Cyclic deformation of ternary nanocomposites: Experiments and modeling

A.D. Drozdov *, J. deClaville Christiansen

Department of Production, Aalborg University, Fibigerstraede 16, 9220 Aalborg, Denmark

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Abstract

Observations are reported on the mechanical response of a ternary composite (blend of polypropylene and a thermoplastic elastomer reinforced with montmorillonite nanoclay) at cyclic tensile deformations with relatively large amplitudes (up to the necking point). Constitutive equations for the viscoplastic behavior of hybrid nanocomposites are derived by using the laws of thermodynamics. Adjustable parameters in the stress–strain relations are found by fitting the experimental data. It is demonstrated that the model adequately predicts stress–strain diagrams of the nanocomposite under cyclic loading.

Keywords: Nanocomposite; Viscoplasticity; Cyclic deformation; Constitutive equations

1. Introduction

This paper is concerned with the experimental analysis and numerical simulation of the mechanical response of ternary composites with polymer matrices and nanoclay fillers under cyclic deformation. The experimental study of the mechanical behavior of ternary composites has attracted substantial attention in the past couple of years (Kelnar et al., 2006; Lee et al., 2005; Mishra et al., 2005; Xiaoyan et al., 2005, to mention a few). This may be explained by the desire to improve substantially stiffness and strength of the main phase (traditionally, low-cost polyolefins) by its reinforcement with a nanofiller (layered silicates or ceramic particles), and to ensure an optimal balance between stiffness and toughness by blending the polymer matrix with an elastomeric component (conventionally, a thermoplastic elastomer (TPE) that guarantees high-speed processability and recyclability of the hybrid nanocomposite).
Although some observations on the mechanical behavior of ternary composites in uniaxial tensile and compressive tests with constant strain rates, as well as in uniaxial relaxation tests have been published, no experimental data are available on their response under cyclic deformation. As the latter type of deformations is of essential importance for biological applications of nanocomposites as parts of implant-supported prostheses (Bergstrom et al., 2002, 2004; Pruitt, 2005), the first aim of this study is to report stress–strain diagrams at cyclic deformations.

For the experimental investigation, a blend of isotactic polypropylene (iPP) with polyethylene–octene elastomer reinforced with montmorillonite (MMT) nanoclay is chosen. The concentration of components in the hybrid nanocomposite is close to that in a composite recently studied by Lee et al. (2005). Filling of the composite with TPE increases the region of strains below the necking point (by about 50% compared with neat iPP), whereas reinforcement with nanoclay results in the growth of the elastic modulus of the polymer blend (by about 40%). Mechanical tests are performed in a strain-control mode conventionally employed in experiments on polymers and polymer composites (Bai and Wang, 2003; Christenson et al., 2005; Kletschkowski et al., 2002, 2005; van Dommelen et al., 2003; Yi et al., 2006) with a constant strain rate and with various maximum strains below the necking point. Observations in tests with various strain rates and in ratcheting tests will be reported in a subsequent publication.

The other aim of this work is to develop a constitutive model for the viscoplastic behavior of hybrid nanocomposites at arbitrary (but small) three-dimensional deformations and to find adjustable parameters in the stress–strain relations by fitting the observations. Unlike metallic materials, in cyclic plasticity of which a number of constitutive equations are available, viscoplastic response of semicrystalline polymers and composites with polymer matrices at cyclic deformations is a relatively new field of research. It is quite natural, therefore, that basic ideas in cyclic plasticity of polymers were borrowed from the plasticity theory of metals and refined in a merely phenomenological manner to account for some phenomena typical of the behavior of polymers. A shortcoming of this approach is that the number of experimental constants in stress–strain relations becomes relatively large. As a result, the use of these constitutive equations for design of polymer composites becomes questionable due to the fact that changes in the preparation conditions and composition lead to noticeable (and unpredictable) alteration of material parameters.

To confirm this assertion, we discuss briefly two constitutive models in cyclic plasticity of metals and their implementation for solid polymers. The first is the concept of isotropic and kinematic hardening (Chaboche, 1994; Yaguchi and Takahashi, 2005). According to this approach, the strain tensor is split into the sum of elastic and inelastic components. The elastic component is connected with the stress tensor by an analog of the Hook law, whereas the rate of changes in the inelastic component is proportional to the over-stress tensor (the difference between the conventional stress tensor and the back-stress tensor). The latter tensor is split, in turn, into a sum of several (two, three or more) tensors, whose evolution is governed by nonlinear differential equations involving the inelastic strain-rate tensor as an input. The coefficients in the kinetic equations for the back-stresses are determined by nonlinear scalar evolution equations with parameters depending on invariants of the current stresses (strains). The shape of these equations is mainly determined by the taste of the researcher. An acceptable agreement between observations and results of numerical simulation is reached when the governing equations involve 33 (Yang, 2004) to 35 (Yaguchi and Takahashi, 2005) adjustable parameters. Tong and Vermeulen (2003) demonstrated good accuracy of fitting by a model with only 14 constants (however, the dependence of these quantities on maximum and minimum stresses in ratcheting tests was not investigated). Application of the hardening concept to modeling the mechanical response of polymers was initiated by Krempfl and his group (Ho and Krempfl, 2002; Krempfl and Khan, 2003), but fitting of a loading–retraction curve (one cycle only) on polyphenylene oxide by a model with 12 adjustable parameters revealed rather poor agreement with experimental data and an additional improvement of the model was necessary (Colak, 2005). For a comparison of several versions of models with isotropic and kinematic hardening and a discussion of their ability to fit data on polyethylene reinforced with short glass fibers, see Remond (2005).

