CYCLIC VISCOELASTICITY AND VISCOPLASTICITY OF POLYPROPYLENE/CLAY NANOCOMPOSITES

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Abstract
Observations are reported in tensile relaxation tests under stretching and retraction on polypropylene/clay nanocomposites with various contents of filler. A two-phase constitutive model is developed in cyclic viscoelasticity and viscoplasticity of hybrid nanocomposites. Adjustable parameters in the stress-strain relations are found by fitting the observations. Ability of the constitutive equations to describe characteristic features of the time-dependent response under loading and unloading is confirmed by numerical simulation.

1 Introduction

This paper deals with experimental investigation and constitutive modeling of the time-dependent response of polypropylene/clay nanocomposites. The study focuses on the so-called anomalous behavior [1] of nanohybrids observed in relaxation tests on specimens stretched up to some maximum strain ϵ_{max} and unloaded down to various minimum stresses σ_{min}.

Experimental data in conventional relaxation tests under tension demonstrate a monotonic decrease in stress with time. The situation changes drastically when relaxation is conducted on samples subjected to tension up to a maximum strain ϵ_{max} and retraction down to a minimum stress σ_{min}. Depending on the difference $\delta\sigma=\sigma_{max}-\sigma_{min}$, where σ_{max} stands for maximum stress under tension, three regimes of relaxation are revealed (i) simple relaxation (stress decays monotonically with time) at $\delta\sigma<0.3\sigma_{max}$, (ii) mixed relaxation (stress increases, reaches its maximum value, and decreases afterwards) at $0.3\sigma_{max}<\delta\sigma<0.8\sigma_{max}$, (iii) inverse relaxation (stress grows with time) at $\delta\sigma>0.8\sigma_{max}$.

Transitions from simple to mixed to inverse relaxations have been observed in semicrystalline and amorphous polymers [1-3]. However, this phenomenon has not yet been examined in hybrid nanocomposites. The objective of this work is twofold: (i) to analyze the effect of clay content on the time-dependent behavior of polypropylene/nanoclay hybrids in three-step (loading–unloading–relaxation) tests, and (ii) to derive a constitutive model for the viscoelastic and viscoplastic behavior of nanocomposites subjected to cyclic deformation.

2 Experimental results

Isotactic polypropylene Moplen HP 400R was purchased from Albis Plastic Scandinavia AB (Sweden). Maleic anhydride grafted polypropylene Eastman G 3015 was supplied by Eastman

Chemical Company (USA). Organically modified montmorillonite nanoclay Delitte 67G was donated by Laviosa Chimica Mineraria S.p.A. (Italy).

Hybrid nanocomposites were manufactured in a two-step process [4]. At the first step, a masterbatch was prepared in a twin-screw extruder Brabender PL2000. At the other step, pellets of the masterbatch were mixed with polypropylene in various proportions corresponding to nanoclay concentrations χ=0, 1, 3, and 5 wt.%. Dumbbell specimens for tensile tests were molded by using injection-molding machine Arburg 320C.

Mechanical tests were performed at room temperature by means of universal testing machine Instron–5568 equipped with an electro-mechanical sensor for control of longitudinal strains. The experimental program involved two series of tests.

The first series was conducted to evaluate the effect of clay content on the time-dependent response of nanocomposites under tension. In each test, a specimen was stretched with cross-head speed d=100 mm/min (which corresponded to strain rate e=1.7·10^{-2} s^{-1}) up to strain ε=0.1. Afterwards, the strain was fixed, and changes of stress σ with time t were monitored.
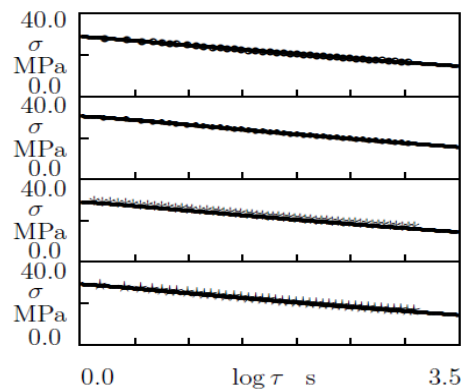

Figure 1. Stress σ versus relaxation time τ. Symbols: experimental data in relaxation tests under tension on nanocomposites with various clay contents χ wt.% (unfilled circles – χ=0, filled circles – χ=1, asterisks – χ=3, stars – χ=5). Solid lines: results of numerical simulation.

