PACKING AND STRUCTURE IN SYSTEMS CONTAINING ROD-LIKE PARTICLES

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ABSTRACT

A non-discrete Monte Carlo algorithm is used to model the packing of static rods. The results establish that inter-rod contact results solely from rod motion, not from space-filling effects. As the concentration of static rods is increased, clusters of aligned rods form and grow. The effects of rod motion are inferred through thermodynamic analysis. At sufficiently high rod concentrations, rod motion is expected to cause structural coarsening wherein the rods rearrange into larger but fewer clusters. These results should be considered when modeling the structure and mechanical behavior of whisker- and chopped-fiber-reinforced composites.

INTRODUCTION

This paper discusses theory and numerical experiments that address two important engineering questions relevant to the packing of rod-shaped particles in whisker- or chopped-fiber-reinforced ceramic composites:

1) How are the rods arranged spatially within the composite?

2) What is the maximum concentration of rods which can be incorporated into the system?

The model systems described herein are highly idealized and the answers provided are by no means complete. Nevertheless, it is hoped that this paper will at least provide some firmly-based partial answers and allow other investigators to see the remaining questions from a fresh viewpoint.

NUMERICAL ROD-PACKING EXPERIMENTS

We began our investigations by constructing an algorithm to place rods, one at a time, into a two-dimensional matrix. Using this program, we can study the effects of axial ratio and rod concentration on the structural arrangements. We chose to begin with two dimensions mainly because it is simpler to observe the arrangement of rods in a monolayer than in the bulk of a three-dimensional system. Trends observed in two dimensions are expected to reflect trends in three dimensions. We worked with monodisperse systems, i.e., all of the rods in a given experiment have the same length and diameter.

Many numerical studies of rod packing have used a discrete lattice in which the rods are represented as contiguous series of occupied square (two-dimensional) or cubic (three-dimensional) cells [1-5]. Although such lattice models greatly simplify the mathematics, the approach suffers from limited positional and orientational choices for the rods; it also distorts their shape. We have used a non-discrete model so that the position and orientation of the rods are continuously variable and the rods do maintain their true shape. This model also uses the "hard-core" assumption wherein the rods cannot interpenetrate. This leads to far more realistic representations of the structural arrangements than do "soft-core" models which allow rods to cross through one another.

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The algorithm for placing the rods is shown in Figure 1. A random number generator chooses the angular orientation of the j^{th} rod. Next, candidate X and Y positional coordinates are chosen randomly. The candidate position is checked to see if it results in interpenetration with existing rods. If interpenetration is detected, a new candidate position is chosen while the original orientation is maintained. The process is continued until an appropriate vacancy for placing the rod is found. The j^{th} rod is then placed in the matrix and the process continues with the choice of an orientation for the $(j+1)^{th}$ rod. The rods are static; once a rod is placed, it is not allowed to move. If rods are placed such that they overlap the boundary of the square lattice, they "wrap around" and penetrate its opposite edge. The program keeps track of the number of tries it takes to place a rod successfully. The significance of this feature is discussed elsewhere [6,7].

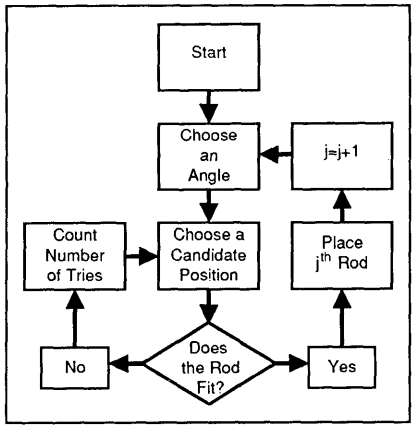

Figure 1. Monte Carlo algorithm for placing rods.

RESULTS AND DISCUSSION OF NUMERICAL ROD PACKING EXPERIMENTS

Figure 2 shows a series of rod configurations with increasing concentration, which were built up during one run of the algorithm described above. Although some rods appear to touch in the figure, these instances are entirely the result of plotter limitations. Since double precision numbers are used to describe the boundaries of each rod, the chance of any of the rods touching without interpenetrating is vanishingly small.

