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Design of yield-stress fluids: a rheology-to-structure inverse problem†

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We present a paradigm for the design of yield-stress fluids, using six archetypal materials for demonstration. By applying concepts of engineering design, we outline a materials design paradigm that includes (i) morphological organization based on jammed *versus* networked microstructures, (ii) collected scaling laws for predictive design, (iii) low-dimensional descriptions of function-valued flow data, (iv) consideration of secondary properties including viscous behavior, and (v) a strategy for material concept synthesis based on the juxtaposition of microstructures. By explicitly specifying these design strategies, we seek to create an ontology and database for the engineering of yield-stress fluids. Our proposed design strategy increases the likelihood of finding an optimal material and prevents design fixation by considering multiple material classes to achieve a desired rheological performance. This flips the typical structure-to-rheology analysis to become the inverse: rheology-to-structure with multiple possible materials as solutions.

1. Introduction

Rheologically-complex fluids have the potential to meet numerous and diverse design objectives.¹ Inspiration can be found in biological systems with complex fluids² and soft solids,^{3,4} and many engineered systems use rheologically-complex behavior as a design strategy.^{5,6} Currently the most utilized rheological phenomenon is the dramatically shear-thinning ‘yield-stress fluid,’ the reversible transition from solid-like to liquid-like behavior at a critical applied stress.

The importance of yield-stress fluids in daily life and industry cannot be overstated as the concept applies to products as pedestrian as paint and toothpaste but also to applications as esoteric as crude oil gelation and rocket fuel.^{7–9} Consider a few other examples. A yield stress was a sufficient property to enable a new production technique for tailorable ceramic beads.¹⁰ In the food industry, the yield stress is of great importance for processing, manufacturing, and functional properties, as well as for correlation with sensory indices.¹¹ In 3D printing applications, yield-stress materials have been taken advantage of for inks that hold their extruded shape, for cellular composites,¹² and for a medium in which to print large complicated structures with microscopic precision.¹³ Electrically or magnetically responsive yield-stress fluids can be used as active mechanical elements that respond to their environment.^{14,15} An

optimal yield stress value in flow batteries balances an increased electrical conductivity through plug flow with the cost of increased mechanical pumping.¹⁶ For biomedical applications, an emerging paradigm of moldable hydrogels is based on yield-stress fluids capable of drug delivery.¹⁷ For design of all these materials, the primary design objective is a fluid that has a yield stress, since that is what enables the novel behavior. Therefore, before considering any constraining secondary objectives (thixotropy, linear viscoelasticity, *etc.*), design of these materials should first consider all the possible ways to achieve a shear-reversible yield-stress fluid, since for this primary objective it is the functionality that matters, not the chemistry that achieves it.¹⁸

In the field of rheology, most works in the public domain focus on the analysis of materials rather than researching and developing more useful design practices and methodologies; these complementary approaches are depicted in Fig. 1A. By analysis, we mean that, starting with known ingredients or a known microstructure, a material is characterized and these properties are related to the macroscopic performance. Of course, carrying out the analysis perspective is non-trivial for rheologically-complex materials; the characterization of properties can be especially arduous due to their function-valued nature, and so several complicated structural and observational dependencies are used to describe a single material. To design a material is the inverse of this analysis process and fundamentally is about making decisions,²¹ starting with the desired macroscopic performance, decisions must be made on what properties might achieve that objective, and in turn what ingredients or microstructure might result in those properties.

The details of the inverse design process are depicted in Fig. 1B.²⁰ We emphasize that designing does not only mean

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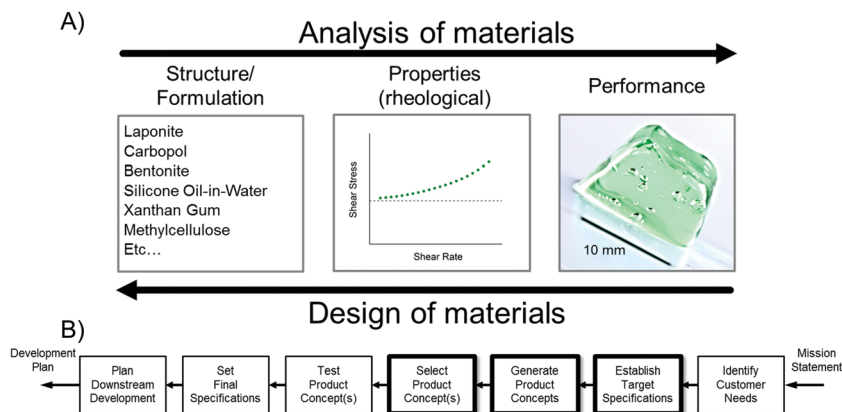


Fig. 1 (A) Engineering design is the inverse of analysis (adapted from ref. 19 and applied to rheological properties). Analysis starts with a specific material structure and connects it to properties and performance, which is non-trivial for rheologically-complex materials. Design starts with a desired performance (e.g. shape-holding with a yield-stress fluid), and a decision is made on what material to best achieve it. (Image from ref. 1.) (B) Full process of design (adapted from ref. 20). Many current material design efforts tend to skip the first four upstream steps, assuming a single material type to test or optimize. Our work focuses on methods for enhancing the upstream steps shown in bold for yield-stress fluids.

formulating or building entirely new materials. It also includes determining a set of target specifications (qualitative or quantitative), as well as generating a set of concepts that may satisfy these specifications by surveying and organizing existing materials as well as ideating new material concepts. After generation of concepts, selection of existing materials and of candidate new material concepts to prototype and formulate is carried out. Additional downstream processes then take place as depicted in Fig. 1B. Our work here contributes to the necessary upstream steps of the design process, providing methodologies for establishing target specifications, generating concepts of yield-stress fluids, and comparing and selecting based on rheological properties. This work does not provide tools for the equally important—but often over-prioritized—downstream steps of the design process such as material formulation, material optimization, and production ramp-up. Predictive tools and models for these downstream steps are, of course, immensely difficult to develop for real materials and likely need to be developed on an individual basis. Specific aspects outside the scope of this work are down-selection based on non-rheological criteria, formulation guidelines or optimization of a specific material microstructure, and application-specific performance objectives; our focus is broader and contributes to earlier stages of the design process.²⁰

Our goal here is to adapt engineering design theories to rheologically-complex materials, specifically yield-stress fluids, thus organizing research efforts across material classes of soft matter by using functional requirements based on desired rheological properties (see ESI† for more discussion). As specific contributions, we examine: (i) organization of structure-to-property design strategies based on jammed *versus* networked microstructures, (ii) collected scaling laws for predictive property design, (iii) low-dimensional descriptions of function-valued flow properties, (iv) property visualization (Ashby-style charts) that consider secondary properties including viscous behavior, and (v) a strategy for material concept synthesis (ideation) based on the juxtaposition of microstructure design strategies to generate new ideas. By successfully applying design techniques to yield-stress

fluids, we will demonstrate design paradigms that can more generically be used with other rheologically-complex properties.

To study and develop design methodologies for rheologically-complex materials, we characterize the bulk rheology of well-studied archetypal yield-stress fluids, *i.e.* materials one may regard as “classic” yield-stress fluids within rheological literature. These yield-stress fluids were chosen to survey a wide variety of chemistries, as well as different microstructures which can be categorized by the mechanism by which the yield stress comes about (discussed in detail in Section IIIA). Characterized materials are Carbopol 940 (jammed microgel), silicone oil-in-water and mineral oil-in-water emulsions, Bentonite and LAPONITE[®] RD (colloidal clays), and xanthan gum (polymer gel). Sample formulation and preparation steps are given in ESI† along with characterization details, experimental results at multiple gaps, and tables summarizing model fit parameters. Although the chemistry and microstructure vary, these materials have overlapping ranges of dynamic yield stress as weight percentage of additive is varied. Clearly there are numerous ways to achieve the same yield stress with these materials, and therefore designing with such materials is an inverse problem.

II. Background

A. Yield-stress fluids

Though it has been debated whether a “true” yield stress exists,^{8,22} yield-stress fluids are accepted as a practical reality, with definitions hinging on the critical value of stress that results in flow. Example definitions include: “[a yield-stress fluid] does not flow if the imposed stress is below a threshold value, but it can flow rather easily after this value is exceeded⁷”, and, “[a yield-stress fluid combines] solid-like behavior at low stresses with a fluid-like response at high stress.²³” The controversy over a “true” yield stress comes from observations of extremely slow flow below any critical stress value,⁸ however on the timescales of many applications this deformation is not significant.

Additionally, several reviews focus on the numerous ways a yield stress may be determined including steady flow tests, oscillatory shear tests, and compressional tests to name a few examples.^{9,11,24} Any yield stress value obtained is representative of a (typically narrow) range of stresses to induce a particular type of flow or irreversible deformation.

For this paper, parallel disk steady flow is used for characterization, with corrected shear-stress values as a function of shear rate (see Section SIII for more details, ESI†). By this method, we obtain the dynamic yield stress and the shear rate dependent flow behavior which is likely to be one of the most important secondary properties of interest. Equally important properties outside the scope of this work include critical yield strain and pre-yield modulus (oscillatory measurement), and static yield stress (creep, increasing shear rate flow tests).²²

B. Design process

In this section, we will briefly describe how we will map concepts from engineering design onto yield-stress fluids. A more thorough review of basic engineering design concepts is given in Section SII (ESI†). This work makes contributions to the concept development phase of design. While the downstream optimization and detail design phases are necessary, they are premature without first considering multiple concepts.

To set the stage for concept development, the functional requirements and target specifications of a material must first be described. Since functional requirements cannot specify a particular solution without imposing creativity-stifling restrictions,^{20,25,26} for the design of a yield-stress fluid, a poor functional requirement might be, “a polymeric network that flows under stress and reversibly solidifies at low stress” (particular material structure specified).

Using a suitable functional requirement (proposed in Section IIIA), a set of numerous possible concepts are obtained through surveying existing materials and through various brainstorming and ideation strategies. Methodologies for these processes build on approaches from lateral thinking²⁷ including generating potentially unfeasible concepts, and delaying concept evaluation to a later stage of the design. In this work, multiple

material structure concepts are considered as ways to achieve a particular rheological behavior, that of a yield-stress fluid. Numerous techniques exist for systematic concept generation; in this paper we use “categorization of concepts” (Section IIIA) and “juxtaposition” (Section IIIE), the latter involves combining two concepts to produce something new.²⁷ Following their generation, concepts would be evaluated for further development. For the design of complex fluids, concept evaluation often involves material formulation and rheological analysis. For more details on the generic design process and a brief example illustrating the importance of creativity and design from the field of mechanical (machine) design, please refer to Section SII in the ESI.†

C. Materials design approaches

The design process of concept generation (surveying and ideation) maps to material selection and material synthesis. For a new product or application, a material can either be selected from existing concepts or newly synthesized.

For materials that are not rheologically-complex, theories and methodologies of material selection have been well developed; the most influential methods are described by Ashby.²⁸ A flowchart depicting Ashby's selection process is shown in Fig. 2 with an example material-property co-plot. For this process, a far-reaching and robustly organized database of material properties is the required starting point; relevant constraints and rankings of suitability are then applied. This process has found great success for simple materials whose properties are scalar parameters (*e.g.* density, modulus), in contrast to the function-valued properties (material functions) that describe rheological behavior.

