

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Elastic and Viscoelastic Properties of Polymers Filled with Solid Particles

V. E. Zgaevsky^a

^a Institute of Chemical Physics, Chernogolovka, U.S.S.R.

To cite this Article Zgaevsky, V. E.(1977) 'Elastic and Viscoelastic Properties of Polymers Filled with Solid Particles', *International Journal of Polymeric Materials*, 6: 1, 109 – 124

To link to this Article: DOI: 10.1080/00914037708075223

URL: <http://dx.doi.org/10.1080/00914037708075223>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Elastic and Viscoelastic Properties of Polymers Filled with Solid Particles

V. E. ZGAEVSKY

Institute of Chemical Physics, Chernogolovka, U.S.S.R.

(Received July 20, 1976)

A filled polymer is modelled by stiff cubic particles with parallel faces joined by polymeric interlayers. The particle centres are located at the centre of the lattice of cubic symmetry. Isotropy of such a body is provided by the assumption of "polycrystalline" structure of the model.

Based on this model, elastic and viscoelastic properties of a composite body are calculated. Discussion of the results and comparison with the experimental data are given. Efficiency of the possible ways of optimizing the mechanical properties of the filled system is evaluated, and the conditions for applicability of the temperature—time analogy to a composite body are analyzed taking into account the properties of a polymer—filler interface.

Polymer filled with solid particles is a structurally inhomogeneous solid. Such a solid possesses two characteristic features:

a) The ratio of moduli of components may vary within 3-5 orders of magnitude.

b) The volume fraction of the fillers may reach 80 per cent. Due to these features the general methods for mathematical estimation of mechanical properties of such composite bodies are cumbersome and often ineffective.

There is a need in less accurate, but simpler methods of calculation of properties of the composites. Such simple methods should provide some general analytical expressions suitable for finding more efficient ways for optimizing structural parameters the composites.

Such methods are usually based on model representations of the composites.

In the present paper elastic and viscoelastic properties of filled polymers are considered within the framework of a multiparticle model. The results obtained are discussed and compared with experimental data. The efficiency of possible ways for optimization of the mechanical properties of filled

systems is also evaluated and the conditions for applicability of the temperature time analogy to the composites are analyzed.

1 ELASTIC PROPERTIES

1.1 Description of the model with ideal adhesion

A filled system is modelled by a set of identical cubic rigid particles with the centres located at the noduses of cubic lattice (Figure 1). There are polymer interlayers of uniform thickness between the parallel faces of particles. The body obtained will be similar to a crystal with pairwise, but noncentral particle interaction. Potential energy of particle interaction should be equal to free energy of deformed polymer interlayers.

Transition to an isotropic body is made by using polycrystal structure of the model. This could be done by assuming that the space orientation of the vectors of an elementary lattice is, on average, equally probable. The calculations are carried out under the following assumptions:

- 1) The adhesion strength of the polymer-particle interface is larger than

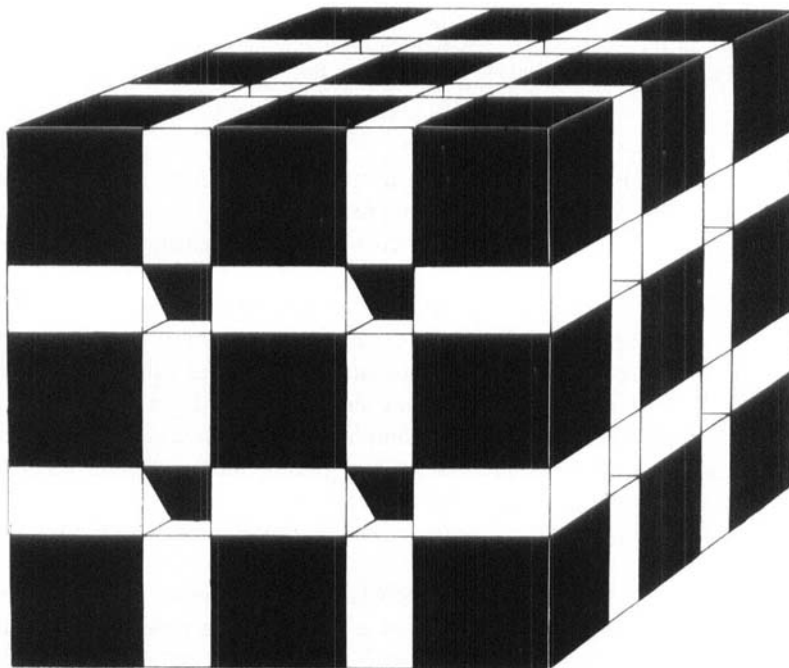


FIGURE 1 The crystal model of a filled polymer.

the cohesion strength of the polymer.

2) The strain of a filler particle can be neglected as compared to polymer strain.

3) Polymeric interlayers are not stressed in the initial condition.

4) The deformation is isothermal and reversible.

5) The stress (or strain) state of the body as a whole is simple (simple tension, simple shear, etc).

