

General theory of composite materials

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INTRODUCTION

Until recently composites have been regarded as a simple combination of two or more materials. In fact, they should be treated as a material system composed of several phases, at least one of which is solid with a macroscopically distinguishable boundary; such a system makes it possible to obtain new properties or a combination of properties which are not attainable by any component separately or by simple addition of them.

The study of these materials has to be interdisciplinary. Several methods and theories have already been derived for description of the deformation and mechanical behaviour and failure. However, for different types of composite the same basic principles apply, there is a definite similarity, and marked

progress can only be achieved by a 'synthesis' based on already analysed data from various fields and scientific disciplines concerning various materials. In the short space of the present article it is only possible to mention the basic principles of the general theory of composites, with particular stress on the philosophy of the approach, without describing the analytical process.

The theories up to now have generally been derived empirically for individual types of composites. If a single substance is replaced or the production method is modified, the theory ceases to operate; subsequent work generally consists of modification of the theory so that the measurement corresponds to the result instead of vice-versa.

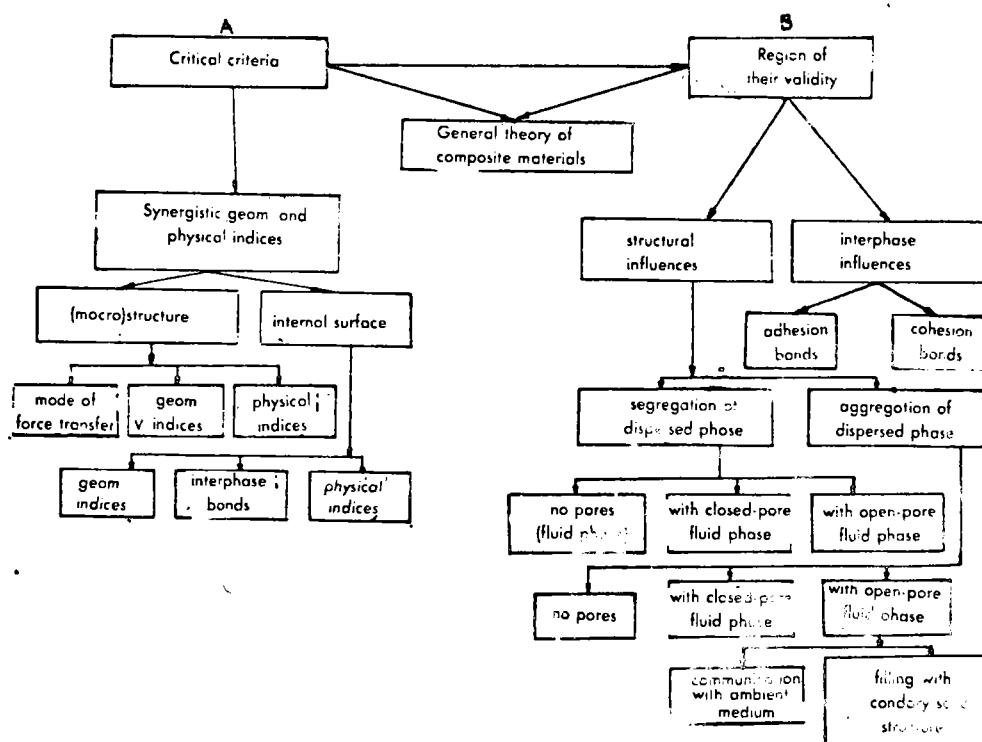


Fig. 1 Basic criteria for the description of composites, and the areas where they are valid

