Rheological Modeling of Polymer / Layered Silicate Nanocomposites

Ehssan Nazockdast[1], Hossein Nazockdast*

Polymer Engineering Department, Amirkabir University of Technology,
P.O. Box 15875-4413, Tehran, Iran
[1] Recent address: Benjamin Levich Institute for Physico-Chemical Hydrodynamics and Department of Chemical Engineering, City College of New York, New York, NY 10031, USA

* Corresponding author: nazdast@aut.ac.ir
Fax: x98.21.66469623

Received: 30.11.2009, Final version: 6.12.2010

Abstract:
This work takes a phenomenological approach to modeling the rheology of polymer/clay nanocomposites in $\dot{\gamma} \leq 1\ s^{-1}$ based on experimental observations [10]. The total stress was divided to three contributions: Matrix stress, σ_M, inter-particle (matrix/particle) stress, σ_P, and hydrodynamic stress σ_H. Based on the superposition of complex viscosities, η^*, plotted against strain rate amplitude, $\gamma_o\omega$, at different nonlinear strain amplitudes, a modified Bingham-type constitutive equation proposed by Doiraswamy et. al [16] was used to model $\sigma_M + \sigma_P$ while σ_H was modeled by using constitutive equation proposed by Lipscomb et. al [25] for ellipsoidal particles. The comparison between experimental and modeling results showed that steady hydrodynamic stress in simple shear flows scales with complex viscosities in oscillatory experiments when compared at $\dot{\gamma} = \gamma_o\omega$. On the basis of this observation, the network-like behavior of the polymer nanocomposite was attributed to retarded chain dynamics as a result of polymer/clay interactions. In order to take into account the thixotropic behavior of network structure, the constitutive equation proposed by Coussot [18] was employed for modeling $\sigma_M + \sigma_P$. Both Coussot and Doraiswamy equations gave a reasonable quantitative prediction of transient stress in simple shear flow up to shear rates as high as $\dot{\gamma} = 0.1\ s^{-1}$.

Zusammenfassung:
Diese Arbeit stellt einen phänomenologischen Ansatz vor, um die rheologischen Eigenschaften von Polymer/Schichtsilikat-Nanokompositen basierend auf experimentellen Ergebnissen [10] zu modellieren. Die Gesamtspannung setzt sich aus drei Beiträgen zusammen, der Matrixspannung, σ_M, den Interpartikel (Matrix/Partikel)-Spannungen, σ_P, und der hydrodynamischen Spannung, σ_H. Basierend auf der Superposition der komplexen Viskosität, η^*, als Funktion der Scherrate, $\gamma_o\omega$, bei verschiedenen nichtlinearen Scheramplituden, wurde eine modifizierte Konstitutivgleichung vom Bingham-Typ von Doiraswamy et al. [16] angewandt, um $\sigma_M + \sigma_P$ zu modellieren, während σ_H unter Verwendung einer Konstitutivgleichung von Lipscomb et al. [25] für ellipsoidale Partikel modelliert wurde. Der Vergleich zwischen experimentellen und Modellierungsergebnissen zeigte, dass die stationäre hydrodynamische Spannung in einfacher Scherung mit der komplexen Viskosität, gemessen in Scheroszillationen skaliert, falls man $\dot{\gamma} = \gamma_o\omega$ setzt. Basierend auf dieser Beobachtung, wird das netzwerkartige Verhalten dieser Nanokomposite der verzögerten Kettendynamik aufgrund der Polymer/Schichtsilikat-Wechselwirkungen zugeschrieben. Um das thixotrope Verhalten der Netzwerkstruktur zu berücksichtigen, wurde die Konstitutivgleichung von Coussot [16] verwendet, um $\sigma_M + \sigma_P$ zu beschreiben. Sowohl die Gleichung von Coussot als auch die Gleichung von Doraiswamy führen zu einer guten quantitativen Vorhersage der transienten Spannung in einfacher Scherung bis zu einer Scherrate von $0.1\ s^{-1}$.

