

STRUCTURE AND PROPERTIES OF HETEROPHASE SOLIDS

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Synopsis—A classification of the wide variety of solids according to physical, structural and chemical characteristics shows the category of heterophase solids to be the largest group of natural and artificial substances. Most manufacturing and manufactured materials fall in this category.

The structure of such materials can be described by the shape, size, concentration, orientation and topology of the constituent phases. Statistical methods—in particular, geometric probability—sometimes supplemented by certain physical or topological restrictions, provide adequate tools for the description of naturally grown or artificially mixed systems.

Mechanical modulus properties as well as thermal and electrical properties can be treated in a fairly general manner, based either on field distortion of one phase by the presence of another phase or by means of phase models that give upper and lower limits for the property.

The problem of strength properties can be seen in terms of fracture mechanisms or as a statistical one, in which case extreme value theory provides a suitable method.

Introduction

THE SOLID state of matter presents itself in a much larger number and variety of phenomena than are encountered in the gaseous and liquid states. The reason for this is the high degree of compaction or density of packing compared with those of gases and liquids. One result of different packing densities is the extent to which individual properties of atoms or molecules (or other building units) influence the macroscopic properties of the substance that they build up. Certain properties of gases at low pressures are practically independent of the nature of their constituent particles. Physical properties of solids, on the other hand, are largely determined by those of the constituent particles and, in particular, by the interaction between them.

A general consequence of increasing interaction is the formation of

surfaces, hence the ability to form isolated aggregates or bodies over a wide range of sizes, which can in turn join to form higher aggregates and so forth. Gases lack completely this ability and fill the available space uniformly. Liquids possess it to a certain degree. They form surfaces and separated, identifiable aggregates (for example, in emulsions or mists), but it is the solid state that derives its broad range of phenomena and material properties to a large extent from the ability to form bodies of almost any size and complexity.

The number of possibilities is very large indeed for a macroscopic piece of solid material to be composed of smaller units, each in turn consisting of microscopic and submicroscopic aggregates of various, but specific orders of magnitude. Paper is as good an example as any, the scale of its constituent units descending from fibres to cell wall layers, then via fibrils to microfibrils and, finally, to cellulose molecule chains. A similar scale can be found in most solids. Since most chemical species, natural or man-made, exist in the solid state, a large number of all the possible structural designs is in fact realised. This is why we observe such a variety of phenomena and properties in solids.

It is also the reason for the lack of a comprehensive theory and indeed phenomenology of the solid state comparable to the well-developed kinetic gas theory. There have been attempts to formulate theories of phenomena in highly ordered crystal lattices. A recent publication is the book by Sachs,⁽¹⁾ whose approach is essentially based on symmetry properties of lattices and electron configurations of the constituent atoms. An earlier publication by Eucken⁽²⁾ approaches the problem from several angles—thermodynamics, electronics, theory of lattice order—and covers a wide range of phenomenological material, although it also is restricted to crystal lattices of perfect or reduced order. The same is true for most of the literature on general solid state physics.

For detailed information on phenomena in and properties of aggregates, one has to turn to the literature on specific materials of technological interest such as metals, ceramics and plastics.

There is also the glassy state of matter believed to be caused by a slow rate of crystallisation because of high viscosity (compared with the rate of cooling) at temperatures when the solid phase is coexistent with the liquid phase.⁽³⁾ The result is a material with only short-range order as in liquids, but with the rigidity and strength of solids.

The general conclusion is that there seems to be at present no way of formulating basic concepts from which the behaviour of solids in their various forms and appearances can be derived and understood. Yet one can classify and select one class of particular interest for further discussion and this will now be attempted.

Classification

DEPENDING on the viewing angle, there are several ways of classifying solids. The following three aspects are each sufficiently general to allow clear demarcation and, at the same time, sufficiently different to define geometric loci for classes with characteristically different properties.

1. The *physical* aspect considers the atomic or molecular constituents and classifies solids according to the bonding forces between them, which are—

- (a) The ionic bond between different atomic species from opposite ends of the periodic table. The bond is strong, non-saturable and non-directional, produced by a central force (electrostatic).
- (b) The valency bond between equal or different atoms is of widely varying strength: it is directional and saturable.
- (c) The Van der Waals' bond can be formed between equal or different atoms. It is weak and caused by a non-saturable and non-directional central force that originates from permanent or induced dipoles.
- (d) The metallic bond is created by the free or almost free movement of valency electrons of the constituent atoms. It is non-saturable and not established by a central force. Its strength is of the order and variation of the valency bond.