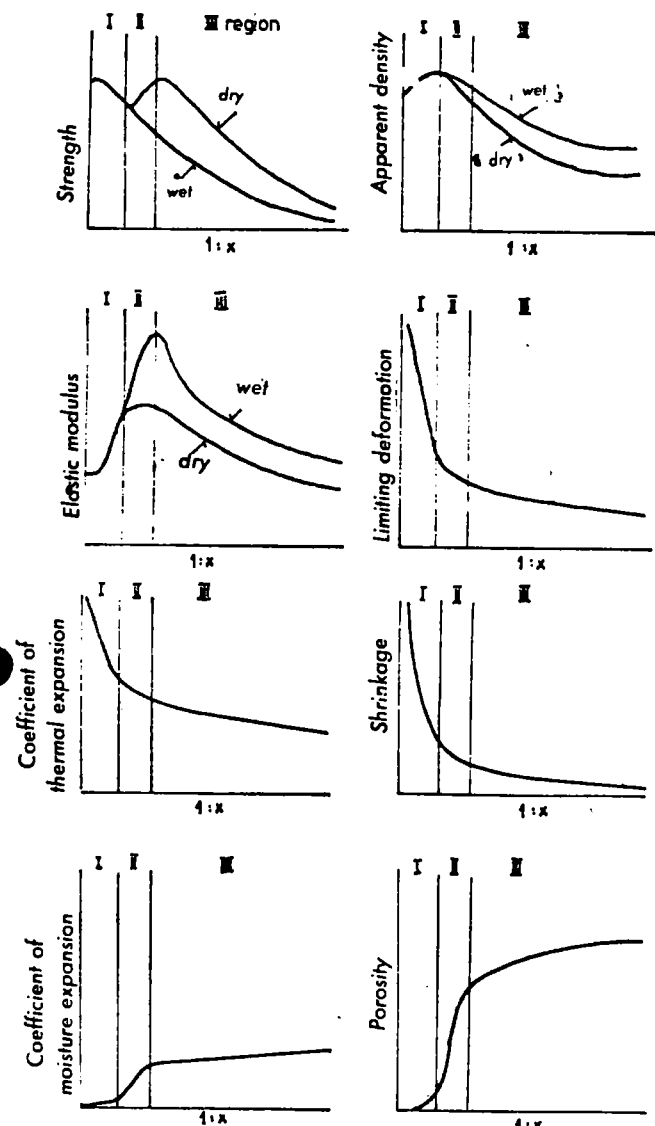


Fig. 2 The change in the properties of possible systems comprising two solid phases with or without a fluid phase, as a function of the mass ratio between the solid phases

The reason for this unsuccessful approach is generally that no basic criteria have been taken into account; that fundamental and non-fundamental, critical and modifying aspects, have been confused; and, in particular, that different classes of composites, which are formed and operate under different conditions, have been confused.

Clearly a basic step in an attempt to understand the behaviour of composites and hence to be able to predict their properties is (Fig. 1):

- a) classification of the critical criteria;
- b) classification of the areas of their validity.

Critical criteria and the areas of their validity

If, using a simple example of a composite consisting of two solid phases with or without the presence of a liquid phase, we study the properties of the composite with different phase compositions (including the extremes, i.e. on the one hand a quasi-homogeneous system consisting of one solid phase, and on the other hand a two-phase non-coherent system consisting only of the second solid phase and a liquid phase), we can find a non-

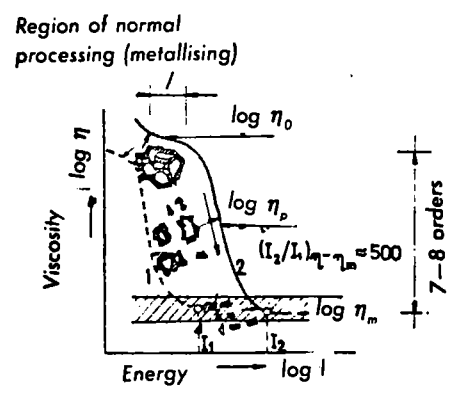


Fig. 3 Structural uniformity achieved by breakdown of the primary structure: 1, with lubricant; 2, without a lubricant

random, systematic change in all the physical indices, as shown in Fig. 2 (ref. 1). The evident similarity of all these dependences on the phase composition of the system lies in the fact that they are markedly different in three regions and that these regions are always the same.

The reason for this change is not only the phase composition nor only the phase geometry, but also the superstructure of the composite, which is, of course, a function of the phase composition and geometry, but is also a function of other physical and geometrical parameters of the system and of the phases.

Let us show by another example (Fig.3) how great an influence the superstructure has on the properties of a composite. A fine particle filler mixed using normal methods, with a binder (a resin) will give a structure formed by aggregations of coagulated particles bound by physical forces. By more energetic mixing, e.g. by high-frequency vibration, it is possible to achieve a breakdown of this primary structure and the formation of a new structure, exhibiting identical dispersion of individual particles and structural uniformity. In this way we can, for example, reduce the true viscosity of a fresh mix by 7-8 orders, increase its mechanical properties after curing several-fold, etc. (ref. 2).

