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Feature article

Some simulations on filler reinforcement in elastomers

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Abstract

This review illustrates how elastomer reinforcement can be modeled using Monte Carlo simulations on rotational isomeric state chains to characterize their spatial configurations 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 those in 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: Elastomers; Mechanical properties; Reinforcing fillers

1. 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 [1–5]. 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 commercial applications. Some of the work on this problem has involved analytical theory [6–12], but most of it is based on a variety of computer simulations [13–40].

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. 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. 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 excludes the chains from the volumes it occupies. 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 [41–43], 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.

2. Description of simulations

2.1. Rotational isomeric state theory for conformation-dependent properties

In rotational isomeric state models, the continuum of

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rotations occurring about skeletal bonds is replaced by a small number (generally three) 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 is then used to predict or interpret various properties of the chains [41–43]. 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 [44].

2.2. 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 [45]. 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 space 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 $P(r/nl)$, where n is the number of skeletal bonds of length l. The histogram generally consisted of 20 equally spaced intervals over the allowed range $0<(r/nl)<1$, since previous studies showed that this choice was the most suitable for obtaining probability distribution functions [46]. The function $P(r/nl)$ was smoothed using the IMSL cubic spline subroutine CSINT. The smoothing procedure is necessary for the proper calculation of the stress–strain isotherms from the Monte Carlo histogram [46].

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 are shown in Fig. 1 [45]. They document 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.

2.3. 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 [45, 47] described below.

The distribution $P(r)$ of the end-to-end distance r is directly related to the Helmholtz free energy $A(r)$ of a chain by

$$A(r) = c - kT \ln P(r) \tag{1}$$

where c is a constant. The resulting perturbed distributions are then used in the 'three-chain' elasticity model [48] to obtain the desired stress–strain isotherms in elongation. For the specific case of this model, the general expression for ΔA takes the form

$$\Delta A = \frac{v}{3}[A(r_0\alpha) + 2A(r_0\alpha^{-1/2}) - 3A(r_0)] \tag{2}$$

for elongations that are 'affine' (in which the molecular deformations parallel the macroscopic deformations in a linear manner). Here α is the elongation ratio L/L_i, v is the number of chains in the network, and r_0 is the value of root-mean-square end-to-end distance of the undeformed network chains.

One quantity of primary interest here is the nominal or engineering stress f^*, defined as the elastic force at equilibrium per unit cross-sectional area of the sample in the undeformed state:

$$f^* = -T\left(\frac{\partial \Delta A}{\partial \alpha}\right)_T \tag{3}$$

Substitution of Eq. (2) into Eq. (3) then gives

$$f^* = -\frac{vkTr_0}{3}[G'(r_0\alpha) - \alpha^{-3/2}G'(r_0\alpha^{-1/2})] \tag{4}$$

where $G(r) = \ln P(r)$, and $G'(r)$ denotes the derivative dG/dr. The modulus (or 'reduced stress') is defined by $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ and is often fitted to the Mooney–Rivlin

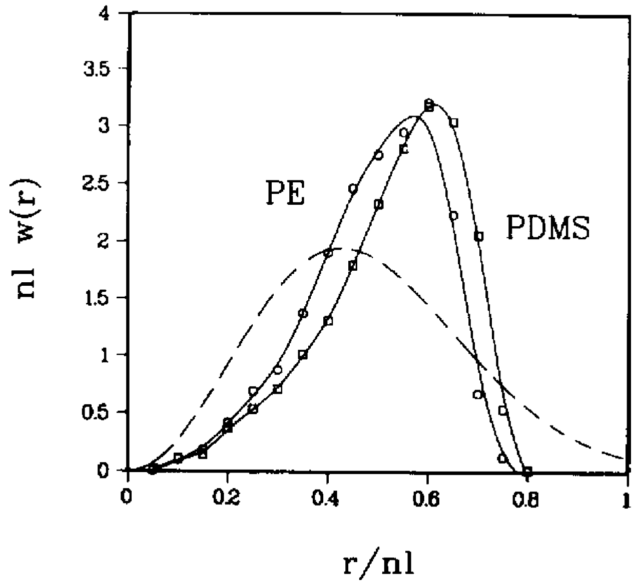

Fig. 1. Comparisons among the rotational isomeric state distribution functions for the end-to-end distance r for polyethylene and poly(dimethylsiloxane) (PDMS) chains having $n=20$ skeletal bonds of length l, and the Gaussian approximation for the PDMS distribution. From Ref. [45], with permission from the American Institute of Physics.

semi-empirical formula $[f^*] \equiv 2C_1 + 2C_2\alpha^{-1}$ [48,49], where C_1 and C_2 are constants independent of deformation α.

