Engineering Yield-Stress Fluids for a Better World

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ABSTRACT

Yield-stress fluids are materials that reversibly transition from solid-like to fluidlike at a critical applied stress and may be the most utilized rheological phenomenon in our world. This paper discusses our research on engineering and design-thinking for yield-stress fluids, addressing the rheologyto-structure inverse problem of the many ways to achieve a yield stress, questioning assumptions of possible properties (extensibility), and research motivated by applications of engineering yield-stress fluids for a better world, including directwrite 3D printing, and fire suppression with sprayable gels.

INTRODUCTION

Yield-stress fluids have found use in drug delivery, food products, batteries, surface coatings, 3D printing materials, concrete, and many other applications. This rheological phenomenon can be achieved by a diverse range of microstructures including polymeric gels, colloidal glasses, emulsions, and more (Fig. 1).

This conference paper reviews our vision and recent research activities associated with the design and engineering of yield stress fluids. We describe a paradigm for applying design-thinking¹, we question properties possible², and discuss two applications where engineering of yield stress fluids allows for novel performance^{3–5}.



Figure 1. Engineering a specific property is an inverse problem because it can be achieved by multiple microstructural design strategies.

DESIGN-THINKING FOR RHEOLOGY

We engineer things for a purpose: a desired objective that motivates our design decisions and eventual creation of something. Here, that something is a material, and we are specifically interested in yield-stress fluids.

When starting with an objective, we consider multiple concepts or strategies to achieve it. This constitutes an inverse problem (Fig. 1), which we will call a problem of *design* (or engineering). This is different than analysis which is a forward problem starting from specific, determined circumstances. Fig. 2 contrasts that forward problem of analysis with the inverse problem of design. Most academic literature in the field of rheology, complex fluids, non-Newtonian fluid mechanics, and soft matter, is framed in terms of analysis. Indeed, most scientific studies are aimed at gathering knowledge about how materials or systems will behave.



Figure 2. Design is the inverse of analysis. It builds upon knowledge acquired through analysis, but organizes that knowledge in different ways and requires different methods. (Image adapted from Nelson & Ewoldt¹.)

Design builds upon the knowledge from analysis, but frames problems differently. It requires information to be organized in different ways, e.g. in comparative ways to contrast how different concepts could achieve a specific desired outcome. Engineering design research is its own field, with a strong community with broad interests ranging from design theory, to design methodologies, to optimization techniques, and beyond.



Figure 3. Ashby-style co-plot showing our measurements of extension properties of several yield-stress fluids and our ability to engineer new designed materials that achieve desired properties. The PEO Emulsion system is used for 3D printing in Figure 5. (Image adapted from Nelson et al.² adding data from Rauzan et al.⁶.)

For rheologically-complex fluids, two key design questions are often asked. First, "What properties do I want?" And second, "How can I achieve the desired properties?" The first question relates properties to performance (Fig. 2, right side), and is often approached from a continuum mechanics perspective (fluid mechanics, solid mechanics, constitutive equations, and conservation of mass and momentum are typically seen here). The second question relates properties to structure (Fig. 2, left side), and might be more common in materials science, formulation chemistry, and textbooks focused on particular material classes (e.g. focused on polymers, or colloids, or emulsions and foams).

Design questions require us to compare across different material classes. For example, to identify generic rheological property targets, which could be achieved by whatever ingredients and microstructure we choose. Several methods and approaches can be adapted from more developed engineering design fields, in particular mechanical design and material selection.

INSPIRED BY ASHBY DIAGRAMS

One of the most commonly taught design tools for engineering mechanical systems involves material selection based on properties. Known as "Ashby diagrams" and named for the researcher that developed their use⁷, we have adapted this approach to rheological material properties.

Fig. 3 shows one example of an Ashbystyle chart, here used for a collection of yield-stress fluids showing their varying extensibility. Extensibility is defined here as strain-to-break in a uniaxial test with defined geometry and extension rate. Example images of these tests are shown in Fig. 4.

All commonly studied yield-stress fluids show negligible extensibility. Indeed, this seems to be the leading paradigm in the open literature. However, real materials can have a yield stress *and* be extensible. Fig. 3 makes this immediately clear.