Résumé:
Ce travail entreprends une approche phénoménologique de la modélisation de la rhéologie des nanocomposites argile/polymère en $\dot{\gamma} \leq 1\ s^{-1}$, en se basant sur des observations expérimentales [10]. La contrainte totale est divisée en trois contributions : la contrainte de la matrice, σ_M, la contrainte inter particule (matrice/particule), σ_P, et la contrainte hydrodynamique σ_H. A partir de la superposition des viscosités complexes, η^*, representées en fonction de l'amplitude de la vitesse de déformation, $\gamma_o\omega$, pour des amplitudes de déformation non linéaire différentes, une équation constitutive modifiée de type Bingham proposée par Doiraswamy et al. [16], a été utilisée pour modéliser $\sigma_M + \sigma_P$, tandis que σ_H a été modélisée en employant une équation constitutive proposée par Lipscomb et al. [25], pour des particules ellipsoïdales. La comparaison entre les résultats expérimentaux et de modélisation montre que la contrainte hydrodynamique stationnaire dans les écoulements de cisaillement simple est proportionnelle aux viscosités complexes des expériences dynamiques lorsque $\dot{\gamma} = \gamma_o\omega$. A partir de cette observation, le comportement de type réseau du nanocomposite polymérique a été attribué à la dynamique retardée des chaînes résultant des interactions polymère/argile. Dans le but de prendre en compte le comportement thixotropique de la structure de réseau, l'équation constitutive proposée par Coussot [18] a été

 DOI: 10.3933/ApplRheol-21-25434

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

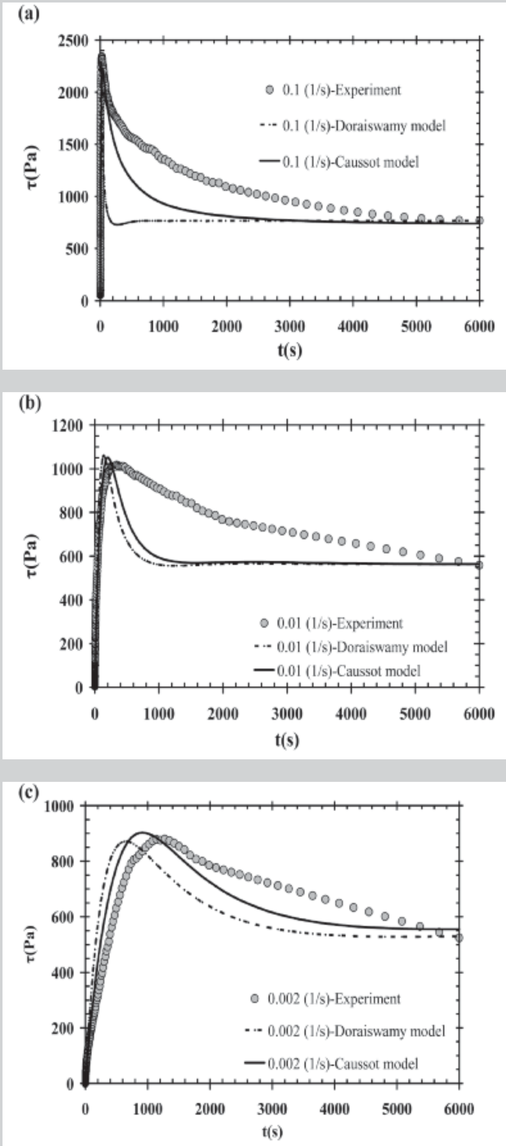

Figure 12: Comparison between the experimental values and model predictions based on Doraiswamy and Caussot equations at different shear rates for PN7.5-3 samples.

to polymer/clay interactions rather than interparticle interactions. Adopting this idea enabled the model to predict transient shear stress qualitatively in different shear rates. However the shear stress predicted from the modeling reached to steady state much faster than experimental results. This was attributed to inability of the Bingham-type constitutive equation to model the transient behavior of network structure of the nanocomposites. Therefore, in the second attempt, the stress due to polymer/clay interactions was modeled using Coussot constitutive equation: a Maxwell model containing a structure parameter, which is determined through a kinetic equation. This model was able to provide more accurate predictions of experimental results of transient shear stress particularly at higher shear rates. Although Coussot equation provided a more reasonable prediction of shear stress, this benefit came in the expense of introducing additional parameters, whose evaluations required separate experiments. This modified model was also incapable of giving a reasonable prediction at $\dot{\gamma}$ = 1(1/s).

REFERENCES

[1] Gilman JW, Jackson CL, Morgan AB, Harris R, Manias E, Giannelis EP, Wuthenow M, Hilton D, Phillips SH: Flammability Properties of Polymer Layered-Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites, Chem. Mater. 12 (2000) 1866 – 1873.

[2] Hotta S, Pau DR: Nanocomposites formed from linear low density polyethylene and organoclays, Polymer 45 (2004) 7639 – 7654.

[3] Manias E, Touny A, Wu L, Strawhecker K, Lu B, Chung TC: Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties, Chem. Mater. 13 (2001) 3516 – 3523.