Some typical results are shown in Fig. 2 [45], in which the ordinate is the calculated value of the reduced stress or modulus normalized by the value given by the Gaussian limit. The value of unity is seen to be obtained for long chains, in this case those having $n=250$ skeletal bonds, as expected. The shorter chains show upturns in modulus with increasing elongation that are similar to those shown in bimodal networks in which short chains are introduced to give advantageous increases in ultimate strength and modulus [50,51].

2.4. 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.

3. Spherical particles

3.1. Particle sizes, shapes, concentrations, and arrangements

The particle sizes of greatest interest are those used commercially, with small particles giving significantly better reinforcement than larger ones. The primary particles are generally assumed to be spherical. The concentrations or 'loadings' in the simulations are generally relatively small, smaller than those used commercially, since larger concentrations lead to unacceptably high attritions from chains running into particles. In actual filled elastomers, the particles are dispersed at least relatively randomly, but it is of interest to do simulations on regular particle arrangements as well [28].

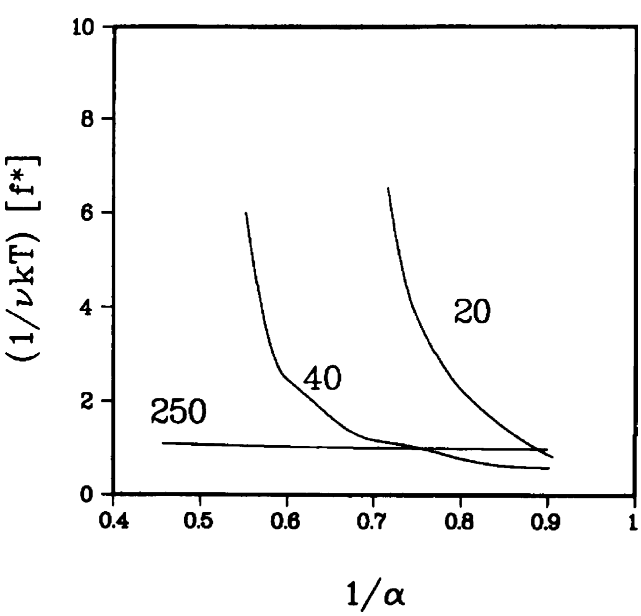

Fig. 2. Elongation moduli of PDMS networks having 20, 40, and 250 skeletal bonds, in the Mooney–Rivlin representation. Values of the modulus have been normalized by the number of network chains, the Boltzmann constant, and the absolute temperature, and α is the elongation ratio or relative length of the deformed sample. From Ref. [45], with permission from the American Institute of Physics.

3.1.1. Regular arrangements, on a cubic lattice

In these 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 [14]. The arrangement is shown schematically in Fig. 3. 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 [52, 53], and some of their mechanical properties have been reported [54,55].

3.1.2. Random arrangements, within a sphere

In a subsequent study [16], the reinforcing particles were randomly distributed, as is illustrated in Fig. 4. The system was taken to be a sphere having a radius equal to the end-to-end distance of the completely stretched out chain. The chain being generated was started at the center of the sphere, and this was the only place a filler particle could not be placed. Otherwise, the particles required to give the desired loading were randomly dispersed over the sample volume shown.

3.2. Distributions of chain end-to-end distances

Of greatest interest here is whether the particles cause increases or decreases in the 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.

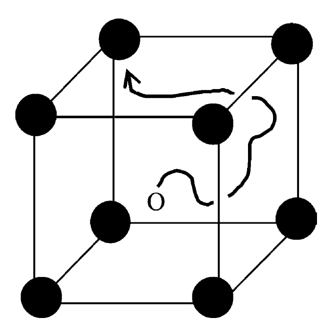

Fig. 3. Schematic view of a polymer chain being generated within part of a three-dimensional cubic filler matrix.