2. The *structural* aspect considers the size and arrangement of constituent units relevant for typical properties of the solid. It is a more technological classification of manufactured or manufacturing materials rather than of physical species of matter. It differentiates between (a) homophase and (b) heterophase materials.

The term phase is in this context used in a descriptive rather than in the thermodynamic sense. It denotes a region of uniform properties, large enough to be considered as a continuum and surrounded or bounded by a surface or an interface with different properties. The phases can be either continuous or disperse.

3. The *chemical* aspect considers the chemical species of which the solid consists. There are—(a) pure and (b) composite materials or phases.

Most manufactured and natural materials are heterophase solids, pure or composite, often with different types of bond within and between their constituent phases. Unfortunately, it is impossible to break down this large category of materials into smaller classes without introducing arbitrary decisions. They concern the scale and the objective that we have in mind. Two examples may illustrate this.

A fibre-reinforced metal is obviously a heterophase material. Isolated parallel fibres, forming a disperse phase, are embedded in a matrix of metal, forming another phase. If we compare properties of this material with those of the unreinforced metal, the metal phase can be considered as continuous.

If we study the properties of the material by itself, however, we would have to take into account the polycrystalline structure of the metal phase, which would then have to be considered as discontinuous with interfaces between the crystallites.

Paper is another heterophase material. Highly porous air filter paper made of cellulose can, in filtering, be considered as two-phase with both cellulose and air forming continuous phases. In its mechanical strength, however, the cellulose phase itself is heterophase, consisting of individual fibres that could be called continuous structural regions. If the oil or water absorbency of such a paper is to be studied, the fibres themselves would add to the observed phenomena the effect of their own heterophase structure.

It is therefore useful, if the structure and properties of heterophase materials are discussed, to bear in mind the objective of the discussion and the scale to which it refers. Much unnecessary controversy can be avoided in this way.

Structure of heterophase materials

Most people will probably agree with Smith⁽⁴⁾ when he states that structure is among the most basic attributes of matter that one can apprehend. 'It is structure that distinguishes between a cornfield and a cake' and it is a change in structure that turns a tree into sheets of paper.

The structure of a heterophase material is described by three mutually independent quantities—the shape, the size and the concentration of the phases. All three quantities have distributions. Often related to them are two more quantities necessary for the description of structure—the orientation and the topology of the phases. These five quantities characterise all phases, whether they are disperse or continuous.*

The structure of the fibre phase in paper, for example, is described by the shape, dimensions and concentration of the fibres and by their distributions. The shape can give rise to orientation and the topological feature is that the fibres are not isolated, but cross and contact each other.

Similarly, the structure of the air phase in a sintered metal is described by the shape, dimensions and number of the channels, also by whether or not the channels have a preferential direction (orientation) and whether or not they are interconnected (topology).

Experimental methods to determine the phase structure are usually based on cross-sectioning and scanning and are widely used by metallographers and mineralogists. The volume fraction of one phase can be found very simply by inspecting a two-dimensional cross-section. Regions occupied by the phase appear as areas and the volume fraction of the phase is given in good approximation either by the fractional area covered by the phase regions or by the

* This system was first used by Holliday⁽⁵⁾ to describe the geometry of disperse phases

fractional length of a scanning line that passes through the phase regions. Several cross-sections have to be scanned if the material is anisotropic—see Underwood.⁽⁶⁾

Smith & Guttman derived a simple expression to find the surface area per unit volume of a phase, a structural parameter of some importance for many physical properties.⁽⁷⁾ It reads $S/V=2N/L$, where S and V are surface and volume of the phase, N is the number of intersections with phase boundaries made by a scanning line in the plane of a cross-section of which the length L traverses the phase regions. The expression is independent of the shape of the phase or phase regions.

The phase dimensions can be obtained by examining cross-sections, only if assumptions are made about the shape of the phase regions. Fullman⁽⁸⁾ has derived for a number of geometrical shapes expressions to calculate three-dimensional structural quantities by scanning cross-sections. Uniform and varying sizes were considered. For rods of uniform size, to quote one example, he finds the following expressions for their radius r and length l —

$$r = N_L/\pi N_A \quad \text{and} \quad l = 2N_A/N_V$$

where N_L and N_A are the number of phase regions per unit length and area covered by the phase of a random line or plane, respectively; N_V is the number of phase regions per unit phase volume.

