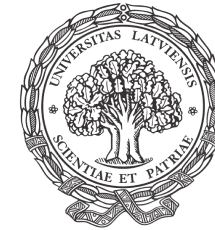


UNIVERSITY OF LATVIA
FACULTY OF PHYSICS AND MATHEMATICS



Tatiana Glaskova

Summary of the Doctoral Thesis

**EXPERIMENTAL AND THEORETICAL
INVESTIGATION OF THERMOPHYSICAL
AND MECHANICAL PROPERTIES
OF POLYMER NANOCOMPOSITES**

Submitted for Doctoral Degree in Engineering
Subbranch: Mechanics of Polymer and Composite Materials

ISBN 978-9984-45-341-5



Riga, 2011

UNIVERSITY OF LATVIA
FACULTY OF PHYSICS AND MATHEMATICS



Tatiana Glaskova

Summary of Doctoral Thesis

EXPERIMENTAL AND THEORETICAL INVESTIGATION
OF THERMOPHYSICAL AND MECHANICAL PROPERTIES
OF POLYMER NANOCOMPOSITES

Submitted for Doctoral Degree in Engineering

Subbranch: Mechanics of Polymer and Composite Materials

Scientific supervisor:

Dr. Sc. Ing. Andrey Aniskevich

Institute of Polymer Mechanics

University of Latvia

Riga, 2011



IEGULDĪJUMS TAVĀ NĀKOTNĒ

This work has been supported by the European Social Fund within the project «Support for Doctoral Studies at University of Latvia».

Type of the work: collection of scientific papers.

Scientific supervisor: *Dr. Sc. Ing. Andrey Aniskevich*, Institute of Polymer Mechanics, University of Latvia.

Reviewers:

1. *Prof. Dr. Habil. Sc. Ing. Robert Maksimov*, Institute of Polymer Mechanics, University of Latvia;
2. *Dr. Phys. Sandris Lācis*, University of Latvia;
3. *Prof. Dr. Sc. Ing. George Papanicolaou*, University of Patras, Greece.

The dissertation defense will take place in the open session of Physics, Astronomy, and Mechanics Dissertation Commission of the University of Latvia to be held on May 20, 2011, at 15:00 in Room 314 of the Institute of Polymer Mechanics.

The dissertation and its summary are available at the Library of the University of Latvia (Kalpaka Blvd. 4) and at the Academic Library of the University of Latvia (Rupniecības Str. 10).

LU Physics, Astronomy, and Mechanics Dissertation Commission chairperson:

Prof. Dr. Habil. Phys. Andrejs Cēbers.

©University of Latvia, 2011

©Tatiana Glaskova, 2011

ISBN 978-9984-45-341-5

Abstract

The doctoral thesis generalizes results of complex research of mechanical and thermophysical properties of epoxy-based nanocomposites and is presented as a set of scientific papers.

Polymers and composites are usually exposed to influence of external factors (temperature, humidity, mechanical loading, etc.) which cause a time-dependent change of their structure and properties due to physical and chemical transformations. Thus, predicting mechanical and thermophysical properties of composite materials, it is necessary to consider results of research about structure and properties time-dependent variability of polymer resins under the influence of external factors.

The aim of the work is to establish features of moisture absorption and to estimate influence of the absorbed moisture on mechanical and thermophysical properties of epoxy-based nanocomposites.

For this purpose at first the kinetics of moisture absorption of epoxy matrix and composites on their basis is experimentally investigated in a wide interval of humidity. For the description of moisture absorption kinetics the comparative analysis of known sorption models is denoted and features of their application are analyzed. The model considering influence of an interphase is offered based on the results obtained for equilibrium moisture content for the nanocomposite. The density of this layer is assumed to be lower than for polymer resin owing to distinction of cross-linking. It is shown that the increase of filler content and consistently interphase leads to greater moisture absorption of composite materials.

Relatively high moisture absorption of epoxy resins causes changes in their structure and properties in time and there is subsequent deterioration of elastic properties of composites. Elastic characteristics of composite materials are investigated experimentally and described by means of micromechanical models. It is shown that elastic modulus of polymer resin in a composite material depends on filler content and decreases with the increase of moisture content. The consideration of morphological features of filler particles (presence of layered structures and formation of an interphase) in a composite material and their influence on elastic characteristics of composite in whole is presented.

Viscoelastic behavior of epoxy resin and epoxy-nanoclay composite is analyzed after long-term influence of moisture. Application of thermomechanical analysis allows establishing the basic regularities for glass transition temperature for nanocomposite with different filler and moisture contents. The experimentally obtained sets of creep and creep recovery curves for nanocomposite with different filler and moisture contents are approximated by means of the linear integral equation of Boltzmann-Volterra, considering a principle of moisture-time analogy.

It is shown that function of a moisture-time reduction correlates with change of a yield stress and volumetric change of nanocomposite samples during moistening that indicates viscoelastic character of deformation of nanocomposites and is confirmed by results of dilatometry.

Main results of doctoral thesis are published in 6 scientific articles [P] and 3 conference proceedings [C], and also discussed in 12 conferences reports.

The investigations were carried out at the Institute of Polymer Mechanics, University of Latvia, in 2003 – 2010.

Table of contents

Abstract	3
1. Introduction, aim, and tasks of the work	6
2. Overview of current scientific verities for investigation of mechanical and thermophysical properties of epoxy resins and epoxy-based nanoclay composites	9
3. Overview of materials and methods used within the work	12
4. Modeling of moisture sorption of composite materials	13
4.1. Application of sorption models to kinetics of moisture sorption of epoxy resins	13
4.2. Moisture sorption by epoxy-based nanocomposite	19
5. Mechanical characterization of epoxy-based composite materials	23
5.1. Strength and elastic properties	23
5.2. Modeling of elastic properties considering layered structure of MMT clay	25
5.3. Modeling of elastic properties considering formation of interphase	31
6. Viscoelastic properties of epoxy-based nanocomposite	36
7. Thermophysical characteristics and structural changes under moistening of epoxy-based nanocomposites	42
8. General conclusions, practical importance, and scientific novelty of the work	48
9. References	51
10. List of publications and conference theses	53
10.1. Papers in journals included in the thesis	53
10.2. Conference proceedings included in the thesis	53
10.3. Conference theses	53
11. Participation in research projects	54
Acknowledgments	55

1. Introduction, aim, and tasks of the work

It's well recognized that all history of mankind development is connected with the invention of some kind of composite materials (CM) which have become a push to technics and civilization development. The very first bricks and the pottery which have appeared app. 5000 years BC contained the crushed stones or reinforcing straw. Ancient potters regulated even porosity of the products. In the beginning of the first millennium Romans have invented the concrete which to high extent influenced building and civilization development.

The present time is remarkable for high rates of scientific and technical progress. The rapid development of modern technics demands more and more new materials having advanced properties. Materials having high durability, hardness, heat and corrosion resistance etc. and a joint combination of these properties are required. The main advantages of polymer composites over traditional kinds of materials (metals, ceramics, wood etc.) is a unique combination of properties (strength, deformation, impact, elastic, rheological, adhesive, electric, frictional, thermophysical etc.) and also a possibility to control material properties changing composition and conditions of manufacture.

Moisture absorption of epoxy resins leads to their time-dependent change in their structure and subsequent deterioration of properties. In order to minimize this negative effect of moisture on functional, structural, and mechanical properties of polymer composites the scientific and industrial interest is devoted to polymer/layered silicate nanocomposites (NC). Polymer NC include different types of matrix (thermoplastic, thermosets, or elastomers) filled with small quantity (less than 6% by weight) of nanosized (less than 100 nm at least in one dimension) particles. The excellent barrier capability with significantly reduced permeability of moisture and gases is one of the most attractive and useful properties that have not been fully explored in the past. The key to such performance rests in the ability to exfoliate and disperse individual, high aspect ratio silicate platelets within the polymer matrix [1]. The complete dispersion of clay nanolayers in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks. The coupling between the tremendous specific surface area of clay ($S \approx 800 \text{ m}^2/\text{g}$) and a polymer matrix facilitates stress transfer to the reinforcement phase, allowing for such tensile and toughening improvements [2].

One of the most prominent silicate nanofillers is montmorillonite (MMT). It belongs to phyllosilicate group of minerals that typically form in microscopic crystals. MMT, a member of the smectite family, is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average thickness of one nanometer and diameter of approximately one micrometer. Due to dispersion of MMT nanoparticles with high

length to thickness ratio in polymer matrix, the obtained system can effectively operate as composite with anisotropic properties that is particularly useful for different applications. The attractive characteristics suggest a variety of industrial applications for NC: automotive (gas tanks, bumpers, interior and exterior panels), constructions (building sections and structural panels), aerospace (flame retardant panels and high performance components), electrical applications and electronics (electrical components and printed circuit boards), food packaging (containers and wrapping films) [3, 4]. The production and investigation of polymers composites belongs to material science area that is one of priority areas in Latvia („Innovation materials and technologies (nano-structured multifunctional materials and nanotechnologies)”) and worldwide.

Epoxy resins widely used as composite matrix are very attractive due to their high strength and stiffness, high temperature resistance, low volatility, creep and shrinkage, good adhesion to metal and ceramic substrates. Nevertheless epoxy resins have a major drawback of moisture absorption, which in turn degrades the functional, structural and mechanical properties of the composites [5, 6].

It is essential to investigate mechanical, thermal and barrier properties of NC and to estimate their steadiness to environmental effects. The improved stability of polymer NC could broaden their application in techniques and construction.

Change of structure and properties of polymers in time due to physical and chemical transformations under the influence of external factors (temperature, humidity, loading, etc.) leads to change of structure and properties of composite materials. The forecast of such changes is necessary to formulate basing on investigation results of time-dependent variability of structure and properties of polymers.

Usually polymer resins in a composite material are non-uniform, forming an interphase with more or less expressed border near the filler particles. The density of interphase could be above or below density of polymer resin owing to distinction of cross-linking and porosity degree. Thus morphological features of filler particles (layered structure and presence of interphase near the border of particles) could influence properties of a composite: elasticity characteristics, durability, and kinetics of moisture absorption, swelling and fracture character.

Therefore the aim of the work is to establish features of moisture absorption and to estimate influence of the absorbed moisture on mechanical and thermophysical properties of epoxy resins and epoxy-clay NC.

For this purpose the following objectives have been set:

1. To ascertain experimental regularities and to model the kinetics of moisture absorption of investigated epoxy resins and epoxy-clay NC in a wide range of humidity;

2. To establish effect of moisture on deformability of epoxy-clay NC and its components, to describe mechanical properties of NC by means of analytical models taking into account filler morphological peculiarities and to verify effect of moisture on deformability of NC incorporating silicate nanoparticles;
3. To forecast long-term creep of investigated materials using method of moisture-time analogy and to estimate change of retardation time spectrum and reduction function of polymer resin by addition of silicate nanoparticles;
4. To establish the interrelation of thermophysical and mechanical characteristics of epoxy-clay NC, having absorbed moisture, with the structural changes accompanying deformation at various schemes of loading and temperatures.

2. Overview of current scientific verities for investigation of mechanical and thermophysical properties of epoxy resins and epoxy-based nanoclay composites

Composite materials based on polymers are frequently exposed to a humid environment. Water molecules, as well as low-molecular substances, are able to move in a polymer resin and change its physical properties. The key parameters determining the mechanism of moisture sorption are the chemical composition and microstructure of the polymer.

The moisture sorption in epoxy resins and composites based on them is investigated rather well. Different models have been suggested for describing the water sorption kinetics [7-9]. It is usually assumed that the moisture sorption in epoxy resins proceeds by diffusion according to Fick's (*Adolf Eugen Fick*) law [7, 10]. Such a model, which suits well the initial stage of moisture sorption, is often inadequate for describing the moisture sorption process as a whole. The moisture sorption can activate different processes in a material, which, in turn, affect the water sorption kinetics (chemical reactions, leaching of low-molecular components, etc.). Therefore, for each investigated material it is necessary to estimate the applicability of different moisture transport models to describing experimental data on water sorption in epoxy binders and to determine the most adequate ones.

In order to minimize the negative effect of moisture on functional, structural, and mechanical properties of polymer composites the scientific and industrial interest devoted to polymer/layered silicate nanocomposites due to their outstanding properties and possible novel applications have resulted in numerous studies [11-13].

Owing to high shape-anisotropy and surface of the exfoliated silicate layers they act as efficient barriers against moisture transport through the material and cause an increase in the path length for molecules diffusing through the polymer. Since absorption of water reduces the elastic characteristics of hydrophilic polymers, the addition of nanoparticles to minimize the negative effects of water uptake is particularly useful [5, 14]. The reduction of moisture absorption in turn can suppress the internal damage and progress to improved long-term performance of the NC.

Although there have been numerous material syntheses, tests and characterizations of layered silicate-filled NC in the literature, the fundamental mechanisms are not fully clear and are rarely discussed [15]. Therefore a better understanding and prediction ability is significant in accelerating development and application of NC.

It should be emphasized that effective properties of two-phase composites have been extensively studied and various micromechanical models have been developed [16-24]. The

basis of these micromechanics models is elastic solution of an infinite matrix containing one inclusion. Nevertheless many authors proposed that apart from two base phases there is an interphase between particle and matrix and its properties should be taken into account [18-20].

In the structural hierarchy of polymer-clay NC at least two states can be assigned: 1) state of total exfoliation of clay platelets with characteristic parameters as thickness and dimensions in the plane of platelets; and 2) state of incomplete exfoliation of clay platelets and characteristic parameters as thickness and dimensions in the plane of intercalated layered stacks [24]. The aspect ratio and orientation of anisometric particles determine their reinforcement degree. Nevertheless, it is difficult to control the orientation of plane particles during processing of composite and the real distribution of their orientation could be rather complex, the determination of the effective elastic constants of transversely isotropic layers of NC with coplanar orientation of such particles is of great importance. The data obtained in this case could serve as initial for a further analysis of the elastic properties of a composite with disoriented nanoparticles taking into account their orientational distribution in the material [24].

Another point is that anisotropy of the layered silicate should be considered. A single layer of montmorillonite clay is a monoclinic crystal composed of two silica tetrahedral sheets and a central octahedral sheet [21]. Taking into account the hexagonal configuration of the tetrahedrons in the two tetrahedral sheets and layered structure of montmorillonite clay it could be assumed that a stack of the silicate layers is a transversely isotropic medium. For the case of intercalated silicate in composite, the layered structure remains while the galleries between layers are filled with polymer. This case also could be represented as transversally isotropic medium from an overall point of view.