Observations in short-term relaxation tests (with duration t_{rel}=20 min) on nanocomposites with χ=0, 1, 3, and 5 wt.% of clay are reported in Figure 1 where stress σ is plotted versus relaxation time τ=t-t_0 (t_0 stands for the instant when relaxation starts). Following common practice, the semi-logarithmic plot is employed with log=log$_{10}$. The following conclusions are drawn: (i) at all concentrations of nanoclay, stress decreases monotonically with τ, and (ii) the relaxation diagrams are weakly affected by clay content χ.

The other series of tests was conducted to examine the influence of filler on the viscoplastic behavior of nanocomposites under loading–unloading and their viscoelastic response under retraction. In each test, a specimen was loaded with cross-head speed d=10 mm/min (which corresponded to strain rate e=1.7·10^{-3} s^{-1}) up to maximum strain ε_{max}=0.1 and unloaded down to minimum stress σ_{min}=1 MPa with the same cross-head speed (this value was chosen instead of σ_{min}=0 MPa to avoid buckling of specimens). Afterwards, the strain was fixed, and evolution of stress σ with time t was measured during t_{rel}=20 min.

An example of the stress–strain diagram under cyclic loading for nanocomposite with χ=5 wt.% is reported in Figure 2. Experimental data in cyclic tests show that reinforcement of polypropylene with nanoclay results in (i) an increase in yield stress σ_y (defined as the maximum stress under tension), (ii) a decrease in yield strain ε_y (the strain at which tensile stress reaches its maximum value), and (iii) evolution of shapes of stress–strain curves under retraction (curvatures of these diagrams increase monotonically with χ).
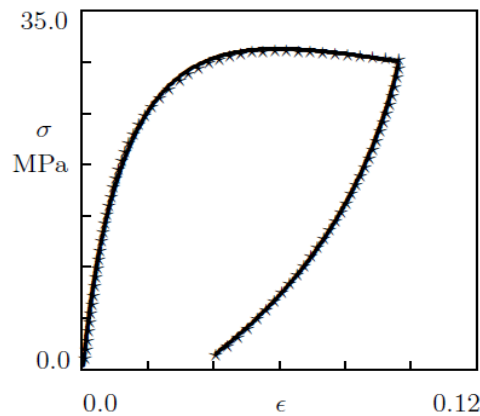
Figure 2. Stress σ versus strain ε. Stars: experimental data in cyclic test with ε_{max}=0.1 and σ_{min}=1 MPa on nanocomposite with χ=5 wt.%. Solid line: results of numerical simulation.

Observations in relaxation tests under retraction are depicted in Figure 3. According to this figure, relaxation diagrams under retraction are weakly affected by clay content χ.
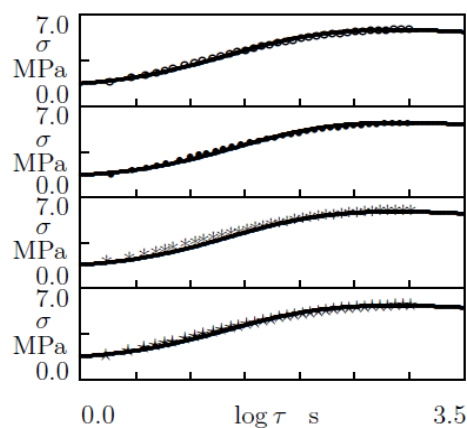

Figure 3. Stress σ versus relaxation time τ. Symbols: experimental data in relaxation tests on nanocomposites with various clay contents χ wt.% stretched up to ε_{max}=0.1 and unloaded down to σ_{min}=1 MPa (unfilled circles – χ=0, filled circles – χ=1, asterisks – χ=3, stars – χ=5). Solid lines: results of numerical simulation.

