, at 50% fiber volume fraction, the axial and transverse Young's loss moduli, axial, and transverse shear loss moduli are improved compared to classic fiber composites by 105%, 23%, respectively. The following question arises. IIs it possible to significantly improve the dissipative properties of the modified composites if to consider the structural features of the interphase layer? In this regard, the authors will approximately estimate the effective characteristics of the interfacial layer damping and qualitatively its effect on the effective properties of the modified composite, since the previous estimates found in the literature were given without taking this factor into account. The

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importance of this study is because, for modified composites, the volume fraction of the whiskered layer with its dissipative properties can be significant and may exceed the volume fraction of the epoxy binder, which ensures the solidity of the whiskered fibers.

4.3. Damping properties of the whiskered layer

Various advanced fibers are used to improve the quality of composite materials. Therefore, modified fiber composites constitute the object of this study. Tables 1 and 2 demonstrate the properties of fiber composites. Table 3 demonstrates the characteristics of the whiskerized layer formed by ZnO nanowhiskers. Consider the whiskered layer due to the presence of nanostructures surrounding the surface of the fiber, a so-called whiskered interphase layer is formed between fiber and matrix when such a fiber system is embedded in the matrix material. Figure 4 shows that the whiskered interphase layer is a nanocomposite system, consisting of nanofibers and matrix material.

To estimate the effective properties of whiskered interphase layer, an approximate geometrical model was developed, which will be used in conjunction with a generalized self-consistent (GSC) method. The representative volume element has three concentric cylindrical phases. The first phase, which represents nanofiber with radius *r*1 is assumed to be linear elastic isotropic material. In contrast, matrix material of the second phase with outer radius *r*2 is linear viscoelastic isotropic material. An equivalent homogenized medium represents the third phase with an infinite outer radius, and its properties are unknown. According to GSC method, the unknown properties of this phase represent the unknown effective properties of whiskered interphase layer. Realistically, when nanofibers are fully wetted by matrix, together, they formed cylindrically orthotropic material around the fiber (radial type of structure (Hashin, 1990)), which has gradient properties along the length of its nanofibers. However, for the analytical study, the authors will assume that the properties of this layer are constant along the length of nanofibers. This simplification seems reasonable because the length of nanofibers is very small. As a result, the whiskered interphase layer can be treated as transversely isotropic material with an axis of symmetry parallel to the principal axis of nanofibers or *r*-axis. Consider a whiskered layer formed by ZnO nanowhiskers. The authors believe that an epoxy matrix, a viscoelastic polymer at a temperature below the glass transition, and a viscoelastic polymer at a glass-transition temperature can be considered a matrix. The properties of nanowhiskers, epoxy matrix, and viscoelastic polymer are given in Table 3.

The evaluation of the specific dynamic properties of the whiskered layer for three types of such layers was carried out in the work. It is proposed to evaluate the specific dynamic properties of the whiskered layer for three types of such layers. Figure 5 shows the longitudinal shear loss modulus dependences obtained using the GSC Eshelby-Christensen's method. The same figures show more approximate estimates obtained using the Reis averaging. A comparison of the curves shown in Figure 5 indicates the effect of a significant increase (by about an order of magnitude) in the effective modulus of loss of the whiskered layer if a viscoelastic polymer below Tg is used instead of an epoxy matrix. Note that the use of carbon nanotubes (fuzzy fiber) as whiskers leads to a significant increase in damping properties or whiskered interphase layer (Figure 6).

However, note that these effects can be significant only for small volumetric contents of the matrix (Figure 6), i.e., for very thin whiskered layers. For the value of the volumetric contents greater than 0.3. the use of CNT NW leads to a slight increase in effective dynamic properties. A much more significant effect of increasing the effective loss modulus (more than 1000 times higher than that of an epoxy matrix) can be obtained if a viscoelastic polymer at Tg is used as a matrix in a whiskered layer. The same effect was previously found for inclusions with very thin viscoelastic coatings (Gusev and Lurie, 2009). However, this anomalous effect manifests itself for small volumetric contents of the matrix V, and in a very small range of V. This must be taken into account in qualitative assessments of the dynamic properties shown in Figure 5. Indeed, taking this circumstance into account, it will be necessary to exclude from consideration a very promising case (Gusev and Lurie, 2009), when a viscoelastic polymer at Tg is used as a matrix.

