

CHAPTER II

LITERATURE REVIEW

It has been revealed recently that approximately 6 % of the population over the age of 15 suffered from some sorts of joint disturbance. The commonest conditions are forms of arthritis, these being either rheumatoid or osteoarthritis, which cause the inflation or degeneration of the joint structures. These may follow specific infection, injury, generalised disease states or change which largely paralleled the ageing process.

Osteoarthritis is present in 80-90 % of people over the age of 50 years. It is characterized by destruction of the central part of the cartilage lining the affected joint. The condition is probably a degenerative one but is definitely accelerated by any trauma to the joint. Hence, it is very common in the knee and hip joints which must withstand the burnt of the bodies weight under day to day circumstances.

Rheumatoid arthritis, on the other hand, is a systematic disease causing joint inflammation. This affects 2 % of the population, but unlike osteoarthritis is not considered to be age related. Rheumatoid arthritis starts in the small joints such as the toes and fingers but can spread to more load bearing ones such as the knee and hip. The hip and knee being synovial joints have cartilage on each articulating surface with a lubricating, shock absorbing fluid between them. Rheumatiod arthritis is characterized by the inflammation of the synovial membrane

which holds the fluid in the joint, becoming inflamed and eventually filling the gap between the articular surface causing stiffening of the joint and consequent pain.

Products from the synovium soon begin to erode into the articular cartilage and the underlying bone. The body's reaction to this is to produce more bone but does so in a non-specific manner. Consequently bony outcrops are formed in the joint and the fibrous synovial membrane becomes calcified causing in extreme cases the two bones to fuse and become completely immobilised. Once the joint surfaces have been damaged to such a degree, pharmacological methods of treatment become ineffective and total joint replacement is required to regain mobility and reduce pain. Total joint arthroplasty may be required in other cases also, such as may be needed following severe fractures to the femur in need of complete reconstruction.

Endoprosthesis and their fixation in the human body by far are the most commonly replaced joint in the human body to date is the hip where it is currently believed that there are 400,000 total hip joint replacements performed worldwide. There are a multiplicity of designs all of which vary only in relatively minor yet crucial detail, but consist basically of a long stem with a hemispherical head at one end, modelled to attain the geometry of the original femoral head. Two early designs of hip prosthesis represent two different approaches in respect of design and materials selection. McKee(8) opted for a large diameter femoral head replacement and a metal-metal combination, while Charnley(9) utilised a smaller diameter head and a metal-plastic system. The latter has proved to be the more successful from the mechanical, biomechanical, and clinical points of view, and most of the current

prostheses are based on this approach. A variety of prostheses are currently on the market with wide ranges of stem lengths and cross-sections as well as variations in ball and cup design.

The majority of femoral components are manufactured from grades of stainless steel such as 316 or cobalt/chrome/molybdenum alloys, such as vitallium, or titanium/aluminium/vanadium alloys such as Ti-6% Al-4 % V.

The single most difficult problem of hip joint as well as other joint replacements is fixation of the implant. When the weight of the body is transmitted from a prosthesis to bone at no more than three or four points of relatively small area, local pressures may be so high that crushing of the bone may occur, and a prosthesis which was tight at the end of the operation may soon become loose after carrying the weight of the body.

In 1960, Sir John Charnley(1) presents the preliminary results of a new method to anchor the femoral head prosthesis. His idea was to distribute the force over a wide area with the use of a plastic filler (bone cement) between the prosthesis and the bone. Charnley was the first to use bone cement on a large scale, and this concept of prosthesis anchorage has gained worldwide acceptance(10,1). Figures 1.1 and 1.2 shows a schematic representation of Charnley's total hip replacement and factors effecting characteristics of the joint.

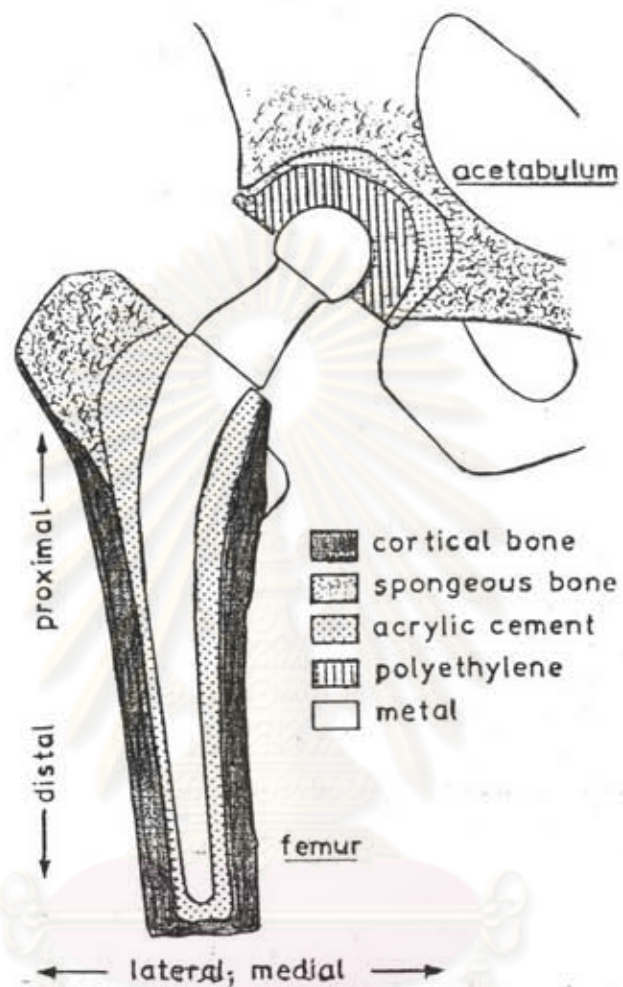


Figure 1.1 Schematic diagram showing Charnley's total hip replacement(1)

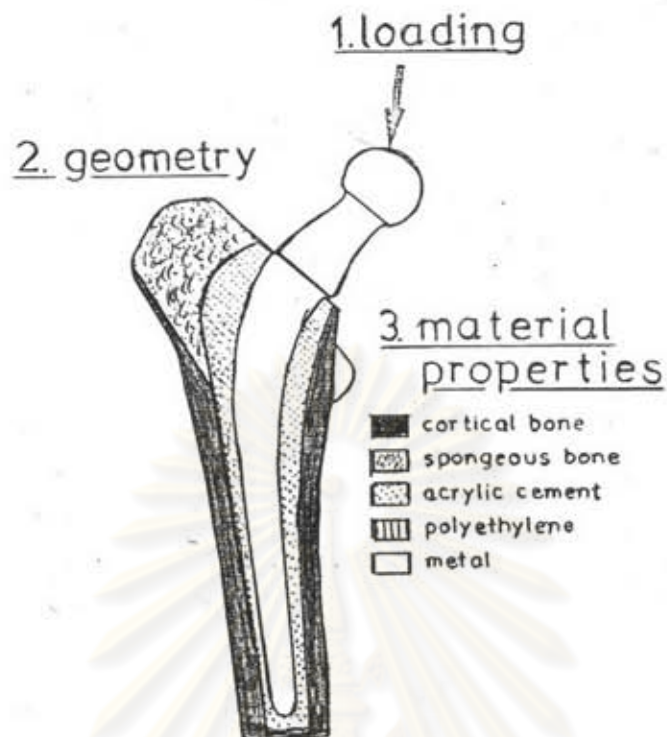


Figure 1.2 Schematic diagram showing factors effecting characteristics of joint(1)

One draw back in Charnley's hip replacement operation is the fact that it is inadvisable to employ this technique in a patient under the age of 50, particulary if the patient is energetic and required to be very active in his work or recreation.

