Chapter 2

Literature Survey

Natural Bone

In biological terms bone is described as a connective tissue. Connective tissue is the tissue which support the various structures of the body. In mechanical terms bone is a composite material with several distinct solid and fluid phases. Human bones may be described as one of the five general categories : long bones such as the femur and humerus, short bones such as wrist and ankle, flat bones such as the skull, irregular bones and sesamoid bones.

Bone is unique within the body because it is hard, and it is hard because the extracellular collagenous matrix, the major organic component of all connective tissue, is impregnated with a mineral phase, principally hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ or very similar crystals. The size of hydroxyapatite about 5 nm x 20 nm x 40 nm (Glimcher and Krane, 1968) and its stiffness is approximately two-thirds that of steel. However, it is also quite brittle with poor impact resistance. The mineral crystallites are in intimate juxtaposition known as epitaxy in an arrangement with the collagen fibrils because there is a nucleating site occur due to collagen provide an array of charged groups spaced in the same manner as the ions in the hydroxyapatite crystal lattice (Glimcher, 1984). In fact bone has a complex hierarchical structure, which is heterogeneous and anisotropic (Fig. 2.1.1).

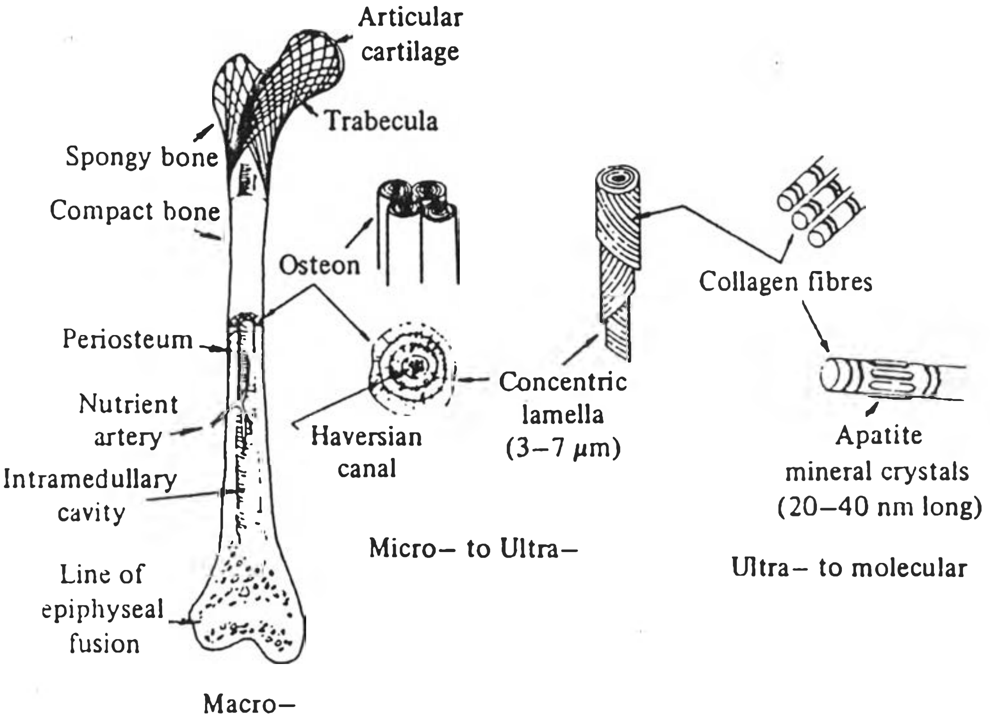

Figure 2.1.1 Microstructure and macrostructure of bone (from Katz, 1980).

In mature cortical bone the collagen-hydroxyapatite composite is formed into densely packed concentric lamellar structures, the Haversian system or osteon. The osteon is a cylindrical structure whose long axis courses somewhat irregularly along the long axis of the bone. The thin layer between adjacent osteons is called the cement line. The osteon so formed is probably the basic mechanical unit of compact Haversian bone. Haversian bone is probably the commonest form of bone in the human skeleton and other vertebrates. In the very young the long bone are composed of woven bone with a few osteons, called primary osteons. With maturation the woven bone is converted to laminar bone and haversian bone, called secondary osteons. Down the middle of the osteon runs a blood vessel.

An assessment of the mechanical behaviour of bone may be made on sections prepared with careful machining into standard specimens, such as those used for conventional material testing. Cortical bone has anisotropic mechanical properties with a maximum parallel to, and a minimum perpendicular to, the long axis (Bonfield, 1984). The stiffness of cortical bone, as represented by the Young's modulus varies between 7-30 GPa, depending on orientation, location and age. A standard tensile test of wet cortical bone at ambient temperature at a quasistatic strain rate gives an almost linear stress-strain curve, with a small viscoelastic component, and reaches a maximum point in brittle fracture at a total strain of only 0.5-3.0 %. The values of ultimate tensile strength (~50-150 MPa) are less critical than a measure of its fracture toughens, which has been established, with a critical stress intensity factor (K_{IC}) of ~2-12 $MNm^{-3/2}$ and a critical strain energy release rate (G_{IC}) of ~ 500-6000 Jm^{-2} (Bonfield, 1987a).

Materials for Bone Replacement

Animal bone and ivory have been employed in orthopaedic prosthesis in the past. But it is difficult to ensure the supply of these materials with adequate and predictable mechanical strengths (Bonfield, Grynpas and Bowman, 1980). Accordingly, surgeons have resorted to a variety of synthetic engineering materials whose maintained in the body over a long period of time. The materials used for implantation should be biocompatible in the body environment. In addition, the materials selected must withstand the normal physiological forces without fracture, either in the short term associated with overloading or in the longer term due to fatigue or stress corrosion.

The bone replacement materials consist of a large group of metals, ceramics, polymers, and composites.

1. Metals

Metal implants are used as structural, load-bearing materials in devices for fracture friction, partial and total joint replacement devices, instruments, and external splints, braces and traction apparatuses (Black , 1988). The principal reasons for this popularity are that metals have high yield stresses and sufficient ductility to ensure that stresses exceeding the yield point produce plastic deformation than brittle fracture and ease of fabrication into parts by a wide variety of conventional techniques.

