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Soft polymeric materials near the transition from liquid to solid state

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Abstract

Soft polymeric materials have gained importance in recent years, namely in food, pharmaceuticals, photographic media, adhesives, vibration dampeners and superabsorbers (to name a few), but also as intermediates for selforganization of molecules or supramolecules into long range order. Many of these soft materials are close to their gel point, i.e. they are liquids just before reaching their gel point or they are solids which have barely passed the gel point. New rheological methods need to be developed for the understanding of these soft materials; the typical liquid properties (viscosity) and typical solid properties (modulus) are not applicable since they diverge at the gel point. This will be discussed in the following. Fortunately, chemical gelation experiments with model polymers has given insight into the behavior at the gel point (Winter and Mours, 1997). This knowledge of the critical gel provides us with a reference state when working with soft polymeric materials. Chemical gels will serve as model materials for the exploration of physical gels. A novel method for detecting the gel point has been proposed: the instant of liquid-to-solid transition(gel point) is marked by the crossover of the normalized dynamic moduli $G'/\cos(n_c\pi/2)$ and $G''/\sin(n_c\pi/2)$.

1. The Gel Point as Reference State

Polymers at their gel point, so called "critical gels" (Vilgis and Winter, 1988), are characterized by a self-similar relaxation modulus (Chambon and Winter, 1985; Winter and Chambon, 1986; Winter and Chambon, 1987)

$$G(t) = S_c t^{-n_c}, \qquad \text{for} \qquad \lambda_0 < t < \infty \tag{1}$$

when probed above a material characteristic crossover time λ_0 (glass time or entanglement time, for instance), see figure 1. The two material parameters are the stiffnes S_c and the relaxation exponent n_c. Subscript c is used here to identify the critical state at the gel point. Universal features of critical gels are that they

- require infinite time to relax,
- relax in a broad distribution of shorter modes which are self-similar.

These features become appearent in experiments which probe the long-time behavior. The stretching of the spectrum has been attributed to two effects, the broadening of the cluster size distribution (molecular clusters, supramolecular clusters) and the branching of the clusters.

When introducing the relaxation modulus of eq.1 into the classical equation of linear viscoelasticity of Boltzmann (Ferry, 1980), this leads to a constitutive equation for the critical gel

$$\tau(t) = \int_{-\infty}^{t} dt' S_c (t-t')^{-n_c}\, \dot{\gamma}(t') \tag{2}$$

which is simplified here for applications where the short modes, with characteristic times below the λ_0 crossover time, do not contribute significantly. The equation is written in terms of the shear stress $\tau(t)$ and the shear rate $\dot{\gamma}(t)$

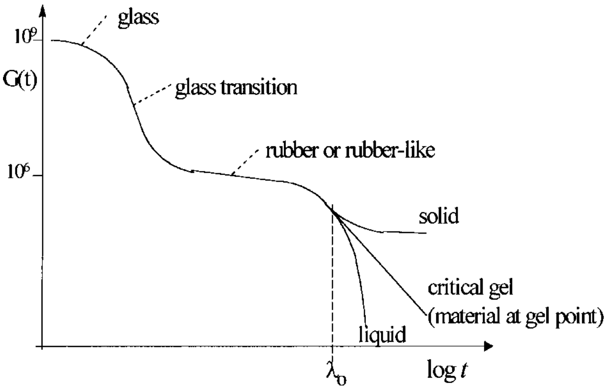

Fig. 1. Relaxation modulus of polymeric materials. The long-time behavior distinguishes between liquids and solids. The critical gel is the material state at the gel point. The material characteristic crossover time λ_0 is the glass transition time or (in this example) the entanglement time. In this sudy, the sample is far away from the glass transition; otherwise, it would not be soft any more.

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but can also be generalized to tensorial form

$$\boldsymbol{\pi}(t) = -P(t)\mathbf{1} + n_c S_c \int_{-\infty}^{t} dt'(t-t')^{-(n_c+1)} \mathbf{C}^{-1}(t;t') \qquad (3)$$

$\mathbf{C}^{-1}(t;t')$ is the well known Finger strain tensor (Larson, 1988) between states t' and t. Large strain behavior and breaking of the structure is not included in this equation. The breaking of critical gels (Venkataraman and Winter, 1990) is a topic which needs to be investigated in the future.