The problem results from the poor mechanical properties of the bone cement which is a self-curing polymethylmethacrylate (PMMA). As PMMA is a brittle material with low fracture toughness, it has been reported that 10 % of all patients with total joint replacement would need a second operation within 10 years. With such long term complications, total joint replacements have been restricted mainly to older patients. Given the large number of total hip replacement operations performed annually (about 400,000) then even a relatively small failure rate has important implications in terms of the need for

revision operations. When to this number is added the unsatisfied need for long-term total hip replacement procedures in younger patients and for other joints such as the knee, then it is readily apparent that improvements in the properties of bone cement would have far-reaching consequences.

There are currently two major research initiatives in progress: first, to eliminate cement completely by developing either bone ingrowth into a porous metal stem or bone apposition at a bioactive surface; and second, to improve the mechanical properties of existing acrylic bone cement by various methods of reinforcement. All these approaches will, if successful, increase the spectrum of procedures for joint replacement.

For a number of years, synthetic materials have been routinely utilized as replacements for bone in a variety of procedures, ranging from bone grafts to total hip replacement. A necessary prerequisite for such an implant material or prosthesis is that it should be biocompatible in the sense of not producing an inflammatory reaction(11). In addition, the implant material would be expected to withstand any anticipated physiological loading, without either substantial dimensional change, catastrophic brittle fracture, or fracture in the longer term due to creep, fatigue, or stress corrosion. These have been the major factors underlying the selection of the three types of materials currently utilized as bone prostheses, namely metals (for example as stainless steel, cobalt alloys, titanium alloys), ceramics (for example as alumina), and polymers (for example as polyethylene, PMMA). The application of these materials in orthopedic surgery has allowed the development of many procedures which are judged clinically successful and will remain

of considerable importance. However, problems do exist, for example as the finite lifetime of a major procedure such as total hip replacement effectively limits its application to elderly patients, although the need exists across a complete spectrum of age. This limit is a direct consequence of utilizing only the criteria of biocompatibility, ductility, and fracture strength for the selection of the appropriate implant material : What is often neglected is a serious consideration of the effect of introduction the synthetic implant on the functional remodelling of the nature tissue, and any attempt to match the elastic deformation characteristics of the synthetic material with those of the nature tissue being replaced (mechanical compatibility).

As none of the synthetic materials utilized currently remotely approaches the elastic behavior of cortical bone, then it is not surprising that there is an intrinsic problem in ensuring stress transfer across a tissue-prosthesis interface and that the dynamic remodelling of cortical bone is significantly affected. Whether an elastic mismatch of this type becomes a problem in clinical practice will depend on the magnitude of the applied load, the nature of the interfacial bond, and the elastic constants of the interfacial materials, but it is certainly the prime cause of "loosening" when "stress shielding" of cortical bone is produced by the significantly stiffer implant. From this standpoint, it would seem desirable to complete the spectrum of available implant materials by developing new materials which, as well as having adequate biocompatibility and "strength", are also mechanically compatible with cortical bone. The development of adjacent surfaces with similar elastic properties is, of course, an essential factor in securing substantial bone ingrowth into a synthetic material. While it is

possible to obtain bone ingrowth into almost any solid with a suitably porous surface in a postoperative stress-free situation, the extent of growth is limited, and it is not obvious that the interfacial bone created by ingrowth bone will survive any subsequent stress application if the surfaces are elastically dissimilar. As a result, bone cement, even with its recognized deficiencies remains an essential procedure for bone-implant fixation. Consequently, any advance in this situation towards the ideal of a cementless bone would appear also to depend on the development of mechanically equivalent materials to bone.

In order to be applicable to younger patients, the new implant materials and/or the new bone cements having analogous mechanical properties to those of cortical bone should be investigated. Thus, mechanical properties of the cortical bone itself should be considered first.

2.1 Mechanical Properties of Cortical Bone

2.1.1 Elastic behavior of cortical bone

increase in flexural strength. ic behavior of cortical bone, the complex nature of its structure must be kept in view. Essential features of the bone may be considered as a two-level composite(12). A hydroxyapatite-collagen lamellae forming osteons as the first level, a preferred orientation with respect to a long axis of the bone, and surrounded by nonoriented bone as the second level(13).

Young's modulus (E) of the cortical bone is not unique in the sense of having one absolute value, but it depends on the precise

details of the associated microstructure. In addition to a variation with location in a particular bone, the Young's modulus varies with orientation in a major support bone, from a maximum value parallel to the long axis to a minimum value perpendicular to the long axis, with a ratio of maximum E to minimum E of about 2. The overall range of E determined experimentally for the cortical bone of all types is relatively large from 7 to 30 GPa. The values of E for the longitudinal and transverse orientations of mature cortical bone from the major load-bearing bones are 18 to 30 and 7 to 15 GPa, respectively.

For intermediate orientations between the limiting directions parallel to the long axis and perpendicular to the long axis, the value of E decreases progressively, but it is not a uniform manner. In contrast to the extensive data on E , there has been relatively little work on the shear modulus (G) and Poisson's value (ν) which is 4.7 to 6.6 GPa and 0.22 to 0.42, respectively.

A precise analysis of the elastic behavior would require a statement of the elastic stiffness coefficients rather than the technical elastic constant such as E , G , and ν . However, such a description is conditioned by the basic assumption as to the symmetry of bone, and is not considered relevant to the present discussion.

A knowledge of Young's modulus of the bone provides a measure of deformation which allows an adequate approach to the design of analogous replacement materials. However, it should be emphasized that bone is not simply a linear elastic solid, but it demonstrates viscoelastic deformation within the range of physiological loading, for example as time-dependent and recoverable deformation. But the essential point demonstrates that the loading-unloading curves

do not coincide above a relatively small applied stress and a hysteresis loop is formed. In general, on unloading to the starting condition, for example as zero stress, a residual strain is noted which is completely recovered with time. It is the property of bone which provides an important energy-dissipating mechanism during deformation. This subject is not sufficiently developed to be incorporated quantitatively into the design of analogous replacement materials, but there is no doubt that the existence of some viscoelasticity should be recognized as an essential feature in an optimized prosthesis.

2.1.2 Fracture toughness of cortical bone

Cortical bone has a limited total elongation to fracture of only 0.5 to 3 % and hence, the presence of random internal, surface cracks, or flaws significantly reduces the energy absorbed during fracture(14). Consequently, an evaluation of fracture toughness provides a more appropriate measure of fracture than a determination of a critical stress, such as the ultimate tensile strength, which gives a variable result for a given orientation and identical experimental procedure. As a result, a variety of fracture mechanics techniques(12,15-22) have been utilized in the past decade to assess the fracture toughness of bone specimens with a single characterized crack which have included measurements of the critical strain energy release rate, G_C and the critical stress intensity factor, K_C , as shown in Table 2.1. The specimen geometries used in the earlier experiments in this series all produced rapid crack propagation, with an unknown and variable crack velocity. More recently, in contrast with the use of the

compact tension method,(19) it has been possible to propagate a crack in bone at a relatively slow and measurable rate, and G_C and K_C values for transversely oriented bovine femur and tibia bone specimens were determined by this method for various crack velocities(12,20-21). The general assumptions involved in the application of fracture mechanics concepts to the fracture of bone have been critically reviewed(23), with particular reference to the physical implications of the single-edge-notched, center-notched cylindrical and compact tension test methods. It was suggested that the compact tension method has a particular advantage, namely that the imposed rate of deformation, or more fundamentally, the resultant crack velocity can be varied in a controlled manner.