Halpin-Tsai equations [24, 25] obtained for isotropic polymer matrix filled with coplanar transversally isotropic cylindrical particles of arbitrary aspect ratio could be used for the case of exfoliated NC. The elastic solution was obtained for the composite consisted of a single fiber encased in a cylinder of matrix, both embedded in an unbounded homogeneous medium, which is macroscopically indistinguishable from the composite. The relations between the stress and strain components have to be averaged throughout the composite. The obtained formulas are curve fitted to exact elasticity solutions and confirmed by experimental measurements in order to get the solution for composite filled with particles of arbitrary aspect ratio.

The mechanical phenomena taking place in the process of sorption and swelling in polymer composite materials, while being of certain theoretical and practical interest, have been studied slightly, especially for nanocomposite that are of interest in developing high-efficiency materials. For example, for clay-containing NC exhibiting improved mechanical, thermal, and

barrier properties compared to unfilled polymers, the majority of papers [2, 5, 13] presented results without conclusions about the processes proceeding in them.

Therefore it is significant to establish the relation between the thermophysical and mechanical characteristics of the clay-containing NC that has absorbed moisture and the structural changes attending the deformation process under different kinds of load and at different temperatures.

Finally the use of modern materials – nanocomposites on the basis of a polymer resin in different areas of techniques, constructions, and also in electronics demands the estimation of long-term deformability and durability in the conditions of influence of different environmental factors (loading, raised and/or variable temperature and/or humidity). For the forecasting of long-term deformability and durability of conventional composite materials: polymers filled with microparticles of minerals, and also reinforced with carbon and glass fibers, the method of stress-time, temperature-time and moisture-time analogies is applied [37, 27]. This method is based on reduction of time by means of acceleration of relaxation processes at increase in level of loading, temperatures, and relative moisture content inside the material, characterized by reduction function. The function of temperature-time reduction which characterizes change of creep rate at change of temperature, for NC is higher in comparison with polymer resin.

Thus the complex research of mechanical and thermophysical properties of various epoxy resins and epoxy-nanoclay composite is necessary in order to determine the steadiness of modern composite materials to different environmental factors (temperature, humidity, loading, etc.) that will allow estimating possible applications of nanoclay composite materials.

3. Overview of materials and methods used within the work

The following thermosetting polymers are investigated in the work: 1) epoxy resin ED-22, hardened by polyethylene polyamine and filled with disperse crystal filler LiF (filler content 0.05, 0.11, 0.23, 0.28, 0.33, 0.38, and 0.46% by weight); 2) epoxy resin Reapox 520; and 3) bisphenol A epoxy resin, hardened by polypropylene oxide filled with particles of montmorillonite clay (filler content 2, 4 and 6% by weight).

Kinetics of moisture sorption is experimentally investigated using sorption method in atmospheres with relative humidity $\varphi = 24, 34, 53, 77, 84$ and 98% using desiccators with silica gel and saturated solution of salts $MgCl_2$, $Mg(NO_3)_2$, $NaCl$, KCl , and K_2SO_4 respectively. Specimens in the form of thin plates are used in order to measure the percentage of weight change due to moisture absorption as a one-dimensional diffusion mode. The specimens are placed then into the humid atmospheres at room temperature and periodically weighed with accuracy 0.00005 g using *Mettler Toledo XS 205DU*. The mass increment $m(t)-m_0$ is used to find the moisture content during sorption

$$w(t) = \frac{m(t) - m_0}{m_0}$$

The investigations are performed by various mechanical methods: 1) quasistatic tension tests according to LVS EN ISO 527 standard by the use of *Zwick 2.5* testing machine with a crosshead rate of 5 mm/min at room temperature; and 2) creep in uniaxial tension according to ASTM D2990 standard by the use of creep-test bench at stress level equal to half of tensile strength for 7 h and recovery tests for 17 h for the specimens at room temperature.

The changes of structure and properties of investigated materials are studied by means of 1) differential scanning calorimetric analysis using *Mettler DSC 30* for temperature range from -50 to 150 °C at heating rate 10 °C/min; 2) thermogravimetry using *Mettler TA 3000* device for temperature range 20–280 °C at heating rate 10 °C/min; 3) differential thermal analysis using *UIP-70M* device with specimens heated to 150 °C at heating rate 2 °C/min with subsequent cooling; and 4) X-ray diffraction analysis using *DRON - 3M* device with photography in transmitted light on CuK_{α} radiation. Scanning of angular intervals was carried out with a 0.01 ° step and with a pulse collection time in each step of 90 sec.

The homogeneity of the filler particles' dispersion in polymer resin is approved by the transparency of all NC specimens. Additional microscopy methods such as scanning electron (SEM) and transmission electron microscopy (TEM) are applied for the micro structural analysis.

4. Modeling of moisture sorption of composite materials

4.1. Application of sorption models to kinetics of moisture sorption of epoxy resins

[P2]

As it was mentioned before moisture absorption of epoxy resins leads to the time-dependent change in the structure and subsequent deterioration of properties. Absorbed moisture can activate different processes in a material, which, in turn, affect the water sorption kinetics (chemical reactions, leaching of low-molecular components, etc.). Therefore, for each investigated material it is necessary to estimate the applicability of different moisture transport models to describing experimental data on water sorption in epoxy binders and to determine the most adequate ones.

Moisture sorption by epoxies is usually [8, 10] described by Fick's model. In this model [7], it is assumed that moisture sorption occurs only by diffusion, and, according to the first Fick's law, the diffusate flow density \mathbf{j} is directly proportional to the gradient of its concentration C

$$\mathbf{j} = -D \text{grad } C, \quad (4.1)$$

where D is the diffusivity describing the rate of moisture sorption, which is independent of moisture concentration. For a non-stationary state, with account of the mass conservation law, the second Fick's equation is valid. For the case of one-dimensional diffusion along the x axis, when the specimen thickness is smaller than its length and width, it has the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (4.2)$$

where $C = C(x, t)$ is the moisture concentration in the specimen which depends on the position x and time t .

The solution to Eq. (4.1) for a plane-parallel plate of thickness h , with initial $C (0 < x < h, t = 0) = C_0$ and boundary $C (x = 0, x = h, t > 0) = C_\infty$ conditions, is the series [7]

$$C(x, t) = C_\infty - 2 \frac{(C_\infty - C_0)}{\pi} \sum_{k=1}^{\infty} \frac{(1 - (-1)^k)}{k} \sin\left(\frac{\pi k}{h} x\right) \exp\left(-\left(\frac{\pi k}{h}\right)^2 D t\right), \quad (4.3)$$

where C_0 is the initial uniform concentration of moisture and C_∞ is a constant concentration of moisture at the surfaces of a plane-parallel sheet. Integrating Eq. (4.3) across the plate thickness, the expression for determining the moisture content in the specimen is obtained:

$$w(t) = w_\infty - 2 \frac{(w_\infty - w_0)}{\pi^2} \sum_{k=1}^{\infty} \frac{(1 - (-1)^k)^2}{k^2} \exp\left(-\left(\frac{\pi k}{h}\right)^2 D t\right). \quad (4.4)$$

Here, w_∞ is the equilibrium moisture content in the specimen. The model considered contains two material characteristics as parameters: the diffusivity D and the equilibrium moisture content w_∞ . In numerous studies [e.g., 7], it is shown that, if the sorption curve is drawn on a diagram whose abscissa axis is \sqrt{t} , the initial section of this diagram will be a straight line passing through the origin of coordinates. Then, using experimental data, the diffusivity can be determined from its inclination:

$$D = \frac{\pi h^2}{16t} L^2, \tag{4.5}$$

where $L = \frac{w(t) - w_0}{w_\infty - w_0}$ is the change in the moisture content $w(t) - w_0$ in the specimen by the instant of time t , normalized to its maximum value.

The second parameter of the model – the equilibrium moisture content – as a rule, is found experimentally as the maximum achieved moisture content in the specimen. It should be noted here that, according to Eq. (4.4), this maximum is achieved only asymptotically at $t \rightarrow \infty$, which in practice leads to an error in determining w_∞ . The relation between the diffusivity found by Eq. (4.5) and φ of the environment is shown in Figure 4.1 for Reapox 520 epoxy resin specimens stored in atmospheres with relative humidity $\varphi = 33, 53, 75, 84$ and 97%.

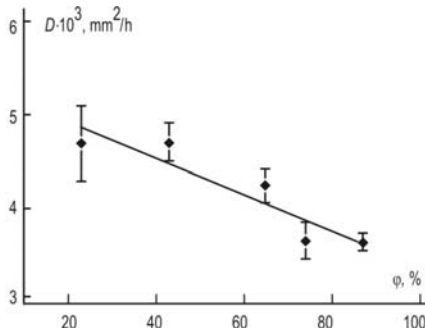


Figure 4.1. Diffusivity in relation to the relative humidity of environment.

The results from calculating the moisture content for Reapox 520 epoxy resin by Eq. (4.4) and experimental data for atmospheres of various humidities are shown in Figure 4.2. It is clear that the Fick’s model describes well the process of moisture sorption in a low-humidity atmosphere, but when the relative humidity exceeds 75%, the moisture sorption process slows down in the middle part of sorption curve.

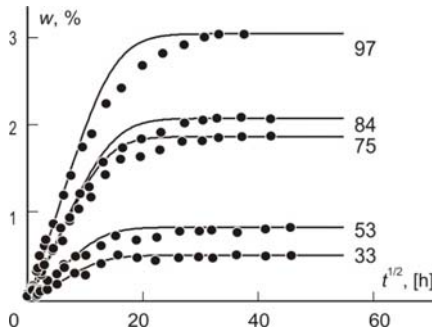


Figure 4.2. Changes in specimen mass with time at different values of ϕ (numbers next to the curves): experimental data (dots) and calculations by Fick's model (4.4) (curves).

In other words, the value of moisture sorption rate used in calculating the moisture content is overestimated, since the model disregards the processes of interaction between the moisture and polymer, swelling, etc., which accompany the process of moisture sorption. It is seen that the adequacy of Fick's model declines with increasing relative humidity of environment, since the diffusion mechanism becomes less dominating, and other mechanisms, such as the interaction between the polymer and the diffusate and/or relaxation processes, start to affect the moisture transport in the polymer [28]. The alternative models of moisture sorption which should be used to explain the deviation of moisture transport in polymers from the classical diffusion mechanism with the diffusivity independent of moisture concentration, take into account different subtle differences in the moisture sorption process in each particular case.

In the model known as Jacob's–Jones model [8], it is assumed that the material consists of two phases of different density and, accordingly, different sorption properties. It is taken that the moisture sorption process in both the phases proceeds simultaneously and obeys Fick's law. The possibility of formation of chemical bonds between water and polymer molecules is neglected. Accordingly, the moisture content in each phase of the material is expressed by the formulas

$$w_1(t) = w_{\infty 1} - 2 \frac{(w_{\infty 1} - w_0)}{\pi^2} \sum_{k=1}^{\infty} \frac{(1 - (-1)^k)^2}{k^2} \exp\left(-\left(\frac{\pi k}{h}\right)^2 D_1 t\right),$$

$$w_2(t) = w_{\infty 2} - 2 \frac{(w_{\infty 2} - w_0)}{\pi^2} \sum_{k=1}^{\infty} \frac{(1 - (-1)^k)^2}{k^2} \exp\left(-\left(\frac{\pi k}{h}\right)^2 D_2 t\right),$$

which contain four unknown parameters, namely the equilibrium moisture content and diffusivity of each of the phases. As a result, the total moisture content in the specimen is

$$w(t) = w_1(t) + w_2(t) \quad (4.6)$$

where $w_1(t) = \frac{\Delta m_1}{m_0}$, $w_2(t) = \frac{\Delta m_2}{m_0}$; $\Delta m_1, \Delta m_2$ are the mass increments of the phases.

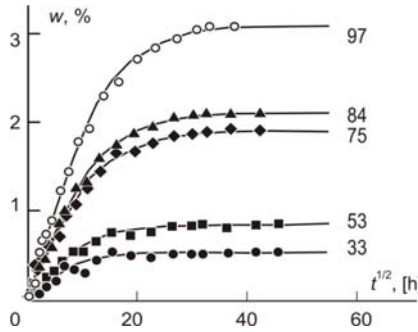


Figure 4.3. Changes in the mass of specimens with time at different values of φ (numbers next to the curves): experimental data (dots) and calculations by Eq. (4.6) (curves).

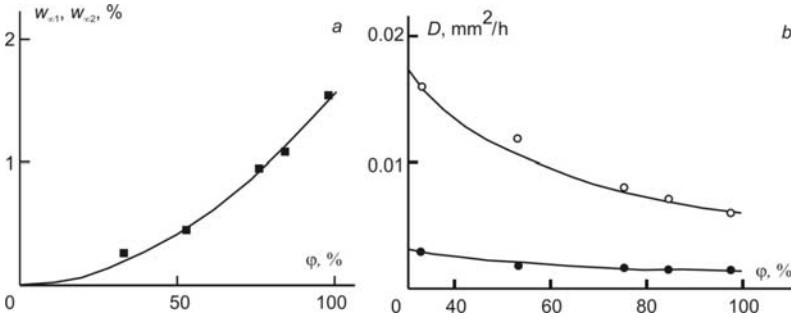


Figure 4.4. Sorption isotherms (a) and diffusivity (b) of the phases D_1 (\circ) and D_2 (\bullet) in relation to φ .

The calculation by Eq. (4.6), presented in Figure 4.3, agrees with experimental data rather well for all the atmospheres considered, which means that the epoxy resin is two-phase. It is known that epoxy resins contain both areas with a sufficiently perfect and dense spatial network and poorly cross-linked regions, which can be regarded as a two-phase structure of the material. This model does not take into account possible changes in the material microstructure during the sorption process, which can be expressed in a worse description of sorption curves with increasing relative humidity of environment, as seen from Figure 4.3. Nevertheless, it can be used for an objective estimation of sorption characteristics of materials with a nonuniform structure.

As seen from Figure 4.4 sorption isotherms of two phases are almost equal. In turn, it follows from Figure 4.4 that, the diffusivity in the different phases differs several times. Probably, this reflects the real material structure with areas of relatively small and high

permeabilities. The account of two-phase nature of the system allows improving the description of the sorption curve.

The last sorption model presented in the thesis is a model with a time-dependent diffusivity [9]. According to this model, owing to the physical processes going on in the material (primarily, the plasticization and associate changes in the relaxation character, as well as aging, aftercure, etc.), the diffusivity decreases with time in proportion to its current value:

$$\frac{dD}{dt} = -\gamma D(t).$$

The solution of this equation is $D = D_0 e^{-\gamma t}$. This model contains three parameters — the diffusivity at the initial instant of time D_0 , the equilibrium moisture content w_∞ , and the coefficient γ describing the rate of change in diffusivity.