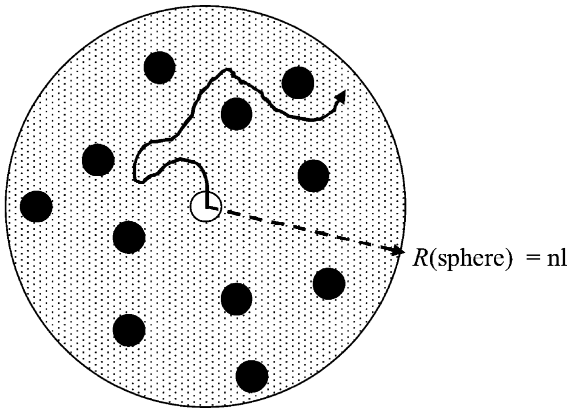

Fig. 4. Schematic view of a polymer chain and randomly-distributed filler particles. The origin of the chain was placed at the center of the sphere of radius R(sphere) $= nl$ (maximum extension, r_{max}). All the filler particles were placed randomly in non-overlapping arrangements within the sphere, except of course 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.

3.2.1. Typical results

Some illustrative results for filler particles within a PDMS matrix is described in Fig. 5 [16]. 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 put them into a larger context.

3.2.2. Relevant neutron scattering results

These simulated results on the distributions are in agreement with some subsequent neutron scattering experiments on deuterated and non-deuterated chains of PDMS [56,57]. 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 also indicated chain extensions when the particles were relatively small, and chain compressions when they were relatively large.

3.2.3. Comparisons with some related simulations

There have been several reports of simulations that have yielded results in disagreement with the described simulations and the corresponding scattering experiments. 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. In particular, the simulations by Vacatello [18,21,24,30,31] show only compressions of the chains.

In a rather different approach, Mattice et al. [37,39] 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!

3.2.4. Improvements in the model

Because of these discrepancies, the present simulations were refined in an attempt to understand the differences described [35]. 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 our earlier results [13–16,19,20]. An additional

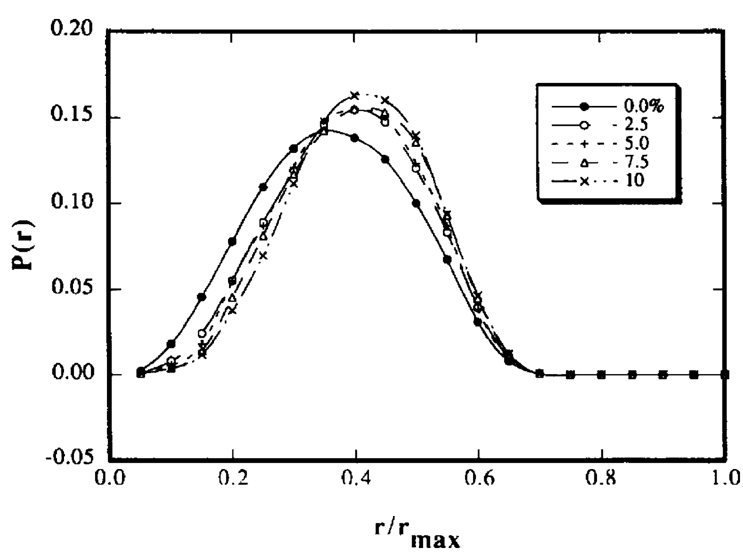

Fig. 5. Radial distribution functions $P(r)$ at $T = 500$ K for network chain end-to-end distances obtained from the Monte Carlo simulations. The results are shown as a function of the relative extension r/r_{max}, for PDMS networks having 50 skeletal bonds between cross links. The radii of the filler particles was 5 Å, and the values of the volume percent of filler present are indicated in the inset. From Ref. [16], with permission from John Wiley and Sons, Inc.

modification, generating dense collections of chains, is in progress [58].

3.2.5. Distributions of particle diameters

Also in progress are simulations to determine any effects of having multimodal distributions of particle sizes [59]. Looking at this issue was encouraged by the improvements in properties obtained by using bimodal distributions of network chain lengths in elastomers [50] and thermosets [60], and bimodal distributions of the diameters of rubbery domains introduced into some thermoplastics [61,62].

3.3. 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 reduced nominal or engineering 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 [63].

3.3.1. Typical results

Fig. 6 shows the stress–strain isotherms in elongation [16] corresponding to the distributions shown in Fig. 5 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.

