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New Developments and Directions in the Area of Elastomers and Rubberlike Elasticity

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Summary: There are number of important developments in the area of elastomeric polymers, including (i) network chains of controlled stiffness, (ii) model elastomers (including dangling-chain networks), (iii) fluorosiloxane elastomers, (iv) new thermoplastic elastomers, (v) other new elastomers, (v) bimodal network chain-length distributions, (vi) cross linking in solution or in a state of deformation, and (vii) gel collapse. Interesting elastomeric composites include those with (i) in-situ generated ceramic-like particles, (ii) ellipsoidal fillers, (iii) clay-like layered fillers, (iv) polyhedral oligomeric silsesquioxane (POSS) particles, (v) porous fillers, (vi) elastomeric domains modifying ceramics, and (vii) controlled interfaces. New characterization techniques are being developed for elastomers, and there have been new developments in elasticity theory and in elastomer processing. Some examples of societal aspects of relevance are (i) synthesis of elastomers in environmentally-friendly solvents, (ii) biosynthesis, (iii), recyclability, (iv) improved adhesion to tire cords, and (v) better barrier properties in anti-terrorism clothing. Educational topics include curriculum development, and mobile laboratories for elastomer experiments and demonstrations.

Keywords: bimodal distributions, biosynthesis, curriculum, elasticity theory, elastomers, gel collapse, interfaces, mechanical properties, model networks, recyclability, reinforcement

Elastomeric Polymers

Network chains of controlled stiffness. The primary interest here is to increase the melting point of an elastomer such as poly(dimethylsiloxane) (PDMS) so that it undergoes strain-induced crystallization. This crystallization is the origin of the superb mechanical properties of natural rubber, and it results from the reinforcing effects of the crystallites. One way of stiffening elastomeric chains such as PDMS is to put a meta or para phenylene group in the backbone.[1]

Model elastomers. Elastomers of this type are made by reacting functionally-terminated chains with a multifunctional end-linking agent. Because of this preparative approach, much more information on their structures is known than on those prepared using more uncontrolled

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methods such as sulfur vulcanization or peroxide thermolysis. They also have unusually good mechanical properties, perhaps because of a reduced number of dangling chains.[2] The same synthesis approach has been used to put known numbers of dangling chains of known lengths into intentionally-imperfect networks.

Fluorosiloxane elastomers. Placing fluorine atoms into siloxane repeat units can be useful for increasing polysiloxane solvent resistance, thermal stability, and surface-active properties.[3-5]

New thermoplastic elastomers. There is a need to develop thermoplastic elastomers that are less expensive than the Kraton® styrene-butadiene-styrene triblock copolymers. The leading candidates are stereochemical copolymers of polypropylene, and chemical copolymers of ethylene and comonomers such as hexene-1.[6-8]

Some other new elastomers. One example of another interesting elastomeric material is a new hydrogenated nitrile rubber with good oil resistance and a wide service-temperature range.[9] Another is a type of "*baro*plastic" elastomer which parallels *thermo*plastic elastomers in that a pressure increase gives the desired softening required for processing instead of the usual temperature increase.[10]

Bimodal network chain-length distributions. End linking a mixture of very short chains with the much longer chains that are typical of elastomers gives networks with unusually good ultimate properties, including toughness. [11] This is illustrated in Figure 1.

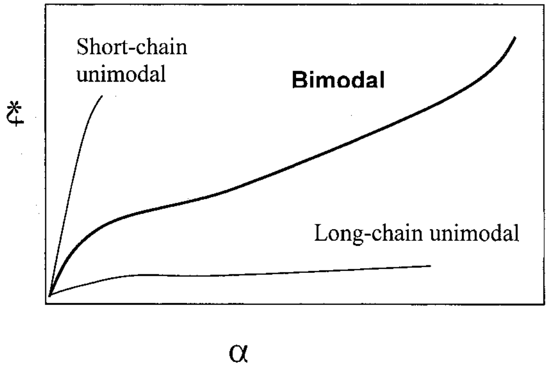

Fig. 1. Typical dependence of nominal stress against elongation for two unimodal networks having either all short chains or all long chains, and a bimodal network having some of both.

Cross linking in solution or in a state of deformation. Forming networks under these unusual conditions has a number of advantages, including the synthesis of elastomers exhibiting less stress relaxation, and stress-strain relationships that are closer to those expected from the simplest molecular theories.[2] Recent studies on networks cross linked in solution have focused on their unusually high extensibilities,[12,13] and changes in their extents of strain-induced crystallization.[14,15]

Gel collapse. Gels, which are networks swollen with a diluent, can be brought to the point where only small changes in a variable such as temperature, pH, ionic strength, etc. can bring about an abrupt shrinkage.[16-19] This is illustrated in Figure 2. The shrinkage occurs rapidly enough in fibers and films to be of interest with regard to producing switches, actuators, artificial muscle, and drug-delivery systems.

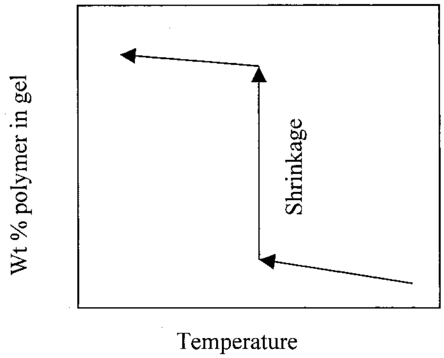

Fig. 2. A gel exuding solvent upon decrease in temperature, with the shrinkage representing "gel collapse".

