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FEATURE ARTICLE

Some Recent Theory, Experiments, and Simulations on Rubberlike Elasticity

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Some recent theory in the area of rubberlike elasticity is illustrated by the analysis of strain-induced crystallization, chain entanglements in networks through constraint models, junction fluctuations and neutron scattering, and phase separations in oriented gels. Experimental techniques for characterizing elastomers involve the usual mechanical property measurements but also include chain orientation by birefringence measurements and infrared spectroscopy, small-angle neutron and X-ray scattering studies, pulse-propagation measurements, and Brillouin scattering. Some unusual types of elastomers described include (i) networks having known structures ("model" elastomers), (ii) networks having bimodal distributions of network chain lengths, (iii) reversibly cross-linked materials ("thermoplastic elastomers"), and (iv) elastomers cross linked in solution. Some novel approaches to reinforcement include (i) sol−gel-generated ceramic phases, (ii) rubbery particles for toughening ceramics, (iii) zeolites and other porous fillers that can be penetrated by network chains, and (iv) exfoliated clays. Examples of simulations involve the gelation process leading to network structures, non-Gaussian distributions, crystallization of elastomers that are chemically or stereochemically copolymeric, and reinforcement from particulate fillers.

Introduction

Elastomers are defined by their very large deformability with essentially complete recoverability. This is a very unusual type of elasticity and requires three molecular characteristics: (i) the material must consist of polymeric chains, (ii) the chains must have a high degree of flexibility and mobility, and (iii) the chains must be joined into a network structure.[1−6] The first requirement arises from the fact that the molecules in a rubber or elastomeric material must be able to alter their arrangements and extensions in space dramatically in response to an imposed stress, and only a long-chain molecule has the required large number of spatial arrangements of very different extensions. The second characteristic required for rubberlike elasticity specifies that the different spatial arrangements be *accessible* (i.e., changes in these arrangements should not be hindered by constraints that might result from inherent rigidity of the chains, extensive chain crystallization, or the very high viscosity characteristic of the glassy state).[1,2,7−9] The long-chain nature and required flexibility are illustrated by the chain being deformed schematically in Figure 1. The network structure cited is required to obtain elastomeric recoverability. It is obtained by joining together or "cross linking" pairs of segments, approximately 1 out of 100, thereby preventing stretched polymer chains from irreversibly sliding by one another. The cross links are generally chemical bonds (as would occur in sulfur-vulcanized natural rubber or a peroxide-cured polysiloxane elastomer). Such junctions in elastomeric network can also be physical aggregates, for example, the small crystallites in a partially crystalline polymer or the glassy domains in a multiphase triblock copolymer.[8] The latter materials are considered separately in comments on "thermoplastic elastomers". In any case, the existence of the required network structure creates a major problem for physical chemists interested in structure−property relationships. Networks are insoluble in all solvents, and this requires forfeiting the standard technique of characterizing a material by dissolving it into a solvent and measuring the properties of the resulting solution.

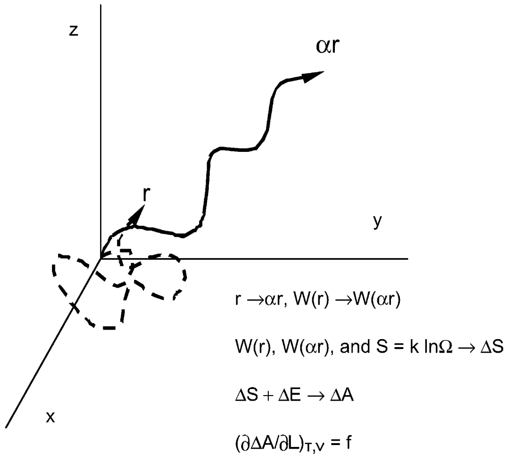

Figure 1. Sketch of a chain being elongated and the series of calculations leading from distributions of chain end-to-end distances to equations of state.

The earliest elasticity experiments involved stress−strain−temperature relationships, or network "thermoelasticity". They were first carried out many years ago, by Gough, back in 1805, and more quantitatively by Joule in 1859.[1,2,7,10] The results

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implicated entropy decreases as the origin of the retractive force. Relevant here is the important experimental fact that mechanical deformations of rubberlike materials generally occurred at essentially constant volume, so long as crystallization was not induced.[1] (In this sense, the deformation of an elastomer is very different from that of a gas.) The source of the entropy decrease is illustrated by the stretching of the chain in Figure 1: the number of arrangements in space corresponding to a given end-to-end distance *r* decreases as *r* increases.

In the 1930s, Kuhn, Guth, and Mark first began to develop quantitative theories based on this idea that the network chains undergo such spatial or configurational changes, by skeletal bond rotations, in response to an imposed stress.[1,2] More rigorous theories began with the development of the "phantom network" theory by James and Guth in 1941,[11,12] and the "affine model" theory by Wall,[13] by Wall and Flory,[14] and by Flory and Rehner[15,16] in 1942 and 1943. In the latter, the chains are viewed as moving linearly with the macroscopic deformation, whereas in the former, fluctuations spoil this simple affine relationship. Modern theories generally begin with the phantom model and extend it, for example, by taking into account interchain interactions.[8]

The basic theoretical approach, further described below, is outlined by the text in Figure 1. A distribution function $W(r)$ is applied to both the original length of a network chain and to its extended length. These distributions are then used in the Boltzmann equation to calculate entropy changes accompanying the deformation. Some contribution for energy changes is then inserted to give the Helmholtz free energy or "work function". Differentiating it with regard to length then gives the elastic force as a function of the number of network chains, the temperature, and the deformation, in other words, the elastic equation of state suitable for comparisons with experiment.

