Modeling of Creep for Multiwall Carbon Nanotube/Epoxy Nanocomposite

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ABSTRACT: The effect of multiwall carbon nanotubes (MWCNTs) on creep of epoxy matrix was evaluated on the basis of short-term creep-recovery tests performed at different stresses and temperatures. Six different compositions of MWCNT and bisphenol A epoxy resin (0–3.8 wt % of MWCNTs) were investigated. Slight reduction of creep compliance, strain rate, and residual strain were revealed experimentally for nanocomposite comparing to the neat resin. The development of viscoelastic strain for creep stage was described by the use of time–temperature–strain superposition principle with the parameters obtained from the approximation of recovery stage using modified Schapery model. The model accounted for the effect of strain on the viscoelastic strain rate for recovery stage. Its application gave better results for approximation of a series of recovery curves at different temperatures and stresses than of time–stress superposition model. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

An appearance of multiwall carbon nanotubes (MWCNTs) with their unique properties including mechanical ones (high stiffness, strength, and flexibility) invoked a great number of investigations on modification of polymer matrices for high strength composites. Epoxy matrices are preferable in structural materials due to relatively high stiffness and strength, good chemical and corrosion resistance, low shrinkage in cure, high adhesion, and dimensional stability.[1–3] Besides high stiffness and strength, a matrix material has to possess viscoelastic and/or viscoplastic properties to eliminate brittle fracture of the composite. These properties determine long-term deformability and strength of the matrix and consequently of the composite. The optimal addition and good dispersion of MWCNTs with their high aspect ratio and interfacial area to epoxy matrix can result in an improvement of its elastic and strength characteristics as well as a decrease of creep strain rate at both room and elevated temperatures.[4] In contrast to elastic and strength characteristics, time-dependent properties, namely, creep and stress relaxation of MWCNT/epoxy nanocomposites (NCs), are not widely and deeply investigated by now. The results of the investigations are conflicting *prima facie*, although some regularities can be found. Soliman et al.[5] found out that MWCNT/epoxy NCs showed a decrease in creep comparing to the neat matrix. The effect of reduction of creep strain is conditioned by good dispersion of functionalized MWCNTs in epoxy matrix.[6,7]

However, functionalization itself results in creation of defects in MWCNTs and chemical bonds in NC. For these NCs, the mechanical approach cannot be applied. Starkova et al.[8] found out that creep resistance of MWCNT/epoxy NC does not differ from that of neat matrix up to tensile stresses of 75% of strength.

It is well known that creep of epoxy matrix is dependent on stress and temperature.[9] With an increase of stress or/and temperature, a creep compliance function becomes nonlinear on stress. The nonlinearity can be described by various phenomenological models. The selection of the model is conditioned by the purpose of its further application, namely, construction of the model useful for subsequent calculation of the composite deformational characteristics or the model useful for comparing the creep of the composite and neat matrix. In the latter case, it should be remembered that creep strain comprises two components: viscoelastic and viscoplastic. The former is reversible, but the latter is irreversible after the load was removed. Provided there is no interaction between various deformational mechanisms, the creep strain is considered as the sum of the two above mentioned components.

Viscoelasticity of MWCNT/epoxy NCs was evaluated by means of dynamic mechanical thermal analysis,[10,11] from which glass transition temperature (T_g) was determined. It was found out[12] that T_g of NC differs from T_g of the neat matrix. In most cases,

it is lower than of neat matrix, i.e., the occurrence of MWCNTs inhibits the curing of epoxy matrix.

An important statement was done by Yang and D'Souza[13] concerning the comparative investigation of MWCNT/epoxy, graphite/epoxy, and carbon nanofibre/epoxy NCs in both glassy and rubbery states. For all glassy NCs, the strains were significantly lower than these of the neat epoxy and decreased with increasing filler content. It limits the use of glassy NCs for many structural applications. The tensile modulus and strength of most rubbery NCs were higher than of neat matrix and increased with the increase of filler content. Most rubbery-like NCs showed higher ultimate strain than the epoxy. So, the reinforced rubbery matrix is more effective than of the glassy matrix. In spite of the fact that the rubbery epoxy is not used for structural composites, the useful temperature range of the composite may include the glass transition region of polymer matrix, especially at high stress levels. In glass transition area, the small increase of temperature may result in a considerable change of the viscoelastic properties[14]: the increase of creep strain rate and decrease of relaxation (retardation) times. The acceleration of creep of polymer material by means of reduction of relaxation times underlines the principle of time–temperature–stress superposition (TTSSP), which is widely used for prediction of long-term deformability. Strictly speaking, the TTSSP principle has ground only in the area of viscoelasticity, where viscoplastic strain does not develop. In this case, creep strain is equivalent to viscoelastic strain. In common case, creep strain comprises also a viscoplastic component, characterizing the accumulation of irreversible changes in the material structure in time.

For MWCNT/epoxy NC, viscoplasticity may be conditioned by pulling out the nanotubes from the epoxy matrix.[15] Viscoplastic strain may be linear function of stress, which is described by use of Burger's model,[16,17] or nonlinear, for example, power function of stress.[18] The nonlinearity form, as well as the dependence on time and temperature for viscoplastic strain, can be obtained from the analysis of creep tests results accounting for the partial reversibility of the process, i.e., evaluation of viscoelastic strain component from the recovery tests. The separation of total creep strain to viscoelastic and viscoplastic components for the material studied in certain conditions can be done on the basis of theoretical model's application to the series of creep-recovery test results.

Nevertheless, the analysis of experimental results and models already reported in the literature showed the lack of information about effect of filler on creep and recovery characteristics of epoxy matrices filled with MWCNTs studied simultaneously at different stresses and temperatures.

That is why the aim of this work was to evaluate an effect of MWCNTs on viscoelastic and viscoplastic properties of epoxy matrix at different stresses and temperatures. To achieve the aim, modeling of time-dependent strain for creep-recovery loading regime and obtaining the model parameters by approximation of the experimental data were done on the basis of short-term creep-recovery tests performed at different stresses and temperatures. Viscoelastic strain component was obtained by fitting a series of recovery curves, corresponding to various stresses and

temperatures. The TTSSP model was modified to account for the effect of initial or elastic strain on viscoelastic strain rate for recovery stage. For evaluation of viscoplastic strain, two approaches were developed, considering it as (i) viscoelastic strain with infinitely long relaxation (retardation) time and (ii) a difference of total and viscoelastic strains for creep stage.

