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Some Simulations on Elastomers and Rubberlike Elasticity

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SUMMARY: A number of examples are given to illustrate the use of computer modeling to elucidate the structures of elastomeric polymer networks, and to provide guidance on controlling network structure to maximize mechanical properties. The first example involves simulations of the gelation process leading to the development of the network structure necessary for a material to exhibit reversible elastomeric properties. The goals here are to characterize the amounts and constitutents of the sol phase, and the structure of the gel phase sufficient for prediction of its mechanical properties. Attempts are also being made to simulate the structure and properties of networks having multimodal distributions of chain lengths, for example to suggest how trimodal distributions might give additional improvements beyond those shown by bimodal networks. Network thermoelasticity can also be elucidated by simulations of the temperature dependence of the unperturbed dimensions of the network chains. Strain-induced crystallization is also being simulated to generate chains having sequence distributions that are representative of various polymerization conditions. The chains are then placed alongside one another to determine matched-sequence runs that could lead to the formation of crystallites. Finally, the long-standing problem of clarifying how fillers reinforce elastomeric materials is being approached using simulations of chains in the vicinity of impenetrable filler particles. In this way it is possible to determine how reinforcement depends on the perturbation of distributions caused by this excluded-volume effect.

Introduction

The present review illustrates how computational modeling has been used in the elucidation of the structures and properties of elastomeric polymer networks, using studies with which the author has been involved. One of the main goals has been to provide guidance on how to optimize the mechanical properties of an elastomer, by control of its network structure and by the incorporation of reinforcing fillers.

Network Formation

The formation of network structures has been extensively simulated by Eichinger and coworkers.1) The basic approach is to randomly end link functionally-terminated precursor chains with a multifunctional reagent, and then to examine the sol fraction with regard to

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amount and types of molecules present, and the gel fraction with regard to its structure and mechanical properties. This is illustrated in Fig. 1. The systems most studied in this regard$^{1)}$ involve chains of poly(dimethylsiloxane) (PDMS) having end groups X that are either hydroxyl or vinyl groups, with the corresponding Y groups on the end linking agents then being OR alkoxy groups in an organosilicate, or H atoms in a multifunctional silane.$^{2)}$

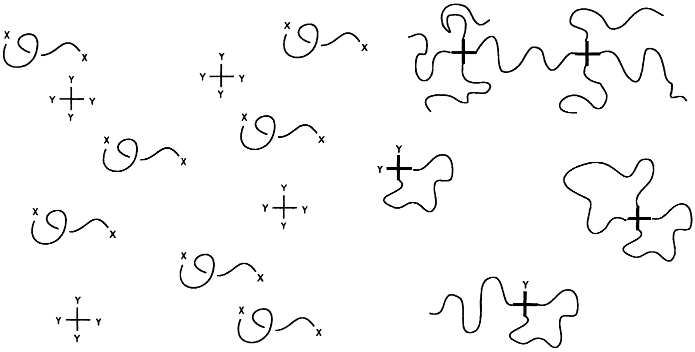

Fig. 1: End-linking reactions to form elastomeric network structures. The left portion of the figure shows the reactants, and the right portion shows some types of expected products.

The Monte Carlo method for simulating these reactions is now part of the Polymer Module in some commercial software (Molecular Simulations, Inc.), and is being used to generate additional information on the vinyl–silane end linking of PDMS.$^{3)}$ Some preliminary results for duplicate experiments for two PDMS molecular weights are shown in Table 1. The simulations are seen to give a very good account of gelation points, but overestimate 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, they are trapped within the network if they are large enough to be penetrated by the precursor chains.$^{2)}$ This "incarceration" process has also been simulated successfully.$^{2)}$

Distributions of End-To-End Distances

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 are used to simulate spatial configurations and thus distribution functions for the end-to-end separations.4-6) 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 Fig. 2. Another example of this approach was to determine how an applied force can change the distributions for a chain that can undergo a coil-to-helix transition.7)

Table 1: Extents of reactiona) for some poly(dimethylsiloxane) end-linking reactions.3)

M_n of PDMSb) (g/mol)	At gelation		At end of reaction	
	Experiments	Simulations	Experiments	Simulations
6,400	0.65	0.65	0.87	0.99
"	0.68	"	0.89	"
7,300	0.67	0.63	0.88	0.96
"	0.67	"	0.89	"

a)As gauged by Si–H consumption.
b)Number-average molecular weights.

These Monte Carlo distributions can be used in the standard three-chain model for rubberlike elasticity to generate, for example, stress-strain isotherms.2) Non-Gaussian effects can cause large increases in modulus at high elongations, because of the limited extensibilities of the network chains.8) 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. One illustration of this approach is the use of multimodal distributions of network chain lengths, as described in the following Section.