Theory

Some Refined Models. Most molecular theories of rubberlike elasticity use the Gaussian distribution for $W(r)$, making it proportional to $\exp(-r^2)$, partly because it is easy to handle analytically. It has the deficiency that it is inapplicable to chains that are too stiff, too short, or stretched too close to the limits of their extensibility. The stiffness shortcoming is not much of a practical problem because there are so many flexible polymers that can be used in elastomers. The shortness limitation is more serious since people would like to interpret elastic properties for "bimodal" networks containing some very short chains[8] or very heavily cross-linked "thermoset" networks (such as Bakelite resins) and even coal![17] Not being able to treat very high deformations severely limits, of course, the interpretation of ultimate properties. The Gaussian distribution is obviously unsuitable in this case because it does not assign zero probabilities to any value of *r* less than infinity. It is for these reasons that there are now a number of non-Gaussian theories, some of which are discussed below.

Another aspect of the molecular theories being extensively refined is the question of how the chains interact with one another, particularly with regard to entanglements (either between two chains remote from their junctions or entanglements between junctions and the surrounding chains). If the entanglements are of the type that can be relieved by the chains simply moving past one another, then their contributions to the mechanical properties such as the modulus would disappear after an extended period of time, and this time-retarded elasticity is an important subject in the area of viscoelasticity. More relevant here are the ones that are not removed by deformation, or swelling, since their contributions can be permanent. Some of their characteristics have been handled by the "constraint" theories described below, but there have been a variety of other approaches as well.[8,9,18] Important related work has, for example, been carried out by Edwards and co-workers,[19] Graessley,[20−22] Doi,[23,24] Grosberg and Khokhlov,[25,26] and de Gennes.[27]

The constraint models are attempts to bridge the affine theory, where there are no junction fluctuations at all, with the phantom theory, where there are significant fluctuations. These fluctuations decrease the strain sensed by the molecular chains to values well below those imposed macroscopically, with corresponding decreases of the predicted modulus. One of its successes has been its explanation for long-troubling large decreases in the modulus observed upon increases in elongation, as represented by the Mooney−Rivlin "$2C_2$ correction" to the form of the stress−strain isotherms predicted by the earliest theories. In the constraint theories, this correction is attributed to increases in elongation causing decreases in the entangling of chains around the junctions, with these increased fluctuations decreasing the strain sensed by the chains and thus the modulus they exhibit.[8] These theories have also successfully explained the decreases in the $2C_2$ correction in swollen networks, in networks prepared in the swollen state and studied dried, and in networks containing junctions of very high functionality.[8]

The original version of the theory ("constrained junctions") placed the constraints entirely on the junctions themselves. The magnitudes of the fluctuations as measured in neutron spin−echo studies,[28] however, were larger than would be expected from this model. This was remedied in the "constrained-chain" theory, where the constraints were placed at the centers of gravity of the chains, and the "diffused-constraints" model, which spread them along the chain contours. The last of these models has been used extensively, for example, to interpret stress−strain isotherms in elongation successfully as well as molecular deformation tensors and strain birefringence.[29]

Some Other Applications of Theory. The constrained-junction model was also found to give good results on strain-induced crystallization of elastomeric networks.[30] Specifically, the model explains the major features of this type of crystallization, including the downturn in the modulus from the straightening out of the chain segments within a crystallite and the subsequent increase from the expected crystallite reinforcement.

As already mentioned, the extent to which fluctuations of junctions occur is of central importance in constraint theories, and considerable theoretical work has addressed this issue[31,32] and the related subjects of scattering and relaxation spectra.[33] Very relevant in this regard is neutron scattering from networks in the undeformed and deformed states.[34,35] Some of the results obtained should be of great utility in further revising the theories of rubberlike elasticity in general, for example, by indicating how best to distribute the constraints as one goes along a chain from one junction to the next.

There is also considerable theory for segmental orientation and phase separation in gels of semirigid chains dried under uniaxial deformation.[36,37] The results were useful in providing guidance for using both uniaxial and biaxial orientation to optimize the mechanical properties of a variety of polymeric films such as those prepared from starch.[38] Drying under uniaxial deformation gave ribbons that were stronger in the axial direction but weaker in the perpendicular direction. Drying under biaxial extension, however, gave mechanical properties that were more uniformly improved in all directions in the plane of the film.

Some Experimental Results

Mechanical Properties and Swelling. The great majority of studies of the mechanical properties of elastomers have been carried out in elongation because of the simplicity of this type of deformation.[7] Agreement between theory and experiment has generally been satisfactory, but the strain-induced crystallization that occurs in some elastomers requires separate treatment. There are a smaller number of studies using types of deformation other than elongation, for example, biaxial extension (equivalent to compression), shear, and torsion. Comparisons between theory and experiment for these less common deformations appear to be satisfactory but will require additional experimental data for definitive analysis.[8]

Stress−strain isotherms for any type of deformation can show very significant hysteretic effects that parallel those in small-molecule systems, for example, in magnetization−demagnetization loops.[39,40] They are particularly important in elastomers since they correspond to wasted energy and overheating ("heat build up", with accompanying increases in thermal degradation). The amount of hysteresis can also be gauged from such stress−strain isotherms. The area below an elongation curve corresponds to the energy required for deformation, and the area below a retraction curve corresponds to the energy recovered. The area between the two curves thus represents the energy not recovered, in hysteresis.

Equilibrium swelling in a solvent is a nonmechanical property that is much used to characterize elastomeric materials.[1,2,7,41] It is an unusual deformation in that volume changes are now of central importance rather than being negligible. The equilibrium extent of swelling can be interpreted to yield the degree of cross linking of the network, provided the polymer−solvent interaction parameter[1] χ_1 is known. Conversely, if the degree of cross linking is known from an independent experiment, then the interaction parameter can be determined. The equilibrium degree of swelling and its dependence on various parameters and conditions provide, of course, additional important tests of theory. Agreement between theory and experiment is satisfactory, and some discrepancies that are observed may be due to different properties responding differently to different deformations.

An interesting area involving some swollen networks or "gels" is their abrupt collapse (decrease in volume) upon relatively minor changes in temperature, pH, solvent composition, et cetera.[7,8,42−45] Although the collapse is quite slow in large, monolithic pieces of gel, it is rapid enough in fibers and films to make the phenomenon interesting with regard to the construction of switches and related mechanical devices, artificial muscle, and drug-delivery systems.