EXPERIMENTAL

Bisphenol A epoxy matrix LH 289, curing agent H 289, as well as masterbatch containing 5 wt % of MWCNTs were provided by Havel Composites (Olomouc, Czech Republic). The masterbatch with previously dispersed MWCNTs was developed by the providing company. This type of resin has low viscosity (520 mPa s at temperature 25°C) and good stability to chemicals. The average dimensions of MWCNTs according to provider's data were 10 nm in diameter and 200 nm in length. Six different MWCNTs contents c in the epoxy matrix ($c = 0$, 0.2, 0.5, 1.0, 1.9, and 3.8 wt %) were prepared in order to investigate the effect of filler on the properties of NC. The intense shear mixing for 5 min was used to get homogeneous batch of epoxy resin with certain amount of the masterbatch. Right after, the necessary amount of hardener (in ratio 33 : 100) was added, and the mixture was degasified for 10 min at room temperature (RT). Then, the silicon molds for dog-bone type samples were filled with the mixture and cured at RT for 22 h and at 50°C for 2 h. The NC specimens were polished to get perfectly flat surfaces. After that, the specimens were post-cured at 80°C for 24 h to remove the technological stresses. The final dimensions of all dog-bone specimens were 150 mm × 10 mm × 4 mm. To avoid any moisture effect on mechanical test results, all the NC specimens were conditioned in desiccators with silica gel of relative humidity 17% at RT for 2 months. After this period of time, no change in the mass of all NC specimens was observed.

The scanning electron microscope (SEM) Hitachi SEM S-4800 was used for investigation of homogeneous dispersion of MWCNTs within the epoxy matrix. The fracture surfaces of the NC specimens with golden spraying (less than 20 nm) were analyzed. At least five photos were made for NC with various filler contents.

To determine the effect of MWCNTs on elastic modulus and strength of NC and choose the stress levels for creep tests within the linear range of elasticity, quasistatic tests were performed. Uniaxial tension of the specimens was done up to their failure using universal testing machine Zwick 2.5 equipped with a load cell of 2.5 kN at a constant crosshead speed of 5 mm min^{-1}, which corresponds to a nominal strain rate of 1×10^{-3} s^{-1}.

Based on the results obtained, three stress levels corresponding to $^1/_4$, $^1/_3$, and $^1/_2$ of strength in the region of linear elasticity were chosen for creep tests. The creep tests lasted for 5 h and were followed by 19 h of recovery. This time scheme was chosen according to ASTM standard (D 2990, 2009) and allows the specimens to recover after the creep. The temperature for each creep-recovery test was constant but was varied from one test to another and equals to 17, 22, and 27°C. The choice of the temperature levels was caused by necessity to investigate time-dependent behavior of the NC at RT and temperatures close to

operational with minor deviation ($\pm5^\circ$C). It provided an opportunity to estimate influence of small temperature changes usually occurring during experiments on viscoelastic behavior of the epoxy and NC. To exclude the effect of physical aging, the temperatures were chosen to be relatively far from glass transition temperature T_g for both epoxy matrix ($45.3 \pm 4.1^\circ$C) and NC ($62.4 \pm 5.3^\circ$C) at the highest filler content (3.8 wt %).[19]

The creep tests at the same temperature were performed simultaneously at three stress levels using creep bench designed in the Institute of Polymer Mechanics, University of Latvia, by account of leverage relation 10. The strain of the NC specimens was determined using displacement data obtained by the half-bridge type extensometer of the basis of 40 mm and digitizing device Spider8 produced by Hottinger Baldwin Messtechnik (Darmstadt, Germany). The data obtained by Spider included time, displacement, and strain for each of three specimens. The frequency of obtaining data was 1 Hz for the first 300 s and further 0.02 Hz till the test end. Temperature during the experiment was measured using thermocouple connected as additional channel to Spider device. Before starting a new creep-recovery test, the strain was reset to zero to exclude any residual strains from the previous test.

MODELING OF CREEP AND RECOVERY

There is a well-elaborated approach for description of creep and recovery responses in the area of linear viscoelasticity, based on Boltzmann's hereditary theory. It is expressed as an integral equation between strain ε, stress σ, and time t

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

where E is the elastic modulus of material.

Creep kernel $K(t)$ may be represented in the form of a series of exponents or Prony series[20]

$$K(t) = \sum_{i=1}^n \frac{b_i}{\tau_i} e^{-(t/\tau_i)}, \tag{2}$$

where τ_i, b_i ($i = 1, \ldots, n$), is a discrete retardation times spectrum.

This form of $K(t)$ allows one to take into account a set of relaxation processes, which underline the creep of polymer material. Integral equation (1) gives a possibility to account for a loading prehistory on strain development. For creep-recovery input, i.e., $\sigma(t) = \sigma_0 H(t) - \sigma_0 H(t - t_0)$, where t_0 is the unloading moment, the response, i.e., compliance $I(t) = \varepsilon(t)/\sigma_0$, will be the following:

$$I(t) = \frac{1}{E} + \sum_{i=1}^n b_i \left(1 - e^{-(t/\tau_i)}\right), \quad \text{if } t < t_0, \tag{3}$$

and

$$I(t) = \sum_i b_i e^{-(t-t_0)/\tau_i} \left(e^{-(t_0/\tau_i)} - 1\right), \quad \text{if } t > t_0. \tag{4}$$

The model parameters, obtained from fitting the creep curves, may be used for the description of recovery curves and *vice versa*.[21]

Linear model is adapted to description of viscoelastic behavior of polymer materials under the action of small stresses and/or low temperatures. Nevertheless, in service life the creep and recovery responses of polymer materials are often nonlinear. The most common thermodynamically consistent theory of nonlinear viscoelastic and viscoplastic materials was developed by Schapery.[22] He suggested that nonlinear viscoplastic response is a particular case of nonlinear viscoelasticity, corresponding to infinite retardation times. Papanicolaou et al.[23,24] have used Schapery's approach to describe nonlinear time-dependent response of unidirectional fiber reinforced composite and also gave the technique how to describe the nonlinearity parameters, while Megnis and Varna[18] performed a systematic investigation of the time-dependent viscoplastic strains occurring in off-axis layers of unidirectional continuous fiber composite (glass fibre/epoxy prepreg system) and suggested a testing methodology for their characterization. According to Megnis and Varna,[18] several authors used Schapery's approach to describe nonlinear time-dependent response of composite giving the technique how to obtain nonlinearity parameters.[24] However, rather little work is done concerning the characterization of time-dependent viscoplastic strain. Megnis and Varna[18] presented the functions describing the stress and time dependence of viscoplastic strain as a product of time- and stress-dependent master curves. The linear viscoelastic response and the final level of viscoplastic strain were determined for recovery, whereas the time dependence of the viscoelastic strain was analyzed in the creep tests at different applied stress levels. It was demonstrated that the time dependence of viscoplastic strain can be described by one master curve that is independent on the stress level.

For uniaxial loading, viscoelastic creep formulation according to Schapery model[22] is the following:

$$\varepsilon(t) = g_0 I_0 \sigma_0 + g_1 \int_0^t \Delta I(\xi - \xi') \frac{d(g_2\sigma)}{ds} ds, \tag{5}$$

where I_0 is the instantaneous compliance, ΔI is the time-dependent part of the compliance, and g_0, g_1, g_2, and a_σ are time-independent, but stress-dependent material parameters. The reduced time arguments are defined by

$$\xi = \int_0^t a_\sigma(s)ds, \quad \xi' = \xi(t') = \int_0^{t'} a_\sigma(s)ds, \tag{6}$$

where $\ln a_\sigma$ is the time–stress shift factor ($a_\sigma < 0$), and s is the integration variable.

