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Modelling the Rheology of Semi-Concentrated Polymeric Composites

Research Team

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Introduction

The rheological characterization of fiber-filled media is of major concern in polymer processing research. A lot of work has been focused on the study of fiber-filled Newtonian liquids, where the rheological effects and the orientation state of the fiber are described and presented [1,2]. In order to properly describe the fiber-filled medium, the constitutive equation should not only describe the rheological properties of the suspension, but also give the final fiber orientation of the composite (Fig. 1). It is essential to examine the role of the polymer rheology and the fiber-polymer interaction.

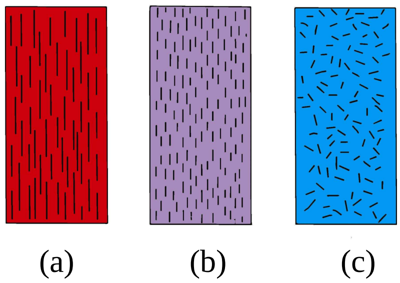


Figure 1. Composites with a polymeric matrix. A semi-concentrated fiber suspension can be made by adding glass fibers in a polymer melt: (a) long fibers oriented in the longitudinal direction, (b) short fibers oriented in the longitudinal direction, (c) short fibers randomly oriented.

The motivation for using a composite constitutive equation arose from the observation of the measured experimental stresses of polymer suspensions. It was noticed that the total stress of the composite is increased with the addition of fibers, and hence an adequate constitutive equation could be had by adding an extra stress term to an already existing constitutive polymeric equation.

Furthermore, it is known that such materials exhibit viscoplastic behaviour, which manifests itself in the existence of a yield stress. Therefore, viscoplasticity must be taken into account in the constitutive equation to distinguish the areas of flow into yielded-unyielded regions, which are important from a processing point of view.

It is the purpose of the current work to develop and test such a composite constitutive equation for composite materials with a polymeric matrix.

Mathematical Modelling

Viscoelastic Modelling

The rheology of polymer melts is best described by integral constitutive equations of the K-BKZ type [3], i.e.,

$$\tau = \frac{1}{1-\theta} \int_{-\infty}^{t} \sum_{k=1}^{N} \frac{a_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) H_k(I, II) \left(C_t^{-1}(t') + \theta C_t(t') \right) dt' \quad \text{(1a)}$$

$$H_k(I, II) = \frac{\alpha}{(\alpha-3)+\beta_k I_C + (1-\beta_k) II_C} \quad \text{(1b)}$$

where N is the number of relaxation modes, λ_k and a_k are the relaxation times and relaxation modulus coefficients at a reference temperature, α, β_k and θ are material constants, and II, I are respectively the first invariants of the Cauchy-Green tensor $\boldsymbol{C}_t$ and its inverse $\boldsymbol{C}_t^{-1}$ the Finger strain tensor. These appear in the strain-memory function $H_k(I,II)$, which has a sigmoidal form. The θ-parameter relates the second normal stress difference N_2 to the first one N_1 according to $N_2/N_1=\theta/(1-\theta)$. The values of the material parameters are found by regression analysis on available rheological experimental data.

Viscoplastic Modelling

The rheology of viscoplastic materials exhibiting a yield stress is best described by the Herschel-Bulkley differential constitutive equation [4], i.e.,

$$\boldsymbol{\tau}_{vp} = \left(K \left|\dot{\gamma}\right|^{n-1} \pm \frac{\tau_y}{\left|\dot{\gamma}\right|} \right) \dot{\boldsymbol{\gamma}}, \qquad \text{for } \left|\tau\right| > \tau_y, \quad \text{(2a)}$$

$$\dot{\boldsymbol{\gamma}} = 0, \qquad \text{for } \left|\tau\right| \le \tau_y, \quad \text{(2b)}$$

where τ_{vp} are the viscoplastic stresses, $\dot{\gamma}$ are the rates-of strain, τ_y is the yield stress, K is the consistency index, and n is the power-law index. Note that when n = 1and K = μ (a constant), the Herschel-Bulkley model reduces to the Bingham model. When τ_y = 0, the power-law model is recovered, and when τ_y = 0 and n = 1, the Newtonian model is obtained. In viscoplastic models, when the shear stress τ falls below τ_y, a solid structure is formed (unyielded). An example of this is given in the process of calendering (Fig. 2a,b), where a solution of the above equation gives the yielded/unyielded regions as shown in Fig. 2c (Sofou and Mitsoulis [5,6]).