Gels are also formed, of course, when elastomers are used to absorb liquids, for example, in diapers and in attempts to control oil spills on bodies of water.[46]

Some Other Important Properties. An example of a relevant optical property is the birefringence of deformed polymer networks.[41,47] This strain-induced birefringence can be used to characterize segmental orientation,[48,49] both Gaussian and non-Gaussian elasticity, crystallization and other types of chain ordering, and short-range correlations.[2,7] Other optical and spectroscopic techniques are also important, particularly with regard to segmental orientation. Some examples are fluorescence polarization, deuterium NMR, and polarized infrared spectroscopy.[41] Such studies are now being used increasingly to determine the effects of reinforcing fillers on network chain orientation and the possible strain-induced crystallization it facilitates.

Measuring scattering intensities is of great utility in the study of elastomers, particularly small-angle neutron scattering from deuterated chains in a nondeuterated host.[7,41] As usual, it is important to avoid phase segration of the deuterated chains. One application has been the determination of the degree of randomness of the chain configurations in the undeformed state, an issue of great importance with regard to the basic postulates of elasticity theory. The chains were found to be in the same unperturbed states they occupy in solvents in which excluded volume effects have been nullified. This supports the use of these "theta state" dimensions for chains in the undeformed state in the molecular theories of rubberlike elasticity. Of even greater importance is the determination of the manner in which the dimensions of the chains follow the macroscopic dimensions of the sample (i.e., the degree of "affineness" of the deformation[50−56]). This relationship between the microscopic and macroscopic levels in an elastomer is one of the central problems in rubberlike elasticity. The results indicated that the deformations generally lay between the affine and phantom limits, as suggested by the constraint theories mentioned above.

Small-angle X-ray scattering techniques have also been applied to elastomers. Examples are the characterization of fillers precipitated into elastomers using sol−gel technology, in which organometallics are hydrolyzed and condensed into ceramiclike phases that reinforce the material. The same reactions have been used to generate elastomeric phases within ceramic matrices, now to improve their impact resistance.[57−59] The scattering techniques mentioned have been used to characterize the morphologies of these materials. One example is the demonstration[60] that basic catalysts in sol−gel reactions give smooth particles, whereas acidic catalysts give fuzzy particles and even wispier structures. This approach to reinforcement is discussed further below.

One example of a relatively new technique for the noninvasive, nondestructive characterization of network structures involves pulse-propagation measurements.[61,62] The goal is the rapid determination of the spacings between junctions and between entanglements in a network structure. Another example is really a resurrection of the Brillouin scattering method,[63] which should be quite useful for looking at glassy-state properties of elastomers at very high frequencies.[64]

Control of Network Structure

Until recently, there was relatively little reliable quantitative information on the relationship of stress to structure primarily because of the uncontrolled manner in which elastomeric networks were generally prepared.[1,2,7,65] Segments close together in space were linked irrespective of their locations along the chain trajectories, thus resulting in a highly random network structure in which the number and locations of the cross links were essentially unknown. New synthetic techniques are now available, however, for the preparation of "model" or "ideal" polymer networks of known structure.[8,66] An example is the condensation end-linking of hydroxyl-terminated chains of poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$] using tetraethyl orthosilicate [$Si(OC_2H_5)_4$]. Characterizing the un-cross-linked chains with respect to molecular weight M_n and molecular weight distribution and then running 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 and cross links having the functionality of the end-linking agent.[65] These networks have been used to estimate the effects of interchain entanglements on the elastic modulus, but experiments that should be equivalent have somehow given contradictory results.[8] At least some experiments gave values of the modulus that were higher than those predicted by theory, and this was taken to indicate substantial contributions from such entanglements.

The end-linking reactions described above can also be used to make networks having unusual chain-length distributions.[67,68] Those having a bimodal distribution are of particular interest with regard to their ultimate properties, as will be described below.

Networks at Very High Deformations

Some (unfilled) networks show a large and rather abrupt increase in the modulus at high elongations.[2,3] This increase is very important since it corresponds to a significant toughening of the elastomer. Its molecular origin, however, has been the source of considerable controversy. It had been widely attributed to either the "limited extensibility" of the network chains,[69] (i.e., to an inadequacy in the Gaussian distribution function) or to strain-induced crystallization.

The issue has now been resolved,[8,69] however, by the use of end-linked, noncrystallizable model PDMS networks. These networks have high extensibilities, presumably because of their very low incidence of dangling-chain network irregularities. They have particularly high extensibilities when they are prepared from a mixture of very short chains (molecular weights around a few hundred g mol^{-1}) with relatively long chains (around 18 000 g mol^{-1}), as further discussed below. Apparently, the very short chains are important because of their limited extensibilities, and the relatively long chains, because of their ability to retard the rupture process.[65] The improvements in properties are thus from an intramolecular division of responsibilities rather than from some intermolecular effect such as strain-induced crystallization.

Comparisons of stress−strain measurements on such bimodal PDMS networks with those in crystallizable polymer networks such as natural rubber and *cis*-1,4-polybutadiene were carried out, particularly as a function of temperature and in the presence of a plasticizing diluent.[70] In the case of crystallizable polymers such as natural rubber, increases in temperature or additions of solvent suppress the anomalous upturns in modulus, which indicates they are largely if not entirely due to strain-induced crystallization. In contrast, the upturns in modulus in the case of the bimodal elastomers are not diminished at all, which is consistent with the described intramolecular origin.