[4] Sinha Ray S, Okamoto M: Polymer layered silicate nanocomposites: A review from preparation to processing, Prog. Polymer Sci. 28 (2003) 1539 – 1641.

[5] Larson RG: The Structure and Rheology of Complex Fluids, Oxford University Press (1998)

[6] Galgali G, Ramesh C, Lele A: A Rheological Study on the Kinetics of Hybrid Formation in Polypropylene Nanocomposites" Macromolecules 34 (2001) 852 – 858.

[7] Krishnamoorti R, Vaia RA, Giannelis EP: Structure and Dynamics of Polymer-Layered Silicate Nanocomposites, Chem. Mater. 8 (1996) 1728 – 1734.

[8] Solomon MJ, Almusallam AS, Seefeldt KF, Samwangthamroj A, Varadan P: Rheology of polypropylene/clay hybrid materials, Macromolecules 34 (2001) 1864 – 1872.

[9] Krishnamoorti R, RenJ, Silva AS: Shear response of layered silicate nanocomposites, J. Chem. Phys. 114 (2001) 4968 – 4973.

[10] Nazockdast E, Nazockdast H, Goharpey F: Linear and nonlinear melt-state viscoelastic properties of polypropylene/organoclay nanocomposites, Polym.Eng. Sci. 48 (2008) 1240 – 1249.

[11] Eslami H, Grmela M, Bousmina M: Structure build-up at rest in polymer nanocomposites: Flow reversal experiments, J. Polym. Sci. Part B: Polymer Physics 47 (2009) 1728 – 1741.

[12] Ren J, Krishnamoortti R: Nonlinear viscoelastic properties of layered silicate based intercalated nanocomposites, Macromolecules 36 (2003) 4443 – 4451.

[13] Letwimolnun W, Vergnesa B, Ausiasb G, Carreauc PJ: Stress overshoots of organoclay nanocomposites in transient shear flow, J. Non-Newtonian Fluid Mech. 141 (2007) 167 – 179.

[14] Havet G, Isayev AI: A thermodynamic approach to the rheology of highly interactive filler polymer

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org

mixtures. Part I – Theory, Rheol. Acta 40 (2001) 570 – 581.
[15] Montes S, White JL: Rheological models of rubber-carbon black compounds: Low interaction viscoelastic models and high interaction thixotropic-plastic-viscoelastic models. J Non-Newtonian Fluid Mech 49 (1993) 277 – 298.
[16] Doraiswamy D, Mujumdar AN, Tsao I, Beris AN, Danforth SC, Metzner AB: The Cox-Merz rule extended: A rheological model for concentrated suspensions and other materials with a yield stress, J. Rheol. 35 (1991) 647 – 685.
[17] Leonov AI: On the Rheology of filled polymers, J. Rheol. 34 (1991) 1039 – 1068.
[18] Coussot P, Leonov AI, Piau JM: Rheology of concentrated dispersed systems in a low molecular weight matrix, J. Non-Newtonian Fluid Mech. 46 (1993) 179 – 217.
[19] Jeffery GB: The motion of ellipsoidal particles immersed in a viscous fluid, Proc. Royal Soc. London. Ser. A 102 (1922) 161 – 179.
[20] Folgar E, Tucker CL: Orientation Behavior of Fibers in Concentrated Suspensions, J. Reinf. Plast. Comp. 3 (1984) 98 – 119.
[21] Advani SG, Tucker III CL: The Use of Tensors to Describe and Predict Fiber Orientation in Short Fiber Composites, J. Rheol. 31 (1987) 751 – 784.
[22] Chung DH, Kwon TH: Invariant-based optimal fitting closure approximation for the numerical prediction of flow-induced fiber orientation, J. Rheol. 46 (2002) 169 – 194.
[23] Hand GL: A theory of dilutes suspensions, Arch. Rat. Mech. Anal. 7 (1961) 81 – 86.
[24] Giesekus H: Elasto-viskose Flüssigkeiten, für die in stationären Schichtströmungen sämtliche Normalspannungskomponenten verschieden gross sind, Rheol. Acta 2 (1962) 50 – 62.
[25] Lipscomb GG, Denn MM, Hur DU, Boger DV: The flow of fiber suspensions in complex geometries, J. Non-Newtonian Fluid Mech. 26 (1988) 297 – 325.
[26] Mobuchon C, Carreau PJ, Heuzey M-C, Sepehr M, Ausias G: Shear and extensional properties of short glass fiber reinforced polypropylene, Polym. Comp. 26 (2005) 247 – 264.

This is an extract of the complete reprint-pdf, available at the Applied Rheology website
http://www.appliedrheology.org