We digress here to discuss some implications of this observation. If our system were set up to simulate rod movement such as random vibration, streaming, stirring, or matrix contraction (due to filtration consolidation, settling or sintering), we would observe many cases where rods touch. Since any real physical experiment involves some degree of rod movement, *all* physical systems exhibit rod connectivity which increases with concentration. Such particle connectivity is commonly modelled by numerical percolation studies, using Monte Carlo algorithms based on discrete square or cubic lattices, as mentioned above. In these discrete models, there is a finite probability of adjacent rods touching without interpenetrating, even when no rod motion is allowed. Therefore, the degree of connectivity in a discrete lattice is, to some extent, an artifact of the choice to use a discrete lattice. By way of example, consider the pair of rods in a discrete, square lattice depicted in Figure 3a. If a rod placement algorithm similar to that described above is used, there is a finite probability of successfully placing a third rod that touches both of the existing rods. Such placement

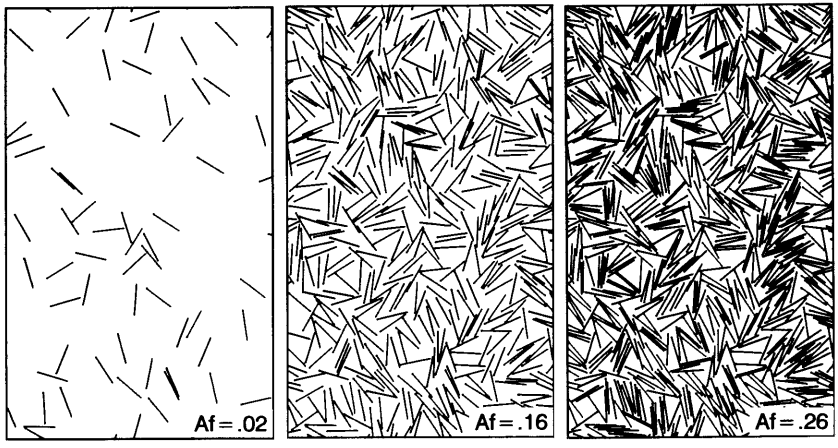

Figure 2. Three stages during the filling of the non-discrete lattice using the algorithm shown in Figure 1. Axial ratio is 25. Area fraction (Af) covered by rods ranges from 0.02 to 0.26.

would result in connectivity or percolation across the group. However, if the existing rods had been placed in a *non-discrete* lattice, as shown in Figure 3b, the probability of similarly placing a third rod in contact would be vanishingly small. The issue that emerges is that *space-filling constraints alone do not result in percolation in realistic hard-core models.* Percolation in a real system is the result of particle motion. Percolation in a discrete lattice model is an artifact of the model.

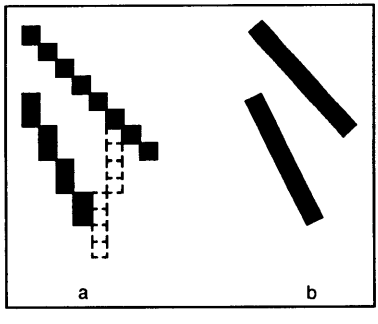

Figure 3. Rods with an axial ratio of 8 represented in a) a discrete lattice, and b) a non-discrete lattice. In the discrete lattice, there is a finite probability that a third rod can be placed so that it touches both existing rods (example shown in broken lines). The chance of this happening in the non-discrete lattice is vanishingly low.

While we have not yet incorporated rod motion into our computer model, we can illustrate the point made above with a simple physical experiment. Wooden sticks were scattered at random onto a level substrate and gently vibrated until all lay flat on the surface. The rods that were originally stacked on top of others tended to "push" their way onto the surface, causing lateral displacement of rods that were already laying flat. Figure 4a is a picture of these wooden sticks (axial ratio of 25) after vibration. Many instances of rods touching can be seen and there are several instances of rods laying close together and parallel. The resulting configuration is close to, if not at, the percolation threshold. Figure 4b was generated by the non-discrete Monte Carlo algorithm for rods with the same axial ratio and

at the same concentration (area fraction of 0.263). Although some of the lines appear to touch, we stress again that these instances are due to plotter limitations; none of the computer-generated rods are mathematically connected. The configuration of the wooden sticks can be viewed as a slightly "annealed" version of the computer-generated structure, with limited movement of the sticks resulting in extensive connectivity. A static, discrete-lattice percolation model might yet predict the degree of connectivity in these sticks. However, agreement would be merely fortuitous.