Elastomeric Composites

In-situ ceramic-reinforced elastomers. One novel way of introducing ceramic-like fillers into a polymer is by the *in-situ* hydrolysis and condensation of an organosilicate, organotitanate, organozirconate, etc. to give silica, titania, zirconia, etc. These "sol-gel" techniques are not much used commercially thus far, because the processing is so different from the usual "*ex-situ*" incorporation of fillers after making them in a separate step, and then mechanically blending them into the polymer matrix.

Ellipsoidal fillers. Reinforcing fillers can be deformed from their usual approximately spherical shapes in a number of ways. For example, if the particles are a glassy polymer such as polystyrene, then deforming the matrix in which they reside above the glass transition temperature will convert them into ellipsoids.[20,21] Uniaxial deformations give prolate (needle-shaped) ellipsoids, and their axes will be in the direction of the deformation, as illustrated in Figure 3. Similarly, biaxial deformations give oriented oblate (disc-shaped) ellipsoids.

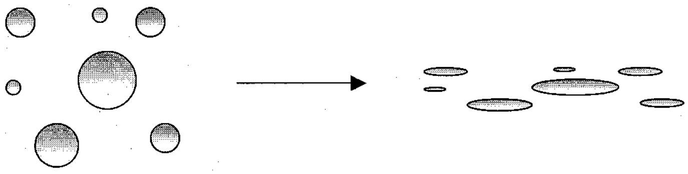

Fig. 3. Deformation of spherical particles into prolate ellipsoids.

One interest here is the anisotropic reinforcements such particles provide, and there have been simulations to better understand the mechanical properties of such composites. [22]

Clay-like filler. Exfoliating layered particles such as the clays, mica, and graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than in the case of solid particles such as carbon black and silica.[23-27] Other properties can also be substantially improved, including increased resistance to solvents, and reduced permeability and flammability.

Polyhedral oligomeric silsesquioxane (POSS) particles. These fillers are cage-like structures, and have been called the smallest possible silica particles. They typically contain between zero and eight organic functional groups per cage. The particles with no functional groups at all can be blended into polymers using the usual mixing or compounding processing, while those with one functional group can be attached to a polymer as side chains. Those with two functional groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross linked networks.[28-32] Nanotubes are also of considerable interest in this regard.[33-35]

Porous fillers. Some fillers such as zeolites are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities, with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix.[34] Because of the constraints imposed by the cavity walls, these confined materials show no glass transition temperatures. A typical structure of this type is illustrated in Figure 4.

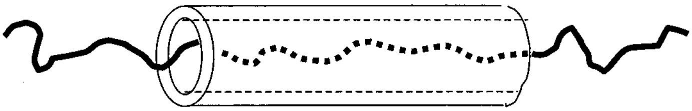

Fig. 4. Sketch of a polymer chain passing through the cavity of a zeolite.

In-situ elastomer-improved ceramics. The sol-gel technique used to precipitate ceramic-like fillers into an elastomer can also be used to precipitate elastomeric domains into a ceramic.[2] The main goal here is to improve the impact resistance of the resulting composite.

Composites with controlled interfaces. By choosing the appropriate chemical structures, chains that span filler particles in a polymer-based composite can be designed so that they are either durable, breakable irreversibly, or breakable reversibly.[36-38]

New Characterization Techniques

IR spectroscopy and birefringence[39] are being used to get new insights into the network chain orientation necessary for strain-induced crystallization. Also of importance are NMR, small-angle x-ray and neutron scattering, atomic force microscopy, Brillouin scattering,[40,41] and pulse propagation measurements.[40,42] In the last of these techniques, the delay in pulses passing through the network is used to obtain information on the network structure.

Theoretical Developments

Some of the most interesting advances in rubber elasticity theory are the various approaches being developed to take better account of chain entanglements.[2,43] In the "constraint" theories, the focus is on the way the constraints are placed within the network structure, some possibilities being illustrated in Figure 5.

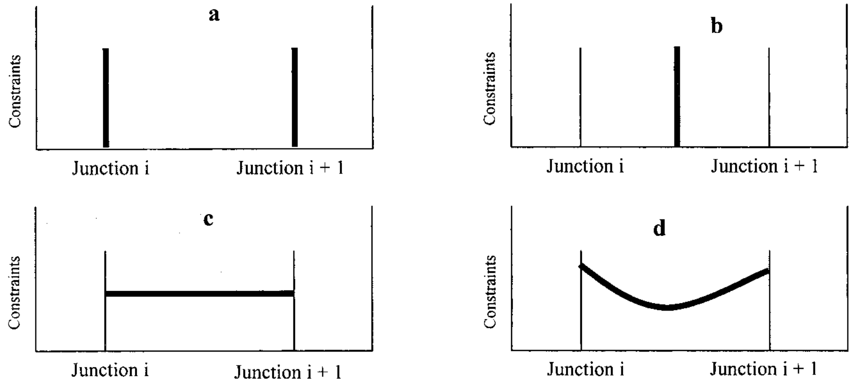

Fig. 5. Locations of constraints in the constraint theories: (a) at the junctions themselves, (b) at the mass centers of the network chains, (c) spread uniformly along the network chains, and (d) at possibly more refined locations based on future experimental information.

New Developments in Processing

Important topics in this area are the use of chaotic mixing to improve compounding,[44] and modeling that includes flow-induced crystallization during molding processes.

Societal Aspects

Of interest here are the possible synthesis of elastomers in environmentally-friendly solvents, and the understanding and exploitation of biosynthetic techniques.[45] Another environmental goal is recyclability.[46,47] Other topics much in the news currently are the improvement of safety aspects of tires (with an emphasis on more reliable bonding to tire cords), and better barrier properties in anti-terrorism protective clothing. Educational topics include curriculum development, and mobile laboratories for elastomer experiments and demonstrations.

Acknowledgments

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