The model includes four stress-dependent parameters: g_0, g_1, g_2, and a_σ to be determined from the experiment. Piecewise continuous functions are usually used[8,18] for the description of $g_1(\sigma)$ and $g_2(\sigma)$. Their values are obtained by fitting the experimental creep-recovery data. The choice of the functions becomes more uncertain and complex if the effect of temperature has to be considered.[25] The procedure is very time, energy, and material costly. Practically, it cannot be used for the prediction of long-

term creep of the materials. In a special case of a linear visco-elastic response, all nonlinear parameters are equal to unity: $g_0 = g_1 = g_2 = 1$, and eq. (5) reduces to eq. (1) having time and integration variables t, s substituted by the reduced times ξ, ξ' [eq. (6)]. For creep kernel $K(\xi)$ in the form of eq. (2), one obtain

$$\varepsilon(t) = \frac{\sigma(t)}{E} + \sum_{i=1}^{n} b_i \int_0^{\xi} \frac{1}{\tau_i} e^{-(\xi-\xi')/\tau_i} \sigma(\xi') d\xi'. \tag{7}$$

The model describing nonlinearity through the reduced time is called by time–stress superposition. It may be especially useful for the description of a series of creep-recovery curves obtained at various stresses and temperatures. An application of TTSSP allows one to extend the time scale by the use of elevated temperatures and stresses for acceleration of relaxation processes.

A multiple time–temperature–stress shift factor $\ln a_{T\sigma}(T,\sigma)$ may be introduced in accordance with Alexandrov–Lazurkin formula for the relaxation times[26,27]:

$$\tau_i = \tau_{0i} \exp\left[-\frac{U_0 - \gamma\sigma}{RT}\right], \tag{8}$$

where U_0 is the effective activation energy, γ is the structurally sensitive parameter, $R = 8.31$ J mol^{-1} K^{-1} is the universal gas constant, T is the temperature in K, or in accordance with free volume concept.[28]

There are two questions to be discussed and experimentally verified: (i) a type of function to be used in description of time–temperature–stress shift factor for creep; and (ii) change of the shift factor when creep stage changes to recovery.

Let us consider the functions, which can be used for description of time–temperature–stress shift factor as a function of temperature and stress increments for creep. In accordance with eq. (8), shift factor for two creep compliance curves, obtained at different temperatures T_0 and T_1 and stress levels σ_0 and σ_1 will be the following:

$$\ln a_{T\sigma} = \frac{\tau_i^{(1)}}{\tau_i^{(0)}} = \left(\frac{U_0 - \gamma\sigma_0}{RT_0^2}\Delta T + \frac{\gamma\Delta\sigma}{RT_0}\right)\frac{1}{1 + \frac{\Delta T}{T_0}}, \tag{9}$$

where $\Delta T = T_1 - T_0$, $\Delta\sigma = \sigma_1 - \sigma_0$, T_0, and σ_0 are the reference temperature and stress, i.e., temperature and stress levels corresponding to reference creep compliance curve, regarding which the shift is considered.

If the relative change of temperature is small, $\frac{\Delta T}{T_0} \ll 1$, then eq. (9) can be written in the form

$$\ln a_{T\sigma} = \alpha_1 \Delta T + \alpha_2 \Delta\sigma, \tag{10}$$

where $\alpha_1 = (U_0 - \gamma\sigma_0)/RT_0^2$ and $\alpha_2 = \gamma/RT_0$.

According to free volume concept[28]

$$\ln a_{T\varepsilon} = \frac{1}{f_0^2}\frac{\alpha_v^T\Delta T + \Delta\varepsilon_v}{1 + \frac{1}{f_0}\left(\alpha_v^T\Delta T + \Delta\varepsilon_v\right)}, \tag{11}$$

where f_0 is the relative free volume characterizing the initial state of the material, α_v^T is the volume coefficient of thermal expansion (CTE), $\Delta\varepsilon_v$ is the difference of volume strains caused by application of different stresses σ_0 and σ_1 ($\Delta\sigma$).

If the relative volume change is small, $\frac{1}{f_0}\left(\alpha_v^T\Delta T + \Delta\varepsilon_v\right) \ll 1$, eq. (11) can be rewritten in the form:

$$\ln a_{T\varepsilon} = \frac{1}{f_0^2}\left(\alpha_v^T\Delta T + \beta_2\Delta\varepsilon_v\right). \tag{12}$$

The use of time–temperature–strain shift factor in the form of eq. (12) complicates the prediction of long-term creep of the material on the basis of eq. (7), because strain variables are found on both the left and right sides of the equation. However, the strain development in time can be explained as follows: current value of strain depends on the strain prehistory. To solve eq. (7) with respect to the reduced time variable, numerical methods, for example, step-by-step approach, can be used. This problem is out of our current discussion. We will consider the difference of eqs. (10) and (12) in their application to creep-recovery curve description.

The difference of volume strains $\Delta\varepsilon_v$ caused by application of different stresses σ_0 and σ_1 may be approximated by the difference of elastic volume strains

$$\Delta\varepsilon_v \approx \frac{\sigma_1}{E_1}(1 - 2v_1) - \frac{\sigma_0}{E_0}(1 - 2v_0), \tag{13}$$

where E_0 and E_1 and v_0 and v_1 are the elastic moduli and Poisson ratios of the material for stresses σ_0 and σ_1, respectively.

If the characteristics of elasticity are stress (or strain) independent, $E_0 = E_1 = E$ and $v_0 = v_1 = v$, then

$$\Delta\varepsilon_v \approx \frac{1 - 2v}{E}\Delta\sigma \tag{14}$$

and eq. (12) reduces to eq. (10) with the parameters $\alpha_{1\sigma} = \alpha_v^T/f_0^2$, and $\alpha_{2\sigma} = (1/f_0^2)((1 - 2v)/E)$.

Thus, the time–temperature–stress and time–temperature–strain shift factors coincide for creep stage.

For two-stage creep regime, Schapery[22] introduced two different time–stress shift factors: $a'_\sigma(\sigma)$ for creep and $a''_\sigma(\sigma)$ for recovery. Since recovery is a passive loading regime with zero stress, it was supposed that $\ln a'_\sigma(\sigma) = 0$ or $a''_\sigma = 1$. Taking into account the change of temperature for transition from one creep-recovery test to another, the reduced times for creep and recovery stages in accordance with Schapery model are the following:

$$\xi = t \cdot a_{T\sigma}(T, \sigma), \tag{15}$$
$$\xi = t_0 \cdot a_{T\sigma}(T, \sigma) + a_T(T)(t - t_0), \tag{16}$$

where $a_{T\sigma}(T,\sigma)$ is the time–temperature–stress shift factor defined by eq. (10).