For rheologically-complex materials, material selection databases and design textbooks are completely absent (in the public domain), with the next best things being rheological modifier handbooks^{29,30} and material class specific texts.³¹ While useful, the available handbooks lack much of the needed information for effective, creative, rational design. The greatest inadequacy of such handbooks is the general failure to express or acknowledge

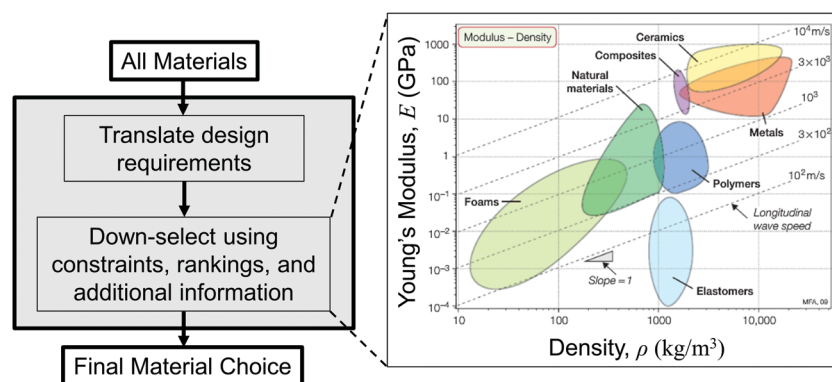


Fig. 2 Flowchart representation of material selection method (adapted from ref. 28). Starting from a database of all surveyed materials, design constraints and further research enable one to down-select to a final material choice. A common tool used in the down-selection process is the “Ashby diagram” (pictured from ref. 28), which is a material-property co-plot used to compare and show trends of multiple material properties across different material types. Rheological properties are challenging to visualize in this way when they are functions, rather than constants.

the function-valued nature of properties. As an example, though the ubiquity of yield-stress fluids has already been stated, available handbooks, Braun²⁹ and Ash,³⁰ only mention the phenomenon once out of all the numerous rheological modifiers they list, with Braun²⁹ providing only viscosity values at a single reference shear rate for particular weight percentages of additive (for a nonlinear viscoelastic material).

The lack of a database of rheological properties in the public domain has been identified previously, along with the necessity for a standard that these data sets conform to for facilitating comparison.³² There are several unique difficulties that must be addressed in establishing a more effective organization and design database for yield-stress fluids: (i) function-valued properties (*e.g.* no single value of viscosity exists), (ii) some rheological phenomena are not achieved by all materials (Fig. S1, ESI[†]), (iii) the conceptual model of a yield-stress fluid still being somewhat controversial as mentioned in Section IIIA. These issues are generally not present in solid materials which all have a basic set of simply-defined material properties such as density and Young's modulus.

There is an increasing interest in using inverse design methods to create materials that achieve functional requirements^{19,33–38} including a focus on properties which may be achieved by numerous formulations.¹⁸ Principles of material selection were applied by Ewoldt^{1,39} in designing a material for use in robotic adhesive locomotion; a minimum yield-stress was the primary design objective and a low post-yield viscosity at a reference shear rate was the secondary objective. This previous work is built upon with the specific contributions mentioned in Section I. By applying inverse design methods to rheologically-complex material properties we hope to enable more creativity for these materials, broadening the concept generation space before fixating on any particular structure. In this work, we explicitly state the fundamental strategies and methodologies known to exist for designing a yield-stress fluid, thereby forming an ontology and the basis for a database for the engineering of rheologically-complex materials.⁴⁰ We then demonstrate the usefulness of this ontology and database through several case studies.

III. Design methods for yield-stress fluids

A. Rheology-to-structure inverse problem & organization

There have been past attempts at categorizing yield-stress fluids based on the presence of a material restructuring time,²² the microscopic mechanism by which the yield stress emerges for certain particulate systems,⁷ and the concepts of glasses and gels,⁴¹ however none are from the perspective of design. To facilitate design, the typical perspective of structure-to-rheology must be flipped to a property-based rather than microstructure-based organization (Fig. S1, ESI[†]). This represents an ontology, or taxonomy, to organize design solutions for yield-stress fluids.

The first step to ideate the many possible ways to achieve a yield-stress fluid is to describe the desired functionality, or

functional requirements.^{25,42,43} As described in Section SII (ESI[†]), it is non-trivial to balance overly-narrow and overly-broad functional requirement descriptions to avoid unnecessarily limiting the possible design options. A good functional requirement contains only what is general and essential.⁴²

Existing functional requirement descriptions are available as definitions of a yield-stress fluid (quoted earlier in Section IIA). These definitions are well-crafted in that they are completely formulation- and structure-agnostic, not presupposing anything about the material and only describing behavior. However, we feel they can be too broad for design ideation, since there is no concept of reversibility or mechanical connectivity, concepts which may help focus creative ideation of new microstructure designs and avoid implausible solutions. For example, the phenomenological definition “[a material] that shows little or no deformation up to a certain level of stress [and] above this yield stress the material flows readily⁴⁴” lacks concepts of mechanical connectivity and reversibility. A formulation chemist might think to use entangled polymer solutions, but topological entanglements in solution do not bear static loads for long times, thus polymer solutions generally will not produce a yield stress fluid. Given a too-broad definition, one may also be limited to relying on only pre-existing lists of materials which, as discussed in Section IIC, are themselves sorely lacking.

We propose the following more precise functional requirement that includes the structural concept of mechanical connectivity, which is fundamental to yield-stress fluids:

A yield-stress fluid is able to bear a static load for long time-scales (suitably high viscosity at low stress) with mechanical connectivity that yields, flows (measured by a dramatic drop in viscosity above a characteristic yield stress), and is recoverable.

While somewhat long-winded to address the debated low-stress behavior, this newly proposed functional requirement provides physical insight into how one might achieve a yield-stress fluid in a precise way that is both formulation- and structure-agnostic, so as to not overly constrain the concept generation process. Rather than attempting to invent a way for viscosity to transition across multiple orders of magnitude, a designer can instead use intuition and experience about methods of bearing static loads that are able to reform after mechanical disruption. Additionally, after significant disruption by shear flow, some materials may show an increasing viscosity over time at low stresses,^{45,46} leading eventually to a stoppage of flow. To an observer it would be unclear if these materials are yield-stress fluids before the flow stoppage event. However, it is this signature of flow stopping for some finite applied stress (*i.e.* bearing a static load) that indicates that though the behavior of these materials is not that of an ideal yield-stress fluid, they are still yield-stress fluids. The buildup or recovery of this capacity to bear a static load is necessary for a material to be considered a yield-stress fluid. To be clear, by “recovery”, we are not referring to elastic strain recovery, but instead the ability to yield, flow, and recover a yield stress again, even if not the same yield stress as before.

For existing yield-stress fluids, there are two known mechanical interactions by which our proposed functional requirement is satisfied: (i) jammed, repulsive interactions; and (ii) networked,

attractive interactions. Of course, these may co-exist in complex systems. These concepts of arrested structures have been well developed as “glasses” and “gels” respectively,^{47,48} and have been used to organize certain yield-stress fluids in the context of particle sedimentation.⁴¹ Here we use this organization to provide insight into designing yield-stress fluids and to compare properties and behavioral trends across different microstructures.

Fig. 3 organizes yield-stress fluids based on the two mechanisms (or design strategies) of jammed *versus* networked microstructures. We use the term “repulsion-dominated” for materials where a static load is borne primarily by the microstructural elements jamming, pushing against nearest neighbors, with macroscopic yielding once the internal structure is able to rearrange and slide past itself to flow. Examples within this repulsion-dominated design strategy include suspensions of polymer microgel particles (*e.g.* suspensions of crosslinked polyacrylic acid (Carbomer)⁵⁵ or poly(*N*-isopropylacrylamide) (PNIPAm)⁵⁶), oil-in-water emulsions,^{57–62} and foams,^{51,57,62,63} which are each pictured in Fig. 3. Additional examples include spherical and star-like micelle solutions,^{64,65} suspensions of hard particles (colloidal^{66–68} and non-Brownian, athermal, granular matter^{69,70}), and suspensions of charged-particles, which are effectively jammed through electrostatic rather than steric repulsion.⁷¹ Though the chemistry varies widely within and across these material classes, yield-stress fluid behavior is caused by the same fundamental mechanism of effectively crowded microstructural elements interacting repulsively. As seen in the images in Fig. 3, morphologically these material classes are very similar. From these examples, one may ideate other possible materials that use this same mechanism. The characterized materials in this work that we will consider as “repulsion-dominated” are Carbopol 940 suspensions of swollen microgel particles that are jammed at sufficiently high

concentrations,⁵⁵ and silicone oil-in-water and mineral oil-in-water emulsions.

We call the second design strategy in our taxonomy “attraction-dominated”, meaning materials where a static load is borne primarily by attractive mechanical connectivity (*i.e.* pulling on nearest neighbors). Attraction-dominated microstructures resist being pulled apart, eventually yielding once these re-formable attractions have been broken. Examples within this group include particulate gels (*e.g.* colloidal clays Bentonite^{22,72–74} and LAPONITE[®]^{75–77}), magneto- and electro-rheological fluids,^{14,15,53,78–80} and fibrillar or polymer solutions that have physical crosslinks that can re-form after rupture (in contrast to covalent or non-recoverable crosslinks).^{41,54,81–85} Morphologically, material microstructures within this group typically are a sparse percolated network spanning the sample that must be destroyed for yielded flow to occur. The characterized materials in this work that we will consider as “attraction-dominated” are suspensions of Bentonite and LAPONITE[®] colloidal clay particles that can attractively interact,²² and xanthan gum which forms structure through self-associative intermolecular attractions.⁸¹

For both of these design strategies, the “-dominated” qualifier has been used to acknowledge that combinations of both mechanisms are possible, such as attractive glasses.⁴⁷ Note that both the repulsion-dominated and attraction-dominated categories are capable of including materials that may have very similar ingredients. For instance, colloidal suspensions can exist as either glasses or gels^{76,86} and thus this structural organization transcends the traditional academic organization by ingredient such as by “particle” *versus* “polymer”.

For material selection, the creation of any material property database is hindered by the fact that not all materials will have all properties. Rather than needing to laboriously characterize the hundreds of entries in a rheological modifiers handbook, one can instead consider if the modifier might possibly satisfy the functional requirement and only characterize those expected to have a yield stress. While mistakes will most certainly be made in this process, *e.g.* materials anticipated to have a yield stress will show no such signature or materials that do have a yield stress may be overlooked, it will be far less onerous and implausible than characterizing every possible formulation of every ingredient hoping to see a particular signature.

With our proposed functional requirement and the resulting classification tree, the material design methodologies of both selection and synthesis are greatly facilitated. Selection strategies benefit by being able to effectively generate lists of existing (but perhaps not relevantly analyzed) candidate materials to choose from, as well as insights into the comparative relations between material classes. With an adequate functional requirement, creative synthesis based on physical insight can occur, with the classification tree allowing for ideation through structured concept generation.

B. Yield stress scaling behavior

When evaluating and comparing concepts, an important aspect to consider is the degree of available predictive analysis. For

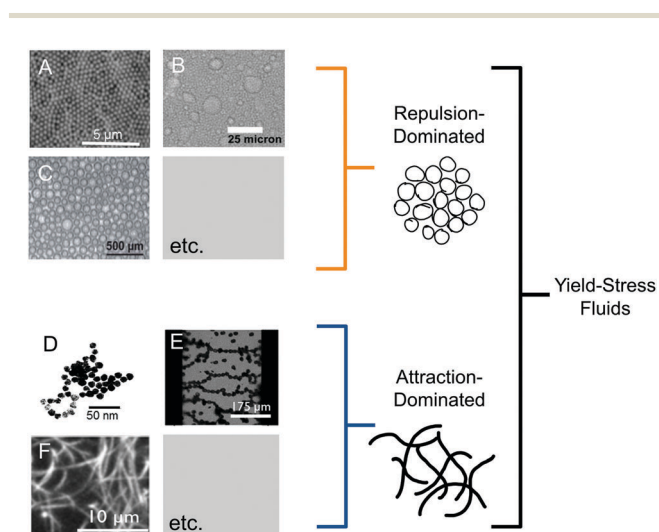


Fig. 3 Organization of design strategies aids in concept generation, for both existing and new materials. For yield-stress fluid design, two generic strategies can be grouped as ‘repulsion-dominated’ and ‘attraction-dominated’ (although combinations also exist, *e.g.* attractive glasses). Examples shown are (A) particulate suspensions,⁴⁹ (B) emulsions,⁵⁰ (C) foams,⁵¹ (D) particulate gels,⁵² (E) electro/magneto-rheological fluids,⁵³ and (F) fiber gels.⁵⁴

example, deterministic models greatly facilitate phases of the design process involving prototyping and testing.⁴³ Models allowing for predictive analysis for yield-stress fluids are reviewed in this paper, but the further downstream phases of the design process are not. The full scientific understanding of all material structures currently known to produce a yield-stress is underdeveloped due to the complexity of calculating macroscopic properties from the underlying microstructure and molecular features. In contrast to complex fluids, developed areas of mechanical design have very clear mathematical models to represent system behavior (*e.g.* stress fields in solid bodies, linkage dynamics, *etc.*).

