Properties and Behavior
of Polymers

VOLUME 2

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Editorial Staff

PREFACE

Owing to their versatility and wide range of applications, polymeric materials are of great commercial importance. The physical and chemical properties of polymeric materials influence their processing and use, so familiarity with the properties and behavior is not only interesting but also crucial to ensure proper utilization of such polymers.

The two-volume set **Properties and Behavior of Polymers** offers over 40 self-contained articles written by prominent scholars from around the world. The articles provide comprehensive, up-to-date information on the physical properties of polymers and the resulting characteristics and behavior, including viscoelasticity, flammability, miscibility, optical properties, surface properties and more.

Containing carefully selected reprints from Wiley's renowned *Encyclopedia of Polymer Science and Technology*, this reference features the same breadth and quality of coverage and clarity of presentation found in the original. This reliable reference will be of particular interest to polymers and materials scientists, chemists, chemical engineers, process engineers, students, researchers and educators in related fields and consultants and suppliers in the plastic and related industries.

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NETWORKS, ELASTOMERIC

Introduction

The most striking features of a rubber-like material are its ability to undergo very large deformations with essentially complete recoverability. In order for a material to exhibit such unusual behavior, it must consist of relatively long polymeric chains that have a high degree of flexibility and mobility, and are joined into a network structure. The requirement of flexibility and mobility is associated with the very high deformability. As a result of an externally imposed stress, the long chains may alter their configurations which takes place relatively rapidly due to their high mobilities (1–13). The requirement of linking the chains into a network structure is associated with the solid-like features, where the chains are prevented from flowing relative to each other under external stresses. As a result, a typical rubber or elastomer may be stretched up to about 10 times of its original length. Upon removal of the external force, it rapidly recovers its original dimensions, with essentially no residual or nonrecoverable strain. As a result of these unique mechanical properties, elastomers find important usages ranging from automobile tires to heart valves, to gaskets in jet planes and space vehicles (14,15).

The above-mentioned general features of elastomeric materials have long been known and, in fact, the area of rubber-like elasticity has had one of the longest and most distinguished histories in all of polymer science (1,2,16). For example, quantitative measurements of the mechanical and thermodynamic properties of natural rubber and other elastomers go back to 1805, and some of the earliest studies have been carried out by such luminaries as Joule and Maxwell. Also, the earliest molecular theories for polymer properties of any kind were, in fact, addressed to the phenomenon of rubber-like elasticity.

Some Rubber-Like Materials

The rubber-like materials described in this section are so designated since they exhibit the high deformability and recoverability so reminiscent of natural rubber itself (2,17). They are thus frequently called "rubbers," and the terms rubber-like materials, rubbers, and elastomers are used essentially interchangeably in the literature. Since high flexibility and mobility are required for rubber-like elasticity, elastomers generally do not contain stiffening groups such as ring structures and bulky side chains (2,13). These characteristics are evidenced by the

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low glass transition temperatures T_g exhibited by these materials. These polymers also tend to have low melting points, if any, but some do undergo crystallization upon sufficiently large deformations. Examples of typical elastomers, which do undergo strain-induced crystallization, include natural rubber, butyl rubber, and high *cis*-polybutadiene, with recent attention focusing on copolymers of high *trans*-polybutadiene (18). In contrast, poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$], poly(ethyl acrylate), styrene–butadiene copolymer, and ethylene–propylene copolymer generally do not undergo strain-induced crystallization.

Some polymers are not elastomeric under normal conditions but can be made so by raising the temperature or adding a diluent ("plasticizer"). Polyethylene is in this category because of its high degree of crystallinity. Polystyrene, poly(vinyl chloride), and the biopolymer elastin are also of this type, but because of their relatively high glass transition temperatures also require plasticization to be elastomeric (13).

A final class of polymers is inherently nonelastomeric. Examples are polymeric sulfur, because of its chains are too unstable, poly(*p*–phenylene) because its chains are too rigid, and thermosetting resins because their chains are too short (13).

There is much current interest in hydrogels, particularly those robust enough to be used in biomedical applications.

Preparation and Structure of Networks

Networks are formed by joining individual chains into a three-dimensional structure. The conventional method of network formation is by random cross-linking with a suitable cross-linking agent. More modern techniques involve end linking in order to obtain better controlled and characterized networks. Polymerization into a cross-linked system by adding a small amount of multifunctional reactants into the polymerizing system or by joining the chains by physical forces such as hydrogen bonding is also utilized.

Random Chemical Cross-Linking.   In random cross-linking, chemical reactions are used that attack a pair of chains, at essentially random locations (1,13). Examples are the addition of sulfur atoms to the double bonds of diene elastomers and the attack of free radicals from peroxide thermolyses or high-energy radiation on side chains (frequently unsaturated) or on the chain backbone itself.

The cross-links formed in this way are generally highly stable. These networks, however, still present the problem that the cross-linking reaction used is highly uncontrolled in that it is not known how many cross-links are introduced or where they lie along the chain trajectories. It is thus very difficult to use these networks for quantitative purposes such as the development of structure–property relationships. Obtaining independent measures of their degree of cross-linking (as represented directly by the number density of cross-links or the number density of network chains, or inversely by the average molecular weight M_c between the cross-links that mark off a network chain) is virtually impossible (13).