Elastomers Having Multimodal Distributions of the End-To-End Distance

One of the most interesting applications of this approach is to PDMS elastomers which have a bimodal distribution of network chain lengths9) and, correspondingly, very good mechanical properties.2) 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.[6,10)]

Because of the improvements in properties exhibited by elastomers having bimodal distributions,[2)] there have been attempts to prepare and characterize "trimodal" networks.[11)]

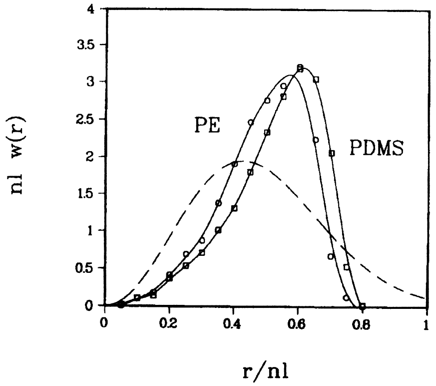

Fig. 2: Comparisons among the rotational isomeric state distributions for polyethylene and PDMS chains having only 20 skeletal bonds, and the corresponding Gaussian approximation.[4)]

The calculations suggest that adding a small amount of very high molecular weight polymer could further improve mechanical properties.

Thermoelasticity

Monte Carlo simulations can also be used to interpret thermoelastic (force-temperature) results generally conducted to estimate the energetic contribution f_e to the elastic force f.[8)] This can be done through the relationship $f_e/f = \mathrm{dln} <r^2>_0 /\mathrm{d}T$, by carrying out calculations of the unperturbed end-to-end dimensions $<r^2>_0$ as a function of temperature. An example is the calculation of f_e/f for the protein elastin,[2)] which showed that the usual random-network model is sufficient to explain its thermoelastic behavior, without the need to postulate more complicated structures.

Crystallization

There is now considerable interest in using simulations for characterizing crystallization in copolymeric materials. In particular, Windle and coworkers[12)] 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, two-dimensional 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, on the other hand, 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.13-16)

One example13,14) 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 two-dimensional array, with black squares representing dimethylsiloxane units and white squares representing diphenylsiloxane units.13,14) "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 non-crystallizable DMS component, or units of the crystallizable DPS component that were not long enough to participate in the crystallization.13,14) 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 the chains. The crystallites thus identified presumably act as crosslinking sites and reinforcing domains, providing the additional toughness the semi-blocky copolymers have over their random counterparts. These methods have also been used in simulations on a stereochemically variable polysiloxane, specifically poly(methyl-3,3,3-trifluoropropylsiloxane).16)

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 been accomplished by some catalysts) is to make the isotactic runs long enough to give crystallites with enough stability to act as cross links, without making their sizes and numbers so large that the material is highly crystalline rather than elastomeric. Some typical chain generations and matchings are shown in Fig. 3.17) Of greatest interest is the case

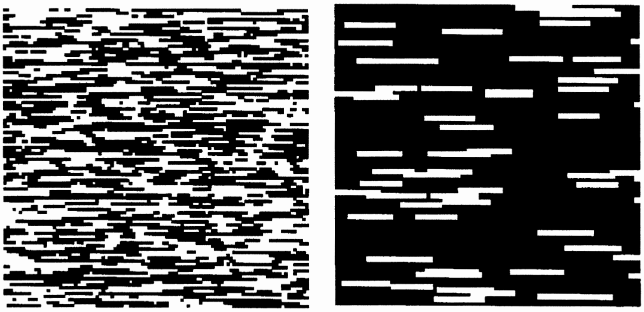

Fig. 3: Results of some simulations on PP chains that were 90 % isotactic. In the left portion of the figure, the black squares represent the *d* isomers and the white squares the *l* isomers. In the right portion, the neighboring like squares coalescing into crystallites of isotactic polymer are shown by the white blocks.

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 (replications of *d*'s or replication of *l*'s). As can be seen in Fig. 4, the simulations are consistent with the presence of crystallinity at overall levels of PP isotacticity sufficiently low to give completely amorphous polymers had the structures not been blocky.

