

Teaching Rheology Using Product Design

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Here we describe two courses on experimental rheology offered over the past several years to seniors and first-year graduate students at our institutions. These laboratory courses use complex materials available from the shelves of our local retailers. We have found that measuring the rheology of face cream, shampoo, paint, chewing gum or plastic bags provides great motivation for students to learn rheology fundamentals. In this communication we describe the structure of the courses and give detailed instructions for others who may wish to duplicate this curriculum.

The two courses in Leuven and Minnesota are somewhat different, but what is common is the product-oriented approach. Typically we have 10-20 students who are asked to pair up (with three students per group one is usually a slacker!). Early on in the course each group selects a material from those listed in Table 1. Care is taken to ensure that all five of the material classes are represented in the materials studied.

Typically, after lectures on rheology fundamentals, rheometry, and a lab tour, each pair submits a plan including which rheometer geometry they will use and the types of linear and nonlinear data they plan to collect. They discuss this plan with the instructor. During this discussion, we put emphasis on how measurement problems need to be addressed. Students then get time in the rheometry lab to carry out their measurements, duly supervised by an experienced graduate student, postdoc, or lab manager. In the last week of semester the student teams give presentations describing their material, why its rheology is important for

its performance in end-use and/or processing, and how their material-function measurements can be used to reverse engineer the structure of their product. Students are also asked to think about the molecular or formulation parameters that they could use to modify the rheological behavior of the products during processing or during the product life cycle.

Each of us has labs with several rotational rheometers capable of linear and nonlinear measurements including of normal stresses. We instruct each team to plan to complete their measurements within a 4-hour lab session. It should be quite possible to carry out this syllabus with just one modern rheometer. Apart from the lab time, students typically need some help with data analysis and interpretation. The latter may be time-con-

Table 1. Commercial materials used to teach rheology

Class of material	Examples	NOTES
Polymeric liquids	grocery bag (LDPE) bottle (PE or PET-E) beer cup (PP)	Molten state, melt rheometer 150-250°C. May require more lab time. PET is somewhat difficult, needs to be dried under vacuum, also not dramatically viscoelastic.
Suspensions	latex paint lime-based paint mustard	Avoid solvent based paints. Be careful with acidity of certain foodstuffs.
Emulsions	face cream (e.g. Nivea) mayonnaise (e.g. comparing light vs. regular)	Slip is often a major issue with these emulsions.
Surfactants	shampoo (e.g. Garnier Ultra Doux for Kids, Clariant)	pH neutral shampoos are best. Some surfactants contain Cl ⁻ ions, be careful for pitting corrosion! Transparent shampoos are nice; they get students thinking about the length scales involved. Some shampoos with suspended particles are often rheologically interesting.
Gels	foodstuff (ketchup, yogurt) hair gels toothpaste	These are difficult to measure and rheologically somewhat disappointing. The LVE properties show solid like behavior and often only the yield stress is rheologically relevant.

suming on the faculty and teaching assistants; in Leuven we have addressed this problem by instating a formal system for spending ‘quality time’ with the teaching staff, where the students get two vouchers, each valid for half an hour of consulting time from the teaching assistants.

During lectures, following the introduction of the different rheological concepts, we draw on examples from the literature to show how measurements of the different material functions can be used to infer relevant aspects about the intrinsic material properties, the processing behavior, or end-use properties. Examples of how this is done are listed in Table 2.

The rheology project aims at four distinct learning goals:

1. Understanding the different material functions and their relevance for material processes and products. Typically we try to emphasize the dual nature of rheology in materials processing and product design: linear viscoelasticity as an analytical tool, as some kind of mechanical microscope – and the non-linear properties as required for product performance or for predicting

the behavior in processing flows. This part needs to be learned by the students early on in the project when they select the material functions that they intend to measure. There is always some feedback required at this stage of the project, typically after they submit their plan.

2. Selecting a measurement technique, performing the measurements and data analysis. This is something the students typically enjoy. It is best that students are warned beforehand about issues such as wall slip, sedimentation or creaming, and it is also advisable to have a good solvent trap in the lab to avoid evaporation. An explicit request is that students determine the limits of linear viscoelasticity and that they check the internal consistency of the data set they have obtained, e.g. use the Cox-Merz relation. This is maybe one of the most important lessons learned for those who will go on to practice rheology.

3. Choosing a constitutive model and fitting it to data. This part of the project is typically most challenging and especially relevant for the polymeric samples (where the relation between structure and rheology – see 4 - is less challenging). Overall, its importance has lost some of its weight in the assignment in recent years with the emphasis in teaching shifting somewhat to structure-

Table 2. Lecture examples linking deformation regimes and material functions with the various material classes.