The mechanical properties of general interest are the modulus, tensile strength, maximum extensibility, and toughess (energy to rupture), and all are affected by strain-induced crystallization. The higher the temperature, the lower the extent of crystallization and, correspondingly, the lower the ultimate properties. The effects of increases in swelling parallel those for increases in temperature since diluent also suppresses network crystallization. For noncrystallizable networks, however, neither change is very important.[65]

In the case of such noncrystallizable, unfilled elastomers, the mechanism for network rupture has been elucidated to a great extent by studies of model networks similar to those already described. For example, values of the modulus of bimodal networks formed by end-linking mixtures of very short and relatively long chains were used to test the "weakest-link" theory[8] in which rupture was thought to be initiated by the shortest chains (because of their very limited extensibilities). It was observed that increasing the number of very short chains did *not* significantly decrease the ultimate properties. The reason[69] is the very nonaffine nature of the deformation at such high elongations. The network simply reapportions the increasing strain among the polymer chains until no further reapportioning is possible. It is generally only at this point that chain scission begins, leading to rupture of the elastomer. The weakest-link theory implicitly assumes an affine deformation, which leads to the prediction that the elongation at which the modulus increases should be independent of the number of short chains in the network. This assumption is contradicted by relevant experimental results, which show the opposite behavior;[69] the smaller the number of short chains, the easier the reapportioning and the higher the elongation required to bring about the upturn in modulus.[65]

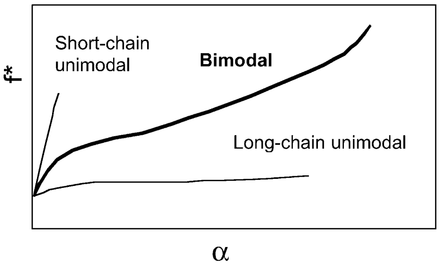

Figure 2. Sketch of stress−strain results for a network having a bimodal distribution of network chain lengths.[65] The nominal stress is shown as a function of elongation, and the area under each curve corresponds to the rupture energy (the standard measure of toughness).

Multimodal Chain-Length Distributions

As already mentioned, there turns out to be an important bonus if one forms a multimodal distribution of network chain lengths by end linking a very large number of short chains into a long-chain network. The ultimate properties are then actually improved![65] 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[66,71,72] and developing theoretical interpretations for their properties.[73−81] The types of improvements obtained are shown schematically in Figure 2, with the results represented in such a way that the area under a stress−strain isotherm corresponds to the energy required to rupture the network. If the network consists of all short chains, then it is brittle, which means that the maximum extensibility is very small. If the network is all long chains, then the ultimate strength is very low. In neither case is the material a tough elastomer because the areas under the stress−strain curves are relatively small. As indicated in the Figure, the bimodal networks are much improved elastomers in that they can have a high ultimate strength without the usual decrease in maximum extensibility.

A series of experiments were carried out in an attempt to determine if this reinforcing effect in bimodal PDMS networks could possibly be due to some intermolecular effect such as strain-induced crystallization. In the first such experiment, temperature was found to have little effect on the isotherms.[82] This strongly argues against the presence of any crystallization or other type of intermolecular ordering. So also do the results of stress−temperature and birefringence−temperature measurements. In a final experiment, swelling was actually found to *increase* the upturn rather than decrease it since the dilation caused by the diluent caused an extension of the chains prior to their further extension in the stress−strain experiment. Apparently, the observed increases in modulus are due to the limited chain extensibility of the short chains, with the long chains serving to retard the rupture process. This can be thought of in terms of what executives like to call a "delegation of responsibilities".[65]

There is an another advantage to such bimodality when the network can undergo strain-induced crystallization, since this can provide an additional toughening effect.[83,84] Decreases in temperature were found to increase the extent to which the values of the ultimate strength of some bimodal networks exceed those of the corresponding unimodal ones. This suggests that bimodality facilitates strain-induced crystallization.

In practical terms, the above results demonstrate that short chains of limited extensibility may be bonded into a long-chain network to improve its toughness. It is also possible to achieve the converse effect. Thus, bonding a small number of relatively long elastomeric chains into a relatively hard short-chain PDMS thermoset greatly improves its impact resistance.[65]

Since dangling chains represent imperfections in a network structure, one would expect their presence to have a detrimental effect on the ultimate properties $(f/A^*)_r$ and α_r of an elastomer. This expectation was confirmed using a series of model PDMS networks in which an excess of chain ends over end-linker functional groups was used to introduce known numbers of dangling ends.[85]

There is also considerable interest in networks that have been prepared in solution but then dried before characterization.[86,87] The chains in such elastomers are “supercontracted”, which gives them great extensibility.

Filler-Reinforced Elastomers and Elastomer-Modified Ceramics

Overview of Filler Reinforcement. One class of multiphase elastomers is that capable of undergoing strain-induced crystallization, as was mentioned above. In this case, the second phase is made up of the crystallites thus generated, which provide considerable reinforcement. Such reinforcement is only temporary, however, in that it may disappear upon removal of the strain, addition of a plasticizer, or an increase in temperature. For this reason, many elastomers (particularly those that cannot undergo strain-induced crystallization) are generally compounded with a permanent reinforcing filler.[8,9,88−90] The two most important examples are the addition of carbon black to natural rubber and to some synthetic elastomers and the addition of silica to polysiloxane rubbers. In fact, the reinforcement of natural rubber and related materials is one of the most important processes in elastomer technology. It leads to increases in modulus at a given strain and improvements of various technologically important properties such as tear and abrasion resistance, resilience, extensibility, and tensile strength.[91] There are also disadvantages, however, including increases in hysteresis (and thus of heat build up) and compression set (permanent deformation).

There is an incredible amount of relevant experimental data available, with most of these data relating to the reinforcement of natural rubber by carbon black.[92] Recently, however, considerable interest has developed in other polymers such as PDMS and even glassy and rigid-rod polymers and other fillers such as precipitated silica, titania, and metallic particles.[65,93−95] One unusual observation is that titania reinforcement of PDMS is reversible whereas silica reinforcement is not, indicating some very interesting differences in surface chemistry.