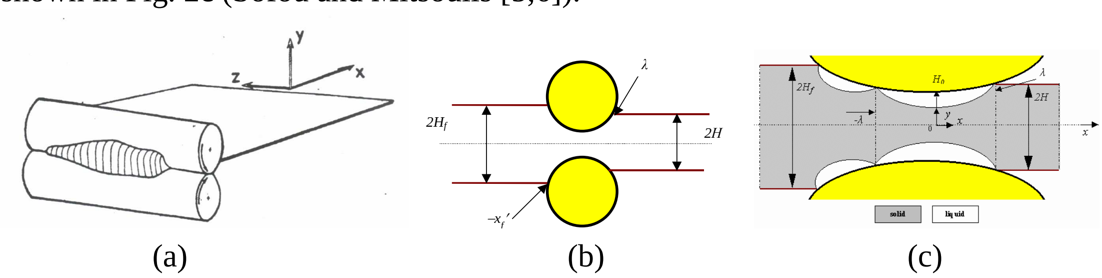


Figure 2. Calendering of viscoplastic materials: (a) the material is passing between two rotating rolls (calenders) to form a sheet, (b) schematic representation of the process for reducing the sheet thickness, (c) calendering of a viscoplastic material, showing the yielded (liquid) / unyielded (solid-shaded) regions [5,6].

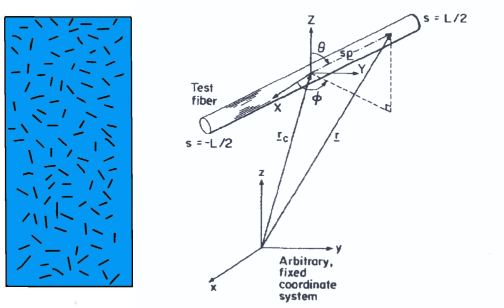
Fiber Suspension Modelling

To describe the probability function for the fiber orientation, a fourth-order orientation tensor, S_{ijkl}, is defined as follows (Advani and Tucker [1]):

$$S_{ijkl} = \oint p_i p_j p_k p_l \psi(\mathrm{p}) d\mathrm{p} \tag{3}$$

where $\psi(\mathbf{p})$ is the probability distribution function for orientation, and **p** is a unit vector denoting the orientation of a fiber. A second-order orientation tensor, S_{ij}, is also used and defined as:

$$S_{ij} = \oint p_i p_j \psi(\mathrm{p}) d\mathrm{p} \tag{4}$$



(a) (b)

Figure 3. (a) Schematic representation of a randomly oriented fiber suspension and (b) a fiber with the relevant variables used in its modelling.

The probability distribution function $\psi(\mathbf{p})$ gives the probability of having a fiber with an orientation **p** at time *t*. The probability distribution function can be defined for both two- and three-dimensional cases. This study focuses on the ability to describe the orientation state in a two-dimensional case, since a first step for numerical simulations would be a two-dimensional field. For two-dimensional descriptions, the probability function has a period of π (Fig. 3),

$$\psi(\theta) = \psi(\theta + \pi) \tag{5}$$

Statistically, the integration over all the possible orientations given by the probability distribution function must be unity:

$$\int_0^{\pi} \psi(\theta) d\theta = 1 \tag{6}$$

The solution to the probability distribution function for a two-dimensional case is given explicitly by Altan et al. [2] for simple shear flow in terms of the deformation gradient tensor:

$$\psi(\theta) = \frac{1}{\pi}\left[\left(\Delta_{11}^2 + \Delta_{11}^2\right) p_1^2 + \left(\Delta_{11}\Delta_{12} + \Delta_{21}\Delta_{22}\right) 2 p_1 p_2 + \left(\Delta_{12}^2 + \Delta_{22}^2\right) p_2^2\right]^{-1} \tag{7}$$

where $\mathbf{\Delta}$ is the deformation gradient tensor. For simple shear flows, the deformation gradient takes the form,

$$\Delta_{ij} = \begin{pmatrix} 0 & -\dot{\gamma} t \\ 0 & 0 \end{pmatrix} \tag{8}$$