6) The strain state of an interlayer between two particles is uniform.

Now the largest deviations of the model from a real body should be mentioned. First of all, the polymeric matrix in the model is assumed to be discrete. This will affect the value of the Poisson's ratio of the filled system. A large underestimation of this value as compared to a real filled system should be expected. A discrete character of the polymer matrix should further lead to incorrect results for dilute systems, since as the filler content approaches zero, the volume fraction of the polymer also approaches zero.

The assumption that a polymeric interlayer between two particles is strained uniformly is not rigorous since the ideal adhesion and the tendency of the polymer to retain its volume during deformation will lead to a non-uniform strain of an interlayer. But this assumption permits the calculations to be carried out in the analytical form. Using this assumption one should expect values of the elastic characteristics of the composite to be underestimated. The model can be modified to take into account the effect of the triaxial stress state of an interlayer.

1.2 Free energy of a deformed polymeric interlayer

Let us consider an arbitrary pair of the neighbouring particles and introduce a system of coordinates related to this pair:

\bar{e}_1 = a unit vector directed along the line connected centres of the particles in the initial state,

\bar{e}_2 = a unit vector normal to \bar{e}_1 ,

\bar{e}_3 = a unit vector chosen so that three vectors \bar{e}_1 , \bar{e}_2 and \bar{e}_3 form a right-hand system.

Obviously, \bar{e}_i will depend on the cell number l and particles number in this cell s .

Let us denote by x_n the coordinates of a point within the polymer in the initial state in this coordinate system.

When displacement of one particle relative to another takes place and this displacement is such that the faces of two cubic particles remain parallel to each other, the coordinates of a point of the interlayer under consideration will be:

$$\begin{pmatrix} X'_1 \\ X'_2 \\ X'_3 \end{pmatrix} = \begin{pmatrix} \left(1 + \frac{\omega_1}{d}\right) X_1 \\ \left(1 - \nu \frac{\omega_1}{d}\right) X_2 + \frac{\omega_2}{d} X_1 \\ \left(1 - \nu \frac{\omega_1}{d}\right) X_3 + \frac{\omega_3}{d} X_1 \end{pmatrix} \quad (1)$$

where ω_n is the displacement of the centre of the particle along the vector \bar{e}_n ,
 d is the thickness of the polymer interlayer in the initial state
 ν is the Poisson's ratio of the polymer.

We have taken into account the assumption 6 above. Using (1), we shall write the strain tensor of the polymer interlayer

$$u_{ik} = \frac{1}{2} \left(\frac{\partial X'_i}{\partial X_k} + \frac{\partial X'_k}{\partial X_i} \right) - \delta_{ik} = \frac{1}{d} \begin{pmatrix} \omega_1 & \frac{1}{2}\omega_2 & \frac{1}{2}\omega_3 \\ \frac{1}{2}\omega_2 & -\nu\omega_1 & 0 \\ \frac{1}{2}\omega_3 & 0 & -\nu\omega_1 \end{pmatrix} \quad (2)$$

The density of free energy of the polymer interlayer can be written in accordance with¹ as

$$f = \mu \left(u_{ik}^2 + \frac{\nu}{1-2\nu} u_{ii}^2 \right) \quad (3)$$

Where μ is shear modulus of the polymer

u_{ik}^2 is the sum of squares of the strain tensor components

u_{ii}^2 is the square of the sum of the diagonal components of the strain tensor.

Substituting Eq. (2) into Eq. (3), we have

$$f = \frac{\mu}{2d^2} [2(1 + \nu)\omega_1^2 + \omega_2^2 + \omega_3^2] \quad (4)$$

1.3 Elastic properties of filled polymer

To calculate the density of free energy ϕ of the model at the given strain state ϵ_{iK} , it is necessary to sum the values of the energy of all interlayers in a elementary cell and to divide it by cell volume U_c .

Then, we obtain

$$\phi = \frac{1}{U_c} \cdot \frac{\mu WR^2}{2d^2} \epsilon_{ij} \epsilon_{kn} \sum_{l's'} A_{ijkln} \left(\frac{l'l'}{ss'} \right) \quad (5)$$

when W is the volume of a polymeric interlayer,

R is the distance between the centres of nearest particles in the initial state,

$$A_{ijkn} = (2\nu + 1)e_{1i}e_{ij}e_{1k}e_{1n} + \delta_{ik}e_{ij}e_{1n}$$

e_{1m} is the projections of vector \bar{e}_1 on the axis x_m of the new co ordinate system chosen arbitrary.