The author now consider an example of the thinnest whiskered layer with a viscoelastic polymer below Tg because it is, in this case, that the effective mechanical properties controlled by the base fibers of the modified fiber composite remain high. It was showed that in this case, very high damping properties can be realized in the composite. Note that for a qualitative assessment of the dynamic characteristics of the whiskered layer and the composite as a whole, the results obtained on the basis of the GSC Eshelby-

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Christensen's method. However, according to curves in Figure 5, approximate analytical estimates obtained based on Reiss formulas or ratios (Equations 3, 4) can be used. The authors consider the modified fiber composite reinforced with IM7 carbon fibers of diameter $D = 5200$ nm with a layer of ZnO nanowires of thin whiskered interphase layer width $L = 500$ nm. Thin viscoelastic polymer below Tg. The average density c_0 of nanotubes/nanowires in the layer can be estimated by formula (Equation 26), where D is the diameter of the base fiber, d is the diameter of the nanofibers in the layer, L is the length of the whisker layer, $h \geq d$ is the distance between nanofibers on the surface of the base fiber, at the maximum density of nanofibers on the surface $h \approx \pi D/d$. For the considered case, the "whisker" layer with width $L = 500$ nmconsists of ZnO nanowires with an average density $c_0 = 0.72$ and with following parameters: $E = 140$ GPa, $\nu = 0.35$. The matrix of the "whisker" layer is assumed to be the viscoelastic polymer at Tg with damping parameters $\mu_M = (1 + i0.02)$ GPa and loss modulus is shown in Figure 4 for volume fracture of matrix $V \geq 03$. Now consider a modified fiber composite with a double modification. Firstly, a composite is reinforced with IM7 carbon fibers, in which the base carbon fibers have a "whisker" layer with ZnO nanowires. Secondly, the "whisker" layer described above has a viscoelastic layer instead of an epoxy matrix. The solidity of the entire double modified composite as a whole is ensured by epoxy resin with damping parameters $\mu_M = 2.5 + i\,0.005\,\text{GPa}$. For an approximate estimate of the effective dynamic properties under longitudinal shear, the Reuss procedure was used, generalized to a four-layer system, which leads to the following simple relations (Equations 27; 28). It is important to note that the proposed new procedure for modifying a fibrous composite leads to a significant increase in the effective loss modulus when the effective loss modulus can be significantly increased in comparison with modified composites obtained based on only an epoxy matrix and even in comparison with the loss modulus of the epoxy matrix itself (more than 40 times the loss modulus of an epoxy matrix (Figure 7)). Simultaneously, it is easy to verify that the effective mechanical properties change insignificantly, and all the useful characteristics and features of the modified fiber composites remain unchanged.

Using the example of longitudinal shear, it is shown that among the considered combinations of materials from which the main structural elements of the whiskered layer of the modified fiber composite are made, the most promising is the interphase layer, in which carbon nanotubes (CNTs) play the role of whiskers, and a viscoelastic polymer acts as a binder at a temperature below the glass transition temperature. Other systems were considered, where an epoxy matrix or a viscoelastic polymer was considered a binder and ZnO nanofibers as whiskers. It is shown that even when an epoxy matrix is used as a binder, the effective loss modulus of the whiskered layer at minimum volumetric matrix contents significantly exceeds the loss modulus of the epoxy matrix itself**.** The paper also shows that most of the estimates, which are the basis for choosing the optimal structures, can be obtained based on analytical expressions found using the Reis relations. It was found that such assessments are adequate not only from qualitative results but also give fairly accurate quantitative results. Using a more accurate procedure for estimating effective properties using the generalized Eshelby-Christensen's method confirms these conclusions. Quite simple analytical solutions are obviously of significant applied interest since they are very convenient in design calculations when determining the optimal characteristics of the structures under study.

