Miraculous Gelation - Unresolved Problems and Open Questions of Gelation Rheology

H. Henning Winter

Department of Chemical Engineering, University of Massachusetts,
Amherst, MA 01003, USA

The most astounding of all gelation phenomena, in my opinion, is the universality of the "critical gel" rheology for a multiplicity of complex materials at the gel point. Rheology is generally known to strongly depend on the internal structure of a material. However, independent of their individual structure that may cause gelation, all these materials look the same rheologically at the gel point, at least at small strain and in long-time experiments: the long-time relaxation modulus is a powerlaw $G(t)= S\, t^{-n}$. Its format is universal while values for S and n vary from material to material. Really puzzling is the physical dimension of S [Pa s^n], which tells us that S should somehow be divided into a modulus G_0 and a characteristic time t_0, and the relaxation modulus should then be written as $G(t)= G_0\, (t/t_0)^{-n}$. A criterion needs to be found for defining G_0 and t_0. Furthermore, S and n depend on each other. Large S was found for small n and vice versa. But why? Further puzzles concern the temperature dependence, the slope of $G'(t,w)$ and $G''(t, w)$ at gel point, the applicability of the time-cure superposition, diverging rheological functions near gel point, physical as compared to chemical gelation, coping with fast gelation, large strain behavior, and the competition with other solidification mechanisms such as crystallization, jamming and the glass transition, to name a few. Data will be shown to define many of the open questions that still need to be addressed before we can claim that gelation rheology may be understood.