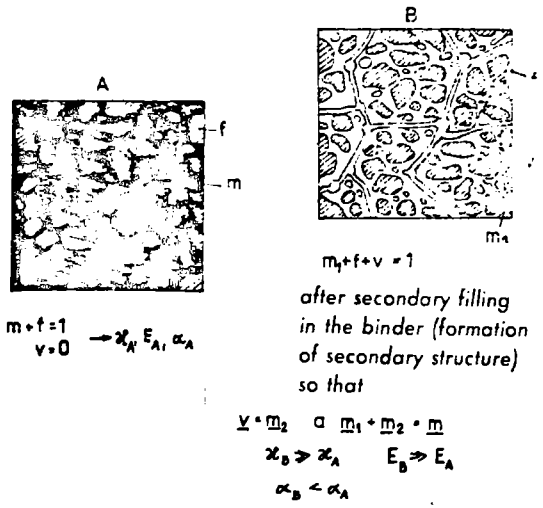


Fig. 4 Comparison of polymer-impregnated polymer concrete (PIPC) with polymer concrete (PC) at an identical amount of binder per unit volume

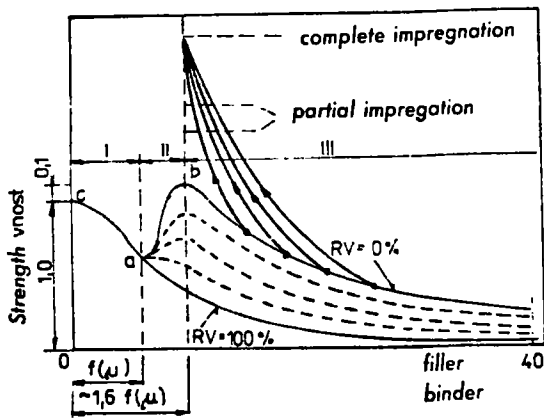


Fig. 5 Change in strength of PC after impregnation with the same polymer (PIPC), as a function of the mass ratio between the solid phases

It would be possible to give several other examples of the decisive influence of the degree of structure. They are all examples of a multi-structure system (Fig. 4), i.e. a system in which there are two or more independent structures extending through the phases and the geometry, as is the case with PIC (Polymer Impregnated Concrete), impregnated ceramics (e.g. the C/C/SiC system) etc.

We have shown, for example, in the case of PIPC (Polymer-impregnated Polymer Concrete) that with a certain amount of binder (polymer) in the system much more advantageous properties are obtained if two independent continuous binder structures are formed than if only one is formed; this will be achieved for example, if, after the formation of PC (Polymer Concrete) with a deficiency of binder and hence with continuous porosity, more binder is added to the system (by impregnation); the latter forms in the pores an independent infrastructure, chemically similar to the original binder but physically, morphologically and crystallographically different. The geometric arrangement of the impregnated phase, as if in microscopic fibres, and the large amount of interfaces, near which the physical properties of the binder differ markedly from the properties in the mass, appreciably alter the nature of the stress flows and breakdown, cause more advantageous stress redistribution, localisation and hindered growth of faults (cracks), etc. As Fig. 5 shows, for example, the strength of the material when the pores are filled with solid binder (as opposed to filling with a liquid) increases above the values achieved with a single-structure system, even when completely dried.

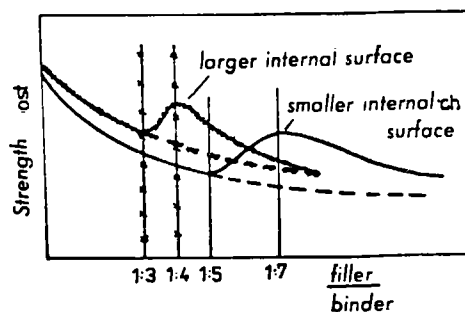


Fig. 6 Influence of the internal surface on the change in the strength of PC, as a function of the mass ratio between the solid phases



Fig. 7 Formation of a transition layer on the phase boundary by orientation of polymers

The above discussion clearly reveals the first critical criterion — the degree of structure of the system (Fig. 1 A). It is particularly critical whether the dispersed phase in the continuous phase (the binder) is segregated (without mutual force contact) or is aggregated (capable of directly transferring a force from one particle to another, possibly through an intermediate layer of binder). Another consideration is the amount and type of fluid phase (gas, liquid) and the degree of its continuity with the external medium (Fig. 1 B).