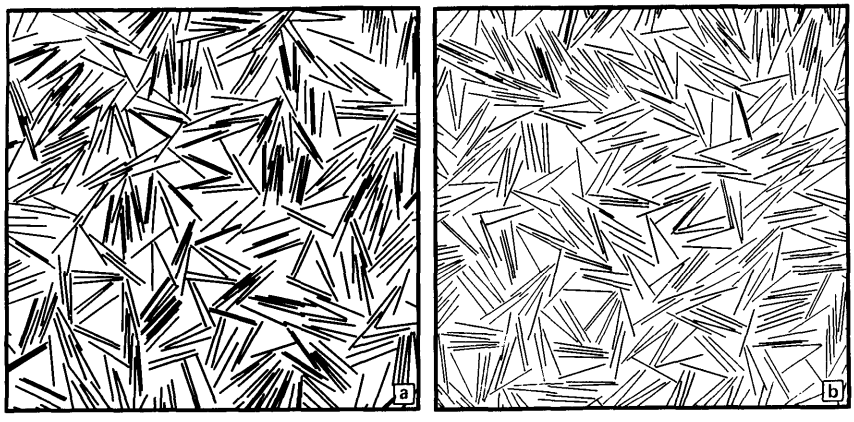

Figure 4. a) Photo of wooden sticks with an axial ratio of 25 at an area fraction of 0.26. Sticks were vibrated until they lay flat on a substrate. Extensive rod connectivity is evident. b) Plot of non-discrete Monte Carlo-generated rod configuration for rods of the same axial ratio and concentration as the sticks. None of the rods actually touch, although plotter limitations result in instances of apparent connectivity.

In addition to the problem of artificially introducing connectivity, models of rods based on discrete lattices lead to another noteworthy difficulty. Rods represented by series of occupied cells can cross through one another without their occupied cells overlapping (i.e., without interpenetrating), as shown in Figure 5. If not specifically prevented within the software, this problem will lead to the construction of physically untenable structures, even when the investigator believes that he or she has implemented the "hard-core" restriction by disallowing overlapping of occupied cells.

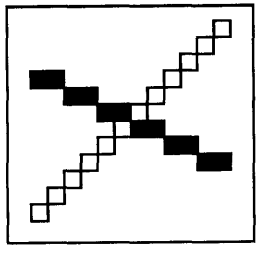

Figure 5. Example of how rods in a discrete lattice can cross without any of their occupied cells overlapping.

Returning to Figure 2 and our discussion of the non-discrete model results, we note that *clusters* of similarly aligned rods are evident. As rods are added to the lattice, both the number of clusters and the average number of rods per cluster increase. We have attempted to characterize the growth of these clusters by setting up rules to determine cluster membership. We say that rod A is clustered to rod B if the following three conditions are met:

1) the angle between them is less than 15°;

2) the distance between their midpoints is less than one half of a rod length; and

3) the distance from the midpoint of either rod to the long axis of the other, measured along a direction at 90° to the long axis of the first rod, is less than one fifth of a rod length.

(These conditions are stated exactly for infinitely thin rods; the rules are actually somewhat more complicated for rods with finite axial ratios.) To propagate the clustering relationship, we say: if A is clustered to B and B is clustered to C, then A is also clustered to C as long as the angle between A and C is less than 15°. The rules are somewhat arbitrary at this point, but result in automatic choice of clusters which at least appear reasonable to the eye. The main point here is that the rules can be applied to obtain an objective *relative* measure of the degree of clustering in various rod configurations. Figure 6 shows the results of cluster membership measurements on the non-discrete Monte Carlo configurations. It is evident that, as the rod concentration increases, the cluster size of the average rod increases smoothly and ever more steeply. Furthermore, at a given rod concentration, cluster size is larger for the longer axial ratios. What causes the formation and growth of clusters in the absence of rod motion? The few small clusters appearing at low concentration are due to chance placement. The clusters that appear at high concentrations arise due to space-filling constraints. Simply put: the majority of the available vacant positions for new rods are next to, and aligned with respect to, existing rods; therefore, the most probable way to squeeze in more rods is by adding to the clusters.