Knowing the behavior at the gel point allows us to use the critical gel as reference state for describing materials in the vicinity of the gel point. Small amplitude dynamic mechanical experiments, when performed over a wide frequency range, show the state of the polymer with respect to the gel point. The complex stiffness

$$S'(\omega) = \frac{G'(\omega)}{\omega^n \Gamma(1-n)\cos\frac{n\pi}{2}} = \frac{G''(\omega)}{\omega^n \Gamma(1-n)\sin\frac{n\pi}{2}} \qquad (4)$$

and the normalized loss angle

$$n = \frac{2\delta}{\pi} \ ; \ \delta = \tan^{-1}\frac{G''}{G'} \qquad (5)$$

are material functions which, at frequencies below $\omega_0 = 1/\lambda_0$, are especially informative near the gel point. G' and G" are the storage and loss moduli, δ is the loss angle, and $\Gamma(\ )$ the gamma function. These material functions are chosen such that, at the gel point, they reduce to

$$n = n_c$$
$$\text{and } S(\omega) = S_c, \quad \text{for} \quad \omega < \omega_0 = 1/\lambda_0. \qquad (6)$$

They become frequency independent; also the loss tangent

$$\tan\delta = \frac{G''}{G'} \qquad \text{for } \omega < 1/\lambda_0 \qquad (7)$$

becomes frequency-independent and equal to $\tan(n_c\pi/2)$ (Winter and Chambon, 1986; Winter and Chambon, 1987). Frequency independence of δ enables the detection of the gel point. This has been used in a convenient experiment for determining the instant of gelation (Holly *et al.*, 1988). It should be noted that the cross-over of $G' \equiv G''$ does not occur at the gel point (Tung and Dynes, 1982); however this problem can be overcome by, instead, plotting $G'/\cos(n_c\pi/2)$ and $G''/\sin(n_c\pi/2)$; the cross-over of these two functions is indeed independent of n_c:

$$\frac{G''(\omega)\cos\frac{n_c\pi}{2}}{G'(\omega)\sin\frac{n_c\pi}{2}} = \frac{\tan\delta}{\tan\frac{n_c\pi}{2}} \equiv 1 \quad \text{for} \quad \delta = \delta_c \qquad (8)$$

This alternative method of detecting gel point is useful for classes of materials for which n_e is known.

2. Chemical Gels

Chemical gels are well defined by their covalent junctions which connect molecules into three-dimensional networks. The evolution of structure is described in the classical theory by Flory (1941; 1942) and Stockmayer (1943) and in the percolation theory (Stauffer, 1985; de Gennes, 1971). Molecular conformations relax with slower and slower modes as the molecules grow in size. The molecular weight distribution is infinitely broad (Flory, 1941; Stockmayer, 1943; Schosseler and Leibler, 1984).

The conversion of the chemical reaction, $0 \leq p < 1$, is the independent variable which defines the progress of the gelation process. The gel point is reached when the largest molecular cluster diverges to infinite size (Florry, 1941; Flory, 1942; Stockmayer, 1943). This defines the threshold value P_c of the chemical conversion. A crosslinking or vulcanizing sample before its gel point, $p < p_c$, can be dissolved in a good solvent; because of this propery, it is called a sol. Beyond the gel point, $p_c < p$, the polymer can only be swollen in a good solvent, but it does not dissolve in its entirety. The polymer is called a gel, even if it contains substantial ammounts of unattached molecules (sol fraction). In this terminology, the liquid-to-solid transition is often called "sol-gel transition".

3. Physical Network Formation

Physical gels are able to form suprarmolecular structures which connect into a sample spanning network. Connectivity can be achieved by a wide range of mechanisms which have been reviewed comprehensively by te Nijenhuis (1997). In analogy to chemical gelation, where large scale connectivity is achieved by covalent bonds between molecules and the gel point is reached when the largest molecular cluster diverges to infinite size (Florry, 1941; Flory, 1942; Stockmayer, 1943), physical gelation may be defined by the growth of physically connected aggregates: the physical gel point is reached when the correlation length of molecular (or supramolecular) motion diverges to infinity. The rheology during gelation has the exact same features as that of chemical gelation, eq.1. The analogy between chemical and physical gelation applies very well to systems with long living bonds. It becomes less defined when renewal of physical bonds occurs on the time scale of observation and the system behaves as a liquid. In this case, a characteristic renewal time, λ_{pg}, of the physical bonds determines long time ordering processes and rheology of a physical gel. The analogy between physical and chemical gelation applies only to time scales shorter than the characteristic renewal time.

Equation 1 changes into

$$G(t) = S_c t^{-n_c}, \quad \text{for} \quad \lambda_0 < t < \lambda_{pg} \tag{9}$$

Physical gels typically have a yield stress beyond which the stucture gets broken and liquid behavior sets in. Below the yield stress, the physical gel is a solid at experimental times shorter than the renewal time and a liquid at experimental times longer than the renewal time.

