

Supramolecular polymeric rheology

Abstract

Supramolecular polymers are a broad class of materials that include all polymers capable of associating via secondary interactions. These materials represent an emerging class of systems with superior versatility compared to classical polymers with applications in food stuff, coatings, cost efficient processes or biomedical areas. Design and development of supramolecular polymers using ionic, hydrogen bonding or transition metal complexes with tailored properties requires deep understanding of dynamics both in linear and non-linear deformations. While linear rheology is important to understand the dynamics under equilibrium conditions, extensional rheology is relevant during the processing or in the usage of polymers utilizing supramolecular associations for example, acrylic based pressure sensitive adhesives are subjected to extensional deformations during the peeling where strain hardening is often desirable. Such data is also needed to develop sophisticated multi-scale models that can later be used for predicting the flow behavior and molecular dynamics of supramolecular networks. We make use of the state of the art rheological measurement devices involving shear rheometer and a unique home built filament stretching rheometer.

Introduction

Supramolecular polymers are relatively new class of polymers with attractive groups that offer reversible interactions and thus the possibility of tuning the properties on will. These associative polymers present superior versatility compared to their covalent polymeric counterparts. They include charged polymers (ionomers, polyelectrolytes, metal-ligands). A very well-known naturally occurring supramolecular system is DNA. Cooperative non-covalent interactions, such as multiple hydrogen bonding and hydrophobic interactions, give rise to its unique architecture. Other example from nature is spider silk whose remarkable strength arises from presence of micro-crystalline domains, formed by secondary interactions, and embedded in a flexible matrix. Amongst the man-made materials, Nylon is a good example in which hydrogen bonding between the polymer chains gives rise to exceptional material properties.

Hydrogen bonding is the most employed non-covalent reversible interaction to create supramolecular polymeric assemblies [1]. The dynamics of hydrogen bonded transient networks can be significantly altered by changing the exchange rate between two hydrogen bonding motifs via external stimuli such as temperature. At high temperatures molecular chains can release stress at a fast rate because of decrease of hydrogen bond life time which can lead to low viscosity melts. This remarkable property thus allows easy processing of such materials for

various applications [2]. Alternatively, at low temperatures the hydrogen bond life can be significantly larger than the experimental time scales leading to transient networks [3]. A schematic of supramolecular hydrogen bonding polymer melt is shown in Figure 1 (Top). Such supramolecular systems have found applications in pressure sensitive adhesives an example of which is shown in Figure 1 (Bottom).

Ionomers represent another class of associative polymers where ionic groups are covalently attached to the polymer backbone. The key feature of ionomers is that a relatively modest concentration of ionic groups attached to a low dielectric constant polymer can provide significant changes in physical, mechanical and dynamic properties of a polymer. Ionomers are nano-structured materials, similar to nanocomposites and block polymers. Ionomers have applications in polymer blends, film and packaging, coatings and adhesives.

The linear rheology of supramolecular polymers is very rich and offers opportunities for property manipulation. Understanding the rich dynamics of such associative polymers is thus interesting from both fundamental and applied standpoints. While the non-linear rheology of supramolecular polymers has been investigated in shear. Literature on extensional rheology remains less understood partly because of the difficulty in attaining stable large extensional deformations. The few available data suggests that they are very promising for tailoring the appearance of strain hardening. Non-

Summary of Ph.D work

linear studies have also revealed fracture in associative polymers. For example in the case of ionomers, although strong transient networks can be obtained, they fracture in a brittle manner in extension.

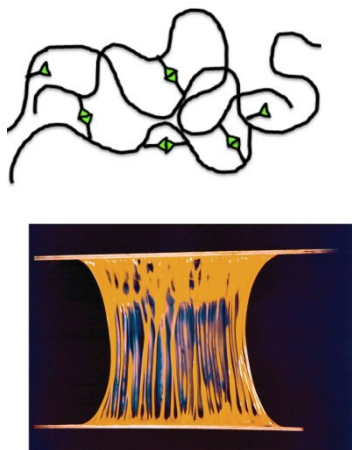


Figure 1. Top: Cartoon of hydrogen bonding polymer melt, green stickers is the hydrogen bonding moieties Bottom: example of pressure-sensitive adhesive

Objective

The project provides new insight by producing presently unavailable experimental results on the extensional rheology of supramolecular polymer melts utilizing hydrogen bonding and ionic bonding (ionomers) respectively. Results have been obtained for:

1. Linear rheology using small amplitude oscillatory shear rheology.
2. Non-linear rheology using filament stretch rheometer to probe the strain hardening behavior. High speed imaging coupled to non-linear provides strong rationale for fracture of these apparently very strong networks.

