Breaking and Healing of Associative Network polymers

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EXTENDED ABSTRACT

Soft solids get easily broken (internally and/or macroscopically) at loads above their yield stress. While chemical network polymers break irreversibly, associative networks are able to heal their structure into long-range connectivity, often of increased order. Typically, the controlling parameters are stress, strain, temperature, and time.

The dynamics of formation, breaking, and reformation of soft polymer gels can be observed with rheology. Polymers at their transition from liquid to solid (critical gels) exhibit a distinct relaxation pattern, which allows detection of the gel point and direct observation of gelation dynamics. The slow molecular dynamics of critical gels is governed by a power law distribution of relaxation modes. The time dependent relaxation modulus, $G(t)=St^{-n}$, decays with a relaxation exponent n and front factor S (stiffness of critical gel). This can be measured, for instance, by mechanical spectroscopy at low frequencies which shows distinct power laws of dynamic moduli, $G' \sim G'' \sim w^n$, and a frequency-independent loss tangent, G''/G'. Not only is rheology a sensitive measure of molecular mobility at a wide range of length scales. Rheology has also become more quantitative due to the recent discovery of the rheological "laws" which govern the gel point. Universality of the transition behavior has been found for chemical and physical gelation[1]. The finite lifetime of physical junctions imposes a problem if the ratio of lifetime and experimental time (gel number) is within a decade below or above order unity.

Block Copolymer Gels

We can use the gel point behavior as reference state for the study of self-organization dynamics in block copolymer gels since the structuring results in a liquid-solid transition[2]. Here we are concerned with S-EB-S (polystyrene- polyethylene/ buthylene-polystyrene) triblock copolymers of which the midblock is selectively swollen with an oil. Below their order-disorder-transition temperature (ODT), such polymer /solvent systems are able to nano-phase separate into spherical polystyrene domains (5-50 nm scale) in a continuous matrix of EB swollen by solvent, hereby ordering into a body centered cubic lattice. The kinetics and dynamics of reverse gelation (breaking) and gelation will be discussed in relation to the S-EB-S model polymer.

ACKNOWLEDGEMENTS

REFERENCES

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2. Soenen et al., Polymer 38:5653-5660, 1997