Besides the degree of structure of the system, a no less important criterion is the existence of detectable phase boundaries, or an internal surface (Fig. 1 A). The internal surface determines the position of the individual regions, shown in Fig. 2, on the axis for the phase composition (by volume or mass), not only by its magnitude, but also by the quality of the boundary (Fig. 6). The individual phases in contacts are bound predominantly (but not exclusively) by physical bonds.

In the direct proximity of the dispersed phase the structure of the binder changes and a 'transition layer' is formed, as also in the case when no chemical reaction occurs. For example, under the action of physical and physicochemical forces, orientation of the polymer occurs (crystallinity) in the proximity of the

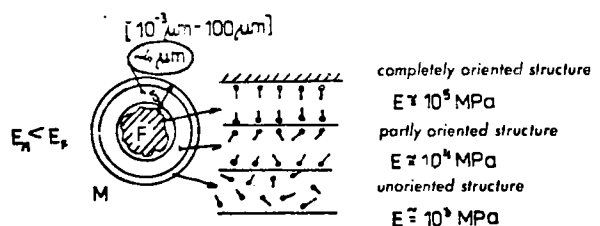
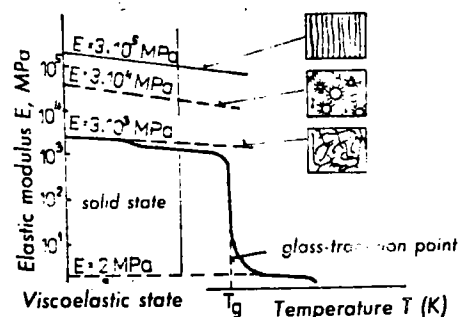


Fig. 8 Properties of the transition layer on the phase boundary

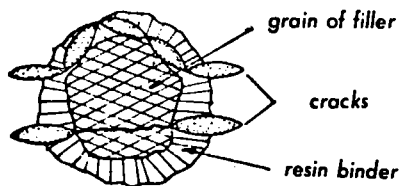


Fig. 9 Formation of micro-defects in the structure in the proximity of dispersed particles (grains, fibres) under the influence of shrinkage during the transition to the solid stage and of the difference in the coefficients of thermal expansion

particles (as the photomicrograph in Fig. 7 shows). These changes on the phase boundary then result in a marked change in the deformation and strength properties of the polymer (see Fig. 8). Micromerements have shown that, for example, the elastic modulus at different distances from the particle varies over two orders (ref. 3).

In the formation of composites, during the transition to the solid state large stresses occur on the phase boundary as a result of shrinkage of the binder during polymerisation and the normally large difference between the coefficients of thermal expansion of the components. At the borders of the particle (Fig. 9), most often in the envelope (modified) layer but also in the particles, microfaults can occur (microcracks or crazing), which are responsible for composites having much lower strength than the strength given by the energy of the bonds formed.

Recent experiments have confirmed that by reducing the internal stress due to shrinkage during polymerisation on the properties of a composite can be greatly improved, e.g. in the case of a composite composed of carbon fibres and an epoxy, with reduction in the shrinkage stress to below 10 MPa the impact strength increases exponentially, from initial values of tens of kJ/m^2 to hundreds ($200\text{--}600 \text{ kJ/m}^2$), as Fig. 10 shows.