An immense variety of metals and alloys have been clinically tested in prosthetic applications (Ludwigson, 1964). However, most metals are either not resistant to the corrosion by body fluids (e.g. aluminium), react with body tissue (e.g. copper) or lack sufficient strength to serve as a structural prosthesis (e.g. gold). The few materials used in endoprostheses are 316 stainless steel, cobalt based chromium-molybdenum alloys and titanium or titanium alloys. The selection between cobalt-chromium alloy and stainless steel is comparable Young's modulus values. Titanium is less stiff than either stainless steel or cobalt-chromium and less stress shielding for a similar cross section. Titanium alloy (Ti-6%Al-4%V) is already effectively optimized in terms of its metallurgical structure.

There have been many attempts to provide better fixation of a metal implant in bone by using porous materials to help ingrowth of bone tissues. Future improvements in fatigue and ultimate strength characteristics may depend on the use of potentially higher strength and lower modulus (Bonfield, 1987b).

2. Ceramics

The class of materials called "ceramic" may include a variety of substances that are nonmetallic and inorganic in nature and generally consist of clay or other silicates. A bioceramic is a ceramic used as a biomaterial. Bioceramics are classified into three sub-groups based on their chemical reactivity in the physiological environment as shown in Table 2.2.1. A fourth classification would be composites consisting of bioceramics used in combination with other material systems such as metals or polymers.

Table 2.2.1 Bioceramic classifications (Hulbert *et al.*, 1987)

A. Nearly Inert Bioceramics
- Al_2O_3 - High alumina ceramics
- LTI carbon - Low temperature isotropic carbon
- ULTI carbon - Ultralow temperature isotropic carbon
- Vitreous carbon - glassy carbon

B. Surface - Active Bioceramics
- Hydroxyapatite (HA) ceramics
- Surface-active glasses
- Surface-active glass ceramics

C. Resorbable Bioceramics
- Calcium sulphate
- Trisodium phosphate
- Calcium and phosphate salts

D. Composites
- Bioceramic coating on metal
- Carbon coating on metals and polymers - ULTI carbon
- Hydroxyapatite - autogenous bone
- Surface-active glass ceramics - PMMA
- Surface-active glass - metal fibers
- Polylactic acid (PLA) - carbon fibers
- Polylactic acid (PLA) - hydroxyapatite (HA)
- PLA - calcium/phosphorous-base glass fibers

Nearly inert bioceramics undergo little or no chemical change during long-term exposure to the physiological environment. Tissue response to inert bioceramics involves the formation of very thin fibrous membrane surrounding the implant material. Alumina ceramics are beginning in orthopaedic compressive load-bearing applications because of the materials low coefficient of friction and excellent wear resistance. LTI carbons are widely used in the construction of prosthetic heart valves because they have exceptional wear and fatigue properties (Bokros and Akins, 1971).

A characteristic of surface-active bioceramics is that they bond to bone with no fibrous tissue at the interface. The glass ceramics containing apatite and wollastenite developed recently by Kokubo and his associates in Japan and used as vertebral prosthesis by Yamamuro (Kokubo *et al.*, 1985). Because of its ability to chemically bond to bone, hydroxyapatite (HA) is rapidly becoming the material of choice for many dental and maxillofacial applications. Moreover, the use of HA to coat porous metal prosthesis to stimulate bone ingrowth shows much promises in cementless fixation of orthopaedic prosthesis.

The resorbable bioceramics include calcium sulphate (Plaster of Paris), trisodium phosphate and a wide variety of calcium and phosphate salts. The purpose of this group is to provide a temporary scaffold or space filler until such time as a body can replace it.

Among these, HA is of particular interest as its chemical composition in very similar to that of the mineral content of bone. It is a calcium phosphate including hydroxide which chemical formula is

$Ca_{10}(PO_4)_6(OH)_2$ and its Ca/P ratio is represented as 1.67. It shows a very slow rate or a complete lack of degradation when implanted in animals. This stability is probably due to its low porosity. The use of high resolution electron microscopy (H.R.E.M.) can show the interpretation of crystallographic structure of pure HA (Hodgskinson and Bonfield, 1988).

3. Polymers

Polymeric materials have gained an important and established place within orthopaedic surgery because they are available with such a variety of compositions and properties. Also, they may be fabricated readily into complex shapes and structures. In addition, their surfaces may be modified physically, chemically, or biochemically (Hoffman, 1984).

The applications of polymers have included use as components of artificial joints due to they provided lower coefficient of friction. Polymethymethacrylate is commonly used as a bone cement for embedding the prosthetic stem within the bone shaft. Newer materials being investigated include biodegradables that eliminate a second operative procedure and employ in forms of drug delivery systems.

4. Composites

Until now, one of the major unsolved problems in orthopaedic surgery has been the mismatch between bone and implant stiffness. From Table 2.2.2 it can be seen that ceramics and metals are stiffer than cortical bone, which is stiffer than polymers. The consideration of equivalence with bone is best suited to an exact structural replacement. In addition, it has become apparent that the lifetime of conventional materials is often limited, not by a failure of them, but by a progressive loss of bone mass from the surrounding tissue leading to loosening of the prostheses (Bonfield, 1989). It should be emphasized that a comparison of mechanical properties of prosthetic materials with those of bone must be related to the design of the prosthesis.

One approach to the development of an analogous implant material for a similar structural configuration is to stiffen a polymer such as polyethylene by the addition of a suitable ceramic second phase. Hydroxyapatite (HA) was used as the particulate filler because the body recognizes HA and high density polyethylene (HDPE) was used as the matrix because its use in prostheses has shown this material to be stable in the body. The processing of such a composite is difficult, and the choice of the compounding / molding route is important to minimize polymer degradation (Abram *et al.*, 1984).

Bonfield *et al.* (1984) reported preliminary tests on various volume fractions of HA reinforcement in the HDPE matrix. The results showed in form of the elastic modulus and stress-strain behavior. From Table 2.2.3, it can be seen that Young's modulus increases progressively with an increase in HA concentration from a starting value of about 1 GPa to a maximum of 9 GPa at ~50 % fraction of HA by volume. The increase in modulus with volume fraction was accompanied by a decrease in the percentage strain to fracture measured during a tensile test at room temperature. The ultimate tensile strength (UTS) remained within a relatively narrow band of values from $\sim$22 to 26 MNm^{-2} for all the composites tested.