3 Constitutive model

A hybrid nanocomposite with a semicrystalline matrix is thought of as a two-phase medium consisting of crystalline and amorphous regions (clay platelets and their stacks are assumed to be randomly distributed in crystalline and amorphous domains, and their influence is accounted for by treating coefficients in the stress–strain relations as functions of nanofiller content χ). Both phases are modeled as viscoelastoplastic continua with plastic deformations governed by different flow rules. The viscoelastic response of the crystalline phase is independent of plastic deformation, whereas relaxation spectrum of the amorphous phase evolves with intensity of plastic strain.

Constitutive equations for uniaxial tension of a nanocomposite with an arbitrary deformation program ε(*t*) involve (i) kinematic relations for elastic strains ε_{ae} and ε_{ce} in the crystalline and amorphous regions

$$\varepsilon_{ae}=\varepsilon-\varepsilon_{ap}, \qquad \varepsilon_{ce}=\varepsilon-\varepsilon_{cp}, \tag{1}$$

where ε stands for tensile strain, and ε_{ap} and ε_{cp} denote corresponding plastic strains, (ii) kinetic equation for plastic strain in the crystalline phase

$$d\varepsilon_{cp}/dt=\varphi d\varepsilon/dt, \tag{2}$$

where coefficient φ obey the equations

$$d\varphi/dt=a(1-\varphi)^2 d\varepsilon/dt \quad \text{(loading)}, \qquad d\varphi/dt=0 \quad \text{(unloading)}, \tag{3}$$

and a is a positive constant, (iii) kinetic equation for plastic strain in the amorphous phase

$$d\varepsilon_{ap}/dt=S[\varepsilon_{ae}-\int_0^\infty f(v)Z_a(t,v)dv]|d\varepsilon/dt|, \tag{4}$$

where S adopts positive values S_1 and S_2 under loading and unloading, dumb variable v stands for dimensionless activation energy for rearrangement, and the function $f(v)$ (it characterizes distribution of relaxation times in a nanocomposite) accepts the quasi-Gaussian expression

$$f(v)=f_0\exp[-v^2/(2\Sigma^2)] \qquad (v\geq 0), \qquad f(v)=0 \quad (v<0) \tag{5}$$

with a positive coefficient Σ, (iv) evolution equations for functions Z_a and Z_c that describe relaxation of stresses in amorphous and crystalline phases

$$\partial Z_a/\partial t=\Gamma_a(\varepsilon_{ae}-Z_a), \qquad \partial Z_c/\partial t=\Gamma_c(\varepsilon_{ce}-Z_c), \tag{6}$$

(v) the Eyring formulas for rates of rearrangement Γ_a and Γ_c in amorphous and crystalline regions

$$\Gamma_a=A\gamma\exp(-v/B), \qquad \Gamma_c=\gamma\exp(-v), \tag{7}$$

where γ stands for the relaxation rate, (vi) linear equations that account for changes in relaxation spectrum of the amorphous phase driven by plastic deformation in crystallites

$$A=1, \quad B=1 \quad \text{(loading)}, \qquad A=1+C(\varepsilon_{cp}^{max}-\varepsilon_{cp}), \quad B=1+D(\varepsilon_{cp}^{max}-\varepsilon_{cp}) \quad \text{(unloading)}, \tag{8}$$

where ε_{cp}^{max} stands for maximum plastic strain in crystalline domains under tension, and C, D are positive constants, (vii) formulas for stresses σ_a and σ_c in amorphous and crystalline domains

$$\sigma_a(t)=E_a[\varepsilon_{ae}(t)-\int_0^\infty f(v)Z_a(t,v)dv], \qquad \sigma_c(t)=E_c(1-\varphi(t))[\varepsilon_{ce}(t)-\int_0^\infty f(v)Z_c(t,v)dv], \tag{9}$$

