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# Application of Time-Stress Superposition to Nonlinear Creep of Polyamide 66 Filled with Nanoparticles of Various Sizes

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## Abstract

The long-term tensile creep of polyamide 66 and its nanocomposites filled with 1 vol.% TiO<sub>2</sub> nanoparticles 21 and 300 nm in diameter is studied. It is assumed that the dominant mechanisms of creep deformation are of viscoelastic nature, while the contribution of plastic strains is not essential in the stress ( $< 0.6$  of the ultimate stress) and time (about 100 h) ranges considered. The creep isochrones obtained show that the materials exhibit a nonlinear viscoelastic behaviour and the degree of nonlinearity is reduced significantly by incorporation of the nanoparticles. The evolution of viscoelastic strains is less pronounced for the nanocomposite filled with smaller nanoparticles. Smooth master curves are constructed by applying the Time-Stress Superposition (TSS). The Boltzmann-Volterra hereditary theory is used for the creep modeling. The nonlinearity of viscoelastic behaviour is taken into account by using the TSS principles and introducing a stress reduction function into an exponential creep kernel. The master curves are employed to predict the creep for time periods more than 60 times exceeding the test time. A comparison of relaxation spectra of the polymers shows that the incorporation of nanoparticles restricts the mobility of polymer chains.

The smaller the nanoparticles, the greater the enhancement in the creep resistance. An empirical approach and a three-parameter law is also used for creep approximation. The efficiency of two models is evaluated by comparing their prediction validity.

*Keywords* A. Nanocomposite; B. Creep; C. Modeling; nonlinear behaviour

## 1. Introduction

Polymer nanocomposites have been attracting considerable interest in the past decade [1-6]. The specific features of nanocomposites are the extremely large interfacial area and the very small average distance between particles, which is comparable with dimensions of macromolecule chains. In this connection, most of the features in the behaviour of nanocomposites are related exactly to the specific matrix-filler and filler-filler interactions. It has been reported by many researchers that the incorporation of a very small amount of inorganic particles into polymers can bring a significant improvement in their thermal and mechanical properties, which is significantly higher than those achieved in traditional filled polymers. This makes nanocomposites a promising new class of materials for various engineering applications and, therefore, requires a comprehensive characterization of their mechanical properties under various testing conditions. In spite of the fact that their strength and elastic properties have been widely investigated in recent years [3-6], there is still a lack of data on the time-dependent behaviour of this kind of materials. It should also be noted that the investigation of their viscoelastic properties in most cases is performed by dynamic or nano-indentation tests [2, 6-9]. However, for characterizing the dimensional stability of nanocomposites, a special attention should be focused on static creep tests [10, 11].

Thermoplastics, and polyamides in particular, are widely used as matrices of nanocomposites with various nanofillers due to their thermal stability and stiffness

together with the relatively easy processing and moderate cost [6, 8-13]. However, the potential applications of thermoplastic matrices and related composites are limited by their poor dimensional stability. It was first reported in [10] that the incorporation of a small amount of inorganic  $\text{TiO}_2$  nanoparticles into a polyamide 66 matrix restricted the motion of polymer macromolecule chains and thus significantly enhanced creep resistance of the nanocomposite. For a comprehensive characterization of the creep of nanocomposites, it is necessary not only to reveal the features of the creep process but also to perform its modelling. The elaboration of an appropriate model for describing the creep is an important task, which would give an opportunity to predict the creep performance for times longer than the test period. Moreover, it will allow one to compare the efficiency of different nanocomposites, for example, filled with various sizes of nanoparticles.

The experimental investigation and modeling of various PA66 based nanocomposites were considered comprehensively in [14, 15]. The present study deals with different approaches to the modelling of nonlinear creep of the materials, which are based on both constitutive equations and empirical approximations. The goals of the present study are (i) to characterize the tensile behaviour and long-term creep of PA66 and its nanocomposites filled with  $\text{TiO}_2$  nanoparticles and to evaluate the effect of nanoparticle size on the creep resistance of the nanocomposites, (ii) to model the creep by using the hereditary theory, together with the TSS principles, and an empirical power law, and (iii) to evaluate the efficiency of the models according to their prediction ability.

## 2. Experimental

A commercial Polyamide 66 (DuPont, Zytel 101) was considered as the matrix material.  $\text{TiO}_2$  nanoparticles (Degussa P25) of diameters 21 and 300 nm were used as fillers. The

density of the nanoparticles was  $4 \text{ g/cm}^3$  and their volume fraction was 1%. Three series of materials were investigated in this study: neat PA66, ITPA (21-nm  $\text{TiO}_2$ ), and PAKRI (300-nm  $\text{TiO}_2$ ). Dog-bone tensile samples with dimensions of  $160 \times 10 \times 4 \text{ mm}^3$  were applied. The details of the extrusion and injection molding procedures used are expounded in [10, 14].

The uniaxial long-term tensile creep tests were performed on a Creep Rupture Test Machine equipped with a double lever system (Coesfeld GmbH, model 2002). Before testing, the desired constant load for each measurement unit was calibrated by using a force transducer. Then, the samples were fixed in clamps. Then samples were tested simultaneously in a testing chamber. The tests were performed under various loads: 20, 30, and 40 MPa ( $\leq 0.6$  of the ultimate stress). A span length of 30 mm was marked on each sample, and the elongation was registered every 60 s. Since the strain measurements after applying the ultimate stress became reliable only after some time and a high data scatter was observed, the first test hour was not taken into consideration. The creep compliance was calculated as the ratio of the measured strain and the applied stress. The measurement procedure was performed based on ASTM 2990-01.

The uniaxial tensile tests were performed on a Zwick universal testing machine using a load cell of 250 kN. The elongation was measured with a strain gage extensometer having a span length of 50 mm. The tests were performed at a crosshead speed of 2 mm/min. At least four samples of each composition were tested. All the tests were performed under room conditions.