A unique aspect of material synthesis for rheological properties is that governing equations are not always known. In the specific case of yield-stress fluids, if any predictive equations are available, they are often scaling laws that relate the yield stress to underlying structure. Available scaling laws for yield-stress fluids are collected in Table 1. While the large variety of model structures of the collected scaling relationships makes it clear that any sort of universal scaling law for a wide range of materials is still a monumental undertaking, general guidelines are still available by using these relationships. Between two otherwise comparable concepts, one would prefer a concept with a readily available predictive scaling law. Thus, this table is useful for the evaluation of concepts and can demonstrate the feasibility of a concept to achieve a particular performance. While not the focus of this paper, these scaling laws are eminently useful further downstream in the design process when attempting to determine final formulations in the system-level and detail design phases. Additionally, all of the listed scaling laws are for the single parameter of the yield stress; predictive structure-rheology equations for entire flow curves are even more difficult to formulate, though in a few cases they do exist.⁶¹

Most of the presented structure-rheology scaling relationships involve the volume fraction of some dispersed phase of the material, however oftentimes in formulation it is much easier to control the weight-percentage of an additive rather than its volume. Carbopol 940 has specific scaling equations obtained by correlation with many different experimental studies

to relate the weight-percentage of additive, C , directly to the yield stress for two different concentration regimes,⁵⁵

$$\sigma_Y = \left(\frac{C}{0.0335} - 1 \right)^3 \quad (9)$$

$$\sigma_Y = 45 \left(\frac{C}{0.124} \right)^{1/3} \quad (10)$$

These correlation formulae agree reasonably well with our experimental results for Carbopol, seen in Fig. 4 alongside the other tested material systems. The weight-percentage of additive is often of great importance when designing a completely new material or modifying an existing material to give it a yield stress.

To the authors' knowledge, the considered material systems besides Carbopol do not have yield stress data organized in the open literature in such a way as to form concentration scaling relationships, except that some type of power law dependence occurs close to a jamming transition. The yield stress of xanthan gum solutions scales approximately linearly with concentration, while the yield stresses of the two-other attraction-dominated systems, Bentonite and LAPONITE[®], have power law slopes of approximately three and nine respectively. The yield stresses of jammed emulsions have the strongest dependence on weight-percentage, with power law slopes of between twelve and fifteen.

Typically, a low percentage of additive is desirable, since it will be less costly and less likely to modify other properties, such as the flavor and texture of food products. Based on the classification tree of yield-stress fluids we can see that the networked, attractive systems achieve yield stresses at moderate values of weight-percentage, while both jammed, repulsive emulsions require a significant percentage of added-oil for comparable yield stress values. The swollen nature of the Carbopol microgels are what result in such a low weight-percentage of additive giving rise to a jammed yield-stress fluid; this is the reason that Carbopol is considered a "high-efficiency" rheological modifier.²⁹ Obviously, there are endless parameters and material properties that might be crucial for

Table 1 Structure-rheology scaling relationships and equations for yield-stress fluid material classes. These relationships are useful for concept evaluation and synthesis as they allow one to predict the resulting yield-stress to varying degrees. See Table 2 for the definitions of all variables

Material class	Scaling relationship	(Eqn #)	Notes
Hard spheres ⁸⁷	$\sigma_Y = \sigma_{\text{crit}} + 112\sqrt{\phi - \phi_{\text{crit}}}$	(1)	$\phi > \phi_{\text{crit}}$
Charged particles ⁸⁸	$\sigma_Y \approx K \left(\frac{W(r_m) - k_B T}{(r_m/2)^3} \right)$	(2)	$r_m < d_{\text{eff}}$ $K = \text{constant}$
Soft particles ⁶¹	See reference		
Emulsions and foams ⁵⁷	$\sigma_Y = \frac{\Gamma}{R_{\text{mean}}} \phi^{1/3} Y(\phi)$	(3)	$\phi > 0.9069$
Particulate gels ⁸⁹	$\sigma_Y \sim \frac{\phi^2}{a^2} W'_{\text{max}}$	(4)	$\phi < 0.64$
Electrorheological fluids ⁷⁸	$\sigma_Y \sim \phi \epsilon_0 \epsilon_s \beta^2 E^2 f_{\text{max}}$	(5)	
Magnetorheological fluids ⁸⁰	$\sigma_Y \sim H^2$	(6)	Low field strength
	$\sigma_Y = \sqrt{6} \phi \mu_0 M_S^{1/2} H^{3/2}$	(7)	Intermediate field strength
	$\sigma_Y^{\text{sat}} = 0.086 \phi \mu_0 M_S^2$	(8)	Fully-saturated induced dipoles

Table 2 Variable definitions for yield stress scaling relationships. Note: F indicates units of force, L units of length, A units of electrical current, t units of time

Variable	Definition
$\phi_{\text{crit}} \doteq [-]$	Critical volume fraction for yield stress scaling to apply
$\sigma_{\text{crit}} \doteq \left[\frac{F}{L^2} \right]$	Yield stress at critical volume fraction
$W(r_m) \doteq [FL]$	Interaction potential at average interparticle separation
$d_{\text{eff}} \doteq [L]$	Effective diameter of particle, where $W(r = d_{\text{eff}}) \approx k_B T$
$\Gamma \doteq [F/L]$	Surface tension
$R_{\text{mean}} \doteq [L]$	Sauter mean radius, $R_{\text{mean}} = 3 \frac{\text{Volume}}{\text{Surface area}}$
$Y(\phi) \doteq [-]$	Scaled contribution per drop to yield stress, $Y(\phi) = -0.08 - 0.114 \log(1 - \phi)$
$a \doteq [L]$	Particle radius
$W'_{\text{max}} \doteq [F]$	Maximum spatial gradient of interaction potential
$\epsilon_0 \doteq \left[\frac{(At)^2}{FL} \right]$	Permittivity of free space
$\epsilon_s \doteq [-]$	Relative permittivity of solvent
$\beta \doteq [-]$	Effective polarizability of particle
$E \doteq \left[\frac{F}{At} \right]$	Electric field strength
$f_{\text{max}} \doteq [-]$	Maximum dimensionless restoring force between particles
$H \doteq \left[\frac{A}{L} \right]$	Magnetic field strength
$M_S \doteq \left[\frac{A}{L} \right]$	Saturated magnetic field strength
$\mu_0 \doteq \left[\frac{F}{A^2} \right]$	Permeability of free space

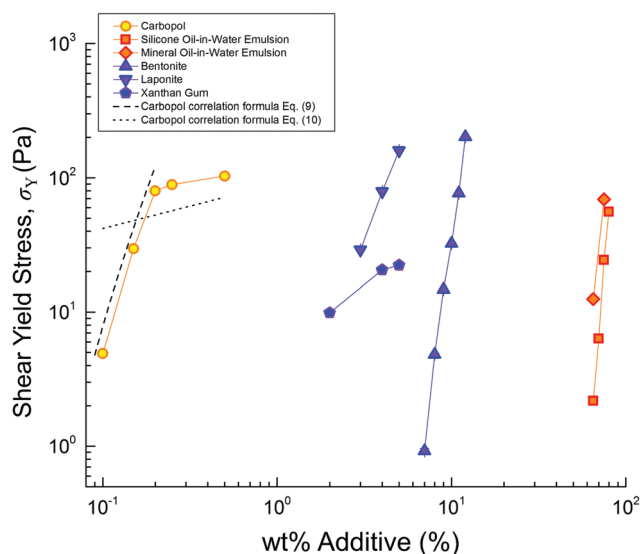


Fig. 4 Shear yield stress versus wt% additive. Percentage of additive, and constraints thereof, is often crucial for achieving design targets. Each data point represents a steady shear flow curve. See ESI† for full steady shear flow data at multiple gaps used for this plot.

one's application such as transparency and other optical properties, conductivity, biocompatibility, and biodegradability. In the next section, we will consider rheological properties beyond the yield

stress by introducing representations of the steady flow behavior to enable the application of material selection principles to function-valued properties.

C. Low-dimensional descriptions for selection of yield-stress fluids

Since a particular value of yield stress can be achieved by multiple materials, applying additional design constraints on secondary parameters or properties is a critical step in converging on a final design choice in a rational, non-arbitrary way. However, due to the function-valued nature of rheologically-complex material properties, low-dimensional representations are necessary for their easy comparison. Fig. S5 (ESI†) shows the full flow curves of all materials measured here and demonstrates how infeasible the rational selection of one particular material would be without using a low-dimensional representation. Of course, information is always lost when representing complicated data in a low-dimensional way. Here we will consider different models which communicate information to varying degrees of completeness and discuss the situations in which the loss of information can be acceptable.

The most common models for yield-stress fluids are the three-parameter Herschel–Bulkley model and two-parameter Bingham model. The Herschel–Bulkley model is typically written as,

$$\sigma = \sigma_Y + K\dot{\gamma}^n \quad (11)$$

which we prefer to re-write as,

$$\sigma = \sigma_Y \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_{\text{critical}}} \right)^n \right]. \quad (12)$$

This updated representation of the Herschel–Bulkley model is better for design comparisons because the dimensions are fixed for all parameters, independent of other parameter values. It results in the parameter $\dot{\gamma}_{\text{critical}}$ that is physically meaningful as a critical shear rate at which the flow stress is twice the value of the yield stress, σ_Y . This physical intuition is desirable compared to the parameter K , which has units that depend on the parameter n . To convert from K , one may use the equation, $\dot{\gamma}_{\text{critical}} = (\sigma_Y/K)^{1/n}$. Unless otherwise specified, our reported values of a material's yield-stress were taken from the Herschel–Bulkley model fit, but the widely-used Bingham model was also fit for comparison. The two-parameter Bingham model which fits the yield stress and infinite shear viscosity, η_∞ , is

$$\sigma = \sigma_Y + \eta_\infty \dot{\gamma}. \quad (13)$$

Shown in Fig. 5 are three possible low-dimensional descriptions of the steady flow behavior of a yield-stress fluid: two values of shear stress (the yield-stress parameter from the Herschel–Bulkley model and the stress at a reference shear rate); the Bingham model, eqn (13); and the Herschel–Bulkley model, eqn (12). Clearly the reference-shear-rate representation loses a significant amount of information about the flow curve, though it has been used when selecting for minimum

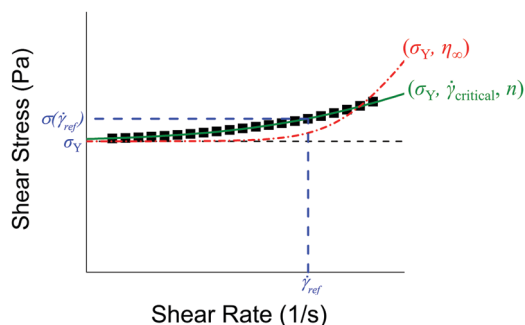


Fig. 5 Low-dimensional representations of function-valued rheological data; here, a steady flow curve. Low-dimensional descriptions are required for easy comparison of materials when selecting or evaluating with Ashby-style diagrams. More accurate representations can come at the cost of decreased physical meaning and added complexity. Here, three possible representations of a yield-stress fluid are shown: (blue dashed) two stress values, the yield stress and the stress at some reference shear-rate; (red dash-dot) the two-parameter Bingham model; and (green solid) the three-parameter Herschel–Bulkley model. (Data is the same as in Fig. S3 (ESI†)).

rheological criteria.³⁹ Our work focuses on the Bingham and Herschel–Bulkley model representations since they preserve substantially more information (see ESI† for discussion of the reference-shear-rate representations). In most cases, the two-parameter Bingham representation can do a reasonable job of capturing the yield stress and the high shear-rate viscosity; it has been useful as the simplest model interpretation and for obtaining a successful dimensionless group to characterize droplet impact of yield-stress fluids.⁹⁰ However, the Bingham model can completely miss information regarding intermediate shear rates for materials shown here, and so in most cases for an accurate representation of the entire flow-curve a model with more parameters, such as Herschel–Bulkley, is necessary; this of course comes at the cost of added complexity (higher-dimensional co-plots) and may result in decreased physical meaning. In the case of the model reformat shown in eqn (12), this latter issue is limited to the interpretation of parameter n , which we interpret as the degree to which a material shear-thickens for $n > 1$ or shear-thins for $n < 1$.

