W.C. Wake

Fillers for plastics

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Preface

This monograph deals with the properties of the various mineral and other powders and some fibres and fibrous materials commonly mixed with polymers to form the material of the familiar plastics article. We shall refer to these materials by the convenient if colloquial word 'fillers'. It is a convenient word because it includes both powders and fibres and can even be stretched to cover such materials as paper; it is commonly used throughout the plastics and rubber industries and is also understood in the paint industry. Although it is necessary to consider the interaction between the polymer and the filler, to consider for example why it is even possible to mix one into the other, it is the properties of the filler and not those of the filled polymer which form the contents of this monograph. The aim is to provide a short reference book dealing with all the main types of filler, listing typical physical properties, describing their origin and morphology. Chapters 2–4 discuss powders, and Chapters 5 and 6 deal with fibres. Chapters 7 and 8 cover glass, paper, felts and woven materials, which, though not strictly fillers in the same sense as the other materials, are considered relevant in this context. Discussion of the properties conferred on the polymer by the use of the filler is avoided except in broad outline and in the particular case of the special nature of the properties conferred by carbon black on elastomeric polymers where it was felt an absence of discussion on the phenomenon of 'reinforcement' would prevent adequate appreciation of the differences between the various types of carbon black. The chapter on carbon fillers has therefore a section on properties conferred on rubbers rather than on plastics.

The term 'filler' is apt to carry with it the implication of a cheap additive to an expensive material but it must be emphasised that

with plastic materials this is not the case. The filler is incorporated with the polymer to give a plastic material in which both the polymer and the filler contribute to the desirable properties of the plastic material. Often, as for example in woodflour filled phenolic moulding materials, the filler is much cheaper than the polymer, but fillers, such as particular forms of glass fibre, may be as expensive as the polymer and in the case of graphitic carbon fibres the filler is much more expensive than the polymer with which it is incorporated.

Although four of the eight authors who have collaborated in producing this monograph hold university appointments almost all have had industrial experience within the polymer industry. It is hoped that the result will be of value not only to the plastics and rubber industries but also to technologists of those branches of the heavy chemicals and textiles industries for which plastics provides one outlet.

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Interfacial phenomena

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1.1   INTRODUCTORY REMARKS

Whether the filler for the plastic is a powder, is fibrous or in the form
of continuous sheet or cloth, contact between it and the polymer must
be intimate and capable of remaining so even when the material
is subjected to deformation. It is also desirable that polymer and
filler should preserve intimate contact when exposed to water or
other liquids or vapours. This cannot be achieved universally as
specific interactions between certain liquids and certain polymers
or fillers result in displacement of the polymer from the filler surface.
The ease with which contact of polymer and filler is achieved, and
the strength and nature of the union are interfacial phenomena
occurring on the surface of the filler and leading to modifications
in the behaviour of the bulk material. How the interfacial behaviour
brings about the changes in mechanical and other properties is not
entirely understood but, after a discussion of the surface properties
that are believed to be important, an indication is given of present
views on the interaction of surface and bulk properties.

1.2   THE WETTING OF POWDERS BY LIQUIDS

It is possible to float on the surface of water powders whose density

is greater than water. Usually, after some time has elapsed, the powder slowly becomes enveloped and sinks. This may never happen with graphite because it is not 'wetted' by water. The powders which are mixed into polymers must similarly be wetted by the polymer and it is customary to approach a discussion of wetting by considering, instead of a powder, an extended plane surface of the same chemical constitution and a simple liquid of low molecular weight and therefore low viscosity, to represent the polymer. This model of the wetting situation enables terms to be introduced that are useful when considering the actual situation of powders or fibres surrounded by polymer. A drop of liquid placed on the imaginary plane surface will either remain as a drop exhibiting a finite angle of contact (θ) with the solid or will collapse by spreading and wetting the surface uniformly and the contact angle is then zero. If γ_s is the free surface energy of the solid, γ_l that of the liquid and γ_{sl} the free interfacial energy between them then the simple form of the Young equation states that $\gamma_s = \gamma_{sl} + \gamma_l \cos \theta$. We can also imagine making the liquid rigid and lifting it to leave a clean dry surface. To do this takes work and Dupré called this the work of adhesion, W_A.

