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Monte Carlo Simulations on Nanoparticles in Elastomers. Effects of the Particles on the Dimensions of the Polymer Chains and the Mechanical Properties of the Networks

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Summary: Reinforcement of elastomers is modeled using Monte Carlo simulations on rotational isomeric state chains, to characterize their spatial configurations in the vicinity of filler particles. The resulting filler-perturbed distributions of the chain end-to-end distances are in agreement with experimental results gotten by neutron scattering. The use of these distributions in a standard molecular theory of rubberlike elasticity produces stress-strain isotherms for elongation that are consistent with available experimental results.

Keywords: computer simulations; mechanical properties of elastomers; Monte Carlo methods; reinforcing fillers; rotational isomeric state theory

Introduction

One of the most important unsolved problems in the area of elastomers and rubberlike elasticity is the lack of a good molecular understanding of the reinforcement provided by fillers such as carbon black and silica.[1–4] This issue has a number of challenging aspects with regard to basic research in polymers in general, and is of much practical importance since the improvements in properties fillers provide are critically important with regard to the utilization of elastomers in almost all commercially applications. Some of the work on this problem has involved analytical theory,[5–7] but most of it is based on a variety of computer simulations.[8–18] In this context, the present review describes one way in which computational modeling has been used to elucidate the structures and properties of elastomeric polymer networks, using illustrative studies from the authors' research groups. In the present approach, the simulations focus on the ways the filler particles change the distribution of the end-to-end vectors of the polymer chains making up the elastomeric network, from the fact that the filler particles exclude the chains from the volumes they occupy. The changes in the polymer chain distributions from this filler "excluded volume effect" then cause associated changes in the mechanical properties of the elastomer host matrix. Single polymer chains are modeled, in the standard rotational isomeric state representation,[19,20] and Monte-Carlo techniques are used to generate their trajectories in the vicinities of collections of filler particles. A brief overview of the approach is given in the following Section.[18]

Description of Simulations

Rotational Isomeric State Theory for Conformation-Dependent Properties

In rotational isomeric state models, the continuum of rotations occurring about

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skeletal bonds is replaced by a small number of rotational states that are judiciously chosen. Preferences among these states is then characterized by Boltzmann factors as statistical weights, with the required energies obtained by either potential energy calculations or by interpreting available conformation-dependent properties in terms of the models. Multiplication of matrices containing these statistical weights is then used to generate the partition function and related thermodynamic quantities, and multiplications of similar matrices containing structural information as well is then used to predict or interpret various properties of the chains.[19,20] Examples of such properties are end-to-end distances, radii of gyration, dipole moments, optical anisotropies, etc. as unperturbed by intramolecular excluded volume interactions between chain segments.[21]

Distribution Functions

The extension of these ideas most relevant in the present context is the use of this model to generate *distributions* of end-to-end distances, instead of simply their averages.[22] The same statistical weights were used in Monte Carlo simulations to generate representative chains, and their end-to-end distances *r* were calculated. The corresponding distribution function was obtained by accumulating large numbers of these Monte Carlo chains with end-to-end vectors within various intervals, and dividing these numbers by the total number of the chains, *N*. The distances were then placed into a histogram to produce the desired end-to-end vector probability distribution function P(r) or $P(r/nl_o)$, where *n* is the number of skeletal bonds of length l_o. The function $P(r/nl_o)$ was smoothed using the IMSL cubic spline subroutine CSINT.[23]

These distributions are very useful for chains that cannot be described by the Gaussian limit, specifically chains that are too short, too stiff, or stretched too close to the limits of their extensibility. Some typical results shown elsewhere[18,22] document exactly how bad the Gaussian distribution is for short chains of polyethylene and poly(dimethylsiloxane) (PDMS), particularly in the region of high extension that is critical to an understanding of ultimate properties.

Applications to Unfilled Elastomers

The present application of these calculated distribution functions is the prediction of elastomeric properties of the chains within the framework of the Mark-Curro theory.[22,24] The distribution P(r) of the end-to-end vectors *r* is directly related to the Helmholtz free energy A(r) of a chain by $A(r) = c - kT \ln P(r)$ where c is a constant. The resulting perturbed distributions are then used in the ‘‘three-chain’’ elasticity model[25] to obtain the desired stress-strain isotherms in elongation for deformations that are ‘‘affine’’ (in which the molecular deformations parallel the macroscopic deformation in a linear manner). One quantity of primary interest here is the normalized or reduced stress $f^*/\nu RT$, where $f^*$is the nominal or engineering stress, ν is the number of network chains, and R and T have their usual significance. The strain α is the elongation ratio L/L_i of the stretched and unstretched lengths of the sample.