The most important unsolved problem in this area is the nature of the bonding between the filler particles and the polymer chains.[91] The network chains may adsorb strongly onto the particle surfaces, which would increase the effective degree of cross linking. This effect will be especially strong if particles contain some reactive surface groups that may cross link (or end link) the polymer chains. Chemisorption, with permanent chemical bonding between filler particles and polymer chains, can be dominant, particularly if the filler is precipitated into the elastomer in situ during curing.[96,97] Another type of adsorption that can occur at a filler surface is physisorption, arising from long-range van der Waals forces between the surface and the polymer. Contrary to chemisorption, this physical adsorption does not severely restrict the movement of polymer chains relative to the filler surface when high stresses are applied. The available experimental data suggest that both chemisorption and physisorption contribute to reinforcement phenomena and that the optimal degree of chemical bonding is quite low (on the order of 0.2 bonding sites per nm^2 of filler surface).[89] Excessive covalent bonding, leading to immobilization of the polymer at the filler surface, is highly undesirable. A filler particle may thus be considered a cross link of very high functionality but transient in that chains at its surface can participate in molecular rearrangements under stress. This transient nature gives rise to the lack of reversibility frequently observed in the stress−strain isotherms of filled elastomers. Apparently, the chains irreversibly slide along the particle surfaces in response to the applied stress and then cannot completely return to their original positions.

There are probably numerous other ways in which a filler changes the mechanical properties of an elastomer, some of admittedly minor consequence.[9,91] For example, another factor involves changes in the distribution of end-to-end vectors of the chains due to the volume taken up by the filler,[91,98] as discussed further below. This effect is obviously closely related to the adsorption of polymer chains onto filler surfaces, but the surface also effectively segregates the molecules in its vicinity and reduces entanglements.[65] Another important aspect of filler reinforcement arises from the fact that the particles influence not only an elastomer’s static properties (such as the distribution of its end-to-end vectors) but also its dynamic properties (such as network chain mobility). More specifically, the presence of fillers reduces the segmental mobility of the adsorbed polymer chains to the extent that layers of elastomer close to the filler particles are frequently referred to as “bound rubber”.[99,100]

Some Novel Composites. As is obvious from the above comments, the mechanism of the reinforcement is only poorly understood. Some elucidation might be obtained by precipitating reinforcing fillers into network structures rather than blending badly agglomerated fillers into the high-molecular-weight polymers prior to their cross linking. This has, in fact, been done for a variety of fillers, for example, silica by hydrolysis of organosilicates, titania from titanates, alumina from aluminates, et cetera.[8,94] A typical, and important, reaction is the acid- or base-catalyzed hydrolysis of tetraethyl orthosilicate:

$$\text{Si(OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH} \qquad (1)$$

Reactions of this type are much used by ceramists in the new sol−gel chemical route to high-performance ceramics.[101,102] In the ceramics area, the advantages are the possibility of using low temperatures, the purity of the products, the control of ultrastructure (at the nanometer level), and the relative ease of forming ceramic alloys. In the elastomer reinforcement area, the advantages include the avoidance of the difficult, time-consuming, and energy-intensive process of blending agglomerated filler into high-molecular-weight and high-viscosity polymers and the ease of obtaining extremely good dispersions.

In the simplest approach to obtaining elastomer reinforcement, some of the organosilicate material is absorbed into the cross-linked network, and the swollen sample is placed into water containing the catalyst, typically a volatile base such as ammonia or ethylamine. Hydrolysis to form the desired silica-like particles proceeds rapidly at room temperature to yield on the order of 50 wt % filler in less than an hour.[8,103]

Impressive levels of reinforcement can be obtained by this in-situ technique.[8,57] The modulus generally increases substantially, and some stress−strain isotherms show the upturns at high elongation that are the signature of good reinforcement. As generally occurs in filled elastomers, there can be considerable irreversibility in the isotherms, which is thought to be due to irrecoverable sliding of the chains over the surfaces of the filler particles.

If the hydrolyses in organosilicate−polymer systems are carried out with increased amounts of the silicate, bicontinuous phases can be obtained (with the silica and polymer phases interpenetrating one another).[96] At still-higher concentrations of the organosilicate, the silica that is generated becomes the continuous phase, with the polymer dispersed in it.[8,104−107] The result is a polymer-modified ceramic, variously called an “ORMOCER”,[108] “CERAMER”,[109,110] or “POLYCERAM”.[104] It is obviously of considerable importance to determine how the polymeric phase, often elastomeric, improves impact resistance and other mechanical properties of the ceramic in which it is dispersed.

Similar approaches can be used to generate rubbery phases, for example, by the in-situ hydrolysis and condensation of *tri*functional materials such as $RSi(OR')_3$.[8]

Some potential fillers are porous, and this has been exploited to obtain unusually intimate bonding between the particles and the host elastomer matrix.[111−113] Examples are zeolites and Vycor glass, and the threading is typically achieved by absorbing monomer into the cavities and then polymerizing it. Good reinforcement has been obtained in these materials, which have also been of interest because the polymer constrained in the cavities no longer exhibits a glass-transition temperature![114,115]

Separating clay layers and dispersing them into a polymeric matrix gives remarkably good reinforcement at low loadings.[116−120] This is due to the unusually high surface area exposed upon such exfoliation. Some recent studies involving natural rubber illustrate the excellent reinforcement that can be obtained in this way.[121,122]

Biomimicry

Minimizing the hysteresis mentioned above is very important in the case of jumping insects such as grasshoppers and fleas. In these cases, the elastomer is a protein called resilin, and the energy is stored by the insect’s use of its muscles to compress a plug of this material.[8] It is released when the insect wishes to jump, for example, away from a predator, and the larger the fraction of the stored energy that is available, the better. Release time is obviously also critically important and is approximately 1 ms. Insects with more sluggish bioelastomers were presumably phased out by natural selection.

Resilin is also important in flying insects such as dragonflies, where plugs under the wings smooth out the flapping by alternating between being compressed and expanding. Large hysteretic effects would be bad not only because of the inefficiencies involved but also because of possible overheating of the dragonfly.[65]

The cross linking in these bioelastomers is carefully controlled by nature. The number and spacing of the cross links is fixed by the ribosome-controlled α-amino acid sequence since the cross linking occurs only through the lysines (using a copper-activated enzyme called lysyl oxidase).[8] Particularly intriguing is the fact that the lysine sites are preceded and succeeded by alanines (which may be in α-helical conformations). Placing these potential cross-linking sites at the ends of two stiff sequences may help control their spatial environment, for example, their entangling with other protein repeat units.