To reduce the diffusion equation to Eq. (4.2) with a constant diffusivity D , the principle of modified time is used, by analogy with the change in D under a nonstationary temperature [29]:

$$dt^* = e^{-\gamma t} dt, t^* = \int_0^t e^{-\gamma t} dt = \frac{1 - e^{-\gamma t}}{\gamma}. \quad (4.7)$$

Then, the diffusion equation takes the form

$$\frac{\partial C}{\partial t^*} = D_0 \cdot \Delta C. \quad (4.8)$$

Using the earlier-found solution (4.4) to Eq. (4.2) and replacing t with t^* , according to Eq. (4.7), the solution to Eq. (4.8) for the one-dimensional case has the form

$$w = w_\infty - \frac{2 \cdot (w_\infty - w_0)}{\pi^2} \sum_{k=1}^{\infty} \frac{(1 - (-1)^k)^2}{k^2} \cdot e^{-\lambda_k^2 F}, \quad (4.9)$$

where $F = \frac{D_0}{\gamma} [1 - \exp(-\gamma \cdot t)]$, $\lambda_k = \frac{\pi \cdot k}{a}$, F is the Fourier criterion, $\gamma = 1/\tau$, and τ is the characteristic time of relaxation. A description of the sorption curve by Eq. (4.9) is shown in Figure 4.5.

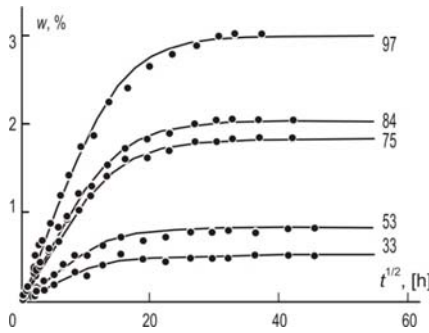


Figure 4.5. Approximation of experimental sorption data according to the model with a time-variable diffusivity for different φ (numbers next to the curves).

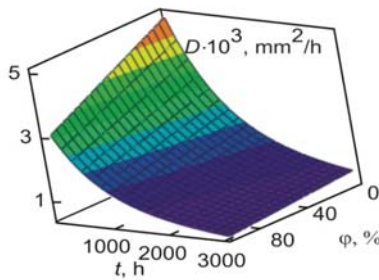


Figure 4.6. Diffusivity D as a function of time t and the relative humidity φ of environment.

The diffusivity D as a function of time and the relative humidity of environment is shown in Figure 4.6. It is seen that, at great times, the diffusivity tends to an infinitesimal value, which describes the saturated state of the system. During moisture sorption (for about 450 h) at $\varphi = 98\%$, $D_0 = 3.61 \cdot 10^{-3} \text{ cm}^2/\text{h}$, and $\gamma = 0.002$, the diffusivity decreased 4-6 times. In general, due to the presence of three parameters, the model is relatively flexible and can describe the sorption curves rather well (Figure 4.5).

Thus the most suitable for describing the sorption kinetics are found to be the model taking into account the two-phase nature of materials and the model with a variable diffusivity. These models give results agreeing rather well with experimental data and in addition contain a relatively small number of parameters, which make them more acceptable in practical applications.

4.2. Moisture sorption by epoxy-based nanocomposite

[P3], [C1]

Properties of multi-component composite materials, as a rule, depend on composition and conditions of their manufacture in a very complicated manner. Therefore for successful forecasting of composite materials' properties it is necessary to investigate properties of each material component separately having equally manufactured material samples.

A series of moisture content measurements of the specimens was executed at different time intervals. The experimental values of moisture content for NC with filler mass content $c = 0\%$ are plotted in Figure 4.7 versus the square root of time. Each of these data points corresponds to the mean value with mean deviation of 4 specimens.

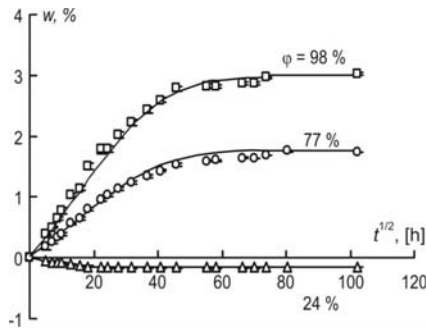


Figure 4.7. The percentage of experimental weight gain (dots) in relation to square root of time in hours for NC with $c = 0\%$ in atmospheres with ϕ (numbers on the curves) and evaluation by Fick's model (solid lines).

From Figure 4.7 it is obvious that sorption process could be described by Fick's model with good agreement for all contents of MMT and in all atmospheres. It should be mentioned that the diffusion coefficients of NC obtained by Eq. (4.5) are independent on relative humidity of atmosphere (see Figure 4.8). The scattering within the atmosphere of equal humidity doesn't exceed 10% of average value. It was experimentally confirmed that sorption process in NC passes much more slowly than in pure epoxy resin (as shown in Figure 4.8), for the highest filler content diffusivity reduces about half of diffusivity as for neat epoxy resin. As it was mentioned above this phenomenon takes place owing to the extremely high aspect ratio of silicate platelets, which increased the tortuosity of the water molecules' path of while moisture diffuses into the NC. According to the tortuous path model and since the moisture permeability is a function of volume fraction and aspect ratio of the platelets the exfoliated NC is more preferred to conventional or intercalated composites in terms of the barrier characteristics [6].

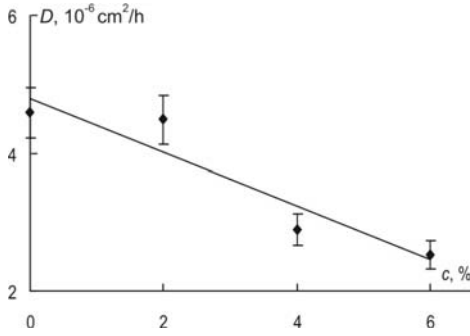


Figure 4.8. Diffusion coefficient of NC evaluated by Eq. (4.5) in relation to filler weight content.

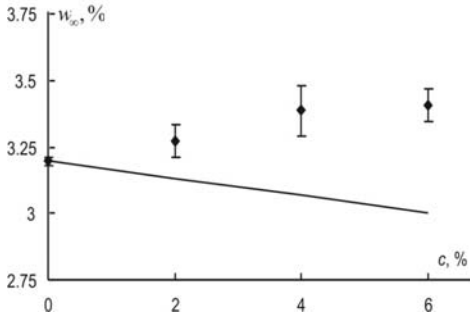


Figure 4.9. Equilibrium moisture content in relation to filler weight fraction in atmosphere with 98% RH (dots - approximation of experimental data, line - evaluation by Eq. (4.10)).

The equilibrium moisture content of NC w_{∞}^{NC} involves the equilibrium moisture content of the NC components: of polymer resin w_{∞}^{ep} and of filler w_{∞}^f , accordingly:

$$w_{\infty}^{NC} = w_{\infty}^{ep} \cdot (1 - c) + w_{\infty}^f \cdot c. \quad (4.10)$$

The use of mass was chosen as a reference in the rule of mixture instead of volume since all the NC specimens revealed swelling of about 3% by volume at the end of the saturation. It is considered that hydrophilic epoxy resin has the main contribution to the moisture uptake and equilibrium moisture content of the filler w_{∞}^f is close to zero since naturally hydrophilic MMT clay has been organically treated.

The increase of equilibrium moisture content with the increase of MMT weight content in NC (shown in Figure 4.9) could be caused by growth of interphase mass content. The estimation of interphase moisture sorption characteristics is created using modified rule of mixture for equilibrium moisture content

$$w_{\infty}^{NC} = w_{\infty}^{ep} \cdot (1 - c - b) + w_{\infty}^i \cdot b, \quad (4.11)$$

where w_{∞}^i is equilibrium moisture contents of interphase, b is interphase content by mass. Such addition of interphase around the filler particles allows preventing the deviation of evaluation by Eq. (4.10) from results of approximation using experimental data. Nevertheless Eq. (4.11) contains 2 unknown parameters (w_{∞}^i and b), that can't be determined independently. That's why the proper analysis is based on the attributing capacity of moisture absorption of the interphase to the deviation between evaluation by Eq. (4.10) and experimental results.

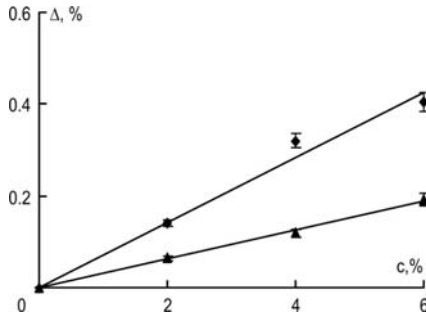


Figure 4.10. Deviation between experimental data of equilibrium moisture content of NC and estimation of it by mixture rule (4.10) for atmosphere with $\phi = 77$ (\blacktriangle) and 98 (\blacklozenge) % RH.

Moreover it should be expected that for atmosphere with higher relative humidity (higher content of absorbed moisture) the difference between the amount of absorbed moisture content measured by experiments and predicted by Eq. (4.10) should increase. This observation is further supported by experiments as shown in Figure 4.10. The higher content of filler leads to greater moisture absorption and greater deviation from estimation by mixture rule without consideration of sorption characteristics of interphase. The general idea is that this deviation that represents moisture content in interphase is linear proportional on filler content (as shown in Figure 4.10). It means that coefficients of proportionality correspond to sorption capacity of interphase in NC per 1% of filler.

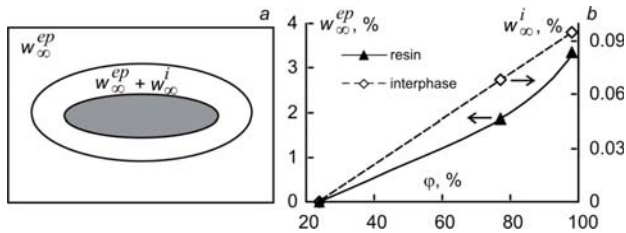


Figure 4.11. Schematic representation of equilibrium moisture content distribution within composite system of one particle (a) and sorption isotherm of epoxy resin and interphase in NC per 1% of clay by weight (b).

At equilibrium the relationship between moisture content in material and equilibrium relative humidity of surrounding atmosphere can be displayed by sorption isotherm. It is estimated that the total moisture content is distributed homogeneously by the section of the NC specimens and according to sorption isotherm for the moisture concentration in NC. For each humidity value, a sorption isotherm indicates the corresponding moisture content at a given, constant temperature. Because of the complexity of sorption processes in composite materials, the isotherms traditionally deviate from Henry's (*William Henry*) law, exhibit nonlinear behavior and should be measured experimentally.

The sorption isotherm of interphase in NC per 1% of clay could be estimated from Figure 4.11. As it was mentioned before the content of interphase in NC couldn't be predicted independently from Eq. (4.11). Nevertheless it's possible to estimate the effect of the interphase on sorption properties of NC in whole. These results could be used for further analysis of the moisture effect on mechanical and thermal properties of NC. Respectively moisture content which exists both in matrix and in interphase of NC could be predicted instead of Eq. (4.10) for given composite system

$$w_{\infty}^{NC} = w_{\infty}^{ep} \cdot (1 - c) + w_{\infty}^i \cdot c, \tag{4.12}$$

where both w_{∞}^{ep} and w_{∞}^i are determined from Figure 4.11, which represents the sorption isotherm of epoxy resin and interphase. This sorption isotherm and formula (4.12) allow approximate estimation of additional moisture content of NC in atmosphere of any relative humidity and any filler content.

Hence it is shown that sorption process could be described by Fick's model with good agreement for all contents of clay and all atmospheres. Based on the results obtained by relating moisture on properties of NC it could be concluded that the addition of impenetrable clay nanoparticles is useful for the reduction of negative effect of moisture on properties of NC allowing the application of modified epoxy resin in environments with higher-operating relative humidity. The effect of absorbed moisture on mechanical and thermophysical properties of epoxy-clay NC is thoroughly discussed in the following chapters.

5. Mechanical characterization of epoxy-based composite materials

5.1. Strength and elastic properties

[P1], [P4], [P6], [C1]

The mechanical behavior of neat epoxy resin and epoxy resin filled with microparticles (LiF crystals) and nanoparticles (MMT) was studied in quasistatic tensile tests for the revealing of filler and absorbed moisture influence on tensile elastic modulus and strength of composite materials. For instance Figure 5.1 shows stress-strain curves of epoxy resin and NC with filler content $c = 6\%$ specimens being preliminary sustained to an equilibrium condition in atmospheres with humidity 24, 77 and 98%. Stress-strain curves of the other NC (with filler contents 2 and 4%) look similarly to curves presented in Figure 5.1 having strongly pronounced limit of forced elasticity.

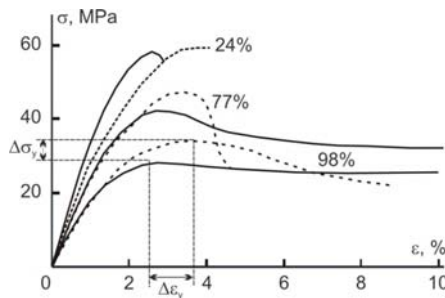


Figure 5.1. Typical stress-strain curves at a fixed rate of deformation (5 mm/min) for neat epoxy resin (dotted line) and NC with $c = 6\%$ (solid line) and different ϕ (numbers on the curves).

As it is clear from Figure 5.2 filling of epoxy resin with MMT nanoparticles led to increase in elastic modulus of dry material approximately by 30% and to reduction of upper yield stress and yield strain app. by 1/3. The increase of moisture content both in epoxy resin and in NC resulted in reduction of elastic modulus and yield stress; while yield strain has almost the same value. Dry (sustained in atmosphere with $\phi = 24\%$) specimens failed in more brittle manner than moistened ones (sustained in atmosphere with $\phi = 98\%$). Durability of the former specimens twice exceeded durability of the latter. Intermediate values of durability are obtained for NC specimens sustained in atmosphere with $\phi = 77\%$.