Eq. (5) allows the tensor of elastic moduli of the model to be readily written in Voigt's notations

$$G_{ijkn} = \frac{1}{U_c} \cdot \frac{\mu WR^2}{2d^2} \begin{pmatrix} 4(1 + \nu) & & & & & \\ & 4(1 + \nu) & & & & \\ & & 4(1 + \nu) & & & \\ & & & 2 & & \\ & & & & 2 & \\ & & & & & 2 \end{pmatrix} \quad (6)$$

Turning to the isotropic polycrystal,² we shall find the elastic characteristics of the composite, namely Young's modulus, E , shear modulus G , bulk modulus K and Poisson's ratio σ

$$\begin{aligned} E &= \frac{2(1 + \nu)(5 + 2\nu)}{5 + 4\nu} \mu\psi(\phi) \\ G &= \left(1 + \frac{2}{5}\nu\right) \mu\psi(\phi) \\ K &= \frac{2}{3}(1 + \nu)\mu\psi(\phi) \\ \sigma &= \frac{\nu}{5 + 4\nu} \end{aligned} \quad (7)$$

where ϕ is the volume fraction of filler particles and $\psi(\phi) = \frac{\phi^{2/3}}{1 - \phi^{1/3}}$.

It is of interest to compare the theoretical formulae obtained with the experimental data. In Figure 2 the experimental data for the dependence of the common logarithm of the ratio of the effective shear modulus of the composite to the modulus of the polymer versus volume fraction of filler are presented.³ The data are denoted by triangles—(polyisobutylene, glass beads); empty circles—(polyurethane, glass beads) and by shaded circles—(polyurethane, crystal salt). Curve 3 shows a theoretical dependence of the shear modulus on the value of ϕ in accordance the Eq. (2) at $\nu = 0.5$. For comparison, dashed lines show the Hashin-Shtrikman's limits for rubber filled by particles of a crystalline material. Where the ratio of the shear

modulus of the crystalline material to the modulus of latex is $2.10^{5,4}$ (the ratio of the bulk moduli is about 10). Curve 1 shows the similar dependence obtained by Van der Poel. In spite of the relative simplicity of the model considered here, theoretical curve 3 lies between the lower limit by Hashin-Shtrikman and the experimental points.

1.4 Case of triaxial strained model

Disagreement between the theory and the experimental data will be much smaller if one takes into account a complex stress state of the interlayers caused by incompressibility the ideal adhesion at the interface.

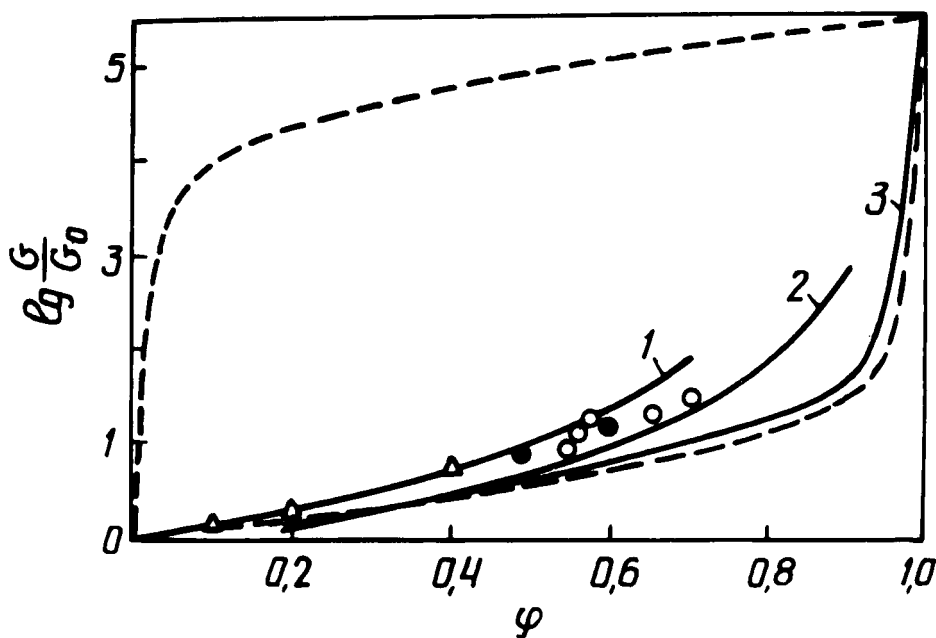


FIGURE 2 The dependence of common logarithm of the ratio of the effective shear modulus of the composite to the modulus of the polymer vs. the volume fraction of filler.

Lindsey⁵ gives Schapery's calculation of the stress distribution in the polymeric interlayer between parallel surfaces of two disks under forces acting normal to the surface of the discs. These calculations were made under the assumption of small deformations.

The interlayer is characterized by the Young's modulus E_0 and Poisson's ratio ν . The ratio of the disk diameter D to the interlayer thickness d was a .