Now, $W_A = $ [Free surface energy of solid] + [Free surface energy of liquid] − [Free interfacial surface energy]. The Dupré equation can be combined with the Young equation to give $W_A = \gamma_l(1 + \cos \theta)$. If the free surface energy of the liquid is equated to its surface tension then the work of adhesion of the liquid to the solid can be calculated from a knowledge of the surface tension and equilibrium contact angle. This very simple model must be modified before wetting can be discussed. The modification necessary is the introduction of the vapour pressure of the liquid, the absorption of the vapour by the solid and the recognition that removal of the liquid from the surface will leave an adsorbed film of the substance behind. The liquid forming the drop will, of course, be volatile to a greater or lesser extent and the atmosphere above the surface on which the drop rests will be saturated with the vapour of the liquid. This vapour will adsorb on the surface of the solid not covered by the drop and, because the atmosphere near the drop is saturated with vapour, the adsorbed layer will be more than a monolayer. In place of γ_s on the left hand side of the Young equation it is then necessary to write γ_{sv} as the tension balancing the drop, and $(\gamma_s - \gamma_{sv})$ is known[1] as the spreading coefficient π_e. The Young equation may consequently be written in the form $\gamma_s = \pi_e + \gamma_{sl} + \gamma_{lv} \cos \theta$. When the contact angle is zero the spreading coefficient governing the wetting of the surface by the bulk liquid is given by $\pi_e = \gamma_s - \gamma_{sl} - \gamma_l$ and we may regard the energy represented by π_e

as providing the driving force which will determine the rate at which the liquid will spread under the constraint of its viscosity. The work of adhesion when an adsorbed film is left on the solid is considerably smaller than that which refers to the clean surface. The work of adhesion is, of course, a free energy which can be split by means of the Gibbs equation into enthalpic (or heat content) and entropic terms. The heat of adsorption can be derived from the direct wetting by the liquid of the solid in the form of a fine powder and this brings us more closely to the real situation. It is then possible to know something of the interaction of the characteristic groups of the polymer, by using a low molecular weight model liquid, with actual fillers. Thus with paraffin hydrocarbons simulating polyethylene, the interaction of —CH_2— groups with a variety of crystalline powders has been examined. More recent work has enabled the work of adhesion to be broken down into energies of interaction due to the London dispersion forces, dipole interaction, electrostatic attraction and so forth[2].

It is now clear that it is the London dispersion forces which are the most important at the short distances which exist between powder and enveloping liquid but the other interactions add additional energy when the adsorbed molecule is already polar or on an ionic crystal where the charges can induce dipoles in the adsorbate. The powders used in plastics range from carbon, through comminuted organic materials to powdered ionic crystals. The interaction is therefore least between carbon and a saturated hydrocarbon such as polyethylene or polyisobutene, and greatest between an ionic powder and a polar polymer such as polyvinyl chloride, but as between various ionic powders there will be very little difference of interaction unless there is some specific chemical reactivity present. Table 1.1 illustrates these points by reference to some typical ionic solids wetted by ethyl acetate, which may be regarded here as

Table 1.1 ENTHALPIES OF ADHESION IN mJ/m^2 OF LIQUIDS TO IONIC SOLIDS AND CARBON

	Ethyl acetate[3]	Carbon tetrachloride[3]	Iso-octane[3]	Benzene[3, 4]	1-methyl cyclohexane[4]
BaSO$_4$	430	280	—	210[3], 411[4]	998
TiO$_2$ (anatase form)	420	300	155	220[3]	—
SiO$_2$	520			220[3], 211[4]	336
ZrO$_2$	—	340	160	260[3]	—
ZrSiO$_4$	—	470	240	330[3]	—
Graphite	—	255	—	295[3]	—
Carbon black	—	—	—	158[4]	200

simulating PVA; carbon tetrachloride, a rather poor model for PVC and iso-octane to simulate a saturated hydrocarbon polymer.

