Broadband viscoelasticity of polymers with initial stress: applicability of time- temperature superposition to macromolecular systems

American Chemical Society Petroleum Research Fund Type AC project
Rod Lakes, University of Wisconsin
Progress report, 22 August 2007

Apply a steady force to a polymer and it will continue to deform, or "creep" with time. This creep occurs more rapidly at high temperature than at low temperature. Creep is objectionable if it results in warp of a plastic part, or loosening of a fastener over its service life. Creep at short time is beneficial for the purpose of absorbing noise and vibration, since it is linked with viscoelastic dissipation of vibration energy.

Droop of a polymer under its own weight is illustrated in the attached video. The blue pyramid was formed of a silicone polymer used as a hand strength exerciser. The clock indicates the true time scale in the accelerated video. In this case, the material droops over a period of several minutes. Other materials may droop more rapidly or much more slowly. Tests of creep and other viscoelastic properties are therefore done on polymers. For example the clear plastic cube which supports the blue pyramid is made of a polymer called PMMA. This polymer retains its shape well at room temperature, though it may droop over many thousands of years, or if heated sufficiently. The present study deals with PMMA as well as polyethylene.

It is, however, difficult to do a test which covers more than a multiple of about 1,000 in time or frequency. For example a test may be done from 10 seconds to 10,000 seconds (a bit less than three hours). That will not suffice to evaluate a material with an expected service life of years under load. Also the test does not reveal how well the material absorbs sound, corresponding to a time scale of from about five hundredths of a second to fifty millionths of a second.

One can get around this experimental limitation and also predict behavior for short and long time periods. To do this, one assumes that a temperature change is equivalent to a multiplication of the time scale by some number. Then, several experiments are done at different temperatures. The results are shifted on a logarithmic time scale to obtain a prediction for an extended time scale. This time-temperature shift approach will work if all the molecules in the polymer have the same temperature sensitivity.

In our laboratory we do tests over a range of a hundred million in effective time or frequency. This is much greater than the factor of 1000 usually used. In this project we use the extended range capability to evaluate the time-temperature shift assumption. The diagram below shows results for an amorphous polymer PMMA, known commercially as Plexiglas. As temperature is raised, the peak in the viscoelastic dissipation does not merely shift to higher frequency, it also becomes larger. Therefore the usual time-temperature shift assumption needs to be modified. Polyethylene, which is partially crystalline, also exhibits deviations from the usual time-temperature shift pattern. Implications in design with polymers are under study.