The dependence of normal stress σ_z on the distance of a point from the disk centre is

$$\frac{\sigma_z(\tau)}{E_0 \epsilon} = \frac{\nu}{(1 + \nu)(1 - 2\nu)} \left\{ 1 - \frac{I_0[\tau\sqrt{3(1 - 2\nu)}]}{I_0[a\sqrt{3(1 - 2\nu)}]} \right\} + \frac{1}{1 + \nu} \left\{ 1 + \frac{1}{2} \cdot \frac{I_0[\tau\sqrt{3(1 - 2\nu)}]}{I_0[a\sqrt{3(1 - 2\nu)}]} \right\} \quad (8)$$

where ϵ is the relative displacement of the disk surfaces, $I_0[\kappa]$ is the modified Bessel's function of argument κ . Now the value of ϕ in our model can be made to be connected with the value of a in Schapery's calculation, namely

$$a = \frac{\phi^{1/3}}{\sqrt{\pi(1 - \phi^{1/3})}} \quad (9)$$

Substituting Eq. (9) into Eq. (8), we obtain the dependence of $\frac{\sigma_z(\tau)}{E_0 \epsilon}$ in terms of both ϕ and ν .

By numerical integrating of the equation obtained with respect to τ and then dividing the resulting surface area, we obtain the value of k , which is the ratio of the effective modulus of the interlayer to the modulus obtained under the assumption of uniform strain in the interlayer.

The value of k now should be substituted as a coefficient into components in three upper lines of the matrix of Eq. (6). Turning as previously to the isotropic polycrystal we shall obtain for the shear modulus G of the filled polymer the following expression:

$$G = \left[\frac{2}{5} (1 + \nu)k + \frac{3}{5} \right] \mu\psi(\phi) \quad (10)$$

Curve 2 in Figure 2 shows the dependence of the relative shear modulus of the filled polymer, which corresponds to Eq. (10). We can see that account for the triaxial stress state leads to a better agreement between the calculated curve and the experimental data.

The value of k depends on both ϕ and ν . At $\phi \leq 0,5$, the dependence of k on ν is weak. For example, at $\phi = 0,5$, when ν changes from 0,4 to 0,5, then k varies from 1,12 to 1,5. At larger volume fraction of the filler ($\phi > 0,5$) the dependence of k on ν becomes stronger. At $\phi = 0,8$, k changes from 1,56 to 7.55 when ν changes from 0,4 to 0.5.

Thus, the shear modulus of a particulate composite with polymer matrix can be changed within an order of magnitude by possible changing of the value of the Poisson's ratio.

1.5 Elastic properties of a filled polymer without adhesion between the matrix and the particles

Let us again choose the arrangement of the cubic particle centres at the

centre of the lattice with cubic symmetry. The particles are placed into a polymeric matrix, adhesion between particles and polymer being absent. During the deformation of the composite cavities will occur between the particles and the matrix. We shall consider the polymer to be incompressible. Calculations are carried out under the above assumptions, except for the first assumption. Furthermore of the deformation of an interlayer between particles the uniforming of will naturally be violated at the interfaces between the single interlayers. Neglecting of deformation non-uniformity in this case, when there is no adhesion, will not lead to significant mistake, especially at intermediate and high volume fraction of the filler. As previously, let us write down a free energy of the deformed polymeric interlayer at $\nu = 0.5$ in the system of Cartesian coordinates, where the axis x_1 is directed parallel to the cube edge, and x_2 and x_3 form with x_1 the right-hand system of vectors.

$$f = \frac{2\mu}{R^2} [\omega_{11}^2 + \omega_{22}^2 + \omega_{11}\omega_{22} + (\omega_{12} + \omega_{21})^2 + \omega_{13}^2 + \omega_{23}^2] \quad (11)$$

Here the first index at the values of displacement ω denotes the plane of the interlayer normal to the axis x_i , and the second index shows the projection of this plane displacement on the axis x_k . Contrary to the previous case, the interactions take place here not only between the nearest particles and therefore in Eq. (11) not only the squares of ω_{ik} is present, but also their products. Then, as previously, elastic moduli of the crystal are calculated and the transition to the isotropic material is made, using the same idea about the polycrystalline composite. We obtain

$$\begin{aligned} G &= \mu(1 - \phi) \\ E &= 2\mu(1 - \phi) \\ K &= \frac{2}{3}\mu(1 - \phi) \\ \sigma &= 0 \end{aligned} \quad (12)$$

As one can see from this formulae, the elastic characteristics of such material decreases linearly with the volume fraction of the filler. At $\phi = 0$, the shear modulus is equal to the modulus of an unfilled polymer, though the Young's modulus and the Poisson's ratio differ from their values for the polymer. This is a result of the violation the continuity caused by consideration of six independent plates of polymer in the elementary cell.

Comparison of the theory and experiment^{6,7} is given in Figure 3 where the relative Young's modulus is shown with respect to the volume fraction of the filler (polyvinylchloride—glass beads, shown by open circles; polyurethane—NaCL, shown by squares). The agreement between the theory and experiment is good enough.

Comparing Eqs. (10) and (12), one can get the limits of changes of the

elastic characteristics of filled system when the adhesion changes. For the volume fraction of filler equal to 70–80 per cent the ratio of the shear modulus of a filled polymer with the ideal adhesion to the shear modulus of the same system with no adhesion exceeds an order of magnitude.