1.3 THE CRITICAL SURFACE TENSION OF SOLIDS

Whether or not a liquid will spread over the surfaces of a solid reflects the extent to which the attraction between molecules of liquid and substrate exceeds the cohesion of the liquid. When discussing the interaction of liquids with surfaces of low free surface energy, Zisman in an important series of papers[5] has introduced the concept of a critical surface tension. This is a property of the *solid* and refers to the surface tension of a liquid which will just wet the solid. It is obtained by plotting the cosines of the contact angles of the homologous series of organic saturated aliphatic hydrocarbons (other homologous organic series give similar though usually slightly higher values) against their surface tension and extrapolating the straight line obtained to $\cos\theta = 1$. This gives the critical surface tension of the solid, usually written as γ_c. Most of the powders used as fillers have surfaces with high free surface energy and as they are polycrystalline they will have many places, such as edges of crystals, dislocation ends, and so forth with exceptionally high surface energy. However, there are the exceptions to this such as carbon black, silica and powders or surfaces which have been treated to render them hydrophobic and which must be regarded as having surfaces of low surface free energy. Such surfaces will not be wetted spontaneously by liquids whose surface tension is greater than the appropriate γ_c. In the case of a polymer instead of a liquid wetting the surface, it is convenient to replace the idea of a high surface tension by a high cohesive energy density (*CED*) since surface tension and *CED* are closely related. (N.B. If E is the total internal energy and V the molar volume $CED = E/V$ and is therefore a measure of the 'internal pressure' of the substance. The internal pressure is given by $\gamma/V^{\frac{1}{3}}$.) There is doubt concerning the wetting relation between some of the more polar polymers and some low energy surfaces. This does not imply that the polymer cannot be adsorbed onto the surface but only that wetting does not proceed spontaneously and that desorption is possible. The work of adhesion of a liquid in similar circumstances is relatively small, not much greater in fact than the work of cohesion of the liquid itself.

1.4 THE MOBILITY OF ADSORBED LIQUIDS ON POWDERS

Vapours or gases adsorbed onto ionic crystals seem to obey

Langmuir's hypothesis that the molecules remain fixed at given sites on the surface. There is, however, an alternative situation when the adsorbing substrate has a low free surface energy namely, that the adsorbed molecule, whilst it remains attached to the surface may, nevertheless, move over the surface at a fixed distance from it without requiring extra energy to overcome potential barriers. This situation could exist with carbon black, and there is some evidence that it does[6], and could also possibly exist on a glass or silica surface treated with a siloxane or a clay surface treated with a long chain aliphatic amine. The nature of the evidence for this is thermodynamic and involves the calculation of the entropy of adsorption for two distinct models, one corresponding to fixed-site adsorption and the other to mobile adsorption; the observed value is then compared with the expected values. The importance of the possibility of mobile adsorption in the present context is that it provides a mechanism for the relief of local stress in a filled polymer without desorption of the polymer from the powder.

1.5   ADSORPTION OF POLYMERS

So far the discussion has concerned theories and data obtained from liquids of low molecular weight and their extension to polymeric materials has been by analogy only. Some work has indeed been carried out on the adsorption of polymers into solid surfaces but this has concerned dilute solutions of polymers and not bulk material. From solution, polymers do adsorb onto the surfaces of solids and whether the polymer is in an extended or closely coiled state depends on the solvent. Initially, only a small part of the polymer chain is adsorbed but gradually adsorption of other parts occurs, with a looped configuration being formed of parts adsorbed and parts still solvated. It is appropriate to emphasise here that all adsorption is a dynamic phenomenon[7] with adsorption and desorption continually occurring. What determines the equilibrium condition is the dwell time of an adsorbate before desorption occurs. The looped adsorbed condition of polymers should not be regarded as a static situation but one where the rates of desorption and resorption of parts of the molecule are equal.

The higher the surface energy of the adsorbing surface, the more likely is any given portion of the polymer chain to be flat on the surface of the adsorbent. A low energy surface with no polar interaction between surface and adsorbate will result in large loops of the polymer chain free in the solvent. In the equilibrium situation, the higher molecular fraction will be preferentially adsorbed[8]

because there are more points of adsorption and less likelihood that all of the larger number of adsorbed points will desorb at the same time. However, in the short term, the smaller molecules, because of their increased mobility, will be preferentially adsorbed.[9] This could be of technological importance because glass reinforced polyester resins are made by dissolving the ester resin in styrene and applying this solution of a polymer in a solvent to the glass surface before polymerising the solvent. The cross-linking of polyester and solvent into one large molecule then impedes molecular diffusion to or from the glass interface and, contrary to the true thermodynamic equilibrium, the smaller molecules may be retained at the interface[9]. The most important of such molecules is phthalic acid[9], present as an impurity in most polyester resins.

The adsorption of polymers from solution onto glass beads has also been examined for its effect on the mobility of the polymer chains[10]. The chain segments which are strongly adsorbed, are not only unable themselves to move but materially restrict the movement of loops to which they are attached. In the case of glass reinforced polyester, adsorption of polyester is established in solvent conditions which afterwards become 'frozen' by polymerisation of the styrene. The material is then at room temperature well below the glass transition temperature of the resin but this temperature, which reflects segment mobility, is influenced by the adsorption phenomena which occurred during the liquid regime. Thus PMMA, unfilled, showed a glass transition temperature of 62°C which was raised to 77°C by the addition of 5 per cent (by weight) of glass beads and to 86°C by the addition of 30 per cent[10].