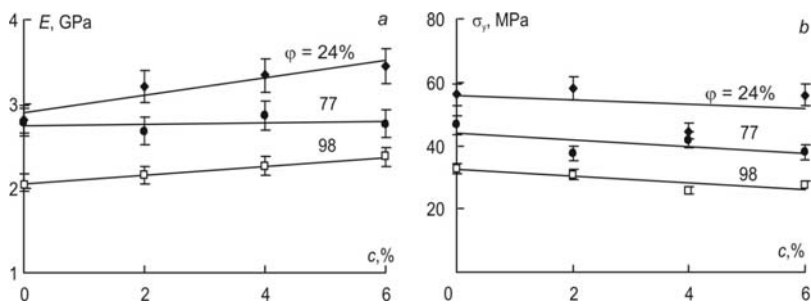


Figure 5.2. Elastic modulus (a) and yield stress (b) of NC in relation to the filler mass content for different ϕ (numbers on the curves).

Consequently due to absorbed moisture both pure resin and NC with $c = 6\%$ show almost same degradation as for elastic modulus by 1 GPa and for tensile strength by 25 MPa, respectively. It should be noted that though the values themselves of elastic modulus and strength are improved with respect to filler content, the positive effect as moisture content increases (in atmosphere from 24% RH till 98% RH) was not established.

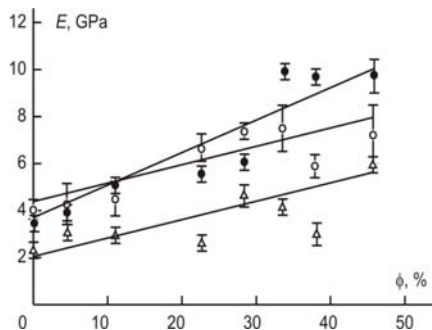


Figure 5.3. Experimental elastic moduli E of the CM in the initial (o) and moisture saturated (Δ) states and after a moistening-drying cycle (\bullet) in relation to the filler volume content ϕ .

Figure 5.3 demonstrates moisture effect on experimentally obtained elastic modulus of epoxy resin filled with different content of LiF crystals. As follows from the data in the figure an increase in the elastic modulus with increasing ϕ is observed for the CM in the conditionally initial state at $\phi \leq 0.33$, in the saturated state at all the values of ϕ considered, and after a moistening-drying cycle at $\phi \leq 0.38$. Thus it is assumed that the structure and properties of polymer resin changes upon filling. This could be explained by the presence of interphase having properties different from the properties of the polymer resin in the bulk. That's why upon modeling of elastic properties of CM it is important to take into account morphological

properties of filler particles in the conditionally initial state and then to estimate effect of absorbed moisture on structure and properties of CM having different filler content.

5.2. Modeling of elastic properties considering layered structure of MMT clay

[P4]

The behavior and properties of NC are dependent not only on properties of its structural components, but also on the material microstructure: the dispersion and orientation of filler particles, and the interactions between filler particles and polymer matrix [30].

Nevertheless one of the main parameters that affect the behavior of the nano-system is the effectiveness of dispersion of filler particles within the polymer matrix [31].

One way to check the morphological peculiarities of clay nanoparticles in a solvent, before incorporating them to a matrix, is to observe their dispersion by TEM. A typical image of acetone suspension of clay nanoparticles is shown in Figure 5.4a.

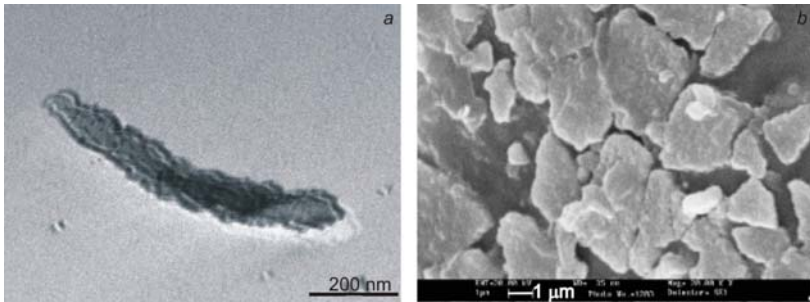


Figure 5.4. Typical TEM image of acetone suspension of clay nanoparticle. The nanoclay appears in black (a); SEM micrograph of fracture surface of NC with $c = 2\%$ (b).

It is obvious from Figure 5.4a that the observed aggregate should be a stack of clay platelets having layered structure and high aspect (diameter to thickness) ratio (50). The aspect ratio of the platelet stack as observed from Figure 5.4a is about 7.

Moreover the platelet shape of the filler particles could be confirmed by SEM micrograph (Figure 5.4b) of fracture surface of NC specimen with $c = 2\%$. It could be seen that the transversal dimension of the filler aggregates is much smaller than longitudinal ones.

Efforts are being made to relate effective tensile elastic modulus of moistened NC with properties of its structural components. It should be emphasized that taking into account complicated structure of real composite material, only evaluative results could be obtained theoretically [16].

Halpin-Tsai equations [24, 25] obtained for isotropic polymer matrix filled with coplanar transversally isotropic cylindrical particles of arbitrary aspect ratio (5.1) are used for the case of exfoliated NC. The elastic solution was obtained for the composite consisted of a single fiber encased in a cylinder of matrix, both embedded in an unbounded homogeneous medium which is macroscopically indistinguishable from the composite. The relations between the stress and strain components were averaged throughout the composite. The obtained formulas were curve fitted to exact elasticity solutions and confirmed by experimental measurements in order to get the solution for composite filled with particles of arbitrary aspect ratio.

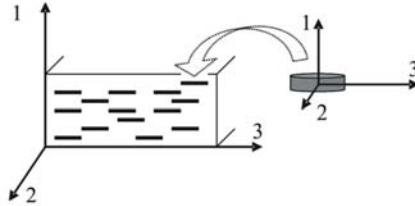


Figure 5.5. Schematic representation of cylindrical filler particles embedded in polymer matrix.

For a completely exfoliated system Halpin-Tsai equations for elastic moduli of NC take form:

$$E_1 = E_m \frac{1 + 2\eta_1\phi}{1 - \eta_1\phi}, \quad (5.1)$$

$$E_2 = E_3 = E_m \frac{1 + 2A_f\eta_2\phi}{1 - \eta_2\phi}, \quad (5.2)$$

where

$$\eta_1 = \frac{R_1 - 1}{R_1 + 2}, R_1 = \frac{E_{f1}}{E_m}, \eta_2 = \frac{R_2 - 1}{R_2 + 2A_f}, R_2 = \frac{E_{f2}}{E_m}.$$

In the equations (5.1)-(5.2) E_1, E_2, E_3 are elastic moduli of given composite, E_m is elastic modulus of matrix and E_{f1}, E_{f2} – elastic modulus of filler for axes' directions shown in Figure 5.5; A_f is the aspect ratio of platelet ($A_f \gg 1$ since it equals to the diameter divided by thickness for cylindrical platelets); ϕ is the volume fraction of filler particles and is determined by formula

$$\phi = \frac{c}{\rho_f} \cdot \frac{1}{\left(\frac{c}{\rho_f} + \frac{(1-c)}{\rho_m} \right)},$$

where c is filler weight content, ρ_f and ρ_m are filler and matrix density, accordingly.

If the exfoliation is incomplete the composite system is considered to consist of matrix and pseudo particles (stacks of individual platelets) [21]. Figure 5.6 shows scheme of filler particles

that are forming a stack (a pseudo particle). N is the number of platelets per stack, L – length (width), t – thickness of the platelet, s – inter-platelet spacing.

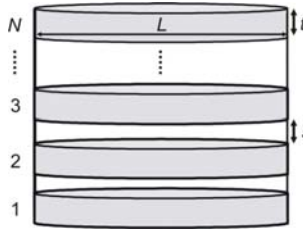


Figure 5.6. Representation of pseudoparticle (platelet stack).

For the case of incomplete exfoliation Halpin-Tsai equations are modified and get form:

$$E_1 = E_m \frac{1 + 2\eta_1' \phi'}{1 - \eta_1' \phi'}, \quad (5.3)$$

$$E_2 = E_3 = E_m \frac{1 + 2A_f' \eta_2' \phi'}{1 - \eta_2' \phi'}, \quad (5.4)$$

where

$$\eta_1' = \frac{R_1' - 1}{R_1' + 2}, R_1' = \frac{E_{p1}}{E_m}, \eta_2' = \frac{R_2' - 1}{R_2' + 2A_f'}, R_2' = \frac{E_{p2}}{E_m}.$$

Here A_f' is the aspect ratio of platelet stack, ϕ' is the volume fraction of platelet stacks, R' is the ratio of platelet stack elastic modulus to elastic modulus of the matrix. Elastic moduli of platelet stack in different axes' directions could be calculated using direct and reverse rules of mixture

$$E_{p1} = \frac{V_{ps}}{\frac{V_p}{E_{f1}} + \frac{V_{ip}}{E_m}}$$

and

$$E_{p2} = \frac{E_{f2}V_p + E_mV_{ip}}{V_{ps}},$$

where V_p is volume of platelets, V_{ip} is volume of inter-platelet spacing, V_{ps} is volume of platelet stacks. Using simple geometrical assumptions (each platelet stack consists of N platelets of thickness t , length L and located at inter-platelet spacing s) the formulas for elastic moduli of platelet stack take form

$$E_{p1} = \frac{E_{f1}E_m(Nt + (N-1)s)}{E_mNt + E_{f1}(N-1)s}$$

and

$$E_{p2} = \frac{E_{f2}Nt + E_m(N-1)s}{Nt + (N-1)s}$$

Accordingly following formulas for aspect ratio of platelet stack A_f' , volume fraction of platelet stacks ϕ' and ratio of platelet stack elastic modulus to elastic modulus of the matrix E_r' were obtained for model parameters [21]:

$$A_f' = \frac{A_f}{N} \left(\frac{1}{1 + \left(1 - \frac{1}{N}\right) \frac{s}{t}} \right),$$

$$\phi' = \phi \left(1 + \left(1 - \frac{1}{N}\right) \frac{s}{t} \right),$$

$$R_1' = R_1 \frac{1 + \left(1 - \frac{1}{N}\right) \frac{s}{t}}{1 + R_1 \left(1 - \frac{1}{N}\right) \frac{s}{t}}, \quad R_2' = \frac{R_2}{1 + \left(1 - \frac{1}{N}\right) \frac{s}{t}} + \frac{\left(1 - \frac{1}{N}\right) \frac{s}{t}}{1 + \left(1 - \frac{1}{N}\right) \frac{s}{t}}$$

Using known values of elastic modulus of matrix in atmospheres with different relative humidity it is possible to determine elastic moduli of NC by equations (5.3) and (5.4). The elastic moduli of montmorillonite clay platelets are ranging from 40 GPa [32] (in transverse direction of platelet) to 180 GPa [24, 33] (in longitudinal direction of platelet) based on the literature values for layered-structure clay minerals, an empirical modulus-density relation for alumina, silica and their compounds and values obtained by simulation for the product of elastic modulus and thickness of the platelets. In the current study elastic moduli of filler are assumed to be $E_{f1} = 55$ GPa, $E_{f2} = E_{f3} = 180$ GPa, aspect ratio of filler platelet $A_f = 50$, number of platelets per stack N is changed from 1 to 6, $s/t = 1$.

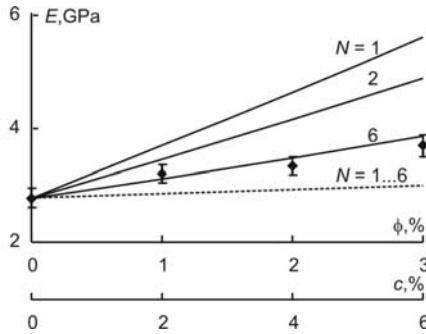


Figure 5.7. Elastic modulus of NC versus filler volume content. Evaluation by (5.1) (solid line) and (5.3) (dashed line) for different number of elementary layers N (numbers on the curves) in a platelet stack.
Dots – experimental data for $\varphi = 24\%$ RH.

Comparing results of evaluation by Eq. (5.1) with experimental data of quasistatic tensile tests of specimens conditioned in dry atmosphere ($\varphi = 24\%$ RH) provided in Figure 5.7 it is obvious that evaluation results for elastic modulus of NC with exfoliated filler particles are higher than experimental ones. Increasing the number of platelets per stack gives the opportunity to get better agreement between them. Although it's rather arguable since it is assumed in the model that filler particles obey coplanar orientation in polymer matrix. On the other hand evaluation by Eq. (5.4) (low bound) is much lower than experimental results even for the case of exfoliated platelets. It means that real orientation distribution of clay platelets is somewhere in between these limits and could be rather complicated.

Nevertheless using obtained results (the same parameters N, t, s) for moistened NC it is possible to estimate structural changes of the polymer resin due to moisture absorption.

The resulting evaluation of elastic modulus of moistened NC by Eq. (5.3) shows the deviation from results obtained experimentally (see Figure 5.8). As it can be seen taking into account platelet stack layered structure (increasing the number of platelets in stack till 6) improves the congruence of results with experimental data. Apparently it could be described by the change of elastic properties of the platelet stacks. It should be emphasized that while elastic modulus of impermeable clay platelets is not dependent on moisture content, the matrix phase that is located in the inter-platelet spacing absorbs moisture. Therefore the elastic properties of the platelet stacks are dependent on absorbed moisture content and cause more significant decrease of moistened NC elastic modulus as presented in Figure 5.8.

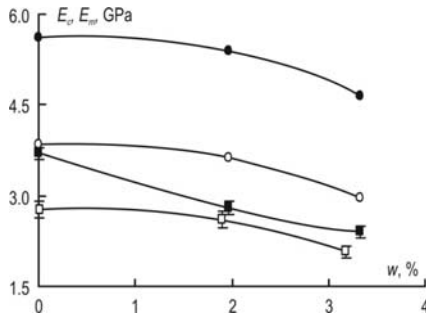


Figure 5.8. Elastic modulus of epoxy resin and NC with $c = 6\%$ in relation to the absorbed moisture content. Experimental data (NC with $c = 6\%$ (■), epoxy resin (□)), evaluation by (5.3) for NC with $c = 6\%$ and $N = 1$ (●) and $N = 6$ (○).

The change of elastic modulus under effect of moisture e. g. NC with $c = 6\%$ proves that moisture which exists in the inter-platelet spacing significantly influences the elastic modulus. Logically enough, the higher content of filler leads to higher content of inter-platelet spacing and as a result to greater moisture absorption and greater change of NC properties that are sensitive to moisture.

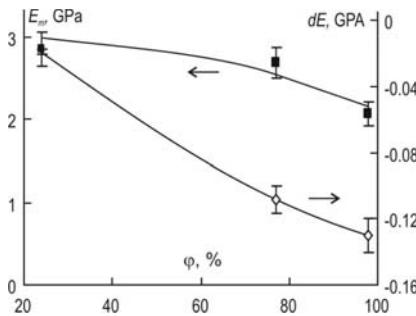


Figure 5.9. Elastic modulus of epoxy resin (■) and normalized to 1% wt. of filler deviation of NC elastic modulus (◇) in relation to the relative humidity of the atmosphere.