2 VISCOELASTIC PROPERTIES

Experimental data on the frequency dependence of mechanical characteristics of the composite contain the complete information on the physical-chemical structure of the material, which in principle permits its ultimate mechanical properties to be characterized. To obtain this information from the experimental results, it is necessary to have some theoretical description

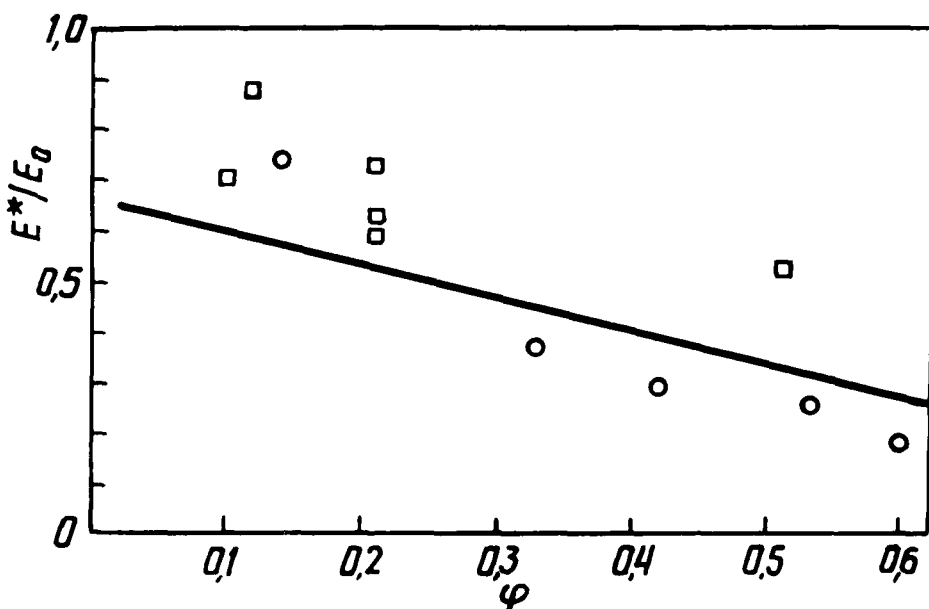


FIGURE 3 The dependence the ratio of the effective Young's modulus of the composite to the modulus of the polymer vs. the volume fraction of filler.

of such behaviour. The necessity of such description is evident from the problem of obtaining the experimental data over the wide range of frequencies. It is known, that in the case of pure polymers the temperature-time superposition (Tts) is commonly used for this purpose. Its validity is well established theoretically and experimentally.⁸ A widespread application of this principle to filled polymers⁹ needs additional proof especially as direct experimental evidence exists.¹⁰

Furthermore, in a paper¹¹ on the basis of an analysis of results of dynamic testing of filled polymers over the frequency range of 0.004 to 0.4 hertz, the concentration-time (Cts) and concentration-temperature (CTS) are superpositions put forward. Analysis of possible causes of validity of these principles seems to be of some interest.

Here we intend to present a model description of viscoelastic properties of a filled polymer, in order to discuss characteristic features of relaxation mechanisms which can satisfy or not satisfy to various superposition principles.

Three modifications of the model considered above are discussed

- 1) a model with the ideal adhesion of the polymer to the filler;
- 2) a model with the ideal adhesion and the polymer with properties near the particle surface which are different from those in bulk;
- 3) a model with poor adhesion at the surface of filler particles.

2.1 Filled polymer with the ideal adhesion

In addition to the assumptions taken above a small amplitude of the deformation involved should be expected. We shall consider only such deformation of the composite, that the wave length is much larger than linear sizes of the composite sample. We shall describe the behaviour of a polymeric material by a linear theory of viscoelasticity and assume the material to be incompressible. Then calculations analogous to those delivered in paragraphs 1.2 and 1.3, lead to expression for the complex shear modulus \hat{G} of the filled polymer, in the case of small periodic deformation:

$$\hat{G} = 1,2\psi(\phi)\hat{\mu} \quad (13)$$

where $\hat{\mu}$ is the complex shear modulus of the polymer. Eq. (13) is directly obtained from Eq. (7) by the common rule, substituting complex moduli for elastic moduli at $\nu=0.5$.

In accordance to Eq. (13), the effective complex modulus of the composite is given as a product of a value, depending only on the volume fraction of the filler, and the complex modulus of the pure polymer. This immediately leads to the conclusion, that tangent of an angle of the mechanical losses, $\tan \delta$ of the composite with the ideal adhesion will be exactly equal to the tangent of the pure polymer, t , at any degree of filling, ϕ . Note that this conclusion is reached without taking into account the peculiarity of the behaviour of the matrix-particle interface zones.

The value of logarithm of the real part of the modulus \hat{G} will increase with ϕ by the value $\log [1, 2\psi(\phi)]$. If for a pure polymer the principle of TtS is valid and the shift factor on frequency scale is equal to a_T , then substituting

$\hat{\mu}(a_T\omega)$ into Eq. (13), we shall see, that the same value a_T will also be a shift factor for the composite.