Little is known of the structure of bulk polymers outside the field of crystallites and crystallisation phenomena. Where the polymer has been prepared by an emulsion process, there is evidence, even after processing, that the latex particle persists as a unit. Possible structural orders have recently been discussed[11, 12] but there are as yet, no generally accepted ideas. The presence of carbon black[11] or silica[12] in natural rubber is known to change the X-ray diagram, and the appearance under the electron microscope encourages the belief in the presence of microcrystallites in the immediate neighbourhood of the filler particle.

Russian workers[13] have emphasised the differences which must exist between wetting of a surface—and therefore of a powder—by a low molecular weight liquid and a polymer. Thus polyacrylic acid, which would be expected to wet crystalline aluminium hydroxide, does not do so according to the appearance of electron photomicrographs which show only occasional point contact between the two materials. Similar photomicrographs were obtained with

polyisobutene and carbon black though when adsorption took place from solution (in toluene) the boundaries of separate particles were no longer apparent and wetting seemed complete. The point is made that adsorption of a polymer chain onto a surface must involve a large entropy term which could completely alter the energetics of the system when polymer and powder come into contact with the former in its fully coiled state. The work of mixing the powder into the polymer may be in part a necessary uncoiling and straining of polymer molecules in contact with powders in order that the polymer may have a conformation suitable for wetting the powder.

1.6   THE INFLUENCE OF FILLERS ON THE PROPERTIES OF POLYMERS

It is not proposed to deal with the very complicated data which exist on the important technological properties of polymers and the way they can be modified by fillers. This section is concerned solely with generalised properties conferred by any filler, independent of its nature.

The theory of the increase in modulus which fine particle fillers cause when incorporated in a polymer is derived from that evolved for the increase in the viscosity of a liquid carrying rigid particles in suspension. This exercise in hydrodynamics was first successfully studied by Einstein[14] who considered the case of a dilute suspension of rigid spheres. Shearing of the liquid by the flow process results in shearing forces across the diameter of the spheres which act as couples producing rotation. This absorbs energy which shows as an increase in viscosity. If the ratio of the viscosity of the suspension to that of the pure liquid is η_{rel}, Einstein showed that for a dilute solution $\eta_{rel} = 1 + 2 \cdot 5c$, where c is the volume concentration of the spherical particles. The equation shows the relative viscosity to be independent of the size of the spheres and of their chemical nature. If the concentration is increased interaction occurs between liquid near the surfaces of neighbouring spheres and further energy is dissipated. The equation becomes[15] $\eta_{rel} = 1 + 2 \cdot 5c + 14c^2$ and further elaborations concern non-spherical particles and higher concentration. This theory, simple in conception, has been applied to elastic behaviour with modulus replacing viscosity and particle shape becoming of greater significance; the development of theories and equations representing elastic behaviour is reviewed by Mullins[16] with particular reference to elastomer behaviour. Because of the importance of the unique reinforcement conferred by carbon black on

hydrocarbon elastomers, this filler has been studied more than any other and discussion of its reinforcing effect is reserved for Chapter 3 of this monograph. However, it is necessary to state here that the reinforcement of elastomers by certain carbon blacks involves enhancement of properties other than modulus. An increase of modulus, that is stiffening, is shown by any filler, though recent work suggests that the magnitude of the effect is not as independent of particle surface as has been assumed and that although physical adsorption and chemisorption is involved, the more nearly the atoms of the polymer can coincide with those of the filler[17], the greater the interaction between polymer and filler and the greater the modulus change. This question of fit between adsorbate and absorbent atoms, the question of valence bond length of the polymer matching the interatomic distances of the crystal face of the filler, involves the entropy of adsorption and was discussed some years ago in relation to adhesive forces[18].

1.6.1   CHANGE IN STRENGTH

With the exception of carbon black in rubbers with hydrocarbon main chain structure and to a lesser extent fine particle silica in the same rubbers but also in silicon rubbers, the addition of particulate fillers will decrease the tensile strength of a polymer more or less in proportion to the volume present. Fibrous fillers behave differently provided that the volume loading is sufficiently high, the length-to-diameter ratio sufficiently large, and the fibres themselves strong. With these conditions satisfied the tensile strength, as also the stiffness and flexural strength, is determined almost wholly by the fibre or filament. The properties are markedly anisotropic and even randomly oriented chopped strand mat from glass or asbestos fibres has properties uniform in two and not three dimensions.