5. CONCLUSIONS:

It has been established that the dissipative properties of modified composites with whiskered fibers largely depend on the dynamic characteristics of an inhomogeneous nanostructured layer of whiskers "grown" on fibers in such composites. The whiskered layer created on the surface of the base fibers can exhibit different physical and mechanical properties depending on the density of whiskers, their rigidity, and the thickness of the interfacial layer. The presence of whiskerising provides the technological possibilities of creating stable nanostructures with specified characteristics. It was shown that the loss modulus of a layer with nanosized whiskers can significantly exceed the loss modulus of a viscoelastic matrix, which is a source of damping effects. It was established that this characteristic is determined mainly by the shear nature of deformation in an inhomogeneous system, increases with an increase in the relative stiffness of whiskers, and decreases significantly with an increase in the volumetric content of the matrix. In the general case, shear deformations in the interphase layer are associated with a longitudinal shear in the direction of the whiskers

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and a transverse shear in the perpendicular direction.

Finally, it was found that taking into account the high damping properties of whiskered layers with an optimal nanostructure around the base fibers makes it possible to significantly increase the damping properties of the modified fibrous composite without reducing its high mechanical stiffness characteristics due to the small thickness of the curved layers. The above estimates show that the value of the effective loss modulus of the modified composite can be tens of times higher than the matrix loss modulus.

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$$1/\mu_{eff}^{*} = (1-V)/\mu_1^{*} + V/\mu_2^{*}, \quad \text{(Eq. 1)}$$

$$\mu_2^{*} = a\,(1+i\eta) = \mu_2' + i\mu_2'' \quad \text{(Eq. 2)}$$

$$V = (a/b)\,\sqrt{(1+\eta^2)},\ \Delta/R \approx V, \quad \text{(Eq. 3)}$$

$$\mu'' \approx b(\sqrt{1+\eta^2}-1)/2\eta \approx b\eta + O(\eta^2) \quad \text{(Eq. 4)}$$

$$[\sigma] = (\sigma_{rr}^{(i)}, \sigma_{\theta\theta}^{(i)}, \sigma_{zz}^{(i)}, \sigma_{rz}^{(i)}, \sigma_{\theta z}^{(i)}, \sigma_{r\theta}^{(i)})^T \quad \text{(Eq. 5)}$$

$$[\varepsilon] = (\varepsilon_{rr}^{(i)}, \varepsilon_{\theta\theta}^{(i)}, \varepsilon_{zz}^{(i)}, \varepsilon_{rz}^{(i)}, \varepsilon_{\theta z}^{(i)}, \varepsilon_{r\theta}^{(i)})^T \quad \text{(Eq. 6)}$$

$$[\sigma] = C[\varepsilon] \quad \text{(Eq. 7)}$$

$$[\sigma] = (\sigma_{rr}^{(i)}, \sigma_{\theta\theta}^{(i)}, \sigma_{zz}^{(i)}, \sigma_{rz}^{(i)}, \sigma_{\theta z}^{(i)}, \sigma_{r\theta}^{(i)})^T, \quad \text{(Eq. 8)}$$

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$$[\varepsilon] = (\varepsilon_{rr}^{(i)}, \varepsilon_{\theta\theta}^{(i)}, \varepsilon_{zz}^{(i)}, \varepsilon_{rz}^{(i)}, \varepsilon_{\theta z}^{(i)}, \varepsilon_{r\theta}^{(i)})^T, \quad \text{(Eq. 9)}$$

$$U^{RVE} = U^0 + U', \quad \text{(Eq. 10)}$$

$$U' = \int_S \left(\sigma_{ij}^1 u_i^0 - \sigma_{ij}^0 u_i^1\right) dS, (i, j = 1,2,3). \quad \text{(Eq. 11)}$$

$$U' = \int_S \left(\sigma_{ij}^1 u_i^0 - \sigma_{ij}^0 u_i^1\right) dS = 0, (i, j = 1,2,3) \quad \text{(Eq. 12)}$$

$$u_z^{(i)}(r, \theta) = \left(D_1^{(i)} r + D_2^{(i)} r^{-1}\right) \cos\theta \quad \text{(Eq. 13)}$$

$$\sigma_{rz}^{(i)}(r, \theta) = C_{44}^{(i)} \left(D_1^{(i)} - D_2^{(i)} r^{-2}\right) \cos\theta, \quad \text{(Eq. 14)}$$

$$\sigma_{\theta z}^{(i)}(r, \theta) = -C_{55}^{(i)} \left(D_1^{(i)} + D_2^{(i)} r^{-2}\right) \sin\theta. \quad \text{(Eq. 15)}$$