Of course, the Bingham and Herschel–Bulkley models are not without limitations. These models are the most common yield-stress fluid models not because they explain the greatest number of complex phenomena, but because they can accurately describe the representative steady shear flow behavior of a large number of yield-stress fluids across a wide range of experimental conditions. Phenomena that the structure of these models obviously cannot describe include pre-yield flow behavior,⁸ sample aging and time-dependent properties,⁹¹ and the effect of flow history including non-monotonic flow curves.^{9,46} Models that describe these phenomena may be important but are far outside the scope of the present work.

As the starting point for a design database, we require a model that gives a reasonable representation of a wide variety of materials at the time of characterization with physically meaningful parameters. As will be discussed in Section IIID, the characterized flow curves are well represented by the

Herschel–Bulkley model. Regarding the effects of aging and flow history, in the worst case scenario, a material could completely lose a yield stress that is recoverable.⁹² In the best case, the yield stress could change over some definable range greater than zero. Similarly, some yield stress fluids are thermodynamically unstable and at long times can lose their yield stress.^{57,63} This does not mean that simple yield-stress fluid models are irrelevant to the description of these materials, it means that when using these models, one must be rigorous in reporting the characterization methodology and time of characterization relative to formulation. In an ideal scenario, the relative time of characterization and application will match. However, if this is not the case, a designer must take into account the time-dependent nature of the materials. Perhaps someday there will be a universal constitutive model that describes all the possible phenomena of all materials capable of apparent yield-stress behavior for any flow history and at any time after formulation only using physically meaningful parameters. However, in order to facilitate the development of a useful design database today, we are required to use simpler models. As previously stated, these simple models of yield-stress fluid behavior have already been demonstrated sufficient in modeling or helping solve real design problems such as enabling adhesive locomotion,³⁹ tuning droplet impact behavior,^{90,93} controlling droplet shape for some yield-stress fluids,^{94,95} and creating field-responsive dampers.⁹⁶ For these and many other situations, the considered models are representative of the behavior in application of many materials, and more complex models are not always necessary.

Low-dimensional descriptions will be relevant for other function-valued rheological properties, beyond just yield-stress fluids, including linear viscoelastic functions such as the relaxation modulus.⁹⁷ Whatever the degree of the low-dimensionality, visualization of the property values will be a relevant question, which we consider in the following section.

D. Visualizing secondary properties

As stated previously, for applications involving yield-stress fluids, the yield stress will most likely be the primary design objective and there is no end to the number of secondary design objectives one might consider. For example, secondary objectives might be material properties such as viscosity, or linear storage modulus, G' ; they might be features such as necessary weight-percentage of additive, or cost of material; or even the presence (or absence) of non-ideal behavior such as fatigue, non-homogeneous yielding, or ductile *versus* brittle yielding.^{7,98,99} The characterization and representation of these properties and effects will be key to the development of a useful design database, however those properties and many others are outside the scope of this work. Rather, we focus on the challenges in representing the steady flow behavior, which is likely to be—but not necessarily—one's most important secondary objective.

Shown in Fig. 6A is the comparative plot of the parameters from the Bingham model fit (eqn (13)), the simplest whole-curve representation of a yield-stress fluid (full flow curves

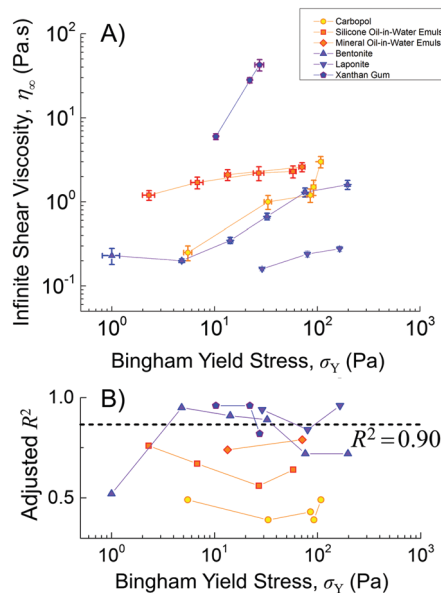


Fig. 6 (A) Ashby-style co-plot of the two-parameter Bingham model description of archetypal yield-stress fluids, $\sigma = \sigma_Y + \eta_\infty \dot{\gamma}$ (cf. Fig. 5, red dash-dot line). (B) Adjusted coefficient of determination from model fitting with variance weighting. See ESI† for the full steady shear flow data which these Bingham parameters describe, verified by testing at multiple gaps. Uncertainty bars indicate the standard error of the parameters from fitting.

shown in ESI†). Important insights into designing new materials can be obtained from the comparison of the trends and regions of the Bingham model parameters of different materials. Until such time as every yield-stress fluid one could possibly want has already been made and characterized, people will always need to try to expand the performance limits of materials; the scaling behaviors and inhabited regions give an idea of what material concepts are likely to be successful strategies when expanding the parameter space. For example, in Fig. 6A both oil-in-water emulsions show the interesting scaling behavior of the infinite shear viscosity, η_∞ , being nearly flat, varying by less than half an order of magnitude, across one-and-a-half orders of magnitude in yield stress, σ_Y . Therefore, one can expect that if one wanted to design a material with an increased yield stress without substantially increasing the high-shear-rate viscosity, an oil-in-water emulsion would be one possible candidate for doing so. Studying the reason for this (analysis of materials, Fig. 1) could lead to other design concepts for achieving this. Similarly, due to the region they inhabit, one can infer that particulate gel systems will have the lowest viscosities at high shear rates.

The simplicity of interpreting the Bingham model comes at the cost of accuracy; the adjusted R^2 values of the model fits are shown in Fig. 6B and indicate that for many materials the Bingham model can be unacceptably inaccurate and thus the three-parameter Herschel–Bulkley model (eqn (12)) is next considered.

The Herschel–Bulkley model fit results in the parameters shown in Fig. 7A with the adjusted R^2 values shown in Fig. 7B indicating a minimum adjusted R^2 value of 0.90. The added complexity of this representation is immediately apparent in

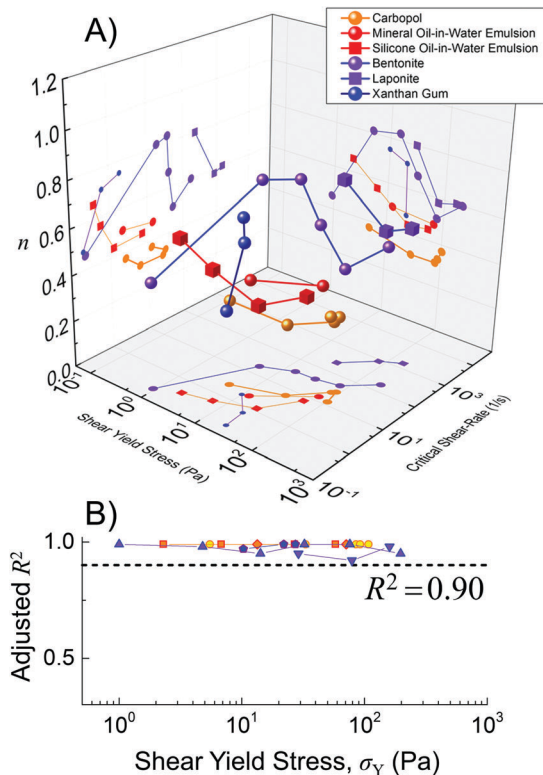


Fig. 7 (A) Ashby-style co-plots of design-appropriate three-parameter Herschel–Bulkley model descriptions of archetypal yield-stress fluids, eqn (12). (cf. Fig. 5, green solid line). Shaded 2-D projections shown in detail in Fig. 8. (B) Adjusted coefficient of determination from model fitting with variance weighting (same symbol labeling as Fig. 6). See ESI† for the full steady shear flow data which these Herschel–Bulkley parameters describe, verified by testing at multiple gaps.

that three separate comparative plot projections are necessary to see the full relationships between fit parameters. In some cases, it is unclear if any meaningful relation can be determined such as in the plot of n versus critical shear rate, where the parameter curves of some materials are non-monotonic, bending back around on themselves with varying concentration. In such a case, this behavior may be more indicative of a region of the property space that a material tends to inhabit, rather than any sort of scaling relationship. Here we will only comment on the behaviors of $\dot{\gamma}_{\text{critical}}$ and n versus σ_Y shown in Fig. 8A and B respectively. Even considering only these two projections, we are still afforded great insight into how the materials will behave across a wide range of shear rates without needing to see the material flow curves at all, and this with just a three-parameter fit.

Starting with Fig. 8A, the critical shear rate, $\dot{\gamma}_{\text{critical}}$, allows us to determine when the flow stress will deviate from the yield stress by a factor of one-hundred percent. The approximate range of critical shear rates for measured systems is $0.2 \leq \dot{\gamma}_{\text{critical}} \leq 3000 \text{ s}^{-1}$ with oil-in-water emulsions having very low values of critical shear rate, followed by Carbopol, then by the particulate gel systems. These trends in critical shear rate can be confirmed by directly examining the full data in Fig. S4 (ESI†), that shows Bentonite and LAPONITE® have comparatively flat

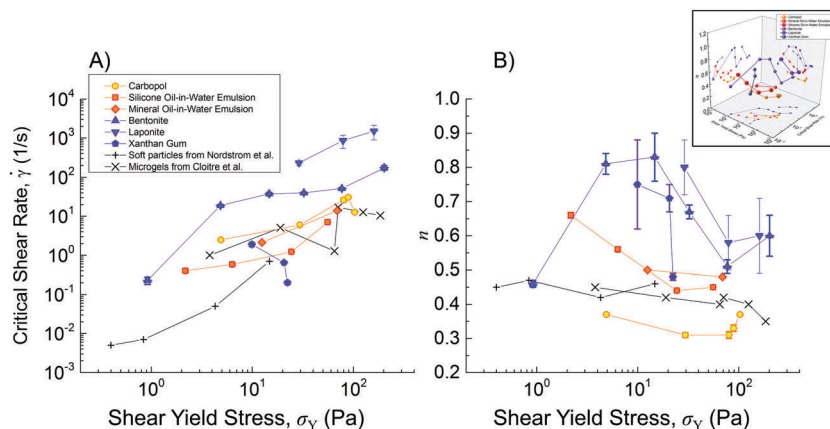


Fig. 8 Detailed projections of Ashby-style co-plot from Fig. 7. See ESI[†], Nordstrom *et al.*,¹⁰⁰ and Cloitre *et al.*¹⁰¹ for the full steady shear flow data which these Herschel–Bulkley parameters describe. Uncertainty bars indicate the standard error of the parameters from fitting (error bars for data from ref. 100 and 101 are smaller than symbol size and are omitted for clarity).

flow curves. Using Fig. 8B, one can also anticipate even more features of the sensitivity of the flow stresses to applied shear rate. As seen in Fig. 8B, all the Bentonite samples have values of n that are significantly higher than the Carbopol samples. Per eqn (12), what this means is that while the Bentonite flow curves are flatter than the Carbopol flow curves for $\dot{\gamma} < \dot{\gamma}_{\text{critical}}$, above $\dot{\gamma}_{\text{critical}}$ the Bentonite flow stresses will increase significantly faster than Carbopol.