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Table 2.1 Some previous investigations of the fracture mechanics parameters for bone(24)

METHOD	ORIENTATION	BONE TYPE	Gc (Jm ⁻²)	Kc (MNm ^{-3/2})
Single-edge notched	Transverse	Bovine femur	1388-2557	3.21
	longitudinal			
	Longitudinal	Bovine femur	3135-5534	5.58
Three-point bending	Longitudinal	Bovine femur	---	6.56
Center-notched (shock tube)	Transverse	Bovine tibia	4	0.23
Single-edge notched	Longitudinal	Bovine tibia	780-1120	2.2-4.6
Compact tension	Transverse	Bovine femur	820	3.5
Compact tension	Transverse	Bovine femur	920-2780	2.4-5.2
Compact tension	Transverse	Bovine tibia	1726-2796	4.46-5.38
Compact tension	Transverse	Bovine tibia	---	3.3-5.7
Compact tension	Transverse	Bovine tibia	630-2884 ^a	2.8-6.3
			630-2238 ^b	2.0-5.6

a Slow fracture

b Catastrophic fracture

In a recent investigation(22), the compact tension specimen approach was extended to evaluate the fracture of transversely oriented, for example as with fracture in the longitudinal direction,

bovine tibia compact bone specimens, in terms of G_C and K_C for a wide range of crack velocities from 10^{-5} to 10^2 msec⁻¹. As density has an important effect on the fracture mechanics parameters, the test specimens were grouped within four narrow bands of density, namely 1.92 to 1.94, 1.94 to 1.96, 1.96 to 1.98 and 1.98 Mg⁻³. It may be demonstrated that, for a given bone density K_C and G_C depend on the loading rate, and resultant crack velocity, with a maximum in fracture toughness at a crack velocity of about 1.0×10^{-3} msec⁻². These figures define the range of K_C and G_C values applicable to bovine compact bone in the weakest direction. Similar tests on longitudinal bone suggest a factor of about 2 increase for any given density/crack velocity, while selected tests on human bone have given similar results(25).

2.2 Development of New Implant Materials

Some of the important mechanical properties of existing prosthetic materials are listed in Table 2.2. It is readily apparent that these do not match the properties of cortical bone with respect to stiffness.

Table 2.2 Comparison of mechanical properties of current implant materials with those of cortical bone(24)

Materials	Young's modulus (GPa)	Ultimate tensile strength, (MPa)	K_c ($MNm^{-3/2}$)	G_c (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 6 wt% Al 4 wt% 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

It can be seen that ceramics such as alumina give the greatest mismatch with respect to Young's modulus. The alloys listed also have a substantially higher Young's modulus than bone, but it is significant that titanium alloys are a factor of 2 less stiff than stainless steel or cobalt chrome. Polymers such as high molecular weight polyethylene are less stiff or more compliant than bone.

With respect to yield or fracture characteristics, such as ultimate tensile strength, the ranking of existing ductile prosthetic materials reflects to stiff that metals are stronger than bone and polymer. Ceramics are so brittle that they can not be ranked in this way as the ultimate tensile strength is sensitively conditioned by the presence of cracks or pores. While the compressive tensile strength is

indeed significantly higher, the general applicability for bone replacement of ceramics should be considered on the basis of fracture toughness, such as K_C and G_C , for example as a measure of stress and crack geometry, as compared with bone. On this basis of fracture toughness, both polyethylene and the metals are superior to bone, while currently used alumina is marginally inferior. In addition, ideally the metal replacing the head and neck of the thigh bone would have the same strength as the bone and also the same elasticity. If a metal is too flexible it will eventually be subjected to fatigue failure and break. If a metal is too stiff, its bonding within the bone will become weak and it will be subject to loosening. As a result, bone cement is a acrylic polymer as use a grouting agent to fill the canal space between implant with nature bone, even with its recognized deficiencies remains an essential procedure for bone-implant fixation. Consequently, any advance in this situation towards the ideal of a cementless bone would appear also to depend on the development of mechanically equivalent materials to bone.

A comparison of mechanical properties of prosthetic materials with those of bone must be conditioned finally by the design of the prosthesis. The consideration of equivalence with bone is best suited to an exact structural replacement. It should not be taken to imply that, for example as the existing design for the stem in total hip replacement, which is "unnaturally" centered along the femoral neural axis and hence requires a much higher ultimate tensile strength than that of bone, can be constructed from a "bone-equivalent" materials.

2.3 Development of New Bone Cements

During the first three decades of this century, a fast chemical science had been developed by providing the basic for choice of high molecular weight materials. Polymers of methacrylate ester, especially, PMMA was the first one for application as biomaterial. It was processed to combine properties of high transparency to relate with high toughness and strength in the industrial field by easily processing. The same properties caused it to be adopted by the dental profession for the fabrication of full dentures and artificial eyes. In an interesting history review, investigations were started to the possible use of the product as denture base material in 1933. Two years later, G.B. Drury *et al.*(26) reported that more than 2,000 employees had received a prosthesis to full satisfaction and studied the released of the material for the dental profession in due time. In 1941, acrylic resins had become a main heading in the Index to Dental Literature and the Index Medicus. These reports on their use as materials for dentures, artificial teeth, inlays, crowns, bridges, eyes, noses, and ears(27). The material was formed into the desired shape either by thermoplastic or by a chemoplastic way which is curing a mixture of polymer and monomer in a mould at elevated temperatures. The potentials of the material to be buried in the body, had received the attention of investigators. Contzen(28) indicated that had investigated the biocompatibility of PMMA in animal experimentals in 1938 and they found that it had suited to use for repairing of cranial defects. During period of World War II, it is required a large demand for reconstructive and cosmetic surgery and there were an explore *Plexiglas* or *Perspex* in orthopeadic

surgery, especially for treatment of coxarthropathy and in hip arthroplasties(29). In 1943, the brothers Judet started their experiments with hip endoprostheses, fabricated from plexiglas and they implanted the first prosthesis in 1946(30). In 1940 and 1943, Sehnebel *et al.*(31) used tertiary amines as accelerators for the peroxide initiating polymerization of MMA monomer, autopolymerizing of cold-curing resins. At the 1950s, several dental restorative resin were provide an *in situ* curing material for the invisible filling. Cranioplastic operations were simplified to other reconstructive procedures because it was no longer to prefabricate the inserts in gypsum molds. In 1952, Drukrey *et al.*(32) mentioned tumor induction, which this polymers was used after implantation in animals. However, it appeared that possible carcinogenicity was related to physical aspects of the material as shape, dimensions, porosity, etc., rather than to the chemical composition of the materials. In addition, tumor formation could only be observed in certain animal species and could be not a single case of malignant degeneration related to implants in the human. The development of biomedical acrylic resins had came in 1960 when Charnley(1) revolutionized orthopaedic surgery by introducing auto polymerization resins as an anchoring medium for metallic hip endoprosthesis. The term bone cement was introduced and the following twenty years have been dedicated to refinements of implantation techniques, assessment of biocompatibility and toxicological, and allergenic aspects of PMMA and its components. Acrylic resin implants are applied clinically today as shown in Table 2.3

Table 2.3 Current clinical applications of acrylic resin implants(11)