All scanning methods are based on the application of geometric probability. Applied to paper, they provide expressions for determining a number of structural features of a sheet such as the number of fibres in the sheet, their length density and orientation, the mean free fibre length and others, some of which are given elsewhere.⁽⁹⁾ The underlying concept of randomness is thus seen to be a universal key to structural approaches not only to paper, but to heterophase materials in general. This has some significant consequences that will be discussed later. Before this, we consider the two main generating principles for random structures in heterophase materials: natural growth and artificial mixing.

Natural growth of isolated particles such as crystals in a liquid medium is controlled by physical as well as geometric factors. The physical principle is that of minimising the energy of the system. A characteristic feature is the distinction between volume and surface energy. [A non-directional, non-saturable bonding force (such as in Van der Waals' and metallic bonds) should always lead to the hexagonal closest packing. In fact, most substances with these types of bond, crystallise in the cubic (face-centred) closest packing, because the surface energy of the initial nucleus is lower in this case.⁽²⁾] The shape of the particle is controlled by the directional growth rates, which in turn are restricted by the equilibrium between the rate of energy loss (owing

to increase in volume) and the rate of energy gain (owing to the increase in surface).⁽¹⁰⁾ Local disturbances can lead to branching and subsequent infilling. The final size is limited by exhaustion of the surrounding medium. The final shape is controlled by geometric factors such as steric hindrances and relative atomic radii, but more fundamentally by topological factors, especially symmetry conditions of lattices. The prediction of the 230 possible crystal structures, all found in nature, was one of the finest successes of group theory.

In most practical cases, however, particles do not grow in isolation, but impinge on each other. Their final sizes and shapes are therefore additionally controlled by the presence of other particles. Impingement shapes and structures are a fairly recent subject of study.⁽⁴⁾

In short, such structures are largely determined by the original spacing of nuclei and their relative growth rates. As shown by Meijering,⁽¹¹⁾ the distribution of shapes of polyhedra grown by random nucleation is similar to that obtained by subdividing space by random planes. The average number of faces per polyhedron was found to be 15.54 and the average number of sides per face (polygon) was 5.23. The distribution of particle lengths has the shape of an unsymmetric modified error function. Coxeter⁽¹²⁾ used elementary topology to describe the structure of a 'statistical honeycomb'. His result was that space-filling structures consist of polyhedra with an average of 13.56 faces, each having an average of 5.115 sides or vertices. These values agree well with experimental results obtained by Matzke,⁽¹³⁾ who compressed lead shot until all interstices were eliminated and examined the shapes thus produced. It may be mentioned that Bernal⁽¹⁴⁾ carried out similar experiments and used Meijering's arguments in an article on the structure of liquids.

In most real cases of growing heterophase, in particular, polycrystalline structures, however, physical and topological requirements interfere with the laws of geometric probability and impose stochastic restrictions upon the growing system—(1) the condition of minimising the surface energy, which restricts the initial local geometry; (2) the condition of filling space, which controls the long-range geometry and later growth.

In a two-dimensional system, minimum surface energy is achieved if three phase boundaries meet at one point at 120°. An n -sided polygon contributes therefore $n/3$ corners and the total number of corners is $C = \frac{1}{3} \sum nP_n$, where P_n is the number of polygons with n sides. The total number of edges is, of course, $E = \frac{1}{2} \sum nP_n$. If these values are inserted in Euler's equation, $C - E + P = 1$ (where $P = \sum P_n =$ number of polygons), the result is $\sum (6 - n)P_n = 6$, if edge effects are neglected. The number of polygons with 3, 4, n sides are thus related to each other as a result of the physical and topological restrictions mentioned. (For every 7-sided polygon that grows, for example,

a 5-sided polygon must also develop in the system.) The average number of sides is 6.

