The Cambridge Polymer Group Silly Putty™ "Egg"

Silly Putty™ is a registered trademark of Binney and Smith

Introduction

Silly Putty™ is a material that vividly demonstrates the richness and complexity of behavior that apparently simple materials can produce. When first handled, the initial impression given by Silly Putty™ is that of a plastic material. It can be easily kneaded, much like dough, into any shape desired. On short time scales these complex shapes appear to be permanent distortions of the material. However, upon longer inspection the material is seen to sag under its own weight although the putty does not flow indefinitely on a flat surface. If rolled into a ball and dropped, the material bounces like an elastic material. In addition, if a shock or impulsive load is applied to the putty, it will shatter. The behavior of this fascinating material gives insight into the rheological behavior of many materials. In rheological terms the experimenter is distorting the Silly Putty™ over a range of *Deborah numbers*. This non-dimensional parameter describes the ratio of the fluid relaxation time scale to that of the experimental time scale. A high Deborah number therefore corresponds to a fast experiment in which the load or impulse is applied over a very short time scale.

Composition

Silly Putty™ is a silicone material produced by Dow Corning® Corporation (under the name of Dow Corning® 3179 Dilatant Compound). According to Dow Corning the composition (by weight percentage) is as outlined in the table below.

PDMS	65%
Silica	17%
Thixotrol	9%
Boric Acid	4%
Glycerine	1%
Titanium Dioxide	1%
Dimethyl Cyclosiloxane	1%

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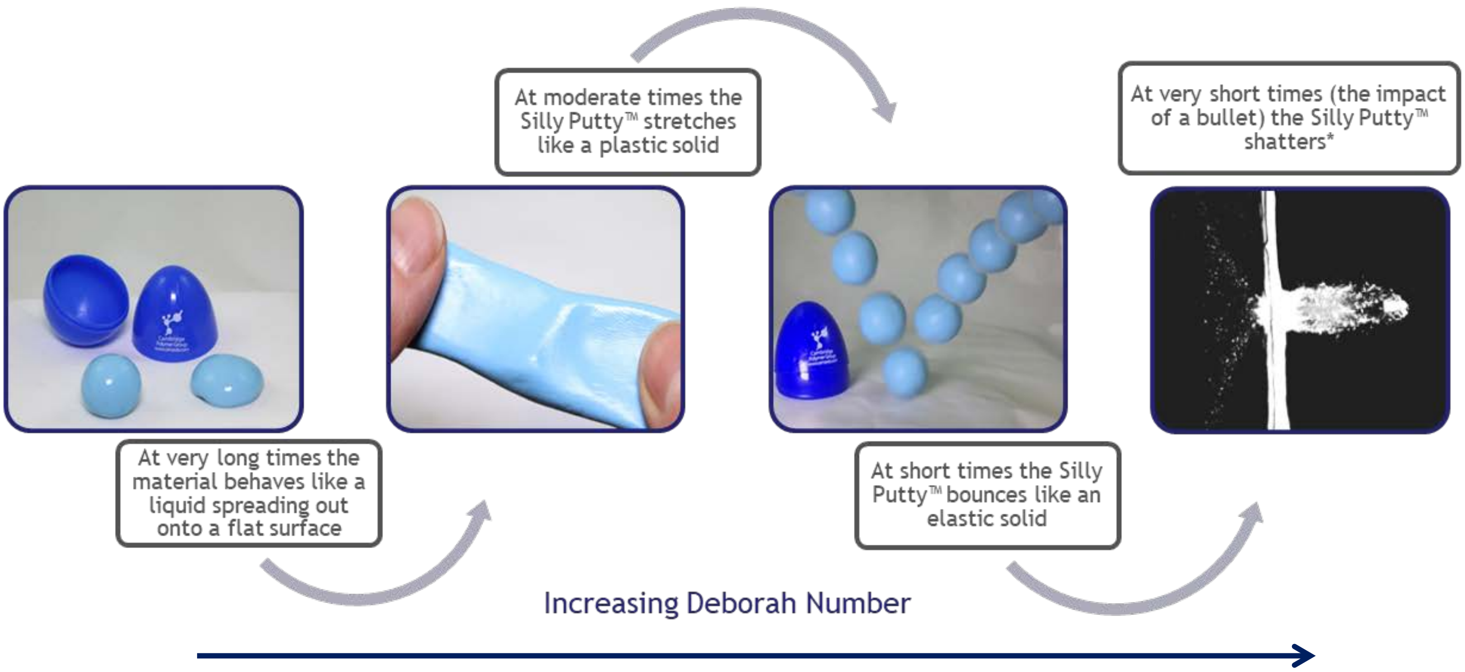