### 3. Creep models

#### 3.1. Constitutive equations and the Time-Stress Superposition

The Boltzmann-Volterra linear hereditary creep theory is commonly used for characterizing the time-dependent properties of viscoelastic materials [16, 17]. The strain response in the simplest loading case of uniaxial tensile creep under isothermal conditions is given by

$$\varepsilon(t) = J_0 \sigma(t) + \int_0^t \sigma(s) K(t-s) ds, \quad (1)$$

where  $J_0$  is the instantaneous creep compliance,  $K$  is the creep kernel, and  $t$  is time. The kernel function  $K(t-s)$ , which characterizes the strain developing after application of a loading impulse, usually is expressed by a sum of exponents

$$K(t-s) = \sum_{i=1}^k \frac{A_i}{\tau_i} e^{-\frac{t-s}{\tau_i}}, \quad (2)$$

where  $(A_i, \tau_i)$  is a discrete relaxation spectrum. The stress history in the simplest case of creep can be written as

$$\sigma(t) = \sigma_0 H(t),$$

$$H(t) = \begin{cases} 0, & t < 0 \\ 1, & t > 0 \end{cases},$$

where  $\sigma_0$  is a constant operating stress and  $H(t)$  is the Heaviside step function. Then, taking into account the independent action of stress impulses applied at different instants of time, Eq. (1) after integration takes the form

$$\varepsilon(t) = J_0 \sigma_0 + \sigma_0 \sum_{i=1}^k A_i \left( 1 - e^{-\frac{t}{\tau_i}} \right). \quad (3)$$

For the creep compliance, Eq. (3) can be rewritten as

$$J(t) = J_0 + F(t), \quad (4)$$

$$F(t) = \sum_i A_i \left( 1 - e^{-\frac{t}{\tau_i}} \right). \quad (5)$$

Obviously, Eqs. (3)-(5) are valid as long as the creep behaviour is linear viscoelastic. Nonlinear viscoelastic constitutive equations can be derived in a number of ways. One of them is an extension of the linear superposition to the nonlinear range by representing the viscoelastic function in a multiply integral form [18, 19]. However, such models are usually ineffective in use due to the complexity of mathematical computations and the great amount of material parameters involved. In spite of the fact that some approaches to the simplification of the constitutive equation in order to obtain a practically useful theory are known, the creep models in the multiply integral form have not found a wide application. Another way for the characterizing the nonlinear creep is to employ the method of reduced variables based on a constitutive equation in a single integral form, which is derived either from the linear hereditary creep theory or from thermodynamics [19-22]. This method, the so-called Time-Stress Superposition (TSS), is analogous to the Time-Temperature Superposition (TTS), which allows one to expand the effective time interval of experimental creep and to describe the nonlinear viscoelasticity. In this case, an increase in the applied stress accelerates the relaxation processes and, therefore, shifts the relaxation spectrum towards the region of shorter times [23, 24]. Similarly to the time-temperature reduction function, an equivalence between the time and stress is established by introducing a the time-stress reduction function  $a_\sigma(\sigma)$ . Then, passing to the reduced time  $t \rightarrow t' = ta_\sigma$  in Eq. (3) the relation for calculating the nonlinear viscoelastic creep compliance is given by

$$J(t, \sigma) = J_0 + F(t, \sigma),$$

$$F(t, \sigma) = \sum_i A_i \left( 1 - e^{-\frac{ta_\sigma}{\tau_i}} \right). \quad (6)$$

It should be noted that initially the relaxation spectra were involved as mathematical descriptions of the macroscopic behaviour of materials, without any their interpretation on the macromolecular basis. Nevertheless, it is possible to find some correlations between the relaxation process observed and certain macromolecular processes [17].

### 3.2. Empirical power law

Another, the most widespread, approach for characterizing the viscoelastic response is the use of power functions [18, 25]. The nonlinearity of viscoelastic response in this case is taken into account by stress-dependent model parameters. In some cases, a stress-dependent parameter is also introduced into the time-dependent kernel function [26, 27]. Generally speaking, different modifications of the power law are special cases of the Schapery nonlinear viscoelastic model, which is based on thermodynamics laws where a power-type kernel function is used [20]. Nevertheless, the power-law models more often are considered as empirical ones without attaching much importance to their physical background. The most used power law is the three-parameter one, the so-called simple power law. In this case, the creep compliance is given by

$$J(t) = J_0 + J_1 t^n, \quad (7)$$

where  $J_0$ ,  $J_1$ , and  $n$  ( $0 < n < 1$ ) are material parameters. In the case of nonlinear response  $J_0$  and  $J_1$  are stress-dependent parameters, while  $n$  either remains constant or takes arbitrary values in order to obtain a better fit of experimental data. Equation (7) can be written in the form

$$\ln(J - J_0) = \ln J_1 + n \ln t. \quad (8)$$

Obviously, Eq. (8) in the axes  $\ln(J - J_0)$  vs.  $\ln t$  gives a straight line with a slope  $n$ , which intersects the ordinate axis at the point  $\ln J_1$ .

It is worth noting that originally  $n$  was assumed to be a stress-independent parameter [18]. Following this assumption, some authors [15, 28] take the average value

of this parameter and reduce the data fitting to the variation of only one parameter,  $J_1$ . However, since one considers the power law as an empirical law, then it is more rationally to use that values of parameters which can be uniquely determined by approximating experimental data with Eq. (8) [25, 27].

When the material parameters are known, Eq. (7) can be used to predict the creep for longer times by simple extrapolation. However, it is worth noting that the simple power law is usually valid only within a limited time domain only. In spite of the fact that the modified power-law models allow one to expand the time interval by introducing additional parameters in Eq. (7) and these empirical models remain good for engineer applications, they are unsuitable for analyzing the underlying processes proceeding in materials.

#### 4. Results and discussion

The typical stress-strain curves of PA66 filled with nanoparticles of various sizes are shown in Fig. 1. The tensile behavior of the neat polymer is characterized by an extensive deformation after yielding and a pronounced necking, while the filled polymers exhibit a lower deformability. It can be seen that the elongation at failure of PAKRI and ITPA is almost 2 and 10 times lower than that of neat PA66, respectively. The tensile modulus of neat PA66 is  $E = 2.28 \pm 0.04$  GPa, while incorporating larger nanoparticles (PAKRI) increases by 16%. Even a greater increase in  $E$  (more than 20% compared to that of the matrix) is observed in the case of small nanoparticles (ITPA).

The stress levels in creep tests were chosen based on the results of tensile tests and did not exceed 0.6 of the ultimate stress. Since this stress region is sufficiently far from the yield point (Fig. 1) and the materials at room temperature are in the glassy state [29], it was assumed that the dominant deformation mechanism of the polymers in creep was of

viscoelastic nature, while the contribution of plastic strains was insignificant in the stress and time ranges considered.