Highly Specific Chemical End Linking. If networks are formed by end-linking functionally terminated chains instead of haphazardly joining chain segments at random, then the nature of this very specific chemical reaction provides the desired structural information (6,13,19–28). Thus, the functionality of the cross-links is the same as that of the end linking agent, and the molecular weight M_c between cross-links and its distribution are the same as those of the starting chains prior to their being end linked.

Because of their known structures, such end-linked elastomers are now the preferred materials for the quantitative characterization of rubber-like elasticity. In addition, bimodal networks prepared by these end-linking techniques have very good ultimate properties, and there is currently much interest in preparing and characterizing such networks (13,22,25,29–33) and developing theoretical interpretations for their properties (34–37). Both subjects are discussed below.

Polymerizations with Multifunctional Monomers. Another way of making a network is by a copolymerization in which at least one of the comonomers has a functionality ϕ of 3 or larger. This is one of the oldest ways of preparing networks but has been used mostly to prepare materials so heavily cross-linked as to be relatively hard thermosets rather than highly deformable elastomers (13,38). Some work in this area involves the use of sol fractions and statistical arguments to obtain information on the structures of the sol phases and gel (elastomeric) phases (39–43).

Physical Aggregation. Preparation of elastomeric networks is also possible by causing physical aggregation of some of the chain segments (3,13). Examples are the adsorption of chain segments onto filler particles, formation of polymer microcrystallites, condensation of ionic side chains onto metal ions, chelation of ligand side chains to metal ions, and microphase separation of glassy end blocks in an elastomeric triblock copolymer (44). These materials are now not much used in quantitative studies of rubber-like elasticity. The nature and extent of the cross-linking can change with the temperature, the presence of diluent, and degree of deformation in an uncontrolled manner, and the "cross-links" are frequently so large as to complicate greatly the theoretical analysis of any experimental results.

Networks Prepared under Unusual Conditions

Several indirect approaches are undertaken in preparing networks of simpler topology with reduced degrees of network chain entangling (4). Some of the techniques employed involve (*i*) separating the chains prior to their cross-linking by either dissolution (45) or stretching (46), (*ii*) simultaneously forming two different but interpenetrating systems, (*iii*) trapping cyclics into the network, (*iv*) simultaneously cross-linking one component highly and the other lightly, and (*v*) using platelets as junctions.

Cross-Linking in Solution. This approach (5) did produce elastomers that had fewer entanglements, as indicated by the observation that such networks came to elastic equilibrium much more rapidly than elastomers cross-linked in the dry state. When a network is cross-linked in solution and the

solvent then removed, the chains collapse in such a way that there is reduced overlap in their configurational domains. It is primarily in this regard—namely, decreased chain-cross-link entangling—that solution cross-linked samples have simpler topologies.

These elastomers also exhibited stress–strain isotherms in elongation that were closer in form to those expected from the simplest molecular theories of rubber–like elasticity. Specifically, there were large decreases in the Mooney–Rivlin $2C_2$ correction constant.

In these procedures, removal of the solvent has the additional effect of putting the chains into a "supercontracted" state (5). Experiments on strain-induced crystallization carried out on such solution cross-linked elastomers indicated that the decreased entangling was less important than the supercontraction of the chains, in that crystallization required larger values of the elongation than was the case for the usual elastomers cross-linked in the dry state (47). More recent work in this area has focused on the unusually high extensibilities of such elastomers (48).

One novel approach involves the use of collapsed cross-link regions that can unfold under stress, and then refold reversibly upon retraction of the elastomer (49). This is essentially biomimicry of some body tissues, such as the muscle protein titin, in which such behavior gives these biomaterials an impressive combination of deformability and strength.

Cross-Linking in the Deformed State. In this approach, a first network is generally introduced in the undeformed state, the resulting elastomer is elongated, and a second series of cross-links is introduced in the stretched state. Release of the stress permits the network to retract, but the second network of this "double-network" structure prevents retraction down to the original dimensions. The most interesting feature of the retracted network is the fact that it is anisotropic in structure and properties.

In some cases, double networks have shown increases in orientability and strain-induced crystallization (50) and improved fatigue resistance (51). In fact, some results show that there may be less of a compromise between failure properties in general and the modulus (52), which may be due in part to the decreased hysteresis observed for some of these elastomers. Theoretical treatment of such materials goes back to 1960 (53), and research has continued on them up to the present time (51,54–56). Better molecular understandings of these observations are being sought with, for example, extensive studies of residual strains and birefringence (55).

Interpenetrating Networks. If two types of chains have different end groups, then it is possible to end link them simultaneously into two networks that *interpenetrate* one another (57). Such a network could, for example, be made by reacting hydroxyl-terminated PDMS chains with tetraethoxysilane (in a condensation reaction), while reacting vinyl-terminated PDMS chains mixed into them with a multifunctional silane (in an addition reaction) (58). Interpenetrating networks can be very unusual with regard to both equilibrium and dynamic mechanical properties (59). For example, such materials can have considerable toughness and unusual damping characteristics.