3.4. Effects of arbitrary changes in the distributions

One additional interesting result is the observation that in some cases, chain compression can also cause increases in modulus. This is being clarified by making some arbitrary changes in the distributions obtained and documenting the effects these changes have on the corresponding simulated stress–strain isotherms. For example, the curves can be shifted to lower and higher values of the chain dimensions, as is illustrated by two of the curves in Fig. 7 [58]. The 'fitted curve' was produced as follows: the distribution of end-to-end distances for the 500,000 Monte Carlo polyethylene chains of 50 bonds at 550 K was fitted to a Gaussian curve. In addition, this curve was shifted in different directions mathematically to obtain other representative curves called left-shifted, right-shifted, and up-shifted.

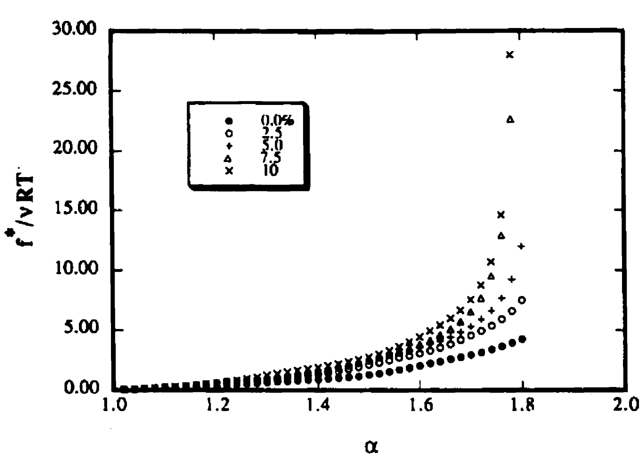

Fig. 6. Nominal stress as a function of the elongation ratio calculated from the distributions shown in Fig. 5. From Ref. [16], with permission from John Wiley and Sons, Inc.

This gives the isotherms shown in Fig. 8, which show the expected increases in modulus when the chains are extended by the filler excluded volume effect, and decreases when the chains are compressed. Unexpected results are obtained, however, when the distribution is narrowed (up-shifted) at the same most-probable value of the chain dimensions as is also shown in Fig. 7 [58]. The narrowing causes the peak defining the most-probable value to shift upward to keep the area under the curve the same, as is required. In this case, the change in the shape of the distribution does indeed cause an increase in the modulus, as shown in Fig. 8. These results are admittedly preliminary, and, therefore, need to be examined further and extended in additional simulations. In any case, these results are consistent with those from other simulations finding increases in modulus even when the chains are compressed, since it demonstrates that the mechanical properties can depend on subtle features of the distribution, beyond merely some average value of the chain dimensions!

3.5. Relevance of cross linking in solution

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 in solution followed by removal of the solvent [63]. This is shown schematically in Fig. 9. Such experiments were initially carried out to obtain elastomers that had fewer entanglements and the success of this approach was supported by the observation that such networks came to elastic equilibrium much more rapidly. They also exhibited stress–strain isotherms in elongation that were closer in form to those expected from the simplest molecular theories of rubberlike elasticity.

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 [63]. 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 [64,65]. The most recent work in this area has focused on the unusually high extensibilities of such elastomers [66–68].

In any case, the present simulations should help elucidate

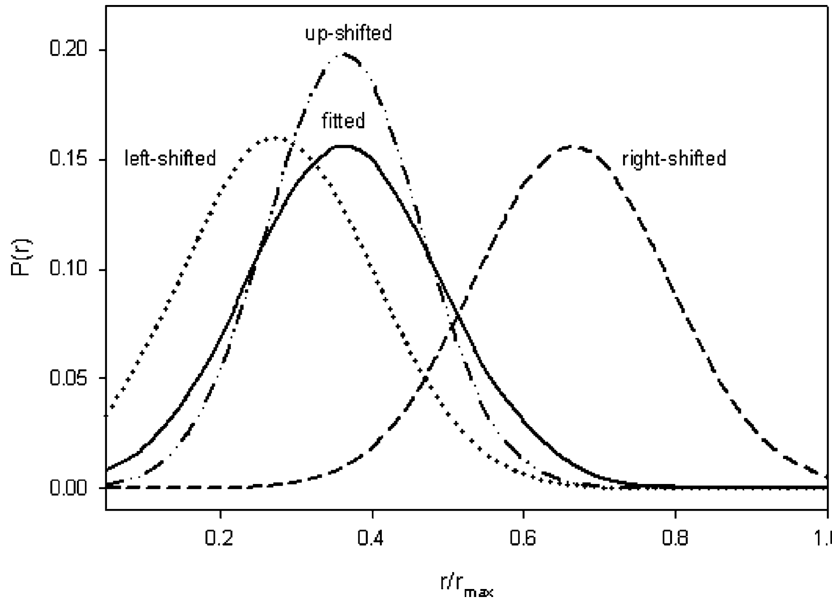

Fig. 7. Arbitrary illustrative shifts in end-to-end distance distributions, to smaller and larger values of r. Also shown is an arbitrary illustrative narrowing of an end-to-end distance distribution, at the same most-probable value of r.

molecular aspects of phenomena in this area of research as well.