The free volume concept gives the time–temperature–strain shift factor [eq. (12)], in which strain-dependent part does not vanish for recovery because volume strains and their difference for

transition from one creep-recovery test with stress σ_0 to another with σ_1

$$\Delta\varepsilon_v = (1 - 2v_1)\varepsilon_1 - (1 - 2v_0)\varepsilon_0 \qquad (17)$$

are not zero. Let us suppose that time–temperature–strain shift factor is the same function for creep and recovery, but its strain argument has different values for creep and recovery. Instead of elastic volume strain taken as a first approximation for creep, the initial value of time-dependent volume strain, which is the sum of viscoelastic and viscoplastic components, can be considered as the first approximation for recovery. Then eq. (12) will take the form

$$
\begin{aligned}
\ln a_{T\varepsilon} &\approx \frac{1}{f_0^2}\left(\alpha_v^T\Delta T + \Delta\varepsilon_v\right)\\
&= \frac{1 - 2v_0}{f_0^2}\left[\frac{\alpha_v^T\Delta T}{1 - 2v_0} + \frac{1 - 2v_1}{1 - 2v_0}\varepsilon^{(1)} - \varepsilon^{(0)}\right],
\end{aligned} \qquad (18)
$$

where ε_0 and ε_1 are the elastic strains for creep and the initial time-dependent strains for recovery, respectively.

Substituting the constant coefficients of eq. (18), it is reduced to

$$\ln a_{T\varepsilon} = \alpha_{1\varepsilon}\cdot\Delta T + \alpha_{2\varepsilon}\cdot\varepsilon_1 - \varepsilon_0, \qquad (19)$$

where $\alpha_{1\varepsilon} = \alpha_v^T/f_0^2$ and $\alpha_{2\varepsilon} = (1 - 2v_1)/f_0^2$.

Keeping in mind that time–temperature–stress and time–temperature–strain shift factors for creep and recovery are different, the designations $\ln a'_{TF}$ and $\ln a''_{TF}$ are used for compliance formulation from eqs. (6) and (7) and eqs. (10) and (19),

$$I(t) = \frac{1}{E} + \sum_{i=1}^{n} b_i\left(1 - e^{-(t/\tau_i)a'_{TF}}\right), \quad \text{if } t < t_0, \qquad (20)$$

and

$$I(t) = \sum_{i}^{n} b_i e^{-((t-t_0)/\tau_i)a''_{TF}}\left(e^{-(t_0/\tau_i)a'_{TF}} - 1\right), \quad \text{if } t > t_0, \qquad (21)$$

where F denotes the factor accelerating the relaxation processes and is σ or ε for TTSSP or time–temperature–strain superposition, accordingly.

Assumptions regarding the viscoplastic strain for creep are the following: (i) it is a particular case of nonlinear viscoelasticity corresponding to infinite retardation times; and (ii) it can be calculated as a difference of total and viscoelastic strains. The latter can be calculated on the basis of eq. (19), by the use of the parameters τ_i, b_i $(i = 1, \ldots, n)$, f_0, α_v^T, $(1 - 2v_1)/(1 - 2v_0)$ (or U_0 and γ), obtained from the approximation of recovery test results using eq. (21). It is worth noting that the production of time–temperature–stress shift factor $a_{T\sigma}(T,\sigma)$ by time t_0 in eq. (21) is large enough to give zero value to exponent in bracket. So, a solution of the optimization problem on the basis of eq. (21) is difficult when the initial values of the parameters are unknown. As the solution of the optimization problem on the basis of eq. (20) is easier, the results of the approximation of a series of creep curves can be used as the initial values of parameters for approximation of the recovery test results.

RESULTS AND DISCUSSION

Microstructural Characterization

The morphological peculiarities of MWCNTs within the epoxy matrix were checked using SEM investigating fracture surfaces of NC specimens. It is well known that SEM analysis is restricted by tiny area rejecting the rest of the specimen. The area investigated should be representative of the whole specimen. That is why dispersion of MWCNTs within a polymer matrix should be characterized at different levels starting from microlevel and proceeding till nanolevel depending on the size of filler particles.[29,30] The dispersion of MWCNTs at micro- and nanoscales within the epoxy matrix for NC with 3.8 wt % of MWCNTs is shown in Figure 1.

The individual nanotubes are randomly spread within the epoxy matrix at both scales. This step-by-step observation allows one to conclude that the dispersion of MWCNTs in the NC is rather homogeneous and the experimental procedure chosen for the manufacturing of NC specimens is efficient.
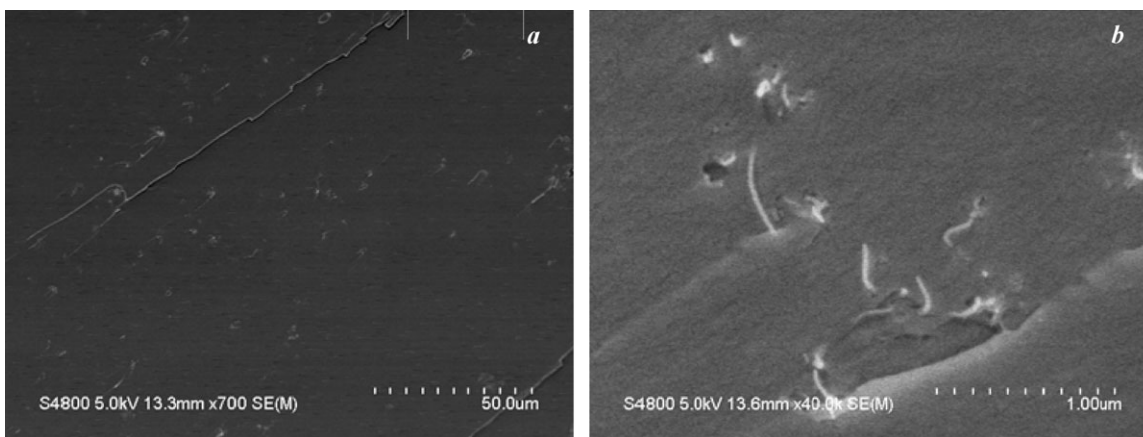

Figure 1. SEM micrograph of epoxy NC with 3.8 wt % of MWCNTs at microscales (a) and nanoscales (b).

Figure 2. SEM micrograph of epoxy NC with 1 (a), 1.9 (b), and 3.8 (c) wt % of MWCNTs.

However, the nanotubes agglomerates in NCs were also observed by SEM. The larger was the nanofiller content in NCs the larger was the agglomerate size (see Figure 2). Similar result was obtained by Martone et al.[31] for MWCNT/epoxy NC, produced by the same experimental procedure.