In three dimensions, the corresponding restriction is expressed by $\sum (6-n)P_n = 6(B+1)$ where B is the number of polyhedra or phase regions in the system. The condition of minimum surface requires that four edges meet in a vertex at 109.5° (the tetrahedron angle whose cosine is $-\frac{1}{3}$). It can easily be shown⁽⁴⁾ that this leads to polyhedra with on average 13.39 faces and 5.104 sides per face, in good agreement with Coxeter's result quoted above,⁽¹²⁾ which was later improved to give an even better agreement.⁽¹⁵⁾ The non-integer numbers indicate that heterophase structures do not naturally grow into a regular pattern.* Shapes and sizes of the phases have distributions with means defined by geometric and physical conditions, the latter controlling in particular the initial stages of growth.

Many heterophase materials, old and new, are made by consolidating an artificial mixture of substances, the mixing having been done in a state of higher mobility of the phases. Examples are the vulcanisation of a mixture of rubber and carbon black, the setting of concrete, the manufacture of paper.

The absence of restricting physical phase boundary conditions permits an even wider variation of phase relations and structures than found in natural heterophase materials. Mixing is primarily a separating process and the main effect that physical (and chemical) forces have is to prevent complete separation of the constituent phases. Uniform dispersion in this type of material is therefore an ideal never completely achieved by mechanical mixing, although addition of chemicals can considerably improve the dispersion.

In the case of an ideal dispersion of the phases, the geometric structure of these materials would be controlled only by statistical laws and the given size and shape of the constituents with results like the following—

1. Equal spheres fill 75 per cent of the space, if close-packed (hexagonal or cubic), but only 60–63 per cent if randomly packed. Unequal spheres in random arrangement can fill up to 85–90 per cent of the space. In general, random packing results in lower bulk density than does regular packing. If paper could be made by distributing the fibres randomly in three dimensions instead of depositing them in layers, the result would probably be a much bulkier product, just as ceramics and metals can be made with a wide range of porosities by sintering an originally random array of isolated particles.

* The only 'regular' body of similar dimensions that can be stacked to fill space is the truncated octahedron, suggested first by W. Thompson (Lord Kelvin) in 1887.⁽¹⁶⁾ It has 14 faces, of which six are squares and eight regular hexagons. The mean number of sides per face is $5\frac{1}{2}$, but these bodies do seem not to occur in naturally grown polycrystalline systems, in which the most frequent number of sides per polygon is always found to be five.

2. Two-dimensional networks of randomly mixed fibres form polygons with an average number of sides of four, whereas randomly growing phases such as polycrystallites or foams, controlled by physical as well as by statistical laws, form on average six-sided polygons, as mentioned earlier.

A very characteristic feature of premixed and consolidated heterophase materials is interaction between the phases in the mixing and in the consolidation process, usually accompanied by a change in volume. Such interaction can alter the shape and properties of the constituents, hence affect the structure and properties of the whole.

A system of glass fibres embedded in a polyester or epoxy resin, for example, goes through a temperature cycle during polymerisation. The heat expansion of resin is approximately ten times that of the glass fibres. When cooling from polymerising to room temperature, considerable compression forces can lead to kinking of the glass fibres, with corresponding effects on the properties of the finished product.⁽¹⁷⁾ A similar effect in paper was observed by Page & Tydeman.⁽¹⁸⁾ Here, a swelling and shrinkage cycle is the effective mechanism.

Summarising, then, the small-scale or local structure of heterophase solids is determined by a number of physical and geometric factors that vary from substance to substance. Common to all of them, however, is the non-uniform large-scale or bulk structure. Except for a few materials such as fibre-reinforced metals with parallel fibres, the complete description of heterophase structures must make use of statistical methods—in particular, geometric probability—possibly with certain physical limitations.

The most general hypothesis on which a quantitative treatment can be based is that the system is ergodic—that is, a large number of small samples (volumes) give the same average for a specific property, structural or physical, as found in a larger volume. The smallest volume to exhibit all the features of the material with a given degree of confidence is called the representative volume element or the representative cell. As Holliday points out,⁽¹⁹⁾ there will generally be different values for the size of the representative cell for different independent parameters such as concentration and size of phases. The choice must be such that the material can be considered, with respect to the property in question, to consist of a large number of independent representative cells. Applied to paper, the concept of the representative cell would mean that the formation of a sheet (the parameter being substance) is not expressed by the size and density distribution of thick or thin spots, but by the size and shape of an area whose substance lies within given limits of the average.

