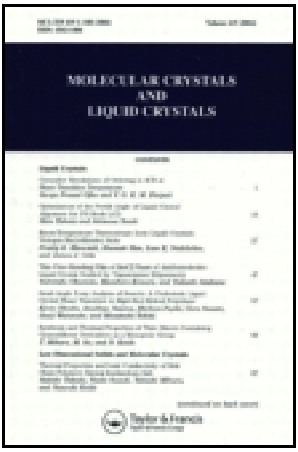

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Some Simulations on Filler Reinforcement in Elastomers

J. E. Mark [a]

[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio, 45221-0172

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Some Simulations on Filler Reinforcement in Elastomers

J. E. MARK

Department of Chemistry and the Polymer Research Center,
The University of Cincinnati, Cincinnati, Ohio 45221-0172

Elastomer reinforcement is being modeled by Monte Carlo simulations on rotational isomeric state chains in order to obtain the spatial configurations of the chains in the vicinity of filler particles. The results are distributions of the chain end-to-end distances as perturbed by this excluded-volume effect, and the results obtained are in agreement with experimental results gotten by neutron scattering. The use of these distributions in standard molecular theories of rubberlike elasticity then produces stress-strain isotherms suitable for comparison with elongation experiments. Such simulations have now been carried out for elastomeric matrices reinforced by spherical filler particles (either on a cubic lattice or randomly dispersed), or by prolate or oblate particles on cubic lattices (either with their axes oriented or randomized). The simulated mechanical properties are consistent with experimental results available at the present time, and should provide encouragement and guidance for additional simulations and experiments.

Keywords: Computer simulations; Elastomers; Reinforcing fillers

INTRODUCTION

The present review describes one way in which computational modeling has been used in elucidating the structures and properties of elastomeric polymer networks, using illustrative studies from the author's research group. One of the main goals has been to provide guidance on how to optimize the mechanical properties of an elastomer, in the present case by the incorporation of reinforcing fillers.

MODELING APPROACH

In brief, Monte Carlo computer simulations are being carried out on filled networks [1-8], 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 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 are obtained by applying Monte-Carlo methods to rotational isomeric state representations of the chains [9]. Conformations of chains which overlap with any filler particle during the simulation are rejected. The resulting perturbed distributions are then used in the three-chain elasticity model [10] to obtain the desired stress-strain isotherms in elongation.

RESULTS AND DISCUSSION

Spherical Particles

On a cubic lattice

In this application, a filled poly(dimethylsiloxane) (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 [3]. This is shown schematically in Figure 1. 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 [11, 12], and some of their mechanical properties have been reported [13, 14].

Particles that are randomly dispersed

In a subsequent study, the reinforcing particles were randomly distributed within the PDMS matrix [7]. 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 2. These results on

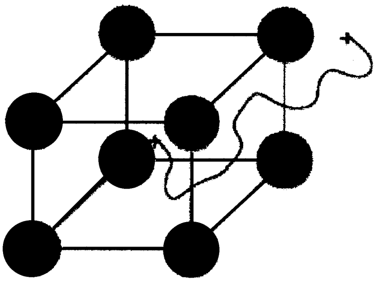

FIGURE 1. Schematic view of a polymer chain being generated within part of a three-dimensional cubic filler matrix [3].

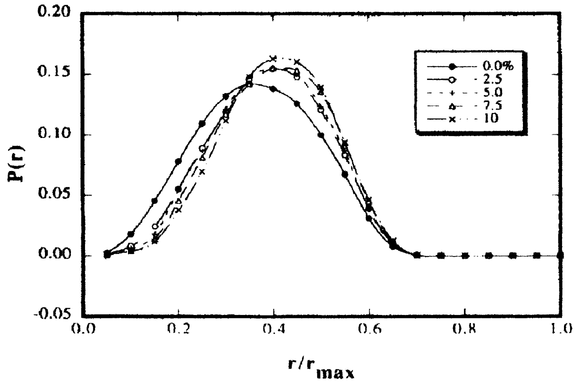

FIGURE 2. Radial distribution functions P(r) at T = 500 K for network chain end-to-end vectors obtained from Monte Carlo simulations. The results are shown as a function of the relative extension r/r_{max}, for PDMS networks having 50 skeletal bonds between cross links [7]. The radii of the filler particles was 5 Å, and the values of the volume % of filler present are indicated in the inset.