Quasistatic Tensile Tests

The quasistatic test results did not show positive effect of MWCNTs on elastic modulus of NC. The elastic modulus of NC was about 3.14 ± 0.1 GPa. Slight effect of MWCNTs was observed on tensile strength of the NC. The strength of the epoxy matrix was about 60 ± 5 MPa; the strength of NC with 3.8% of MWCNT was 70 ± 6 MPa. As it is shown widely in the literature,[8,13,15,32] tensile properties of NCs are quite insensible to the incorporation of MWCNTs into the polymer matrix due to their stronger dependence on the presence of agglomerates and defects in the NCs which can appear during manufacturing

of the specimens as well as on the carbon nanotube (CNT)–polymer interfacial bonding. Relatively weak bonding leads to poor stress transfer from polymer matrix to CNTs, and the CNTs would have a low reinforcing efficiency, resulting in the insensitivity of the NC tensile properties to the CNT content.[15,29]

Experimental Creep-Recovery Strain Curves

Keeping in mind that the creep of polymer material is accelerated by an increase of temperature and stress levels, one can suppose that the effect of nanofiller will be more noticeable at larger values of T and σ. To show the effect of nanofiller, the creep-recovery test results for NC with $c = 3.8\%$ of MWCNTs and neat epoxy matrix at highest temperature [Figure 3(a,c)] and stress [Figure 3(b,d)] levels are compared. Creep strains of NC are smaller than of neat epoxy matrix [Figure 3(a,b)]. The difference appears as earlier (in time), as the temperature and
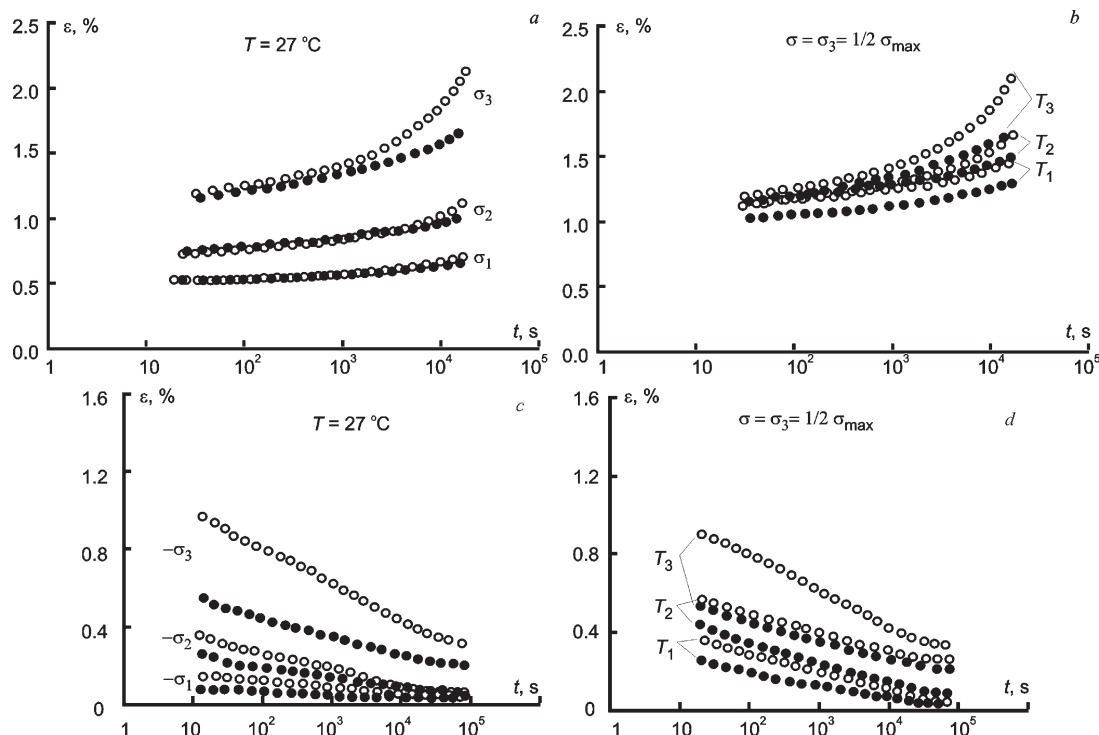
Figure 3. Creep (a,b) and recovery (c,d) curves for MWCNT/epoxy NC with $c = 0$ wt % (○), 3.8 wt % (●); (a,c) $T = 27°C$, σ_1, σ_2, $\sigma_3 = 16$, 22, 29 MPa; (b,d) $\sigma_3 = 29$ MPa, T_1, T_2, $T_3 = 17$, 22 and 27°C.

stress levels are increased. This means that the occurrence of nanofiller in epoxy matrix decelerates the relaxation processes underlying the creep. Thus, high modulus MWCNT, having high aspect ratio, acts as restriction sites for regrouping of polymer macromolecules. As the increase of temperature and stress results in the decrease of relaxation (retardation) times [eq. (8)], the effect of nanofiller is more noticeable at larger temperatures and stresses. So, the addition of MWCNTs improves creep resistance of epoxy matrix affected by two factors, i.e., stress and temperature. Papanicolaou et al.[33] reported similar results for creep of MWCNT/epoxy NC at lower stress level. Such improvement in creep resistance was attributed to the increased tendency of epoxy to exhibit its elastic rather than its viscous nature with the addition of MWCNTs. However, due to agglomeration of MWCNTs at high filler content, this effect is insignificant taking into account the potential impact of highly elastic MWCNTs to the improvement of creep resistance of epoxy matrix.

The recovery tests [Figure 3(c,d)] gave viscoelastic strain $\varepsilon_{ve}(t)$, in which rate increased with the increase of stress and temperature, and residual strain ε_{res}, in which value also increased with the increase of stress and temperature. Comparing the graphs in [Figure 3(c,d)], one can note that the effect of stress and temperature on viscoelastic strain rate is less expressed for NC than of neat resin. Similar result with the reduction of creep strain rate due to addition of MWCNTs to epoxy resin was obtained by Tehrani et al.[4] As for the value of residual strain, the effect of nanofiller is expressed at highest temperature and stress. There was quite large data spread for the residual strain of NCs at different filler contents as a function of applied stress and temperature. Therefore, values of ε_{res} were considered in approximation for each creep-recovery test.

Approximation of Creep-Recovery Compliance Curves

To select the nonlinearity form, the creep-recovery compliance curves were approximated using time–temperature–stress [eq. (10)] and time–temperature–strain (eq. (19)) superposition models along with eqs. (20) and (21). A series of creep (or recovery) compliance curves, corresponding to various σ and T, were simultaneously approximated by the use of SIMPLEX algorithm in FORTRAN environment. The objective function in the form of root-mean-square deviation was used. Initially, a series of $n = 7$ exponents were chosen, but during the optimization process the number of exponents was reduced to 4: the summands with small amplitudes b_i (of two orders of magnitude) were removed. The initial values of the parameters were obtained from approximation of creep compliance curves of epoxy matrix. Then, the recovery curves of the matrix and NCs with various c were approximated. As a result of the approximations, the parameters τ_i, b_i $(i = 1, \ldots, n)$ of eqs. (20) and (21), f_0, α_v^T, $(1 - 2v_1)/(1 - 2v_0)$(or U_0 and γ) were obtained for NCs with all considered c.

The Case of $\varepsilon_{res} \xrightarrow[t \to \infty]{} 0$. It was already mentioned above that viscoplastic strain component for creep can be modeled as viscoelastic one with infinitely long retardation time, i.e., residual strain will recover for long time. Thus, a series of recovery curves without deduction of residual strains were approximated

by the use of TTSSP and time–temperature–strain superposition models. As an example, the results for NC with $c = 3.8\%$ of MWCNTs are given in Figure 4. Comparing the solid and dotted lines, which are the approximation results using the above two models, one can note that the time–temperature–strain superposition gives better fit of experimental data. Similar result was obtained for NCs with other c and neat epoxy matrix.