Bonfield (1988) reported that K_{IC} (determined as 3 $MNm^{-3/2}$) are strictly valid for the 40%-50% volume fraction range, which gave completely brittle behavior. Initial *in vivo* tests that, hydroxyapatite - reinforced polyethylene gave a satisfactory response in no adverse reaction. It was also reported that one application of the composite had been envisaged as a sleeve for a growing prosthesis.

It is important to study the *in vivo* response that the composite invokes. Bonfield *et al*., 1986 observed the composites of 0.3-0.5 volume fraction were implanted into the lateral femoral of rabbit up to 6 months. The response of the surrounding tissue was assessed using histology and electron microscopy technique. Push-out tests also presented the level of the interfacial shear strength of the implant/bone interface. Also, Doyle *et al*. (1990) studied the stages of new bone formation in tissue surrounding implants of polyethylene filled with 40 volume% hydroxyapatite.

Such a system may also be considered analogous to bone in that the components used that the collagen matrix in replaced by polyethylene, while hydroxyapatite remains as a common reinforcement. However, none of the existing materials are bone-like with respect to stiffness and fracture toughness or microstructure. The development of composites only provided an approach to an analogous bone material. The general effect has been demonstrated for polymer that Young's modulus will increase with concentration of filler, while the fracture toughness will show the reverse effect. Hence, starting with a ductile polymer matrix, and transition into brittle behavior is observed. A balance between modulus and fracture toughness is required if the properties of bone are to be matched.

Table 2.2.2 Comparison of mechanical properties of current implant materials with those of cortical bone (Bonfield, 1985).

Material	E (GPa)	UTS (MPa)	K_{IC} ($MNm^{-3/2}$)	G_{IC} (Jm^{-2})
Alumina	365	6 - 55	≈ 3	≈ 40
Co-Cr alloy	230	900 - 1,540	≈ 100	≈ 50,000
Austenitic stainless steel (EN 58)	200	540 - 1,000	≈ 100	≈ 50,000
Ti-6wt%Al-4wt%V	106	900	≈ 80	≈ 10,000
Cortical bone	7 - 30	50 - 150	2 - 12	600 - 5,000
PMMA(bone cement)	3.5	70	≈ 1.5	≈ 400
Polyethylene	1	30	–	≈ 8,000

E = Young's modulus

UTS = ultimate tensile strength

K_{IC} = critical stress intensity factor

G_{IC} = critical strain energy release rate

Table 2.2.3 Mechanical behaviour and bioactivity of various hydroxyapatite particle reinforced polyethylene composites (Bonfield *et al.*, 1984).

Hydroxyapatite volume fraction	Young's modulus (GPa)	Strain to fracture (%)	Fracture mode	Bioactivity[a]
0	1.3 ± 0.2	> 90	Ductile	x
0.10	1.4 ± 0.2	79 ± 10	Ductile	?
0.20	2.0 ± 0.1	50 ± 4	Ductile	?
0.25	2.5 ± 0.2	43 ± 3	Ductile	?
0.30	3.0 ± 0.2	34 ± 5	Ductile	?
0.35	3.7 ± 0.4	32 ± 8	Ductile	?
0.40	4.4 ± 0.7	29 ± 5	Ductile	√
0.45	5.9 ± 0.5	7 ± 3	Brittle[b]	?
0.50	7.7 ± 1.3	3 ± 1	Brittle[c]	√

[a] Bone apposition around implant.

[b] $K_{IC} = 2.9 \pm 0.3\ \mathrm{MNm^{-3/2}}$

[c] $K_{IC} = 2.4 \pm 0.2\ \mathrm{MNm^{-3/2}}$

x = not bioactive

? = not tested

√ = showed bioactivity

Biocompatibility of Implant Materials

Biomaterials, which are used in contact with biological fluids, have to meet certain chemical, physical and biological requirements in order to ensure optimal and lasting function of the implant. Technical requirements have been discussed with respect to physical and chemical properties such as strength, wear behaviour, corrosion resistance, as well as workability and sterilizability. Body tolerance and body stability constitute the biological requirements, being the important factor. In general, biologic responses devided into two types according to the body systems : tissue and blood responses (Hoffman, 1984).

1. Tissue responses

The major response to implants is the inflammatory process. Whether the foreign body is a molecule or a solid particle or object, there is inflammation in the vicinity and the proteins and cells attempt to digest the foreign element and convert it to tolerable metabolites. However, most implants are not readily metabolized and then the alternative fate is to be encapsulated in a fibrous collagen scar tissue capsule. If the biomaterial is porous, their tissue may be deposited within the pores, and the thickness of the encapsulation is decreased. The thinner the membrane, the better the compatibility.

In some cases the material may evolve toxic substances and cause tissue necrosis-reactive and remodeling changes from physically induced tissue damage. For example, a loose acetabular cup in a total hip replacement may cause the formation of necrotic debris (Meachim, 1976).

2. Blood responses

The major response of blood to any foreign surface is first to deposit a layer of proteins called a thrombus. The character of the thrombus will depend on the rate and pattern of blood flow in the vicinity. Thus, the design of the biomaterial system is particularly important. The thrombus may break off and flow downstream as an embolus and this can be a very dangerous event. In some cases the biomaterial interface may eventually "heal" and become covered with a "passive" layer of protein and/or cells. Growth of a continuous monolayer of endothelial cells onto this interface is the one most desirable end-point for a biomaterial in contact with blood.

As a result, a compatible implant should have no deleterious effect on the adjacent tissue. The cells should show no abnormalities, no variant type cells, there should be no inflammatory reactions and no cell necrosis. The histology of the tissue surrounding the implant should be normal.

Particulate-filled Polymer Composites

In general, the behaviour of the composite depends not only on the individual properties of the two components and on their relative proportions, but also on the size, shape and state of agglomeration of the minor component, and on the degree of adhesion between the filler and the matrix.

When considering the general behaviour of particle-filled plastics, it is convenient to consider the behaviour of brittle glassy plastics, such as the epoxides, unsaturated polyesters and polymethylmethacrylates, separately from that of the tougher semi-crystalline plastics such as polyethylenes and nylons. The former generally have relatively low elongations to failure, of the order of a few percent, and low fracture energies of a few hundred Jm^{-2}, while the latter have fracture strains which can be over 100% and fracture energies of the order of several tens of thousands of Jm^{-2}.