The theory of endochronic plasticity (Valanis and Lee, 1984; Watanabe and Atluri, 1986) provides another concept in viscoplasticity introduced firstly for metals and applied later to polymers. This approach introduces some internal time that is determined by history of plastic deformations and presumes that the current stress equals an integral of the plastic strain-rate tensor (where the rate is calculated with respect to the internal time).
with a kernel (hereditary function) that, in general, depends on the internal time and some characteristic parameters of the plastic strain curve in the Ilyushin space. Adopting a number of simplifying assumptions, Zhao and Kuang (2006) developed stress–strain relations with 15 material constants and reported an acceptable (but far from being perfect) accuracy of matching observations in cyclic tests with given maximum and minimum stresses. It should be noted, however, that the adjustable parameters strongly depend on the amplitudes of ratcheting, which implies that the number of experimental constants in the full model is substantially higher. Kletschkowski et al. (2002, 2005) developed a simple version of the endochronic theory of plasticity for polymers (7 constants) and applied it to approximate experimental data on polytetrafluoroethylene (PTFE) and composites with PTFE matrices. Unfortunately, the quality of fitting observations in cyclic tests (one cycle only) was rather poor.

It is worth also mentioning a merely phenomenological approach in cyclic plasticity, according to which a constitutive model is designed by composing several standard rheological elements (springs, dashpots and Coulomb friction units) connected in parallel or in sequel. Yoon et al. (2004) studied a series of the Jenkin elements (a linear spring in sequel with a hardening plastic unit) and found good agreement between observations in ratcheting tests on steel and results of numerical analysis when the model involved 22 adjustable parameters (these quantities, however, are strongly affected by amplitude of ratcheting). Bergstrom et al. (2002, 2004) and Bergstrom and Hilbert (2005) analyzed several combinations of elastic and nonlinear viscous elements (a spring in sequel with a Voight element, a spring in sequel with a group consisting of a Voight element in parallel with a dashpot, and a dashpot in sequel with a group consisting of a Maxwell element in parallel with a spring). The number of adjustable parameters in the models varied from 12 to 15 depending on the choice of a rheological model and assumptions regarding the nonlinearity of viscous units. It was demonstrated that the constitutive equations could reproduce the first cycle of deformation (experiments on ultra high molecular weight polyethylene and polytetrafluoroethylene) only when the experimental constants for retraction differed substantially from those for the loading part of the stress–strain curve. Anand and Ames (2006) introduced a rheological model consisting of an elastic spring in parallel with a group that involved several Voight elements in sequel with each other and with another spring. It was shown that the stress–strain relations with 27 adjustable parameters could reproduce qualitatively stress–strain curves for the first cycle of deformation on poly(methyl methacrylate), but the discrepancies at unloading were relatively large. Lai et al. (2005) showed that a nonlinear Zener model with only 10 material constants can correctly approximate experimental data on isotactic polypropylene in the interval of very small strains (less than 2%), but no attempts were reported to examine its abilities at larger strains.

This brief discussion shows that the constitutive equations for the mechanical response of solid polymers involve large numbers of experimental constants and reveal rather modest quality of fitting stress–strain diagrams at cyclic deformation (to the best of our knowledge, the accuracy of predictions of these models has not been studied). The objective of the present study is to develop stress–strain relations for the viscoplastic response of polymers at cyclic loading that obey the following requirements: (i) the number of material constants is less than that in most of the above models, (ii) these quantities can be easily found by matching observations, and (iii) when the adjustable parameters are determined, the model adequately predicts the mechanical response in independent tests.

Two starting points in our derivation of constitutive equations should be mentioned. The first is the concept of pseudo-elasticity proposed by Ogden and Roxburgh (1999). We borrow from this theory its hypothesis that some internal parameters in the stress–strain relations may be treated as piece-wise constant functions: they accept fixed values along the loading and retraction paths, but change their values when the sign of the strain rate is altered. The other is the assumption introduced in our previous studies (Drozdov and Christiansen, 2003, 2004) that the strain-rate tensor for plastic deformation is proportional to the strain-rate tensor for macro-deformation (not to the stress tensor as it is presumed in conventional theories of elasto- and viscoplasticity).

The exposition is organized as follows. Experimental data on a ternary composite are reported in Section 2. Constitutive equations are derived in Section 3. Adjustable parameters in the stress–strain relations are determined in Section 4. The model is validated by comparison of its predictions with observations in Section 5. Some concluding remarks are formulated in Section 6.
2. Experimental procedure

Homopolymer of isotactic polypropylene Moplen HP 501L was supplied by Basell Polyolefins (density 0.90 g/cm³, melt flow rate 6.0 g/10 min). Thermoplastic elastomer Engage 8102 was purchased from DuPont-Dow Elastomers (polyethylene–octene copolymer with a comonomer content 31 wt.%, density 0.885 g/cm³, and melt flow index 30.0 g/10 min). Masterbatch MB 1001E was purchased from PolyOne Inc. (nanocomposite with polypropylene matrix filled with 40 wt.% of Nanoblend concentrate, chemically modified MMT nanoclay). Pellets were carefully mixed in proportion 50:30:20 by weight, which corresponded to ≈8 wt.% of nanoclay in the ternary composite. Dumbbell specimens (ASTM standard D638) with length 148 mm, width 9.85 mm and thickness 3.74 mm were molded by using injection-molding machine Ferromatic K110/S60-2K.

Mechanical tests were carried out at ambient temperature with the help of an universal testing machine Instron–5568 equipped with electro-mechanical sensors for control of longitudinal strains in the active zone of samples. The tensile force was measured with a standard load cell. The engineering stress $\sigma$ was determined as the ratio of the tensile force to the cross-sectional area of specimens in the stress-free state.

Uniaxial tensile tests were performed with a constant cross-head speed of 20 mm/min, which corresponded to the engineering strain rate $\dot{\varepsilon} = 4 \times 10^{-3} \text{ s}^{-1}$. The value of the cross-head speed was chosen as a compromise between the following contradictory requirements: (i) the strain rate should be maximal to neglect viscous properties of the composite, and (ii) it should be minimal to reproduce correctly the required cyclic deformation programs with maximal strains as small as 0.025.