Fig. 8B showcases differentiation of the materials correlating with the classification tree (Fig. 3); systems with networked attractions have higher values of n that vary significantly with the yield stress, while the repulsive jammed systems have lower values of n that are much flatter as the yield stress is varied. Taken together, Fig. 8A and B allow one to make qualitative comparative statements on the behavior of the material classes. For example, the resultant stress on the networked systems will increase as a function of shear-rate much more strongly than for the jammed systems, but the stress to flow the jammed systems will typically deviate from the yield stress earlier (excepting xanthan gum). A simple case study of how these property spaces might be used is presented in Section IV A.

This initial database can be continually grown by fitting the proposed Herschel–Bulkley model in eqn (12) to new and existing published data, as was done in Fig. 8A and B with other published data.^{100,101} As the database grows, the broader possibilities of material behavior are immediately apparent. For example, though many studies consider only $n = 0.5$,^{57,61,62,100} this assumption is shown to only apply to a limited subset of the yield-stress fluids shown here.

It is important to note that these comparative co-plots with the Herschel–Bulkley model are only possible due to the re-write of the model seen in eqn (12); the parameter K in the traditional Herschel–Bulkley model (eqn (11)) cannot be used in co-plots as K changes units as a function of the n parameter. These qualitative comparisons come in addition to being able to accurately reproduce the complete flow curve for a wide range of shear rates if one's application dictates it since all the necessary parameters are specified. All the reported fit

parameters are available in the ESI[†] that the authors invite others to add to.

E. Synthesis approaches for yield-stress fluids

In addition to the physical insight afforded by our functional requirement (Section III A), which is crucial to successfully ideate new material concepts, the classification tree (Fig. 3) allows for a systematic framework for concept generation and further organization and understanding of existing materials.

Here we present one possible strategy for ideating new design concepts, a vision for the future design of yield-stress fluids. Shown in Fig. 9 is a visualization of a juxtaposition/combination concept generation process (a known design methodology^{27,102}) applied to material microstructures that can achieve a yield stress. This framework organizes ideated combinations of two individual material classes with representative classes pictured. In Fig. 9, the general state of knowledge for each entry is indicated in the matrix. Each entry will be referred to using “(row, column)” notation with each grey square representing an individual material class using the same A–F notation as in Fig. 3. Combinations of microstructures exist off-diagonal and include studied materials, as in the case of a mixture of a magnetorheological fluid and fibrillar gel (grease),⁷⁹ and material structures that have never been described in the open literature to the authors' knowledge. Of course, any particular combination is subject to the constraints of chemical compatibility or the ability to actually synthesize the material. Additionally, just as in mechanical design, a conceptual combination in no way assures that the functional specifications will be met, but it does broaden the available possibilities.

Though many of the presented juxtapositions in Fig. 9 at first glance may not necessarily suggest any additional benefit over others, this method is a quick and simple way of generating a very large number of possible ideas. In fact, many of the combinations in Fig. 9 are being studied because they are either scientifically interesting, have novel properties, or both. For example, a combination of particulates and emulsion droplets,

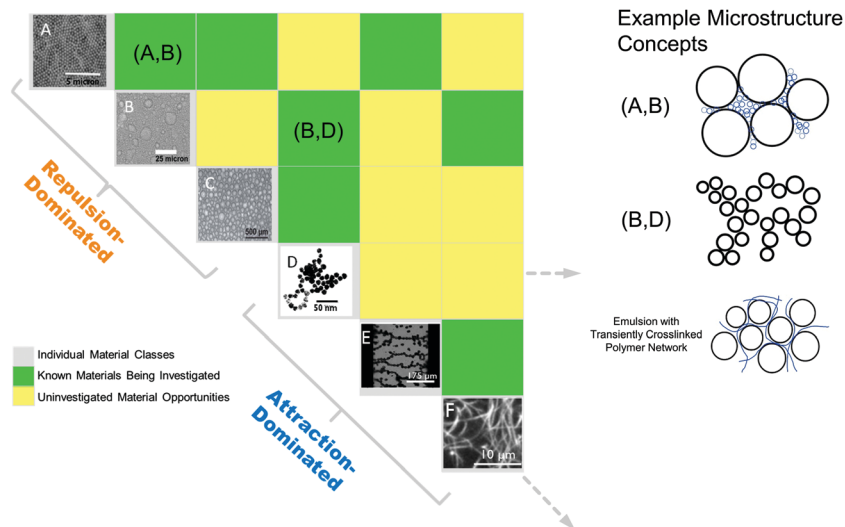


Fig. 9 One possible concept generation strategy for material microstructures and combinations thereof. Each entry on the diagonal (same labeling as Fig. 3, (A) particulate suspensions,⁴⁹ (B) emulsions,⁵⁰ (C) foams,⁵¹ (D) particulate gels,⁵² (E) electro/magneto-rheological fluids,⁵³ and (F) fiber gels⁵⁴) represents an individual material class and serves as a label for off-diagonal combinations. Off-diagonal entries represent combinations of microstructures. Two example combinations are shown schematically: (A and B), a particulate suspension as the interstitial fluid in an emulsion; and (B and D), emulsified droplets networked in a structure similar to a particulate gel. A combination of an emulsion with a microstructure with no yield-stress, a transiently crosslinked polymer network, is shown on the right.

as pictures in (A and B) is being investigated in the form of bimodal dispersions of starch and fat droplets.¹⁰³ Microgels made field-responsive would correspond to (A and E).¹⁰⁴ Entry (C and D) applies to whipped cream which can be conceptualized as a foam stabilized by a particulate gel network.¹⁰⁵ Entries on this juxtaposition table are not limited to a single incarnation. For example, entry (A and C) could describe a foam stabilized by a crowded colloidal suspension,¹⁰⁶ or a particulate suspension that has been foamed as in the case of foamed concrete.¹⁰⁷

Composite microstructures appearing very recently in scientific literature include photocrosslinkable nanoemulsions which fall into the category of emulsion gels (B and D),^{108,109} and nanoparticle solutions used as an adhesive between polymer gels.¹¹⁰ The latter concept is not pictured but can be conceptualized as a composite of particulate and polymer gels. Other composite materials not pictured include field-responsive polymer gels¹⁰⁴ and yogurt, which is a combination of a polymer gel and an emulsion.¹⁰⁵ Of course, in juxtaposition, one is not limited only to combining two yield-stress fluid concepts. For example, ice cream might be conceptualized not as a combination of two concepts, but three: a foam, an emulsion, and a jammed particulate suspension.¹⁰⁵ Using the technique of juxtaposition, one could combine any number of concepts, or perhaps combine a yield-stress fluid concept with a structure that would have no yield stress, but attains a different rheological function. An example of the usefulness of this juxtaposition process is provided in the next section on case studies.

IV. Case studies

Here we demonstrate the usefulness of our proposed paradigm through two simple design problems that make use of the different methods presented in Section III.

A. Case study 1: yield-stress fluid adhesive design (material selection)

This design problem is to constrain one surface to another. Additional context for this type of problem in mechanical design is given in Section SIIB (ESI[†]). Here we will assume the following requirements as our “customer needs” (Fig. 1B, step 1): the surfaces must resist a peak separating force of at least 8 Newtons (for context, approximately the weight of a piñata filled with candy), one of the surfaces is a semi-infinite flat plate that cannot be modified (no permanent deformation), the surfaces must be separable without destroying either surface. Of the (limited) concepts discussed in Fig. S2 (ESI[†]), typical solutions to this problem such as mechanically separable fasteners and welding are unable to satisfy all design constraints, leaving us with the strategy of using an adhesive. The use of yield-stress fluids as adhesives has been investigated,^{111–113} and for obvious reasons we will limit our consideration of this problem to yield-stress fluids.

Derks *et al.*¹¹¹ derived the following equation for the peak adhesive force for an incompressible yield-stress fluid between circular flat surfaces for small gaps (shear-dominated deformation) at very low shear rates,

$$F_{\text{Peak}} = \frac{2}{3} \sigma_Y (\pi R_0^2) \left(\frac{R_0}{D_0} \right) \quad (14)$$

for surface radius, R_0 , and initial gap height, D_0 . This equation was validated using a material with behavior well described by Herschel–Bulkley model parameters. Thus, this simple model (that neglects thixotropy and many other phenomena) is entirely sufficient for this design problem provided the properties at the time of characterization are representative of the properties at the time of use.

Whether a static or a dynamic yield-stress is more relevant for this particular design problem is entirely dependent on unspecified details of the application. However, it is nearly always the case that a static yield stress will be greater than or equal to the dynamic yield stress. Given the vague nature of this (and many) design problems, since our primary design objective translates only to a minimum yield-stress, it is prudent to use the dynamic yield stress regardless of which yield stress is closer to application conditions.

Choosing for now that the radius of the circular surface and initial gap height are to be 27 and 0.5 millimeters, respectively, solving for σ_Y gives us approximately 100 Pa as our minimum yield stress target specification (Fig. 1B, step 2). Consulting Fig. 4 to generate product concepts from the limited number of formulations presented here (Fig. 1B, step 3), there are 3 materials for us to choose from: 0.5 wt% Carbopol, 12 wt% Bentonite, and 5 wt% LAPONITE[®]. With multiple materials satisfying our primary design objective, we could stop our design process here and select all 3 formulations as candidates to formulate and validate in application, however this would be premature since we have yet to consider any secondary properties. Additionally, the geometry here was chosen simply for demonstrative purposes. For a situation where the surface radius is 40 millimeters, the minimum yield stress would be approximately 30 Pa, and the number of candidate materials increases four-fold to 12. Thus, it is easy to see how a more open-ended design, as well as a larger database, quickly lead to situations where it is impractical to compare, formulate, and test all material concepts, and therefore secondary properties are necessary to down-select to materials more likely to be best (see also Fig. S5, ESI[†]).

Eqn (14) was derived assuming low shear rates, and therefore the peak force only depends on the yield stress value and not the flow behavior. However, if yielding and larger shear rates were to occur in application, a material with a strongly increasing stress response would lower the risk of catastrophic debonding. Thus, we can use sensitivity of the flow curve as a measure of the robustness of the material, and rank the suitability of the 3 candidate materials. In terms of the parameters we have characterized, a material with a lower $\dot{\gamma}_{\text{critical}}$ has a more sensitive flow curve. Of less importance here, a higher value of n contributes to a more sharply increasing flow curve after $\dot{\gamma}_{\text{critical}}$ and could be used as an additional ranking index were two materials to have the same critical shear rate. In general, the decision of which parameter is more important depends on the details of the functional requirements and application conditions.

Consulting Fig. 8A to select our product concepts (Fig. 1B, step 4), we are seeking a material in the lower-right portion of this plot. Ranking the three formulations that meet the minimum yield stress requirement, Carbopol has the lowest critical shear rate, followed by Bentonite, with LAPONITE[®] in last. While the number of materials a designer selects to move on to downstream design processes can be subjective, this ranking of suitability based on secondary criteria is not dependent on designer input. Should these materials fail in the concept

testing phase (e.g. due to non-ideal conditions), a designer could use the scaling behavior seen in Fig. 4 and 8 to predict how more concentrated formulations might behave in further tests. Additionally, if there is need to look beyond the current set of known materials, surveying using only a rheological modifiers hand-book or similar tool would be an overwhelming process given the issues discussed in Section IIC. If this is the case, the functional requirement and organization presented in Section IIIA can be used to select candidate materials based on anticipated microstructure rather than ingredient.