Some typical results on networks having either a unimodal or a bimodal distribution of network chain end-to-end distances are shown elsewhere.[18,22] In the case of a unimodal distribution of relatively long chains, the reduced stress had the expected theoretical value and was independent of elongation. iIn the case of the networks containing some short chains, however, there were upturns in modulus with increasing elongation that were similar to those shown in bimodal networks, in which short chains are introduced to give advantageous increases in ultimate strength and modulus.[26,27]

Applications to Filled Elastomers

In this case, the same Monte Carlo simulations were carried out as was done for the unfilled networks, but now each bond of the chain was tested for overlapping with a filler particle as the chain was being generated.[28] If any bond penetrated a particle surface, the entire chain conformation was rejected and a new chain started. Some specific illustrative examples of such investigations are given below.

Spherical Particles

Particle Sizes, Shapes, Concentrations, and Arrangements

The particle sizes of greatest interest are those used commercially, with small particles generally giving significantly better reinforcement than larger ones. The primary particles are generally assumed to be spherical. In actual filled elastomers, the particles are dispersed at least relatively randomly, but it is of interest to describe some simulations on regular particle arrangements as well.[28]

In some of the earliest simulations, 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.[18,29] The filler particles were found to increase the non-Gaussian behavior of the chains and to increase the moduli, as expected. It is interesting to note that composites with such structural regularity have actually been produced,[30] and some of their mechanical properties have been reported.[31]

In the first of a series of subsequent studies,[9] the reinforcing particles were randomly distributed, as is illustrated in Figure 1.

Distributions of Chain End-to-end Distances

Of greatest interest here is whether the particles cause increases or decreases in the chain end-to-end distances, with this expected to depend particularly on the size of the filler particles, but presumably on other variables such as their concentration in the elastomeric matrix as well.

Some illustrative results for filler particles within a PDMS matrix are described in Figure 2.[9,18] One effect of the particles was to increase the dimensions of the chains, in the case of filler particles that were small relative to the dimensions of the network chains. In contrast, particles that were relatively large tended to decrease the chain dimensions.

Since these changes in dimensions arising from the filler excluded volume effects are of critical importance, it is necessary to

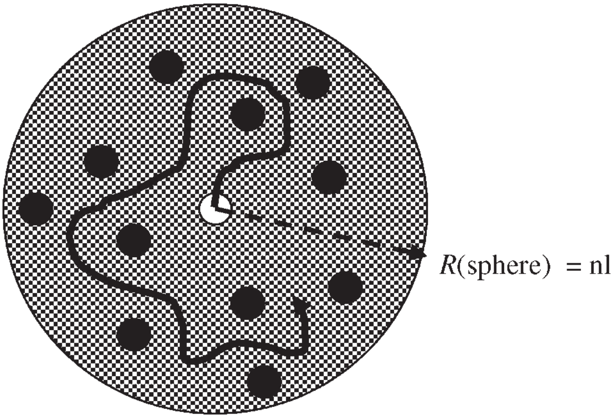

Figure 1.
Schematic view of a polymer chain and randomly-distributed filler particles. The origin of the chain was placed at the center of the sphere of radius R(sphere) = nl (maximum extension, $r_{\max}$). All the filler particles were placed randomly in non-overlapping arrangements within the sphere, except at its center (where the chain started its trajectory). Chain conformations that trespassed on any particle were rejected, and statistical calculations were performed on the remaining, acceptable conformations.

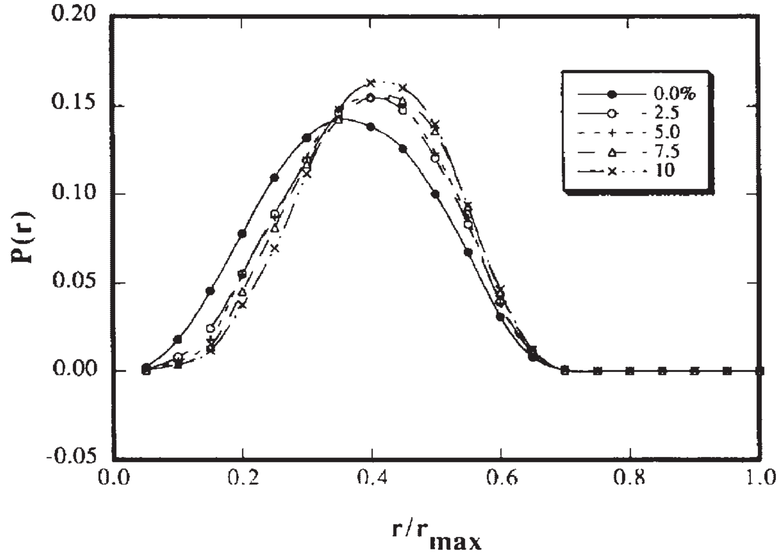

Figure 2.
Radial distribution functions P(r) at T = 500 K for network chain end-to-end distances obtained from the Monte Carlo simulations. The results are shown as a function of the relative extension r/r_{max}, for PDMS networks having 50 skeletal bonds between cross links.[9] The radius of the filler particles was 5 Å, and the values of the volume % of filler present are indicated in the inset.