Cyclic tests were carried out according to the following program: (i) loading with the constant cross-head speed up to the maximum strain $\varepsilon_{\text{max}}$, (ii) retraction with the same cross-head speed down to the zero minimum stress (in order to avoid buckling of specimens, the minimum force was chosen as 10 Pa), and (iii) subsequent reloading and retraction (at least 10 cycles of deformation).

The experimental program consisted of two groups of tests: basic and additional. Basic tests (10 cycles of loading–retraction with the maximum strains $\varepsilon_{\text{max}} = 0.025, 0.05, 0.075, 0.10, 0.125$ and 0.15) were employed to find material constants in the governing equations. Additional tests were used to validate the constitutive model by comparison of its predictions with observations. These tests include (i) loading–retraction tests (10 cycles) with the maximum strains $\varepsilon_{\text{max}} = 0.09, 0.11$ and 0.14, (ii) loading–retraction tests (20 cycles) with the maximum strains $\varepsilon_{\text{max}} = 0.06$ and 0.08, and (iii) two-step cyclic tests (2 cycles) with the maximum strains $\varepsilon_{\text{max}_1} = 0.125$ and 0.15 in the first cycle and $\varepsilon_{\text{max}_2} = 0.10$ in the other cycle.

![Graph](image-url)  
Fig. 1. The engineering stress $\sigma$ versus engineering strain $\varepsilon$ in cyclic tensile tests with various maximum strains $\varepsilon_{\text{max}}$. Symbols: experimental data. Solid lines: results of numerical simulation.
Each test was performed on at least four specimens. No necking of samples was observed. The stress–strain diagrams for basic tests are depicted in Fig. 1 (only two cycles of deformation are shown to avoid overlapping of the curves). The following conclusions may be drawn from this figure:

1. The first loading part of the stress–strain diagrams is non-monotonic: the engineering stress \( \sigma \) increases with strain, reaches its maximum in the vicinity of \( \epsilon = 0.085 \) (which is in good agreement with the yield strain of polypropylene \( \epsilon_y = 0.09 \) provided by the supplier), and slowly decreases afterwards. The maximum tensile stress along the loading path equals about 24 MPa, which is less than the yield stress for PP reported by the supplier (34 MPa). The latter may be explained by the presence of TPE in the composite, whose modulus is substantially lower than that of PP.

2. The retraction parts of the stress–strain curves are strongly nonlinear, which distinguishes the mechanical response of polymer nanocomposites from that of metals and metallic alloys.

3. At cyclic deformation, the apparent residual strains (the strains measured when the stress vanishes) grow with number of cycles, whereas the maximum stresses decay slowly with number of cycles.

Our aim now is to derive constitutive equations that adequately describe observations depicted in Fig. 1.

3. Constitutive model

As the internal structure of a ternary composite is rather complicated and its detailed description requires a number of experimental parameters, we adopt a merely phenomenological approach and treat the composite as an isotropic incompressible elastic medium. Although isotactic polypropylene demonstrates slight compressibility [its Poisson's ratio is estimated as \( v = 0.43 \), see Kolarik and Pegoretti (2006) to \( v = 0.49 \), see El-Farahaty (1996)], the effect of compressibility is disregarded since the other phases (thermoplastic elastomer and nanoclay) are strongly incompressible.

In the derivation of constitutive equations, we concentrate on isothermal deformation processes with small strains and disregard viscoelastic phenomena observed in standard creep and relaxation tests. The focus on isothermal processes is explained by our interest to biomedical applications of ternary composites as well as the fact that substantial softening of the elastomeric phase occurs at temperatures as low as 60–70 °C. We confine ourselves to the analysis of the viscoplastic response at small strains because necking of hybrid composite specimens is observed at uniaxial tension with longitudinal strains as low as 0.17. Finally, our neglect of creep and relaxation phenomena is explained by the fact that the maximum duration of our cyclic tensile tests (10 cycles of loading–retraction with the maximum strain 0.15) does not exceed 5 min. Observations in standard relaxation tests on the ternary nanocomposite (not presented) show that the decay in stress during this period is less than 20%. Even this effect of viscoelasticity on the mechanical response is strongly reduced in cyclic tests, when the stress increases and decreases at each cycle of deformation.

We adopt the conventional assumption in viscoplasticity with small strains and split the strain tensor for macro-deformation \( \dot{\epsilon} \) into the sum of strain tensors for elastic, \( \dot{\epsilon}_e \), and plastic, \( \dot{\epsilon}_p \), deformations

\[
\dot{\epsilon} = \dot{\epsilon}_e + \dot{\epsilon}_p,
\]

where both tensors, \( \dot{\epsilon}_e \) and \( \dot{\epsilon}_p \), are assumed to be traceless.

It is postulated that the plastic strain tensor vanishes at the initial instant, whereas the rate-of-strain tensor for plastic deformation is proportional to the rate-of-strain tensor for macro-deformation:

\[
\frac{d\dot{\epsilon}_p}{dt} = \phi \frac{d\dot{\epsilon}}{dt}, \quad \dot{\epsilon}_p(0) = \hat{0},
\]

where \( \hat{0} \) is the tensor with zero components, \( t \) stands for time, and \( \phi \) is a scalar function to be determined in what follows. It should be emphasized that we use the term “plastic strain” for brevity. According to Eq. (2), it may be more accurate to refer to the tensor \( \dot{\epsilon}_p \) as the viscoplastic strain tensor, because it is determined by the entire history of deformation.
The strain energy (per unit volume) of an isotropic incompressible medium at small strains is given by

\[ W = \frac{1}{2} \mu \dot{\varepsilon} : \dot{\varepsilon}, \]

(3)

where \( \mu \) stands for an elastic modulus, and colon denotes convolution of tensors. Differentiating Eq. (3) with respect to time and using Eqs. (1) and (2), we find that

\[ \frac{dW}{dt} = \mu (1 - \phi) \dot{\varepsilon} : \dot{\varepsilon}, \]