Figure 4. Extensional behavior of yield-stress fluids. A) Bentonite clay suspension, a commonly studied material that fails to match the extensibility of other yield-stress fluids; B) a resin used in printing by the company HexArmor; C) the bubble gum, Hubba

Bubba Bubble Tape; and D) a model material introduced here. (Image adapted from Nelson et al.²)

The use of Ashby-style charts can be extended to many other complex rheological properties, and some examples exist in our own work.^{1,8–10} A challenge going forward will be to represent complex, *function valued* rheological properties with condensed, low-dimensional metrics that allow for visualization in terms of two or three scalar quantities.

ENGINEERING EXAMPLES

Beyond Ashby diagrams, below we describe two example studies from our research that demonstrate design thinking and, to various degrees, seek answers to the two key design questions for rheological materials, "what properties are important?" and "how can the properties be achieved?".



Figure 5. Engineering a yield-stress fluid ink with extensibility for direct-write 3D printing. Extensibility increases printing speeds and improves stability of un-supported structures. (Image adapted from Rauzan et al.⁶)

Example 1: Extensible yield-stress fluids for direct-write 3D printing

Figure 5 outlines our work to develop a novel class of particle-free emulsions with polymer additives for direct-write 3D printing, which is of current interest for fabrication of soft actuators and sensors. It is perhaps easy to see that a yield-stress fluid is required for direct-write 3D printing, which is based on extrusion of material from a nozzle that must retain its shape. But, how can this property be achieved? Many microstructure options are available (Fig. 1). Here, we engineer an emulsion-based material to achieve the yield stress which allowed us to independently study a new hypothesis, that the property of extensibility could also improve performance.

This particular material structure and formulation was used to build 3D structures and to pattern at filament diameters below that of any other known yield-stress fluid material (less than 10 μ m). To engineer the extensibility, we used a polymer additive (PEO at different molecular weights) to tune the extensibility of the material, a property of yield-stress fluids that has only recently been acknowledged (Fig. 3, Fig. 4).

High extensibility of the emulsion correlates to the ability of filaments to span relatively large gaps (over 10 mm) when extruded at large tip diameters (330 μ m) and the ability to extrude filaments at high print rates (20 mm/s). Post-printing transformation is used to convert the emulsion into an elastomer, which can buckle and

recover from extreme compressive strain with no permanent deformation, a characteristic not native to the emulsion.



Figure 6. Aqueous yield-stress fluids can extinguish fires better than water alone. Here demonstrated with droplets of a 0.1% by weight Carbopol microgel particle suspension impacting a burning substrate. (Still image from full video, available online, Blackwell et al.¹¹)



Figure 7. A new dimensionless group identifies which rheological properties are important for splash regimes in droplet impacts of yield-stress fluids, allowing for design guidelines across a range of different material classes. (Image adapted from Blackwell et al.³)

Example 2: Droplet impact and coating

Among the many engineering applications of yield-stress fluids, one is the unique ability of shear-thinning yield-stress fluids to extinguish fires by coating and sticking to substrates (Fig. 6). This has motivated our work to answer "what properties are important?" For the complex application of fire suppression, the question is still unanswered. Yet, motivated by potential engineering of such fluids, we have experimentally studied the phenomena of droplets impacting surfaces and understanding the regimes of splash behaviour.

Fig. 7 shows experimental results from a large data set of droplet impact observations. Different regimes are notes for droplets impacting a solid substrate with a thin coating of the same material.^{3,5} We have identified a new dimensionless group that simplifies the understanding of the splash regimes. Doing so helps identify what rheological properties matter. Here, the yield stress and the high rate viscosity, as fit to a Bingham model, is sufficient. This enables engineering with these materials since this dimensionless group governs the behaviour. Moreover, the properties involved could serve as design targets, if one knew whether they wanted incoming droplets to splash, or not, when impacting and coating a substrate. We have used this processing map to assess other complex yield-stress fluids, including paints, with successful predictions of splash behaviour (unpublished work). This demonstrates the value in identifying properties (rather than formulation) that corresponds to desired performance. Paints are composed of complex formulations, but if only certain continuum-level properties matter, this simplifies the design targets.

CONCLUSIONS

There is much left to learn about how to engineer yield-stress fluids. Application areas are numerous, and design-thinking will help lead us to an ability to truly engineer these materials, and to engineer systems that involve these materials. Engineering design textbooks exist in other fields of engineering, and the methods and approaches described here may be a start at developing our own discipline to rationally design these materials to achieve a diverse range of objectives that help make for a safer and better world.

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