Class of material	Linear viscoelastic properties	Generalized Newtonian behavior	Other non-Linear material functions
Polymeric liquids	Data on silly putty and LDPE (from [1,2]) are shown with a brief discussion on how MW and MWD affect properties [2]	Shear thinning is discussed, with an example of fitting an Ellis model [3,5]. Evaluations of shear rates in extrusion and injection molding.	Normal stress differences, transient normal stress differences [3] and transient elongational viscosities [1,4,5] and their role in extrusion and fiber spinning or blow molding [3,5]
Suspension	Stable suspensions : Effect of volume fraction and interaction potential on the moduli [6,7]	Range of shear rates and role of shear thinning in paints and inks [8] and shear thickening and liquid body armour [9]	Thixotropy (necessarily brief) using a model suspension of fumed silica in PDMS [10]
Emulsion	Emulsions as single relaxation time fluids (Maxwell), using rheology to measure droplet size [11]	Evaluation of shear rates in settling/creaming and product usage (‘feel’), as discussed for example in [12]	Transient normal stress differences to evaluate morphology evolution [13]
Surfactants	Surfactant solutions as single relaxation time fluids (Maxwell) [14]	Flow curves of simple surfactants and relation to shear rates in filling, rubbing [12]	Demonstrate the Kaye effect [16,17] and extensional properties [18]
Gels	Solid-like behavior [15]	Yield stress and its relevance for toothpaste. Methods to measure yield stress [19,20]	Breakdown and recovery of gel structure, thixotropy [21]

rheology relations (see 4).

4. Reverse engineering of the product: the relation between structure and rheology. In this part of the project, students have to establish the link between rheology and structure by trying to understand how the rheological behavior has been 'built-in' to the material. They should

Table 3. Examples of parameters to be discussed for reverse engineering or product modification.

Class of material	Reverse engineering / structural parameters
Polymeric liquids	Polymer type, chain architecture, molecular weight and distribution
Suspension	Particle size, size distribution, (effective) volume fraction Effect of changing the interaction potential, medium viscosity
Emulsion	Droplet size (emulsification technique), volume fraction, stabilizers
Surfactants	Identify rheologically relevant components and suggest phase behavior (wormlike micelles or cubic phases) Concentration, presence of salt; solvent viscosity (e.g. glycerol)
Gels	Crosslink density, volume fraction of polymer Interaction potential

be able to discuss how parameters related to formulation or material design control its rheology and what they would measure when something goes wrong with the product or process. Some of the parameters that are discussed are listed in Table 3.

In our experience, students are particularly eager to understand the microstructural bases for different rheological responses in anticipation of having to solve a real problem by the end of the course. They also seem to be able to differentiate between the usage of rheology as an 'analytical method' and as a valuable engineering tool for finding parameters relevant for processing conditions or for designing end-use properties. Student response has been overwhelmingly positive, and we have enjoyed teaching it and exchanging our experiences. A detailed description of the course contents at the two institutions is given below. More information and materials are available on the web at cit.kuleuven.

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This course is designed as an elective for the first semester of the final (5th) year of the chemical engineering master program. Typically also some material science and engineering students join the class. The number of students varies between 10 and 20. The course builds to a large extent on the book *Rheology: Principles, Measurements and Applications* (Macosko, Wiley, 1994) supplemented with *The Structure and Rheology of Complex Fluids* (Larson, Oxford, 1999). The course is 3 (ECTS) credits with 10 lectures of 2 hours.

U Minnesota ChEn 8102

This course is designed as an elective for first year graduate students in chemical engineering in their second semester. However, typically, in addition to 5-7 chemical engineers, we have 3-6 materials majors and 1-2 biomedical engineers and often an aeronautical engineering, chemistry, pharmacy or even a food science grad student. Typically 2-4 seniors also take the course under 4702. They do the same exercises and exam but are graded separately.

Like the Leuven course we follow the structure of *Macosko*, supplemented with *Larson*. The course is 2 credits with 22 lectures, 50 min each. In addition to the laboratory exercise described above, two assignments contain rheometer data from the US National Institute of Standards viscoelastic standard, NIST 2491, polyisobutylene in pristane. The students are asked to evaluate the range of reliability of these data, test them against limiting relations, and fit them to several models.

A less intensive alternative:

For those who do not have the facilities to allow students to perform measurements, we experimented with a different approach a few years ago. Students were given a rheology-related problem in processing or formulation, such as instability in a film-blowing line or splashing and dripping paint. Subsequently, students were

(continues, *Product Design*, page 26)

asked to look for the material functions to be measured that could help solve the problem along similar lines to what is discussed above. They then had to propose the purchase of a type of rheometer to a 'board of directors' with a presentation. The 'board' was composed of senior graduate students and postdocs who were very keen to play this role and formed a very challenging audience.

When graduate students take the course, they sometimes lobby to choose materials that they want to characterize for their thesis research. This can be very helpful to the students who need rheology for their research, but it leads to a wide disparity in the quality and scope of the reports. Moreover, it is hard to cover all the classes of materials.

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