(4)

At isothermal deformation of an incompressible medium with small strains, the Clausius–Duhem inequality reads

\[ Q = -\frac{dW}{dt} + \dot{\sigma} : \dot{\varepsilon} \geq 0, \]

(5)

where \( Q \) is the energy dissipation per unit time and unit volume, \( \dot{\sigma} \) stands for the stress tensor, and prime denotes the deviatoric part of a tensor. Inserting Eq. (4) into Eq. (5) and assuming dissipation of energy to vanish, we arrive at the stress–strain relation

\[ \dot{\sigma}(t) = -p(t) \hat{I} + \mu (1 - \phi(t)) (\dot{\varepsilon}(t) - \dot{\varepsilon}_p(t)), \]

(6)

where \( p(t) \) is an unknown pressure, and \( \hat{I} \) stands for the unit tensor. Eqs. (2) and (6) are satisfied for an arbitrary isothermal deformation program \( \dot{\varepsilon}(t) \) with small strains.

With reference to the experimental data reported in Section 2, we distinguish between the first loading (when \( \dot{\varepsilon}(t) \) changes monotonically from 0 to some ultimate tensor \( \dot{\varepsilon}_{\text{max}} \)) and subsequent retractions and reloadings. At the first loading of a virgin medium, the function \( \phi \) is determined by the stretched exponential relation

\[ \phi = 1 - \exp \left( -a J_e^\beta \right), \]

(7)

where \( a \) and \( \beta \) are positive constants, and

\[ J_e = \sqrt[3]{\frac{2}{3} \dot{\varepsilon} : \dot{\varepsilon}}, \]

(8)

denotes the conventional intensity of elastic deformation. Our choice of Eq. (7) may be explained by the following reasons: (i) it appears to be physically plausible (the rate of plastic strain equals zero at the initial instant, does not exceed the rate of macro-deformation at any time, and reaches the strain rate for macro-deformation at large elastic strains), (ii) it contains only two adjustable parameters, and (iii) it ensures good approximation of stress–strain diagrams at elongation of a virgin sample, see Section 4.

When the macro-strain reaches its maximum value, and retraction and subsequent reloading begin, changes in the pre-factor \( \phi \) are governed by the first-order kinetic equation:

\[ \frac{d\phi}{dt} + b|\dot{\varepsilon}| \phi = \frac{a}{\mu} \dot{\sigma} : \dot{\varepsilon}, \]

(9)

where \( a \) and \( b \) are dimensionless scalar parameters, and \( |\dot{\varepsilon}| \geq 0 \) is the strain-rate intensity. Eq. (9) is chosen for two reasons: (i) it is relatively simple and involves only two quantities, \( a \) and \( b \), to be determined by matching observations, and (ii) the work of external forces \( \dot{\sigma} : \dot{\varepsilon} \) is included into Eq. (9) as an input, which seems physically plausible. The initial condition for Eq. (9) is determined by the assumption regarding continuity of the function \( \phi \), see Eq. (6). Following the concept of pseudo-elasticity, we presume the quantities \( a \) and \( b \) to be constant for each path of the stress–strain diagram at cyclic loading (which means that \( a \) and \( b \) remain constant during each subsequent retraction and reloading), but they alter their values at the instants when the strain rate changes its sign.

It is worth emphasizing that all theories of cyclic plasticity with yield surfaces are grounded of the hypothesis that the rate of plastic strain changes discontinuously at the points where the sign of strain rate is altered (they employ different kinetic equations for active loading and unloading and presume continuity of the plastic
straining tensor only). Unlike these concepts, governing Eq. (9) ensures a higher level of smoothness of the plastic strain tensor: not only this tensor, but the rate-of-strain tensor for plastic deformations remain continuous at the points where the direction of deformation is altered, while only the coefficients \( a \) and \( b \) in kinetic Eq. (9) change their values.

The present study focuses on the analysis of cyclic deformations, when the macro-strain tensor \( \varepsilon(t) \), after reaching the value \( \varepsilon_{\text{max}} \), “decreases” down to \( \varepsilon_{\text{min}} \), “increases” once more up to \( \varepsilon_{\text{max}} \), and so on. To complete description of the model, it is necessary to define (i) the values \( a_0^+ \), \( b_0^+ \) of coefficients in Eq. (9) at the first time when \( \varepsilon = \varepsilon_{\text{max}} \), (ii) their values \( a_0^- \), \( b_0^- \) at the first time when \( \varepsilon = \varepsilon_{\text{min}} \), and (iii) a rule that allows these quantities to be transformed into the coefficients in Eq. (9) for any subsequent cycle. The following phenomenological equations are introduced:

\[
\begin{align*}
    a_0^+ &= A_+ \exp (\Gamma a_0^+ \rho_e), \\
    b_0^+ &= B_+ \exp (-\Gamma J_0^+), \\
    a_0^- &= A_- \exp (-\gamma J_0^-), \\
    b_0^- &= B_- \exp (-\gamma J_0^-),
\end{align*}
\]

where \( A_+, A_- \), \( B_+, B_- \), \( \Gamma, \gamma \) are positive material constants, and \( J_0^+ \) is the intensity of elastic strains when the tensor \( \varepsilon \) reaches its “maximum” \( \varepsilon_{\text{max}} \) and “minimum” \( \varepsilon_{\text{min}} \) values for the first time. Although Eq. (10) are relatively simple, they provide the main source of adjustable parameters in the governing equations. To explain the physical meaning of Eq. (10), it is convenient to present them in the differential form:

\[
\begin{align*}
    \frac{1}{a_+} \frac{da_+}{dJ_e} &= \Gamma a_+, \\
    \frac{1}{b_+} \frac{db_+}{dJ_e} &= -\Gamma b_+, \\
    \frac{1}{a_-} \frac{da_-}{dJ_e} &= -\gamma, \\
    \frac{1}{b_-} \frac{db_-}{dJ_e} &= -\gamma,
\end{align*}
\]

where the superscript index 0 is omitted. Eq. (11) mean that evolution of the quantities \( a_{\pm} \) and \( b_{\pm} \) at first loading and first retraction is described by the first-order kinetic equations, where the intensity of elastic strain \( J_e \) plays the role of internal time. This conclusion is in agreement with conventional assumptions in the endo-chronic theory of plasticity.