Of course, this simplified down-selection process was performed only with the available parameter space. Secondary properties of interest that may affect performance for this particular design that are outside the scope of this work include pre-yield (ultra-low shear rate) viscosity and aging behavior if the adhesive is to be used for long times, thixotropic restructuring times that will affect the initial adhesion process, and pre-yield modulus that will dictate how well the material adheres to a rough surface similar to the Dahlquist criterion.¹¹⁴ This is not to say that we should be paralyzed and rendered impotent in our design process due to our lack of description of all possible properties and phenomena. Relevant and meaningful decisions can still be made using the simplified—but still representative—descriptions that are present in this initial work.

B. Case study 2: extensible yield-stress fluid design (material concept synthesis)

Obtaining a highly-extensible yield-stress fluid is the second design problem case study. The motivation for this design target is the subject of work in preparation,^{115,116} but we briefly describe a portion of the work here as an example of the presented design paradigm, specifically the juxtaposition process (Section IIIE). For the materials formulated here, the characterized shear data does not necessarily allow one to draw any conclusions about “stretchability”. However, extending these materials between one’s thumb and index finger suggests they are generally incapable of stretching to a length comparable to materials such as the bubble gum in Fig. 10B. High extensibility of materials is known to be important for sensory characteristics for foods including bubble gum.¹¹⁷ It has also been conjectured that high extensibility stabilizes a filament extrusion process such as in direct-write 3D printing.^{116,118}

We have no options from our surveyed concepts capable of satisfying our qualitative target specifications, and chose to generate a set of new concepts using the process detailed in Section IIIE (Fig. 1B, step 3). To be explicit, we carried out this process to ideate numerous concepts that we could choose to develop based on qualitative arguments of suitability. At this very early phase of the design process (Fig. 1B), we were not seeking to evaluate the feasibility of formulation, we were not seeking a list of chemicals that could be used to make such a material, and we certainly were not seeking to generate constitutive models to predict the properties of completely new concepts for materials. This last task in particular is not feasible during a typical design process given that a model for a radically new material cannot be validated until after the

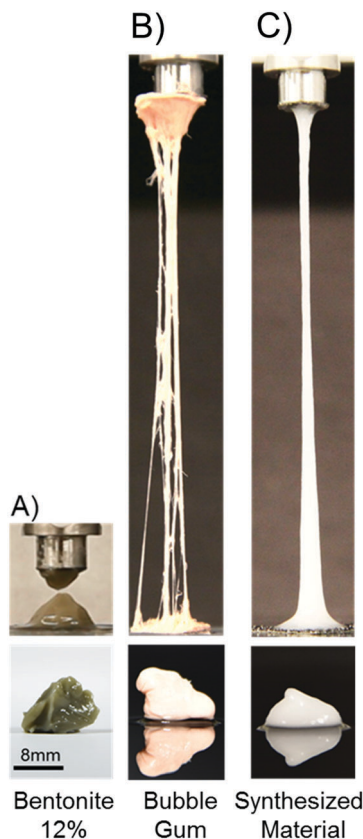


Fig. 10 Preliminary results of the extensional behavior of a material synthesized using the concept generation strategy depicted in Fig. 9 compared to (A) Bentonite, one of the archetypal yield-stress fluids discussed in this work, (B) Hubba Bubba Bubble Tape, a bubble gum. The synthesized material, (C) an oil-in-water emulsion with a transiently crosslinked polymer network is based on one of the concepts schematically shown in Fig. 9.

design has already been decided upon and formulated.²¹ Certainly, after the concept generation process (Section III E), the process of selecting a product concept (Fig. 1B, step 4) requires consideration of how a given concept might be formulated, but prescribed methodologies for this are outside the scope of this work. Though many concepts were generated, we will focus on the qualitative reasoning for the final concept we selected for downstream design process development.

Shown in Fig. 9 is a schematic for a concept for a material that has not yet been investigated in the open literature (except for the first author's Masters thesis and work in preparation^{115,116}), a juxtaposition of an emulsion that is a yield-stress fluid with an interstitial transiently crosslinked polymer network of moderate molecular weight. A major reason this concept was selected was to attempt to minimize interactions between the juxtaposed microstructures, since interactions have the potential to be enormously complex. The emulsion microstructure provides a yield stress and little-to-no extensibility, whereas the polymer network microstructure provides high extensibility but no yield stress. In this way, the material has conceptually decoupled design parameters.¹¹⁹ Interactions will always be present with multi-component systems, *e.g.* the emulsion stability may be affected by the polymer component. However, some structures are, of course, more sensitive than

others. For example, the Bentonite, LAPONITE[®], Carbopol, and xanthan gum are sensitive to salt concentration and pH to different degrees. The emulsion structure, while still having multi-component interactions, is, in principle, robust in the compartmentalization of additives (water- and oil-soluble additives separated). This aspect of emulsions allowed for more freedom when choosing the high-extensibility microstructure and formulation.

This material is shown in the uniaxial extension tests in Fig. 10 (see ref. 115 for full material and methods details). The full microstructural and mechanical characterization of this material is the subject of our ongoing work,¹¹⁶ and though it is highly improbable that the real material microstructure will exactly match the synthesized concept, the generated juxtaposed idea is what enabled the formulation to occur at all. Additionally, only through generating a large number of material concepts—many of which were not feasible to formulate or did not satisfy the functional requirement—was it possible to carry out the downstream design processes and obtain a completely new material. To create completely new material systems, one cannot be limited to incrementally modifying existing systems or only considering material structures with properties that are predictable in a straightforward way. If these approaches are all that one considers, this is tantamount to design fixation,¹²⁰ and radically new solution spaces of materials will never be achieved without the provocation of approaches such as juxtaposition.²⁷

V. Conclusions

Yield-stress fluids are the most utilized and perhaps the most useful rheologically-complex materials. Here we have presented an ontology for the design of yield-stress fluids. We have provided methodologies and insights for broadening the available design space, and for the evaluation of design concepts based on available predictive analysis and the comparison of simply represented flow data. Moving forward, we recommend usage of our revised representation of the Herschel–Bulkley model since it preserves the flow data while having physically meaningful parameters. Anyone wishing to utilize yield-stress fluids in some product or application would benefit from the methods presented here, by making use of our early-stage database framework and more importantly considering all possible concepts rather than blindly accepting the most immediately obvious approach.

The design-space presented here is obviously incomplete. Not all materials and microstructure types that produce a yield-stress fluid are known by the authors or by anyone else. However, by following the functional requirement proposed here, significant progress can be made on effectively deciding what materials are capable of producing a yield-stress fluid to then be evaluated and characterized appropriately. These same methods of design can and should also be applied to other rheological phenomena (*e.g.* linear viscoelasticity) that are currently under-utilized.

Everything presented here has only been to relate a particular rheological parameter, the yield-stress, to numerous structures, the lower level stage of the “Design of materials” schematic outlined in Fig. 1A (left portion). To effectively design complex materials in the

future will mean completely integrating the higher-level stage of performance-to-rheology target setting (e.g. ref. 1, 39 and 97) with the lower level stage of rheology-to-structure ideation (the focus of our work), followed by formulation and the optimization of specific material formulations, e.g. with computational material science or otherwise.^{121–123} To further develop the full design toolbox for yield-stress fluids and other materials, the fields of engineering design,^{42,124} product design,^{18,20,31,125} and design science^{19,25,34,43,126,127} can be embraced for other methodologies and insight. This will enable the rheology and soft matter communities to better design and engineer materials to achieve novel functionality due to the unique aspects of rheologically-complex soft materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- R. H. Ewoldt, Extremely soft: design with rheologically complex fluids, *Soft Robot.*, 2013, **1**, 12–20, DOI: 10.1089/soro.2013.1508.
- M. Denny, The role of gastropod pedal mucus in locomotion, *Nature*, 1980, **285**, 160–161, DOI: 10.1038/285160a0.
- K. Autumn, Mechanisms of adhesion in geckos, *Integr. Comp. Biol.*, 2002, **42**, 1081–1090, DOI: 10.1093/icb/42.6.1081.
- R. E. Shadwick, Mechanical design in arteries, *J. Exp. Biol.*, 1999, **202**, 3305–3313, <http://www.ncbi.nlm.nih.gov/pubmed/10562513>.
- C. Laschi, M. Cianchetti, B. Mazzolai, L. Margheri, M. Follador and P. Dario, Soft robot arm inspired by the octopus, *Adv. Robot.*, 2012, **26**, 709–727, DOI: 10.1163/156855312X626343.
- E. Cheung and M. Sitti, Adhesion of biologically inspired polymer microfibers on soft surfaces, *Langmuir*, 2009, **25**, 6613–6616, DOI: 10.1021/la900997p.
- D. Bonn, M. M. Denn, L. Berthier, T. Divoux and S. Manneville, Yield stress materials in soft condensed matter, *Rev. Mod. Phys.*, 2017, **89**, 35005, DOI: 10.1103/RevModPhys.89.035005.
- H. A. Barnes, The yield stress—a review or ‘panta rhei’—everything flows?, *J. Non-Newtonian Fluid Mech.*, 1999, **81**, 133–178, DOI: 10.1016/S0377-0257(98)00094-9.
- P. C. F. Møller, J. Mewis and D. Bonn, Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice, *Soft Matter*, 2006, **2**, 274, DOI: 10.1039/b517840a.
- C. J. E. Santos, A. Z. Nelson, E. Mendoza, R. H. Ewoldt and W. M. Kriven, Design and fabrication of ceramic beads by the vibration method, *J. Eur. Ceram. Soc.*, 2015, **35**, 3587–3594, DOI: 10.1016/j.jeurceramsoc.2015.05.018.
- A. Sun and S. Gunasekaran, Yield stress in foods: measurements and applications, *Int. J. Food Prop.*, 2009, **12**, 70–101, DOI: 10.1080/10942910802308502.
- B. G. Compton and J. A. Lewis, 3D-printing of lightweight cellular composites, *Adv. Mater.*, 2014, 5930–5935, DOI: 10.1002/adma.201401804.
- T. Bhattacharjee, S. M. Zehnder, K. G. Rowe, S. Jain, R. M. Nixon, W. G. Sawyer and T. E. Angelini, Writing in the granular gel medium, *Sci. Adv.*, 2015, **1**, e1500655, DOI: 10.1126/sciadv.1500655.
- W. Wen, X. Huang and P. Sheng, Electrorheological fluids: structures and mechanisms, *Soft Matter*, 2008, **4**, 200–210, DOI: 10.1039/B710948M.
- J. de Vicente, D. J. Klingenberg and R. Hidalgo-Alvarez, Magnetorheological fluids: a review, *Soft Matter*, 2011, **7**, 3701, DOI: 10.1039/c0sm01221a.
- K. C. Smith, Y.-M. Chiang and W. Craig Carter, Maximizing energetic efficiency in flow batteries utilizing non-newtonian fluids, *J. Electrochem. Soc.*, 2014, **161**, A486–A496, DOI: 10.1149/2.011404jes.
- E. A. Appel, M. W. Tibbitt, M. J. Webber, B. A. Mattix, O. Veisoh and R. Langer, Self-assembled hydrogels utilizing polymer–nanoparticle interactions, *Nat. Commun.*, 2015, **6**, 6295, DOI: 10.1038/ncomms7295.
- G. D. Moggridge and E. L. Cussler, *Chemical product design*, 2nd edn, Cambridge University Press, Cambridge, 2012.
- G. B. Olson, Designing a new material world, *Science*, 2000, **288**, 993–998, DOI: 10.1126/science.288.5468.993.
- K. Ulrich and S. D. Eppinger, *Product design and development*, 5th edn, McGraw-Hill, New York, 2012.
- G. A. Hazelrigg, A framework for decision-based engineering design, *J. Mech. Des.*, 1998, **120**, 653, DOI: 10.1115/1.2829328.
- P. Møller, A. Fall, V. Chikkadi, D. Derks and D. Bonn, An attempt to categorize yield stress fluid behaviour, *Philos. Trans. R. Soc., A*, 2009, **367**, 5139–5155, DOI: 10.1098/rsta.2009.0194.
- N. J. Balmforth, I. a. Frigaard and G. Ovarlez, Yielding to stress: recent developments in viscoplastic fluid mechanics, *Annu. Rev. Fluid Mech.*, 2014, **46**, 121–146, DOI: 10.1146/annurev-fluid-010313-141424.
- Q. D. Nguyen and D. V. Boger, Measuring the flow properties of yield stress fluids, *Annu. Rev. Fluid Mech.*, 1992, **24**, 47–88.
- J. Hirtz, R. Stone, D. McAdams, S. Szykman and K. Wood, A functional basis for engineering design: reconciling and evolving previous efforts, *Res. Eng. Des.*, 2002, **13**, 65–82, DOI: 10.1007/s00163-001-0008-3.