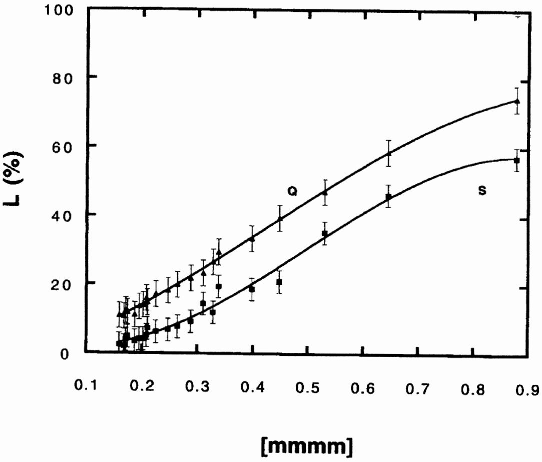

Fig. 4: Degrees of crystallinity for stereoblock polypropylene samples as a function of the isotactic pentad content, with Q and S representing the results for quenched and annealed (searched) samples, respectively.[22)]

Filler Reinforcement

Monte Carlo computer simulations have been carried out on filled networks[18-21)] in an attempt to obtain a better molecular interpretation of how such dispersed fillers reinforce elastomeric materials. The approach taken enables estimation of the effect of the excluded volume of the filler particles and the non-Gaussian characteristics of the chains on the elastic properties of the filled networks. Distribution functions for the end-to-end vectors of the chains were obtained using a Monte-Carlo rotational isomeric state technique.[4)] Conformations of chains which overlapped with any filler particle during the simulation were rejected. In one of the earliest simulations of this type, the filled polymer network was modeled as a composite of crosslinked polymer chains and spherical filler particles arranged in a regular array on a cubic lattice.[20)] The filler particles were found to increase the non-Gaussian behavior of the chains, and to increase the normalized moduli of the networks above the reference value of unity.

In a more realistic portrayal, the reinforcing particles were randomly distributed within a PDMS elastomeric matrix.[21)] 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 in agreement with some subsequent neutron scattering experiments on silicate-filled PDMS.[23)] The substantial increases in stress and modulus with increase in filler content and elongation are in at least qualitative agreement with experiment.

Simulations[24)] have also been carried out to model networks reinforced with polystyrene (PS) particles that were deformed into prolate ellipsoids by first generating spherical particles within an elastomer, heating the elastomer above the glass transition temperature of the PS, stretching it, and then cooling the material under the deformation.[25)] The model employed is shown in Fig. 5. The distributions simulated for this anisotropic system were then used to calculate values of the elastic modulus in units of νRT (where ν is the number density of network chains) The results are shown in Fig. 6,[24)] for the spherical particles (axial ratio $\delta = 1$), and the prolate particles at $\delta = 4$. The unusual maxima and minima are pathological and indicate that a slight change in the shape of the distribution function can have a pronounced effect on stress-strain behavior. The simulated results are in qualitative agreement with the experimental differences in longitudinal and transverse moduli.[25)] Quantitative comparisons are difficult because of the non-uniform stress fields around the particles after the deforming matrix is allowed to retract, and also because the present simulations apply to the particles on an ideal cubic matrix.

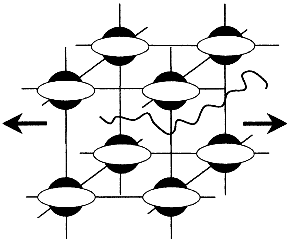

Fig. 5: A three-dimensional cubic lattice of filler particles as they would originally appear as spheres, and then as deformed into aligned prolate ellipsoids. The aspect ratios δ of the ellipsoids were varied by changes in the extent of the deformation applied uniaxially in the direction shown by the arrows. Also shown is a polymer chain which was randomly generated among the ellipsoidal filler particles to determine the particle-induced changes in its spatial configurations and thus its end-to-end distributions.[24)]

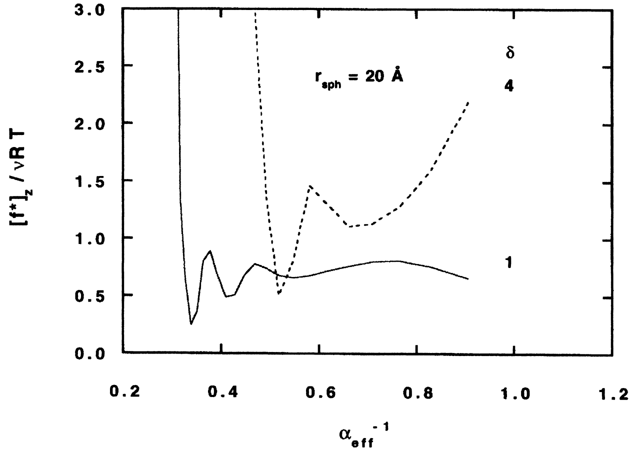

Fig. 6: Normalized longitudinal moduli shown as a function of the inverse elongation for particles which were originally spheres with a radius r_{sph} of 20 Å.

Acknowledgements

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