where E_a and E_c denote elastic moduli, and (viii) the expression for tensile stress in a nanocomposite

$$\sigma=\sigma_a+\sigma_c. \tag{10}$$

Stress–strain relations (1)–(10) involve nine adjustable parameters with transparent physical meaning: (i) E_a, E_c denote Young's moduli, (ii) γ and Σ characterize the linear viscoelastic response, (iii) a determines rate of plastic deformation in the crystalline phase under tension, (iv) S_1, S_2 denote rates of plastic flow in the amorphous phase under loading and unloading, (v) C, D describe evolution of relaxation spectrum in amorphous domains at retraction.

4 Fitting of observations

Adjustable parameters in the stress–strain relations are found by matching the observations reported in Figures 1–3. Each set of experimental data is approximated separately. As an example, the effect of clay content χ on elastic moduli E_a and E_c is illustrated in Figure 4 where the data are approximated by linear dependencies.
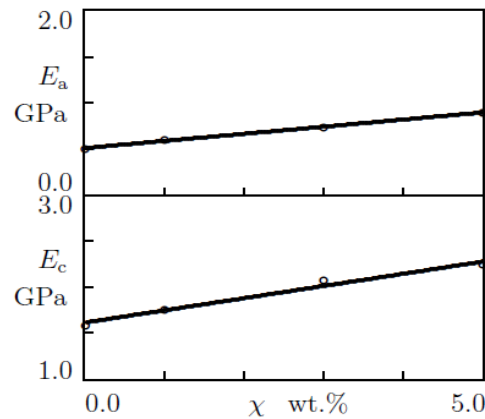

Figure 4. Elastic moduli E_a and E_c versus clay content χ. Circles: treatment of observations in three-step tests. Solid lines: results of numerical simulation.

5 Numerical simulation

To demonstrate ability of the constitutive model to predict the viscoelastic and viscoplastic responses of nanocomposites with various concentrations of filler χ in three-step (loading–unloading–relaxation) tests, numerical integration is conducted of the stress–strain relations with the adjustable parameters found by matching observations.

Simulation is carried out for nanocomposites with $\chi=0$, 5, 10, and 15 wt.% subjected to cyclic loading with strain rate $e=1.7\cdot10^{-3}$ s^{-1}, maximum strain $\varepsilon_{max}=0.1$, and minimum stresses $\sigma_{min}=0$, 5, 10, 15, 20, 25 MPa.

The stress–strain diagrams under loading and unloading are depicted in Figure 5. This figure demonstrates that an increase in clay content χ causes (i) a noticeable growth of yield stress σ_y, (ii) a strong reduction of yield strain ε_y, and (iii) a growth of curvature of the stress–strain diagrams under retraction.

Relaxation curves under retraction toward various minimum stresses σ_{min} are reported in Figure 6 (as an example, only data for $\chi=0$ wt.% are presented). This figure demonstrates that the model predicts adequately transitions from simple (at $\sigma_{min}>20$ MPa) to mixed (at $5<\sigma_{min}<20$ MPa) to inverse (at $\sigma_{min}<5$ MPa) relaxations (the critical stresses at which these transitions occur coincide with the data on semicrystalline polymers reported in [1-3]). Results of numerical simulation show that these stresses are practically independent of clay content χ. Reinforcement of polypropylene with nanoclay does not affect relaxation curves at $\sigma_{min}>15$ MPa and induces a decrease in peaks on the relaxation diagrams at $\sigma_{min}<15$ MPa. The effect of clay content becomes substantial at low minimum stresses only. For example, at