The ergodic hypothesis has been found very powerful in other fields of

physical statistics. It could also prove a powerful tool in dealing with heterophase materials. Until now, only very few steps seem to have been made in this direction.

Properties of heterophase materials

IN ITS most general form, the objective of a theory of bulk behaviour of heterophase solids is to predict the response R of a macroscopic sample to some physical condition x_i , to which its representative cells are subjected. It is assumed that a function of the form $R = Gx_i$ exists, where G denotes an operator that, for static phenomena, is a function of the material properties of the representative cells and their stochastic relationship. If, for example, the x_i are elastic deformations of the elementary cells, G would contain the elastic moduli of the cells, their distribution and correlations; R would then be the bulk stress necessary to produce this pattern of deformations, determined by a system of linear equations with random coefficients. According to an extensive review by Hashin,⁽²⁰⁾ the problem has not yet been treated in this form, except for attempts by Brown⁽²¹⁾ and Prager⁽²²⁾ to express the dielectric constant of heterophase systems.

Usually, the approach is based on continuum physics and simplifying models or assumptions such as stochastic independence are introduced to incorporate the statistical nature of the problem. Furthermore, most of the work done deals with mechanical properties.

One of the first systems that seem to have been investigated is that of a continuous phase (matrix) containing a disperse phase of individual, independent particles. A bulk property T of the system is related to the property of the matrix T_0 and the volume fraction c of the disperse phase by the expression⁽²⁰⁾ $T = T_0(1 + ac)$, where a is a constant. Einstein⁽²³⁾ was the first to derive this expression for the viscosity of suspensions of spherical particles in a Newtonian liquid, for which he found $a = 2.5$. The theory has since been adapted to a number of different shapes and other properties of the disperse phase.

A similar expression was derived by Smallwood⁽²⁴⁾ for the increase in Young's modulus of rubber produced by a dispersed solid. The constant was again 2.5. The above equation holds only for small particle concentrations. The effect of carbon black in concentrations up to 30 per cent by volume on Young's modulus of rubber can be described, according to Guth,⁽²⁵⁾ by expanding the equation to higher terms of c —

$$E = E_0(1 + 2.5c + 14.1c^2).$$

Most types of carbon black tend to form chains and higher aggregates. It is

possible to take this into account by adjusting the constants and by introducing shape factors for the aggregates. Clearly, the original rigorous theory of field distortions by the presence of dispersed particles thus gradually develops, with increasing complexity of the system, into a method of interpolating experimental results, a characteristic tribute to the limitations of existing theoretical tools. A comprehensive review is given by Rutgers.⁽²⁶⁾ Amstein & Reiner⁽²⁷⁾ reported the interesting observation that Einstein's law for dilute suspensions describes the behaviour of concrete mixes with up to 60 per cent fractional volume of sand, a result not yet understood.

Hill⁽²⁸⁾ applied variational methods to investigate the elastic behaviour of fibre-reinforced materials of regular geometry. A different model is one in which the material is considered, at a certain distance from a dispersed particle, to be homogeneous with different elastic properties. This method was applied to fibre-reinforced materials.⁽²⁰⁾

In all the previous cases, the disperse phase was treated as a disturbance of the field in the homogeneous, continuous phase. If both (or more) phases are comparable in the part they play in the elastic behaviour of the material, one of two models is often used as a suitable starting point for a phenomenological description: the phases are considered to be arranged either in parallel or in series.

In the first case, an applied stress produces a constant strain in each phase. Young's modulus is given by $E = \sum c_i E_i$, where c_i is the volume fraction of the i th phase with Young's modulus E_i .

In the second case, the stress is the same in all phases and the strains are different. Young's modulus is given by—

$$\frac{1}{E} = \sum \frac{c_i}{E_i}$$

For a two-phase system, this reduces to—

$$E = \frac{E_1 E_2}{E_1 c_2 + E_2 c_1}, \quad c_1 + c_2 = 1.$$

The phase with the lower modulus has a greater effect on the modulus of the system in the series model than in the parallel model.