Skull	Repair of cranial defects, correction of deformities	Precured of <i>in situ</i> curing resins
Ear, nose	External prosthese, correction of deformities	Precured, plasticized precured resin
Eyes	Repair of orbital fractures Intra-ocular lensed	Self-curing resin or precured resin Precured, high purity resin
Jaws	Internal fixation of mandibular fractures, contour correction	Self-curing resin
Teeth	Tooth replica implants	Various experimental resins
Thorax	Correction of deformities	Precured resin
Back	Spinal fixation	<i>In situ</i> curing cement
Penis	Penile inserts Testicular implants	Precured resin, largely replaced by silicones
Extremities	Fixation of traumatic and pathological fractures	<i>In situ</i> curing cements

2.3.1 Characteristics of Acrylic Bone Cement

2.3.1.1 General and Chemical Composition

From a chemical standpoint in autopolymerization of acrylic bone cement, the rigid mass of acrylic cement surrounding orthopedic implants and penetrating bone surfaces is a rather complex network of organic macromolecules plus some low molecular weight impurities. Two factors occur in structural complexity to this organic

matrix, are matter molecular discontinuities due to the entrapment of voids, as well as the presence of embedded, and radiopaque inorganic particles. Furthermore, finite amounts of volatile impurities are probably contained within the voids which disrupt molecular continuity in the matrix and affect to mechanical properties of acrylic cement. However, in work procedure must be tried to the most reduce some low molecular weight impurities. And in surgery must be having easy design and economic time for a safety of patience. Thus, polymerization of acrylic bone cement in laboratory need to molded as same as in a real surgery which mixing acrylic bone cement from polymer of PMMA and MMA monomer by stirring with hand. In the present , bone cement for orthopaedic surgery consists of a powder and a liquid.

Powder : approximate 90 % by weight of the powder component of bone cement is composed of particles of PMMA and/or random co-polymers of mostly MMA monomer with small amounts of other monomers such as styrene. Most of the polymeric particles in the powder component tend to be spherical in shape. The size usually ranges from 30 to 150 μm in diameter. The remaining 10 % of the powder weight is composed of particulate radiopacifiers such as barium sulphate or zirconium dioxide. Benzoyl peroxide (BPO), a polymerization initiator, is also present in small amounts in the powder component (0.75 to 2 % by weight). The chemical structures of possible organic components in the powder are shown in Figure 2.1.

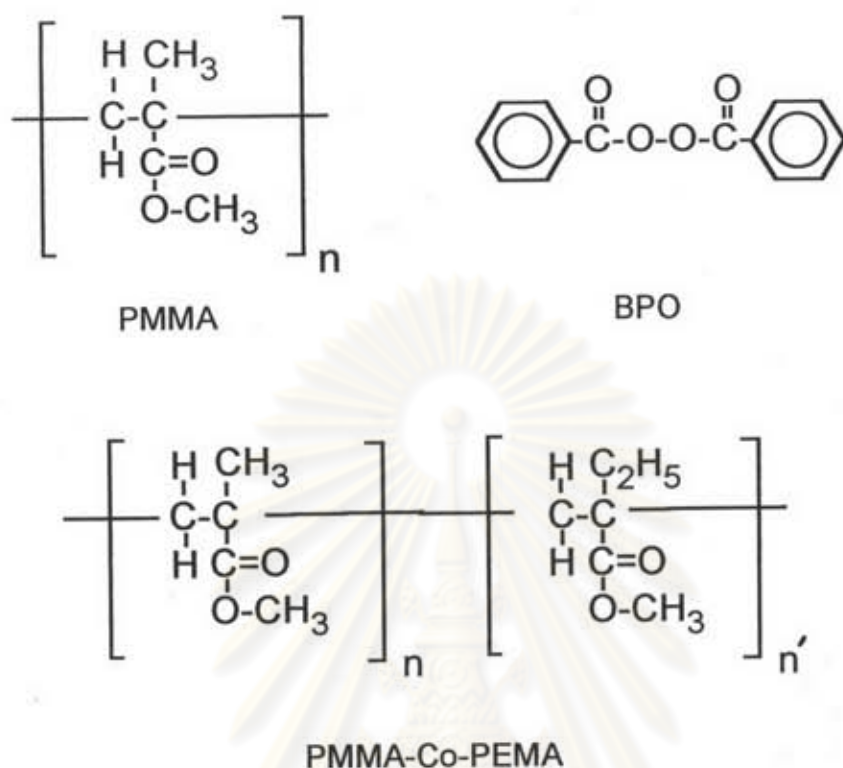


Figure 2.1 Chemical structure of organic components in the powder

The polymeric spherical beads are commonly prepared by chain (addition) polymerization of MMA monomer using a process known as suspension polymerization. This process involves dispersion of initiator containing liquid monomer in an immiscible medium, for example as water, alcohol, etc. The dispersed monomer forms spherical droplets which maintain their integrity in the aqueous medium by mechanical agitation and the use of stabilizers. Stabilizers may include water soluble polymers, electrolytes, or water insoluble inorganic compounds. Polymerization of the monomeric droplets begins as soon as production of free radicals from the initiator is thermally activated. The chemical microstructure forms during this process is of

crucial importance since it will constitute approximately 70 % by weight of the polymeric matrix of the cement.

Other chemical features of the bead matrix include addition defects, tacticity, residual monomer or other impurities, and, particularly, the nature of end groups. Addition defects involve both head-to-head and tail-to-tail polymerization. Bone cement powder have recently characterized tacticities by Nuclear Magnetic Resonance (NMR). This analysis revealed the following ranges of triad distributions having sequence of three repeating units as syndotactic about 50 to 60 %, atactic about 37 to 42 %, and isotactic about 3 to 6 %, as shown in Figure 2.2.



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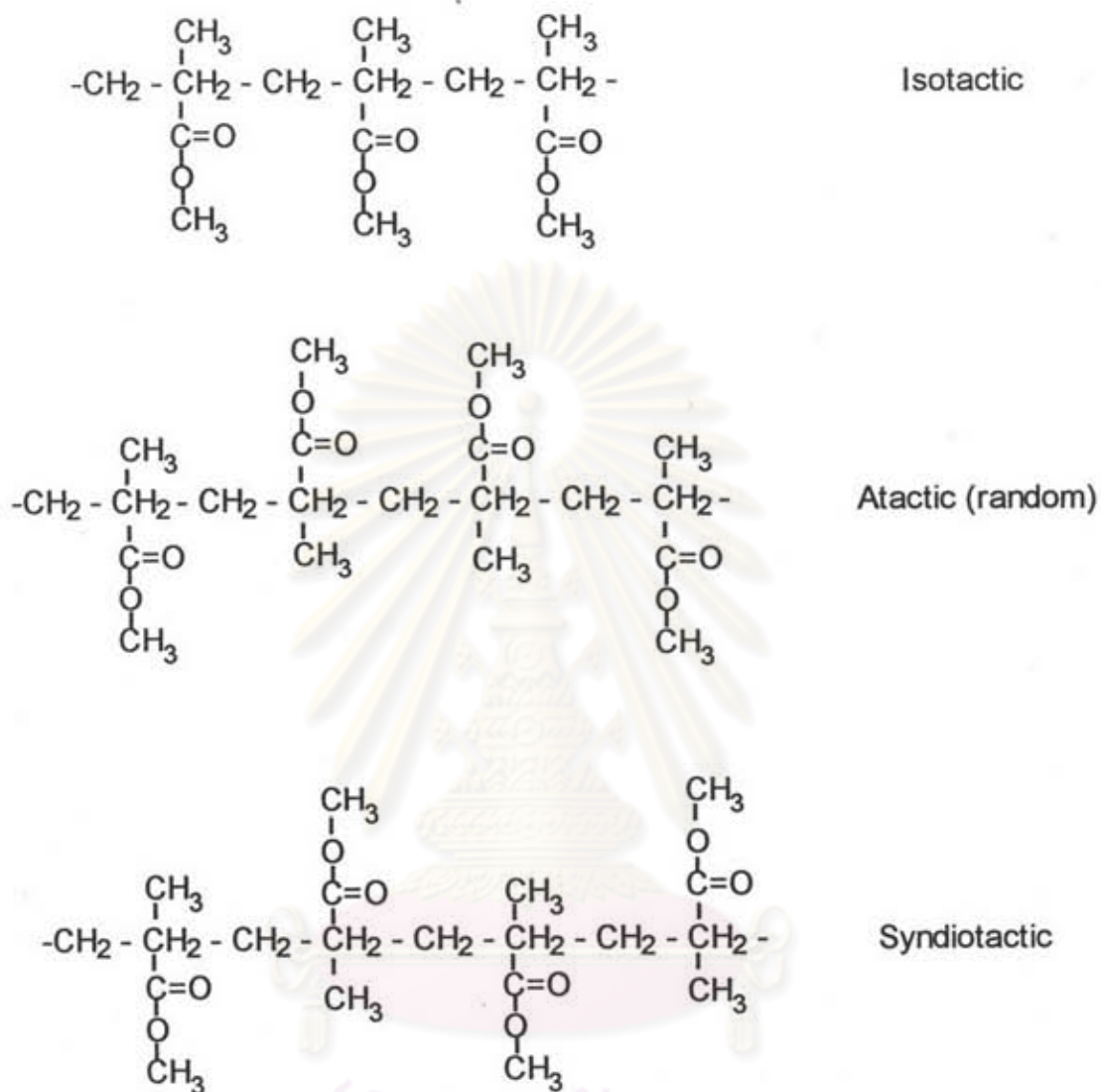