Together with the superstructure (sometimes also called the

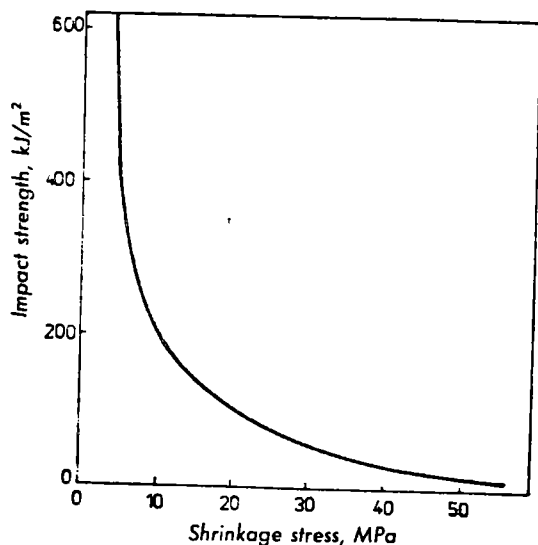


Fig. 10 Influence of internal stress due to shrinkage and during the transition to the solid state and cooling from the solidification temperature on the impact strength of a composite consisting of carbon fibres and an epoxy resin

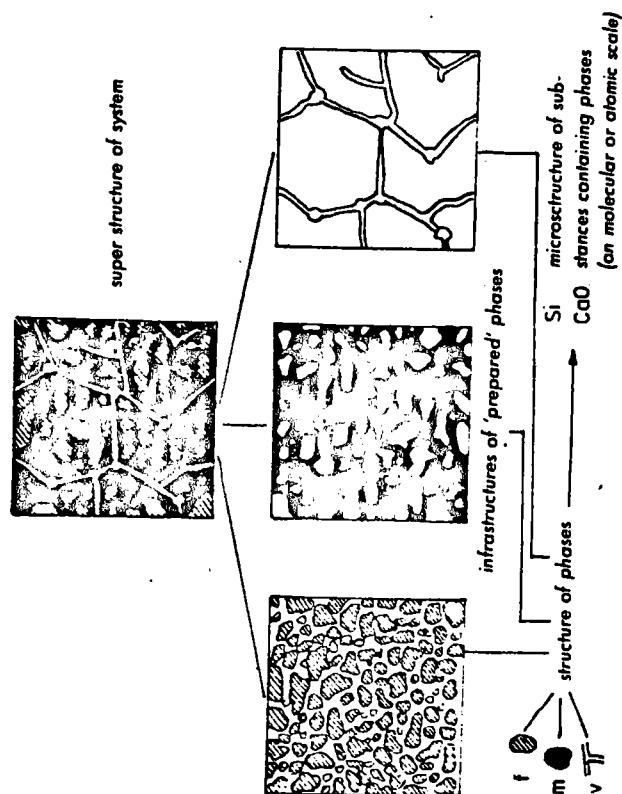


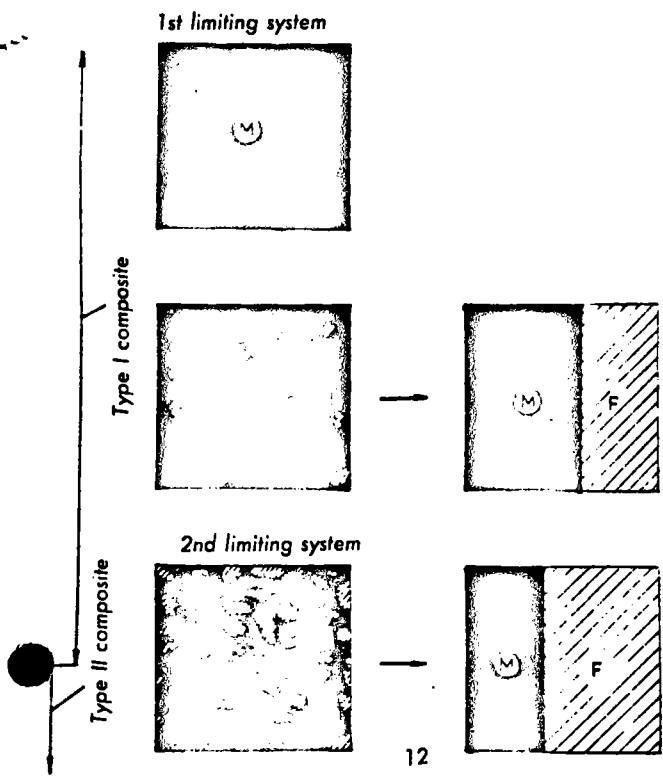
Fig. 11 Structure of systems at various levels

macrostructure), which expresses the arrangement of the system as a whole, a composite contains a more or less regular structure of systems on different levels (Fig. 11). Each phase has its own structure. The infrastructure is formed by the prepared phases in their original arrangement in the composite. In the systems of which the phases are composed, each substance has its own microstructure.