The parallel model was found to apply very well, to quote one example, to fibreglass-reinforced resins, when the fibres were fairly long and parallel to the direction of applied stress. The physical mechanism in this case is transfer of shear stresses across the fibre/resin interface. If the fibres are not parallel, stresses normal to the fibre/resin interface cause local ruptures and Young's modulus drops almost discontinuously to a lower value, which depends on fibre orientation and fibre length.⁽¹⁷⁾ The effect of fibre orientation on

'reinforcement efficiency' was treated by Krenchel,⁽²⁹⁾ who derived an efficiency factor—

$$\eta = \int_0^\pi \cos^4 \phi f(\phi) d\phi$$

where $f(\phi)$ is the distribution of the angle ϕ between the fibres and the direction of applied stress. For parallel fibres, $\eta = 1$. For fibres randomly oriented in the plane, $\eta = \frac{3}{8}$.

The factor η also depends on the fibre length l as $\eta = (l - 2x)/l$. Here, x is the length of fibre near the ends that becomes ineffective for stress transfer, owing to the failure of glass-resin adhesion caused by the high stress concentration at the fibre ends. This was investigated by Outwater.⁽³⁰⁾ The length x is constant for a given fibre diameter, which means that there is a critical length for a particular type of fibre, below which the fibres become virtually ineffective. The existence of a minimum 'transfer length' was also observed in fibre-reinforced metals.⁽³¹⁾

In most systems, the elastic behaviour falls between those given by the parallel and series model. The two models then represent the upper (parallel model) and lower (series model) limits of bulk moduli. The derivation of bounds (upper and lower limits) of bulk properties is one of the primary objectives of most theories of heterophase materials, using different mathematical tools and geometric models. Hashin⁽²⁰⁾ arrives by statistical methods at the following expression for the lower limit of the bulk modulus of a two-phase system of arbitrary geometry—

$$E = E_1 + \left[(E_2 - E_1)c_2 / 1 + \frac{3(E_2 - E_1)}{3E_1 + 4G_1} \cdot c_1 \right]$$

(G = shear modulus), instead of the expression for the simple series model quoted previously. The upper limit is obtained by interchanging the indices 1 and 2. The limits are much closer than for the simpler models as one can easily verify by using arbitrary numerical values for E_i ($= G_i$) and c_i in both sets of equations. Experimental verification is presented by Hashin & Shtrikman.⁽³²⁾ Analogous expressions for dielectric properties were derived by the same authors.⁽³³⁾ These and similar model approaches are equally applicable to other bulk properties such as thermal and electrical conductivity.

Often, there is a phase inversion with increasing volume fraction of one phase: the formerly disperse phase becomes continuous and the formerly continuous phase becomes disperse. (An example of this is cream with water as continuous phase and fat as disperse phase, which changes into butter, in which fat is the continuous and water the disperse phase.) In such cases, the bulk property often obeys the parallel model in compositions for which the

phase with the higher value is the continuous phase and follows the series model at the other end. This is demonstrated by the thermal conductivity of magnesium oxide/magnesium silicate ($\text{MgO-Mg}_2\text{SiO}_4$) systems as a function of the composition.^(19,34) It is highest for the pure oxide, decreases with increasing silicate contents according to the parallel model and approaches the lower value for pure silicate according to the series model.

A problem of particular importance is that of fracture. It can be approached in two ways: from a physical point of view (mechanism of fracture) and from a phenomenological-statistical point of view (ultimate bulk strength).

The most interesting feature of heterophase materials in this respect is obviously the nature of the interfaces between the phases. It is reasonable [Bikerman⁽³⁵⁾] to consider an interface as a separate phase (interphase) with a gradual transition of the bulk properties of one phase to those of the adjacent phase.

Most theories of fracture assume perfect adhesion—that is, absence of impurities such as air and water, which constitute flaws in the interphase. Theories of the strength of crystallised solids usually give values that are orders of magnitude higher than the observed ones,⁽²⁾ because of local imperfections of the lattice. In heterophase materials in which the stresses concentrate at or near the interfaces, it is sometimes possible (with due precautions) to produce interfaces largely free from impurities. The assumption of perfect adhesion is then somewhat more realistic. The strength of carefully produced fibreglass-reinforced metals, for example, is known to be determined by minute cracks on the surface of the glass fibres rather than by imperfect adhesion between glass and metal.

If perfect adhesion is a reasonable assumption, it is unlikely for two reasons as Holliday points out^(19,34,35) that failure at the interface occurs.

Firstly, if failure begins between two atoms A and B belonging to different phases, it can continue either between two atoms A or two atoms B or between another pair AB. Since both A and B are backed by their bulk phases, it is much more likely for a crack to proceed between atoms of the same kind than along a path that lies in its whole length between A and B. In other words, fracture occurs within one phase rather than in the interface.