the distributions are in agreement with some subsequent neutron scattering experiments on silicate-filled PDMS [15]. The corresponding stress-strain isotherms in elongation are shown in Figure 3. The substantial increases in modulus with increases in filler

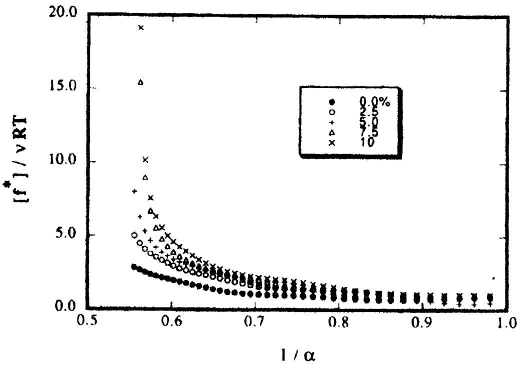

FIGURE 3. Mooney-Rivlin representations of the moduli calculated from the distributions shown in Figure 2 [7], where ν is the number of network chains and α is the elongation.

content and elongation are in at least qualitative agreement with experiment.

Prolate Particles

Parallel orientations

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 [16] and the long fibers frequently used for this purpose in thermoplastics and thermosets [17]. Oblate (disc-shaped) particles can be considered as analogues of the much studied clay platelets used to reinforce a variety of materials [18-21].

In one example in this area, simulations were carried out to model networks reinforced with polystyrene (PS) particles [22]. These initially spherical particles were deformed into prolate ellipsoids by first polymerizing 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 imposed deformation [23]. The model employed is shown in Figure 4. The approach can be illustrated by an elastomeric matrix of amorphous polyethylene (PE)

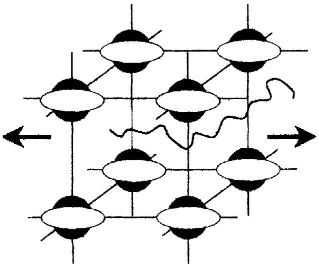

FIGURE 4. A three-dimensional cubic lattice of filler particles as they would originally appear as spheres, and then as deformed into aligned prolate ellipsoids. The aspect ratios δ of the ellipsoids were varied by changes in the extent of the deformation applied uniaxially in the direction shown by 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 distribution [22].

chains having 300 skeletal bonds in a cubic lattice of oriented prolate filler particles having radii r_{sph} = 20 or 40 Å, at 425 K and a volume fraction of filler of 0.2. Typical results are shown in Table 1, including the root-mean-square end-to-end distance of the chains as a measure of their sizes. Of particular importance are the last two columns, which document the anisotropic changes of initial chain dimensions (relative to the spherical ones) in directions longitudinal and transverse to the particle axial directions, respectively. These anisotropic changes in chain dimensions are also shown graphically in Figure 5. This anisotropy gives rise to values of the modulus in the longitudinal direction that are significantly higher than those for the spherical particles. Typical results are shown in Figure 6. 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 the stress-strain behavior [22]. It could also be due to using too large an interval in constructing the histograms used to obtain the distance distributions.

In any case, the simulated results are in qualitative agreement with the experimental differences in longitudinal and transverse moduli [23]. 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.

TABLE 1 Results of Monte Carlo calculations for PE chains in a cubic lattice of oriented prolate filler particles

δ[a]	a[b]	$\langle r^2\rangle_o^{1/2}$[c]	λ_{iz}[d]	$\lambda_{I,x,y}$[e]
r_{sph} = 20 Å				
0.0	55.1	71.2	1.0	1.00
1.0		61.2	1.0	1.00
1.5		63.3	1.2	0.97
2.0		64.4	1.3	0.97
4.0		65.9	1.3	0.99
6.0		66.5	1.3	1.00
r_{sph} = 40 Å				
0.0	110.	71.2	1.00	1.00
1.0		65.3	1.00	1.00
1.5		65.2	1.06	0.97
2.0		66.1	1.09	0.98
4.0		67.0	1.10	0.99
6.0		67.6	1.10	1.00

[a] Aspect ratio of oriented prolate particles.