put them into a larger context. In particular, these simulated results on the distributions are in agreement with some subsequent neutron scattering experiments on deuterated and non-deuterated chains of PDMS.[32] The polymers contained silica particles that were surface treated to make them inert to the polymer chains, as was implicitly assumed in the simulations. These experimental results agreed with the present simulations in that they also indicated chain extensions when the particles were relatively small, and chain compressions when they were relatively large. Increases in chain dimensions have also been recently been reported in scattering studies on heavily cross-linked polystyrene (PS) spheres introduced as filler particles into a PS matrix.[33]

Some recent dynamic Monte Carlo simulations have also reported increases in chain dimensions in filled systems.[34] There have been several reports of simulations, however, that have yielded results in disagreement with the described simulations and the two corresponding scattering reports mentioned above. The major difference in approach was the use of dense collections of chains instead of single chains sequentially generated in the vicinities of the filler particles. Specifically, the simulations by Vacatello,[10,16] and by Kumar et al.[17] find chain dimensions that are either unchanged by the filler particles or are decreased.

In a rather different type of simulation, Mattice et al.[35] generated particles within a matrix by collapsing some of the chains into domains that would act as reinforcing filler. They found that small particles did lead to significant increases in chain dimensions, while large particles led to moderate decreases, in agreement with the single-chain simulations and scattering experiments. These simulations parallel the already cited experimental scattering study of PS spheres in a PS matrix.[33]

Because of these discrepancies, the present simulations were refined in an attempt to understand the differences

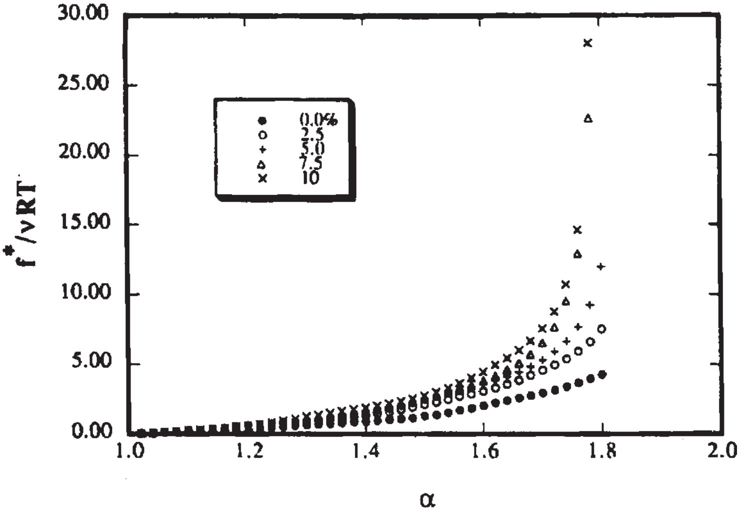

Figure 3.
Stress-strain isotherms calculated from the distributions shown in Figure 2.[9,18]

described.[15] This involved (i) relocating the particles periodically during a simulation, (ii) starting the chains at different locations, (iii) using Euler matrices to change the orientations of the chains being generated, and (iv) replacing the "united atom" approach by detailed atom specifications. None of these modifications significantly changed the results obtained.

Also in progress are simulations to determine any effects of having multimodal distributions of particle sizes.[36] Looking at this issue was encouraged by the improvements in properties obtained by using bimodal distributions of network chain lengths in elastomers[26] and thermosets,[37] and bimodal distributions of the diameters of rubbery domains introduced to improve the properties of some thermoplastics.[38–40]

Stress-Strain Isotherms

There are two items of primary interest here, specifically increases in modulus in general, and upturns in the modulus with increasing deformation. Results are typically expressed as the nominal stress or reduced stress as a function of deformation. The area under such curves up to the rupture point of the sample then gives the energy of rupture, which is the standard measure of the toughness of a material.[41]

Figure 3 Shows the stress-strain isotherms in elongation[9,18] corresponding to the distributions shown in Figure 2. There are substantial increases in modulus that increase with increase in filler loading, as expected. Additional increases would be expected by taking into account other mechanisms for reinforcement such as physisorption, chemisorption, etc., as described below.