The experimental results are expected to redefine the field of extensional rheology of supramolecular polymers.

Hypothesis

The hypothesis of this research work has been based on our thinking that by using well defined model systems one can tailor strain hardening behavior with increasing amount of supramolecular bonding content. We also hypothesize that although these systems appear

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strong but intrinsically they are brittle because supramolecular associations lack the diffusional relaxation process as opposed to conventional entangled polymers like entangled linear polyethylene (LDPE) which appears to be very ductile and tough when stretched.

DTU Filament Stretching Rheometer

The project has been mostly based on the unique DTU Filament Stretching Rheometer (DTU-FSR) capable of constructing well defined extensional flow fields of polymer melts. Designed with thermostat, nitrogen atmosphere and on-line feedback control of plate motion (required for non-Newtonian liquid experiments) this instrument placed at DTU Chemical Engineering is unique in the world. The key feature that sets the DTU-FSR from any other extensional flow rheometer is the on-line feedback control from the on-line laser sheet scanning of the filament diameter designed and implemented is cooperation between the CAPEC and DPC research groups at DTU Chemical engineering.

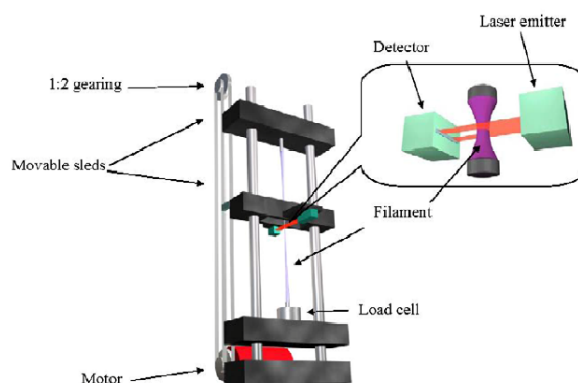


Figure 2. Sketch of Filament Stretching Rheometer at DTU. A test sample placed between two plates is drawn into a bridge.

Experimental Details

We used pure Polybutyl-n-acrylate (PnBA) and three of its hydrolyzed variants mentioned here in increasing amount of hydrogen bonding content. These include samples: AA6, AA12, AA38. The numbers used in this nomenclature denote the percentage of acrylic acid groups. On the other hand we have also used supramolecular systems utilizing ionic bonding as the other class of supramolecular polymers for this project. The emphasis has been on ionomers based on

polyethers and sulphonated phthlates with sodium counterions hereafter represented by PTMO-Na.

The extensional stress growth coefficient as a function of time was measured by a filament stretching rheometer (DTU-FSR). Measurements were performed at a constant hencky strain rate imposed at the mid-filament diameter using an online control scheme [4].

Results

Linear rheology results indicate deviation of terminal power law slopes from 1 and 2 to a slope of 0.5 with the increase of hydrogen bonding (see Figure 3).

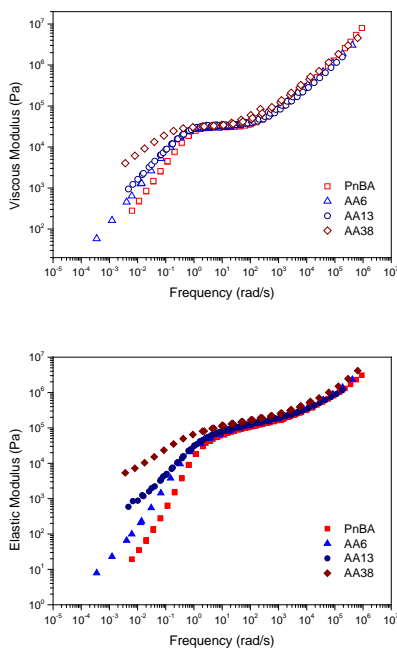


Figure 3. LVE master curves for PnBA and its hydrolyzed derivatives.

The non-linear rheology measured using the DTU-FSR is shown in Figure 1. The strain rates increase from right to left in Figure 4. The solid lines represent the LVE envelope obtained from a multimode Maxwell fit to the linear rheology data.