Thus we have a tool to observe rod structures under very idealized conditions, with no rod motion. As stated above, these conditions will never be observed in a physical experiment. However, the results clearly demonstrate the structural effects of space-filling constraints and thereby provide a starting or limiting condition for observing the effects of rod motion. We have already seen in Figure 4 that limited rod motion can cause

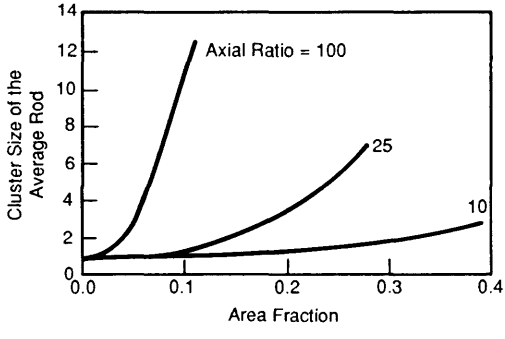

Figure 6. Data illustrating the growth of rod clusters as the rod concentration is increased in the static, non-discrete, Monte Carlo-generated configurations.

extensive rod contact. The effects of motion induced by processing operations have been studied both theoretically and empirically, using physical experiments. For example, the alignment of chopped fibers as a result of shear during extrusion or injection molding has been discussed by several investigators [8-10]. Also, the preferential orientation of fibers perpendicular to the axis of compaction has been noted in composites that were consolidated by colloidal filtration, settling or uniaxial pressing [11,12]. Other investigators [13] and our studies show that short fibers can be made to form into tightly aligned rows by the influence of sonic or ultrasonic vibration (see Figure 7). These examples all address the results of specialized, highly directed motion. Though they are extremely important technologically, they are not easily described by a single, general theory. Each case must be handled by using a model of rod motion tailored to the specific processing operation. For example, a good way to model uniaxial consolidation might be to begin with a configuration formed by non-discrete Monte Carlo space-filling and then mathematically compact the system along the axis. It would be necessary to select rules to decide when a rod becomes fixed (e.g., rod translates until it touches another rod in one spot, then rotates until it touches in a second spot, whereupon it is fixed). The results of such models might be useful, but their accuracy in modeling physical behavior will always depend upon the investigator's skill in selecting amongst all possible assumptions regarding the positions at which rods become fixed. On the other hand, certain aspects of the structural effects of *completely random rod motion* are understandable in terms of thermodynamics. The thermodynamic approach, which we have adapted from theory that was developed for molecular rods, involves only two, clearly defined assumptions: that the motion of the rods is random (thermal agitation) and that there are no attractive or repulsive forces affecting the rods. For macroscopic rods (sticks) or microscopic rods (chopped fibers or whiskers), the assumption of completely random motion within a composite certainly represents a considerable simplification of reality. Nevertheless, the results of the model have been found to explain some physical phenomena which are observed in systems containing rods.

THERMODYNAMIC ANALYSIS OF RODS

Additional details of our thermodynamic approach are described elsewhere [6,7]. In this paper, we will confine discussion to the main concepts involved in the calculations, and move on to present the results.

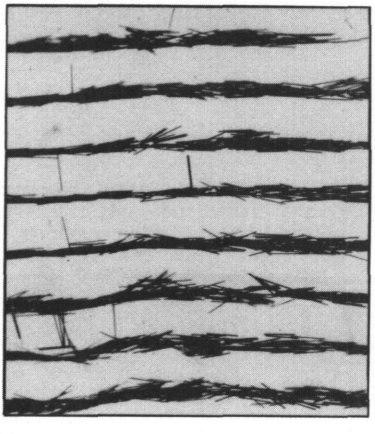

Figure 7. Optical micrograph of chopped graphite fibers (10 μm diameter; 300 μm long) which were aligned into rows by the application of sonic vibration.