1. Particle-filled brittle plastics

In tension and flexure, unfilled thermosets have fracture with little or no yielding at strains of the order of two or three percent. In compression and shear they generally yield and are capable of relatively large amounts of plastic deformation before fracture. Addition of particulate fillers usually decreases the stress at which fracture occurs in tension and flexure, increases the stress at which yielding occurs in compression and improves the elastic moduli (Phillips and Harris, 1977).

Roulin-Moloney, Cantwell and Kausch (1987) found that increasing filler volume fraction increases the modulus and toughness and can give castings with strength comparable to the matrix. Changing the filler particle size at constant volume fraction does not have significant influence on the modulus of the composite.

Increasing the filler modulus increase the modulus of the resulting composite. This is clearly shown in Fig. 2.4.1 for an epoxy resin filled with silica, alumina and silicon carbide particles. The modulus of these fillers are 94, 320 and 469 GPa respectively. Similarly, increasing the modulus of the filler increase the stress intensity factor (K_c).

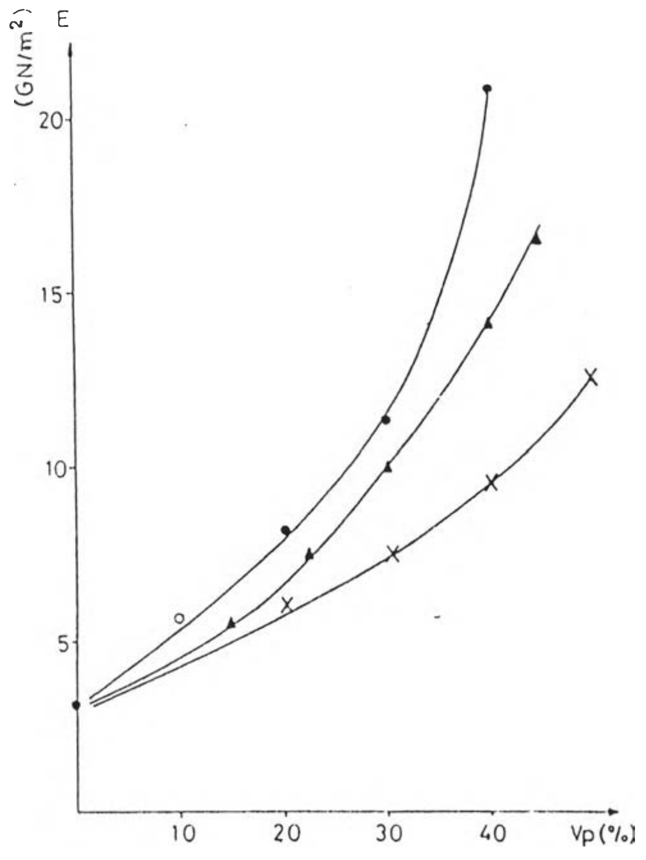

Figure 2.4.1 Flexural modulus as a function of volume fraction of filler: x,silica ; ▲,alumina ; ●,silicon carbide (from Roulin-Moloney, Cantwell and Kausch, 1987).

Phillips and Harris (1977) reported that the effect of the fracture surface energy is complex, and significant increases can be obtained because the particles inhibit crack growth. In absolute terms this added resistance to crack propagation is not large, but because the fracture energies of the unfilled resins are low so it can be quite significant and may be two or three times the fracture energy of the resin.

The enhancement of the fracture energy of a brittle plastic by the addition of particulate fillers has important implications for strength by reducing its strength. The strength of a brittle solid is controlled by a combination of its fracture energy, Young's modulus and the size of the fracture initiating flaw, through the Griffith equation

$$\sigma = \sqrt{\frac{2E\gamma_F}{\pi c}} \qquad (2.4.1)$$

where γ_F is the fracture energy and c is the size of fracture initiating flaw. It can be seen that the size of the primary fracture flaw is the significant effect for strength of a brittle solid.

2. Particle-filled tough plastics

Addition of particulate fillers to tough thermoplastics tends almost always to reduce their toughness. The tough plastics are intrinsically capable of absorbing a great deal of energy during fracture, primarily through shear deformation processes or crazing, having values of fracture energy of 10^3 to 10^4 Jm^2. Particulate fillers are generally added to thermoplastics to reduce their cost, improve their stiffness, compression strength and moulding characteristics.

Table 2.4.1 shows data for Nylon 66 and Nylon 66 containing 30 wt% of glass beads. Addition of filler considerably reduces the tensile elongation at break and the impact energy, while the tensile strength is relatively unaffected and the compressive strength and stiffness are increased. The general nature of the behaviour can be discussed by considering the influence of glass sphere fillers on nylons (Scott and Phillips, 1974) and poly(phenylene oxide) (Wambach *et.al.*, 1968; Trachte and DiBenedetto, 1971).

Figure 2.4.2 shows the general tensile deformation behaviour of unfilled Nylon 6 (Scott and Phillips, 1974) . At low loads the material is elastic, but as the load is increased the load versus extension behaviour becomes non-linear as some yielding occurs. The load reaches a maximum at the upper yield stress and there follows a period of homogeneous yielding during which deformation occurs under a fairly constant load. Deformation then becomes inhomogeneous with the formation of a neck which gradually extends into the unnecked region (cold-drawing). Fracture finally occurs in a brittle manner in the necked region. Nylon 6 containing 30% of glass spheres also exhibits an upper yield stress, but there is no necking and fracture occurs at a relatively low elongation(<10% compared with values in excess of 30% for unfilled Nylon 6).

PPO is a fairly tough plastic with a fracture energy of 5.3 kJm^{-2}. Fracture energies of the filled and unfilled PPO were measured (Wambach *et.al.*, 1968; Trachte and DiBenedetto, 1971) by linear elastic fracture mechanics techniques using double-edge-notched specimens. A significant

Table 2.4.1 The mechanical properties of unfilled nylon 66, and nylon 66 containing 30% of glass spheres (Scott and Phillips, 1974).