The averaged creep compliance curves for the neat and filled polymers at different stress levels are presented in Fig. 2. The different shape of the compliance curves point to a different contribution of the time-dependent strain component to the overall strain with growing stress and thus to the nonlinearity of viscoelastic behaviour of the materials. Obviously, the higher the stress level, the greater this contribution. The development of nonlinear effects of the viscoelastic behaviour can be clarified by comparing creep isochrones constructed for various instants of time, which are shown in Fig. 3. It is seen that the degree of their nonlinearity increases noticeably with time growing from 10 to 50 hours. It is worth noting that nonlinearity of the isochrones and its development are less pronounced for the filled polymer than for the neat one. A great enhancement in the creep resistance of nanocomposites was revealed by comparing the stress dependences of the purely viscoelastic strain (the measured strain minus the initial strain determined at the first valid experimental point) after different periods of creep. In addition, this effect was more pronounced at higher stress levels. Stress dependences for the purely viscoelastic strain after 20 hours of creep, as an example, are presented in Fig. 4. It can be evaluated that, at the highest load, the viscoelastic strain of PAKRI and ITPA is about 30 and 70% respectively lower than that of neat PA66.

The nonlinear creep model based on the TSS principles was applied to the description of creep data (Eq. (6)). According to the character of the creep isochrones (Fig. 3), it was assumed that time-dependent behaviour of the polymers at the lowest stress level of 20 MPa was mainly linearly viscoelastic. Then, to cover the wide interval of test time, the relaxation times  $\tau_i$  were chosen with a sufficient density, and nine coefficients  $A_i$  were determined for each material. The coefficients of the time-stress reduction function

$a_{\sigma}(\sigma)$  were determined by constructing master curves. To this end, only the time-dependent components of creep compliances were drawn and then shifted to the reference curve for  $\sigma_0 = 20$  MPa along the logarithmic time axis. Quite smooth master curves were obtained by this means, as shown in Fig. 5. One can see that the master curves obtained could predict the creep behaviour of the materials for a period of time more than 60 times exceeding the test time, which means more than one year. In addition, it is seen that the incorporation of nanoparticles into the neat PA66 led to a sufficient enhancement in the material creep resistance. The highest creep resistance for long times is demonstrated by the polymer filled with the small nanoparticles. According to the master curves, the creep strains of ITPA after 3 months under a stress of 20 MPa will be 2 and 1.4 times lower than those of neat PA66 and PAKRI, respectively. Figure 2 shows that the nonlinear viscoelastic model of creep based on the TSS principles (Eq. (6)) fits the experimental data with a reasonable accuracy in the stress and time ranges considered. Moreover, the good agreement between the calculation and master curves in Fig. 5 attests to the validity of the model for long-term creep predictions.

As seen from Fig. 5, curves of the creep compliances for different stress levels have undergone the parallel shifts along the time axis without a noticeable violation of their similarity. As known, this indicates to a fact that an increase in the creep rate is mainly caused by the shortening of relaxation times or, in other words, by acceleration of the mobility of polymer chains. According to the TSS principles,  $a_{\sigma}$  is a quantitative characteristic of this acceleration. Therefore, it is possible to compare the long-term creep resistance of materials by comparing their time-stress reduction functions determined under the same test conditions. The time-stress reduction functions of the neat and nanoparticle-filled polymers are compared in Fig. 6. Obviously, the higher

value of  $\ln a_\sigma$  value, the greater the acceleration of the mobility of polymer chains. Thus, the neat PA66 exhibits the highest sensitivity to the stress action, while the incorporation of nanoparticles diminishes this effect. It is also worth noting that the degree of nonlinearity of the time-stress reduction function of the filled polymers is noticeably lower.

It is mentioned in [10, 14] that  $\text{TiO}_2$  nanoparticles restrict the chain mobility of neat PA66. Obviously, this fact should be reflected by changes in the relaxation spectrum of the filled polymers. Let us assume that each coefficient  $A_i$  in Eq. (6) represents the intensity of motion of polymer macromolecule chains occurring at a time  $\tau_i$ . The higher the value of  $A_i$ , the more intense the motion of a certain chain segment and the higher the contribution of the viscoelastic component to the overall strain. Thus, comparing the relaxation spectra for the neat and nanoparticle-filled polymers should give a quantitative estimate for the degree of restriction of the mobility of polymer chains. The relaxation spectra of the materials investigated are presented in Fig. 7 in double logarithmic coordinates. It is found that the spectra are similar and the proportion 1:0.8:0.55 exists between the coefficients  $A_i$  for the neat PA66, PAKRI, and ITPA, respectively. One can conclude from here that the mobility of polymer chains in the polymer filled with small  $\text{TiO}_2$  nanoparticles is almost 2 times lower than that in the neat polymer.

An empirical model, the simplest three-parameter power law Eq. (7), was also applied to the description of creep. The parameters of the power law were determined directly from experimental data. The quantity  $J_0$  represents the initial compliance, which characterizes the material response at the beginning of loading. For the determination of  $J_1$  and  $n$ , the experimental data were drawn in double logarithmic coordinates and approximated by a linear trend. As seen from Eq. (8), the slope of the straight line gives

the parameter  $n$ , while the free term of the equation determines the value of  $J_1$ . The parameters of the power law determined for the materials investigated are listed in Table 1. As follows from Fig. 2, the power law gives satisfactory approximation results for all the materials.

Owing to the simplicity of determining its parameters, the power law is an empirical model convenient for engineering applications. However, as already mentioned, in most cases, it gives satisfactory results only for a limited time domain. Noticeable discrepancies between experimental and calculated data are observed in Fig. 2 for relatively short times ( $\ln t < 10$ ), while for longer times, the power law is in a good agreement with the experiments. Moreover, if the power law is used for predicting the long-term creep and for approximating the master curves given in Fig. 5, Eq. (7) with the parameters given in Table 1 becomes inadequate already at  $\ln t > 13$ .