Figure 2.2 A characterized tacticities of bone cement powder

Residual monomer is expected to be in powder beads for thermodynamic reasons or due to viscosity induced entrapment of unpolymerized species in the matrix. Residual monomer in the polymer particles has been reported to be in the order of 0.28 %. Several other trace impurities are possible in polymeric particles of the powder and these could include residual initiator, chain transfer agents, stabilizers,

or species present in the dispersing medium during suspension polymerization.

Liquid : the liquid component of acrylic bone cements contains three basic ingredients, MMA monomer approximately 97 % by volume, N,N-dimethyl-p-toluidine (DMPT) approximately 2.7 % by volume, and hydroquinone or hydroquinone monomethylether approximately 75 ppm. The chemical structures of these three components are shown in Figure 2.3.

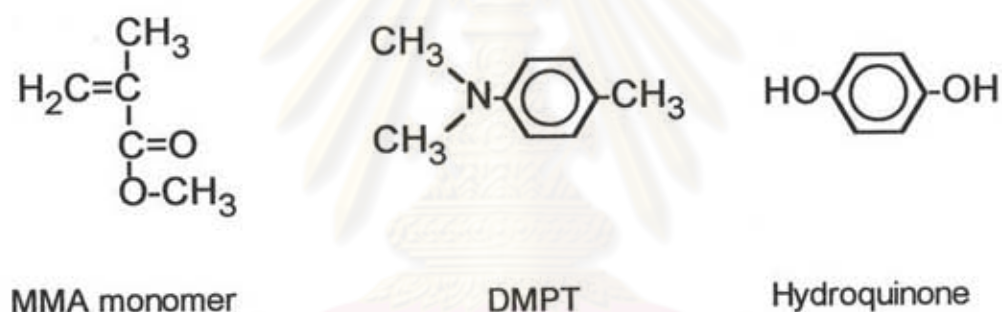


Figure 2.3 The chemical structure of 3 liquid components.

Polymerization of MMA monomer commonly occurred at about 60 °C by thermal decomposition of benzoyl peroxide to form free radicals. Thus, polymerization may be achieved by heating a mixture of MMA monomer and benzoyl peroxide, giving the so-called heat-cured acrylic. At room temperature, the decomposition of peroxides can be accomplished by a redox reaction with easily oxidizable compounds such as tertiary amines. In biomedical room temperature, curing acrylic resins the commonly used accelerator is N,N-dimethyl-p-toluidine. In addition, uncontrollable sources, such as

light, radiation, oxygen, and environmental heat, can initiate the polymerization of MMA monomer. Thus, when the monomer is stored in a pure form without any precautions, it will have a very short shelf life. To prolong the shelf life of the monomer, small quantities of a radical scavenger or the stabilizers commonly are hydroquinone or its monoethers must be added.

The properties of the cured resins could be modified to some extent by cross-linking the polymer chains. This could be accomplished by addition of comonomers having two double bonds. Such a comonomer could be incorporated in two growing chains, which can be linked together with chemical bond. When enough cross-linking monomer is added, the resulting polymer molecules form complex three dimensional networks of chains, rendering the polymer insoluble and improving some of its mechanical properties. The most commonly used cross-linking monomer is ethyleneglycol dimethacrylate. Other esters of methacrylic acid, especially ethyl- and butyl-methacrylate are sometimes added as comonomers to improve working properties or to plasticize the polymer.

2.3.1.2 Reaction Mechanisms of Bone Cement

Most medical and dental acrylic resins are shaped and formed *in situ* or in moulds. They are available as a two component system as a powder which mainly consists of small PMMA spheres and beads, and a liquid component containing the monomers. For convenience of user, the peroxide is already added to the powder component and in self-curing formulations the amine accelerator is

dissolved in the monomer. Prior to use, the powder and liquid are mixed in a ratio of approximately 2:1 by weight, and an easily mouldable dough is obtained, within about 10 minute or after heating in a gypsum mould. This is a far more convenient method than polymerizing monomer alone without any polymer already present.

Table 2.4 shows the composition of a regular type of bone cement. Finally, it should be mentioned that the polymerization reaction is strongly exothermic. Consequently, after the polymerization has started, the released heat will cause the temperature of the curing dough to rise. The high temperature increases with the polymerization rate. In this respect the term "cold-curing resin" is misleading, as the maximum temperature in larger masses of curing resin can easily reach value of 120 °C. Advantage of this autoaccelerative process is to permit the polymerization to proceed with high degrees of conversion in a relatively short time.

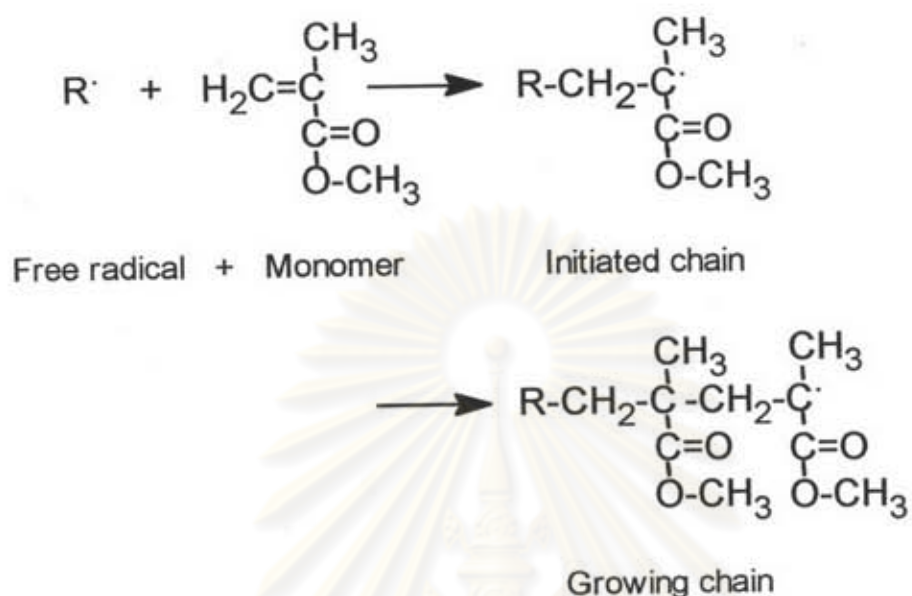
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Table 2.4 Composition of mouldable room temperature curing^(a)
acrylic resin⁽¹¹⁾