The isotherm shown in Figure 5.9 concludes the proposed analysis of moisture and filler effect on deformability of epoxy/MMT NC taking into account filler morphological peculiarities. Using this figure it's possible to estimate NC elastic modulus of any filler content in atmosphere with any relative humidity. It is obvious that due to moisture absorption NC elastic modulus is substantially decreased. Since the value of elastic modulus of epoxy resin is improved with respect to filler content in spite of no positive effect for the decrease of elastic modulus of NC due to moisture absorption (in atmosphere from 24 till 98% RH) epoxy resin modified by

impenetrable stiff MMT clay nanoparticles could be applied in environments with higher-operating relative humidity.

5.3. Modeling of elastic properties considering formation of interphase

[C2]

As pointed out before the silicate platelets could be dispersed in the polymer in three ways: in aggregates, as in intercalated layered NC and in exfoliated platelets. In the current work only the last case is considered due to primary emphasis on the interphase problem. The exfoliated platelets are represented as transversally isotropic spheroids with high aspect ratio that is equal to app. 50.

Since special attention is given to the evaluation of interphase problem and efficiency of adhesion in NC appropriate formulas for the elastic properties of NC filled with randomly oriented transversally isotropic oblate spheroids are applied. For the small filler volume fractions Norris (*Andrew Norris*) approximate expressions [17] for bulk and shear moduli of composite material reinforced with isotropic oblate spheroids with high aspect ratio can be written as

$$K = K_1 + \frac{4}{9} \cdot \phi \cdot \left(\frac{1}{A_f} \frac{\pi}{8} \frac{3-4 \cdot \nu_1}{\mu_1 \cdot (1-\nu_1)} + \frac{1}{\mu_2} \frac{1-\nu_2}{1+\nu_2} \right)^{-1}, \quad (5.5)$$

$$\mu = \mu_1 + \frac{1}{15} \cdot \phi \cdot \left(\frac{1}{A_f} \frac{\pi}{8} \frac{3-4 \cdot \nu_1}{\mu_1 \cdot (1-\nu_1)} + \frac{1}{\mu_2} \frac{1-\nu_2}{1+\nu_2} \right)^{-1} + \frac{2}{5} \cdot \phi \cdot \left(\frac{1}{A_f} \frac{\pi}{16} \frac{7-8\nu_1}{\mu_1 \cdot (1-\nu_1)} + \frac{1}{\mu_2} \right)^{-1}, \quad (5.6)$$

where ϕ is filler volume fraction, A_f is aspect ratio of filler, K , μ and ν are the bulk, shear moduli and Poisson ratio of composite, respectively. Indices 1 and 2 represent matrix and filler properties. The aspect ratio χ is defined as filler particle's diameter related to its thickness and is for the case of NC filled with MMT platelets much higher than 1.

In the numerical calculations, the bulk and shear moduli of the matrix and filler are chosen in such way that they reflect the typical properties of epoxy resin and montmorillonite silicate, respectively. Therefore, the Young's modulus and Poisson's ratio of the matrix are considered to be $E_1 = 3.45$ GPa and $\nu_1 = 0.35$. The elastic modulus is also experimentally determined value. Unfortunately there is lack of the complete elastic constants of montmorillonite silicate. As it was mentioned above in the literature it is usually assumed that elastic modulus in the longitudinal direction is ranging from 140 GPa [20] to 180 GPa [14, 24, 33]. In this work it is assumed that $E_2 = 180$ GPa and $\nu_2 = 0.2$. The aspect ratio is chosen to be about 50.

Then the calculated values of formulas (5.5) and (5.6) are used to evaluate the elastic modulus by the equation

$$E = \frac{9 \cdot K \cdot \mu}{3 \cdot K + \mu} \quad (5.7)$$

The interphase was introduced as a region with gradient of properties nearby the interface of matrix and filler particles. At nanolevel the elastic properties of one single particle containing interphase were considered. The effect of adhesion efficiency was taken into account in the region of the interphase. Previously it was shown that existence of interphase results in increase of equilibrium moisture content during sorption experiments and as a result a significant decrease of elastic moduli was observed. Since the analytical evaluation for both elastic and sorption properties was higher than that for experimental results it was concluded that interphase has elastic properties lower than the matrix and this conclusion will be used in current work.

The expression of the bulk modulus for the system of filler particle-interphase-matrix is assumed to follow the formula

$$K(x, k, R_f) = \begin{cases} K_2 & \text{if } 0 \leq x \leq R_f \\ K_1 \cdot \left(1 - \frac{(K_2 - K_1)}{K_2} \cdot \exp\left(\frac{-(x - R_f)}{k \cdot R_f}\right) \right) & \text{if } R_f \leq x \leq R_i(k, R_f) \\ K_1 & \text{otherwise} \end{cases} \quad (5.8)$$

where x is the coordinate in one-dimensional approach, k is the efficiency of adhesion, R_f is the thickness of the filler particle. The adhesion efficiency is varying from 0 to 1 and expresses the strength of interaction between filler and matrix. The thickness of interphase R_i is denoted as the distance from filler particle to the matrix material with the deviation from matrix properties $\delta = 0.1\%$ and is evaluated by formula

$$R_i(k, R_f) = R_f - R_f \cdot k \cdot \ln\left(\delta \frac{\delta \cdot K_2}{(K_2 - K_1)}\right).$$

The similar formulas could be written for the shear modulus.

Figure 5.10 shows the change of bulk modulus within the system of filler-interphase-matrix material. Four different filler contents corresponding to experimental ones are used in the analysis. It is evident from the figure that increasing filler radius the thickness of the interphase increases. This leads to decrease of effective bulk modulus for the system in whole.

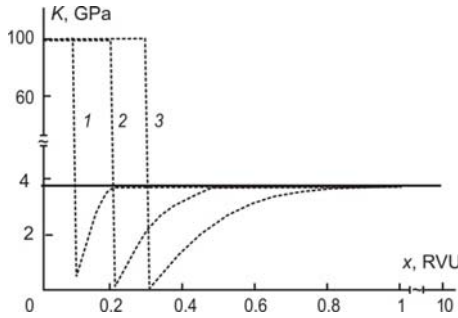


Figure 5.10. Bulk modulus of the 3-phase system for different filler contents $R_f = 1, 2$ and 3% (numbers on the curves) and constant line – neat resin, $k = 0.3$.

Moreover the adhesion efficiency strongly influences the thickness of the interphase and in this way lowers the value of the elastic moduli with the increase of R_i . The dependence of interphase thickness on the filler thickness and adhesion efficiency is shown in Figure 5.11. It is clearly seen that with the increase of filler content or thickness of filler particle the thickness of interphase increases reaching maximal value for the highest adhesion efficiency $k = 1$.

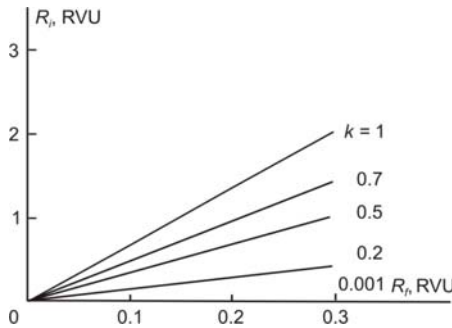


Figure 5.11. Thickness of the interphase vs. thickness of filler particle for different values of adhesion efficiency.

Then the derived variations of moduli were averaged for system of filler particle-interphase in order to get quasi-particle with constant properties using formulas

$$\bar{K}(k, R_f) = \frac{1}{x_{\max}} \cdot \int_0^{R_i(k, R_f)} K(x, k, R_f) dx, \quad (5.9)$$

$$\bar{\mu}(k, R_f) = \frac{1}{x_{\max}} \cdot \int_0^{R_i(k, R_f)} \mu(x, k, R_f) dx. \quad (5.10)$$

These elastic characteristics are used to evaluate the elastic modulus of NC taking into account degree of adhesion and presence of quasi-particles with averaged properties. The elastic modulus is determined by well known relation between elastic characteristics

$$\bar{E}(k, R_f) = \frac{9 \cdot \bar{K}(k, R_f) \cdot \bar{\mu}(k, R_f)}{3 \cdot \bar{K}(k, R_f) + \bar{\mu}(k, R_f)}. \quad (5.11)$$

The final result for the elastic modulus of the composite is showed in Figure 5.12. As it was mentioned before the elastic moduli in the interphase were assumed to be lower than that of the matrix. As seen from the figure adhesion efficiency greatly influences elastic properties of the composite and lowers the effective elastic modulus. It is interesting to notice that with the increase of adhesion efficiency the thickness of the interphase increases and so the content of the quasi-filler particles grows as well. Nevertheless the averaging by the diameter of the particle gives results which are monotonically growing functions in dependence of filler content.

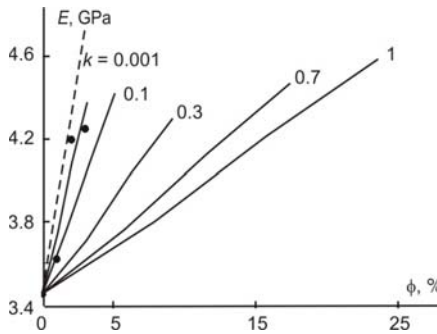


Figure 5.12. Effective elastic modulus in relation to the filler volume content (dots – experimental data, dotted line - evaluation by Eq. (5.7), solid lines – evaluation by Eq. (5.11)).

The expressions for the bulk and shear moduli of the composite were presented using expressions of Norris for randomly oriented platelets which are suitable for low filler contents. First the properties of quasi-particle were estimated at nanolevel considering efficiency of adhesion at different filler contents. It should be noted that the stiffness of filler particles in the direction of major axis is the dominating parameter in these calculations. Since the literature data for the elastic constants of montmorillonite is incomplete it could be concluded that these values could be varied in order to get better agreement with the experimental data.

According to the results obtained in the work the theoretical prediction using expressions of Norris describes the results of quasistatic tensile test quite well. Nevertheless the results of this prediction are higher which can be described by the lack of precise values of parameters like elastic constants and aspect ratio of montmorillonite clay. The possibility to describe this deviation is to introduce interphase. It is clear that taking into account adhesion efficiency and

high surface of filler particles quite high content of quasi-particles is obtained in the case of NC. That's why the thickness of the interphase and adhesion efficiency can greatly influence the mechanical behavior of the NC and should be considered. This analysis at nano- and microlevels provides possibility to estimate the effect of filler and interphase properties and content on effective elastic properties of NC in whole. However polymers are not elastic solids and they behave as viscoelastic materials and therefore viscoelastic properties of NC have to be investigated as described in the following chapter.

6. Viscoelastic properties of epoxy-based nanocomposite

[P6], [C3]

For different kinds of application of NC on the basis of a polymer resin the estimation of long-term deformability and durability in the conditions of influence of different environmental factors (loading, raised and/or variable temperature and/or humidity) is of particular importance [34, 35]. Addition of moisture impenetrable MMT platelets should affect overall viscoelastic properties of NC and result in decrease in NC compliance during moisture absorption process. The viscoelastic behavior of moisture saturated NC specimens with different filler content is an objective of the study and is analyzed in this chapter.

To describe the family of creep and creep recovery curves of NC with different filler content at various values of moisture content w , and basing on Boltzmann (*Ludwig Boltzmann*) superposition principle, the linear integral equation [36, 37] for linear viscoelastic material that is represented with an array of Kelvin (also called Voigt) models is used

$$\varepsilon(t) = \frac{\sigma(t)}{E} + \frac{1}{E} \int_0^t K(t-s)\sigma(s)ds \quad (6.1)$$

with the creep kernel as a sum of exponents:

$$K(t) = \sum_{i=1}^n \frac{b_i}{\tau_i} e^{-\frac{t}{\tau_i}}, \quad (6.2)$$

where τ_i , and b_i , $i = 1, \dots, n$, form the spectrum of retardation times. According to the principle of moisture-time analogy [38],

$$t = t' a_w, \quad (6.3)$$

where $a_w(w)$ is the function of moisture-time reduction, describing variations in the spectrum of retardation times with changes in the relative moisture content in the material.

If the stress varies according to the law

$$\sigma(t) = \sigma_0 H(t) - \sigma_0 H(t - t_0), \quad (6.4)$$

where $t = 0$ and t_0 are the instants of loading and unloading, respectively, and $H(t)$ is the Heaviside function, the compliance $I(t) = \frac{\varepsilon(t)}{\sigma_0}$ has the following expression

for the creep at $t < t_0$,

$$I(t) = \frac{1}{E} + \frac{1}{E} \sum_{i=1}^n b_i \left(1 - e^{-\frac{t a_w}{\tau_i}} \right), \quad (6.5)$$

for the creep recovery at $t > t_0$,

$$I(t) = \frac{1}{E} \sum_i^n b_i e^{-\frac{t \alpha_w}{\tau_i}} \left(e^{\frac{t_0 \alpha_w}{\tau_i}} - 1 \right). \quad (6.6)$$

The function of moisture-time reduction was chosen in the form

$$\ln a_w = \alpha_1 w + \alpha_2 w^2. \quad (6.7)$$

Such functions were used earlier for epoxy binders and composites based on them [39].

The results of short-term (7.5 h) creep of dry (nonmoistened) materials show that creep compliance curves for NC with filler content $c = 0$ and 4% almost coincide (except for instantaneous compliance $I_0 = 1/E$) (Figure 6.1a). That is the filler effect appears in relation of instantaneous compliance to filler content. Moistening of investigated material leads to remarkable increment in creep compliance (Figure 6.1a). Obviously this is caused by case that material is close to viscoelastic state.

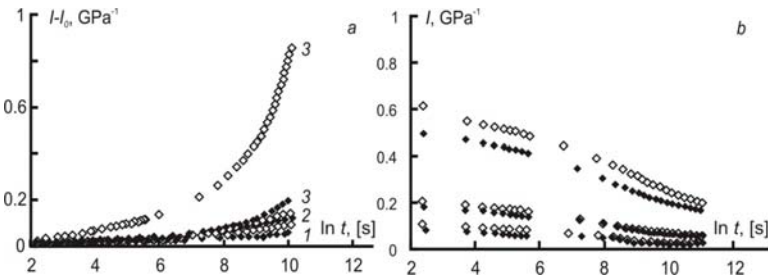


Figure 6.1. Compliance curves of the NC with the filler content $c = 0$ (\blacklozenge) and 4 (\diamond)% for $\varphi = 24$ (1), 77 (2) and 98% (3) in creep (a) and creep recovery (b).