4. Temperature and Molecular Weight Dependence

For chemical gelation, the temperature dependence of the two parameters is known (Izuka et al., 1994). While the relaxation exponent is constant when raising the material temperature from T_0 to a second temperature T,

$$n_c(T) \equiv n_c(T_0) \qquad \text{with} \quad 0 < n < 1, \tag{10}$$

the relaxation modulus

$$G(t,T) = \underbrace{S_c(T_0)\frac{(a_T)^{n_c}}{b_T}}_{S_c(T)} t^{-n_c} \tag{11}$$

shifts with the monomeric friction coefficient and the density as known for polymeric liquids or solids (compare to Ferry (1980)). Remarkable is the power law exponent for the shift: only a fraction of the shift factor becomes effective; the fraction is larger for a soft critical gel (large n_c) than for a stiff one (small n_c).

Physical gels show distinctly different temperature dependence since not only the chain friction is affected by temperature but also the character of the physical junctions (functionality, characteristic renewal time of bonds).

The molecular weight dependence of the relaxation exponent is not clear. However, experiments with model chemical gels suggest a value of n near 0.5 for high molecular weight systems (Mours and Winter, 1996) and larger values (near 0.7) for critical gels which are made from small precursor molecules (Martin and Wilcoxon, 1988).

Better known is the molecular weight dependence of the front factor, the stiffness (De Rose *et al.*, 1997),

$$S_c = \Gamma(n_c) m G_N^o \lambda_e^{n_c} (M/M_e)^{n_c 3.4} \tag{12}$$

as long as the precursor molecules are of a molecular weight above the entanglement limit, $M > M_e$. With n_c about 0.5, the molecular weight dependence is about 1.7. The other parameters belong to the linear viscoelasticity of the precursor which in this case is a polymer of long, linear, flexible molecules of (nearly) uniform molecular weight (Baumgärtel *et al*., 1990) : m is the slope of G" in the entanglement region, G_N^o is the plateau modulus, λ_e is the crossover time from entanglement behavior to glass transition modes and M_e is the entanglement molecular weight. $\Gamma(n_c)$ is the gamma function at n_c.

5. Gelation and Ordering in Physical Gels

Physical gelation and ordering are related processes. Ordering into suprarmolecular structures requires molecular mobility. However, increased order also correlates motion over longer and longer distances, i.e. it reduces mobility and may cause gelation. This gelation phenomenon will interrupt the ordering process. Higher states of order are inherently excluded by the ordering process itself. The challenge is to find suitable ordering dynamics which give the highest order in the material.

Crystallization of polymers is an example of such interplay between ordering and gelation. A deep quench from the (disordered) melt state to a temperature below the crystallization temperature T_C results in rapid crystallization (ordering) of molecular strands into small crystals. The growth of thick crystals is intercepted by gelation. However, when reheating the polymer to some temperature close to T_C, the small crystals melt and enable molecular motion. Thicker crystals start to grow in a so called re crystallization process. Crystallization occurs more slowly at small $\Delta T = T_C - T_X$ and higher order is achieved before the gel point is reached. Beyond the gel point, the large scale order is very much fixed. Further crystallization occurs onto the sample spanning template and on local scale. Examples will be selected from recent experiments of Pogodina *et al.* (Pogodina and Winter, 1998; Pogodina *et al.,* 1999), Gelfer and Winter (1999) and Horst and Winter (2000).

Microphase separating block copolymers also show the interplay of ordering and gelation. After quenching below the ordering temperature, ordered structures nucleate and grow until they border with neighboring grains (Sakamoto and Hashimoto, 1998). The result is a granular structure with uniformly ordered regions of about 1 µm size, but random order (disorder) over longer distances. Development of long range order is not possible due to the lack of molecular mobility. Keller *et al.* (1970) overcame this problem by slowly shearing the microphase separated structure. The shear deformation breaks the solid structure and enhances molecular mobility. Long range order is facilitated by reversing the gelation process temporarily, in this case by mechanically breaking the structure. Keller's sample was a strongly micro-phase separated block copolymer which formed cylindrical microdomains which initially aligned within grains of random direction. Shear rates were chosen such that they preferentially mobilize domains which were directed sideways to the shear direction while domains with cylinders in shear direction have a higher survival probability and are able to grow in length as the shearing process continues. Examples will be shown from the work of Soenen *et al.* (1997) and of unpublished experiments.

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