Powder		Liquid	
Polymethylmethacrylate ^(b) in spheres of 10-150 μm	> 90 %	Methyl methacrylate monomer	> 85 %
Dibenzoyl peroxide	2-3 %	Comonomers (crosslinking agents, butyl methacrylate)	10-15 %
BaSO ₄ or ZrO ₂ ^(c)	4.80%	N-dimethyl-p-toluidine	2-3 %
		Hydroquinone	50-100 μm

- (a) Heat-curing dental formulations are similar, apart from absence of toluidine accerlerator.
- (b) Sometimes copolymer of methyl methacrylate and styrene or butyl methacrylate.
- (c) In dental formulations : fillers and pigments.

The polymerization of MMA monomer is an addition type process taking place in three stages, initiation, propagation, and termination. It is an addition reaction that is initiated through intermediates having an unpaired electron, such as free radicals or active center. When free radicals are generated in the presence of MMA monomer, the double bone will be broken with regeneration of another radical as show below.



This regenerated radical can react with another monomer and so on, thus forming a growing chain. The propagation of chains continues until the reaction is terminated, for example as by two growing chain radicals combining their unpaired electrons to a single bond. The termination is possible in two ways : combination and disproportionation. PMMA is terminated exclusively by disproportionation at high temperature but at low temperature both mechanism are found(33). Once initiated, the rate of successive monomers are added to the chain radical or so-called the polymerization rate, is very high and up to several thousand monomer units until they can be linked together in a single polymer molecule in a few seconds.

2.3.2 Mechanical Properties of Bone Cement

All the materials used in total hip replacement should be biocompatible in the body environment. The materials selected must withstand the normal physiological forces without fracture, either in the short term associated with overloading or in the long term due to fatigue or stress corrosion. The friction and wear characteristics between the alloy stem and the polymeric acetabular cup are also important, both to give the required joint function and to ensure an adequate lifetime. The initial selection of a combination of an alloy stem/PMMA bone cement/ polyethylene cup for a total hip system appeared to meet these requirements adequately, even though a detailed specification is not available. However various combinations of alloys, ceramics, and polymers have been utilized in the past 20 years as stems and cups, PMMA has remained as an almost universal choice for bone cement. A remarkable record of 90 % clinical success has been achieved for a prosthesis lifetime of 10 years or more by PMMA which can be mixed and inserted in the femoral cavity. However, these advantages should be balanced the poor mechanical properties of PMMA and the exothermic nature of the polymerization. The structure of bone cement as used in operative procedures does not possess ideal mechanical properties. It is a very brittle material with poor tensile strength about 30 MPa, low fracture toughness about 1.2 MPa, and inadequate fatigue resistance. It is not adequately suited for applications where cyclic tensile loads are encountered as in a femoral implant. Moreover, the interfaced between bone and the stem will only remain stable under physiological loading if the bone cement layer remains both contiguous

and continuous. For the intrinsic brittle character of PMMA, is difficult in surgery to avoid to producing a void-free bone cement layer, which can lead to a non-continuous layer, then the mechanical mismatch. The resulting structure is heterogeneous, such as voids, which act as stress concentrators, causes occur sites for nucleation and crack propagation through the bone cement. It is no surprise therefore that instances of implant loosening have frequently been reported. According to Feith(34) 20 % of all patients with total hip replacements will need a second operated within 10 years. Therefore the orthopaedic application of PMMA has improved with mechanical by vacuum aids introduced to reduce the level of porosity retained during polymerization, which it is a difficult and not convenience in surgery too. In addition, a polymerization is relative high exotherm about 90°C which causes a reduction in blood pressure and bone necrosis. Consequently, investigations into improvement of the properties of the cement, the cement-bone interface and the cement-implant interface are in fact two major research initiatives in progress as first, to eliminate cement completely by developing either bone ingrowth into a porous metal stem or bone apposition at a bioactive surface and second, to reduce the exothermic temperature and/or improve the mechanical properties of existing acrylic bone cement by various methods of reinforcement and various types of polymer.

2.3.3 Factors Affecting Mechanical Properties of Bone Cement

As previously mentioned the mechanical properties of PMMA cement are sensitive to a number of factors including handling, cementing technique, antibiotic, environment, radiopacifying materials, irradiation, porosity, and strain rate.

2.3.3.1 Effect of Handling and Cementing Technique

2.3.3.1.1 Effect of Handling

Variation in cement handling has been suggested as one of the major causes in the deterioration of the performance of bone cement *in vitro*. As it has mentioned the reason for using a grouting layer between the stem of the prosthesis and the endosteal bone is that it produces an immediate mechanical interlock. Several modification to total hip orthroplasty have been developed in response to clinical need requirements and/or new ideas from the research laboratory.

Lee and Ling(35) investigated how variations in the method of preparing the bone cement affected its mechanical properties. The change of beating frequency from 60 to 260 times per min led to 0.85-3.4 g (~14 %) of liquid monomer loss by evaporation, increasing with higher frequency.

Haas, Brauer, and Dickson(36) suggested some guidance for proper handling techniques in order to optimise other

properties of the cement. They stated that the initial temperature of cement (and of the mixing bowl) greatly affect the time taken to reach the dough stage. The setting time was reduced as kneading was increased porosity ranged from 1 to 10 % of the cement volume and it increased with rapid mixing speed and reduced by the application of pressure during polymerization. Temperature rise, handling time, dough time, and setting time were all affected by the ambient temperature and kneading of the dough mass.

Fumich and Gibbons(37) showed that a slow rate of hand mixing (5 beats per minute) reduced air entrapment when compared with a fast rate of mixing (120 beats per minute) and increased the flexural strength by 29.3 % whereas it did not demonstrate any significant differences in the compressive strength.

2.3.3.1.2 Effect of Cementing Technique

It has been shown that improved cementing techniques in surgery helps to achieve better mechanical interlock between bone and cement simple procedures such as preparation of the osseous bed to create a clean, dry intermedullary canal that allows space for the cement to penetrate as well as reduce the admixture of blood and debris into the cement mass all contribute to improved performance. Pulsed water lavage(38), pushing the canal(39) and pressurization of the cement mass(40) are further techniques used to increase the interlock at bone cement interface.

The use of pressurised injection helps increase cement penetration into cancellous bone. The use of a cement gun

allows retrograde filling of the cannal and avoids the entrapment of air and debris(41) while an intermedullary plug of bone(42) cement or plastic prevents the flow of cement distally, allowing pressure applied proximally to push the cement out into the bony bed. The use of bone cement in its low-viscosity state has been suggested(43-45) as a way of improving interdigitation with the spicules of trabecular bone. Weinstein *et al.*(46) demonstrated that a high pressure insertion technique using a specially designed mechanical injector resulted in approximately 20 % increase in the mechanical strength properties.