$$u_z^{(i)}(R_i, \theta) = u_z^{(i+1)}(R_i, \theta), \sigma_{rz}^{(i)}(R_i, \theta) = \sigma_{rz}^{(i+1)}(R_i, \theta), (i = 1,2,3). \quad \text{(Eq. 16)}$$

$$\int_S \left(\sigma_{rz}^{N+1} u_z^{eff} - \sigma_{rz}^{eff} u_z^{N+1}\right)_{r=r_N} dS = 0. \quad \text{(Eq. 17)}$$

$$\mu_{23}^{eff} = \frac{1}{2\varepsilon_0} C_{55}^{(3)} \left(D_1^{(3)} - D_2^{(3)} R_3^{-2}\right). \quad \text{(Eq. 18)}$$

$$1/\mu_{eff}^* = (1 - V)/\mu_1^* + V/\mu_2^*, \quad \text{(Eq. 19)}$$

$$1/E_{eff}^* = (1 - V)/E_1^* + V/E_2^*, \quad \text{(Eq. 20)}$$

$$\mu_2^* = a\,(1 + i\eta) = \mu_2' + i\mu_2''. \quad \text{(Eq. 21)}$$

$$\varepsilon = \varepsilon_0 \sin\omega t, \quad \text{(Eq. 22)}$$

$$\sigma = \sigma_0 \sin(\omega t + \delta). \quad \text{(Eq. 23)}$$

$$\mu^* = \sigma_0/\varepsilon_0 \quad \text{(Eq. 24)}$$

$$\tan\delta = \mu''/\mu', \quad \text{(Eq. 25)}$$

$$c_0 = \frac{\pi D}{4(D+L)} \left(\frac{d}{h}\right)^2 \quad \text{(Eq. 26)}$$

$$\frac{1}{\mu_{23}^{eff}} = V_1 \left(\frac{1}{\mu_{23}^{(1)}}\right) + V_1 \left(\frac{2\Delta}{d}\right) \left(\frac{1}{\mu_{23}^{(2)}}\right) + V_3 \left(\frac{1}{\mu_{23}^{(3)}}\right); \quad \text{(Eq. 27)}$$

$$V_1 = (1 - V_3)/(1 + 2\Delta/d, V_3 \equiv V. \quad \text{(Eq. 28)}$$

Table 1. *The assumed phase properties for phases in a lamina (Gusev and Lurie, 2009).*

Material	**Bulk Modulus, K (GPa)**	**Shear Modulus, μ (GPa)**
Glass fiber	50	30
Viscous polymer coating	3	0.02 + i 0.01
Epoxy matrix	2.5	2.5 + i 0.005

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Table 2. *Characteristics of a composite with whiskerized fibers*

Fiber: IM7 carbon fiber:	Epoxy matrix:	ZnO NW
EL=256.76 GPa	K=2.5 GPa	E=140 GPa
ET=25.51 GPa	μ=2.3	ν=0.35
μL=22.06 GPa		
μT=9.25 GPa		
νL=0.289		

Source: (Gusev and Lurie, 2009; Kumar and Talreja, 2003; Asthana et al., 2011).

Table 3. *Material characteristics*

Parameters	Binder			Inclusion	
	Epoxy matrix	Polymer at glass-transition temperature	Polymer below glass-transition temperature	ZnO	CNT
Shear modulus, GPa	2.5+0.005i	0.01(1+i)	1+0.02i		
Modulus of elasticity of the first kind, GPa				140	1100
Volume modulus of plane deformation, GPa	2.5	3.5(1+0.1i)	4		
Poisson's ratio				0.35	0.14