In order to confirm the results for the effect of nanoparticles on the mobility of polymer chains obtained by the indirect approach, let us consider some results from direct investigations. The microstructure of the polymers has been investigated based on their thermal properties from the results of DSC and DMTA tests [29]. It was found that a small amount of nanoparticles did not affect the degree of crystallinity, the melting point, and the crystallization temperature of the matrix. It follows from here that the influence of crystallinity on the matrix stiffness and the creep resistance upon introducing the nanoparticles is negligible. Moreover, the results of DMTA tests showed that, by incorporation of only 1 vol.% of small nanoparticles, the glass transition temperature was shifted to higher temperature by about 10 °C (from about 60 °C), while the  $\tan \delta_{\max}$  was slightly changed compared to that of neat PA66. Thus, these results confirm that small amounts of nanoparticles can effectively restrain the movements of polymer chain segments, which in turn affects the matrix creep resistance.

A schematic representative structure of nanofiller-semicrystalline polymer composites is illustrated schematically in Fig. 8 [14]. The following essential elements can be distinguished in such a system: crystallized chains, amorphous regions, an interphase between the filler and matrix characterized by polymer-filler junctions, and bridging segments between filler particles. Each of the elements gives its own contribution to the overall deformation behaviour of the polymer at different stages of creep. For a neat semicrystalline polymer, for example, the instantaneous response to an external mechanical load applied, as well as its load-bearing ability, is mainly determined by the crystallized chains, while time effects and the development of viscoelastic strains is caused by the amorphous regions. The deformational behaviour of nanocomposites is also affected by the bridging segments and the filler-matrix interphase, characterized by polymer-filler junctions. Obviously, the closer the particles, the shorter the bridging elements and the segments of the amorphous polymer and, therefore, the stiffer network. Moreover, one may assume that properties of the interphase regions are different from those in a bulk polymer. Then, the overall behaviour of the material is mostly determined by the width of the filler-matrix interphase.

The polymer filled with the 21-nm nanoparticles (ITPA) showed a greater enhancement of creep resistance than that filled with the 300-nm nanoparticles (PAKRI). The higher efficiency of ITPA compared to that of PAKRI can be explained by the higher specific area of nanoparticles at the same reinforcement ratio. It is easy to show by simple geometrical calculations that a decrease in the nanoparticle diameter (increase in the specific area) leads to a proportional reduction in the width of the nanofiller-polymer interphase or interparticle distance, as shown schematically in Fig. 9 for the case of a simplest cubic distribution of spherical particles perfectly bonded to the matrix. The distance between two neighboring nanoparticles 20 nm in diameter, at a reinforcement

ratio of 1vol.%, is about 55 nm, while in the case of 300-nm particles, this distance is about 15 times greater. One may expect that a network with relatively large distances between the particles is not stiff enough to restrict the small-range of mobility of polymer chains. Taking into account the fact that the crystallinity of both the materials is similar and assuming that the degree of dispersion is relatively high in both the cases, one may conclude that the greater effect caused by the restriction of polymer chain motion in ITPA is mostly associated with the ability of the nanodimensional fillers to form a very dense and stiff network with an extensive interphase.

## 5. Conclusions

The tensile behavior and the long-term creep of PA66 and its nanocomposites filled  $\text{TiO}_2$  nanoparticles of various sizes have been investigated in this study. The creep behaviour of the polymers had a viscoelastic nature, while the nonlinear effects were revealed by investigation the creep compliances and creep isochrones. The degree of nonlinearity of the isochrones, as well as its development in time, was less pronounced for the filled polymers. A considerable enhancement in the creep resistance of the nanocomposites was revealed by comparing the stress dependences of the viscoelastic strain components after different periods of creep. A nonlinear viscoelastic model with an exponential creep kernel, based on the TSS principles, was found to be appropriate for description of the creep, data comparisons for various nanocomposites, and creep predictions. The master curves obtained can be used for predicting the creep behaviour of the materials for time periods more than 60 times exceeding the experimental one. By comparing the relaxation spectra of the materials, it was found that the incorporation of nanoparticles into the neat polymer restricted the mobility of polymer chains. The character and absolute values of the time-stress reduction functions also indicated to an enhanced creep resistance of the nanocomposites. The three-parameter power law

showed satisfactory approximation results only in a limited time domain and was unfit for predicting a long-term creep with the same parameters. The smaller the nanoparticles, the greater the growth in the creep resistance.

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### Figures captions

Fig. 1. Tension diagrams of neat PA66 and its nanocomposites filled with 1vol.%  $\text{TiO}_2$  with diameters of 300 (PAKRI) and 21 nm (ITPA).

Fig. 2 Creep compliance curves of neat PA66 (a), PAKRI (b), and ITPA (c). Experimental data and calculations according to various models.

Fig. 3. Creep isochrones of neat PA66 and ITPA after 10 and 50 hours of creep.

Fig. 4. Stress dependences of the viscoelastic strain component after a 20-hour creep.

Fig. 5. Master curves for the viscoelastic creep compliance component shifted to the reference curve at  $\sigma_0 = 20$  MPa and creep predictions by various models.

Fig. 6. Time-stress reduction functions:  $\sigma_0 = 20$  MPa.

Fig. 7. Relaxation spectra of the materials in double logarithmic coordinates.

Fig. 8. Schematic representative structure of nanoparticle-semicrystalline polymer composites [14].

Fig. 9. Correlation among nanofiller diameter, interparticle distance and volume percentage [1]. Based on the assumptions of cubic distribution and perfect dispersion of nanofillers, a relationship between interparticle distance,  $2h$ , and filler content,  $v_p$ , can be expressed by the equation,  $2h = d \left[ \left( \pi / 6 v_p \right)^{1/3} - 1 \right]$ , where  $d$  symbolizes diameter of a nanofiller.

