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13. ABSTRACT (Maximum 200 words)

Lamellar microstructures can provide excellent control of polymer permeability. For example, they can stop toxic organic vapors yet transmit water vapor, be produced economically, and provide increased resistance to mechanical impact; however, the methods to create and stabilize lamellar blends are not well understood.

Key to creating lamella during melt blending is understanding transient deformation of viscous and viscoelastic drops. In this research, we sheared polymer drops to very large deformation and measured their transient dimensions. By fluorescent labeling and confocal microscopy, we showed diblock copolymers adsorbed on drop surfaces are convected to drop edges where they can lower interfacial tension. Drops deformed further than without block copolymer and generated more lamellar microstructures. At high stress, slip was observed between immiscible polymer surfaces. Slip appears to be caused by reduced chain entanglement, which generates a thin low-viscosity region in the interface. Block copolymer can eliminate this slip.

Drop deformation breakup and coalescence were modeled with new adaptive 3D finite element methods. Calculations compared well to experiments and gave insight into observation of drop widening for low-viscosity drops. The effect of block copolymer on interfacial tension was included in the model and predicted the role of block copolymer in suppressing coalescence.

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4. Statement of the problem studied

Blending two or more polymers optimizes properties of plastics and elastomers. Most blends are immiscible, thus control of their multiphase microstructure is key to property optimization. This microstructure is typically generated by melt mixing. An important class of microstructures is lamellar, which can provide excellent control of polymer permeability. For example, they can provide toxic organic vapors barriers yet transmit water vapor, be produced economically, and provide increased resistance to mechanical impact; however, the methods to create and stabilize lamellar blends are not well understood. Research performed under this Army Research Office grant studied how drops deform to create lamellar microstructures. Drops were deformed in shear flow and analyzed by finite element methods.

5. Summary of the most important results

The key to creating lamella during melt blending is understanding transient deformation of viscous and viscoelastic drops. In this research we sheared polymer drops to very large deformation and measured their transient dimensions. We found that due to their high viscosity, the viscous stresses in polymer drops are much higher than surface stresses so the drops deform affinely into large, flat ellipsoids (see references: 6a.4, 6a.6, 6d.1). But at strains of ~4, curvature at the drop edges becomes high enough to cause drop width to retract. At strains >10, curvature at the tips become high enough to begin to cause retraction in the flow direction.

Adding block copolymer resulted in larger drop deformation, especially for when the viscosity and elasticity of the drop was lower than the matrix. By fluorescent labeling and confocal microscopy, we found that diblock copolymers adsorbed on the surfaces of the drops are convected to the edges of the drops where they can lower interfacial tension (6d.1). This caused drops to deform further than without block copolymer and generate larger lamellae.

At high stress, slip was observed between immiscible polymer surfaces. The slip appears to be caused by reduced chain entanglement, which generates a thin low-viscosity region in the interface. Block copolymer can eliminate this slip (6a.3, 6b.1-3). To quantify interfacial slip, a multilayer coextrusion line was built (6a.3). It was also used to produce 256 layer nylon rubber sheets with potential for ballistic applications (6b.5).

Drop deformation breakup and coalescence were modeled with new adaptive 3D finite element methods (6a.1, 6a.2, 6b.4). Calculations compared well to experiments and gave insight into the observation of drop widening for low-viscosity drops (6a.4). The effect of block copolymer on interfacial tension was included in the model and able to predict the role of block copolymer in suppressing coalescence (6d.2). These adaptive 3D finite element methods are powerful new tools for modelling two phase flows and understanding how to create new microstructured materials.