Convey and Malcom(47) have shown that by pressurising cement to 0.7 MPa, the penetration increased to 80 %, and the interface shear was enhanced by 38.8 %, Halawa *et al.*(48), using fresh human femoral sections, demonstrated that bone-cement interface shear strength increased by 100 % when cement injection pressure was increased from 0.15 MPa to 0.3 MPa. The shear strength also increased by up to 60 % with early application of low viscosity cement. Geiger and Greenwald(49), using fresh cadaver metaphysical specimens, improved interface shear strength by 300 % with the use of pulsatile lavage and concurrent suction of the medullary bone surface, before pressurised cement injection. From these investigations it is evident that, pressurised injection of cancellous bone to increase three dimensional interlock appears to be mechanically effective and hence clinically attractive.

However, the ability to maintain these high curing pressures at surgery has not yet been achieved and the creation of excessive medullary pressure carries an increased risk of pulmonary marrow embolisation, Breed and Drinker *et al.*(47,48). Many small

refinements have combined to produce what seems to be a significant improvement in long term fixation(47). The other approaches, include, centrifugation(48) and mixing the cement component under partial vacuum(49,50), both of which to eliminates the large voids in the cement mantle.

Another approach to improve the mechanical integrity of the prosthesis-cement interface is to coat a thin coat of PMMA polymerized on the proximal stem under high temperture and pressure, which results in a much stronger metal-acrylic bond(51,52).

2.3.3.2 Effect of Antibiotic and Other Inclusions

All surgeons involved in joint replacement surgery are concerned with the problem of effects of infection, which is in the range of 0.5-9.0 %(53). Another form of preventing infection is with the use of systemic antibiotic therapy. Buchholz *et al.*(54) approach was to impregnate bone cement with antibiotics believing that the antibiotic would leach out from the cement into the area of the wound, thus preventing wound infection, with no need for subsequent high serum concentrations of antibiotics.

Lee, Ling, and Vangola(55) studied the effect of addition of 0.4-0.5 g of antibiotics with 40 g of polymer powder of various types. They showed that the addition of antibiotics had only marginal effects on the mechanical strength and stiffness of bone cement. Other work has shown that up to 2 g of antibiotic powder had little effect on the mechanical strength after leaching in 37 °C water had occured. However, large addition of up to 5 to 10 g of antibiotic

powder, significantly altered the compressive and diametrical tensile strength of cement.

The incorporation of antibiotics in liquid form had a significant detrimental effect on both compressive and diametrical tensile strength, inhibiting the growth and interaction of polymer chains(56). Inclusions of blood or fat during application, it is reported also affect the cement strength. These inclusions may act as a stress raisers and may initiate cracks. Holm(57) reported that the flexural modulus of elasticity of CMW cement was decreased by 12 and 21 % by adding 1 and 3 ml blood, respectively.

2.3.3.3 Effect of *In Vivo* Environment

Several authors have studied the change in mechanical properties of cement with time when placed in an *in vivo* environment. Jaffee, Rose, and Radin(58) stored bone cement samples in bovine serum at 37 °C up to two years and found no deterioration in static or compression-fatigue behaviour. They suggested that the working stress in the cement should not exceed 14-17 MPa to ensure long term viability of any implant design.

Freitag and Cannon(59) recorded higher fracture toughness when testing was conducted on cement specimens immersed in bovine serum at 37 °C compared with specimens tested in air. Fostoker, Lereim, and Galante(60) tested cement samples in flexure after implanation from rabbit tibiae during an implanation period ranging between 6-26 months. They did not observe any significant

decrease in bending strength, and there were no adverse effects on the tissue that developed around the bone cement test bars.

2.3.3.4 Effect of Radiopacifying Materials

The two types of radiopacifying materials in common use are, barium sulphate : BaSO_4 (CMW) and zirconium dioxide : ZrO_2 (Palacos, Sulfix). The inclusion of barium sulphate or zirconium dioxide renders the cement radiopaque, enabling detection and monitoring of discontinuities in the bone/cement prosthesis system.

Radiopacifiers are particulate materials and show different effects on different properties of PMMA cement as shown in Table 2.5.

Table 2.5 Effect of mechanical properties for radiopacifiers added
PMMA cement(61)

Mechanical properties	CMW bone cement	CMW + 4 % BaSO_4
Tensile strength, MPa	32.60	28.90
Compressive strength, MPa	93.10	91.70
Flexural strength, MPa	105.00	80.30
Impact strength, MPa	0.58	0.32

Hass *et al.*(36) reported that the addition of BaSO_4 decreased the tensile and compressive strength by 10 %. while according to Freitag and Cannon(59) fracture toughness of Simplex and

Zimmer cements were reduced by 10 % with the addition of 10 % by weight of BaSO₄. Beaument(62) showed a proportional reduction of the fracture toughness of Simplex cement by 5 % for each 1 % volume addition of BaSO₄.

2.3.3.5 Effect of Irradiation

During the course of management of difficult pathological fractures, irradiation is sometimes applied as a part of the treatment. Eftekhar and Thurston(63) studied the irradiation effect on bone cement. They investigated Simplex-p and CMW cement samples irradiated by 10,000 rads for 20 minutes which was assumed as the maximum single dose for a human subject. The samples were then tested in compression, tension, and flexural strength. They concluded that there was no significant difference in mechanical properties of irradiated and normal cement.

Greenwad, Wilde, and Matejczyk(64) investigated the effect of irradiation up to 20,000 rads, well above the usual clinical dose, on shear strength of acrylic bone cement. They reported a slight increase in shear strength which was 41.34 MPa for the control and 42.71 MPa at the clinical dose of 3000 rads.

2.3.3.6 Effect of Temperature

Most investigators have performed mechanical tests at ambient temperature of 20-21 °C. Many of them have kept the samples soaked in water 24 hours before and during testing. Since bone

cement has to function at 37 °C, Lee, Ling, and Vangola(55) determined the temperature dependence of the properties. They observed a 4 % decrease in Young's modulus (compression), 10 % in the ultimate compression strength, and 16 % all in the 1 % proof stress for surgical bone cement when compared with test resulted at room temperature.

Lautenschiager and Marshall(56) also investigated the compressive strength of the plane of Palacos R cement tested at 0°, 23°, and 37°C and reported values of 125.7 ± 1.8 , 90.5 ± 1.1 , and 86.9 ± 2.5 MPa, respectively, when tested at a cross head speed of 2.5 mm/min, showing a significant temperature dependency.

2.3.3.7 Influence of Porosity

Manual mixing of the powder and liquid components of the cement leads to a porous structure caused by the entrapment of air bubbles, which further expand during polymerization. In clinical practice, the cement applied to the femur or acetabular cavity will in certain cases also be higher porous(65). Porosity will obviously influence the mechanical properties adversely, and the investigation of de Wijn *et al.* confirmed this.

Porosity can be reduced clinically by subjecting bone cement mixtures to ultrasonic vibrations. Such work has increased both the compressive strength and energy absorption capacity by 10-15 %. Vacuum mixing has also been shown to improve bending and compressive strength by 15-30 %.



2.3.3.8 Effect of Strain Rate

All types of surgical PMMA are viscoelastic in nature, for example as a material it may be idealised as a linear spring and dashpot connected in series(66). Therefore, it is expected that the resisting force developed will be velocity dependent. It is expected that with increasing strain rate, the modulus of elasticity and ultimate strength in various modes of loading will increase (55,67-68). Therefore, it is important to mention the average strain rate used during testing while reporting any strength data. Only then it will be possible to compare results with other authors.

Lee, Ling, and Vargola(55) AkZ cement showed a 50 % increase in strength at a strain rate of 1.8 sec^{-1} when compared to quasistatic rate. At the very high strain rate of 5.2 sec^{-1} , a 67 % increase in compressive strength was observed. The Young's modulus also increased similarly with strain rate. Astleford *et al.*(69) reported a 30 % increase in direct shear strength when strain rate was increased from 0.001 sec^{-1} to 0.1 sec^{-1} .