**Table 1.** Parameters of the power law

Material	Neat PA66			PAKRI			ITPA		
Stress, MPa	$J_0$ , GPa <sup>-1</sup>	$J_1 \cdot 10^4$ , GPa <sup>-1</sup> s <sup>-n</sup>	n	$J_0$ , GPa <sup>-1</sup>	$J_1 \cdot 10^4$ , GPa <sup>-1</sup> s <sup>-n</sup>	n	$J_0$ , GPa <sup>-1</sup>	$J_1 \cdot 10^4$ , GPa <sup>-1</sup> s <sup>-n</sup>	n
20	0.27	0.89	0.60	0.24	4.87	0.45	0.23	1.65	0.50
30	0.29	0.99	0.60	0.25	2.09	0.56	0.23	1.35	0.56
40	0.40	41.19	0.42	0.31	32.88	0.41	0.27	2.66	0.56

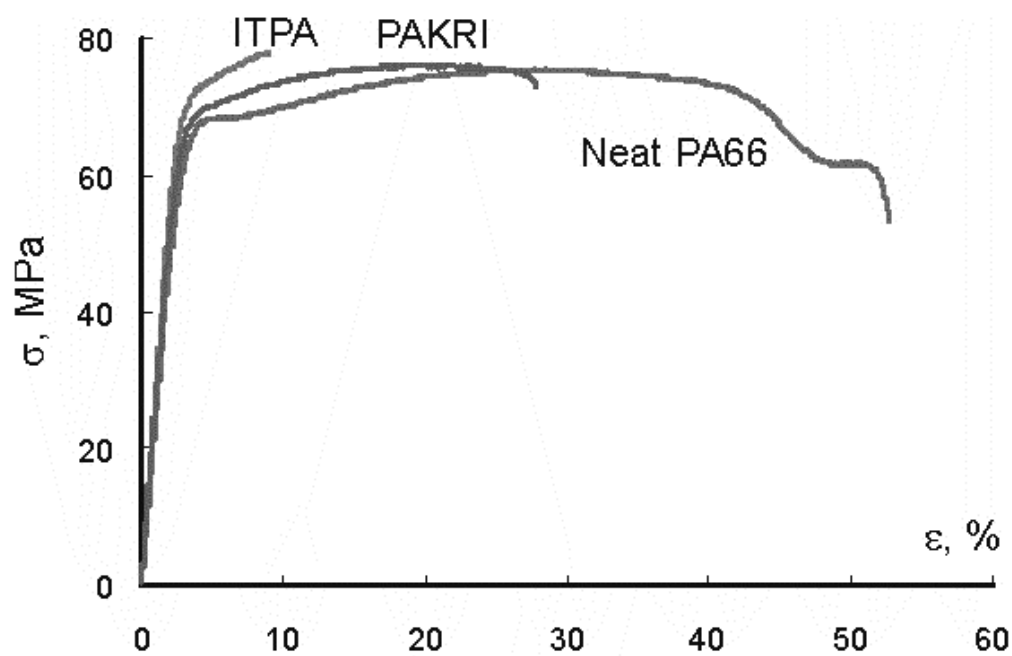


Figure 1

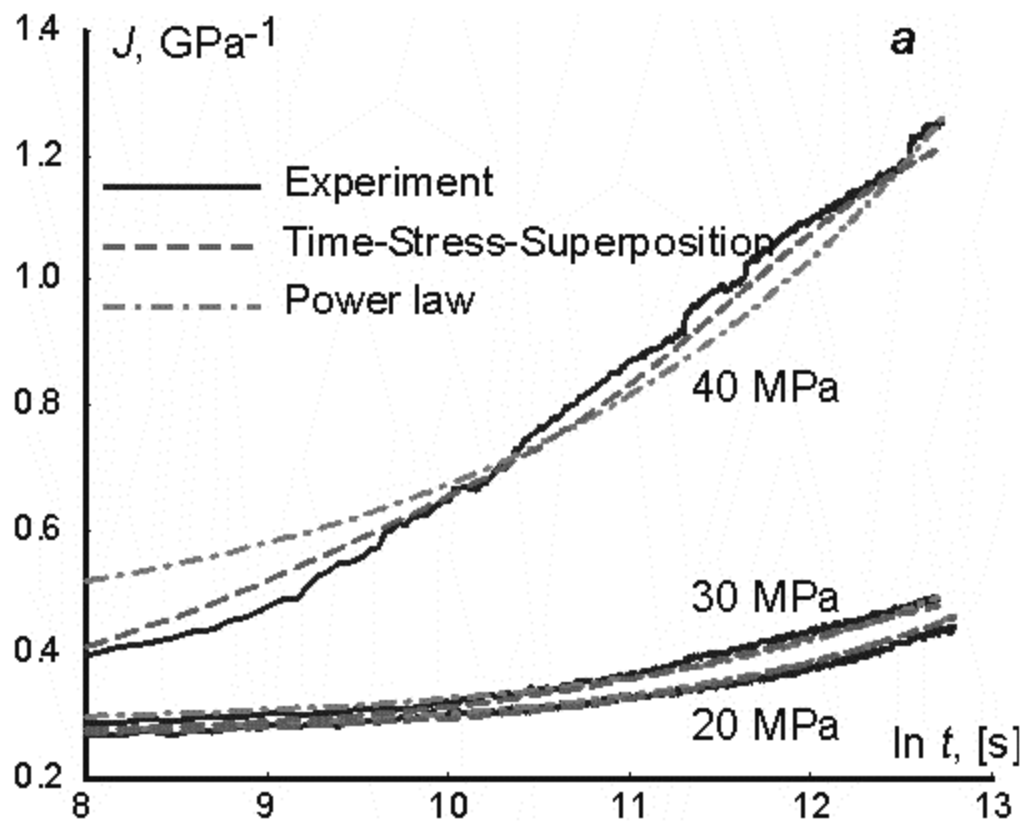


Figure 2a

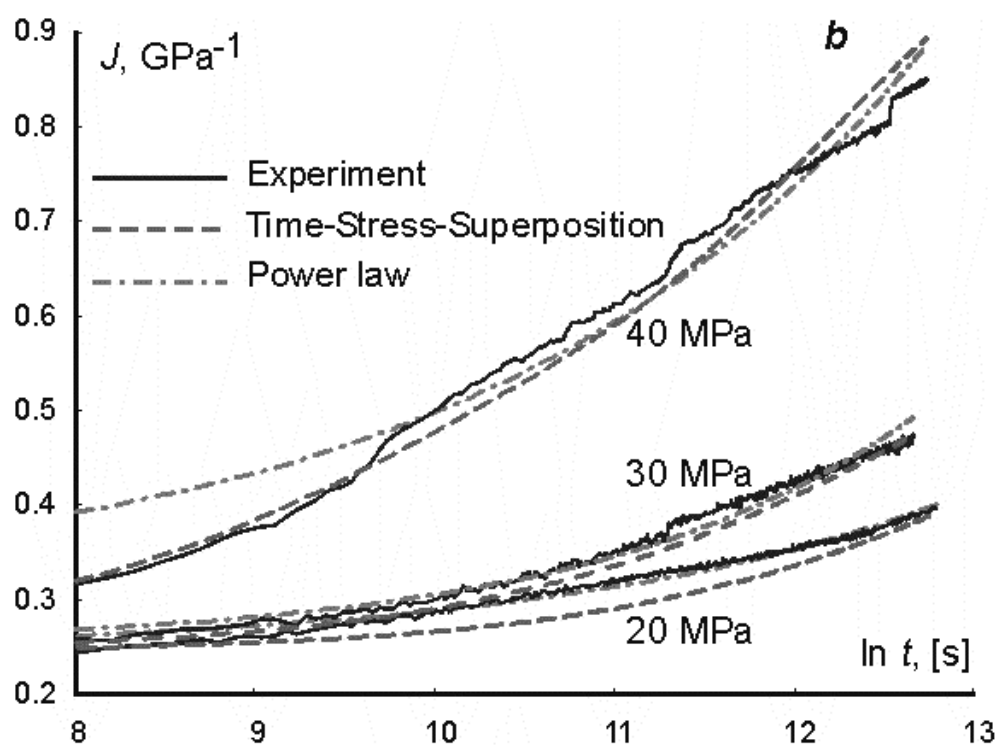