Secondly, between two phases attraction forces of the Van der Waals' type that are caused by induced or permanent dipoles are equal to the geometric mean of the forces within each phase. Thus, the adhesion must be stronger than the cohesion in the weaker of the two phases.

The fracture of fibre-reinforced materials can be understood to consist of discontinuous fibre fractures (in the case of glass fibres, for example, induced by surface damage) until the fibres have reached the transfer length (see above) at which point the matrix (continuous phase) breaks. The interface in

these materials consists usually of atomic groups coupling the fibres to the matrix. In glass-resin materials, these groups are provided by such keying agents as organo-metallic or organo-silicon compounds, of which the metallic or silicon atom attaches itself to the glass surface, whereas the organic group provides the bond to the resin matrix or even takes part in the polymerisation process.⁽¹⁷⁾ The interface forms in this case a separate phase between the two phases that it joins.

In fibreglass-reinforced aluminium, valency bonds between aluminium and the glass can be established, thus forming a transition phase between the two phases.

The reinforcing effect of carbon black in rubber is caused by reactive groups of the phenol, keto or quinone type on the surface of carbon black particles that cross-link the rubber molecules. The surfaces of fracture zones always show a carbon black concentration higher than the bulk average. Thus, as Payne⁽³⁶⁾ points out, the paradox exists that the very particles that produce reinforcement are also the weak spots in the system. The explanation is that stress concentrations are highest near the carbon black inclusions. Fracture occurs near the particle/rubber interface and proceeds to the next particle. This diverting of the path of fracture is the most likely mechanism of the reinforcing effect. Obviously, good dispersion of the particles and adhesion to the rubber matrix are essential to produce this effect. In rubber with poorly dispersed particles, fracture occurs within the aggregates and low strength values result.

In concrete, to quote a last example, fracture is initiated by microcracks at the sand/cement interfaces, caused mainly by differential shrinkage. Initial crack propagation is slow, follows Griffith's theory⁽³⁷⁾ and can lead to re-stabilising the system when the excess potential energy is dissipated in the formation of new surfaces. Since this process is irreversible, a point will be reached under continued stress when the system becomes unstable and fast crack propagation sets in, which leads to ultimate failure.⁽³⁹⁾

Thus, every system has its own particular mechanism of fracture controlled by the type of bonding forces—that is, the atomic structure and the chemical nature of the phases—and by the phase geometry and structure.

Independent of the detailed mechanism, the phenomenon of fracture can be described in statistical terms. Here again, the ergodic hypothesis and the concept of representative cells provide the necessary basis. As in the case of describing the structure, this hypothesis in its general form is too abstract and concrete models and assumptions have to be resorted to.

It may suffice to mention the work by Daniels,⁽³⁹⁾ who investigated the fracture of bundles of threads and by Weibull,⁽⁴⁰⁾ who postulated a specific distribution of local strength of heterogeneous materials, to which he applied

extreme value statistics. A particular result, the dependence of tensile strength on the sample size, was found to apply to paper.⁽⁴¹⁾ Another version of this weak spot approach⁽⁴²⁾ allows, at least in principle, the determination of the size of the representative cell by adjusting the parameters of the statistical model to fit experimental observations of the decrease of the tensile strength of paper with increasing strip length. The theory of extreme values was used by Epstein & Brooks⁽⁴³⁾ in a study of the dielectric strength of paper capacitors, also by Corte, Kallmes & Jarrot⁽⁴⁴⁾ in an investigation of fibre bond fractures in thin paper sheets.

Conclusion

THE CLASS of heterophase materials is so large and varied that no general theory or even phenomenology exists nor is likely to emerge in the near future to cover all the observed facts in one single approach. A multitude of approaches from various directions has to be used at present, which may gradually converge towards a central, unifying and workable concept to understand the behaviour of these materials in their different theoretical and practical aspects.

A vast body of empirical knowledge and a variety of theoretical tools are available. Their discussion had of necessity to be brief and general. Paper was deliberately not put in the centre of the discussion. It may have become apparent, however, that the newly emerging and rapidly growing materials science is resourceful enough to embrace the whole of the class of heterophase materials, of which paper is such a fine example.

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