The equation of change for the second-order tensor (Advani and Tucker [1]) was formulated with the upper-convected derivative of S_{ij}, which is written as follows:

$$\dot{S}_{ij} = \frac{\partial S_{ij}}{\partial t} + u \cdot \nabla S_{ij} - \nabla u \cdot S_{ij} - S_{ij} \cdot \nabla u^T \tag{9}$$

This allows us to define the orientation tensors in steady-state rather than transiently. The fiber contribution to the total stress of the composite is determined using the approach of Dinh and Armstrong [7], who included a term for the fiber contribution to the component of the drag force parallel to the fiber:

$$\tau_f = \eta(\dot{\gamma}) \frac{nL^3}{24 \ln(2h/D)} u_{k,l} S_{ijkl} \tag{10}$$

where $\eta(\dot{\gamma})$ is the viscosity of the polymer, $\dot{\gamma}$ is the shear rate, f is the fiber volume fraction, D is the diameter of the fiber, L is the length of the fiber, n is the number density of the suspension, and h is the average distance from a given fiber to its nearest neighbour. In order to find the distance between two given fibers, Dinh and Armstrong [7] proposed the following expressions based on the alignment of the system:

$$h = (nL)^{-1/2} \quad \text{for aligned systems} \tag{11a}$$

$$h = (nL^2)^{-1} \quad \text{for random systems} \tag{11b}$$

and showed how to determine whether a system of fibers is either aligned or random.
A *closure approximation* is also used to evaluate the fourth-order orientation tensor, S_{ijkl}, in terms of the second-order orientation tensor, S_{ij}. This study used what is known as the *quadratic closure* (Advani and Tucker [1]). The quadratic-closure approximation is given as:

$$S_{ijkl} = S_{ij} S_{kl} \tag{12}$$

New Constitutive equation

The new constitutive equation proposed in this work gives the stresses τ_c of the composite material as the sum of contributions from the *viscoelastic* stresses τ_p of the polymer matrix (eq. 1), the *viscoplastic* stresses τ_{vp} due to the presence of a yield stress of the composite (eq. 2), and the *fiber suspension* stresses τ_f (eq. 10). Thus we have:

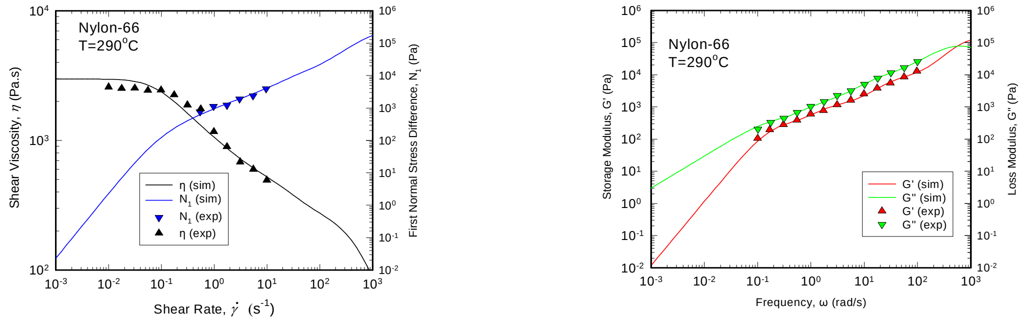
$$\tau_c = \tau_p + \tau_f + \tau_{vp} \tag{13}$$

Rheological Characterization

Three polymer melts were studied, PP, PC and nylon 6/6, reinforced with short and long fibers for different volume fractions [8]. Representative rheological data are shown for nylon 6/6 in Fig. 4, along with the fitting curves by using the K-BKZ model with the damping function of eq. (1b). The parameter values are given in Table 1 for all 3 polymers. Four (4) relaxation modes are used to fit the data. The predictions of the new proposed constitutive model K-BKZ/D-A for the composite nylon 6/6 are shown in Fig. 5a, along with the variation of ratio between the aligned and the random fibers, for which the model best describes the composite material, as shown in Fig. 5b.