Figure 2b

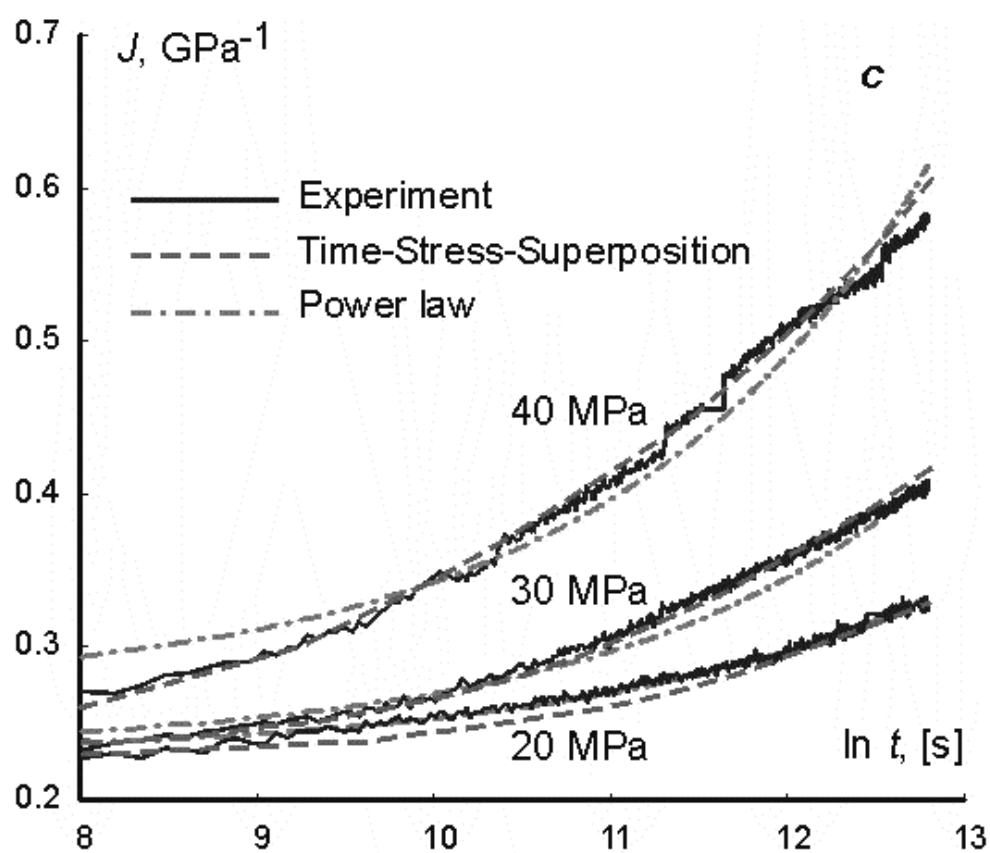


Figure 2c

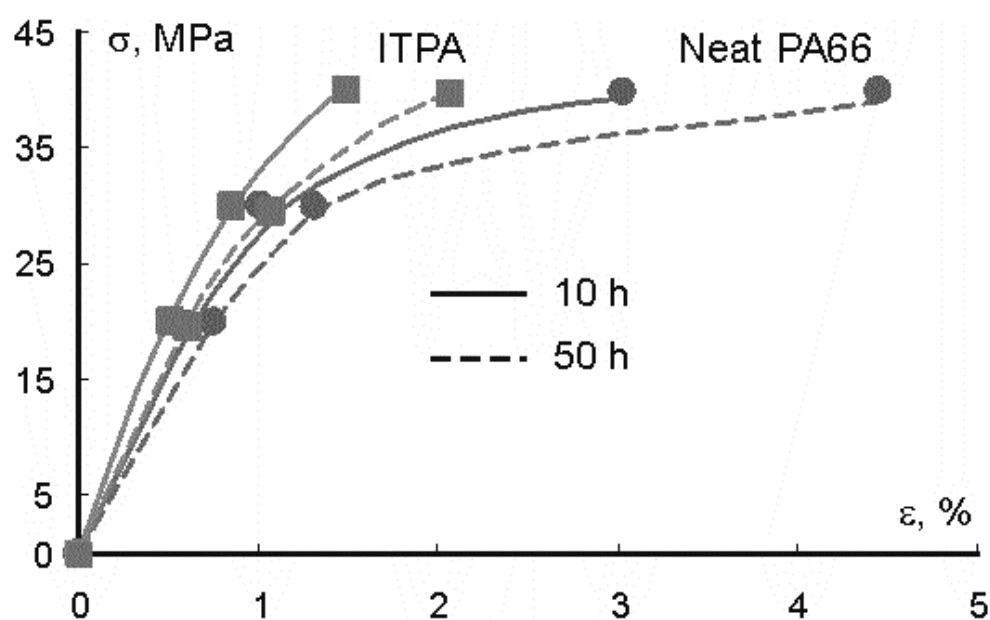


Figure 3

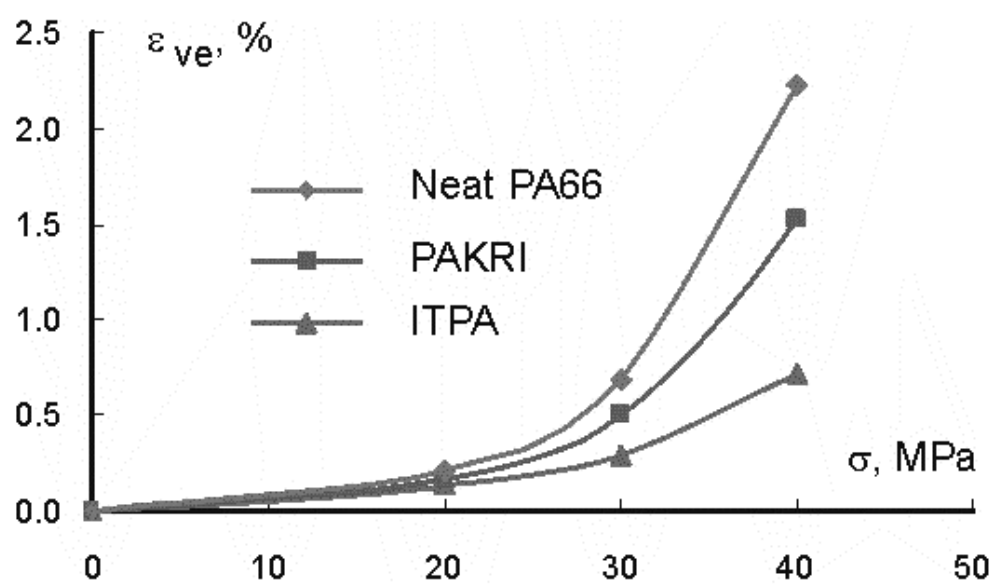


Figure 4

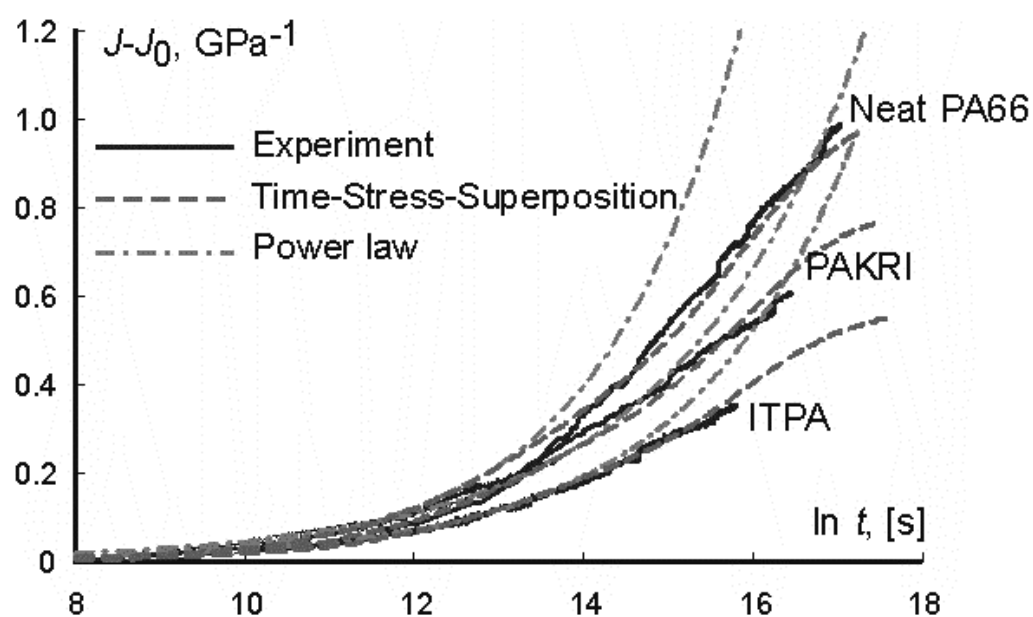


Figure 5

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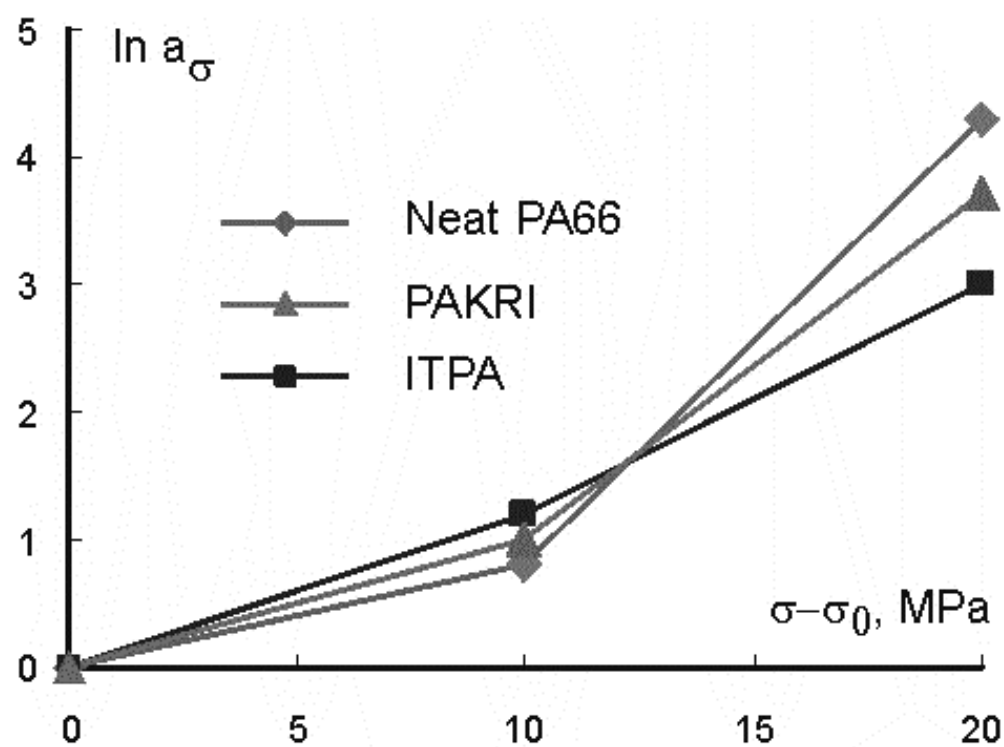