The creep recovery experiments revealed that after 17 h of observation the creep recovery strain still continues to decrease with time (Figure 6.1b). In other words, there is a reason to believe that the creep deformations are reversible. To verify this assumption, it is necessary that the model parameters determined from the results of creep tests can be applied to the case of creep recovery or vice versa. The spectra of retardation times τ_i , b_i , $i = 1, \dots, n$ (6.2) and the function of moisture-time reduction (6.7) of the NC with different filler content can be found from the results of creep recovery tests. For each value of c , the family of compliance curves in creep recovery corresponding to different levels of moisture content w is approximated by Eq. (6.6) with account of Eq. (6.7). The approximation is performed using the SIMPLEX algorithm in FORTRAN. The objective function was specified as the root-mean-square deviation of the calculation from experiment. The initial values of retardation times are chosen at uniform steps in the logarithmic scale, i.e., 1, 10, 100, etc.; the number of exponential functions in creep kernel (6.2) was $n = 7$. During minimization of the objective function, the summands whose pre-

exponential multiplier was of the order of magnitude 10^{-3} and smaller are rejected, and only four exponents remained in Eq. (6.2).

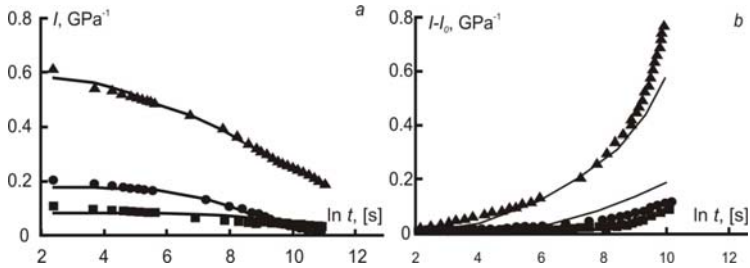


Figure 6.2. Experimental compliances in creep recovery (a) and creep (b) of the NC with $c = 4\%$ at $w = 0$ (■), 2.04 (●), and 3.52% (▲), their approximations by Eq. (6.6) with account of Eq. (6.7) (a), and calculations by Eq. (6.5) with account of Eq. (6.7) (b).

As an example, Figure 6.2a presents the approximated compliance curves in creep recovery for the NC with a filler content of 4%. The verification of applicability of the model used shows a satisfactory description of creep experiments (Figure 6.2b). The spectra of retardation times and the function of moisture-time reduction of NC with different filler content obtained from the approximation are given in Figure 6.3 and Figure 6.4, respectively. The spectra of retardation times for the NC with $c = 2$ and 4% (Figure 6.3) practically do not differ from the spectrum for the binder in a block: they have a common amplitude envelope. However, at $c = 6\%$, these spectra differ: the retardation times increase, but the intensity slightly decreases. As a result, the spectrum envelope is more flat than that for the binder in a block and the NC at $c < 6\%$.

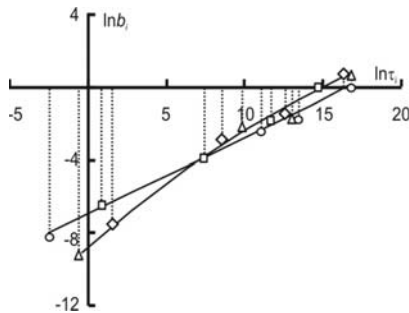


Figure 6.3. Spectra of retardation times of the NC at $c = 0$ (◇), 2 (□), 4 (Δ), and 6% (○).

The functions of moisture-time reduction of the NC with different filler content (Figure 6.4) are nonlinear, and their graphs are concave lines describing the growing influence of the absorbed moisture as its content in the material increases. A comparison of the functions of

moisture-time reduction of the NC at different values of c shows that the addition of a small amount of filler ($c = 2\%$) weakens the influence of moisture on the viscoelastic properties of the binder in the CM. Probably, this is caused by the interaction of filler particles with binder macromolecules with the formation of physical bonds. It is also possible that some part of the absorbed moisture occurs in the interfacial layer. With increasing degree of filling, the influence of moisture on the viscoelastic properties of the binder in the CM grows, and at $c = 6\%$ it becomes equal to that of the binder in a block. The filler particles loosen the binder structure in the NC, and the rate of relaxation processes in the region of great times decreases.

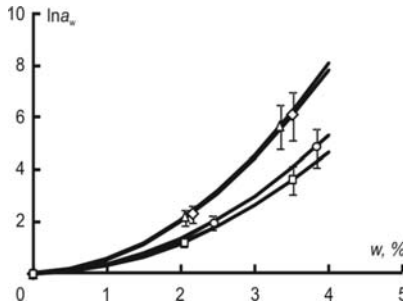


Figure 6.4. Functions of moisture-time reduction of the NC at $c = 0$ (◇), 2 (□), 4 (△), and 6% (○) obtained by approximating the families of creep recovery curves of the material with different moisture content by using Eqs. (6.6) and (6.7).

The influence of the equilibrium moisture content in the NC on its viscoelastic properties is expressed as a changing limit of forced elasticity in quasi-static tests (see Figure 5.2b). Yield stress characterizes the transition of a polymer from glass to rubbery state, which has a relaxation nature.

For its description the equation of Alexandrov-Lazurkin can be applied [40]

$$\tau = \tau_0 \exp\left(\frac{\Delta U - \gamma\sigma}{RT}\right), \quad (6.8)$$

where τ is relaxation time, which characterizes the rate of molecular rearrangements; τ_0 – period of atomic oscillations and is equal to $\sim 10^{-13}$ s; ΔU – activation energy of molecular rearrangements, i.e. the difference between active and initial state of molecules; γ – constant; σ – yield stress; R – gas constant; and T – temperature.

Thus, yield stress is dependent on characteristic relaxation time

$$\sigma = \frac{\Delta U}{\gamma} - \frac{RT}{\gamma} \ln \frac{\tau}{\tau_0} \quad (6.9)$$

The change of moisture content in the polymer results in the change of relaxation times in accordance with moisture-time analogy

$$\ln \frac{\tau_i}{\tau_{0i}} = -\ln a_w. \quad (6.10)$$

Thus a correlation between the yield stress and time-moisture shift factor can be estimated. Such a correlation does exist: for NC with different filler content, the variation in the limit of forced elasticity is directly proportional to the value of the function of moisture-time reduction (Figure 6.5). This correlation can serve as a basis for an alternative determination of the function of moisture-time reduction, namely by using the results of quasi-static tests in the mode of constant strain rate.

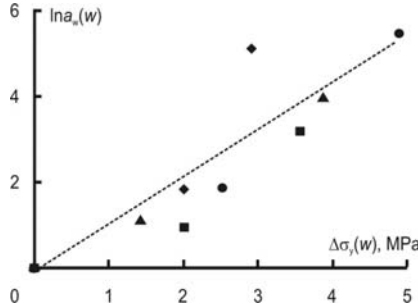


Figure 6.5. Correlation between the function of moisture-time reduction (6.7) and changes in the limit of forced elasticity in quasi-static tests for the NC at $c = 0$ (◆), 2 (■), 4 (▲), and 6% (●).

There is another way for determining the reduction function - according to the volumetric strain [39]. Assuming the binder in a block to be isotropic, the volumetric swelling strain $\frac{\Delta V}{V_0} = 3\varepsilon_h$ can be calculated and using the relation between the reduction function and the change in volume [41]

$$\ln a_w = \frac{1}{f_0^2} \frac{\Delta V}{V_0} \frac{1}{1 + \frac{1}{f_0} \frac{\Delta V}{V_0}}, \quad (6.11)$$

the function of moisture-time reduction is derived (Figure 6.4), which coincides with that determined from creep experiments with $f_0 = 0.062$.

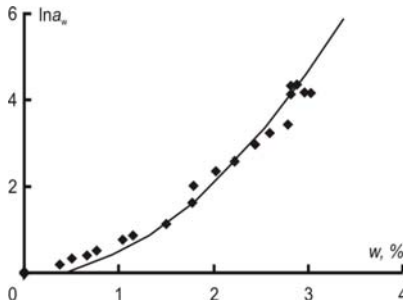


Figure 6.6. Function of moisture-time reduction of the epoxy binder: dots - calculation by Eq. (6.11) with the use of relation between the swelling strain and the relative moisture content; the line - approximation of the family of creep recovery curves given in Figure 6.4.

Thus, based on the principle of moisture-time analogy the function of moisture-time reduction of epoxy resin is derived which correlates with varying volume of specimens upon moistening that allows estimating the function by the results of swelling. In turn the revealed correlation function of moisture-time reduction with the change of limit of forced elasticity indicates viscoelastic character of deformation of NC specimens at different moisture content.

Viscoelastic properties of polymer based composites are fully connected to environmental conditions (temperature, moisture) since with the increase of temperature the frequency of molecular rearrangements increases but delay time decreases. Thus NC specimens having absorbed moisture behave differently due to distinction in glass transition temperature. The features of thermophysical characteristics and their interrelation with structural changes of epoxy-based NC under moistening are explicitly discussed in the next chapter.

7. Thermophysical characteristics and structural changes under moistening of epoxy-based nanocomposites

[P5], [C3]

The features of the phase and relaxation transitions in heating the NC specimens have been studied by the method of thermomechanical analysis (TMA) in the absence of external load. The typical TMA curves of the NC specimens held in an atmosphere with a relative humidity of 24 and 98% until they reached the equilibrium state are presented in Figure 7.1. The general rule for all NC modifications, including those held in an atmosphere with a humidity of 77%, is the presence on the thermal expansion curves of a narrow (5–10°C) temperature range of a sharp change in the character of deformability when in the course of heating the expansion at T_1 is replaced by a shrinkage, and then at T_2 a new growth of deformation begins just as quickly. Such dependences are characteristic of amorphized polymers in which, after passing through glass transition temperature T_g , crystallization occurs very quickly to cause hardening of the material. Then, also spontaneously, melting of the crystallites formed in them begins, which just causes a rise on the TMA curve.

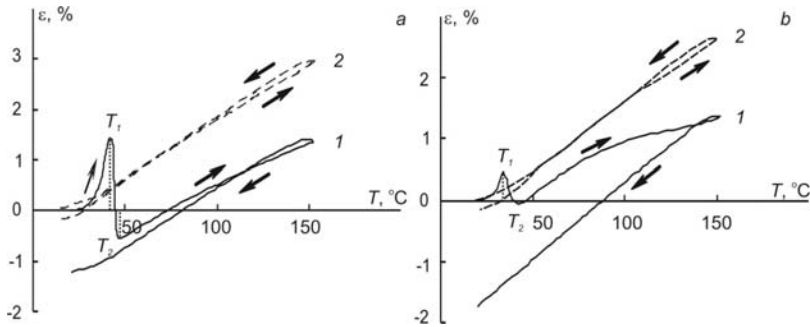


Figure 7.1. TMA curves of NC specimens with $c = 4\%$, $\phi = 24\%$ (a) and 98% (b) (number of heating-cooling cycle (1, 2)).

The fact that the process of shrinkage of the binder in the NC is caused by crystallization is confirmed by experiments with multiple heating of specimens to 70°C and their cooling to 20°C. Figure 7.2 gives the thermomechanical curves for three heating-cooling cycles and shows that the crystallization process was accompanied each time by shrinkage and the melting process — by spontaneous extension. Consequently, in the 20–70°C temperature range the restructuring process in the binder appears to be reversible; crystallization begins at $T_1 = 41\text{--}45^\circ\text{C}$, and melting at $T_2 = 46\text{--}50^\circ\text{C}$.

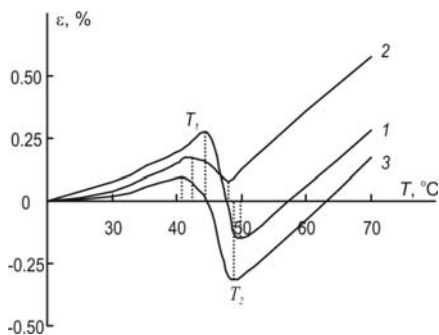


Figure 7.2. TMA curves of the binder at $\phi = 24\%$ (number of heating-cooling cycle (1, 2, 3)).

X-ray structural analysis also confirms that upon preliminary annealing of specimens at 80°C and subsequent drying in a medium of humidity 24% in the binder the crystalline phase is preserved (Figure 7.3, diffractogram 1). The introduction into the NC composition of MMT nanoparticles (diffractogram 2) leads to a change in the parameters of the crystalline reflex of the binder, for example, an increase in the interplanar spacing d and, accordingly, a change in the internal stress in the NC.

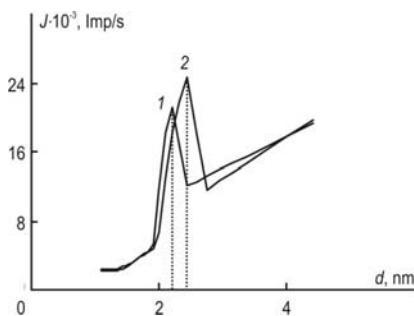


Figure 7.3. Diffractograms of NC specimens with $c = 0\%$ (1) and 6% (2).

It was somewhat difficult to determine T_g from the TMA curves since the attaining by it of the glass transition temperature served as a prerequisite to the binder crystallization in the NC. It was assumed that both processes (devitrification and onset of crystallization) proceeded practically simultaneously. Therefore, the deformation maximum temperature T_1 on the TMA curves (Figure 7.1) is assumed to correspond to the crystallization temperature, and the T_g value was assumed to be slightly different from it. Thus application of thermomechanical analysis to NC with different filler content under moisture effect has shown the following (Figure 7.4): glass transition temperature of NC decreases from 45 to 35°C with the increase of moisture content in NC; the change of glass transition temperature of NC in relation to filler content is insignificant (lies within scattering of experimental data) within atmosphere of equal humidity.

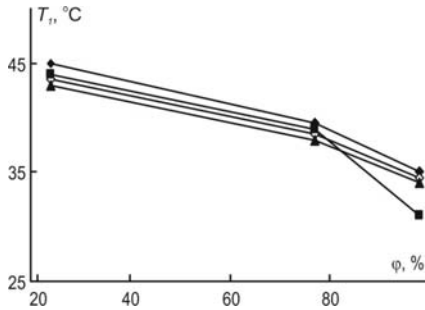


Figure 7.4. Glass transition temperature as a function of the atmospheric humidity for NC at $c = 0$ (♦), 2 (◻), 4 (▲), and 6% (●).