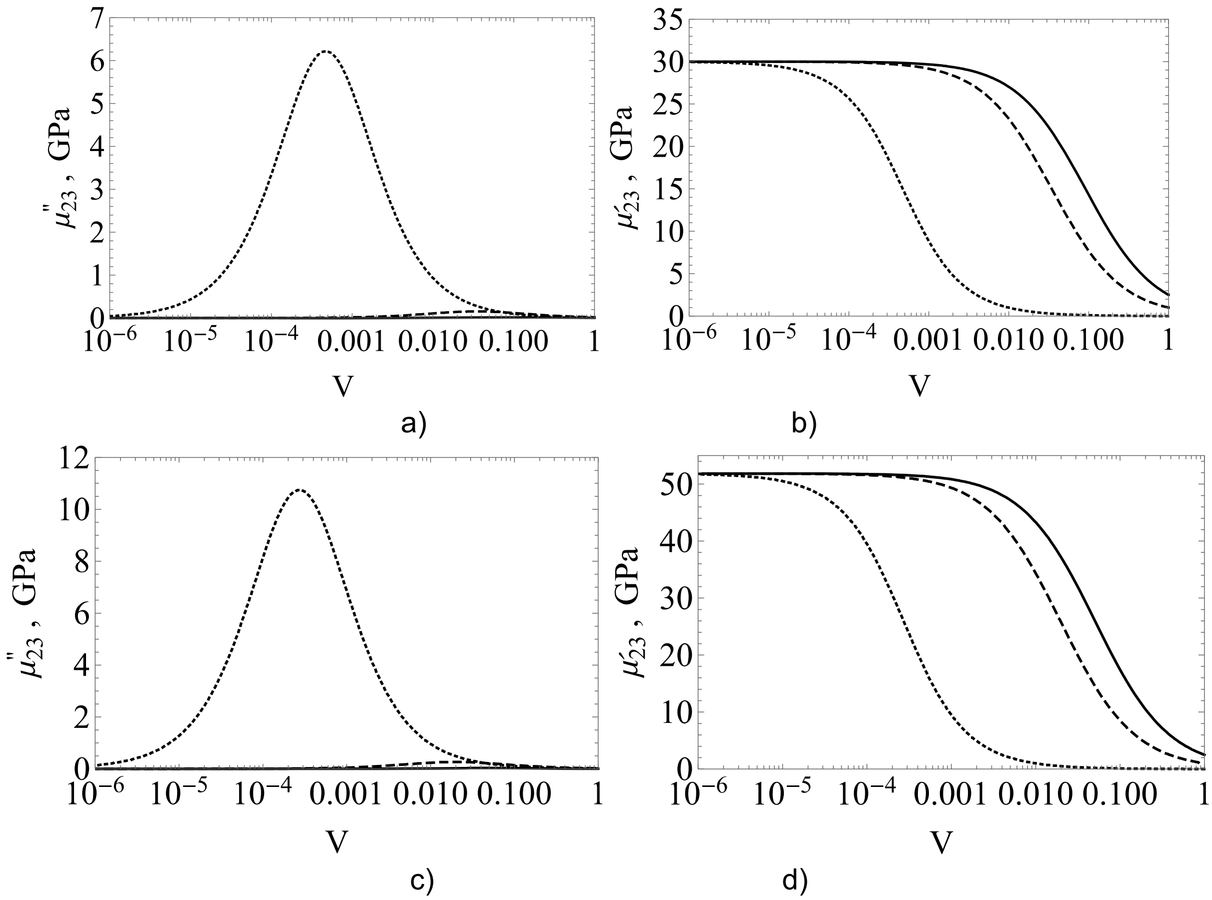

Figure 1. *Effective shear complex modulus of lamella composite with different types of polymers: (a), (c) Loss modulus (dotted line – at T_g, dashed line – below T_g); (b), (d) – storage modulus (dotted line – at T_g, dashed line – below T_g, solid line – epoxy matrix)*

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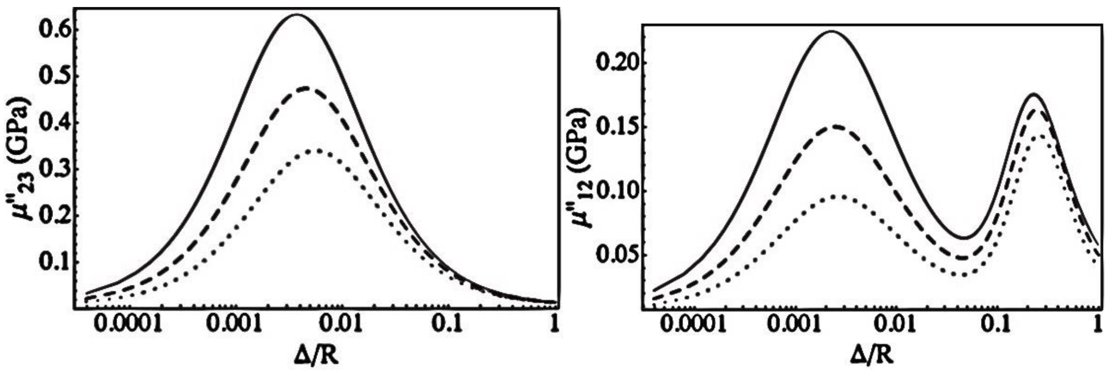