Trying to parallel the control nature exerts in cross linking bioelastomers, for example, by end-linking reactions, is an example of “biomimicry” or “bioinspired design”. Other relevant examples are the use of (i) irregular copolymer sequences to suppress crystallinity, (ii) small side groups to enhance flexibility and mobility, (iii) nonpolar side groups to reduce intermolecular interactions, and (iv) plasticizers to reduce brittleness.[8] It is useful, however, to give one illustration of how such bioinspiration can lead one astray. All of the early work on trying to mimic the flight of birds by designing aircraft with flapping wings turned out to be disastrous! The successful approaches involving propellers or jets were probably not inspired at all by analogies with biological systems. Circular motions and jets of fluids for locomotion are relatively rare in biology and are used in aqueous fluids rather than in air.[65]

Simulations

The formation of network structures necessary for rubberlike elasticity has been extensively simulated by Eichinger and coworkers.[123] The basic approach is to end link functionally terminated precursor chains randomly with a multifunctional reagent and then to examine the sol fraction with regard to the number and types of molecules present and the gel fraction with regard to its structure and mechanical properties. This is illustrated in Figure 3. The systems most studied in this regard[123] involve PDMS chains having end groups X that are either hydroxyl or vinyl groups, with the corresponding Y groups on the end-linking agents then being either OR alkoxy groups in an organosilicate or H atoms in a multifunctional silane.[8] There has been very good agreement between theory and experiment.[124]

The Monte Carlo method for simulating these reactions was used to generate additional information on the vinyl−silane end linking of PDMS.[124,125] The simulations gave a very good account of the extent of reaction at the gelation points but overestimated the maximum extent of reaction attainable. The discrepancy may be due to experimental difficulties in taking a reaction close to completion within a highly viscous, entangled medium.

If cyclic molecules of PDMS are present during the end linking, then they are trapped within the network if they are large enough to be penetrated by any of the precursor chains.[8] This “incarceration” process has also been simulated successfully.[126]

One novel approach to obtaining non-Gaussian distribution functions utilizes the wealth of information that rotational isomeric theory provides on the spatial configurations of chain molecules. Specifically, Monte Carlo calculations based on the rotational isomeric state approximation were used to simulate spatial configurations and thus distribution functions for the end-to-end separations.[127] The results obtained documented the expected fact that the Gaussian distribution is generally a very poor approximation for short chains or for the high extensions that are of primary importance with regard to ultimate properties. Some typical results are shown in Figure 4. The rotational isomeric state distributions for polyethylene and PDMS chains having only 20 skeletal bonds are seen to be poorly represented by the Gaussian approximation. Another example of this approach is to determine how an applied force can change the distributions for a chain that can undergo a coil-to-helix transition.[128]

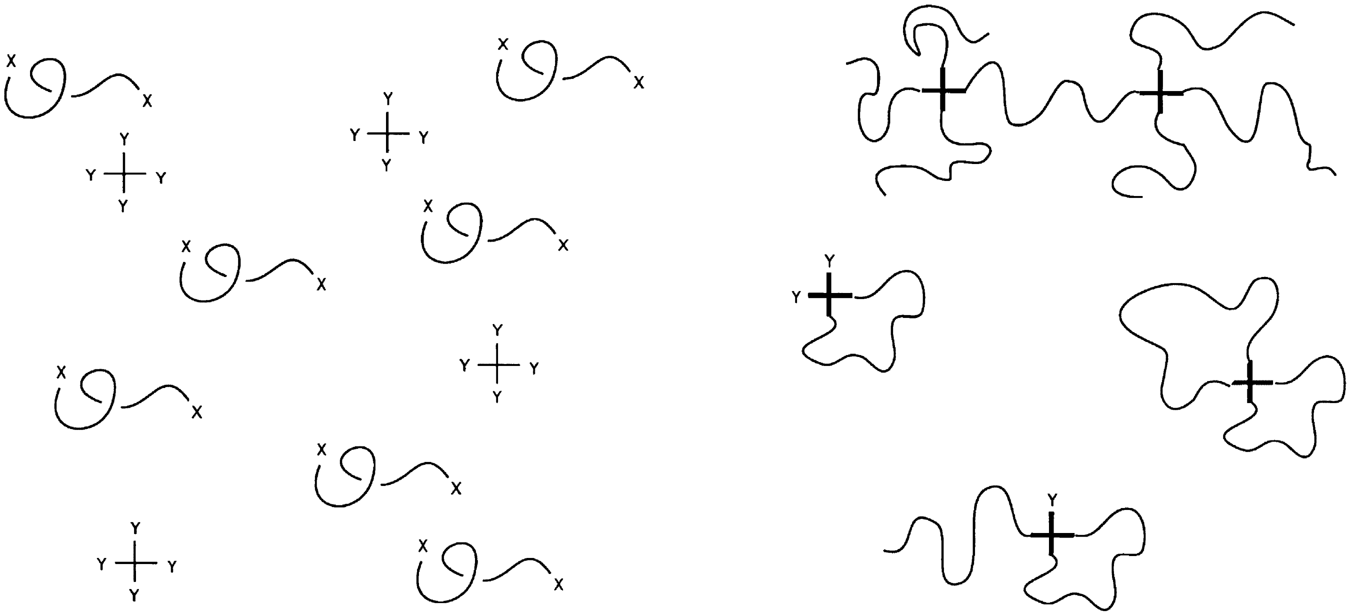

Figure 3. End-linking reactions to form elastomeric network structures. The left side shows the reactants, and the right side shows some types of expected products.