The weak strengthening effect of filler probably is associated with low cross-linking density of polymer's macromolecules located around filler particles and also with possible agglomeration of filler particles [13]. In turn reduction of glass transition temperature of epoxy resin and NC with the increase of moisture content (Figure 7.4) indicates that absorbed moisture softens the materials, i.e. facilitates reduction of intensity interaction between polymer macromolecules and mobility increment of the segments which results in acceleration of relaxation processes. Glass transition temperature of epoxy resin and NC is shifted to temperature region which is only 10-20 °C above room temperature, i.e. temperature during mechanical tests. Therefore loading can lead to transition of epoxy resin to viscoelasticity region which is characterized by large deformations. At least considered epoxy resin with the raised moisture content belongs to transition region from glassy to viscoelastic state.

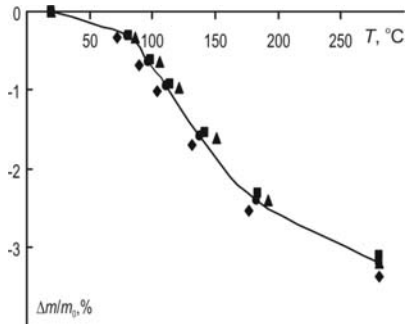


Figure 7.5. Mass loss curves of NC specimens at $\phi = 98\%$ with $c = 0$ (♦), 2 (◻), 4 (▲), and 6% (●).

From the mass loss curves of the thermogravimetric analysis (Figure 7.5) it is seen that in the 80–170°C temperature range the mass loss process is the fastest, which agrees with the decrease in the thermal expansion coefficient. The maximum mass loss is observed in specimens held in an atmosphere with humidity of 98%. For instance, at clay content of 6% the NC mass

loss at 150 °C is 1.5%, and in the binder it is 2% under the same conditions; however, no strict dependence on the degree of filling is observed. A further increase in the temperature leads to a decrease in the mass loss rate. Proceeding from the practically linear interrelation between the moisture content and the mass loss (Figure 7.6), it may be stated that upon heating the NC up to 280 °C the moisture desorption process prevails.

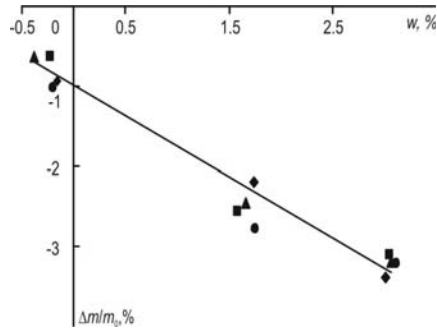


Figure 7.6. Moisture content of NC specimens with $c = 0$ (♦), 2 (■), 4 (▲), and 6% (●) in relation to the mass loss in heating.

In order to establish the relationship between the thermal characteristics and the structural changes attending the NC deformation process TMA analysis has been applied to epoxy-based NC specimens after quasistatic (Figure 5.1) and creep tension experiments (Figure 6.1). For these purpose moist specimens from atmosphere with $\phi = 98\%$ RH were pre-deformed in the air in the regime of quasi-static tension with $\dot{\epsilon} = \text{const}$ and creep with $\sigma = \text{const}$ until the whole of the working part material went into the "neck." Then the specimens were cut along and across the direction of stretching. From the analysis of the TMA curves (Figure 7.7a) it is seen that the thermal expansion of the NC specimens cut in mutually perpendicular directions differs markedly and there are anisotropic changes in the thermomechanical characteristic. Analogous laws have also been obtained for specimens upon creep tests. For heated NC specimens cut along the stretching direction, in both quasi-static tension and creep experiments, their clear similarity to the TMA curves is observed (Figure 7.7b). For instance, in the glass transition temperature range their linear sizes sharply decrease. However, specimens oriented in the creep regime (curve 2) shrink to a greater extent and the process proceeds in a narrower temperature range than for specimens oriented under quasi-static tension (curve 1). Next, when temperatures of 37 °C (under creep) and 64 °C (under quasi-static tension) are attained, the process of their spontaneous stretching begins as sharply as shrinkage.

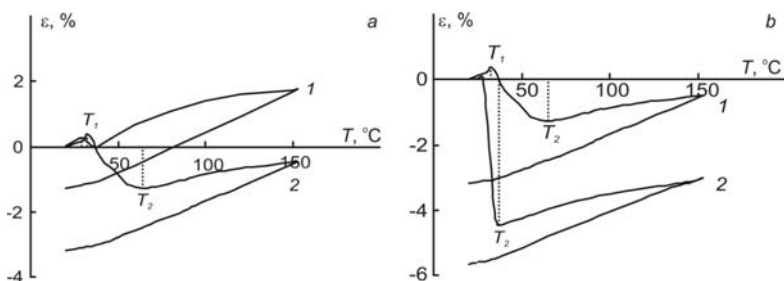


Figure 7.7. TMA curves of NC specimens cut across (1) and along (2) the stretching directions under quasi-static tension (a) and specimens cut along the stretching direction under quasi-static tension (1) and creep (2) (b).

From a comparison with the TMA curves of unloaded NC specimens (Figure 7.1b), it is seen that crystallization of oriented specimens begins at lower temperatures, and the shrinkage value (assumed to be proportional to the degree of crystallinity) is much larger than that for loaded specimens. This is explained by the fact that at orientation a considerable ordering of the NC structure occurs, which is a kind of a crystalline "blank," and therefore its transition to the crystalline structure is considerably facilitated. As a consequence of the crystallization of fibrillar aggregates the NC specimens do not completely regain their sizes either. At the same time, the TMA curves of the specimens cut across the orientation, as the results of quasi-static tension and creep experiments show, practically coincide in terms of the character of the change in the deformability and in its value. The TMA curves of the second heating cycle of specimens reflect, as for unloaded specimens, only one transition connected with the NC devitrification.

The data of X-ray structural analysis correlate well with the assumptions about structural changes in the NC at its deformations to high values. Figure 7.8 presents meridian and equatorial diffraction patterns of NC specimens pre-stretched to failure. It is seen that in the region of small angles on the equatorial diffraction pattern a peak caused by the crystalline phases is present, while it is absent from the meridian diffraction pattern. This effect can be explained by the fact that at large stretches the material acquires an almost completely fibrillated oriented structure, which leads to the disappearance of interfaces characteristic of microcrack walls. Apparently, joining of microcrack walls occurs and, therefore, no diffuse scattering is observed on the diffraction pattern meridian.

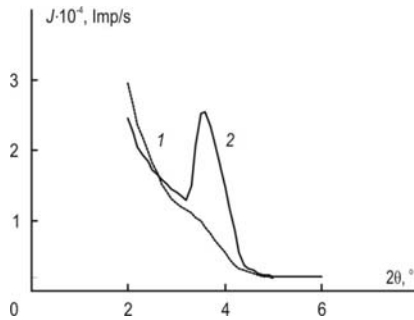


Figure 7.8. Diffraction patterns of a tension pre-deformed NC specimen with $c = 6\%$ cut from the "neck" region: meridian (1); equator (2).

Thus, from the above data it follows that the specific features of the thermomechanical behavior of the non-equilibrium structure of the NC upon stretching is largely determined by the quantity of the initial binder, which has gone to the oriented state, from which fibrillar aggregates of microcracks have been constructed. Changes take place in the region of T_g and, consequently, they have a supermolecular character. In heating, the fibrils acquire a greater mobility, and the coagulation process proceeds. This leads to a disorientation of fibrils with respect to one another and a decrease in the interface area, which shows up macroscopically as shrinkage of the NC.

This chapter concludes the description of complex investigation of mechanical and thermophysical properties of epoxy-based NC filled with nanoparticles of MMT platelets under effect of moisture. The interrelation of thermophysical and mechanical behavior with the structural changes accompanying deformation of epoxy-based NC specimens having absorbed moisture is established in the thesis at various schemes of loading and temperatures. The main conclusions and results, as well as practical importance and scientific novelty of the complex investigation are discussed and analyzed in the next chapter of the thesis.

8. General conclusions, practical importance, and scientific novelty of the work

The results of complex investigation on sorption, mechanical and thermophysical properties of various epoxy resins and epoxy-clay nanocomposite are summarized as follows:

1. Sorption process of investigated epoxy-nanoclay composite is described by Fick's model with good agreement for filler content 0-6% wt. and atmospheres 24, 77, and 98%RH. It is experimentally confirmed that sorption process in NC passes more slowly than in pure epoxy resin, and for the composite with highest filler content diffusivity reduces about half of diffusivity as for epoxy resin. The clay nanoparticles act as efficient barriers against moisture transport. The increase in equilibrium moisture content observed with the increase of clay weight content in NC is explained by growth of interphase content. The specific sorption capacity of interphase in NC per 1% of filler is determined and the sorption isotherm of interphase is derived.

2. Substantial effect of moisture on mechanical properties was shown. Absorbed moisture essentially plasticizes the composite changing its fracture character. Tensile strength of moistened composite decreases twice. Elastic modulus both of moistened pure epoxy resin and NC is reduced approximately 1/3 in comparison to initial state.

2.1. In order to estimate effect of filler morphological peculiarities on elastic properties of NC Halpin-Tsai equations are modified for the case of layered silicate platelets and applied to estimate effective elastic modulus of NC conditioned in atmospheres of different relative humidity. The equation parameters obtained for specimens conditioned in dry atmosphere are used for moistened NC and provided opportunity to estimate structural changes of the polymer resin because of moisture absorption.

2.2. In order to estimate effect of interphase on elastic properties of NC the expressions for the bulk and shear moduli of epoxy-clay NC are derived by modification of Norris expressions for randomly oriented platelets. The properties of quasi-particle are estimated at nanolevel considering efficiency of adhesion at different filler contents. Epoxy resin is further filled with these quasi-particles and micro-model was applied to quantify elastic properties of epoxy-clay NC. This analysis at nano- and microlevels provides possibility to estimate the effect of filler and interphase properties and content on effective properties of NC in whole.

3. Viscoelastic properties of epoxy resin and NC in relation to absorbed moisture content are described on the basis of the principle of moisture-time analogy.

- 3.1. The spectrum of delay times for NC with filler content 6% differs from a spectrum of delay times for epoxy resin: delay times increases, the intensity decreases slightly. Value of moisture-time reduction function for NC with filler content 2% is smaller in comparison with epoxy resin. The further increase in filler content leads to increase in parameters of reduction function.
- 3.2. It is established that moisture-time reduction function correlates with change of upper yield point of NC that indicated viscoelastic character of NC specimens' deformation having different moisture content.
- 3.3. Presence of correlation between moisture-time reduction function and volume change of epoxy resin upon moistening allows its estimating based on the data on swelling.
4. Moisture sorption causes plasticization of NC and leads to decrease of glass transition temperature by 10 °C. The deformation mechanism of NC changes significantly under affect of moisture. Large plastic deformations and formation of transition regions to orientated state ("necking") reveals during tension of moistened specimens of NC. Thermal expansion of the NC specimens cut in mutually perpendicular directions after tensile quasistatic and creep tests differs markedly and there are anisotropic changes in the thermomechanical characteristic. The data of X-ray structural analysis correlates well with the assumptions about structural changes in the NC at its deformations to high values.
5. Incorporation of impenetrable clay nanoparticles with high mechanical characteristics doesn't reduce the negative effect of absorbed moisture on mechanical properties of NC. But since the value of elastic modulus of epoxy resin is improved with respect to filler content up to 20% epoxy resin modified by impenetrable stiff montmorillonite clay nanoparticles can be applied in environments with higher-operating relative humidity.

The **practical importance** of the complex investigation of sorption, mechanical and thermophysical properties of various epoxy resins and composites on their basis rests in the obtained results of steadiness to different environmental factors (temperature, humidity, loading, etc.) determination for novel composite materials. These results will allow estimating possible applications of nanoclay composite materials under influence of environment factors (moisture, temperature, constant and time-varying loading) that will facilitate expanding a scope of polymer composite materials in civil engineering and technological sectors. Since the use of composites in different spheres of life becomes inevitable due to loss of nonrenewable natural resources the efficiency and safety of composites' applications should be guaranteed by correct research of operational properties under the influence of different factors.

Following theses having **scientific novelty** are defended within the work:

1. The account of heterogeneity and formation of the interphase is significant upon modeling of moisture absorption and determination of sorption characteristics of epoxy-clay NC;
2. Modification of Halpin-Tsai equations for isotropic polymer matrix filled with coplanar transversally isotropic cylindrical particles of arbitrary aspect ratio and Norris equations for polymers filler with randomly oriented platelets for the bulk and shear moduli allows determination of effective elastic moduli of epoxy-clay NC taking into account filler morphological peculiarities (layered structure of filler particles and formation of inhomogeneous interphase);
3. The correlation between moisture-time reduction function with the change of upper yield point and volume change of NC specimens upon moistening is established which indicates viscoelastic character of NC specimens' deformation having different moisture content and allows its estimating based on the data on swelling;
4. Anisotropic changes in the thermomechanical characteristic of the NC in mutually perpendicular directions after tensile quasistatic and creep tests are revealed. These results correlate well with data of X-ray structural analysis.

Main results of doctoral thesis are published in 6 scientific articles [P] and 3 conference proceedings [C], and also discussed in 12 conference reports (the conference theses are not included in the thesis).