Definition of composites on the basis of their structure
For simplicity, let us for the moment again consider a system comprising two solid phases. Then, taking into account the previous conclusions, we can find several types differing in the ratio and arrangement of the phases.

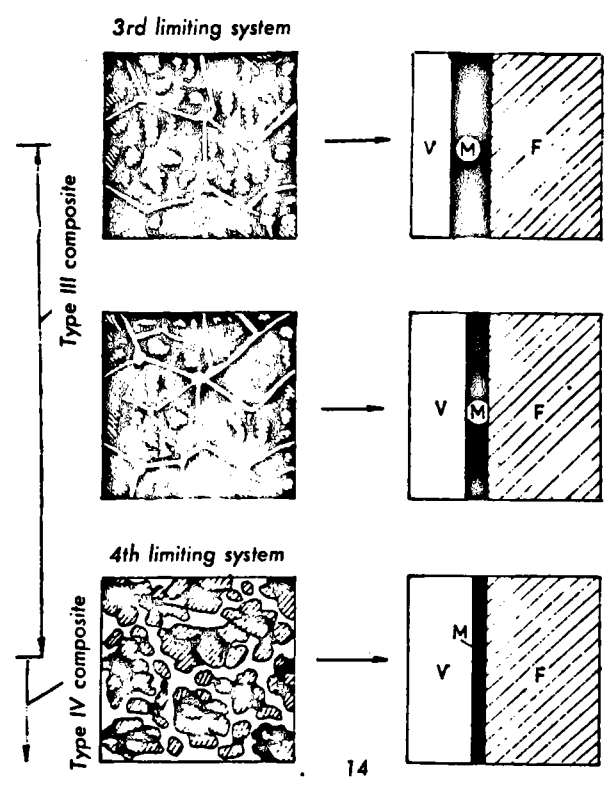
There are several different systems which completely fill a given space (Fig. 12), ranging from a pure binder (i.e. a quasi-homogeneous system) as the first limiting system via dispersed particles, to a system with the dispersed phase in the densest possible arrangement, with aggregated particles (the second limiting system); the critical aspect of the geometrical arrangement in these systems is the segregation of the particles, and the critical component of the properties is the binder. The whole of this group, between the first and second limiting systems, will be termed 'Type I composites'.

From the final (boundary) type I composite onwards it is already impossible to change the volume of the dispersed phase (the dispersed phase remains aggregated), and further change in the volumetric ratio between the two phases is only possible by reduction of the binder, in place of which a third, fluid phase is introduced into the system (Fig. 13). Closed pores are formed in the binder and the overall ratio of the volume of solid phase to the volume of the test specimen falls below unity and continues to fall. A system is formed which is at least three-

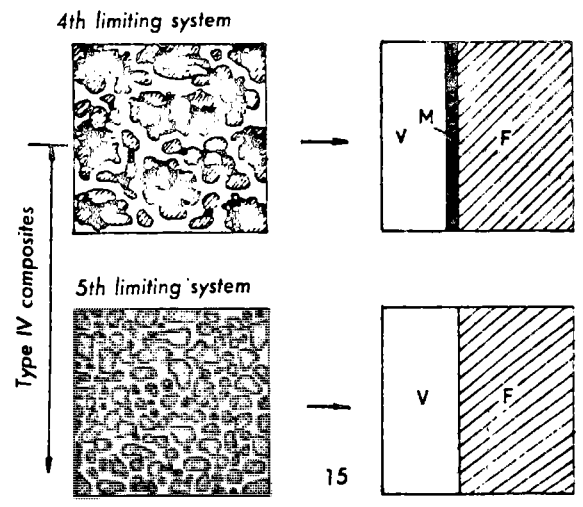
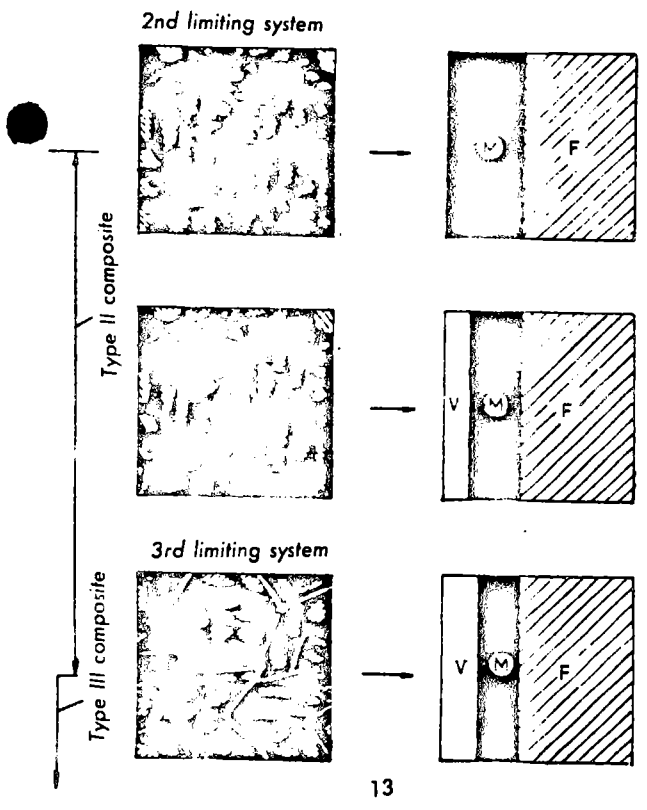