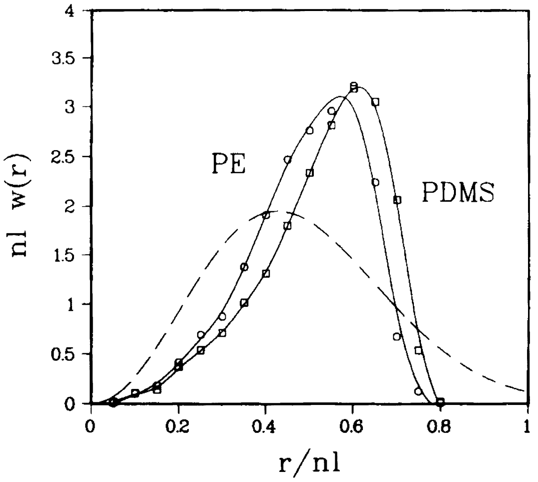

Figure 4. Comparisons among the rotational isomeric state distributions for polyethylene and PDMS chains having only 20 skeletal bonds and the corresponding Gaussian approximation.[138]

These Monte Carlo distributions can be used in the standard three-chain model for rubberlike elasticity to generate, for example, stress−strain isotherms.[8] Non-Gaussian effects can cause large increases in modulus at high elongations because of the limited extensibilities of the network chains.[2] Thus, it is very useful to identify chain structures and chain lengths giving the largest increases in stress without unacceptable decreases in extensibility. This will, of course, maximize the area under the stress−strain curve, which represents the energy for rupture or toughness of the material.[125]

One of the most interesting applications of this approach is to PDMS elastomers which have a bimodal distribution of network chain lengths[129] and, correspondingly, very good mechanical properties.[8] The upturns in modulus observed at high elongations are thought to be due to the very limited extensibilities of the short chains in the bimodal structures, with the long chains increasing extensibility, and this seems to be supported by the simulated results.[127,130]

Because of the improvements in properties exhibited by elastomers having bimodal distributions,[8] there have been attempts to prepare and characterize “trimodal” networks.[78] The calculations suggest that adding a small amount of a very high molecular weight end-linkable polymer could further improve mechanical properties.

There is now considerable interest in using simulations to characterize crystallization in copolymeric materials. In particular, Windle and co-workers[131] have developed models capable of simulating chain ordering in copolymers composed of two comonomers, at least one of which is crystallizable. Typically, the chains are placed in parallel, 2D arrangements. Neighboring chains are then searched for like-sequence matches in order to estimate extents of crystallinity. Chains stacked in arbitrary registrations are taken to model quenched (Q) samples. Annealed samples, however, are modeled by sliding the chains past one another longitudinally to search for the largest possible matching densities. The longitudinal movement of the chains relative to one another, out of register, approximately models the lateral searching (S) of sequences in copolymeric chains during annealing.[125]

One example[132] of such a study involved modeling random and semi-blocky poly(diphenylsiloxane-co-dimethylsiloxane) copolymers. In this example, the chains were placed alongside one another in a 2D array, with black squares representing dimethylsiloxane (DMS) units and white squares representing diphenylsiloxane (DPS) units.[132] “Like” squares neighboring each other in the same row are then viewed as coalescing into blocks, the lengths of which are under scrutiny. It is thus possible to identify crystallizable DPS regions as distinct from noncrystallizable DMS components or units of the crystallizable DPS component that were not long enough to participate in the crystallization.[132] A value of the degree of crystallinity L of a simulated sample can then be determined by counting the units involved in the matching sequences with respect to the total number of units of all of the chains. The crystallites thus identified presumably act as cross-linking sites and reinforcing domains, providing the additional toughness the semi-blocky copolymers have over their random counterparts.

A similar approach was used for polypropylene (PP), a stereochemically variable hydrocarbon polymer. It is of particular interest since it can be prepared in the form of a thermoplastic elastomer in which there are alternating runs of blocks of isotactic and atactic sequences. The trick (which has

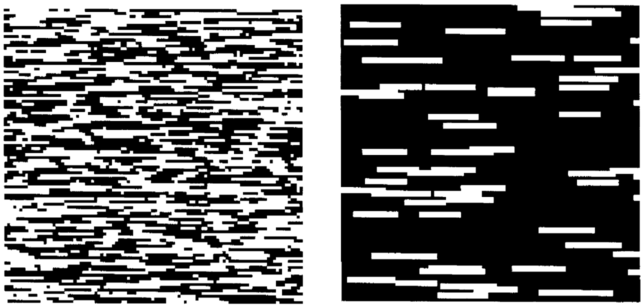

Figure 5. Results of some simulations on PP chains that were 90% isotactic. In the left panel, the black squares represent the d isomers, and the white squares, the l isomers. In the right panel, the number of neighboring like squares coalescing into crystallites of isotactic polymer are shown by the white blocks.

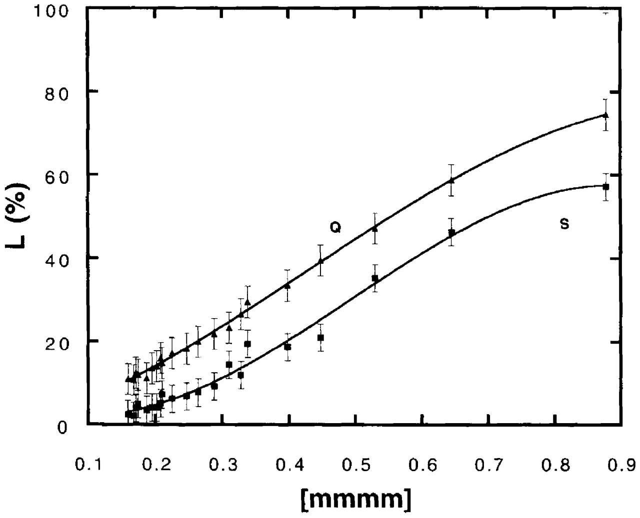

Figure 6. Degrees of crystallinity for stereoblock polypropylene samples as a function of the isotactic pentad content, with Q and S representing the results for quenched and annealed (searched) samples, respectively.[154]

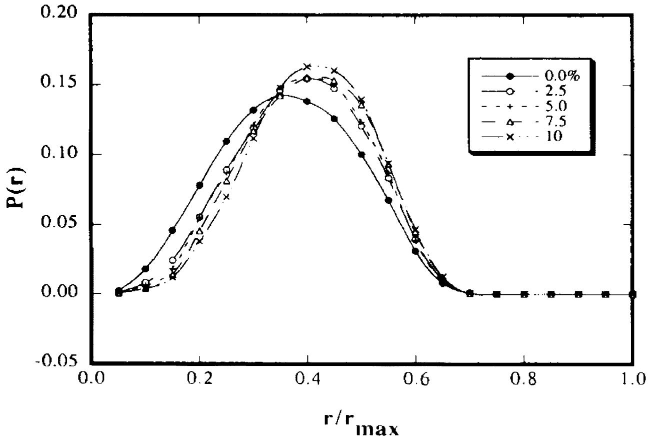

Figure 7. Radial distribution functions $P(r)$ at $T = 500$ K for network chain end-to-end vectors obtained from Monte Carlo simulations. The results are shown as a function of the relative extension $r/r_{\max}$ for filled PDMS networks having 50 skeletal bonds between cross links.[98] The radii of the filler particles was 5 Å, and the values of the volume percent of filler present are indicated in the inset.

