The University of Akron

Rheology Group, Polymer Dynamics, Interfaces

Polymer Dynamics, Interfaces and Rheology Group

Shi-Qing Wang

Kumho Professor
Ph.D. (Physics), University of Chicago (1987)
Fellow of the American Physical Society (1997)
Member of American Physical Society, Society of Rheology
***and American Association for the Advancement of Science***

Research Interests

Physics and engineering of polymeric and other structured materials. Experimental and theoretical foundations of polymer rheology and processing: phenomenology of linear and nonlinear viscoelastic processes; flow instabilities and processing phenomena including wall slip and melt fracture. Time-dependent yielding and fracture behaviors of polymer glasses.

The seven real-time movies below illustrate (a) sharkskin formation (extrusion of polybutadiene) followed by wall slip at higher pressure, (b) particle-tracking velocimetric (PTV) observations of (c) startup shear on an entangled PBD solution, see **Macromolecules 2008, 41, 2663.** (d) Elastic yielding after a sudden stretching due to residual elastic forces. (e) The animated movie based on a rubber band to elucidate the processes of yielding during or elastic yielding after sudden startup deformation (in the example of stretching). (f) PTV revelation of elastic yielding after a SBR melt experienced 7 shear strain units. PTV method has been described in some detail in **Macromol. Mater. Eng, 292, 15** (2007). For the relevant publications, see **Macromolecules 2009, 42, 6261.** (g) Strain localization at the die entry during extrusion of a monodisperse 1,4-polybutadiene of 200 Kg/mol. See **J. Rheol. 57(1): 349-364 (2013)**. (h) PTV evidence of shear yielding during startup uniaxial extension to initialize (unstable) necking. See **J. Rheol. 57, 223 (2013)**

A one hour **seminar** is available at both YouTube and **TuDou**, summarizing what we know now after six years of intense studies and some forty publications (between 2006 and 2012), which was given at the University of Akron on March 2, 2012. The corresponding Powerpoint document (~ 233 Mb) containing all the embedded movies to play in real time is available for online download by request. More recently, we have presented our analysis of the theoretical status of nonlinear polymer rheology at the 2013 Society of Rheology meeting (Pasadena, CA, Feb. 11), "Emerging signs calling for a different framework for nonlinear rheology of entangled polymers", which is available upon request. Moreover, a new **publication** will appear to discuss the construction and structure of the tube model and indicate the emergence of an alternative conceptual framework. There is also a **lecture** given in Jiao Tong University in August 2012 (in Chinese).

(a)

(b)

(c)

(d)

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(e)   (f)

(g)   (h)
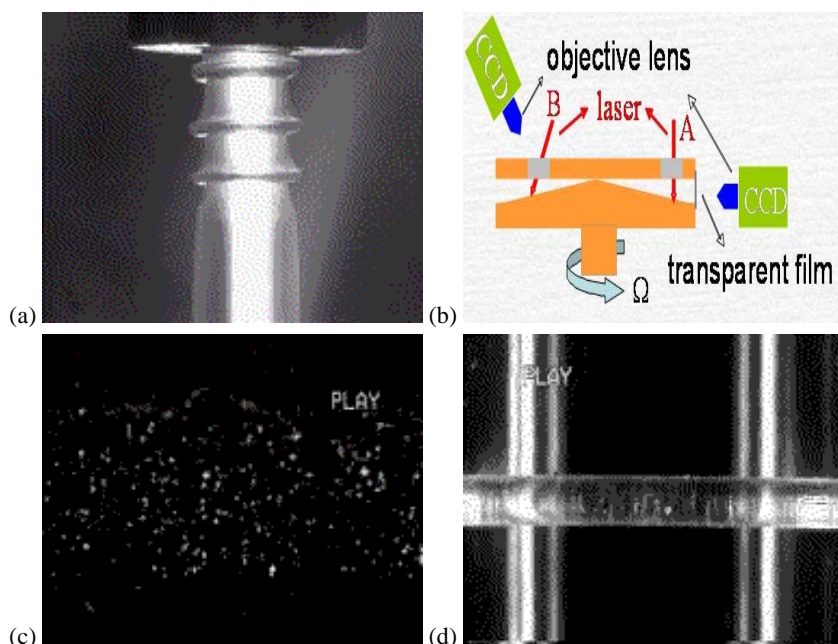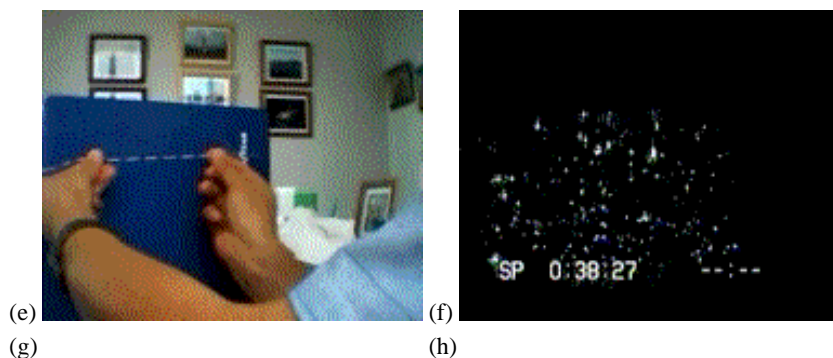
Current Activities

Our current research focuses on two major subjects in polymer science: rheology of polymeric liquids and mechanics of glassy polymers. Several hundred billion pounds of polymers are annually consumed to make commercial plastic (milk bottles) and rubber (e.g., auto tires) products for worldwide consumption. Before they turn into their final forms, most are brought to their liquid states for processing. Thus, it is essential to understand rheological behavior of polymer liquids under large and rapid deformation. Many of these polymers, such as polyethylene and polybutadiene, are well entangled. Their apparent viscosities decrease during processing flow. This basic phenomenon of shear thinning has been recognized for decades although its origin remained elusive. In the past eight decades since M. Reiner, J. Rheol. 1, 5 (1929), polymer flow has been perceived to usually take place homogeneously, and shear thinning has been characterized in rheometric instruments under such an assumption.