Figure 6

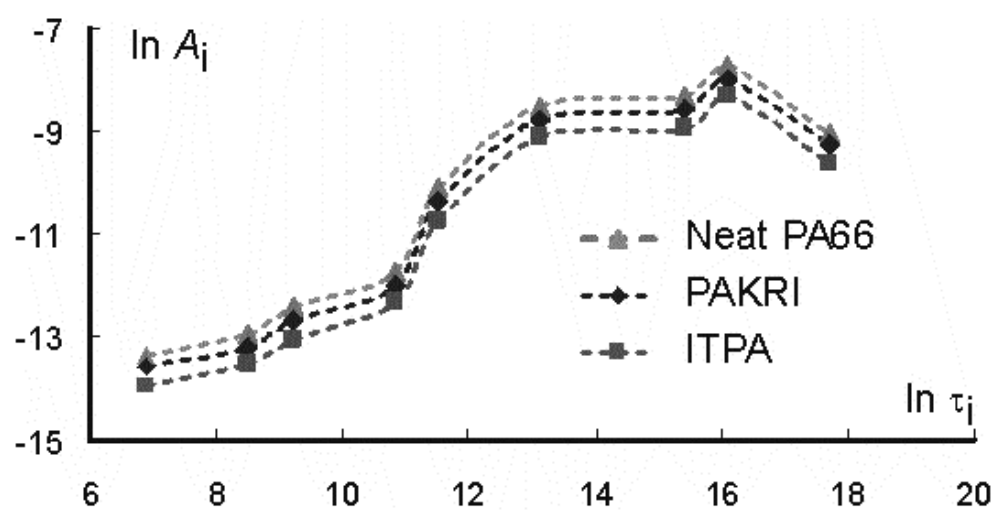


Figure 7

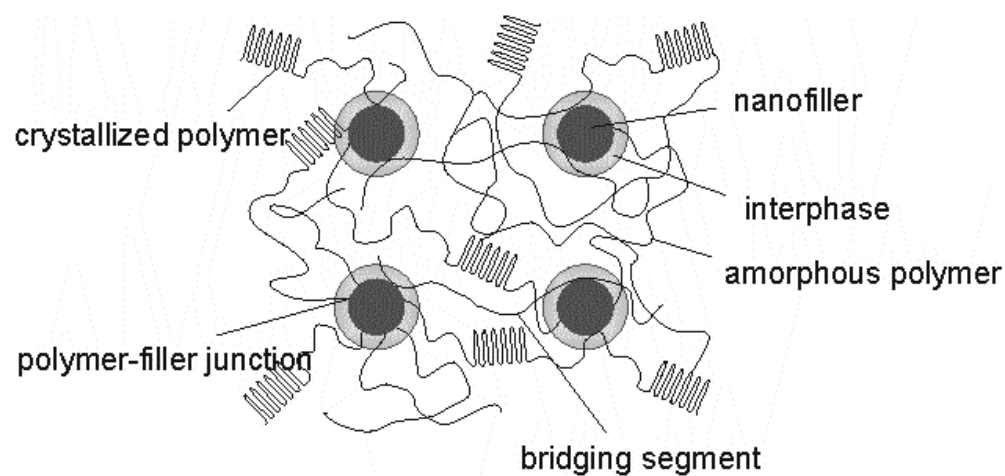


Figure 8

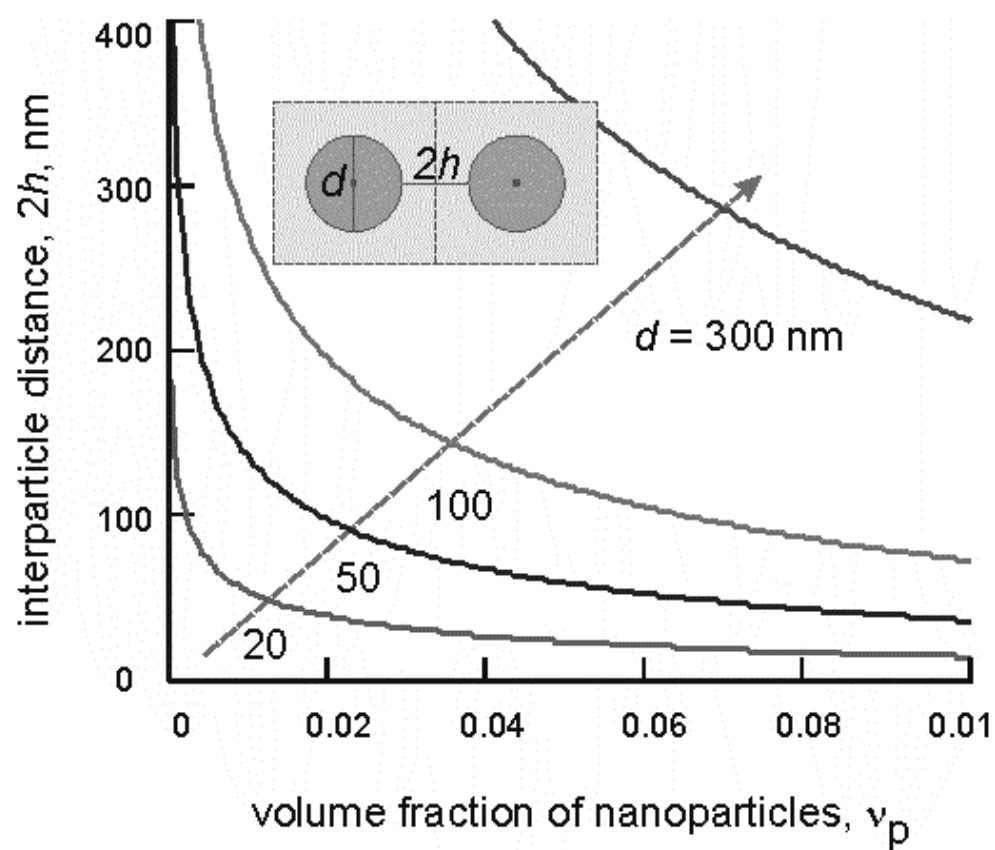


Figure 9

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