Property	Test Method	Nylon 66	Nylon 66 + filler
Tensile strength	ASTM D638-64T	72 - 79 MNm^{-2}	86 - 90 MNm^{-2}
Elongation at break	ASTM D638-64T	30 - 35 %	5 - 10 %
Impact energy	BS 306B and C	7 J	1 J
Compressive strength	ASTM D695	83 MNm^{-2}	138 MNm^{-2}
Flexural modulus	ASTM D790-66	2.5 GNm^{-2}	2 - 4.5 GNm^{-2}

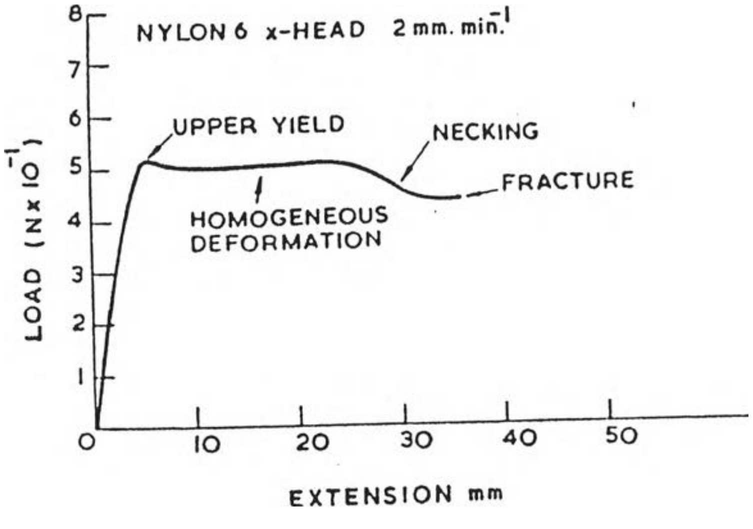

Figure 2.4.2 The tensile behaviour of unfilled nylon 66 (from Scott and Phillips, 1974) .

difference between the filled and unfilled material was the effect of specimen thickness on measured toughness values.

The glass bead used to fill the PPO were used both in an untreated state, and also treated with a silane coupling agent to increase the filler-matrix adhesion. Improving this adhesion affected the tensile yield behaviour considerably, as shown in Fig. 2.4.3, but had a far smaller effect on the fracture energy (Fig. 2.4.4). Both the treated and the untreated glass filler reduced the fracture energy with increasing filler volume fraction. Although the fracture energies were not very different for the two surface conditions, the better-bonded filler produced a rather less tough composite and this was reflected in the appearance of the fracture surfaces.

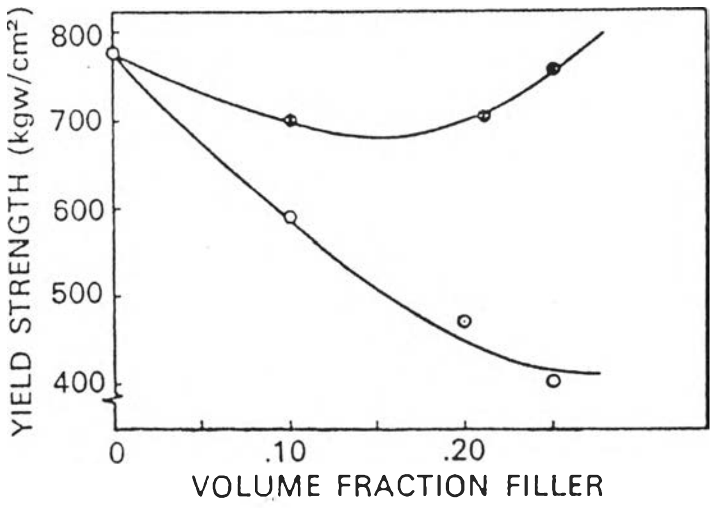

Figure 2.4.3 Effect of volume fraction of glass beads on yield strength of poly (phenylene oxide). (◎) Untreated ; (⊗) A-1100 treated (from Wambach *et.al.*, 1968). Note that the upper curve corresponds to ultimate strength, for fracture occurred prior to yielding.

Similar effects have been observed in Nylon 6 an Nylon 66 filled with similar, untreated glass spheres (Scott and Phillips, 1974). The Nylon 66 tends to bond better to the glass than does the Nylon 6 and, as in the case of treated and untreated glass spheres in PPO, this results in a material with lower toughness. In the tougher composites of glass beads in Nylon 6 and untreated glass beads in PPO, there are regions in which the matrix debounds from the spheres and necks down between them to produce a locally ductile fracture. In the less tough composites, such debounding and necking down is not observed.

Good adhesion between filler and plastic is desirable because it improves strength, but unfortunately it increases the tendency to brittle failure and makes the material more notch sensitive. In practice a compromise must be sought.

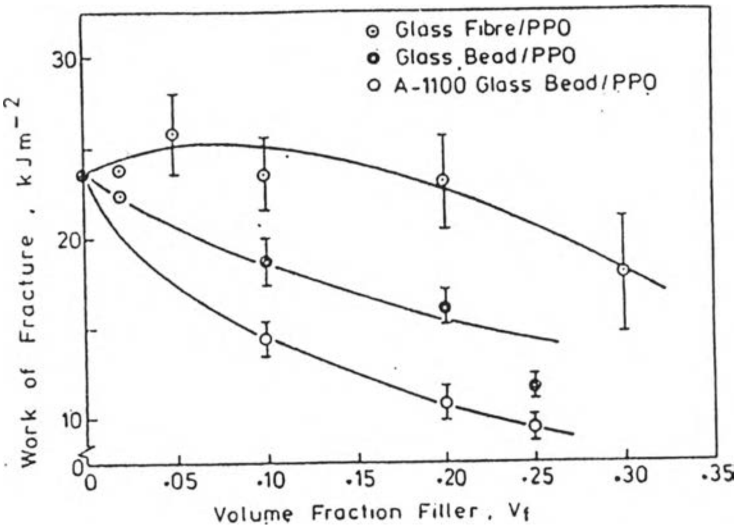

Figure 2.4.4 Effect of volume fraction of filler on fracture toughness of PPO composites (from Trachte and DiBenedetto, 1971).

Theoretical Models in Particulate-filled Polymers

The use of reinforced polymeric materials has been growing steadily and will continue to do so. It is important to have a physical understanding of polymer-filler interactions so that the best models can be developed for use. Although the mechanical behaviour in terms of the two components to the mechanical properties is complicated.

This complication arises not only from complexities of filler concentration, but also from uncertainties in the magnitude of interaction. In addition there are uncertainties in filler size distribution complicated by any agglomeration, and to what extent void formation has occurred during fabrication, and the related problem of imperfect interfacial contact between the matrix and the filler. Nevertheless, theories to describe the mechanical properties of particulate-filled polymers have been developed, with often one theory applying to one situation better than another.