Changes in \( a \) and \( b \) driven by cyclic deformations are described by the equations:

\[
\begin{align*}
    a_+ &= a_0^+, \\
    a_- &= a_0^- \exp (-\varepsilon(J_e - J_0^+)), \\
    b_+ &= b_0^+ \exp (-\eta_+(J_e - J_0^+)), \\
    b_- &= b_0^- \exp (-\eta_-(J_e - J_0^-)),
\end{align*}
\]

where \( \varepsilon, \eta_+ \) and \( \eta_- \) are positive quantities. Eq. (12) postulate that \( a_+ \) is not affected by cyclic deformations, whereas \( a_- \), \( b_+ \) and \( b_- \) decrease exponentially with intensity of elastic strains.

The coefficients \( \xi, \eta_+ \) and \( \eta_- \) in Eq. (12) are given by

\[
\begin{align*}
    \xi &= \xi_0 \exp (\lambda J_e^0), \\
    \eta_+ &= \eta_0^+ \exp (-\kappa_+ J_e^0), \\
    \eta_- &= \eta_0^- \exp (-\kappa_- J_e^0),
\end{align*}
\]

where \( \xi_0^-, \eta_0^+, \lambda, \kappa_+ \) and \( \kappa_- \) are positive material constants.

To ascribe some physical meaning to Eq. (12), we re-write these relations in the differential form similar to Eq. (11):

\[
\begin{align*}
    \frac{1}{a_+} \frac{da_+}{dJ_e} &= 0, \\
    \frac{1}{b_+} \frac{db_+}{dJ_e} &= -\eta_+, \\
    \frac{1}{a_-} \frac{da_-}{dJ_e} &= -\xi, \\
    \frac{1}{b_-} \frac{db_-}{dJ_e} &= -\eta_-,
\end{align*}
\]

where

\[
\Delta J_e = J_e - J_0^0,
\]

is the increment of intensity of elastic deformation. Eq. (14) show that the coefficients \( a_{\pm} \) and \( b_{\pm} \) change with \( \Delta J_e \) monotonically. Evolution of these quantities is described by the first-order kinetic Eq. (14), where \( \Delta J_e \) plays the role of an “internal time”.

The presence of two sets of evolution Eqs. (11) and (14) may be explained as follows. A ternary nanocomposite is thought of as a three-phase system consisting of amorphous regions, crystalline domains and inclusions of nanoclay. Plastic deformations of this system induce transformations of its morphology (Lin and Argon, 1994; Seguela, 2005). The strongest transformations occur along the first loading and first retraction paths and may be associated with inter-lamellar separation and shear, rotation of lamellar stacks and micro-necking of lamellae. These micro-processes induce changes in the rate of plastic strain that are described by
Eqs. (9) and (11). At subsequent cycles of reloading–retraction, only minor changes occur in the crystalline structure that may be attributed to transformations in the interphase regions and associated with sliding of chains along crystallites and clay stacks, diffusion of micro-cavities from the amorphous into crystalline phase, and creation and annihilation of dislocations at the lamellae surfaces. These transformations alter the plastic rate-of-strain relatively weakly, and their influence is described by the evolution Eqs. (9) and (14). An important conclusion of this physical picture is that the intensity of elastic strain $J_e$ serves as the only internal variable that affects the viscoplastic flow. The rate of plastic deformations is mainly determined by evolution of the crystalline morphology at the first cycle of deformation (and is characterized by $J_0^0$). Subsequent “tuning” of this rate with an increase in number of cycles is governed by the increment of this intensity $\Delta J_e$.

Stress–strain relations Eqs. (1), (2), (6), (7), (9), (10), (12) and (13) involve 16 constants to be found by matching observations:

$$\mu, \sigma, \beta, A_+, A_-, B_+, B_-, t_{\alpha}, \Gamma_{\beta}, \gamma, \xi_0^0, \eta_+^0, \eta_-^0, \lambda, \kappa_+, \kappa_-.$$  
This number of experimental parameters is comparable with the number of constants in the models proposed by Bergstrom et al. (2002, 2004) and Lai et al. (2005) that could fit the first cycle of loading–retraction only. Our aim is to demonstrate that the above constitutive equations (i) ensure good agreement with observations for an arbitrary number of cycles, and (ii) correctly predict experimental data in independent experiments.

4. Material parameters

Determination of experimental constants provides the main source of difficulties in application of conventional models for cyclic plasticity, as a large number of parameters should be found simultaneously by fitting a relatively small interval of a stress–strain diagram, see, e.g., Anand and Ames (2006) for a discussion. An advantage of our stress–strain relations is that they are free from this shortcoming: adjustable parameters are determined one after another, and no more than three constants are found by using a particular set of data for loading and retraction.