Under certain conditions, it is reasonable to expect that the behavior of large rods will be exactly like that of rigid, rod-like molecules. These conditions, as mentioned above, include the assumption that the rods move randomly, as do thermally excited molecules. Brownian motion of microscopic rods suspended in low-viscosity fluids is analogous to molecular agitation. The other assumption, that there are no attractive nor repulsive forces affecting the rods, is less restrictive than it may at first seem. Attractive forces between the fibers or whiskers and between the rods and the matrix particles in a ceramic composite are normally avoided during processing by implementation of slight electrostatic and/or steric repulsion. This is just good processing practice. It turns out that the effects of slight *repulsive* forces on the thermodynamic results are minor [14,15]. Therefore, the assumption that *no* forces affect the rods will not itself lead to unreasonable predictions. On the other hand, the effect of gravity (or centrifugal force), resulting in uniaxial compaction of large-particle systems, is analogous to directed attraction between the rods and, as such, is not implemented at present in our thermodynamic approach. To clarify these assumptions, it is useful to point out that a *stable* suspension of microscopic whiskers undergoing Brownian motion should be thermodynamically analogous to an *athermal* (no forces) system of rigid molecular rods. Under these athermal conditions, the behavior of the rods is determined solely by their *shape* (and concentration), and so their *size* should not affect the results. Randomly excited fir logs confined to a large vessel floating in space should behave like an athermal solution of molecular rods with the same axial ratio.

Our thermodynamic approach is directed by the well-accepted, athermal, three-dimensional model of Flory and Ronca [16]. We adapted their approach to a two-dimensional system and, whereas they used a discrete lattice model, we used our non-discrete model [6,7]. In thermodynamic terms, the athermal assumption means that the free energy of the system of rods is determined solely by *entropy*. Due to their asymmetric shape, the rods have a total entropy that is composed of two terms, one for *translational* (positional) entropy and one for *orientational* entropy. This treatment results in the phase diagram shown in Figure 8. To interpret the phase diagram, consider a system of rods with an axial ratio of 25. At low concentrations, the rods are randomly oriented. Minimum free energy is established by maximization of

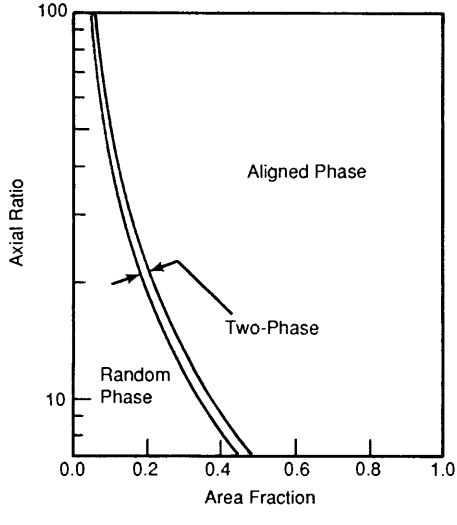

Figure 8. Phase diagram for rods based on the non-discrete Monte Carlo studies [6,7].

both positional and orientational entropy. As rods are added to the system, we reach a critical concentration, the lower phase boundary (0.16), at which an aligned phase appears. At a somewhat higher concentration, the upper phase boundary (0.18), the random phase disappears and all the rods belong to the aligned phase. It is the trade-off between positional and orientational entropy which results in the formation of the aligned phase at high rod concentrations. At high concentrations, the positional freedom of the rods is restricted. If the rods align, sacrificing orientational freedom, more than enough positional entropy is gained back to make up for the lost orientational entropy. It is simply easier to fit more rods into the system when they are aligned. As with any phase transformation governed by thermodynamics, the appearance of the aligned phase above the critical concentration will be spontaneous given that the rods experience sufficient agitation. Figure 9 is a plot showing rods in an aligned phase. Notice that the rods are not perfectly aligned, but are characterized by an average angle of disorientation from the preferred domain axis. Thus, the rods retain a small degree of orientational freedom, even in the aligned phase. As the concentration of rods is increased within the aligned phase field (above 0.18 for an axial ratio of 25), the average angle of disorientation from the preferred domain axis decreases.