The parameters $\alpha_{1\sigma} = (U_0 - \gamma \sigma_0)/RT_0^2$, $\alpha_{2\sigma} = \gamma/RT_0$ of time–temperature–stress shift factor [eq. (10)], and $\alpha_{1\varepsilon} = \alpha_v^T/f_0^2$, $\alpha_{2\varepsilon} = (1 - 2v_1)/f_0^2$ of time–temperature–strain shift factor [eq. (19)], for MWCNT/epoxy NCs with various c are shown in Figure 5. Comparing the nonlinearity parameters α_{2F} of time–temperature–strain superposition $(F = \varepsilon)$ and TTSSP $(F = \sigma)$ [Figure 5(b)], one can note that the values of former are at least two times larger than of latter. The difference is evident because α_{2F} characterizes the dependence of retardation times on strain and stress, respectively, in the former and latter cases. For both cases, the value of nonlinearity parameter α_{2F} decreases with the increase of nanofiller mass content. The values of parameter α_{1F} obtained by approximation of recovery curves with time–temperature–strain shift factor (eqs. (19) and (21)), practically coincide with the values, obtained by approximation of creep curves with time–temperature–stress shift factor (eqs. (10) and (20)), but differ from the parameters obtained by approximation of recovery curves with time–temperature–stress shift factor (eqs. (10) and (21); (a)). This fact can be considered as an indirect confirmation of our suggestion to modify Schapery model for recovery by the use of time–temperature–strain superposition instead of TTSSP. Parameter α_{1F} characterizes the acceleration of relaxation/retardation processes in NCs with temperature increase. In accordance with definition [eq. (19)], α_{1F} is proportional to volume CTE α_v^T and inversely proportional to free volume f_0. Thus, the change of α_{1F} with the increase of c may be conditioned by the changes of the material CTE and/or f_0. This is in line with the dilatometric test results of NC considered.

As the parameters of time–temperature–strain and time–temperature–stress shift factors differ by value, the amplitudes of the retardation spectra obtained by the use of time–temperature–strain superposition and TTSSP principles are also different by value (Figure 6). However, the forms of spectra are similar. It is difficult to establish some strong relation of the spectra on filler content. Thus, one can conclude that the NCs with various c are characterized by the same retardation spectrum, but their shift factors are different.

To check the applicability of models considered with the parameters obtained from the fitting of a series of recovery curves, a series of creep compliance curves were described by the use of eqs. (19) and (20) for the case of time–temperature–strain superposition, and eq. (10) for the case of TTSSP, replacing a'_{TF} with $a'_{T\varepsilon}$ and $a'_{T\sigma}$ respectively. As an example, the description results for creep compliance curves are shown in Figure 7. Comparison of the graphs reveals that time–temperature–strain superposition gives better description of experimental data than the TTSSP. Similar result was obtained for NCs with other c. It was already shown above that the approximation of recovery
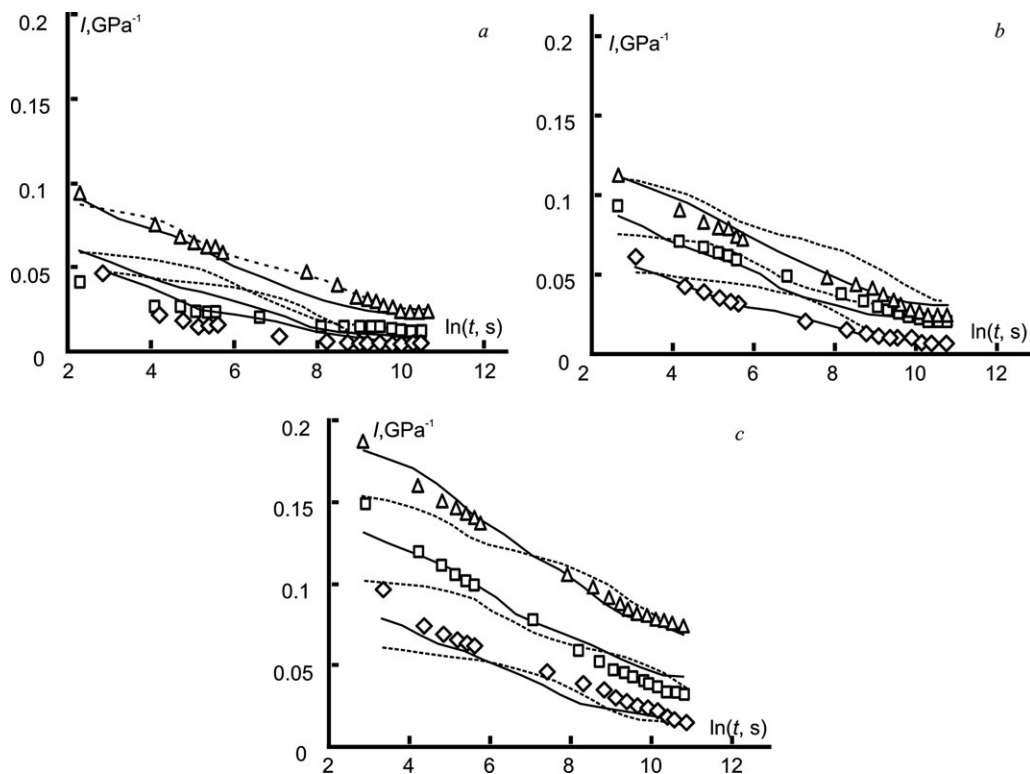
Figure 4. Recovery compliance curves of NC with $c = 3.8\%$ of MWCNTs after creep at stresses: 16 (a), 22 (b), and 29 MPa (c), at temperatures 17 ($\diamond$), 22 ($\square$), and 27°C ($\triangle$). Symbols are experimental data; curves are approximation based on time–temperature–strain superposition (solid lines) and TTSSP (dotted lines).

curves using this model also gives better results. Thus, the application of time–temperature–strain superposition gives better fit of experimental data for both creep and recovery.

The Case of nonzero ε_{res}. To separate viscoelastic and viscoplastic strains, a series of recovery curves with deduction of residual strains were approximated by the use of time–temperature–strain superposition model similar to the case of $\varepsilon_{res} \xrightarrow{t\to\infty} 0$ considered above. The obtained retardation time spectra for NCs with various filler mass contents do not show any dependence on filler content. Parameters $\alpha_{1\varepsilon}$ and $\alpha_{2\varepsilon}$ of time–tempera-