However, although fibre reinforcements are discussed in Chapters 5–8, it is in many of the cases discussed a colloquial misuse of language to call the fibrous material a filler for the polymer. The question concerns whether the stress is borne substantially by the fibres or filaments, the polymer serving only as a binder or coating material, or whether the stress is substantially sustained by the polymer. Glass reinforced polyester, for example is load-bearing in tension solely because of the strength of the glass, the resin being the means of transferring the stress in shear over the large interface, from the the outside to the filaments and from filament to filament inside the bulk.

1.6.2 EFFECT OF EXTENSION

The increased modulus caused by fillers is associated with a reduction in the breaking strain. Apart from the carbon black and silica reinforced rubbers, the strain energy of the polymer (the product of tensile strength and strain or 'the area under the curve'; sometimes called the *toughness* of the material) is reduced by particulate fillers. At strains approaching the breaking strains, many transparent polymers show internal crazing which gives a whitened appearance due to the formation of internal flaws, the boundaries of which act as reflecting surfaces. It might be expected that such flaws would develop when a crystalline powder is mixed into a polymer for whether this is rigid or flexible it will be far less rigid than the powder. If the particles are spherical, elongation of the filled material might be expected to cause separation at the interface due to imperfect wetting of the powder and the prior existence of microflaws. The wetting of the powder by the polymer should, however, be almost perfect because crystalline powders have surfaces of very high energy and mixing is carried out at temperatures where surface tension and viscosity are relatively low. The adhesion of polymer to powder will then exceed the cohesion of the polymer and failure should occur in the polymer were it not for additives of low cohesive strength which preferentially adsorb at the interfaces and allow separation to occur.

A PVC compound filled at 25 per cent of its volume with glass beads showed a 10 per cent increase in volume on extension[19]. This was just the theoretical increase if complete breakaway occurs with the formation of cone-shaped voids on the aspects of the spheres in the stress axis. On the other hand a range of rubbers showed very little breakaway from barium sulphate and calcium carbonate particles at 100 per cent extension and even at elevated temperatures the volume increase on extension was only a small fraction of that predicted for cone-shaped voids[20].

1.7 THE POSSIBILITY OF CHEMICAL INTERACTION SURFACE ENERGY AND THE DISPLACEMENT OF ADSORBED MATERIALS

The interface which has been studied the most is that of resin–glass in glass reinforced plastics[21]. If untreated glass is used with a polyester resin, immersion in water is rapidly followed by the appearance of water at the glass–resin interface. Water diffuses through the resin and displaces it from the glass surface. The surface free

energy of glass is, for a number of reasons, not easy to define, but if the glass is treated with vinyl trichlorosilane, a low energy surface is obtained whose γ_c can be measured easily. The work of adhesion of water to this surface can also be obtained and since the water displaces the resin from the surface treated with the siloxane as easily as from the bare surface, the work of adhesion of water must be greater than that of resin[22]. When certain other so-called coupling agents are used on the glass, the appearance of water at the interface is delayed and some process other than diffusion determines the rate. In these cases physical displacement of the resin is impossible until hydrolysis of chemical bonds has occurred indicating a true coupling of the surfaces by chemical linkages[23]. The various ways of achieving this are discussed in Chapter 7.

1.7.1   CHEMISORPTION

Although there is not much unambiguous, direct evidence, there is also little doubt that siloxane molecules are irreversibly adsorbed (chemisorbed) onto glass and silica surfaces and, by suitably reactive organic groups attached to the silicon atom by a carbon chain of sufficient length to render them accessible, chemical linking to polymers can be achieved. Similarly, amines are strongly adsorbed onto clay minerals and can thus provide, by giving them a long hydrocarbon chain, a low energy, hydrophobic surface. It must be emphasised that such a surface does *not* provide better adhesion with a hydrocarbon; the work of adhesion will be less but so also will the work of adhesion of water, and hence water is *not* preferentially adsorbed and it is therefore a surface from which polymers are not displaced when the compound is placed in water. As has already been explained, the low surface energy probably also results in a modification in the mode of adsorption, some surface mobility allowing adjustment to strain and thus preventing immediate desorption on extension of the compound. This may also be of importance in procuring dispersion of the powder in the polymer although the reason for increased dispersibility of coated fillers is most likely the direct reduction in inter-particle adhesion due to replacement of electrostatic charge attraction by simple van der Waals dispersion forces.

1.8 , CONCLUSIONS

Powders interact with the polymer matrix but much of this interaction is general in nature and is independent of the chemical