6. Listing of all publications and technical reports

6a. Papers published in peer-reviewed journals

1. R.W. Hooper, C.W. Macosko, and J.J. Derby, "Assessing a flow-based finite element model for the sintering of viscoelastic particles," *Chemical Eng. Sci. 55*, 5733-5746, **2000**.
2. R. Hooper, V. Cristini, S. Shakya, J. Lowengrub, C. W. Macosko & J. J. Derby, "Modeling multiphase flows using a novel 3D adaptive remeshing algorithm," in *Computational Methods in Multiphase Flow*, 2001, Eds.: C.A. Brebbia and H. Power, Series: Advances in Fluid Mechanics, *Vol. 29*, 33-42, Wessex Institute of Technology Press, UK.
3. R. Zhao and C.W. Macosko, "Slip at polymer-polymer interfaces: rheological measurements on coextruded multilayers," *J. Rheology 46(1*), 145-167, **2002**.
4. V. Cristini, "Flow-independent drop deformation with zero surface tension," *Physics Fluids 14*, 2929-2932, **2002**.
5. V. Cristini, C.W. Macosko, and T. Jansseune, "A note on transient stress calculation via numerical simulations," *J. of Non-Newtonian Fluid Mech. 105*, 177-187, **2002**.
6. V. Cristini, R. W. Hooper, C. W. Macosko, Stefano Guido and Mariano Simeone, "A numerical and experimental investigation of lamellar blend morphologies," *Ind. Eng. Chem. Res.*, **2002** in press.

6b. Papers published in conference preprints

1. R. Zhao and C.W. Macosko, "Multilayer coextrusion reveals interfacial dynamics in polymer blending," *Proceedings of PPS-15*, s'Hertogenbosch, Netherlands, **1999**.
2. R. Zhao, "The role of interfacial slip in melt rheology of immiscible polymer blends," *Soc. Plast. Eng. Tech. Papers (ANTEC)*, 1076-1080, **2000**.
3. R. Zhao and C.W. Macosko, "Rheology of immiscible polymer blends—interfacial slip," *13th International Congress on Rheology*, D.M. Binding, N.E. Hudson, J. Mewis, et al, eds. Cambridge, UK, 2000, p. 225-227.
4. R. Hooper, V. Cristini, S. Shakya, J. Lowengrub, J.J. Derby, and C.W. Macosko, "Modeling multiphase flows using a novel 3D adaptive remeshing algorithm," *Proceedings of the First International Conference on Computational Methods in Multiphase Flow*, March **2001**.
5. G. Severe, D. Harris, and C.W. Macosko, "Dynamic mechanical analysis of aromatic polyamide/ethylene-propylene-diene terpolymer laminates," *Soc. Plast. Eng. Tech. Papers (ANTEC),* 1910-1914, **2001**.

6c. Papers presented at meetings but not published in preprints

1. R. Zhao and C.W. Macosko, Polymer Processing Society, Shanghai, June 2000.
2. R. Hooper, V. Cristini, J.J. Derby, C.W. Macosko, S. Guido and M. Simeone, "Creating lamellar microstructures in polymer blends," AIChE, Los Angeles, Nov. 2000.
3. H.K. Jeon, "Effect of block copolymers on drop deformation in immiscible blends," AIChE, Los Angeles, Nov. 2000.
4. R. Zhao and C.W. Macosko, "Visualizing slip at polymer-polymer interfaces," Polymer Processing Society, Montreal, June 2001.
5. V. Cristini, H. Zhou, J. Lowengrub, and C.W. Macosko, "The effect of surfactants on drop deformation, collisions and breakup," APS Fluids Meeting, San Diego, CA, Nov. 2001.
6. V. Cristini, T. Jansseune, J.J. Mewis, P. Moldenaers, and C.W. Macosko, "Calculation of transient stress behavior in dilute immiscible blends via experiments and numerical simulations," Society of Rheology Meeting, Washington, DC, Oct. 2001.
7. H. Zhou, V. Cristini, J. Lowengrub, and C.W. Macosko, "The effect of surfactants on drop deformation, collisions and breakup," Society of Rheology Meeting, Washington, D.C., 2001.
8. R. Zhao and C.W. Macosko, "Slip at polymer-polymer interfaces: Rheological measurements on coextruded multilayers," Society of Rheology Meeting, Washington, D.C., 2001.
9. V. Cristini, H. Zhou, J. Lowengrub, and C.W. Macosko, "Numerical simulations of drop breakup and coalescence with soluble surfactant in 3D," Society of Rheology Meeting, Minneapolis, Oct. 2002.
10. S. Velankar, H.K. Jeon, H. Zhou, C.W. Macosko, "Measuring interfacial tension by retraction of surfactant-laden drops: Numerical simulation and experiments," Society of Rheology Meeting, Minneapolis, Oct. 2002.