This thermodynamic analysis predicts how much of each phase will be present for a given concentration of rods at equilibrium. However, it does not give us a complete picture of the structure. For example, for a system containing only aligned phase, the analysis does not predict the expected average size of the domains. This is because the analysis does not take into account the extra entropy which could be gained by having narrow regions of disorder at the domain boundaries, i.e., what one could call "grain-boundary entropy". When both the aligned and the random phase are present at equilibrium (within the narrow, two-phase region on the phase diagram), the analysis again tells us nothing about domain sizes for either phase. In spite of these limitations, however, the predictions based on the phase diagram are illuminating, as we shall see in the next section.

IMPLICATIONS OF THE PHASE DIAGRAM FOR COMPOSITE ENGINEERING

The phase diagram predicts that, given sufficient random agitation, rods above the critical concentration at the lower phase boundary will rearrange, forming an aligned phase. Such spontaneous phase transitions are well documented in liquid crystalline systems [17-19]. In such systems of molecular rods, thermal agitation of the molecules is sufficient to bring about their rearrangement. Spontaneous formation of aligned clusters has

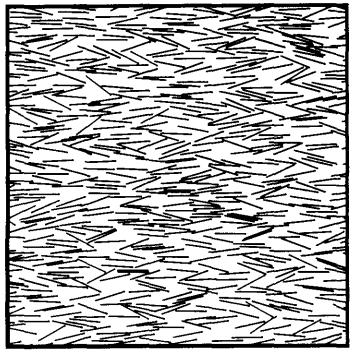

Figure 9. Example of an aligned phase generated by the non-discrete Monte Carlo algorithm [6,7]. Axial ratio is 25, area fraction is 0.19.

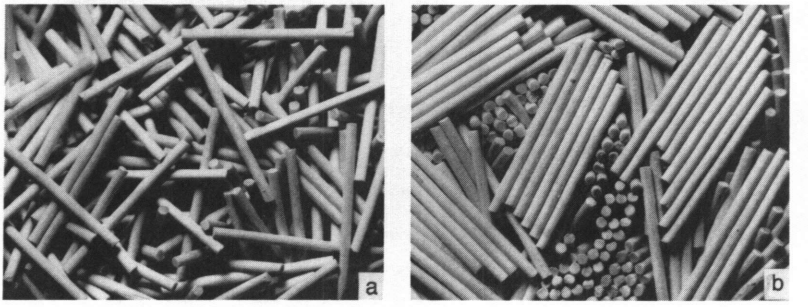

Figure 10. a) Wooden sticks with an axial ratio of 25 were dumped randomly into a beaker. b) During mechanical vibration of the beaker, the rods formed into tightly aligned clusters.

also been observed in suspensions of microscopic rods such as tobacco mosaic virus [20] and colloidal gold particles [21]. In these systems, Brownian motion is sufficient to cause rod rearrangement. Can we expect to observe spontaneous clustering during the processing of slurries for composite systems? Here, the rods are often too large and the intervening matrix particles provide too much kinetic hindrance for Brownian motion to be effective. The motion induced by common processing operations such as high-shear mixing, milling and sonication cannot be characterized as truly random. Yet, our experiments with vibration of macroscopic rods demonstrate spontaneous clustering. Figure 10a is a picture of wooden sticks dumped randomly into a beaker. The view is through the bottom of the beaker. Mechanical vibration (60 Hz) was applied to the bottom of the beaker for several minutes. During this process, the distinct, tightly-aligned clusters seen in Figure 10b were formed and the bulk density of the compact increased. Although the kinetic hindrance of matrix particles was not present, and although the role of gravitational compression was undoubtedly important, this experiment demonstrates that very large rods can spontaneously rearrange and cluster due to the type of motion commonly imposed during composite processing operations.