(a) (b)

Figure 2. *The dependence of effective shear complex moduli of unidirectional composite lamina on the coating thickness of viscoelastic polymer. The straight line represents 50% volume fraction, the dashed line represents 40%, and the dot-line represents 30% volume fraction. Symbol Δ represents thickness of coating layer ($\Delta = R_2 - R_1$) and R_1 is the radius of fiber, R_2 is the radius of fiber with coating: a) axial shear moduli, b) transverse shear moduli*

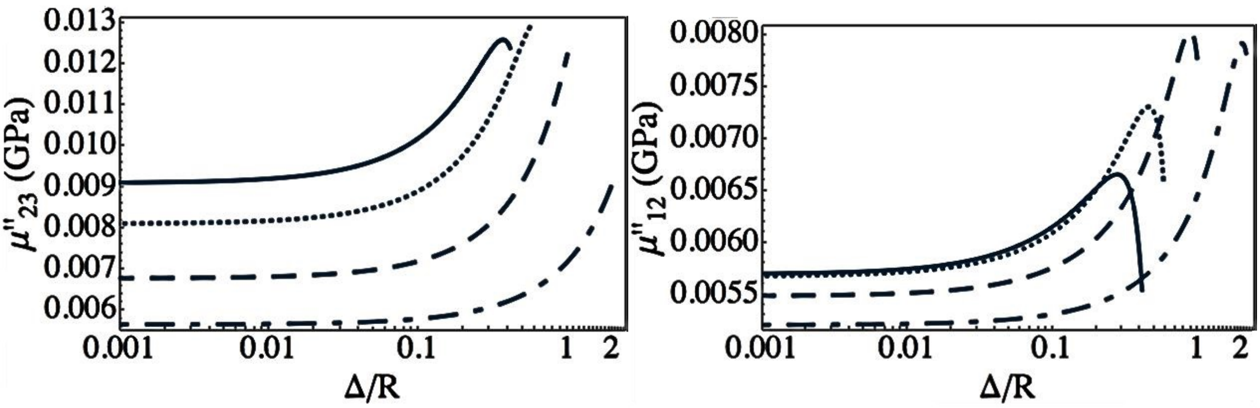
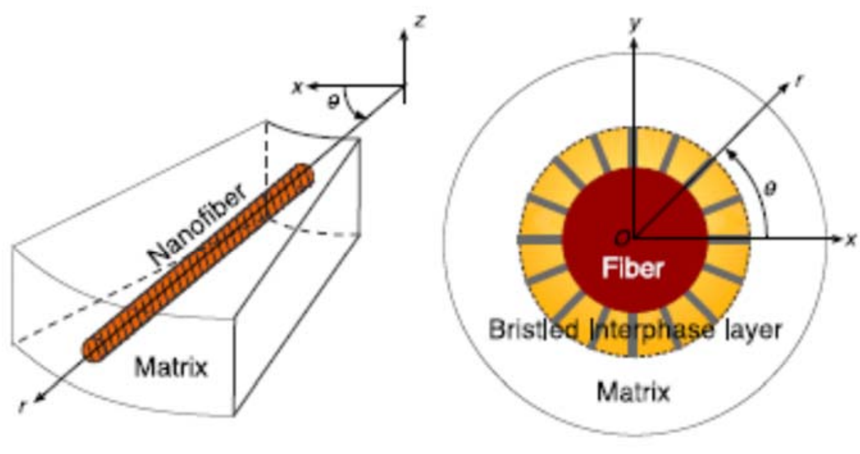