ture–strain shift factor [eq. (19)] for NCs with various c are shown in Figure 8. The value of nonlinearity parameter $\alpha_{2\varepsilon}$ decreases by passage from neat epoxy matrix to NC with $c = 0.2\%$ and then increases with the increase of c from 0.2% to 1%. The alteration of $\alpha_{2\varepsilon}$ is opposite to the alteration of the parameter $\alpha_{1\varepsilon}$ value. The $\alpha_{1\varepsilon}$ value has a pronounced maximum for NC with $c = 0.2\%$, whereupon decreases with the increase of c. The change of $\alpha_{1\varepsilon}$ value with the change of filler mass content c is in line with the dilatometric test results of NC considered,[19] which allowed one to obtain the T_g and CTEs of NCs in both glassy and rubbery states. The densification of the NC was also
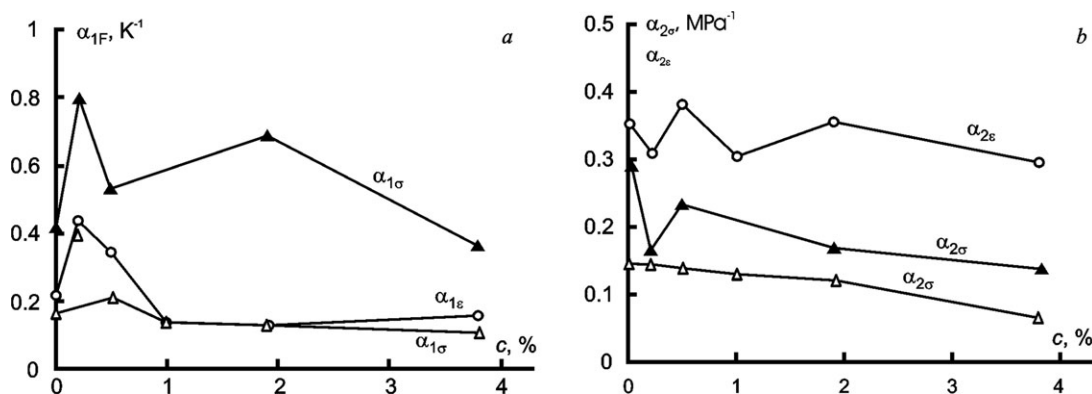
Figure 5. Parameters: α_{1F} (a) and α_{2F} (b) of time–temperature–stress ($F = \sigma$) and time–temperature–strain (F = ε) shift factors from eq. (10) for creep ($-\triangle-$) and recovery ($-\blacktriangle-$) and eq. (19) ($-\circ-$), respectively, for MWCNT/epoxy NC with various nanofiller mass contents c.
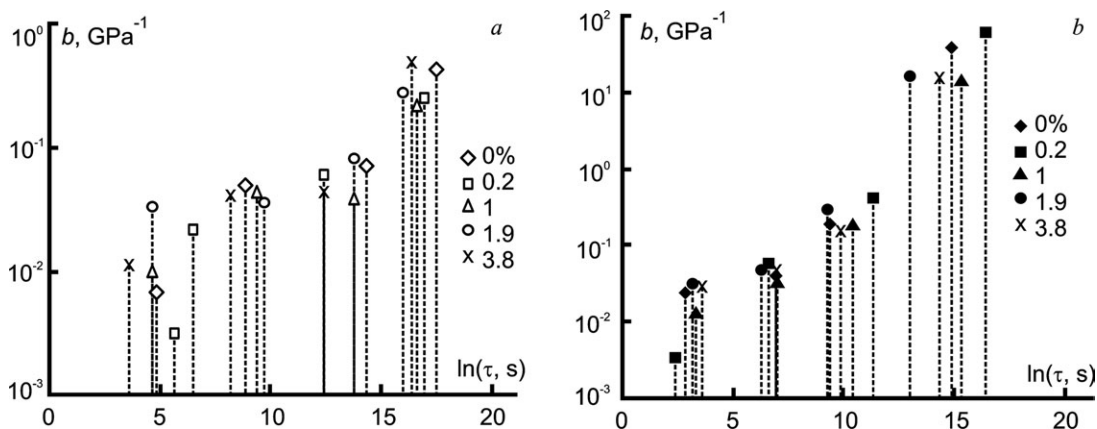
Figure 6. Retardation spectra of MWCNT/epoxy NCs with various filler mass contents, obtained from approximation of a series of recovery curves on the basis of time–temperature–strain superposition (a) and TTSSP (b) principles.

obtained by direct density measurement.[19] The larger is the material density, the larger is its CTE and, consequently, the value of parameter $\alpha_{1\varepsilon}$. As a result, the retardation times are more affected by the increase of temperature. For more dense material, the nonlinear viscoelasticity is less expressed, i.e., the nonlinearity parameter decreases. With the increase of c, the size of filler agglomerates increases and their density decreases. As a result, the effects of temperature and stress become less and more noticeable, respectively.

In contrast to the case mentioned above considering the viscoplastic strain as a viscoelastic one with infinitely long retardation time, this approach allows one to detail the viscoplastic strain in an explicit form. As an example, the viscoplastic strain component defined as a difference of total and viscoelastic strains for creep, neat resin, and NC with $c = 1$ wt % at largest temperature, i.e., 27°C, is shown in Figure 9. It is obvious that for all stress levels considered, the viscoplastic strain of NC is smaller than of epoxy matrix. This means that the occurrence
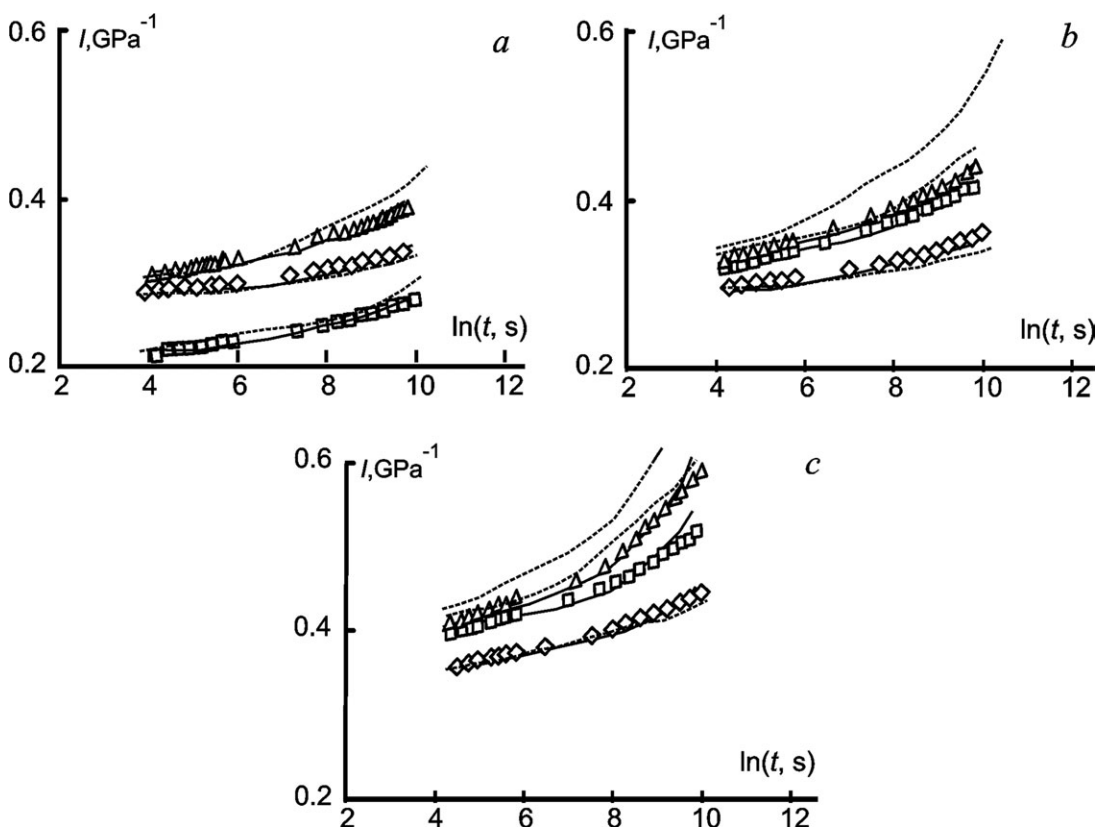
Figure 7. Creep data for MWCNT/epoxy NC with $c = 3.8\%$ at stress levels: 16 (a), 22 (b), and 29 MPa (c) at temperatures: 17 ($\diamond$), 22 ($\square$), and 27°C ($\triangle$). Symbols are experimental data; curves are approximation based on time–temperature–strain superposition (solid lines) and TTSSP (dotted lines) principles.
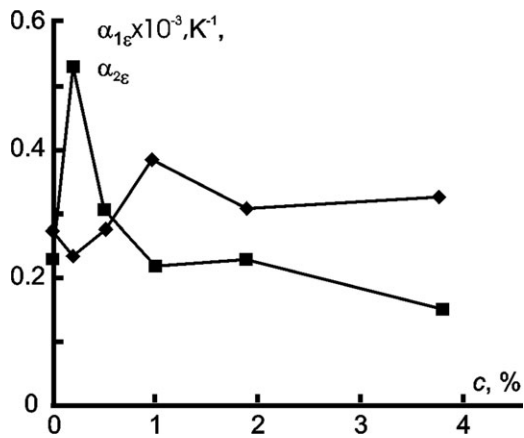
Figure 8. Parameters of time–temperature–strain shift factor for NCs with various MWCNT contents.
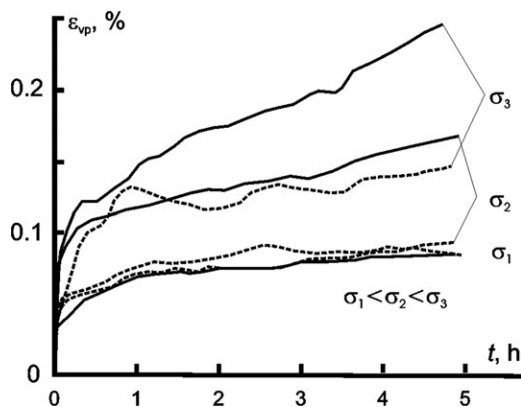
Figure 9. Viscoplastic strain as a function of time for epoxy matrix (solid lines) and NC with $c = 1$ wt % (dotted lines) at 27°C and various stresses.