6d. Manuscripts submitted, but not published

1. H. K. Jeon and C. W. Macosko, "Visualization of block copolymer distribution on a sheared drop," *Macromolecules*, submitted 2002.
2. H. Zhou, V. Cristini, J. Lowengrub and C.W. Macosko, "3D adaptive numerical simulation of deformable drops with soluble surfactant: Pair interactions and coalescence in shear flow," *Phys. Fluids*, submitted 2002.

6e. Technical reports submitted to ARO

Interim Progress report for Aug. 1999 – Dec. 1999

Interim Progress report for Jan. 2000 – Dec. 2000

Interim Progress report for Jan. 2001 – Dec. 2001

Manuscript report, April 2000, "Slip at molten polymer-polymer interfaces."

Manuscript report, August 2001, "Lamellar microstructure of emulsions."

Manuscript report, August 2001, "Modeling multiphase flows using a novel 3D adaptive remeshing algorithm."

Manuscript report August 2002, V. Cristini, "Flow-independent drop deformation with zero surface tension," *Phys. Fluids 14*, 2929, **2002**.

V. Cristini, C.W. Macosko, and T. Jansseune, "A note on transient stress calculation via numerical simulations," *J. of Non-Newtonian Fluid Mech*, in press **2002**.

V. Cristini, R. W. Hooper, C. W. Macosko, Stefano Guido and Mariano Simeone, "A numerical and experimental investigation of lamellar blend morphologies," *Ind. Eng. Chem. Res.*, **2002** in press.

7. Personnel

Ph.D. Researchers:

Russell Hooper, Ph.D. 2001, now at Sandia, Albuquerque, NM
Rui Zhao, Ph.D. 2002, now at Exxon Mobil, Baytown, TX

Postdoctoral researchers:

Dr. Hua Zhou
Dr. Vittorio Cristini
Dr. Hyun Jeon

Faculty:

Professor Chris Macosko

8. No inventions were made under this grant.

9. N/A

10. Appendices

Abstracts of Ph.D. theses research supported by this grant

Russell W. Hooper
Thesis title: "Drop Dynamics in Polymer processing Flows," Dec. 2001
Abstract: attached

Rui Zhao
Thesis title: "Multilayer coextrusion reveals interfacial dynamics in polymer blending," July 2002
Abstract attached

Drop Dynamics in Polymer Processing Flows

A Thesis Submitted to the Faculty of the Graduate School of the University of Minnesota

by

Russell W. Hooper

in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

December 2001

Chapter 1

Introduction & Thesis Overview

Contents

The broad applicability and relatively cheap cost of commodity polymers has led to their widespread use in a growing number of applications. Polymer blending has been and continues to be a viable means of furthering their use. This stems from the economy and efficiency with which blends can be produced compared to other routes, such as polymer synthesis, and from synergism in which blend properties exceed a simple averaging of its components. Hence, blends give new properties from existing polymers.

In general, thermodynamic incompatibility results in most polymer blends being immiscible [1]. The rheology, flow history and relative amounts of blend components then determine the blend structure. In dilute systems, typically defined as blends with $\leq 10\%$ minor phase, the blend structure is normally comprised of a dispersion of small ($O(10\mu m) - O(1mm)$) drops. Blend properties are then intimately related to the morphology which refers collectively to the size, shape and orientation of the structure (drops) [2]. Thus, mechanical, optical and rheological properties can be tailored by proper control of the blend microstructure.

A commercially important example which motivates this thesis involves creation of barrier materials through intelligent processing of dilute polymer blends. Ideally, barriers against aroma, moisture, hydrocarbons, etc. are obtained by generating flat preferentially-oriented drops, i.e. lamellae, of an appropriate (often more expensive) impermeable polymer within a less costly, easily processed polymer of desirable mechanical strength. The latter property is important since many important impermeable polymers such as nylon often possesses poor mechanical properties, e.g. brittleness, which would preclude their use in the absence of blending with a more robust polymer material. Employing this technique has led to reductions in permeability of several orders of magnitude in some commercially important systems [3–6]. Successful creation of these barrier materials has mostly been somewhat of an art, relying on trial-and-error and heuristics. Optimization of barrier properties by controlled generation of lamellar microstructures requires a fundamental understanding of factors influencing blend morphology.