Figs. 12–15 Systems of composites which fill a given space to different degrees, and classification into basic types in terms of the (macro)structural arrangement

phase, all of whose properties will start to differ diametrically from the preceding systems. Composites of this type form another independent group, which we shall term 'Type II composites'. Theoretically this region finishes with a system in which a third, liquid phase is added and forms an independent



infrastructure so that the system is continuously and reversibly connected to the external medium. In practice, of course, this boundary, i.e. the third limiting system, cannot be precise, since the combining of individual closed cells into continuous channels is gradual. The solid phase in these systems, by contrast to type I, does not occupy the whole space delineated by the material. If the fluid phase in the free spaces in the binder is gaseous it is easily compressible; if it is liquid, it is completely incompressible. The primary internal stress in the system (resulting from the formation of the material), just like the secondary internal stress (resulting from external influences), changes when free spaces are formed, the energy dissipation is different, etc. If the pores are filled with gaseous phase, the system has greater capacity for transverse deformation, preventing the development of micro-defects and dissipating larger amounts of energy; this gives an increase in impact strength, fatigue strength and service life. In the



parameters which determine the properties, in addition to the factors which apply to type I composites (i.e. the volumetric ratio and properties of the solid phases, the magnitude and properties of the internal surface of the dispersed phase) other parameters appear: the ratio between the fluid and solid phases, and the magnitude and properties of the internal surface of the fluid phase.

As soon as the porosity of the system becomes continuous (without any change in the arrangement of the dispersed phase, which remains in the aggregated state as at the start of type II composites) a further value (often critical) becomes relevant: internal interaction of the composite with the external medium. This again decisively alters the behaviour of the system, which is characteristic of Type III composites (Fig. 14). Another essential parameter for describing these systems is therefore the external medium, its properties and the method of interaction with the internal surface. The solid phase occupies a continually decreasing part of the total (external) volume of the composite, and there is a loss of binder up to the moment when the primary structure of the binder breaks down and it loses its phase continuity (this is the fourth limiting system). The material becomes free-flowing (Fig. 15) and its properties are determined mainly by the liquid phase (as the secondary dispersing phase). We shall term this group 'Type IV composites'. The boundary of this system is the fifth limiting system, in which the primary continuous phase (the binder) is completely absent, so that the system contains only one solid phase, dispersed in a fluid medium. Type IV composites are not important for design materials, and are encountered mostly as clays.