of nanofiller in epoxy matrix decreases its viscosity. Thus, high modulus MWCNT, having high aspect ratio, imposes restrictions to relative displacement of polymer chains. Time depend-

ence of viscoplastic strain can be described by the use of logarithmic function

$$\varepsilon_{vp} = A \ln t + B \qquad (22)$$

with stress- and temperature-dependent parameters A and B.

As an example, the values of A and B as functions of stress for NC with $c = 0$ ($\diamond$), 1 ($\square$), and 1.9 (Δ) wt % are shown in Figure 10. For NC with $c = 1$ wt %, the value of parameter B is lower than of neat resin; the effect is more pronounced for larger stress levels. For NC with $c = 1.9$ wt %, both the parameters A and B are smaller than of the neat epoxy resin, however, their increase with the increase of stress is more rapid than of the neat resin.

The viscoplastic strain of MWCNT/epoxy NC may be conditioned by the nanotubes pulling out from the agglomerates and subsequent destruction of agglomerates. It was already noted above that the size of nanofiller agglomerate increases with the increase of nanofiller mass content in the NC. Consequently, density of the agglomerate decreases and lower stress levels are sufficient for the nanotube pulling out from the agglomerate.[15]

CONCLUSIONS

Short-term creep-recovery tests of epoxy/MWCNT NCs at various temperatures and stresses showed that NCs reveal smaller creep (recovery) rate and residual strains compared to neat epoxy resin. The enhancement in creep resistance could be caused by the decreased mobility of polymer chains since CNTs having relatively high aspect ratio act as restriction sites. However, due to agglomeration of MWCNTs at high filler content, this effect is insignificant taking into account the potential impact of highly elastic MWCNTs to the improvement of creep resistance of epoxy matrix.

The approximation of a series of short-term creep and recovery curves using modified Schapery model and time–temperature–strain superposition principle gave better fit to the experimental data than by the use of TTSSP principle. The main deviation between approximation parameters of these two models was obtained for nonlinearity parameter, which characterizes the
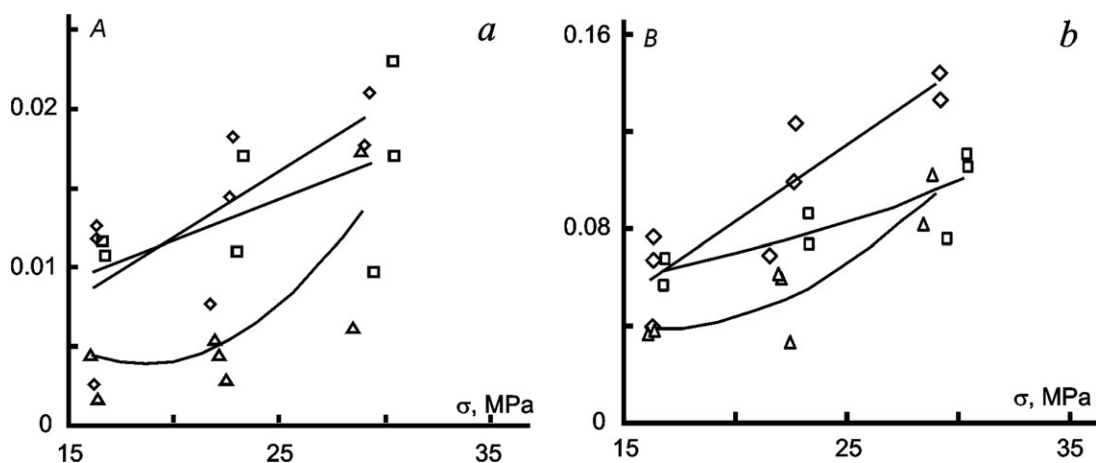
Figure 10. Dependence of parameters A and B of eq. (22) on stress for NC with $c = 0$ ($\diamond$), 1 ($\square$), and 1.9 (Δ) wt %.

dependence of retardation times on strain and stress, respectively. No systematic effect of filler content on the retardation spectra for both approaches was found.

By separating viscoelastic and viscoplastic strains, it was established that the main effect of MWCNTs was observed on viscoplastic strain of NC. It was shown that for all stress levels considered the viscoplastic strain of NC is smaller than of epoxy matrix. This effect was described by pulling out of MWCNTs from the agglomerates and subsequent destruction of agglomerates. Since the size of nanofiller agglomerates increases with the increase of nanofiller mass content in the NC, the density of the agglomerates decreases, and lower stress levels are sufficient for the nanotube pulling out from the agglomerate.

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