1. Tensile modulus

The Young's modulus of filled materials has been represented by a large number of equations. The initial theoretical work on the effects of fillers on materials was by Einstein (1906). He has proposed a formula considering rigid, spherical, non-solvated filler particles. For the case where there is no adhesion with the matrix the model gives

$$E_R = \frac{E_c}{E_m} = 1 + \phi_f \qquad (2.5.1)$$

whereas for perfect adhesion, the relative modulus is given by

$$E_R = 1 + 2.5\phi_f \tag{2.5.2}$$

where E_R is the relative modulus, E_c and E_m are the elastic moduli of the composite and the matrix respectively and ϕ_f is the filler volume fraction.

Smallwood (1944) and Guth (1945) both considered that due to the similarity in the equation of elasticity and those of hydrodynamics it is permissible to use the approach of Einstein's equation as a basis for considering the effect of carbon black particles in rubber. Smallwood found $M^* = M(1+2.5\phi)$ by ignoring the higher powers of ϕ. Guth considered both the viscosity and modulus of elasticity and found the ratios of either the coefficient of viscosity or the moduli of elasticity of the filled to unfilled material to be

$$E_R = 1 + 2.5\,\phi + 14.1\,\phi^2 \tag{2.5.3}$$

An equation based on a mathematical model to describe the moduli of composites of a spherical filler randomly dispersed in a glassy (not elastomeric) matrix is Kerner (1956) equation. For filler which are much more rigid than the polymer matrix, assuming good adhesion between the phases, so the equation becomes;

$$E_R = 1 + \frac{15(1-\nu_m)\phi_2}{8-10\nu_m\phi_1} \tag{2.5.4}$$

where ν_m is the Poisson's ratio of the matrix and ϕ_2, ϕ_1 are the volume fraction of filler and matrix, respectively.

For the special case of the matrix and filler respectively taking on values of Poisson's ratios of 0.5 and 0.25, Van der Poel (1958) has reported the following equation which has found some application :

$$E_R = 1+\left(1.25\phi_2 / (1-1.28\phi_2)\right)^2 \qquad (2.5.5)$$

Thomas's equation (1965) is a semiempirical relationship based on data generated with monodispersed spherical particles ;

$$E_R = 1+2.5\phi+10.05\phi^2+A\exp(B\phi) . \qquad (2.5.6)$$

The coefficient A and B were 0.00273 and 16.6, respectively, and the variance of equation was 0.152.

Halpin (1969) and Tsai (1968) have shown that the Kerner equation and many other equations for moduli can be put in a more general form. Lewis and Nielsen (1970) then showed how the equation can be generalized still further to :

$$M_R = \frac{1+AB\phi_2}{1-B\psi\phi_2} \qquad (2.5.7)$$

where M_R is the relative of any modulus--shear, Young's or bulk. The value of A for any Poisson's ratio of the matrix (ν_m) is

$$A = \frac{7-5\nu_m}{8-10\nu_m} \qquad (2.5.8)$$

and $$B = \frac{M_2/M_1-1}{M_2/M_1+A} \qquad (2.5.9)$$

where M_2 and M_1 are the modulus of filler and matrix, respectively. The factor ψ depends upon the maximum packing fraction ϕ_m of the filler. Two empirical functions are :

$$\psi = 1 + \left(\frac{1-\phi_m}{\phi_m^2}\right)\phi_2 \qquad (2.5.10)$$

and $$\psi\phi_2 = 1 - \exp\left(\frac{-\phi_2}{1-\phi_2/\phi_m}\right) . \qquad (2.5.11)$$

(reduced volume fraction)

Table 2.5.1 gives values of ϕ_m for different packing of spheres and aligned rods. Some of the effect due to filler agglomeration or flocculation can be considered from the Mooney (1951) equation for the modulus of suspension of spheres :

$$E_R = \exp\left(\frac{K\phi}{1-\phi/\phi_m}\right) \qquad (2.5.12)$$

where K is a constant usually 2.5. A comparison of the Mooney, Kerner and modified Kerner equations is given in Figure 2.5.1.

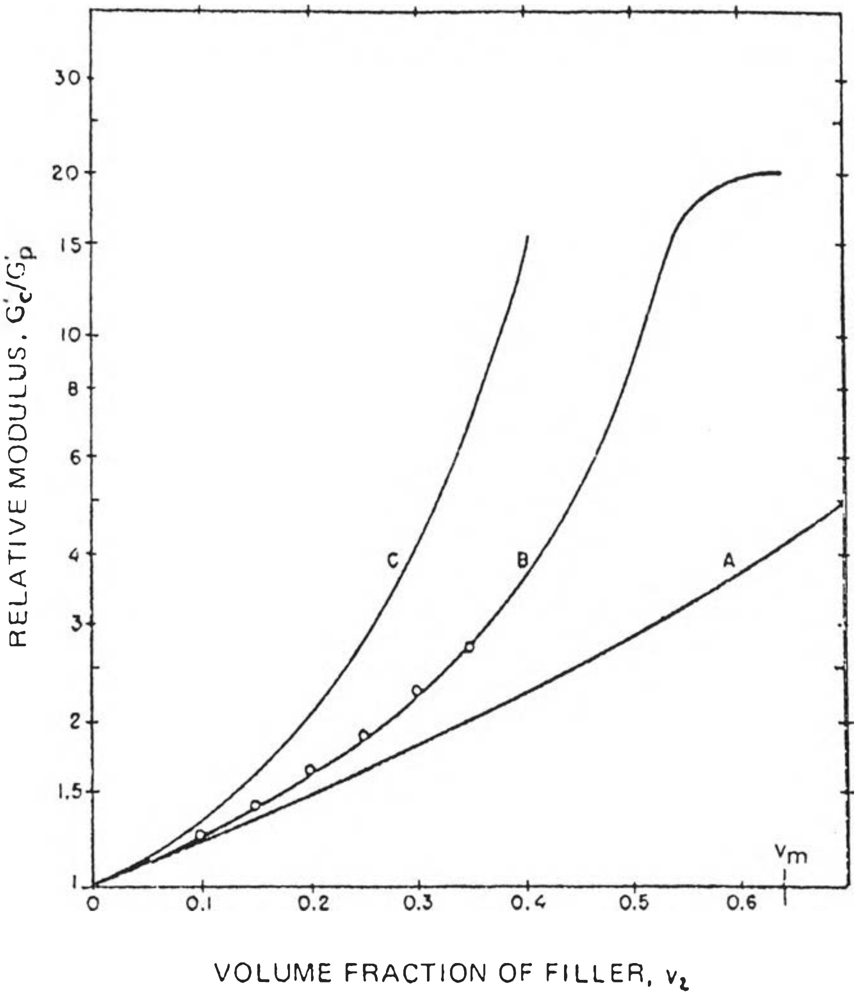

Figure 2.5.1 Dependence of relative modulus (composite/polymer) on concentration for (A) the original Kerner equation ; (B) the modified Kerner equation ; (C) the Mooney equation. Circles correspond to experimental results. Solid curves are calculated with $\nu = 0.35$, G_f/G_p (relative modulus) = 25, and ϕ_m = 0.64 (from Lewis and Nielsen, 1970).