Figure 3. *The dependence of effective dynamic properties of* whiskered *fiber composite lamina on the length of nanofibers for a) axial shear moduli; b) transverse shear moduli, Δ= R2 – R1 is the length of nanowires and R is the radius of base fiber*
Note: Continuous line: Vf =50%, dotted line: Vf =40%, dashed line: Vf =25%, dash-dotted line: Vf =10%).



a) b)

Figure 4. *Unidirectional* whiskered *fiber composite (a) – a cell of a* whiskered *interfacial layer; (b) – a cell of a* whiskered *fiber composite*

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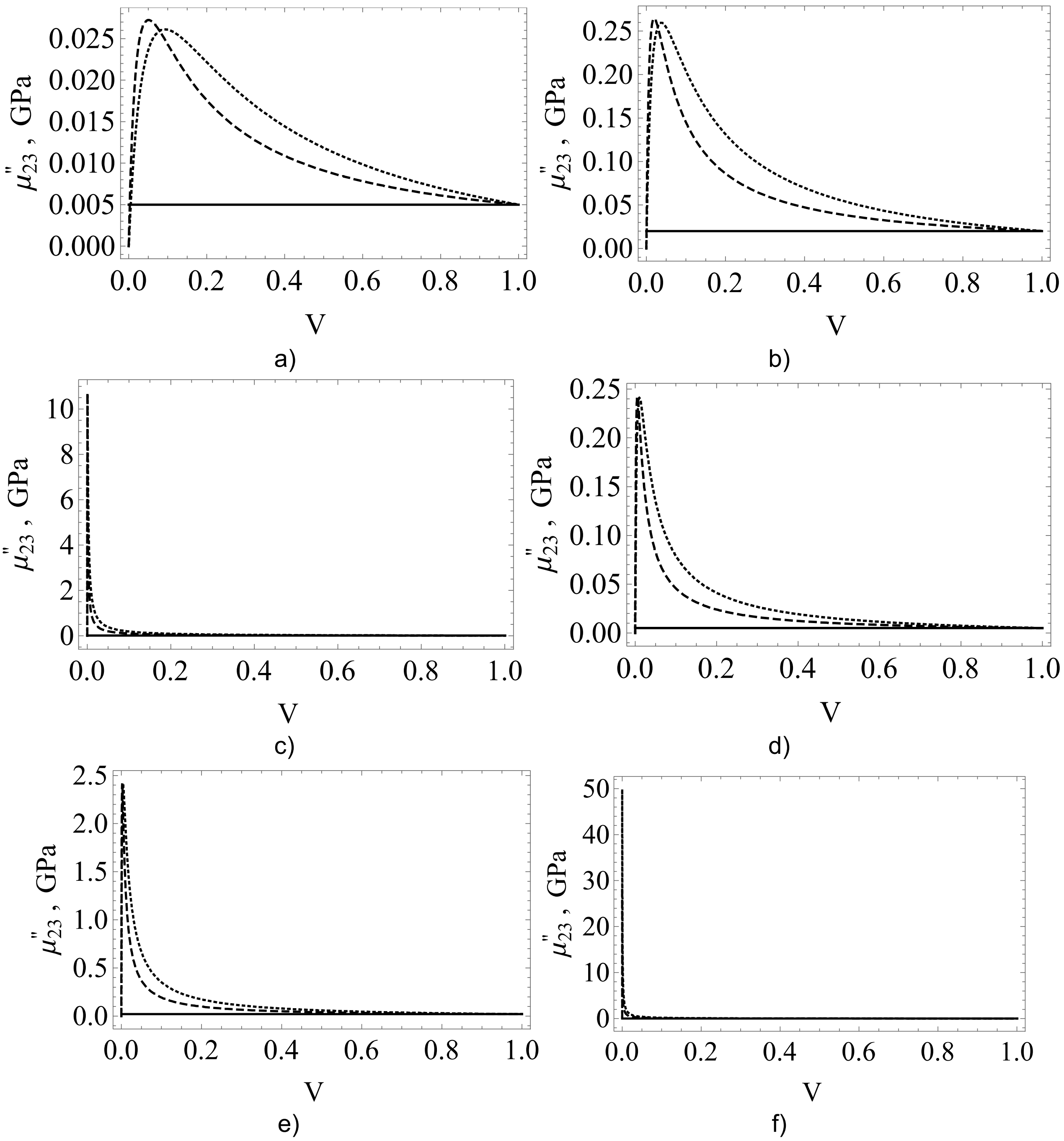

