Illustrative Modeling Studies on Elastomers and Rubberlike Elasticity

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ABSTRACT

Examples are given to illustrate the use of computer modeling to elucidate the structures of elastomeric polymer networks, and to provide guidance on controlling these structures to maximize mechanical properties. The first example involves simulations of the gelation process leading to the network structures necessary for rubberlike elasticity. In other examples, Monte Carlo simulations of network chains are used to characterize non-Gaussian effects, to simulate the structures and properties of networks having multimodal distributions of chain lengths, and to interpret network thermoelasticity. Crystallization is simulated by generating chains having representative sequence distributions and then identifying matched-sequences that could lead to the formation of crystallites. Finally, elastomer reinforcement by fillers is being modeled by simulations of chains in the vicinity of filler particles to determine the importance of this excluded-volume effect.

Keywords: Elastomers, Elasticity, Mechanical Properties, Crystallization, Reinforcement.

1 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 in 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.

2 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 amount and types of molecules present, and the gel fraction with regard to its structure and mechanical properties. This is illustrated in Figure 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 either OR alkoxy groups in an organosilicate, or H atoms in a multifunctional silane [2].
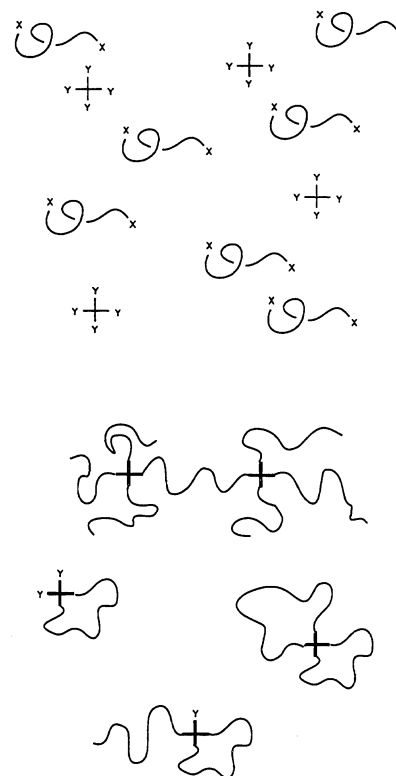

Figure 1: End-linking reactions to form elastomeric network structures. The upper portion of the figure shows the reactants, and the lower portion shows some types of expected products.

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 in the present investigations to generate additional information on the vinyl–silane end linking of PDMS [3]. The simulations were found to give a very good account of extents of reaction at the gelation points, but to overestimate the maximum extent of reaction attainable. The discrepancy may be due to experimental difficulties in taking the end-linking 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 results network if they are large enough to be penetrated by the precursor chains [2]. This "incarceration" process has also been successfully simulated [4].

3 DISTRIBUTIONS OF THE 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 [5]. 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 [6-8]. 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 critical importance with regard to ultimate properties.

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 [9]. 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.

4 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 lengths [10, 11] 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 [8, 12].

Because of the improvements in properties exhibited by elastomers having bimodal distributions [2], there have been attempts to prepare and characterize "trimodal" networks [13-15]. The calculations suggest that adding a small amount of very high molecular weight polymer could further improve mechancal properties.

5 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 [9]. This can be done through the relationship $f_e/f = d\ln<r^2>_0/dT$, 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 [16, 17], which showed that the usual random-network model is sufficient to explain its thermoelastic behavior, without the need to postulate more complicated structures.

6 CRYSTALLIZATION

There is now considerable interest in using simulations for characterizing crystallization in copolymeric materials. In particular, Windle and coworkers [18] 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 that could lead to the formation of crystallites, in order to estimate extents of crystallinity. Chains stacked in arbitrary registrations are taken to model quenched samples. Annealed samples, on the other hand, are modeled by sliding the chains past one another longitudinally to search for the largest possible number of matches. The longitudinal movement of the chains relative to one another, out of register, approximately models the lateral searching of sequences in copolymeric chains during annealing [19-22].

One example [19, 20] 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 (DMS) units and white squares representing diphenylsiloxane (DPS) units [19, 20]. "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 sequences, or units of the crystallizable DPS component that were not long enough to participate in the crystallization [19, 20]. A value of the degree of crystallinity of a simulated sample can then be determined by counting the units involved in the crystalline sequences with respect to the total number of units of all the chains. The crystallites thus identified presumably act as cross-linking sites and reinforcing domains, thereby providing the additional toughness the semi-blocky copolymers are known to have over their random counterparts. These methods have also been used in simulations on a stereochemically-variable polysiloxane, specifically poly(methyl-3,3,3-trifluoropropyl-siloxane) [22].