- 26 A. Winter and V. Govindarajan, Engineering reverse innovations, *Harv. Bus. Rev.*, 2015, **93**, 80–89.
- 27 E. de Bono, *Lateral thinking*, Penguin Books, New York, NY, 1977.
- 28 M. F. Ashby, *Material selection in mechanical design*, 4th edn, Butterworth-Heinemann, Boston, MA, 2011.
- 29 D. D. Braun and M. R. Rosen, *The rheology modifiers handbook practical use & application*, William Andrew Publication, Norwich, NY, 2000.
- 30 M. Ash and I. Ash, *Handbook of rheology modifiers*, Synapse Information Resources Inc., 2006.
- 31 U. Brockel, W. Meier and G. Wagner, *Product design and engineering*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2013, DOI: 10.1002/9783527654741.
- 32 H. H. Winter and M. Mours, The cyber infrastructure initiative for rheology, *Rheol. Acta*, 2006, **45**, 331–338, DOI: 10.1007/s00397-005-0041-7.
- 33 H. M. Jaeger, Celebrating soft matter's 10th anniversary: toward jamming by design, *Soft Matter*, 2015, **11**, 12–27, DOI: 10.1039/C4SM01923G.
- 34 M. Z. Miskin and H. M. Jaeger, Evolving design rules for the inverse granular packing problem, *Soft Matter*, 2014, **10**, 3708–3715, DOI: 10.1039/c4sm00539b.
- 35 P. M. Reis, H. M. Jaeger and M. van Hecke, Designer matter: a perspective, *Extreme Mech. Lett.*, 2015, **5**, 25–29, DOI: 10.1016/j.eml.2015.09.004.
- 36 S. C. Glotzer, Assembly engineering: materials design for the 21st century (2013 P.V. Danckwerts lecture), *Chem. Eng. Sci.*, 2015, **121**, 3–9, DOI: 10.1016/j.ces.2014.09.045.
- 37 A. Jain, J. A. Bollinger and T. M. Truskett, Inverse methods for material design, *AIChE J.*, 2014, **60**, 2732–2740, DOI: 10.1002/aic.14491.
- 38 A. Zakutayev, X. Zhang, A. Nagaraja, L. Yu, S. Lany, T. O. Mason, D. S. Ginley and A. Zunger, Theoretical prediction and experimental realization of new stable inorganic materials using the inverse design approach, *J. Am. Chem. Soc.*, 2013, **135**, 10048–10054, DOI: 10.1021/ja311599g.
- 39 R. H. Ewoldt, C. Clasen, A. E. Hosoi and G. H. McKinley, Rheological fingerprinting of gastropod pedal mucus and synthetic complex fluids for biomimicking adhesive locomotion, *Soft Matter*, 2007, **3**, 634, DOI: 10.1039/b615546d.
- 40 T. R. Gruber, Toward principles for the design of ontologies used for knowledge sharing, *Int. J. Hum. Comput. Stud.*, 1995, **43**, 907–928, DOI: 10.1006/ijhc.1995.1081.
- 41 H. Emady, M. Caggioni and P. Spicer, Colloidal microstructure effects on particle sedimentation in yield stress fluids, *J. Rheol.*, 2013, **57**, 1761–1772, DOI: 10.1122/1.4824471.
- 42 G. Pahl and W. Beitz, *Engineering design – a systematic approach*, Springer London, London, 1996, DOI: 10.1007/978-1-4471-3581-4.
- 43 M. Graham, A. Slocum and R. M. Sanchez, Teaching high school students and college freshmen product development by deterministic design with PREP, *J. Mech. Des.*, 2007, **129**, 677, DOI: 10.1115/1.2722334.
- 44 C. W. Macosko, *Rheology principles, measurements, and applications*, Wiley, New York, 1994.
- 45 F. Da Cruz, F. Chevoir, D. Bonn and P. Coussot, Viscosity bifurcation in granular materials, foams, and emulsions, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2002, **66**, 1–7, DOI: 10.1103/PhysRevE.66.051305.
- 46 P. Coussot, Q. D. Nguyen, H. T. Huynh and D. Bonn, Viscosity bifurcation in thixotropic, yielding fluids, *J. Rheol.*, 2002, **46**, 573–589, DOI: 10.1122/1.1459447.
- 47 F. Sciortino, Disordered materials: one liquid, two glasses, *Nat. Mater.*, 2002, **1**, 145–146, DOI: 10.1038/nmat752.
- 48 F. Sciortino and P. Tartaglia, Glassy colloidal systems, *Adv. Phys.*, 2005, **54**, 471–524, DOI: 10.1080/000187305000414570.
- 49 A. Burmistrova and R. von Klitzing, Control of number density and swelling/shrinking behavior of P(NIPAM-AAc) particles at solid surfaces, *J. Mater. Chem.*, 2010, **20**, 3502, DOI: 10.1039/b923969c.
- 50 C. Clasen, B. P. Gearing and G. H. McKinley, The flexure-based microgap rheometer (FMR), *J. Rheol.*, 2006, **50**, 883, DOI: 10.1122/1.2357190.
- 51 M. Le Merrer, R. Lespiat, R. Höhler and S. Cohen-Addad, Linear and non-linear wall friction of wet foams, *Soft Matter*, 2015, **11**, 368–381, DOI: 10.1039/C4SM01557F.
- 52 D. A. Weitz and J. S. Huang, Self-similar structures and the kinetics of aggregation of gold colloids, in *Kinetics of aggregation and gelation*, Elsevier, 1984, pp. 19–28, DOI: 10.1016/B978-0-444-86912-8.50010-9.
- 53 Y. D. Liu and H. J. Choi, Electrorheological fluids: smart soft matter and characteristics, *Soft Matter*, 2012, **8**, 11961, DOI: 10.1039/c2sm26179k.
- 54 W. Mickel, S. Münster, L. M. Jawerth, D. A. Vader, D. A. Weitz, A. P. Sheppard, K. Mecke, B. Fabry and G. E. Schröder-Turk, Robust pore size analysis of filamentous networks from three-dimensional confocal microscopy, *Biophys. J.*, 2008, **95**, 6072–6080, DOI: 10.1529/biophysj.108.135939.
- 55 J. M. Piau, Carbopol gels: elastoviscoplastic and slippery glasses made of individual swollen sponges meso- and macroscopic properties, constitutive equations and scaling laws, *J. Nonnewton. Fluid Mech.*, 2007, **144**, 1–29, DOI: 10.1016/j.jnnfm.2007.02.011.
- 56 H. Senff and W. Richtering, Temperature sensitive microgel suspensions: colloidal phase behavior and rheology of soft spheres, *J. Chem. Phys.*, 1999, **111**, 1705–1711, DOI: 10.1063/1.479430.
- 57 H. Princen and A. Kiss, Rheology of foams and highly concentrated emulsions: IV. An experimental study of the shear viscosity and yield stress of concentrated emulsions, *J. Colloid Interface Sci.*, 1989, **128**, 176–187, DOI: 10.1016/0021-9797(89)90396-2.
- 58 Y. Otsubo and R. K. Prud'homme, Rheology of oil-in-water emulsions, *Rheol. Acta*, 1994, **33**, 29–37, DOI: 10.1007/BF00453461.
- 59 R. Pal, Effect of droplet size on the rheology of emulsions, *AIChE J.*, 1996, **42**, 3181–3190, DOI: 10.1002/aic.690421119.
- 60 T. G. Mason, New fundamental concepts in emulsion rheology, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 231–238, DOI: 10.1016/S1359-0294(99)00035-7.