9. References

1. *Fornes T. D., Yoon P. J., Hunter D. L., Keskkula H., Paul D. R.* Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. *Polymer*, 2002, Vol. 43, No. 22, p. 5915-5933.
2. *LeBaron P., Wang Z., Pinnavaia T. J.* Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science*, 1999, Vol. 15, No. 1, p. 11-29.
3. *Gay D., Hoa A., Tsai S.* Composite materials. Design and applications. CRC Press, 2003, 503 p.
4. *Roco M.* Broader social issues of nanotechnology. *Journal of Nanoparticle Research*, 2003, Vol. 5, No. 3-4, p. 181-189.
5. *Vlasveld D., Groeneveld J., Bersee H., Mendes E., Pichen S. J.* Analysis of the modulus of polyamide-6 silicate nanocomposites using moisture controlled variation of the matrix properties. *Polymer*, 2005, Vol. 46, No. 16, p. 6102-6113.
6. *Kim J.-K., Hu Ch., Woo R. S. C., and Sham M.-L.* Moisture barrier characteristics of organoclay-epoxy nanocomposites. *Composites Science and Technology*, 2005, Vol. 65, No. 5, p. 805-813.
7. *Crank J.* The Mathematics of Diffusion, Oxford, 1956, 224 p.
8. *Maggana C. and Pissis P.* Water sorption and diffusion studies in an epoxy resin system. *Journal of Polymer Science. Part B — Polymer Physics*, 1999, Vol. 37, No. 11, p. 1165-1182.
9. *Andrikson G. A., Mochalov V. P., and Aniskevich A. N.* Principle of modified time scale for tasks of nonstationary moisture diffusion in polymer materials. *Mekh. Kompoz. Mater.*, 1980, Vol. 16, No. 1, p. 153-170.
10. *Xiao G. Z. and Shanahan M. E. R.* Swelling of DGEBA/DDA epoxy resin during hydrothermal ageing. *Polymer*, 1998, Vol. 39, No. 14, p. 3253-3260.
11. *Koo J. H.* Polymer nanocomposites. McGraw-Hill, 2006.
12. *Ajayan P. M., Schadler L. S., Braun P. V.* Nanocomposite science and technology. Wiley, 2003.
13. *Yasmin A., Luo J. J., Abot J. L., Daniel I. M.* Mechanical and thermal behaviour of clay/epoxy nanocomposites. *Composites Science and Technology*, 2006, Vol. 66, No. 14, p. 2415-2422.
14. *Maksimov R. D., Gaidukov S., Zicans J., and Jansons J.* Moisture permeability of a polymer nanocomposite containing unmodified clay. *Mechanics of Composite Materials*, 2008, Vol. 44, No. 5, p. 505-514.
15. *Wang J., Pyrz R.* Prediction of the overall moduli of layered silicate-reinforced nanocomposites – part I: basic theory and formulas. *Composites Science and Technology*, 2004, Vol. 64, No.7-8, p. 925-934.
16. *Christensen R. M.* A critical evaluation for a class of micromechanics models. *Journal of Mechanics and Physics of Solids*, 1990, Vol. 38, p. 379-404.
17. *Norris A. N.* The mechanical properties of platelet reinforced composites. *International Journal of Solids and Structures*, 1990, Vol. 26, p. 663-674.
18. *Odegard G. M., Clancy T. C., Gates T. S.* Modeling of the mechanical properties of nanoparticle/polymer composites. *Polymer*, 2005, Vol. 46, p. 553-562.
19. *Papanicolaou G.C., Bakos D.J, Kosmidou Th.V.* Effect of the interface stiffness and skin-core adhesion efficiency on the interfacial stress distribution of sandwich structures. *Composites: Part A*, 2007, Vol. 38, p. 1099-1106.
20. *Wang J., Pyrz R.* Prediction of the overall moduli of layered silicate-reinforced nanocomposites-part II: analyses. *Composites Science and Technology*, 2004, Vol. 64, p. 935-944.
21. *Bicerano J.* Prediction of polymer properties. 3d ed., Marcel Dekker, 2002, 756 p.

22. *Giannelis E.* Polymer layered silicate nanocomposites. *Advanced materials*, 1996, Vol. 8, p. 29-35.
23. *Pal R.* Mechanical properties of composite of randomly oriented platelets. *Composites: Part A*, 2008, Vol. 39, p. 1496-1502.
24. *Maksimov R. D., Gaidukov S., Kalnins M., Zicans J., Plume E.* A nanocomposite based on styrene-acrylate copolymer and native montmorillonite clay. Part 2. Modeling of the elastic properties. *Mechanics of Composite Materials*, 2006, 42, p. 163-172.
25. *Halpin J. C., Kardos J. L.* The Halpin-Tsai equations: a review. *Polymer Engineering and Science*, 1976, Vol. 16, No. 5, p. 344-352.
26. *Ferry J. D.* Viscoelastic properties of polymers. John Wiley & Sons. New York, 1961, 218 p.
27. *Perez C. J., Alvarez V. A., Vazquez A.* Creep behaviour of layered silicate/starch-polycaprolactone blends nanocomposites. *Materials Science and Engineering A*, 2008, Vol. 480, No. 1-2, p. 259-265.
28. *Bond D. A.* Moisture diffusion in a fiber-reinforced composite. Pt.I. Non-Fickian transport and the effect of fiber spatial distribution. *Journal of Composite Materials*, 2005, Vol. 39, No. 23, p. 2113-2129.
29. *Weitsman Y.* Diffusion with time-varying diffusivity with application to moisture sorption in composites. *Journal of Composite Materials*, 1976, Vol. 10, p. 193-204.
30. *Masenelli-Varlot K., Chazeau L., Gauthier C., Bogner A., Cavaillé J.Y.* The relationship between the electrical and mechanical properties of polymer–nanotube nanocomposites and their microstructure. *Composites Science and Technology*, 2009, Vol. 69, p. 1533-1539.
31. *Tsai J., Sun T.* Effect of platelet dispersion on the load transfer efficiency in nanoclay composites. *Journal of Composite Materials*, 2004, Vol. 38, p. 567-579.
32. *Chen B., Evans J. R. G.* Elastic moduli of clay platelets. *Scripta Materialia*, 2006, Vol. 54, p. 1581-1585.
33. *Anthoulis G. I., Kontou E.* Micromechanical behavior of particulate polymer nanocomposites. *Polymer*, 2008, Vol. 49, p. 1934-1942.
34. *Luo J.-J., Daniel I. M.* Characterization and modeling of mechanical behavior of polymer/clay nanocomposites. *Composites Science and Technology*, 2003, Vol. 63, p. 1607–1616.
35. *Starkova O., Yang J., Zhang Zh.* Application of time-stress superposition to non-linear creep of polyamide 66 filled with nanoparticles of various sizes. *Composites Science and Technology*, 2007, Vol. 67, p. 2691-2698.
36. *Ward I. M., Sweeney J.* Mechanical properties of solid polymers. 2nd edition. Wiley, London, 2004.
37. *Ferry J.* Viscoelastic properties of polymers. Wiley, New York, 1961.
38. *Urzhumtsev Yu. S., Maksimov R. D.* Prediction of the deformability of polymer materials (in Russian), Zinatne, Riga, 1975.
39. *Aniskevich K., Krastev R., Hristova Yu.* Effect of long-term exposure to water on viscoelastic properties of an epoxy-based composition. *Mechanics of Composite Materials*, 2009, Vol. 45, No. 2, p. 137-144.
40. *Tager A. A.* Physics and chemistry of the polymers. 2nd edition. Himija, Moscow, 1968 (in Russian).
41. *Aniskevich A. N., Yanson Yu. O., Aniskevich N. I.* Creep of epoxy binder in a humid atmosphere. *Mechanics of Composite Materials*, 1992, Vol. 28, No.1, p. 12-18.

10. List of publications and conference theses

10.1. Papers in journals included in the thesis

- [P1] *Aniskevich K., Glaskova T., Janson Yu.* Elastic and sorption characteristics of an epoxy binder in a composite during its moistening. *Mechanics of Composite Materials*, N. Y., Kluwer Academic/Plenum Publishers, 2005, Vol. 41, No. 4, p. 341-350.
- [P2] *Glaskova T. I., Guedes R. M., Morais J. J., Aniskevich A. N.* A comparative analysis of moisture transport models applied to epoxy binder. *Mechanics of Composite Materials*, N. Y., Kluwer Academic/Plenum Publishers, 2007, Vol. 43, No. 4, p. 377-388.
- [P3] *Glaskova T., Aniskevich A.* Moisture absorption by epoxy/montmorillonite nanocomposite. *Composites Science and Technology*, 2009, Vol. 69, p. 2711-2715.
- [P4] *Glaskova T., Aniskevich A.* Moisture effect on deformability of epoxy/montmorillonite nanocomposite. *Journal of Applied Polymer Science*, 2010, Vol. 116, No. 1, p. 493-498.
- [P5] *Faitel'son E. A., Glaskova T. I., Korkhov V. P., Aniskevich A. N.* Structural changes in a clay-containing nanocomposite with a different moisture content caused by its deformation. *Journal of Engineering Physics and Thermophysics*, 2010, Vol. 83, No. 3, p. 443-451.
- [P6] *Aniskevich K. K., Glaskova T. I., Aniskevich A. N., and Faitelson Ye. A.* Effect of moisture on the viscoelastic properties of epoxy-clay nanocomposite. *Mechanics of Composite Materials*, 2010, Vol. 46, No. 6, p. 573-582.

10.2. Conference proceedings included in the thesis

- [C1] *Aniskevich A., Glaskova T., Spacek V., Svirglerova P.* Effect of moisture sorption on deformability of epoxy/montmorillonite nanocomposite. *Proceedings of European conference on Composite Materials*, 2006, CD, No. 90.
- [C2] *Glaskova T., Aniskevich A.* Modeling of effective elastic properties of composite material containing nanoparticles with an inhomogeneous interphase. *Proceedings of European Conference on Composite Materials*, 2008, CD, No. 1454.
- [C3] *Glaskova T., Aniskevich A.* Creep behavior of epoxy/clay nanocomposite. *Proceedings of International Conference on Composite Materials*, 2009, CD, No. F1:14.

10.3. Conference theses

1. *Glaskova T., Aniskevich K., Korkhov V.* Structure and properties of epoxy resin in filled composite during its moistening. *Baltic Polymer Symposium*, November 24-25, 2004, Kaunas, Lithuania. Book of abstracts p. 28.
2. *Glaskova T., Aniskevich A., Spacek V., Svirglerova P.* Effect of moisture sorption on the mechanical properties of epoxy/montmorillonite nanocomposite. *Mechanics of Composite Materials*, May 29-June 2, 2006, Riga, Latvia. Book of abstracts p. 58.
3. *Aniskevich A., Glaskova T., Spacek V., Svirglerova P.* Effect of moisture sorption on deformability of epoxy/montmorillonite nanocomposite. *12-th European conference on Composite Materials*, August 29 – September 1, 2006, Biarritz, France. Book of abstracts p. 101.
4. *Glaskova T., Aniskevich A., Starkova O., Merijs Meri R., Zicans J.* Mechanical performance of organo-clay-epoxy nanocomposite under moisture effect. *Baltic Polymer Symposium*, September 20-22, 2006, Riga, Latvia. Book of abstracts p. 51.
5. *T. Glaskova, A. Aniskevich, Yu. Jansons.* Organoclay-epoxy nanocomposite: properties modeling including interphase layer. *ICSAM - The international Conference on Structural*

- Analysis of Advanced Materials, September 2-6, 2007, Patras, Greece. Book of abstracts p. 42.
6. *T. Glaskova, A. Tuchs, A. Aniskevich*. Modeling of volume-dependent properties of disperse filled composite material considering inhomogeneous interphase. Baltic Polymer Symposium, May 13-16, 2008, Otepaa, Estonia. Book of abstracts p. 65.
 7. *E. A. Fätelson, T. I. Glaskova, A. N. Aniskevich, and V. P. Korhov*. Thermomechanical properties of epoxy/clay nanocomposite depending on filler and moisture content. Mechanics of Composite Materials, May 26-30, 2008, Riga, Latvia. Book of abstracts p. 84.
 8. *T. Glaskova, A. Aniskevich*. Modeling of effective elastic properties of composite containing nanoparticles with an inhomogeneous interphase. European Conference on Composite Materials, June 2-5, 2008, Stockholm, Sweden. CD, No. 1454.
 9. *T. Glaskova, A. Aniskevich, R. M. Guedes, and J. J. Morais*. Application of moisture absorption theories for epoxy resin system. Duracosys'08 (Durability Analysis of Composite Systems), July 16-18, 2008, Porto, Portugal. Book of abstracts p. 119, 120.
 10. *T. Glaskova, A. Tuchs, A. Aniskevich*. Modeling of nanocomposite scalar properties taking into account inhomogeneity of the interphase. Functional materials and nanotechnologies, March 31-April 3, 2009, Riga, Latvia. Book of abstracts p. 190.
 11. *T. Glaskova, A. Aniskevich*. Creep behavior of epoxy/clay nanocomposite. 17th International Conference on Composite Materials, July 27-31, 2009, Edinburgh, United Kingdom. CD.
 12. *T. Glaskova, K. Aniskevich, A. Aniskevich*. Creep behavior of epoxy/clay nanocomposite. Mechanics of Composite Materials, May 24-28, 2010, Riga, Latvia. Book of abstracts p. 71.

11. Participation in research projects

1. "Development of modern functional and constructive materials and corresponding technologies for microelectronics, nanoelectronics, photonics, biomedicine". State research program in Material Science, 2005-2008 yrs. The head of project Dr. Sc. Ing. *Juris Jansons*, full member of Latvian Academy of Science.
2. "Investigation of deformation and strength properties of nanocomposites with non-elastic matrices". Grant of Latvian Scientific Council No. 05.1933, 2006-2010 yrs. The head of project Dr. Sc. Ing. *Juris Jansons*, full member of Latvian Academy of Science.
3. "Foundation of young scientist group for investigation of mechanical and physical properties at nano-, meso- and microlevel of modern polymer composite materials with a disperse filler". Research project of the University of Latvia No. Y2-ZP119-100, 01.06.-30.11.2009. The head of the project Dr. Phys. *Olesja Starkova*.
4. "Support for doctoral studies at University of Latvia". Project of European Social Fund No. 2009/2009/0138/1DP/1.1.2.1.2/09/IPIA/VIAA/004, 01.10.2009.-31.09.2010.
5. "Involvement of human resources to complex investigation of modern composite materials". Project of European Social Fund No. 2009/0209/1DP/1.1.1.2.0/09/APIA/VIAA/114, 2009-2012 yrs. The head of project Dr. Sc. Ing. *Juris Jansons*, full member of Latvian Academy of Science.

Acknowledgments

I would like to express my sincere thanks to my scientific supervisor Dr. Sc. Ing. *Andrey Aniskevich*, to director of Institute of Polymer Mechanics (IPM), head of our laboratory Dr. Habil. Sc. Ing *Juris Jansons*, Dr. Phys. *Olesja Starkova* and Dr. Sc. Ing. *Mauro Zarrelli* and the rest non-mentioned but really close colleagues from IPM and CNR for their guidance and encouragement throughout this work.

I am also grateful to L'ORÉAL Baltic (scholarship for „Women in science” with the support of Latvian National Committee of UNESCO and Latvian Academy of Sciences) and European Social Fund (project „Support for doctoral studies at University of Latvia” and project „Involvement of human resources to complex investigation of modern composite materials”) for the financial support in all stages of this research.

And finally last but HUGE thanks I would like to express to my family and friends for their invaluable support and infinite patience. Owing to my elder brother whose first education is physics I've done my choice once. As a result I still do research with gusto. My parents and my husband have also stimulated me a lot to work as good as possible and make them really happy with me 😊.