The shift along the logarithm modulus axis unlike that for a pure polymer $\log \frac{T_0\rho_0}{T\rho}$, where ρ_0 and ρ are the densities of the polymer at T_0 and T_1 respectively, will correspond to value

$$\log \frac{T_0\rho_0}{T\rho} + 2,3(\phi - \phi^{2/3} - \phi^{1/2} - 2)(\alpha_p - \alpha_f)(T - T_0) \quad (14)$$

This is associated with different thermal expansion coefficients of the polymer, α_p , and the filler, α_f . If $\alpha_p \sim 10^4$ 1/degree, $\phi \sim 10^{-1}$ and $(T - T_0) \approx 100^\circ\text{C}$, then at the case of the crystalline filler, the terms of the Eq. (14) may turn to be of the same order. In so far as ω and ϕ , as well as ϕ and T in the expression Eq. (13) do not occur in multiplicative combinations, there is no possibility in the case given to explain the principles of CtS and CTS suggested in Ref. 11. These authors suppose that the validity of the CtS and CTS principles is connected with the peculiar state of the polymer in some layer near the interface polymer-filler. We shall analyze this possibility in the next section.

2.2 A model taking account of the structure of polymer in the interface zones

The main ideas about the structure of matrix-particle interface zones connect with the fact, that at some distance from the surface of the filler particles the conformations of macromolecules differ from those in the bulk of polymer. This results in different mechanical characteristics of polymer near the surface and in bulk.¹² Let us assume the existence of the interface zone of a certain thickness and the properties of the material within the whole zone to be constant. Now a polymeric interlayer between particles will be inhomogeneous and be part of three layers structure. Let us assume deformation in each layer to be uniform. Polymer at the surface of a filler particle in zone of the thickness d_1 will be characterized by modulus $\hat{\mu}_1$ and in the rest of the interlayer (on the thickness d_2)—by modulus $\hat{\mu}_2$. The obvious procedure of calculations gives on effective modulus of the filled polymer at the presence of the interface zone:

$$\hat{G} = 1, 2\psi(\phi) \frac{\hat{\mu}_2}{1 + 2f \frac{\hat{\mu}_2 - \hat{\mu}_1}{\hat{\mu}_1}} \quad (15)$$

where

$$f = \frac{d_1}{2d_1 + d_2}$$

Now let us note that the geometrical considerations lead to the critical value ϕ_c such that at $\phi = \phi_c$ the value of f can be equal to $1/2$. It means that the whole polymer matrix consists of the material with the shear modulus $\hat{\mu}_1$. Obviously

$$\phi_c = \left(1 + \frac{d_1}{R}\right)^{-3} \quad (16)$$

If changes in the properties of the polymer layer of the particle surface is connected only with effect of the surface itself, the value d_1 should be about 100\AA .^{13,14} If the properties of the surface layer are connected with contraction of thermal or chemical nature, then d_1 seems to be about 1μ . And finally, specially created layers of arbitrary thickness d_1 are possible. If $d_1 \approx 100\text{\AA}$, then for particle diameter of about 10μ we have $\phi_c > 90$ per cent and this case it may be assumed that $f = 0$ up to $\phi \leq 90$ per cent and hence viscoelastic properties of the filled polymer will depend only on the properties of polymer in bulk.

If $d_1 \approx 1\mu$, then $\phi_c = 75$ per cent and at $\phi \geq 75$ per cent the properties of the filled system will depend only on the properties of polymer in the surface layer.

Let us consider the case when $\phi < \phi_c$. Then we can assume $f \ll 1$ in Eq. (15) and $\frac{\hat{\mu}_2 - \hat{\mu}_1}{\hat{\mu}_1}$ to be a finite quantity. Expanding the value of \hat{G} (Eq. (15)) into the series in small f and keeping only the first terms of the expansion and representing the complex moduli as $\hat{\mu} = \mu' - i\mu''$ we obtain the following expressions for real G' and imaginary G'' parts of the effect modulus

$$G' = 1, 2\psi(\phi)\mu_2'[1 - 2(a - bt)f]$$

where

$$\begin{aligned} G'' &= 1, 2\psi(\phi)\mu_2'' \left[1 - 2 \left(a + \frac{b}{t} \right) f \right] \\ a &= \frac{(\mu_2' - \mu_1')\mu_1' + (\mu_2'' - \mu_1'')\mu_1''}{|\hat{\mu}_1|^2} \\ b &= \frac{(\mu_2'' - \mu_1'')\mu_1' - (\mu_2' - \mu_1')\mu_1''}{|\hat{\mu}_1|^2} \end{aligned} \quad (17)$$

and t denotes tangent of an angle of the mechanical losses of the polymer in bulk. Directly from Eq. (17), we find the tangent of an angle of the mechanical losses, $\tan \delta$ of the filled polymer.

$$\tan \delta = t \left[1 - \frac{b}{t} (1 + t^2)f \right] \quad (18)$$

A possible shift of maximum of the value of $\tan \delta$ in accordance with

Eq. (18) is connected not with ϕ , but with f , and the direction of the shift may change its sign depending on the sign of b . Since in Eq. (17) ϕ does not enter into the combination with frequency, the CtS principle again cannot be explained. Fulfilment of the CtS principle for the filled system in accordance to Eq. (17) should mean validity of the following equation.

$$\mu_2'(\omega)[1 - 2(a(\omega) - b(\omega)t(\omega))f] = \mu_2'(\omega\alpha_\phi) \quad (19)$$

at any values of frequency ω . This expression is not obviously at all and it may be expected to be valid in some particular cases only.