Table 2.5.1 Maximum packing fraction, ϕ_m (Nielsen, 1974).

Particle	Type of Packing	ϕ_m
Spheres	Hexagonal close packing	0.7405
”	Face centered cubic	0.7405
”	Body centered cubic	0.60
”	Simple cubic	0.5236
”	Random close packing	0.637
”	Random loose packing	0.601
Fibers	Parallel hexagonal packing	0.907
”	Parallel cubic packing	0.785
”	Parallel random packing	0.82
”	Random orientation	0.52

2. Tensile strength

This property has not received the same level of theoretical attention as the modulus of the composites because of the complexity of fracture mechanisms such as the failure modes, the nature of the polymer-filler adhesion and the particle size and shape. Tensile strength increases as particle size decreases. The reason for this phenomenon is not entirely clear, but the increase in interface area per unit volume of filler as particle size decreases must be an important factor.

Nielsen (1966) has proposed a model for estimating the tensile strength for the case of no adhesion between the filler and matrix, as follow ;

$$\frac{\sigma_c}{\sigma_m} = (1 - \phi_f^{2/3})S \tag{2.5.13}$$

where S is the stress concentration function, which can have a value between 0.5 to 1.0. According to this model filler particles cannot carry any of the load and all the load must be carried by the polymer. When the material breaks, the fracture travels from one filler particle or void space to another.

According to the Schrager (1978) model, a volume of matrix is associated with each embedded spherical particle, which is affected by the presence of the embedded particle. The equation proposed by Schrager is

$$\frac{\sigma_c}{\sigma_m} = \exp(-\gamma\phi_f) \tag{2.5.14}$$

where experimental constant γ was found to be equal to 2.26.

3. Elongation to break

Generally fillers cause a dramatic decrease in elongation to break, for the reason that the actual elongation experienced by the polymer matrix is much greater than the measured elongation of the specimen (Nielsen, 1966). The theory is complex, depending upon the exact fracture mechanism. However, simple models give a qualitative and often a semi-quantitative understanding of experimental results.

If the adhesion between the rigid filler and matrix is good and if the fracture surface is not smooth but propagates from particle to particle, the following equation is expected to be approximately correct :

$$\frac{\varepsilon_c}{\varepsilon_m} = (1- \phi_f^{1/3}) \qquad (2.5.15)$$

where ε_c and ε_m are the elongation to break of the composite and matrix, respectively. This equation is plotted in Figure 2.5.2.

It can be shown that the dramatic decrease occurred by only small amounts of filler. If there is poor adhesion, or if the fracture surface is smooth, the elongation to break may decrease more gradually than equation 2.5.16 would indicate.

Compounding Process

The need for new application areas of polymeric materials results in increasing modified the properties of polymers to produce high performance or added value polymer systems. This may be achieved by incorporating additives such as filler and reinforcements, by blending polymers of differing chemical composition and physical characteristics or by controlled morphological tailoring by a reactive process.

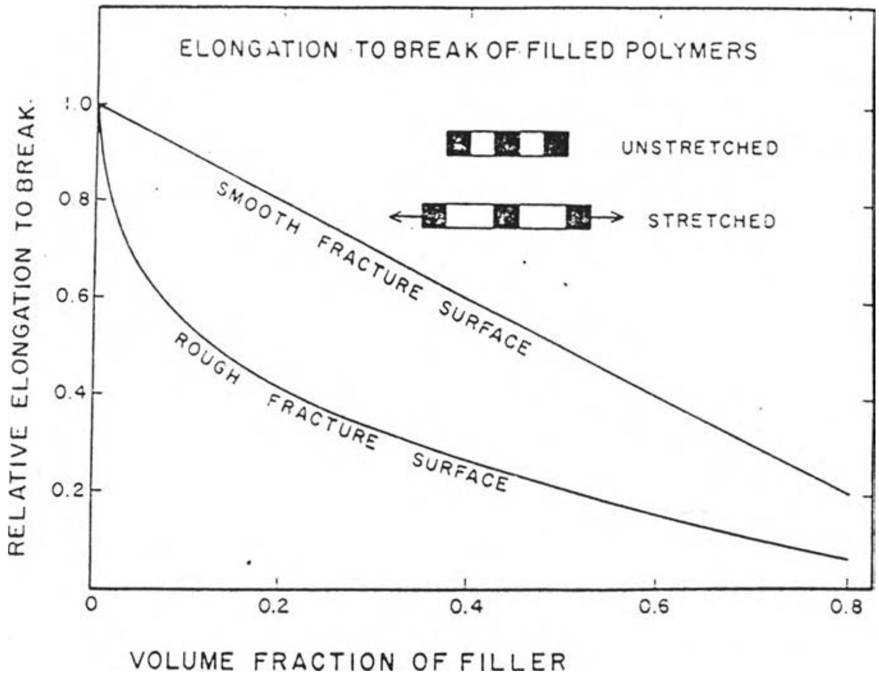

Figure 2.5.2 Theoretical curves for the relative elongation to break of filled polymers as a function of filler concentration (from Nielsen, 1974).

The basic aim of any compounding process is to mix together two or more different materials into a single homogeneous mass with uniform composition. The correct choice of compounding machinery will depend on a number of factors related to the nature of constituent materials. The mechanism involved in continuous compounding operations is to bring together controlled ratios of the constituent materials and to induce physical motion of the ingredients in such a manner that mixing occurs. With high viscosity liquids, such as polymer melts, the motion induced is primarily connective and mixing occurs by laminar flow.