We have already seen that, as the rod concentration is increased, space-filling constraints result in the formation of clusters, even in the absence of rod motion (Figure 6). We believe that, for rod configurations *at fixed concentration* above the lower phase boundary, the introduction of motion will cause the "space-filling-nucleated" clusters to grow. That is, motion will cause structural coarsening wherein the rods rearrange into larger but fewer clusters. The Monte Carlo-generated rod configurations, used for the measurements of cluster size in Figure 6, contained randomly oriented rods. The phase diagram predicts that, above the critical concentration at the lower phase boundary, these randomly oriented configurations will be unstable with respect to the aligned phase. Careful comparison of Figure 6 with the phase diagram, Figure 8, shows that, above a cluster-membership number of about two, the random configurations described in Figure 6 should be unstable. Therefore, we believe that the lines in Figure 6 represent *minimum cluster size* for the given concentration; the clusters are expected to grow if the rods are set in motion. Figure 11 illustrates the starting and end-point structures for a phase transition which begins with an unstable random configuration and ends with a stable aligned phase containing the same concentration of rods. Free energy curves are shown for each of these configurations. As discussed above, we would expect that the inclusion of a grain-boundary entropy term would actually predict that the minimum free

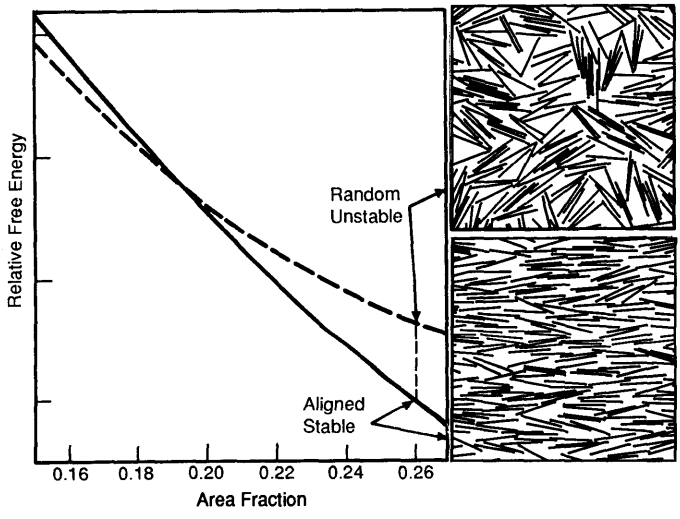

Figure 11. Monte Carlo-generated representations of an unstable random phase (above) and the stable aligned phase predicted for the rod area fraction of 0.26. Free energy curves for the two phases are shown as a function of rod concentration. The random phase has lower free energy at area fractions to the left of the point where the two curves intersect.

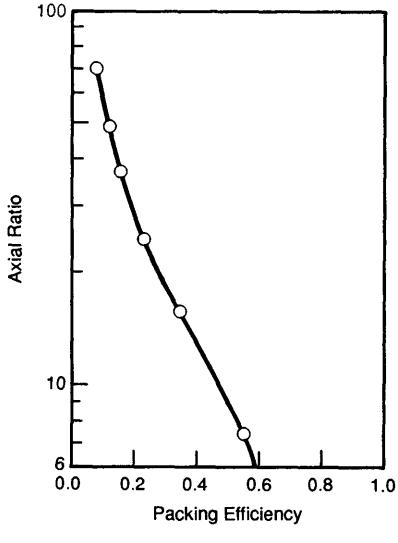

Figure 12. Proposed "maximum packing fraction" data from Milewski's three-dimensional experiments with wooden sticks and glass rods [22].

energy would be reached before the structure had coalesced into a single, large domain.

To summarize our answer to the first question at the beginning of this paper: the thermodynamic analysis, combined with the space-filling observations, set limits on the structures possible at any given rod concentration. The degree of domain coarsening experienced in a real composite will obviously depend upon such factors as the effective viscosity imposed by the matrix (particles, solvents, surfactants) and the type, magnitude and duration of motion imposed during processing.

The possible effects of rod clustering at high concentration have not been taken into account by mechanical modelers. Mechanical models for chopped fiber- or whisker-reinforced composites generally assume a scenario in which the rods are independently as well as randomly oriented. Rods within clusters should not always be considered as independent mechanical entities. For example, a crack could easily propagate along the preferred domain axis of a cluster. Further propagation would be hindered by advance of the crack into a cluster with a different orientation. Therefore, for a given stress, the unanticipated presence of extended clusters may allow some cracks to propagate further than expected. Also, during the consolidation or sintering of a system containing clusters, the parallel rods within a cluster could be easily forced together in directions perpendicular to the domain axis.