$$De = \frac{\lambda_{material}}{t_{flow}}$$

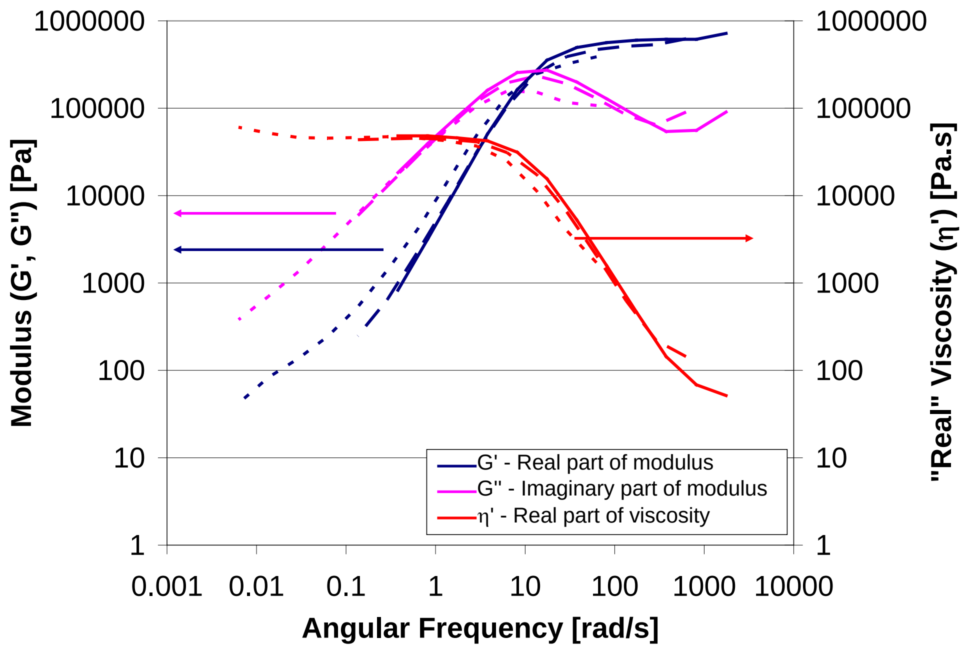
Rheology

As Dow Corning's name suggests, this material possesses some interesting mechanical properties. A dilatant material is one where the viscosity (*i.e.* the resistance to flow) increases faster than the strain rate. Although not common, some materials do exhibit dilatant behavior (concentrated aqueous corn starch suspensions for example). However this phenomena on its own is not enough to explain the behavior of Silly Putty™. In fact there are two mechanisms (and hence two characteristic time scales) at work in this material. The high molecular weight PDMS has a characteristic polymeric relaxation time, λ_{relax} (defined by the time that a random walk allows the chain to relax from a stretched state through thermal vibrations). However due to the Boric acid there are also transient Boron mediated "crosslinks" arising from associating Boron linkages. These act to give the Silly Putty™ a behavior more like an elastic solid than a liquid. However since these "crosslinks" are dynamic (with a characteristic time, λ_{assoc} that is much shorter than λ_{relax}) the material is not permanently locked in place and can consequently flow under the correct conditions. Therefore at time scales longer than λ_{assoc} the Silly Putty™ behaves like a high molecular weight polymeric fluid (with a characteristic relaxation time of λ_{relax}). Over time scales much shorter than λ_{assoc} Silly Putty™ behaves like a crosslinked elastic solid.

When this interesting material is examined experimentally, this rate-dependent behavior becomes more obvious. A simple test was conducted with Cambridge Polymer Group's TA Instrument AR1000 controlled stress rheometer. The experiment conditions are described in the table below. A large gap was used because of the very high viscosity of the sample, which aided in loading the material, and reduced the maximum stress required to shear the material. Fluids are usually tested at a fixed temperature because the modulus varies with temperature. However, the temperature behavior of most relatively simple "fluids" can be described by an Arrhenius expression that allows a direct mapping of oscillatory rate to temperature. For practical purposes, this phenomena allows the apparent dynamic range of the instrument to be extended to both higher and lower frequencies. The resulting data for Silly Putty™ is presented in the figure below.

In the figure at the foot of the page, three sets of data are presented, with two sets representing the complex modulus of the Silly Putty™. The reported parameters are the storage modulus (G') and loss modulus (G"), which are related to the recoverable energy (*i.e.* elasticity) of the material and the damped energy, respectively. The third set of data is the real part of the complex viscosity. The key points to be taken from this graph are: 1) at low frequencies, G" exceeds G'. This indicates that the material is predominantly viscous, i.e. it flows; 2) at about 10 rad/s, the elastic modulus (G') exceeds G" and at this point the material becomes predominantly elastic. This region clearly represents the transition between images two and three on the previous page; 3) finally the elasticity appears to enter a plateau region and the loss modulus goes through a point of inflection and appears to start to rise again. This behavior is characteristic of a concentrated (*i.e.* entangled), high molecular weight system that is above its glass transition temperature. In this context, the Boron linkages discussed above act as virtual entanglements, reducing the mobility of the polymer chains.

Experimental parameter	**Value**
Geometry	4 cm Stainless steel parallel plates
Geometry gap	500 μm
Temperature control	Peltier thermoelectric
Temperature	5, 25, 60 ºC
Control mode	Controlled Stress
Torque values	40000, 30000, 20000 μN.m
Experiment type	Small amplitude oscillatory
Frequency range	0.01 – 100 Hz



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