- 61 J. R. Seth, L. Mohan, C. Locatelli-Champagne, M. Cloitre and R. T. Bonnecaze, A micromechanical model to predict the flow of soft particle glasses, *Nat. Mater.*, 2011, **10**, 838–843, DOI: 10.1038/nmat3119.
- 62 M. Dinkgreve, J. Paredes, M. A. J. Michels and D. Bonn, Universal rescaling of flow curves for yield-stress fluids close to jamming, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2015, **92**, 12305, DOI: 10.1103/PhysRevE.92.012305.
- 63 S. Cohen-Addad, R. Höhler and O. Pitois, Flow in foams and flowing foams, *Annu. Rev. Fluid Mech.*, 2013, **45**, 241–267, DOI: 10.1146/annurev-fluid-011212-140634.
- 64 J. Buitenhuis and S. Förster, Block copolymer micelles: viscoelasticity and interaction potential of soft spheres, *J. Chem. Phys.*, 1997, **107**, 262–272, DOI: 10.1063/1.474346.
- 65 F. Renou, J. Stellbrink and G. Petekidis, Yielding processes in a colloidal glass of soft star-like micelles under large amplitude oscillatory shear (LAOS), *J. Rheol.*, 2010, **54**, 1219, DOI: 10.1122/1.3483610.
- 66 R. C. Kramb and C. F. Zukoski, Nonlinear rheology and yielding in dense suspensions of hard anisotropic colloids, *J. Rheol.*, 2011, **55**, 1069–1084, DOI: 10.1122/1.3613978.
- 67 R. C. Kramb and C. F. Zukoski, Exploration of the volume fraction above which suspensions of spherical and weakly anisotropic colloid particles cannot flow, *J. Rheol.*, 2011, **55**, 1085, DOI: 10.1122/1.3613983.
- 68 T. Jiang and C. Zukoski, Dynamic localization and shear-induced hopping of particles: a way to understand the rheology of dense colloidal dispersions, *J. Rheol.*, 2014, **58**, 1277–1299, DOI: 10.1122/1.4866038.
- 69 H. M. Jaeger, S. R. Nagel and R. P. Behringer, Granular solids, liquids, and gases, *Rev. Mod. Phys.*, 1996, **68**, 1259–1273, DOI: 10.1103/RevModPhys.68.1259.
- 70 E. Brown and H. M. Jaeger, Dynamic jamming point for shear thickening suspensions, *Phys. Rev. Lett.*, 2009, **103**, 1–4, DOI: 10.1103/PhysRevLett.103.086001.
- 71 I. M. Krieger, The second electroviscous effect in polymer lattices, *J. Rheol.*, 1976, **20**, 29, DOI: 10.1122/1.549428.
- 72 N. P. Chafe and J. R. de Bruyn, Drag and relaxation in a bentonite clay suspension, *J. Nonnewton. Fluid Mech.*, 2005, **131**, 44–52, DOI: 10.1016/j.jnnfm.2005.08.010.
- 73 N. J. Alderman, G. H. Meeten and J. D. Sherwood, Vane rheometry of bentonite gels, *J. Nonnewton. Fluid Mech.*, 1991, **39**, 291–310, DOI: 10.1016/0377-0257(91)80019-G.
- 74 P. Coussot, Q. D. Nguyen, H. T. Huynh and D. Bonn, Avalanche behavior in yield stress fluids, *Phys. Rev. Lett.*, 2002, **88**, 175501, DOI: 10.1103/PhysRevLett.88.175501.
- 75 S. Jabbari-Farouji, H. Tanaka, G. H. Wegdam and D. Bonn, Multiple nonergodic disordered states in Laponite suspensions: a phase diagram, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2008, **78**, 1–10, DOI: 10.1103/PhysRevE.78.061405.
- 76 B. Ruzicka and E. Zaccarelli, A fresh look at the laponite phase diagram, *Soft Matter*, 2011, **7**, 1268, DOI: 10.1039/c0sm00590h.
- 77 S. Jataw and Y. M. Joshi, Rheological signatures of gelation and effect of shear melting on aging colloidal suspension, *J. Rheol.*, 2014, **58**, 1535–1554, DOI: 10.1122/1.4887344.
- 78 D. J. Klingenberg and C. F. Zukoski, Studies on the steady-shear behavior of electrorheological suspensions, *Langmuir*, 1990, **6**, 15–24, DOI: 10.1021/la00091a003.
- 79 P. J. Rankin, A. T. Horvath and D. J. Klingenberg, Magnetorheology in viscoplastic media, *Rheol. Acta*, 1999, **38**, 471–477, DOI: 10.1007/s003970050198.
- 80 J. M. Ginder, L. C. Davis and L. D. Elie, Rheology of magnetorheological fluids: models and measurements, *Int. J. Mod. Phys. B*, 1996, **10**, 3293–3303, DOI: 10.1142/S0217979296001744.
- 81 W. E. Rochefort and S. Middleman, Rheology of xanthan gum: salt, temperature, and strain effects in oscillatory and steady shear experiments, *J. Rheol.*, 1987, **31**, 337, DOI: 10.1122/1.549953.
- 82 D. G. Wallace and J. Rosenblatt, Collagen gel systems for sustained delivery and tissue engineering, *Adv. Drug Delivery Rev.*, 2003, **55**, 1631–1649, DOI: 10.1016/j.addr.2003.08.004.
- 83 M. J. Solomon and P. T. Spicer, Microstructural regimes of colloidal rod suspensions, gels, and glasses, *Soft Matter*, 2010, **6**, 1391–1400, DOI: 10.1039/B918281K.
- 84 C. P. J. Bennington, R. J. Kerekes and J. R. Grace, The yield stress of fibre suspensions, *Can. J. Chem. Eng.*, 1990, **68**, 748–757, DOI: 10.1002/cjce.5450680503.
- 85 G. M. H. Wilkins, P. T. Spicer and M. J. Solomon, Colloidal system to explore structural and dynamical transitions in rod networks, gels, and glasses, *Langmuir*, 2009, **25**, 8951–8959, DOI: 10.1021/la9004196.
- 86 V. Trappe, V. Prasad, L. Cipelletti, P. N. Segre and D. A. Weitz, Jamming phase diagram for attractive particles, *Nature*, 2001, **411**, 772–775, DOI: 10.1038/35081021.
- 87 M. Fuchs and M. E. Cates, Schematic models for dynamic yielding of sheared colloidal glasses, *Faraday Discuss.*, 2003, **123**, 267–286, DOI: 10.1039/b205629a.
- 88 R. Buscall, Effect of long-range repulsive forces on the viscosity of concentrated lattices: comparison of experimental data with an effective hard-sphere model, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1365–1370, DOI: 10.1039/ft9918701365.
- 89 W. B. Russel, D. A. Saville and W. R. Schowalter, Rheology, in *Colloid. dispersions*, Cambridge University Press, Cambridge, 1989, pp. 456–506, DOI: 10.1017/CBO9780511608810.017.
- 90 B. C. Blackwell, M. E. Deetjen, J. E. Gaudio and R. H. Ewoldt, Sticking and splashing in yield-stress fluid drop impacts on coated surfaces, *Phys. Fluids*, 2015, **27**, 43101, DOI: 10.1063/1.4916620.
- 91 A. S. Negi and C. O. Osuji, Time-resolved viscoelastic properties during structural arrest and aging of a colloidal glass, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2010, **82**, 1–4, DOI: 10.1103/PhysRevE.82.031404.
- 92 G. Ovarlez, L. Tocquer, F. Bertrand and P. Coussot, Rheopexy and tunable yield stress of carbon black suspensions, *Soft Matter*, 2013, **9**, 5540, DOI: 10.1039/c3sm27650c.
- 93 B. C. Blackwell, M. E. Deetjen, J. E. Gaudio and R. H. Ewoldt, Quantitative measures of yield-stress fluid drop impacts on coated surfaces, *Atomization Sprays*, 2017, **27**, 337–343, DOI: 10.1615/AtomizSpr.2017017381.

- 94 P. Coussot and F. Gaulard, Gravity flow instability of viscoplastic materials: the ketchup drip, *Phys. Rev. E*, 2005, **72**, 31409, DOI: 10.1103/PhysRevE.72.031409.
- 95 G. German and V. Bertola, The free-fall of viscoplastic drops, *J. Nonnewton. Fluid Mech.*, 2010, **165**, 825–828, DOI: 10.1016/j.jnnfm.2010.03.012.
- 96 N. M. Wereley and L. Pang, Nondimensional analysis of semi-active electrorheological and magnetorheological dampers using approximate parallel plate models, *Smart Mater. Struct.*, 1999, **7**, 732–743, DOI: 10.1088/0964-1726/7/5/015.
- 97 R. E. Corman, L. Rao, N. Ashwin Bharadwaj, J. T. Allison and R. H. Ewoldt, Setting material function design targets for linear viscoelastic materials and structures, *J. Mech. Des.*, 2016, **138**, 51402, DOI: 10.1115/1.4032698.
- 98 V. Grenard, T. Divoux, N. Taberlet and S. Manneville, Timescales in creep and yielding of attractive gels, *Soft Matter*, 2014, **10**, 1555, DOI: 10.1039/c3sm52548a.
- 99 N. C. Acevedo and A. G. Marangoni, Functionalization of non-interesterified mixtures of fully hydrogenated fats using shear processing, *Food Bioprocess Technol.*, 2014, **7**, 575–587, DOI: 10.1007/s11947-013-1110-z.
- 100 K. N. Nordstrom, E. Verneuil, P. E. Arratia, A. Basu, Z. Zhang, A. G. Yodh, J. P. Gollub and D. J. Durian, Microfluidic rheology of soft colloids above and below jamming, *Phys. Rev. Lett.*, 2010, **105**, 1–4, DOI: 10.1103/PhysRevLett.105.175701.
- 101 M. Cloitre, R. Borrega, F. Monti and L. Leibler, Glassy dynamics and flow properties of soft colloidal pastes, *Phys. Rev. Lett.*, 2003, **90**, 68303, DOI: 10.1103/PhysRevLett.90.068303.
- 102 E. Walz, K. Jahnke, M. Holinger, E. Gast, B. Elliot-Litchfield and M. Ludeke, *Building your creativity: tools for having ideas and bringing them to be*, Stipes Publishing Co., 2016.
- 103 C. Chung, B. Degner and D. J. McClements, Rheology and microstructure of bimodal particulate dispersions: model for foods containing fat droplets and starch granules, *Food Res. Int.*, 2012, **48**, 641–649, DOI: 10.1016/j.foodres.2012.06.011.
- 104 M. Zrinyi, Intelligent polymer gels controlled by magnetic fields, *Colloid Polym. Sci.*, 2000, **278**, 98–103, DOI: 10.1007/s003960050017.
- 105 H. McGee, *On food and cooking: the science and lore of the kitchen*, Scribner, New York, NY, 2004.
- 106 U. T. Gonzenbach, A. R. Studart, E. Tervoort and L. J. Gauckler, Ultrastable particle-stabilized foams, *Angew. Chem., Int. Ed.*, 2006, **45**, 3526–3530, DOI: 10.1002/anie.200503676.
- 107 C. Krämer, M. Schauerte, T. L. Kowald and R. H. F. Trettin, Three-phase-foams for foam concrete application, *Mater. Charact.*, 2015, **102**, 173–179, DOI: 10.1016/j.matchar.2015. 03. 004.
- 108 M. Helgeson, S. Moran, H. An and P. Doyle, Mesoporous organohydrogels from thermogelling photocrosslinkable nanoemulsions, *Nat. Mater.*, 2012, **11**, 344–352, DOI: 10.1038/nmta3248.
- 109 E. Dickinson, Emulsion gels: the structuring of soft solids with protein-stabilized oil droplets, *Food Hydrocoll.*, 2012, **28**, 224–241, DOI: 10.1016/j.foodhyd.2011.12.017.
- 110 S. Rose, A. PrevotEAU, P. Elzière, D. Hourdet, A. Marcellan and L. Leibler, Nanoparticle solutions as adhesives for gels and biological tissues, *Nature*, 2014, **505**, 382–385, DOI: 10.1038/nature12806.
- 111 D. Derks, A. Lindner, C. Creton and D. Bonn, Cohesive failure of thin layers of soft model adhesives under tension, *J. Appl. Phys.*, 2003, **93**, 1557–1566, DOI: 10.1063/1.1533095.
- 112 R. H. Ewoldt, P. Tourkine, G. H. McKinley and A. E. Hosoi, Controllable adhesion using field-activated fluids, *Phys. Fluids*, 2011, **23**, 73104, DOI: 10.1063/1.3608277.
- 113 Q. Barral, G. Ovarlez, X. Chateau, J. Boujlel, B. Rabideau and P. Coussot, Adhesion of yield stress fluids, *Soft Matter*, 2010, 1343–1351, DOI: 10.1039/b922162j.
- 114 C. A. Dahlquist, An Investigation into the nature of tack, *Adhes. Age*, 1959, **2**, 25.
- 115 A. Z. Nelson, *Extending yield-stress fluid paradigms*, Masters thesis, University of Illinois, 2015.
- 116 A. Z. Nelson, R. Bras, J. Liu and R. H. Ewoldt, *Extending yield-stress fluid paradigms*, Submitted.
- 117 L. Martinetti, A. M. Mannion, W. E. Voje, R. Xie, R. H. Ewoldt, L. D. Morgret, F. S. Bates and C. W. Macosko, A critical gel fluid with high extensibility: the rheology of chewing gum, *J. Rheol.*, 2014, **58**, 821–838, DOI: 10.1122/1.4874322.
- 118 A. L. Rutz, K. E. Hyland, A. E. Jakus, W. R. Burghardt and R. N. Shah, A multimaterial bioink method for 3D printing tunable, cell-compatible hydrogels, *Adv. Mater.*, 2015, **27**, 1607–1614, DOI: 10.1002/adma.201405076.
- 119 N. P. Suh, *Axiomatic design: advances and applications*, Oxford University Press, New York, NY, 2001.
- 120 J. S. Linsey, I. Tseng, K. Fu, J. Cagan, K. L. Wood and C. Schunn, A study of design fixation, its mitigation and perception in engineering design faculty, *J. Mech. Des.*, 2010, **132**, 41003, DOI: 10.1115/1.4001110.
- 121 D. K. Schneiderman and M. A. Hillmyer, Aliphatic polyester block polymer design, *Macromolecules*, 2016, **49**, 2419–2428, DOI: 10.1021/acs.macromol.6b00211.
- 122 U. Akalp, S. J. Bryant and F. J. Vernerey, Tuning tissue growth with scaffold degradation in enzyme-sensitive hydrogels: a mathematical model, *Soft Matter*, 2016, **12**, 7505–7520, DOI: 10.1039/c6sm00583g.
- 123 N. A. Lynd, F. T. Oyerokun, D. L. O'Donoghue, D. L. Handlin and G. H. Fredrickson, Design of soft and strong thermoplastic elastomers based on nonlinear block copolymer architectures using self-consistent-field theory, *Macromolecules*, 2010, **43**, 3479–3486, DOI: 10.1021/ma902517v.
- 124 R. Budynas and K. Nisbett, *Shigley's mechanical engineering design*, 10th edn, McGraw-Hill Education, 2014.
- 125 M. F. Ashby and K. Johnson, *Materials and design: the art and science of material selection in product design*, 2nd edn, 2010.
- 126 B. M. Kudrowitz and D. Wallace, Assessing the quality of ideas from prolific, early-stage product ideation, *J. Eng. Des.*, 2013, **24**, 120–139, DOI: 10.1080/09544828.2012.676633.
- 127 H. Dubberly, *How do you design? A compendium of models*, Dubberly Design Office, 2008.