Twin screw extruders are being used preferentially for a wide variety of polymer compounding operations. Janssen and Smith (1976) presented four different types of twin screw extruders. The screws can rotate in the same or in the opposite directions (co-rotating or counter-rotating extruders). In either case the screws can be intermeshing or non-intermeshing (Fig.2.6.1). In particular co-rotating twin screw extruders are being used in preference to counter-rotating twin screws due to their greater mixing efficiency and their ability to process heat and/or shear sensitive polymers and additives.

Non-intermeshing twin screw extruders can be regarded more or less as two single screw machines with some interaction. With intermeshing screws the process fluid is displaced positively from hopper to die in C-shaped chambers which are moved by the screw rotation. The nature of flow and leakage in co-rotating twin screw extruder is determined by the geometry of the intermeshing zone between two screw forms.

Arising from the need for an advanced form of co-rotating twin screw compounding extruder particularly suited to the processing of polymer systems incorporating high filler loadings and heat or shear sensitive additives, the BTS series of closely intermeshing co-rotating twin screw extruder have been developed by Betol Machinery Limited (Brenner, 1987). The major constructural features of this type of extruder are shown in Figure 2.6.2.

Inherent in the design of the extruder is the high torque characteristic of the processing screws generated by judicious gear design. The high torque capability allows high shear stresses to be used which are needed for the intensive mixing action required for dispersive mixing in highly filled compounds. Accordingly, twin screw extruders are often claimed to have good flow mixing and residence time distribution characteristics. Control of residence time and enhanced dispersive mixing is achieved by the use of staggered mixing barrier elements and a variety of forms of kneading elements.

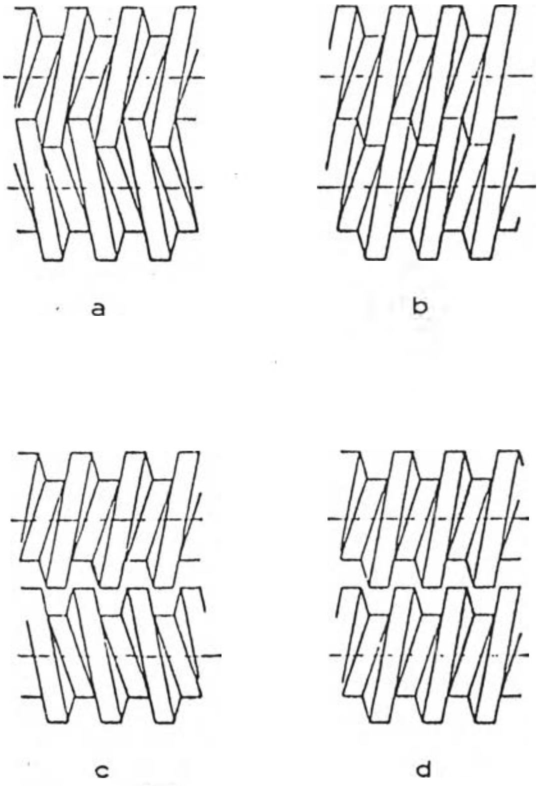

Figure 2.6.1 Different twin screw extruders *a.* intermeshing counter-rotating *b.* intermeshing co-rotating *c.* non-intermeshing counter-rotating *d.* non-intermeshing co-rotating (from Janssen and Smith, 1976).

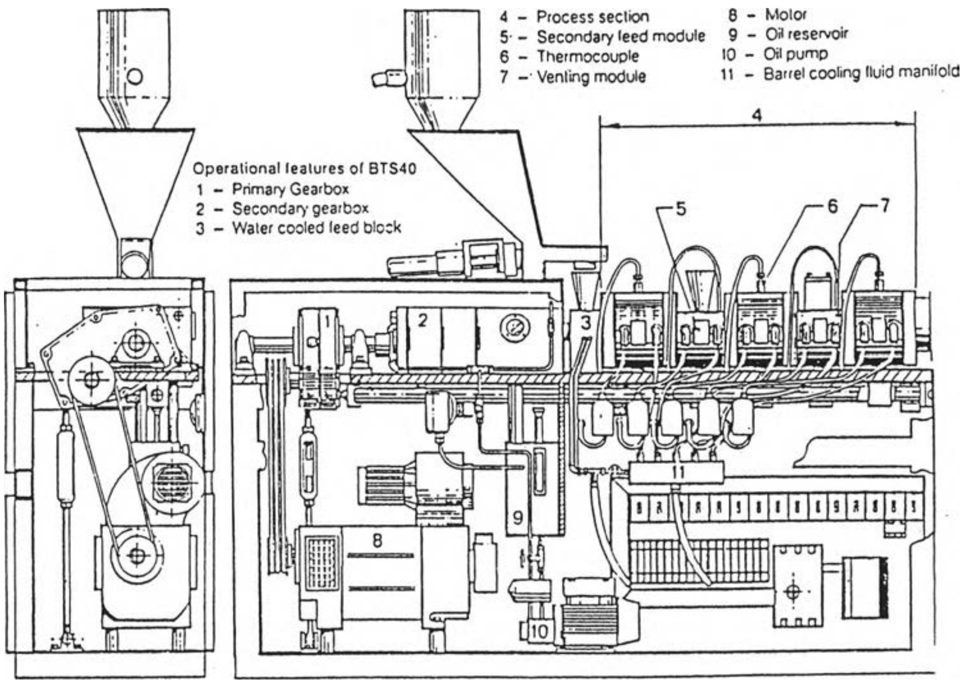

Figure 2.6.2 Constructural features of BTS extruder (from Brenner, 1987).

Abram *et al.* (1984) reported on the importance of the processing route for obtaining high toughness, high modulus, particulate reinforced composites. In this study a co-rotating twin screw compounding extruder was able to prepare highly filled compounds (based on a high density polyethylene (HDPE) matrix filled with particulate calcium hydroxyapatite) more quickly and with less damage to the molecular structure of the HDPE matrix phase when compared with compounding on a two roll mill.

Injection moulded samples of the twin screw extruded composites were tougher in terms of strain-to-break and fracture toughness at equivalent volume fractions of filler than samples from compounded on the two roll mill. However, the two roll milled composites were found to have the higher failure stresses. Significant emphasis is now being placed upon the toughness as well as the stiffness of filled thermoplastic compounds and this study demonstrates that toughness can be sensitive to the choice of compounding route whilst stiffness is relatively unaffected.