As the constitutive equations were developed in Section 3 for an arbitrary three-dimensional deformation, we begin with their simplification for uniaxial tension of a specimen. For uniaxial deformation of an incompressible medium, the strain tensor reads

$$\dot{\epsilon} = \epsilon(t) \left[ e_1 \otimes e_1 - \frac{1}{2} (e_2 \otimes e_2 + e_3 \otimes e_3) \right],$$

where $\epsilon(t)$ stands for longitudinal engineering strain, $e_k (k = 1, 2, 3)$ are unit vectors of a Cartesian coordinate frame, whose vector $e_1$ coincides with the direction of deformation, and $\otimes$ denotes tensor product. The plastic strain tensor $\dot{\epsilon}_p$ is assumed to be presented in the form (15),

$$\dot{\epsilon}_p = \epsilon_p(t) \left[ e_1 \otimes e_1 - \frac{1}{2} (e_2 \otimes e_2 + e_3 \otimes e_3) \right],$$

where $\epsilon_p(t)$ is a function to be found. Substitution of Eqs. (15) and (16) into Eq. (2) results in

$$\frac{d\epsilon_p}{d\epsilon} = \phi, \quad \epsilon_p(0) = 0.$$  
It follows from Eq. (8) that the function $\phi$ in Eq. (17) is given by

$$\phi = 1 - \exp[-\sigma(\epsilon - \epsilon_p)^0].$$

Inserting expressions (15) and (16) into Eq. (6) and excluding the unknown pressure $p$ from the boundary condition on the lateral surface of the specimen, we calculate the tensile stress $\sigma$,

$$\sigma = E \Sigma, \quad \Sigma = (1 - \phi)(\epsilon - \epsilon_p),$$

where $E = \frac{1}{2} \mu$ stands for an analog of the Young’s modulus.

Eqs. (17)–(19) serve for the determination of $E, \sigma$ and $\beta$ by matching the first loading path of a stress–strain curve. The following algorithm is employed. We fix some intervals $[0, \sigma_0]$ and $[0, \beta_0]$, where the best-fit
parameters $x$ and $\beta$ are located and divide these intervals by the points $x_i = i\Delta x$ and $\beta_j = j\Delta \beta$, where $\Delta x = x_0/J$ and $\Delta \beta = \beta_0/J$ ($i, j = 1, \ldots, J - 1$). For each pair $\{x_i, \beta_j\}$, Eqs. (17) and (18) are integrated numerically (by the Runge–Kutta method with the step $\Delta \epsilon = 1.0 \times 10^{-5}$) from $\epsilon = 0$ to $\epsilon = 0.15$. The pre-factor $E$ in Eq. (19) is found by the least-squares method from the condition of minimum of the functional

$$
F = \sum_n \left( \sigma_{\exp}(\epsilon_n) - \sigma_{\text{num}}(\epsilon_n) \right)^2,
$$

where the sum is calculated over all points $\epsilon_n$ at which observations are reported in Fig. 1, $\sigma_{\exp}$ is the stress measured in the test, and $\sigma_{\text{num}}$ is given by Eq. (19). The best-fit values $\bar{x}$ and $\bar{\beta}$ are chosen to minimize $F$ on the set of pairs $\{x_i, \beta_j\}$. Then, the initial intervals $[0, x_0]$ and $[0, \beta_0]$ are replaced with the new intervals $[\bar{x} - \Delta x, \bar{x} + \Delta x]$ and $[\bar{\beta} - \Delta \beta, \bar{\beta} + \Delta \beta]$, and the above calculations are repeated. To ensure an acceptable quality of fitting observations, we set $J = 10$ and repeated this procedure three times. The material constants $E$, $\bar{x}$ and $\bar{\beta}$ are given in Table 1.

The elastic modulus $E$ of the ternary nanocomposite exceeds the Young’s modulus of polypropylene provided by the supplier (1.5 GPa) by 34%, which means that the effect of nanoclay is substantial. Another interesting conclusion may be drawn if we re-write Eq. (18) in the form

$$
\phi = 1 - \exp \left[ - \left( \frac{\epsilon - \epsilon_p}{\epsilon_a} \right)^{\beta} \right],
$$

where

$$
\epsilon_a = \frac{1}{2^\beta}.
$$

Calculation of $\epsilon_a$ by means of this formula results in $\epsilon_a = 0.098$, which is close to the yield strain $\epsilon_y = 0.09$ provided by the supplier.

To find other adjustable parameters, we approximate each part (retraction and reloading) of each stress–strain diagram separately. Keeping in mind that the stress tensor has the only non-zero component $\sigma$ and using Eqs. (15) and (19), we present Eq. (9) in the form:

$$
\frac{d\phi}{d\epsilon} = a\Sigma - b\phi
$$

for loading, and

$$
\frac{d\phi}{d\epsilon} = a\Sigma + b\phi
$$

for retraction.

To find the best-fit parameters $a_i^0$ and $b_i^0$ for the first retraction path of a stress–strain diagram (characterized by the maximum strain $\epsilon_{\text{max}}$), we fix some intervals $[0, a_0]$ and $[0, b_0]$ where these quantities are located and divide these intervals by the points $a_i = i\Delta a$ and $b_j = j\Delta b$ with $\Delta a = a_0/J$, $\Delta b = b_0/J$ ($i, j = 1, \ldots, J - 1$). For any pair $\{a_i, b_j\}$, Eqs. (17), (19) and (21) are integrated numerically (by the Runge–Kutta method with the step $\Delta \epsilon = 1.0 \times 10^{-5}$) from $\epsilon = \epsilon_{\text{max}}$ to $\epsilon = 0$. The initial conditions for Eqs. (17) and (21) reflect the continuity conditions for the functions $\epsilon_p(\epsilon)$ and $\phi(\epsilon)$.

Table 1

<table>
<thead>
<tr>
<th>$E$ (GPa)</th>
<th>$x$</th>
<th>$\beta$</th>
<th>$A_i$</th>
<th>$B_i$</th>
<th>$\Gamma_a$</th>
<th>$\Gamma_b$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.01</td>
<td>17.0</td>
<td>0.82</td>
<td>$2.63 \times 10^2$</td>
<td>$1.42 \times 10^2$</td>
<td>4.77</td>
<td>91.17</td>
<td>69.91</td>
</tr>
<tr>
<td>7.52 $\times 10^3$</td>
<td>1.17 $\times 10^2$</td>
<td>22.16</td>
<td>17.12</td>
<td>75.39</td>
<td>45.52</td>
<td>27.41</td>
<td>13.52</td>
</tr>
</tbody>
</table>

Adjustable parameters of the model
replaced with the new intervals \( [\tilde{a}_+ - \Delta a, \tilde{a}_+ + \Delta a] \) and \( [\tilde{b}_+ - \Delta b, \tilde{b}_+ + \Delta b] \), and the calculations are repeated. To ensure good agreement between the experimental data and the results of numerical simulation, the above procedure is repeated three times with \( J = 10 \).