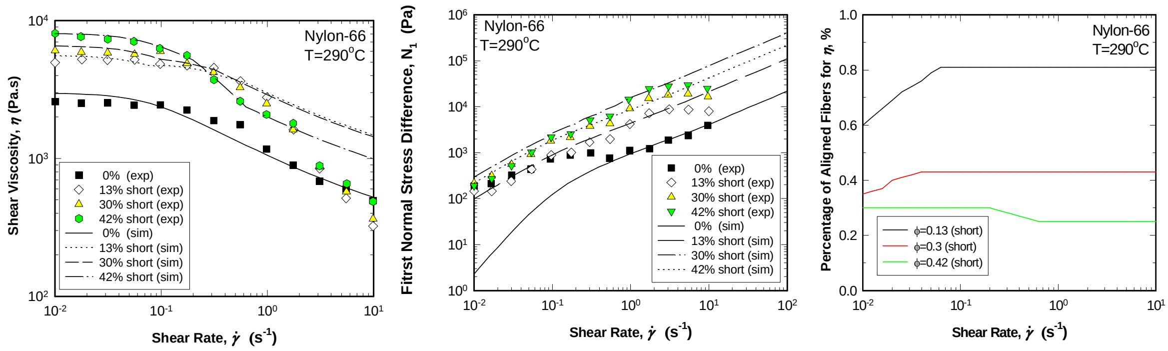
Table 1. Material parameters for fitting data of polymer melts with the K-BKZ model (eq. 1).

PP (α=15.809, β=0.05, θ=-0.1)					PC (α=33006, β=0.99, θ=-0.111)					nylon 6/6 (α=2.5785, β=0.5, θ=-0.1)				
k	1	2	3	4	k	1	2	3	4	k	1	2	3	4
λ_k (s)	0.55E-3	0.34E-1	0.43	5.19	λ_k (s)	0.161E-1	0.107E-1	0.6	228.54	λ_k (s)	0.157E-2	0.138E-1	0.58	5.95
a_k (Pa)	1567E2	9072.6	1037.4	55.336	a_k (Pa)	5402.3E2	1696.3	15.247	0.372	a_k (Pa)	1567E2	7290	951.81	317.13



(a) (b)

Figure 4. (a) Viscosity, normal stress and (b) dynamic moduli data for nylon 6/6 melt and their best fit with K-BKZ model.



(a) (b) (c)

Figure 5. Predictions of the K-BKZ/D-A model for nylon 6/6 data: (a) viscosity, (b) N_1, (c) percentage of aligned fibers.

Results and Discussion

The composite under investigation is the nylon 6/6 polymer melt at 290°C with short fiber suspensions with volume fractions of 0%, 13%, 30% and 42%. The short fibers are 3 mm in length and 12.7 μm in diameter. Figure 5 shows the predictions of the new constitutive model K-BKZ/D-A along with the experimental measurements for the shear viscosity η_S and the first normal stress difference N_1 as a function of shear rate. For the η_S it can be seen that the model predicts well η_S at low shear rates, but at higher shear rates, extra shear thinning due to the presence of the fibers develops, which the model does not predict. However, the model still qualitatively predicts the viscosity of the composite for all shear rates. For N_1 it can be seen that the model predicts well qualitatively and quantitatively at high shear rates but does not fit the experimental values at lower shear rates. This can be explained by the fact that the N_1 cannot be measured at low shear rates with the parallel-plate viscometer [8]. Only at shear rates > 1 s^{-1} can the N_1 be measured properly. This is also the reason why only the last six experimental values were used in the fit of the polymer constitutive equation as can be seen in Fig. 5(b). Hence, the composite constitutive equation describes rather well N_1. The predictions of the model were also good for the other two polymers (PP and PC) with the only exception being the predictions of N_1 for the PC. The ratio between the aligned and randomly oriented fibers for the predictions of η_S is presented in Fig. 5c.

Conclusions

The present work developed a novel rheological constitutive equation for fiber-filled polymeric composites. It includes effects of viscoelasticity of the polymer, viscoplasticity of the composite, and fiber-matrix interaction of the suspension. The model has been tested against experimental rheological data rather successfully. Having demonstrated its usefulness in rheological characterization, the new constitutive model can thus be used for flow simulations of these fiber suspensions in such important polymer processes as extrusion, calendering and injection molding for the production of useful composite products.

References

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