3.6. Detailed descriptions of conformational changes during chain extension

An illustration of this application involves the nominal stress for syndiotactic polypropylene at $T=481$ K as a function of elongation for different chain lengths, for a filler radius of 10 Å [40]. The Monte Carlo simulations were performed using recently derived conditional bond probabilities for stereo-regular vinyl chains [36]. The results are shown schematically for chains having either 100 or 200 skeletal bonds in Fig. 10. At the beginning of the elongation, the chains of the two different lengths followed the same linear curve, which corresponds to the elastomeric region. This linearity is consistent with the equation for the deformation of a single chain in which the stress f^* is directly proportional to its end-to-end distance r [69]. Specifically,

$$f^* = \left(\frac{3kT}{\langle r^2\rangle_0}\right) r \qquad (5)$$

where $\langle r^2\rangle_0$ represents the mean-square unperturbed dimension of the chain.

The 'plastic' region appears at lower elongations for chains having 100 skeletal bonds, as compared with those having 200. Chains of 100 bonds require greater stresses to

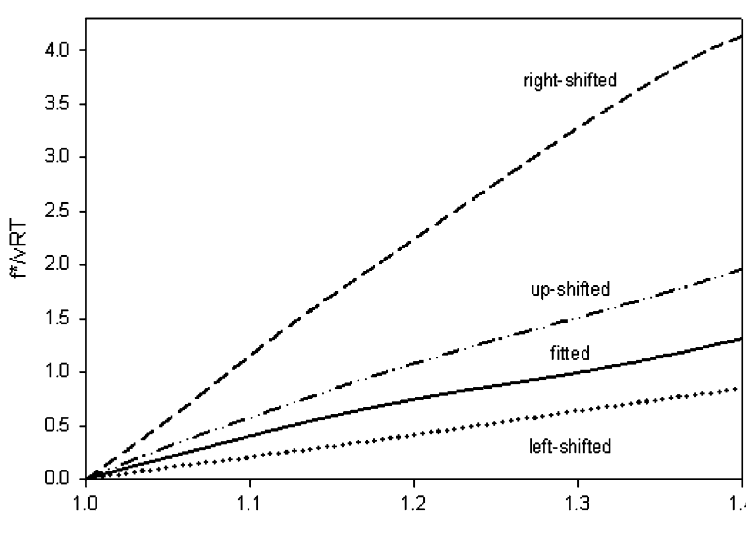

Fig. 8. Normalized stresses calculated for the distribution changes shown in Fig. 7.

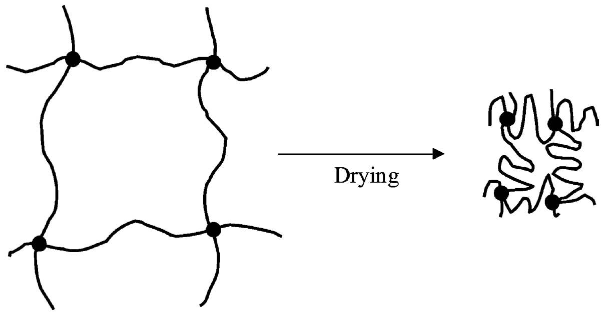

Fig. 9. Forming a 'super-compressed' network by cross linking in solution, followed by drying.

be elongated once this critical point is reached, and this need for higher stresses can be explained in terms of its end-to-end distance distribution [40]. Since the chains of 100 bonds are already more extended than the chains of 200 bonds, the amount of additional elongation they can endure until the elastic region ends is more limited. Once the plastic region is reached, the stress development shows the non-linear character illustrated here, as the elongation is increased.

4. Ellipsoidal particles

4.1. 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 [70] and the long fibers frequently used for this purpose in thermoplastics and thermosets [71]. Oblate (disc-shaped) particles can be considered as analogues of the much studied clay platelets used to reinforce a variety of materials [72–81].