After determination of the best-fit values \( a^0_+ \) and \( b^0_+ \) for the first retraction part of each stress–strain diagram, we integrate Eqs. (17), (19) and (21) from \( \epsilon = \epsilon_{\text{max}} \) to \( \sigma = 0 \) with these constants and apply the above algorithm to approximate the first reloading path of the stress–strain curve. The only differences are that (i) Eq. (20) is replaced with Eq. (21), (ii) numerical integration is performed from \( \sigma = 0 \) to \( \epsilon = \epsilon_{\text{max}} \), and (iii) the best-fit parameters are referred to as \( a^0_0 \) and \( b^0_0 \).

When \( a^0_+, b^0_+, a^0_0 \) and \( b^0_0 \) are found for all stress–strain curves of the main group of tests, these quantities are plotted versus the elastic strain \( \epsilon_{\text{e}}^0 \) (the elastic strain \( \epsilon_{\text{e}} = \epsilon - \epsilon_p \) at the beginning of first retraction and the first reloading). The experimental data are depicted in Figs. 2 and 3 together with their approximations by formulas (10):

\[
\begin{align*}
\ln a^0_+ &= \ln A_+ + \Gamma a^0_{\text{e}e}, \\
\ln b^0_+ &= \ln B_+ - \Gamma b^0_{\text{e}e}, \\
\ln a^0_0 &= \ln A_0 - \gamma \epsilon_{\text{e}}^0, \\
\ln b^0_0 &= \ln B_0 - \gamma \epsilon_{\text{e}}^0.
\end{align*}
\]

(22)

The coefficients \( A_+, A_-, B_+ , B_-, \Gamma_a, \Gamma_b \) and \( \gamma \) in Eq. (22) are determined by the least-squares method and are listed in Table 1. Figs. 2 and 3 demonstrate good agreement between the observations and the results of numerical simulation based on Eq. (22) for cyclic tests with all maximum strains \( \epsilon_{\text{max}} \) except for the smallest one. The latter is not surprising, as a cross-head speed of 20 mm/min is too large in order to perform cyclic deformation with a constant strain rate and the maximum strain \( \epsilon_{\text{max}} = 0.025 \).

After determining the quantities \( a^0_+, a^0_0, b^0_+ \) and \( b^0_0 \) by fitting the experimental data for the first retraction and reloading, we approximate each part of the stress–strain diagrams (corresponding to subsequent retractions and reloadings) separately with the help of one parameter, \( b_+ \), for retraction and two parameters, \( a_- \) and \( b_- \), for reloading, by using the above algorithm. An example of matching observations is presented in Fig. 4, which shows excellent agreement between the experimental data (10 cycles of loading–retraction) and the results of numerical analysis. The same quality of fitting is reached for the other stress–strain curves, but appropriate figures are omitted for the sake of brevity.

The adjustable parameters \( b_+ , a_- \) and \( b_- \) are plotted in Figs. 5–7 versus elastic strain \( \epsilon_{\text{e}} \) at the instant when the strain rate changes its sign. The experimental data are approximated by Eq. (12). For uniaxial deformation, these relations read:

![Fig. 2. The adjustable parameters \( a_+ \) and \( b_+ \) versus elastic strain \( \epsilon_{\text{e}}^0 \) at the beginning of first retraction. Symbols: treatment of observations in cyclic tensile tests. Solid lines: approximation of the experimental data by Eq. (22).](image-url)
\[
\ln b_+ = \tilde{b}_+ - \eta_+ \varepsilon_e, \quad \ln a_- = \tilde{a}_- - \zeta \varepsilon_e, \quad \ln b_- = \tilde{b}_- - \eta_- \varepsilon_e, \quad (23)
\]

where
\[
\tilde{b}_+ = \ln b^0_+ + \eta_+ \varepsilon_e^0, \quad \tilde{a}_- = \ln a^0_- + \zeta \varepsilon_e^0, \quad \tilde{b}_- = \ln b^0_- + \eta_- \varepsilon_e^0.
\]

The coefficients \(\zeta, \eta_+\) and \(\eta_-\) in Eq. (23) are determined by the least-squares technique. Figs. 5–7 show that Eq. (23) provide an acceptable accuracy of fitting the observations.

After finding the parameters \(\zeta, \eta_+\) and \(\eta_-\) for each stress–strain diagram with a maximum strain \(\varepsilon_{\text{max}}\), these quantities are plotted versus elastic strain \(\varepsilon^0_e\) at the first retraction and reloading. The experimental data are depicted in Fig. 8 together with their approximations by Eq. (13), which, at uniaxial deformation, read...
\begin{equation}
\ln \xi = \ln \xi^0 + \lambda \epsilon^0_e, \quad \ln \eta_+ = \ln \eta_+^0 - \kappa_+ \epsilon^0_e, \quad \ln \eta_- = \ln \eta_-^0 - \kappa_- \epsilon^0_e. \tag{24}
\end{equation}

The material constants \( \xi^0, \eta_+^0, \eta_-^0, \lambda, \kappa_+ \) and \( \kappa_- \) in Eq. (24) are calculated by using the least-squares method. The best-fit values of these parameters are collected in Table 1. Fig. 8 demonstrates good agreement between the observations and the results of numerical simulation at all maximum strains \( \epsilon_{\text{max}} \) except for the smallest one, \( \epsilon_{\text{max}} = 0.025 \).