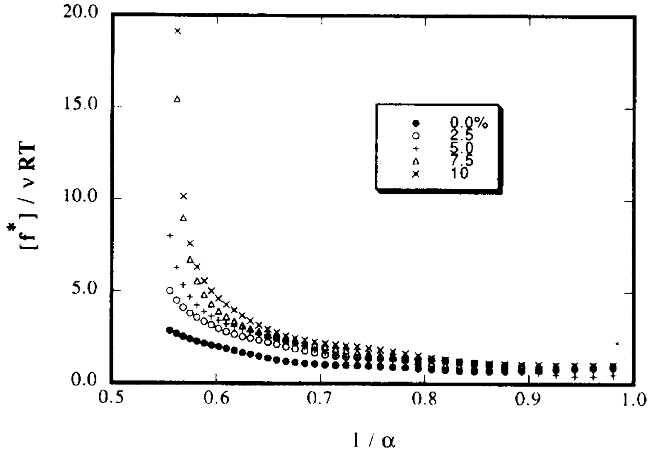

Figure 8. Mooney–Rivlin representations of moduli calculated from the distributions shown in Figure 1,[98] where ν is the number of chains and α is the elongation of the network.

been accomplished by some catalysts) is to make the isotactic runs long enough to give crystallites enough stability to act as cross links without making their sizes and numbers so large that the material is highly crystalline rather than elastomeric.[133] Some typical chain generations and matchings are shown in Figure 5.[134] Of greatest interest is the case where the isotactic lengths are kept at a constant, relatively large value while the atactic sequences are increased in length, thereby decreasing the overall content [mmmm] of meso placements. (For convenience, meso placements can be written explicitly as replications of d's or replication of l's, but this should not be taken to indicate the presence of optical activity since each such substituted carbon atom essentially has a plane of symmetry.) As can be seen in Figure 6, the simulations are consistent with the presence of crystallinity at overall levels of PP isotacticity that are sufficiently low to give completely amorphous polymers had the structures not been blocky.

Monte Carlo simulations were also carried out on filled networks[98,135–137] in an attempt to obtain a better molecular interpretation of how such dispersed fillers reinforce elastomeric materials. The approach taken enabled the estimation of the effect of the excluded volume of the filler particles on the network chains and on the elastic properties of the networks. In the first step, distribution functions for the end-to-end vectors of the chains were obtained by applying Monte Carlo methods to rotational isomeric state representations of the chains.[138] Conformations of chains that overlapped with any filler particle during the simulation were rejected. The resulting perturbed distributions were then used in the three-chain elasticity model[2] to obtain the desired stress–strain isotherms in elongation.

In one application, a filled PDMS network was modeled as a composite of cross-linked polymer chains and spherical filler particles arranged in a regular array on a cubic lattice.[139] The filler particles were found to increase the non-Gaussian behavior of the chains and to increase the moduli, as expected. It is interesting that composites with such structural regularity have actually been produced[140] and that some of their mechanical properties have been reported.[141] In a subsequent study, the reinforcing particles were randomly distributed within the PDMS matrix.[137] One effect of the filler was to increase the extensions of the chains, at least in the case of relatively small filler particles. This is illustrated in Figure 7. These results on the distributions are in agreement with some subsequent neutron-scattering experiments on silicate-filled PDMS.[142] The corresponding stress–strain isotherms in elongation are shown in Figure 8. The substantial increases in stress and modulus with an increase in filler content and elongation are in at least qualitative agreement with experiment.

Nonspherical filler particles are also of considerable interest.[137,143] Prolate (needle-shaped) particles can be thought of as a bridge between the roughly spherical particles used to reinforce elastomers and the long fibers frequently used for this purpose in thermoplastics and thermosets. Similarly, oblate (disc-shaped) particles can be considered to be analogues of the much-studied clay platelets used to reinforce a variety of materials.[144−147] In the case of nonspherical particles, their orientations are also of considerable interest.

Current Problems and Future Trends

There is a real need for more high-performance elastomers, which are materials that remain elastomeric to very low temperatures and are relatively stable at very high temperatures. In addition to the polysiloxanes, some phosphazene polymers, [−PRR′N−],[148] are in this category. These polymers have rather low glass-transition temperatures although the skeletal bonds of the chains are thought to have some double-bond character. There are thus a number of interesting problems related to the elastomeric behavior of these unusual semi-inorganic polymers. There is also increasing interest in the study of elastomers that also exhibit mesomorphic behavior.[8]

A particularly challenging problem is the development of a more quantitative molecular understanding[149−151] of the effects of filler particles, in particular, carbon black in natural rubber and silica in siloxane polymers. Such fillers provide tremendous reinforcement in elastomers in general, but how they do this is still only poorly comprehended. A related but even more complex problem involves much the same components, namely, one that is organic and one that is inorganic. When one or both components are generated in situ, however, there is an almost unlimited variety of structures and morphologies that can be generated.[8] How physical properties such as elastomeric behavior depend on these variables is obviously a challenging but very important problem.

An example of an important future trend is the study of single polymer chains, particularly with regard to their stress−strain isotherms.[152,153] Although such studies are obviously not relevant to the many unresolved issues that involve the interactions among chains in an elastomeric network, they are certainly of interest in their own right.

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