4.1.1. Regular arrangements of prolate ellipsoids

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 [82]. The technique is illustrated schematically in Fig. 11. It is important to note that this approach also orients the axes of the now-elliptical particles, as shown in the middle section of the figure. If desired, the orientation can be removed by dissolving away the host matrix, and then redispersing the particles randomly within another polymer that is subsequently cross linked. This is illustrated in the bottom part of the sketch.

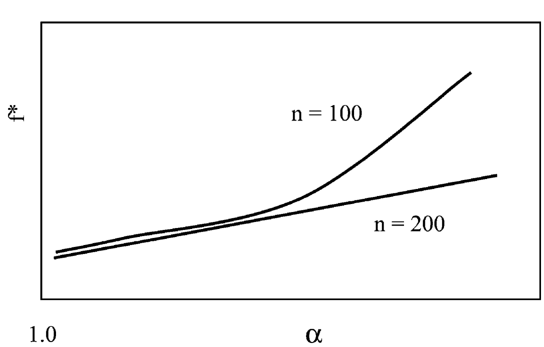

Fig. 10. The nominal stress at $T=481$ K for syndiotactic polypropylene shown as a function of elongation ratio for filler particles having a radius of 10 Å, for two values of the number of skeletal bonds in the chain.

Some relevant simulations are summarized in Fig. 12 [59], which shows the moduli as a function of reciprocal elongation for particles having the specified radius and volume fraction loading. The values of the moduli pertain to directions longitudinal (z) and transverse (x) 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 [82]. Quantitative comparisons are difficult, in part because of the non-uniform stress fields around the particles after the deforming matrix is allowed to retract.

4.1.2. Randomized arrangements of prolate ellipsoids

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. 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.

4.2. Oblate ellipsoids

In spite of their inherent interest, relatively few simulations have been carried out on fillers of this shape.

4.2.1. Regular arrangements

The particles were again placed on a cubic lattice [20], and were oriented in a way consistent with their orientation in PS-PDMS composites that were the subject of an experimental investigation [83]. In general, the network chains tended to adopt more compressed configurations relative to those of prolate particles having equivalent volumes 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