5. Validation of the model

It was demonstrated in Section 4 that the constitutive equations adequately describe the mechanical response of the hybrid nanocomposite at cyclic deformations, and phenomenological relations (10)–(13)
correctly reflect the effect of maximal strain $\varepsilon_{\text{max}}$ on parameters in the stress–strain relations. Our aim now is to show that the model can predict the viscoplastic behavior of hybrid nanocomposites in cyclic tensile tests with various maximum strains $\varepsilon_{\text{max}}$.

We begin with the study of observations obtained in the first series of additional tests (10 cycles of loading–retraction with the maximum strains $\varepsilon_{\text{max}} = 0.09, 0.11$ and $0.14$ and the minimum stress $\sigma_{\text{min}} = 0$ MPa). The experimental data are plotted in Figs. 9–11. To avoid overlapping of curves, only the data for the first cycle (loading of a virgin specimen, retraction, and subsequent reloading) and for the last cycle (reloading and retraction) are presented. To assess the quality of the stress–strain relations, numerical integration of Eqs. (17)–(21) together with formulas Eqs. (22)–(24) is performed by the Runge–Kutta method with the step $|\Delta \varepsilon| = 1.0 \times 10^{-5}$ and the material constants listed in Table 1. Comparison of the experimental data (symbols)
with the results of simulation (solid lines) depicted in Figs. 9–11 demonstrates that the constitutive model adequately predicts these observations.

To show that the model can also predict (with an acceptable accuracy) experimental data in cyclic tests with a higher number of cycles, observations in the other series of additional tests are employed (20 cycles of loading–retraction with the maximum strains $\epsilon_{\text{max}} = 0.06$ and $0.08$ and the minimum stress $\sigma_{\text{min}} = 0$ MPa). The experimental stress–strain diagrams (symbols) are plotted in Figs. 12 and 13 together with the results of numerical simulation (solid lines). To make the exposition clear, only the observations in the first, tenth and twenties cycles are reported. Figs. 12 and 13 demonstrate good agreement between the observations and their predictions by the model. Some deviations, however, are to be mentioned between the experimental data.

Fig. 9. The engineering stress $\sigma$ versus engineering strain $\epsilon$ in a cyclic tensile test with the maximum strain $\epsilon_{\text{max}} = 0.09$. Symbols: experimental data. Solid lines: prediction of the model.

Fig. 10. The engineering stress $\sigma$ versus engineering strain $\epsilon$ in a cyclic tensile test with the maximum strain $\epsilon_{\text{max}} = 0.11$. Symbols: experimental data. Solid lines: prediction of the model.
data at the 20th cycle and the results of numerical analysis: the stress–strain relations slightly underestimate
the tensile stress in the vicinity of the maximum strain $\varepsilon_{\text{max}}$.  

Finally, we analyze observations in two-step cyclic tests, when a specimen is subjected to tensile deformation
with the maximum strain $\varepsilon_{\text{max1}}$, retraction down to the zero stress, reloading with the maximum strain $\varepsilon_{\text{max2}} < \varepsilon_{\text{max1}}$ and subsequent retraction. The experimental stress–strain curves with $\varepsilon_{\text{max1}} = 0.125$, $\varepsilon_{\text{max2}} = 0.1$
and $\varepsilon_{\text{max1}} = 0.15$, $\varepsilon_{\text{max2}} = 0.1$ are depicted in Figs. 14 and 15, respectively. To predict the viscoplastic response
in a two-step cyclic test, the following algorithm is applied: (i) the loading path for a virgin specimen is found
by numerical integration of Eqs. (17)–(19) from $\varepsilon = 0$ to $\varepsilon = \varepsilon_{\text{max1}}$, (ii) the first retraction path is determined by
integration of Eqs. (17), (19) and (21) with the parameters $a$ and $b$ calculated according to Eq. (22), where $\varepsilon_0$ is
the elastic strain at $\varepsilon = \varepsilon_{\text{max1}}$, (iii) the first reloading path is determined by integration of Eqs. (17), (19) and

Fig. 11. The engineering stress $\sigma$ versus engineering strain $\varepsilon$ in a cyclic tensile test with the maximum strain $\varepsilon_{\text{max}} = 0.14$. Symbols: experimental data. Solid lines: prediction of the model.

Fig. 12. The engineering stress $\sigma$ versus engineering strain $\varepsilon$ in a cyclic tensile test with the maximum strain $\varepsilon_{\text{max}} = 0.06$. Symbols: experimental data. Solid lines: prediction of the model.
(20) with $a$ and $b$ given by Eq. (22), where $\epsilon^0_e$ is the elastic strain at $\sigma = 0$, (iv) the second retraction path is calculated by integration of Eqs. (17), (19) and (21) with $a = a^0_+,$ $b = b^0_+ \exp \left[-\eta_+ (\epsilon_e - \epsilon^0_e)\right]$,

where $a^0_+$ and $b^0_+$ are found from Eq. (22). In the latter formulas, $\epsilon^0_e$ is the elastic strain at elongation of a virgin sample up to $\epsilon = \epsilon_{\text{max}2}$, and $\eta_+$ is given by Eq. (24). This is equivalent to the assumption that the entire memory of the nanocomposite about its deformation history is determined by its current elastic strain only. Figs. 14 and 15 show excellent agreement between the observations and their predictions by the constitutive model.
6. Concluding remarks

Experimental stress–strain diagrams are reported at cyclic tensile deformations of a ternary nanocomposite with various maximum strains $\varepsilon_{\text{max}}$ (including the regions of sub-yield and post-yield deformations). Constitutive equations are derived for the viscoplastic response of a nanocomposite at arbitrary three-dimensional cyclic deformations with small strains. After simplification of these relations for uniaxial tension, adjustable parameters in the governing equations are found by fitting the experimental data. It should be noted that although the number of material constants in the model is not small, these quantities are determined by matching each interval of loading–retraction independently, which means that no more than three parameters are found by fitting of each cycle of deformation. The model is validated by comparison of its predictions with observations in independent tests. Good agreement is revealed between the results of numerical simulation and the experimental data.

References