Certainly in the general case, the shift factor α_ϕ on the frequency scale cannot be meaning full for our model, but it is possible to calculate the dependence of G_1 on ω having the value of $\hat{\mu}_1$ and $\hat{\mu}_2$ Eq. (17)).

2.3 A model with imperfect adhesion at the surface of filler particles

This case is of interest since there appears an additional relaxation mechanism connected with the friction between the particle surface and the polymeric matrix.

Making use of the above model with the ideal adhesion, we shall write down the balance of the forces exerted on the particle $\left(\frac{l}{s}\right)$ in the case of periodic deformation

$$\gamma \left(\dot{u}_s^l - \dot{U}_s^l \right) + \phi_{ii'}^{ii'} u_{i'}^{i'} = 0 \quad (20)$$

where γ is the coefficient of friction between free particle surface and the polymer, \dot{u}_s^l and \dot{U}_s^l are the rate of the particle numbers s in the cell number l

and the rate of the polymer surface around the particle $\left(\frac{l}{s}\right)$ respectively.

Hence the force matrices $\phi_{ii'}^{ii'}$ should be as

$$\phi_{ii'}^{ii'} = -\frac{S\hat{\mu}}{d} (3e_{1i}e_{1i'} + e_{2i}e_{2i'} + e_{3i}e_{3i'})$$

$$\phi_{ii'}^{ii'} = \frac{S\hat{\mu}}{d} \sum_{e's'} (3e_{1i}e_{1i'} + e_{2i}e_{2i'} + e_{3i}e_{3i'})$$

where S is the sectional area of the part of polymeric interlayer with ideal adhesion. Value S will be now a variable and at zero adhesion throughout the whole particle surface, S should be equal to zero. The value of γ by definition is proportional to the particle surface $S'(\gamma = \gamma'S')$ where adhesion

is equal to zero. The sum of the values of S and S' should naturally be equal to surface of the whole particle. By solving Eq. (20), us can be found for given value of Us . From known us a mean stress can be written which is induced by a particular movement of the particles. The latter permits viscoelastic moduli of the model to be calculated and offer transition to the polycrystal situation and an expression for the shear modulus of a filled polymer. Omitting somewhat cumbersome calculations, let us write down the final result

$$\begin{aligned} G' &= \alpha\psi(\phi)\mu'(\omega)[1, 2 + Q'(\omega_1, t)] \\ G'' &= \alpha\psi(\phi)\mu'(\omega)[1, 2t + Q''(\omega_1, t)] \end{aligned} \quad (21)$$

where $\alpha = \frac{S}{L^2}$ is the fraction of particle surface with ideal adhesion, $Q'(\omega_1, t)$ and $Q''(\omega_1, t)$ are analytical functions of reduced dimensionless frequency ω_1 and tangent of an angle of the mechanical losses of polymer t

$$\omega_1 = \frac{2\gamma(1-d)}{\alpha} \cdot \frac{\omega d}{\mu'(\omega)} \quad (22)$$

Note that at $\omega_1 = 0$, functions $Q'(\omega_1, t)$ and $Q''(\omega_1, t)$ are equal to zero. In the present paper we shall not need explicit forms of these functions, and so we shall not give them here. Also we note the Eq. (21) describe viscoelastic behaviour of the model when deformation of the part of the polymeric interlayer only is taken into account, namely of the part which is joined with the filler particles.

The formal account for viscoelastic properties of the whole polymeric matrix can be made by addition of complex moduli of the filled polymer into the right part of Eq. (21) at zero value of the adhesion and $\gamma = 0$.

Viscoelastic properties of the polymeric matrix in the filled system at zero adhesion and $\gamma = 0$ can be obtained substituting the elastic moduli in Eq. (12) by the complex ones.

$$\hat{G}(\omega) = (1 - \phi)\hat{\mu}(\omega) \quad (23)$$

Taking the sum of the values given by Eq. (21) and Eq. (23), we finally obtain

$$\begin{aligned} G' &= \alpha\psi(\phi)\mu'(\omega)[1, 2 + Q'(\omega_1, t)] + (1 - \phi)\mu'(\omega) \\ G'' &= \alpha\psi(\phi)\mu'(\omega)[1, 2t + Q''(\omega_1, t)] + (1 - \phi)\mu''(\omega) \end{aligned} \quad (24)$$

It follows from Eq. (24) that at $\phi = 0$ the effective moduli become equal to the moduli of a polymer matrix ($\psi(0) = 0$), while at $\phi \rightarrow 1$ the moduli approach infinity due to assumption of absolute rigidity of the particles. In the case when $\gamma \rightarrow 0$, we have $\omega \rightarrow 0$, as well as the second terms in the

square brackets of the Eq. (24) approaches to zero. Here the effective moduli are expressed as a product of a certain value, depending on ϕ only, and the viscoelastic moduli of a matrix. Analysis of this case was considered above. In the case when $\gamma \neq 0$, there appears an additional relaxation mechanism which leads to appearance of the dimensionless frequency ω_1 , along with the main frequency ω .