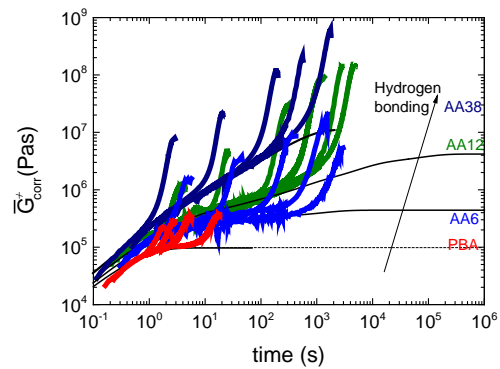


Figure 4. Stress growth coefficients at various strain rates for PnBA and its hydrolyzed derivatives as a function of time.

We interpret the increase of strain hardening behaviour with increasing acrylic acid group density, as an increase of life time of hydrogen bonds causing more extension of sticky rouse modes thus resulting in an increased strain hardening. This reasoning correlates well to the slope of 0.5 observed in the linear rheology data for AA38.

Finally, we have studied the fracture mechanisms for the PTMO-Na ionomer by combining extensional rheometry with high speed imaging. Extensional rheological response of the PTMO-Na ionomer is shown in Figure 5.

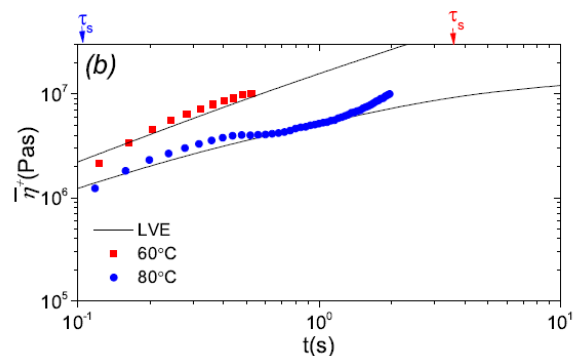


Figure 5. Extensional viscosity curves for PTMO-Na ionomer at two different temperatures. The arrows represent association life time of stickers (ionic bonds).

It shows the transient stress growth coefficient as a function of time for fixed strain rate at two different temperatures. The LVE envelope obtained using a multimode Maxwell fit from LVE oscillatory shear data is plotted as solid lines. The

extensional data are seen to be consistent with the predictions of linear viscoelasticity. The end of each experiment represents brittle fracture of the PTMO-Na filament. At low temperatures, the experimental time scale is smaller compared to association lifetime and the material fractures at relatively lower Hencky strain without showing any departure from the LVE envelope (often termed as strain hardening). By contrast, at high temperatures the experimental time scale exceeds association lifetime and a noticeable strain hardening is observed before brittle fracture. A complete evolution of the ionomer filament during extensional deformation is shown in Figure 6. During extensional deformation, a notch appears from the right edge of the filament orthogonal to the camera lens before it fractures into two halves. The sequence of images demonstrates the decoupling of time scale associated with extensional deformation (of the order of seconds) from the fracture event time which is of the order of *ms*. The fracture profile exhibits a parabolic shape from the beginning of crack propagation to complete fracture of the filament into two halves. This is an attribute associated with fracture of solids under tension.

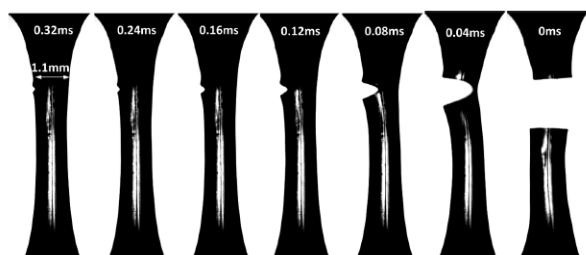


Figure 6. Complete evolution of filaments under constant strain rate extensional deformation. Sequence of images demonstrate parabolic growth of the crack leading to complete fracture of filament into two halves.

Conclusions

The incorporation of acrylic acid groups resulted in significant increase in strain hardening behaviour of hydrolyzed PnBA melts indicating that the life of hydrogen bonds increases with increasing concentration. These results suggest a potential in utilizing hydrogen bond transient networks in melt rheology to tailor strain hardening behaviour. Finally, we have studied the fracture for the PTMO-Na ionomer by combining extensional rheometry with high speed imaging. This project

was inspired by the fact that although ionomers find so many applications, a detailed study to delineate the fracture mechanisms was missing in literature. We have shown that these ionomers are intrinsically very brittle under extensional deformations because they appear like solid with minimal dissipation as evidenced by the shape of fracture profiles.

References

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