Perhaps, by now, the answer to the second question at the beginning of this paper is obvious to the reader: the concentration of rods which can be introduced into a composite is limited by kinetics. There are no absolute "maximum packing fractions", as set forth by Milewski [22]. These limits are artifacts of the degree of rod motion introduced in the physical experiments. Figure 12 shows Milewski's data, which were obtained by briefly tumbling wooden or glass rods, dumping them into cylindrical containers and measuring the bulk density attained by the random compacts. We feel that his trend may be close to the lower phase boundary for three-dimensional systems, although we cannot verify this because we have not yet extended our Monte Carlo analysis into three dimensions.

CONCLUSIONS

Though we have used assumptions which are highly idealized, and though we have left many questions unanswered, we feel that we have established the following points which are relevant to composite engineering:

1) Accurate, non-discrete models of rod packing demonstrate that rod contact and percolation in physical systems are due solely to rod motion. Although rod shape and concentration are undoubtedly important variables, the specific type, magnitude, and duration of motion induced in physical experiments must be regarded as influencing the degree of contact between the rods.

2) Whiskers or chopped fibers will inevitably form clusters due to space-filling constraints, even when no inter-rod attractive forces are present, and even in the absence of motion.

3) Above the critical concentration, predicted by the phase diagram, the application of common processing operations such as high-shear mixing, milling, or sonication will cause the clusters to grow.

4) So-called "maximum packing fractions", established by physical experiments, represent kinetic barriers which will be overcome to an extent dependent upon the kinetic hindrance of the matrix and the type, magnitude, and duration of rod motion imposed during processing.

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REFERENCES

1. E.A. Di Marzio, J. Chem. Phys. 35, 658 (1961).
2. F.L. McCrackin, J. Chem. Phys. 69(12), 5419 (1978).
3. D.Y. Yoon and A. Baumgartner, Macromolecules, 17(12), 2864 (1984).
4. J. Boissonade, F. Barreau, and F. Carmona, J. Phys.A, 16, 2777 (1983).
5. E.A. Holm and M.J. Cima, J. Am. Ceram. Soc., 72(2), 303 (1989).
6. L.A. Chick, C. Viney, and I.A. Aksay, in Rigid Rod Polymers, edited by W.W. Adams, R.K. Eby and D.E. McLemore (Mater. Res. Soc., Pittsburgh, PA) in press.
7. L.A. Chick, C. Viney, and I.A. Aksay, in Fourth International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, edited by D.R. Uhlmann, M.C. Weinberg, and S.H. Risbud (Wiley Interscience, New York) in press.
8. H. Menendez and J.L. White, Pol. Eng. and Sci, 24(13), 1051 (1984).
9. M. Vincent and J.F. Agassant, Rheol. Acta, 24, 603 (1985).
10. H.T. Kau, Pol. Comp., 8(2), 83 (1987).
11. T.T. Meek, R.D. Blake, and J.J. Petrovic, Caram. Eng. Sci. Proc., 8(7-8), 861 (1987).
12. T.N. Tiegs and P.F. Becher, Ceram. Bull., 66(2), 339 (1987).
13. J.L. Dion, J.J. Garceau, and J.C. Morissette, Pulp Pap. Can., 88(3), 87 (1987).
14. P.J. Flory, Proc. Roy. Soc. London A, 234, 73 (1956).
15. M. Warner and P.J. Flory, J. Chem. Phys. 73(12), 6327 (1980).
16. P.J. Flory and G. Ronca, Mol. Cryst. Liq. Cryst. 54, 289 (1979).
17. P.J. Flory, Adv. in Polymer Sci. 59, 1 (1984).
18. S.P. Papkov, Adv. in Polymer Sci. 59, 75 (1984).
19. C. Viney, D.Y. Yoon, B. Reck and H. Ringsdorf, Macromolecules (1989) in press.
20. J.D. Bernal and I. Fankuchen, J. Gen. Physiol. 25, 111 (1942).
21. S. Hachisu, J. Colloid and Interface Sci., 55, 499 (1976).
22. J.W. Milewski, PhD Dissertation, Rutgers Univ. (1973).