The key to intelligent optimization of blend properties lies in quantitative prediction and control of blend microstructure, which in dilute systems amounts to understanding drop dynamics as a function of rheology, flow and concentration. Each of these poses its own set of challenges. Rheological behavior of polymer blends and blend components typically deviates from Newtonian fluid behavior by exhibiting such phenomena as shear thinning and viscoelasticity (i.e. fading memory effects) [7]. These become more pronounced as the processing flow rate and flow strength are increased. As will be discussed shortly, 'strong' flows are characterized by a greater tendency to stretch drops compared to weaker flows which possess a greater rotational (i.e. vorticity) component. Strong flows also lead more readily to significant shape changes which can include coalescence and breakup events. Interparticle interactions increase with the concentration of drops within the blend. Taken together, these characteristics of polymer blending make prediction and control of blend morphology a formidable challenge.

This thesis attempts to improve the current understanding of morphology evolution in polymer blending by devloping numerical tools to predict large deformations of drops in polymer blends. This will complement ongoing independent experiemental studies [8–10] and is based on applying a robust numerical methodology, the finite element method (FEM), to approximate solutions to the equations governing drop dynamics in polymer flows. The FEM is selected for its ability to account for such relevant features as wall effects, nonlinear viscoelasticity, and irregularly shaped, evolving fluid domains. Taken together, accurate accounting of these is awkward or beyond reach of other methods such as finite difference methods, boundary integral methods and finite volume methods. Complete description of the problem is also beyond reach of analytical methods. Nevertheless, these do provide important information such as scaling behavior and exact results for simplified problem descriptions which can be used to validate numerical methodology.

With the problem narrowed to a study of drop dynamics in polymer flows, the remainder of this chapter is devoted to a review of what can be gleaned from simple theory and earlier works. This is followed by an outline of presentation of the thesis.

Multilayer Coextrusion Reveals Interfacial Dynamics in Polymer Blending

A Thesis Submitted to the Faculty of the Graduate School of the University of Minnesota

by

Rui Zhao

in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

July 2002

ABSTRACT

Blending two or more polymers together has been used as an alternative to tailor the end-use properties of polymeric materials. Most of the polymers of practical interest in blends are immiscible, thus multiple phases coexist in the blends. The micro-morphology of each phase developed during mixing dictates the final properties of the blends. It has been understood that micro-morphology is determined by interfacial and rheological properties of the blends, and many works have been done to understand their roles in controlling micro-morphology in blending. However, most of these works have been done in the melt blend itself where interfacial properties and rheology interact with each other. This makes it difficult to clearly investigate their individual effects. In this PhD thesis work, a multilayer coextrusion line was constructed in our laboratory. This coextrusion setup is interfaced with a series of layer multiplication dies which are capable of making multilayer sheets with number of layers range from 2 to 2048 layers. One unique aspect of this process is large amount of interfacial area generated in a fast and well controlled manner, and the rheology of the components do not play an important role up to the point of layer breakup. Thus this coextruded multilayer provides a model system to study interfacial dynamics and blends rheology. Using coextruded multilayers, a novel technique is developed to measure the interdiffusion between a high density polyethylene and a linear low density polyethylene. In this technique the interdiffusion is followed by monitoring the increase of apparent viscosity of the multilayers of these two polyethylenes. A mathematical model using the fast diffusion theory by Kramer *et. al.* was developed to simulate the kinetics of this diffusion. The simulation results favor their theory. This technique is also applied to measuring the interfacial reaction kinetics of maleic anhydride and glycidel methacrylate coupling in a miscible and an immiscible pairs. The kinetics obtained from this technique is in agreement with that from

FTIR spectrum measurements on the same system. Comprehensive rheological measurements were done on coextruded multilayers. These measurements show strong evidence of slip at the melt interfaces of immiscible polymers. The slip velocity is calculated and appears to be dependent on shear stress. A modified Ellis model is used to describe the relation of slip velocity to shear stress. In addition to rheological measurements, the slip is also directly visualized at the interface of a bilayer sample. In this experiment, a technique is developed to imbed carbon black particles (about $1\mu m$) across the interface of a bilayer sample. After shear, particles on each side of the interface move away from each other due to slip. The estimated slip velocity agrees with our rheological measurements. These studies provide the first reliable experimental measurements for the slip.

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