[b] Cubic unit cell dimension in Å.

[c] Root-mean-square end-to-end distance in Å.

[d] Anisotropic changes of initial chain dimensions relative to the spherical ones in the longitudinal direction of the oriented particles (z axis).

[e] Anisotropic changes of initial chain dimensions relative to the spherical ones in the transverse direction of the oriented particles (x,y axes).

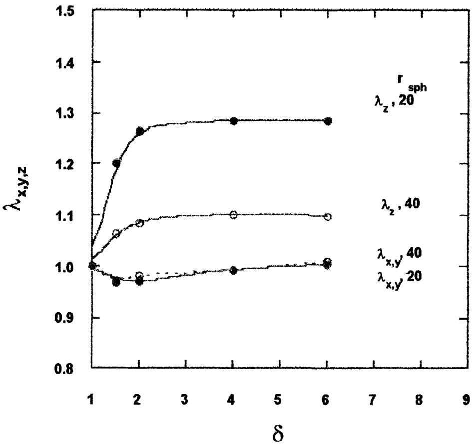

FIGURE 5. Anisotropic changes of the intial chain dimensions for the prolate particles [relative to the dimensions in the presence of spherical particles (δ = 1.0)] [22]. The results are shown as a function of the aspect ratio for filler particles having r_{sph} of 20 or 40 Å.

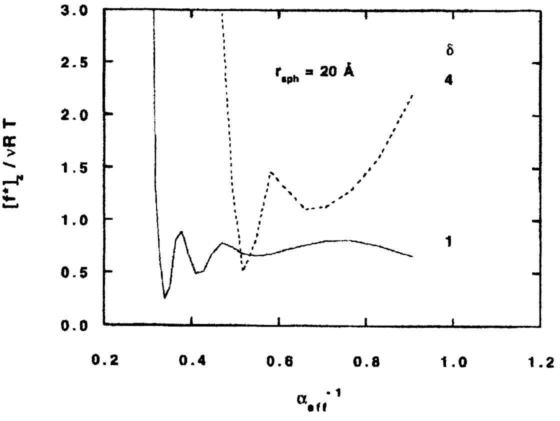

FIGURE 6. Normalized longitudinal moduli shown as a function of the inverse elongation for particles which were originally spheres (axial ratio δ = 1) with a radius r_{sph} of 20 Å, and also deformed to δ = 4 [22].

Random orientations

In this case, isotropic behavior is expected, due to the lack of orientation dependence between the non-spherical particles and 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 [24]. There may be difficulties on the experimental side in obtaining completely randomized orientations (and dispersions), because of the tendency of non-spherical particles to order themselves, particularly in the types of flows that accompany processing techniques or even the simple transfers of polymeric materials.

Oblate Particles

Parallel orientations

The particles were again placed on a cubic lattice [25], and were oriented in a way consistent with their orientation in PS-PDMS composites that were the subject of an experimental investigation [26]. In general, the network chains tended to adopt more compressed configurations relative to those of prolate particles having equivalent sizes and aspect ratios. The elongation moduli were found to depend on the sizes, number, and axial ratios of the particles, as expected. In particular, 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 [26]. 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 [26]. It was not possible to obtain moduli in the perpendicular direction, owing to the nature of the thin film that had to be used in the experimental design.

Random orientations and distributions

With regard to the simulations, it would be of considerable interest to investigate the reinforcing properties of such oblate particles when they are randomly oriented and also randomly dispersed. Such work is in progress [27].

FUTURE WORK

This excluded volume effect is only one aspect of elastomer reinforcement, but some additional effects could be investigated by modeling the adsorption of the elastomer chains onto the filler surface. 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).

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