Slide Ring Gels. Slide ring gels are topological networks with some similarities to linear rotaxane assemblies (60,61). In these gels, a number of cyclic

molecules are threaded onto a linear polymer chain and then trapped by placing bulky capping groups at the two ends of the chain. Some of the cyclics are then fused together to form mobile cross-links. In the case of two fused cyclics, the result is a figure-eight structure: ∞ (62–66). These cross-links are called slide rings, and act like pulleys for the chains threading through them. The sliding is thought to thus equalize any network tensions, cooperatively. This gives the gels unusual mechanical properties, in particular very high deformabilities and degrees of swelling. There has been considerable interest in the theoretical treatment of such materials (67,68).

Double Networks. Double networks belong to a class of hydrogels that consist of two independently cross-linked networks, one consisting of a rigid polyelectrolyte and the other a flexible uncharged polymer. (69–73) The term "double networks" is an unfortunate choice of terminology since this name has long been applied to the completely different elastomeric materials described above as networks in which some of the cross-links are introduced in the deformed state.

Double networks are used as water-swollen gels and exhibit the best mechanical properties when the first network is highly cross-linked and the second only lightly cross-linked. The molar ratio of the second component to the first should be a factor as high as 10 or more, which makes them rather different from most interpenetrating networks (IPNs) (57). The enhanced mechanical properties of these double-network hydrogels are thought to be a result of the second network preventing cracks from growing to the point of producing catastrophic failure of the material. More specifically, this dissipation of crack energy may be facilitated by the second network appearing as clusters in voids occurring in what is apparently an inhomogeneous matrix of the first network. There is expected to be considerable entangling of the two types of chains in these domains. In some cases, a third component is used to form a triple network with, for example, uncross-linked polymer being added to reduce surface friction (74). Considerable modeling has been carried out to better understand the properties of these double network hydrogels (75–77).

Nanocomposite Gels. Nanocomposite gels use exfoliated platelets of clay as the cross-linking junctions (78–81). Ends of the polymer chains absorb strongly on the surfaces of the platelets and enough of the chains attach to *different* platelets to provide the bridges that constitute a network structure. The fact that the cross-links are planar sheets of considerable dimensions and junction functionality somehow yields unusual mechanical properties, including very good toughness.

Network Structure

The elastic activity of a network depends directly on the molecular structure. Perfect networks with no dangling chains, which are connected to the network structure at one end only and no loops where the two ends of a chain terminate at the same junction, serve as suitable references. The structure of a perfect network may be defined by two variables, the cycle rank ξ and the average junction functionality ϕ (3,13). Cycle rank is defined as the number of network chains that must be cut in order to reduce it to a tree (82), which is a giant molecule

containing no closed structures or cycles. The number of junctions μ, the number of chains ν, and the molecular weight M_c, of chains between two junctions, may be obtained from ξ and ϕ by the following three relations (6):

$$v = \xi/(1 - 2/\phi) \tag{1}$$

$$\mu = 2v/\phi \tag{2}$$

$$M_C = \frac{(1 - 2/\phi)\rho N_A}{\xi N_0} \tag{3}$$

where ρ is the density, V_0 is the reference volume of the network, and N_A is Avogadro's number. The number of junctions, μ, and the number of chains, ν, are typically given as number *densities*, by dividing them by the volume of the unswollen network. They are the standard two direct measures of the degree of cross-linking. The molecular weight M_c, of the network chains between two cross-links, is an inverse measure, and typically has a value ranging from 5,000 to 15,000 g/mol. This corresponds to using approximately one of a hundred repeat units for a cross-link (13).

Effects of Network Structure on Elastomeric Properties

Effects of Chain Length.   The length of a network chain between two cross-links decreases with increasing number of cross-links as can be seen from equations (1) and (3). As will be elaborated further in the following sections, the modulus of a network varies inversely with chain length (5,13).

Effects of Chain Length Distribution.   Elastomeric networks are generally prepared in an uncontrolled manner such as peroxide curing (1,2). In such cross-linking, segments close together in space are linked irrespective of their locations along the chain trajectories. This results in a highly random network structure in which the distribution of chain lengths between cross-links is essentially unknown. New synthetic techniques are now available, however, for the preparation of "model" polymer networks of known structure. More specifically, if networks are formed by end-linking functionally terminated chains of known length distribution instead of haphazardly joining chain segments at random, then the nature of this very specific chemical reaction provides the desired structural information (5,13,26,83). Thus, characterizing the uncross-linked chains with respect to molecular weight M_n and molecular weight distribution, and then carrying out the specified reaction to completion gives elastomers in which the network chains have these characteristics, in particular a molecular weight M_c between cross-links equal to M_n, a network chain-length distribution the same as that of the starting chains, and cross-links having the functionality of the end-linking agent. A widely investigated system is end-linked PDMS using tetraethyl orthosilicate. The reaction is shown in Figure 1 (83–85). One reason for this choice is the fact that the polymer is readily available with either hydroxyl or vinyl end groups, and the reactions these groups participate in are relatively free of complicating side reactions. In the application of interest here, a mixture of two