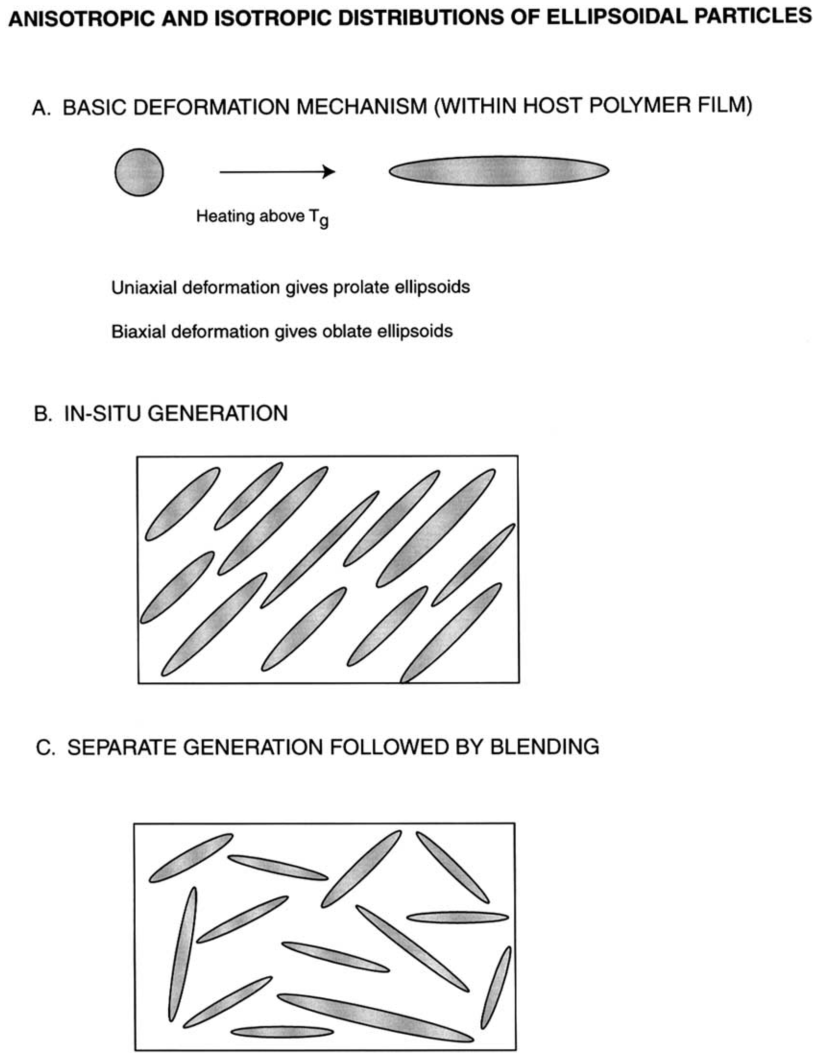

Fig. 11. (A) An originally spherical filler particle being deformed into a prolate (needle-shaped) ellipsoid by stretching a polymer matrix in which it resides. (B) This in situ approach also orients the axes of the deformed particles in the direction of the stretching. (C) This orientation can be removed by dissolving away the film matrix and then redispersing the ellisoidal particles isotropically within another polymer, to reinforce it.

agreement with the corresponding experimental results [83]. 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 [83]. 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.

4.2.2. Randomized arrangements

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 [59].

5. Aggregated particles

5.1. Real systems

The silica or carbon black particles used to reinforce commercial materials are seldom completely dispersed [1–5], as is assumed in the simulations described. As is shown schematically in Fig. 13, the primary particles are generally aggregated into relatively stable aggregates and these are frequently clustered into less stable arrangements called agglomerates.

5.2. Types of aggregates for modeling

Simulations should be carried out on such more highly ordered structures, some limiting forms of which are

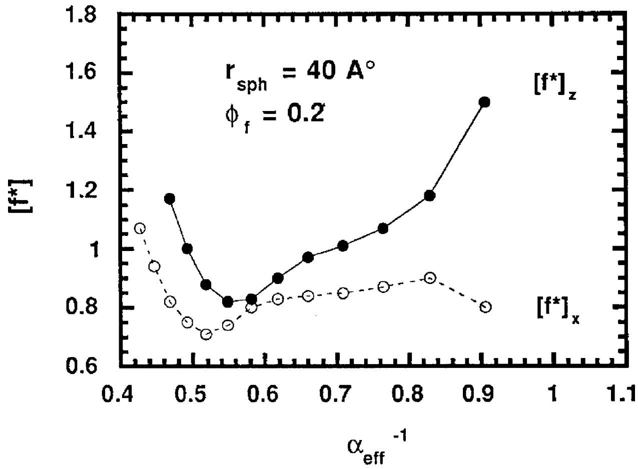

Fig. 12. Mooney–Rivlin representations of simulated elongation isotherms for an elastomer reinforced by prolate filler particles. The subscript z designates values in the direction of the stretching used to generate the ellipsoidal particles, and the subscript x designates values in either of the perpendicular directions. The elongation has been corrected for stain amplification [20].

sketched in Fig. 14 [59]. 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 [1–5].

5.3. 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 [84–89]. 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 contribute to 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.

6. Potential refinements

This excluded volume effect is only one aspect of

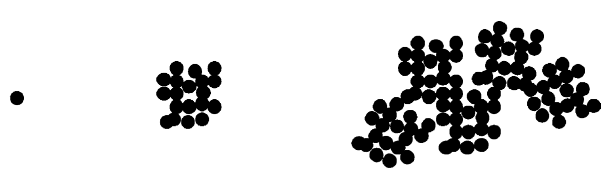

Fig. 13. Sketches of primary particles, aggregates, and agglomerates occurring in fillers such as carbon black and silica.

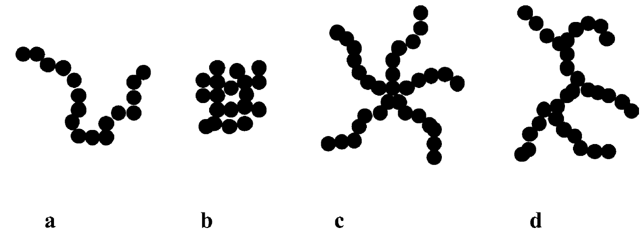

Fig. 14. Four illustrative types of aggregates: a, chainlike, b, globular, c, star-shaped, and d, branched.

elastomer reinforcement [6–12], 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). 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 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.

7. 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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