***Figure 5.** Dependences of the effective modulus of longitudinal shear loss, GSC method (dotted lines), Reiss method (dashed lines), (a) –* whiskered *layer with ZnO and epoxy matrix; pure epoxy matrix-solid lines; (b) –* whiskered *layer with ZnO and viscoelastic polymer below Tg, pure viscoelastic polymer below Tg – solid lines, (c) –* whiskered *layer with ZnO and viscoelastic polymer at Tg, solid line is the pure viscoelastic polymer at Tg, (d) –* whiskered *layer with CNT and epoxy matrix; pure epoxy matrix – solid lines; (e) –* whiskered *layer with CNTs and viscoelastic polymer below Tg, pure viscoelastic polymer below Tg – solid lines, (f) – whiskrised layer with CNTs and viscoelastic polymer at Tg, solid line is the pure viscoelastic polymer at Tg*

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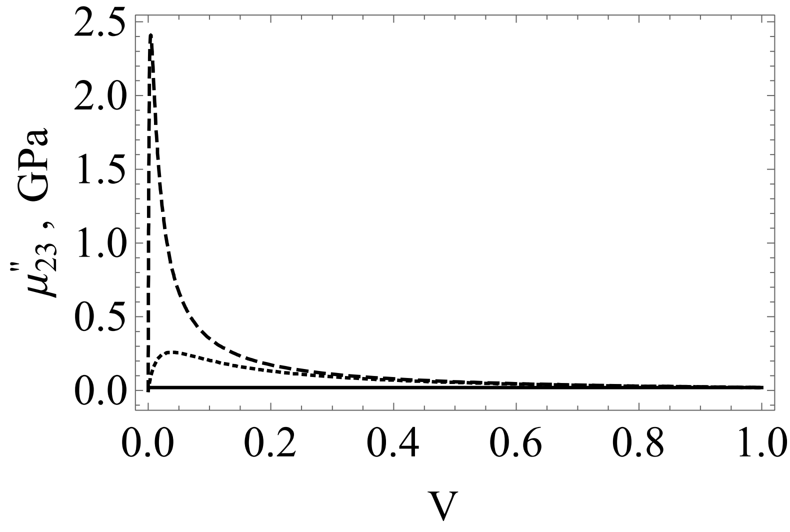

Figure 6. *The dependence of effective dynamic axial shear moduli for* whiskered *interphase layer with viscoelastic polymer below Tg and with two different nanowires: CNT NW – dashed line, ZnO NW – dotted line, pure viscoelastic polymer below Tg – solid line*

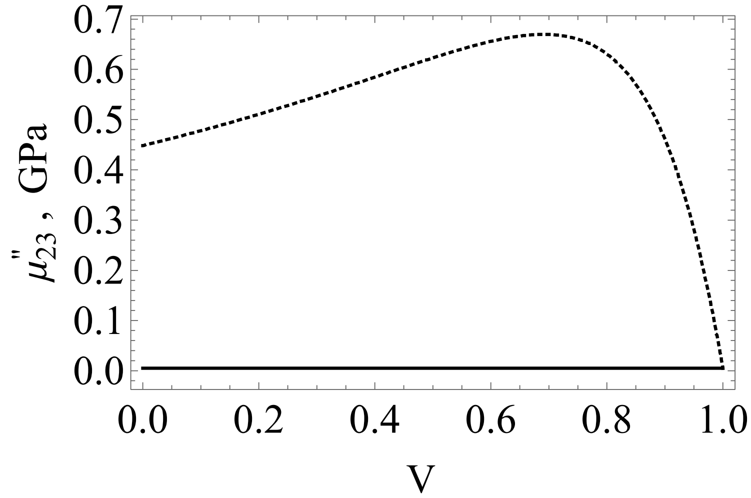

Figure 7. *The dependence of effective dynamic axial shear moduli for double modified fibers composite with* whiskered *interphase viscoelastic polymer below Tg and with nanowires: ZnO NW – dotted line, pure epoxy matrix – solid line*

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