In accordance with the equation (22) at fixed values of α and γ' , the frequency ω_1 will be proportional to $\omega d/\mu'(\omega)$ and thus it is not explicitly expressed in terms of ϕ , though with increasing of ϕ at a fixed size of the particles the value of d should decrease, and therefore ω_1 should decrease, and hence values of both $Q'(\omega_1, t)$ and $Q''(\omega_1, t)$ should also decrease. The latter may lead to the fact that maximum of the value of $\tan \delta$ for the filled polymer will be shifted towards low frequencies with increasing of ϕ . Maximum of the value of $\tan \delta$ for the filled polymer may also decrease, if dissipation energy of the filled polymer is mainly associated with γ' . This follows from the fact that with increasing ϕ both Q' and Q'' decrease, and the values in the square brackets the Eq. (24) will decrease. Frequency dependence of ω_1 is mainly associated with dependence $\mu'(\omega)$. At low frequencies, when $\mu'(\omega)$ is practically independent of ω , ω_1 will be proportional to ω , but in the region of intermediate frequencies, decrease of ω , may be expected due to a strong growth of $\mu'(\omega)$. The square bracket of the expression of the actual part of the shear modulus (24) which affects the value of G' deviation from μ will behave itself in the analogous way.

A more detailed analysis of behaviour of G' and G'' can be carried out when the characteristics of the polymer and the conditions of filling are known.

However, it follows from the above considerations that again we cannot confirm the validity of the TtS, TCS and CtS principles for the filled system, though for each particular case the dependence of G' and $\tan \delta$ on ω for the filled system can be calculated from the known properties of the polymer and values of the above mentioned parameters of filling (α , ϕ , γ').

CONCLUSIONS

1) The shear modulus of a particulate composite with polymer matrix can be changed within an order of magnitude by possible changing of the value of the Poisson's ratio.

2) At volume fraction of the filler equal to 70–80 per cent the range of variation of the shear modulus of a composite can be more than one order of magnitude if there is a change in adhesion between the matrix and the particles.

3) In the case of the ideal adhesion and without consideration of the special structural state of the polymer within the interface zone the TtS principle should be valid. The value of the shift factor on the frequency scale is equal to the corresponding value for the polymer matrix. The shift factor for the shear modulus in the direction of the logarithm modulus axis depends on the volume fraction of the filler. This is determined by the difference in the value of the coefficient of thermal expansion of the matrix and the filler.

4) When the adhesion is imperfect or there exist an interface zone with special properties, the model considered does not confirm the general validity of TtS principle.

Acknowledgement

The author expresses his gratitude to G. V. Vinogradov.

References

1. L. D. Landau, E. M. Livshits, *Elasticity Theory*, Moscow, Nauka, 26 (1965).
2. I. M. Livshits, L. Rozenzweig, *Zh. Eksp. & Toer. Fiz. (USSR)* **16**, 967 (1946).
3. R. F. Landel, T. L. Smith, *Amer. Rocket Soc. J.* **31**, 599 (1961).
4. A. S. Lodge, *Elastic Liquids*, London and New York, Academic Press (1964).
5. G. H. Lindsey, *J. Appl. Phys.* **38**, N. 12, 4843 (1967).
6. T. L. Smith, *Trans. Soc. Rheology*, **3**, 113 (1959).
7. R. Schwarzl, Proceedings of the 4th International Congress on Rheology. Interscience, Part 3, p. 241 (1965).
8. J. Ferry, *Viscoelastic Properties of Polymers*, New York (1961).
9. G. Kraus, *Reinforcement of Elastomers*, Interscience Publishers (a Division of John Wiley and Sons) (1966).
10. S. K. Ordjonikidze, A. D. Margolin and P. F. Pokhil, *Mekh. Polim.* **4**, 688 (1968).
11. Yu. S. Lipatov, V. F. Babich and V. F. Rosovizky, *J. Appl. Polym. Sci.* **18**, 1213 (1974).
12. Yu. S. Lipatov, Transactions of the Second All-Union Conference on the relaxation phenomena in polymers, Baku, pp. 64–85 (1972).
13. Van Fo Fy, *The Theory of Reinforced Materials*, Kiev, Naukova Dumka, p. 100 (1972).
14. Structure and Properties of Polymer Surface Layers, Kiev, Naukova Dumka (USSR), pp. 136, 246 (1972).