Thus, in a schematic and very simplified way we can represent the sub-division of constructional composites (as the basis of a general theory) in terms of structural arrangement as shown in Fig. 16. Only if the study, description and experimental investigation are sub-divided on this basis is there any prospect of obtaining less ambiguous results, which

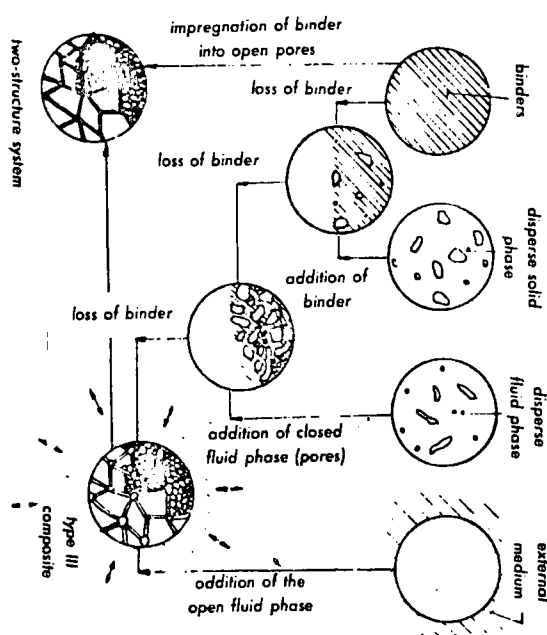


Fig. 16 Schematic division of composites in terms of the (macro-) structural arrangement

are objective, reproducible and non-contradictory.

Let us also remember that a physical description of the structure comprises physical indices of each component of the system, of their interaction and phase boundary. Because the physical constants (functions) of the composite are random spatial functions, they can only be described statistically. For this, however, it is necessary to know the complete geometrical description of the structure and the physical properties of the components; a knowledge of the volumetric phase composition alone is inadequate.

The mechanical processes, which are a function of the relationship of the geometric and physical parameters, take place in the structure through two basic mechanisms (Fig. 17):

- Deformation processes acting by shear flows depending on the phase boundaries and causing changes of mechanical energy of dissipation into thermal energy or into mechanical energy expended on the formation of new surfaces (cracks) in the structure. The proportion of other types of energy (chemical, changes in the electromagnetic field) in the final effect is negligible. These deformation processes are typical of type I composites
- Deformation processes causing the formation of force configurations and force flows in the structure and hence the occurrence of stressed and unstressed areas in the structure. Then the external load is resisted by a framework of force paths which is formed in the structure and is often orthogonal or hexagonal. This process is particularly important for type II and III composites. The most important parameters are the size distribution, the concentration distribution, the phase continuity and the ratio of the physical properties of the phases. The fact that both deformation processes evidently act in multi-structural composites is therefore one of the reasons for the markedly different properties of such systems.

Elastic constants of composites

On the basis of the above-described proposal for a theory of composites, equations have already been derived which accurately characterise the elasticity of these systems. In

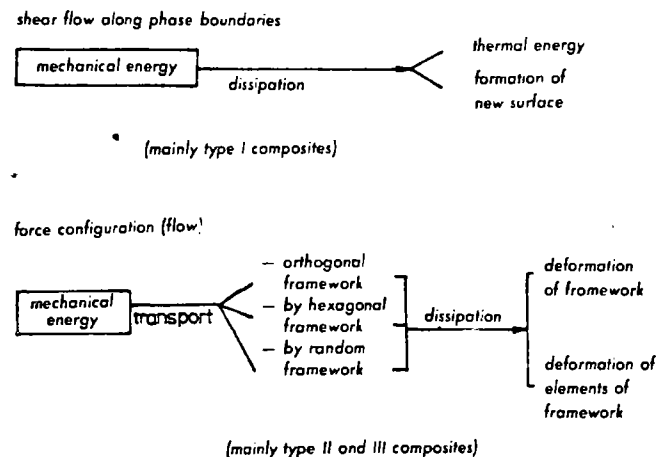


Fig. 17 Two basic mechanisms of deformation processes in a structure

addition to the interaction of the individual phases and their intensive participation in the process (as is normal for practically all so-called mixing rules), the degree of structure of a system with a definite internal surface and its interaction with the ambient medium have also been introduced. This makes it possible also to take account of a fluid phase in the system, not only in terms of its volume and elastic modulus, but also in terms of the magnitude of the internal surface to which it is bound.

CONCLUSIONS

It is the author's desire that the above-described outline of the general theory of composites, based on a structural survey and a synthetic rather than analytical approach, should provide users of composite materials with an effective aid to understanding and mastering planned formation of composites. The author considers this aim particularly important because in the future growth of population, accompanied by restriction of material and energy sources, composites will play

a decisive role in all industries, since of current materials they have the highest specific (energy) efficiency.

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