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 [23]. 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 Figure 2 [24]. Of greatest interest is the case where the isotactic lengths are kept at a constant relatively large value while the random
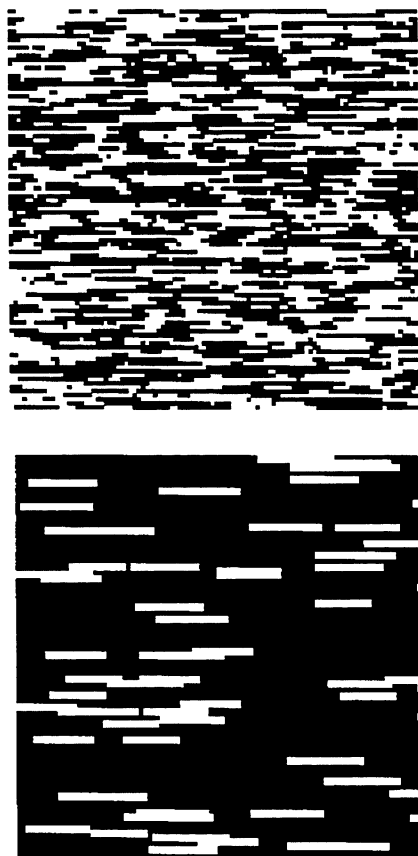
Figure 2: Results of some simulations on PP chains that were 90 % isotactic. In the upper portion of the figure, the black squares represent the *d* isomers and the white squares the *l* isomers. In the lower portion, the number of neighboring like squares coalescing into crystallites of isotactic polymer are shown by the white blocks.

(atactic) sequences are increased in length, thereby decreasing the overall content of *meso* placements (replications of *d*'s or replication of *l*'s). The simulations are consistent with the presence of crystallinity at overall levels of PP isotacticity sufficiently low to give only completely amorphous polymers had the structures not been blocky.

7 FILLER REINFORCEMENT

Monte Carlo computer simulations have been carried out on filled networks [25-28] 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 [6]. Conformations of chains which overlapped with any filler particle during the simulation were rejected.

In an illustrative study, the reinforcing particles were randomly distributed within a PDMS elastomeric matrix

[28]. 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 [29]. The substantial increases in stress and modulus with increase in filler content and elongation are in at least qualitative agreement with experiment.

Simulations have also been carried out to model networks reinforced with polystyrene (PS) particles [30]. These initially spherical particles were deformed into prolate (cigar-shaped) ellipsoids by first generating 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 [31]. The model employed is shown in Figure 3. The distributions simulated for this anisotropic system were then used to calcuate values of the elastic modulus. The simulated results are in qualitative agreement with the experimental differences in longitudinal and transverse moduli [31]. 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. In any case, the results should encourage additional work in this important area of filler reinforcement [32-34].

Specifically, there are a number of directions in which such filler simulations could be extended. For example, one could investigate different particle-size distributions, various distributions of the particles in space, and the effects of particle aggregation. In the case of particles that are non-spherical (including disc-shaped oblate ellipsoids), it would be important to study both particles in regular (parallel) orientations [30] and those that are randomly oriented. It would also be interesting to model physical adsorption of chains onto the filler surfaces, using standard Lennard-Jones interaction potentials. Chemical adsorption, on the other hand, could be modeled by randomly distributing active particle sites, and then interacting chains with them through a Dirac δ-function type of potential (with chains at less than some short-range interaction distance becoming chemi-
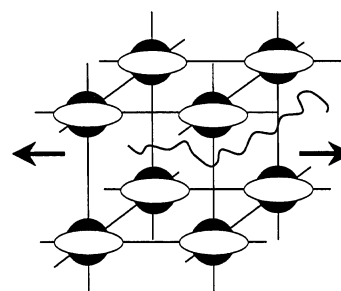

Figure 3: A three-dimensional cubic lattice of filler particles as they would originally appear as spheres, and then as deformed into aligned prolate ellipsoids. The aspect ratios of the ellipsoids were varied by changes in the extent of the deformation applied uniaxially in the direction shown by the 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 distribution [30].

sorbed). Of particular interest would be simulations for chains sufficiently long to partially adsorb onto several filler particles, and to model chain-contour distributions between the bulk polymer and the filler particles.

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