σ_{min}=0, maximum stress under relaxation of neat polypropylene exceeds that under relaxation of nanocomposite with χ=15 wt.% by 81%.
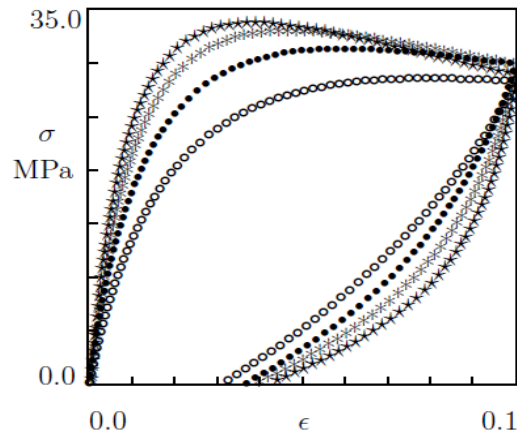

Figure 5. Stress σ versus strain ε. Symbols: results of numerical simulation for cyclic tests with ε_{max}=0.1 and σ_{min}=0 on nanocomposites with various clay contents χ wt.% (unfilled circles – χ=0, filled circles – χ=5, asterisks – χ=10, stars – χ=15).

6 Conclusions

Observations are reported on isotactic polypropylene/organically modified montmorillonite clay nanocomposites with various concentrations of filler in (i) relaxation tests under tension, (ii) loading–unloading tests with various maximum strains, and (iii) relaxation tests under retraction down to the zero stress. Experimental data in relaxation tests show a monotonic decrease in stress with time (simple relaxation) under tension and a monotonic growth of stress with time (inverse relaxation) under retraction.
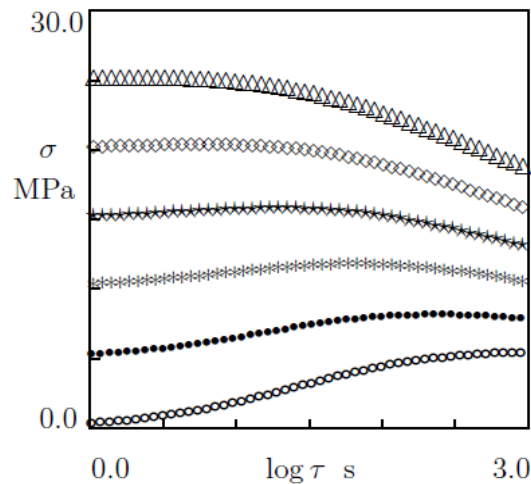

Figure 6. Stress σ versus relaxation time τ. Symbols: results of numerical simulation for relaxation tests on nanocomposites with χ=0 wt.% stretched up to ε_{max}=0.1 and unloaded down to various stresses σ_{min} MPa (unfilled circles – σ_{min}=0, filled circles – σ_{min}=5, asterisks – σ_{min}=10, stars – σ_{min}=15, diamonds – σ_{min}=20, triangles – σ_{min}=25).

Constitutive equations are derived for the viscoelastic and viscoplastic responses of nanocomposites with semicrystalline matrices. A nanocomposite is treated as a two-phase continuum. Both phases are modeled as viscoelastoplastic media with different kinetic

equations for plastic flow and different assumptions regarding the influence of plastic deformation on the viscoelastic behavior. The stress–strain relations involve nine adjustable parameters that are found by fitting the observations.

Ability of the model to predict the mechanical response of nanocomposites with various concentrations of clay is confirmed by numerical simulation.

References

[1] Kitagawa, M., Zhou, D., Qiu, J. Stress-strain curves for solid polymers. *Polymer Engineering and Science*, **35**, pp. 1725–1732 (1995).

[2] Khan, F. Loading history effects on the creep and relaxation behavior of thermoplastics. *Transactions of the ASME. Journal of Engineering Materials and Technology*, **128**, pp. 564–571 (2006).

[3] Drozdov, A.D. Time-dependent response of polypropylene after strain reversal. *International Journal of Solids and Structures*, **47**, pp. 3221–3233 (2010).

[4] Drozdov, A.D., Hog Lejre, A.-L., Christiansen, J.deC. Viscoelasticity, viscoplasticity, and creep failure of polypropylene/clay nanocomposites. *Composites Science and Technology*, **69**, pp. 2596–2603 (2009).