Lately, we learned that well entangled polymers undergo cohesive breakdown upon either startup deformation or large step strain or large amplitude oscillatory shear[Phys. Rev. Lett. **96**, **016001**, **196001**, **97**, **187801** (2006), **99**, **237801** (2007), Macromol. Mater. Engr. **292**, **15** (2007), J. Chem. Phys. **127**, **064903** (2007) and a **sub-list** of our publications on the subject of nonlinear polymer rheology]. The localized yielding phenomenon leads to subsequent inhomogeneous flow. The emerging new understanding has allowed us to make specific predictions of unexpected behavior that would appear counterintuitive to the conventional views. Two such phenomena are arrested wall slip and filament failure after sudden extension, listed below as G and I. The new theoretical picture has also allowed us to unify the description of deformation and flow in shear and extension. A short list of publications on Nonlinear Polymer rheology is provided **here**.

Given the rapidly accumulating evidence, a new textbook on the subject of Nonlinear Polymer Rheology is in the preparation stage. Click **TOC** for the book outline (**TOC** in Chinese). A one-credit course is being taught every year based on the **TOC** and is available for viewing through **stream-video** upon request. The rapidly accumulating results suggest that entangled polymers yield to fast large deformation as if they are breakable solids of finite cohesive strength. The animated movie above (also available as Movie 18 under I. Yield in melt extension) uses a rubber band to elucidate the process of yielding during sudden startup deformation (in the example of stretching). Whether the initial shear banding would surrender to homogeneous shear at long time remains a conceptually and academically interesting question. Nevertheless, the metastability of shear banding appears to be very strong even in solutions. This longevity of shear banding is elusive and also makes shear banding an important phenomenon to reckon with in practice. There is little doubt that yielding must take place when the applied rate is significantly higher than the polymer relaxation rate: Disintegration of the entanglement network begins when each chain can no longer take on further deformation and mutual molecular sliding occurs as shown in the illustrative movie **Elastic Yielding** - the chain (rubber band in the movie) retracts as disentanglement sequentially occurs via chain ends where the fingers represent inter-chain interactions, acting to cause affine deformation initially. We are currently also actively pursuing any possible direct evidence for chain scission that could occur in rupture like material failure.

We summarize the growing experimental evidence in the form of movie video clips that captured the essence of various phenomena in entangled polymer solutions and melts, in each category listed below.

   A. **Yielding in startup shear**
   B. **Large amplitude oscillatory shear**
   C. **Flow birefringence**
   D. **Large step shear**
   E. **Continuous shear**
   F. **PTV observations of other complex fluids**
   G. **Wall slip during and after shear**
   H. **Elastic breakup in simple shear of melts**
   I. **Yield in melt extension**

Many of these several hundred billion pounds of polymers have good mechanical strength because they are glassy, such as PC, PET, PS, PMMA, to mention a few common polymer glasses. Thus, it is essential for us to understand how and why glassy polymers fail mechanically under external deformation. How to make polymer glasses tough by increasing their ductility is a practical

question of significant industrial relevance. We have started to explore and verify a conceptual picture of a hybrid structure that appears applicable in the case of polymer glasses of high molecular weight undergoing large deformation. As an example, we demonstrated how the insights gained in the studies of polymer rheology can be helpful in the subject of nonlinear mechanics of polymer glasses. See *Macromolecules* **2012**, *45*, 6719-6732. An invited **talk** at APS March 2013 provides a glimpse of the ongoing research in our lab.

Footnote:

In response to our statement "The transition from elastic deformation to flow must occur upon startup shear or extension. It occurs essentially at the force maximum", review 2 of our 2011 JOR asserted 'Polymer melts are always in a liquid state and therefore flows. It may be viscoelastic flow but they are not elastic (in) nature.' In 2008, another reviewer of our 2008 JOR paper indicated 'The imposed flow (constant strain rate) is such that flow must take place right from the start of the experiment.'

This disagreement highlights the difference in how to understand responses of entangled polymers to large deformation. In our understanding, entangled polymers cannot be regarded as liquids when suddenly subjected to external deformation. Upon sudden deformation with $Wi = tau/t1 >> 1$ where the time $t1$ to take 100 % deformation, i.e., the reciprocal rate, is much shorter than the relaxation time tau, such systems would essentially suffer elastic deformation until the system breaks apart to allow irrecoverable deformation, i.e., flow. The evidence for the elastic response before the force maximum also comes from the fact that the mechanical stress arises from zero monotonically upon startup deformation, and there is no evidence of flow that would produce a finite stress at $t= 0+$ according to the Newtonian law for liquids.

There is also confusion about the linear viscoelasticity. During the review of our first 2013 JOR, reviewer 1 stated in the two rounds of review respectively "The idea that the zero-rate limit will give an elastic initial response is contrary to my understanding." and "A zero-rate limit is one for strain rate tending to zero which must mean extremely slow flow, so I cannot understand how any elastic deformation can take place." But even when $Wi << 1$, a viscoelastic material still deforms predominantly elastically upon startup deformation for a period up to tau although the elastic strain is as low as Wi.