The cases where the filler causes compression of the chain are relevant to another area of rubberlike elasticity, specifically the preparation of networks by cross linking chains in solution followed by removal of the solvent.[18,41] In these procedures, the solvent disentangles the chains prior to their cross linking, and its subsequent removal by drying puts the chains into a "supercontracted" state.[41] 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.[42,43] The most recent work in this area has focused on the unusually high extensibilities of such elastomers.[44,45]

Ellipsoidal Particles

General Features

Non-spherical filler particles are also of considerable interest. Prolate (needle-shaped) particles can be thought of as a bridge between the roughly spherical particles used to reinforce elastomers[46] and the long fibers frequently used for this purpose in thermoplastics and thermosets.[47] Oblate (disc-shaped) particles can be considered as analogues of the much studied clay platelets used to reinforce a variety of materials.[48–52]

In one particularly relevant series of experiments, initially spherical particles of polystyrene (PS) were deformed into prolate ellipsoids by (i) heating the elastomeric PDMS matrix in which they resided above the glass transition temperature of the PS, (ii) stretching the matrix uniaxially, and then (iii) cooling it under the imposed deformation.[18,53] Some relevant simulations[18,54] show values of the moduli pertaining to directions longitudinal and transverse to the particle axial directions. The anisotropy in structure causes the values of the modulus in the longitudinal direction to be significantly higher than those in the transverse directions. These simulated results are in at least qualitative agreement with the experimental differences in longitudinal and transverse moduli obtained experimentally.[53]

Randomized arrangements of prolate ellipsoids were also of interest. In this case, isotropic behavior is expected, due to the lack of orientation dependence between the non-spherical particles and the deformation axis regardless of the shapes of the particles. The simulated results confirmed this expectation that the reinforcement from randomly-oriented non-spherical filler particles is isotropic regardless of the anisometry of their shapes.

Oblate Ellipsoids

In spite of their inherent interest, relatively little has been done on fillers of this shape. For regular arrangements, the particles were again placed on a cubic lattice[11] and were oriented in a way consistent with their orientation in PS-PDMS composites that were the subject of an experimental investigation.[55] In general, the network chains tended to adopt more compressed configurations relative to those of prolate particles having equivalent sizes and aspect ratios. The reinforcement from the oblate particles was found to be greatest in the plane of the particles, and the changes were in at least qualitative agreement with the corresponding experimental results.[55] In the experimental study, axial ratios were controllable, since they were generally found to be close to the values of the biaxial draw ratio employed in their generation. The moduli of these anisotropic composites were reported, but only in the plane of the biaxial deformation.[55] It was not possible to obtain moduli in the perpendicular direction, owing to the thinness of the films that had to be used in the experimental design.

Aggregated Particles

Real Systems

The silica or carbon black particles used to reinforce commercial materials are seldom completely dispersed,[1–4] as is assumed in the simulations described. The primary particles are generally aggregated into relatively stable aggregates and these are frequently clustered into less stable arrangements called agglomerates.[18]

Types of Aggregates for Modeling

Simulations should be carried out on such more highly organized structures, some limiting forms of which would be chainlike, globular, star-shaped, and branched.[18] It is well known in the industry that such structures are important in maximizing the reinforcement, as evidenced by the fact that being too persistent in removing such aggregates and agglomerates in blending procedures gives materials with less than optimal mechanical properties.[1–4]

Deformabilities of Aggregates

Friedlander et al. have demonstrated that such aggregates have a remarkable deformability, by carrying out elongation experiments both reversibly, and irreversibly to their rupture points.[56–58] This is of considerable importance, since when these structures are within elastomeric matrices, their deformations upon deformation of the filled elastomer means that they must participate in the storage of the elastic deformation energy. This would have to be taken into account both in the interpretation of experimental results and in more refined simulations of filler reinforcement.

Potential Refinements

This excluded volume effect is only one aspect of elastomer reinforcement,[5–7] but some additional effects could be investigated by modeling the adsorption of the elastomer chains onto the filler surfaces. This could be done by first assuming Lennard-Jones interactions between the particles and chains, in physical adsorption. These aspects could then be extended to include chemical adsorption by assuming that there are randomly-distributed, active particle sites interacting very strongly with the chains (by a Dirac δ-function type of potential). If the distance between the chain (generated using the Monte Carlo method) and the active site becomes less than the range of the short-range interactions, then the chain would become chemisorbed. The distribution of other active sites on the filler surface and the Lennard-Jones interactions would determine if the remaining parts of the chain are absorbed onto the surface. Simulations for chains that are sufficiently long to partially adsorb onto several filler particles would be especially illuminating, in that they could shed new light on the general problem of polymer adsorption. The distribution of the chain contours between the polymer bulk and various filler particles could also be of considerable importance.[18]

Conclusions

Although there are obviously unresolved issues, the broad overview presented here should demonstrate the utility of simulations to give a better molecular understanding of how fillers reinforce elastomeric materials. It is also hoped that some of the unsolved problems described will encourage others to contribute to elucidating this important area of polymer science and engineering.

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