Wilde and Greenwald(68) reported about 10-12 % change in direct shear strength when deformation rate varied from 0.125 to 125 mm/min. Saha and Pal(67) studied the effect of strain rate on compressive properties of normal and carbon fiber reinforced bone cements. They observed a 23 % increase of ultimate compressive strength for a strain rates greater than $0.62 \times 10^{-3} \text{ sec}^{-1}$.

Weinstin *et al.*(70) tested three varieties of acrylic in five conditions over a strain rate of $1.3 \times 10^{-3} \text{ sec}^{-1}$ to 1.3 sec^{-1} and the compressive yield and ultimate strengths were shown to

be linearly related to logarithm strain rate. The yield strength doubled over the range of strain rates but the modulus was not dependent on strain rate.

In addition, ageing had effect to mechanical properties of PMMA. Lee(55) used compressive strength as a typical parameter for PMMA cement, finding that all cements tested gained strength between mixing and seven days. By six months this strength was beginning to fall by one year it had decreased by 8.5 %. The performance would fall by more than 10 % in the long term.

2.3.4 Modified Bone Cement

Like brittle materials bone cement is weaker in tension than in compression and fracture of the cement due to fatigue crack growth have led to modifications to the cement by increase tensile strength and fracture toughness. Various additions have been made to the cement which have followed widespread materials engineering principles. Numerous investigations have tried to study of strengthening and toughening by the addition of reinforcements, such as metal wires, carbon fibers, aramid fibers, glass spheres, inorganic bone particles, sugar, and rubber particles. Most of the work has concentrated that bone cement is only 25 % as strong in tension as bone and is lacking in strength of elastic modulus. However, increase in the elastic modulus of the cement may lead to lower interface stresses, but they increase the stresses in the bulk of the cement. Thus, an alternative, such as less brittle material of lower modulus, higher fracture toughness, and overall improved energy absorbing characteristics, which is produce a

brief review on previous investigations to modify and consequently improve the properties of the cement.

The method of most relevance is the addition of a particulate or short fiber to the polymer to form a composite material. The potential benefit may be illustrated by the linear rule of mixtures(71).

$$E_c = E_m V_m + E_f V_f$$

in which E_c , E_m and E_f are the Young's modulus of the composites, matrix and short fiber, respectively and V_m and V_f are the volume fraction of matrix and short fiber, respectively. This equation applies to unidirectional, continuous short fibers, for example as significantly longer than the length requires to transfer stress to the short fiber, and a consideration of the existing commercial fibers give the following possibilities for stiffening. These models are simplistic and they assume perfect adhesion between the filler and matrix and totally elastic strain behavior. Failure to transmit ve.r and tensile load across the interface result in a loss of load sharing between the fiber and the matrix. Therefore, the wetting, coupling, and mechanical bonding between the matrix and filler are all critical in determining the composite strength.

2.3.4.1 Fiber Reinforcement

For acrylic bone cement is significantly weak and less stiff than human bone. Bone cement is also weaker in tension than in compression, as shown in Table 2.6. This limits its use in the orthopaedics to areas where tensile stresses are minimum. Other

investigators have attempted to improve the mechanical properties of PMMA by reinforcing it with metal wire, and graphite and aramid fibers. Normal, carbon fiber reinforced and aramid fiber reinforced bone cement specimens are tested in compression. Addition of a small percentage about 1 to 2 % by weight for carbon fibers and up to 6 % for aramid fibers improve the mechanical properties significantly. Due to improved mechanical properties of fiber reinforced bone cement, its clinical use may reduce the incidence of cement fracture and thus loosening of the prosthesis.



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Table 2.6 Mechanical properties of human bone ,PMMA, and prosthesis material(72)

	UTS (MPa)	E (GPa)	UCS (MPa)	USS (MPa)
Industrial PMMA (injection molded)	68.9	2.1	103	
Orthopaedic PMMA (hand mixed)	30.8	2		
	27.6		66.3	29.7
	25		77	41
Wet femoral cortical bone	123	17.2	166	84
Wet lumber vertebrae (adult average)	3.7	0.34	4.6	2.8
Wet cervical vertebrae (adult average)	3.1	0.55	10.1	
Stainless steel	1724	199.96		

Note : UTS = ultimate tensile strength, UCS = ultimate compressive strength,
USS = ultimate shear strength, E = modulus of elasticity

Carbon fibers have been shown to be compatible in animal tests. Pilliar *et al.*(72) found that the tensile strength, elastic modulus, and fatigue life of the cement were all increased. The introduction of the fibers in a random orientation have resulted that Young's modulus of the bone cement from 2.7 to 5.5 MPa and additionally increased the ultimate tensile strength from 24 to 35 MPa

and increased fatigue resistance, as shown in Table 2.7, but the total strain of failure was slightly lower for the carbon fiber reinforced PMMA. The impact resistance using an Izod impact tester was lowered by introduction of a notch for both reinforced and unreinforced systems, but the carbon fiber reinforced bone cement was far less sensitive to this notch effect. The presence of the carbon fibers also increased the impact resistance of the material. In addition, Saha, S., and Pal, S.(73) studied to prepare samples of normal low-viscosity cement and carbon fiber reinforced cement and to test mechanically. Carbon fiber increased the tensile strength and modulus by 30 % and 35.8 %, respectively. However, the compression strength and modulus, increased by on 10.7 %. Similarly, bending and shear strengths improve by 29.5 % and 18.5 %, respectively. The maximum temperature rise during polymerization was also reduced significantly by the fiber reinforcement.

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Table 2.7 Mechanical properties of carbon fiber reinforced PMMA(73)

Author	Cement	Type	Fiber property	% used	Strength, MPa				Modulus of Elasticity (MPa)
					Tensile	Compressive	Shear	Flexure	
Knoell <i>et al.</i> (1975)	Osteobond	Graphite GY-20	l = 6 mm chopped	1,2,3 and 10 by w/o		1.7		47	4600 (c)
Piliar <i>et al.</i> (1976)	CMW	Carbon	l = 6 mm d = 7 μ m	2 w/o	38				5560 (T)
Piliar <i>et al.</i> (1976)	CMW-porous	Carbon	l = 6 mm d = 10-15 μ m E = 380 to 460 GPa	1 and 2 w/o					Static : 3700 5800 Cyclic : E = 4000 (T) E = 3750 (c)
Saha <i>et al.</i> (1979)	Simplex P R.O.	Chopped Carbon	l = 6 mm d = 8 μ m	1 and 6.6 w/o		74 72	35 47		
Litchman <i>et al.</i> (1978)	Surgical simplex RO.	GRaphite Thovnel-300 Union Carbide	l = 12.5 d = 5.0	0.53, w/o 1.05, v/o 1.57, v/o	34.1 37.8 42.2				3241 (T) 4008 (T) 5730 (T)

Wright and Robinson(74) looked at fatigue crack propagation studies in carbon fiber reinforced polymethylmethacrylate cement and showed that crack propagation rates were approximately an order of magnitude less than those of conventional bone cement at the same range of stress intensity factor.

Pourdeyhimi, B., and Wagner, H.D.(75) studied the fracture behavior of PMMA bone cement reinforced with short ultra-high-molecular weight polyethylene (Spectra 900). These results were demonstrated that linear elastic and non-linear elastic fracture mechanics results indicated that a significant reinforcing effect was obtained at fiber contents as low as 1 % by weight, but this concentration a plateau value was reached and the fracture toughness became insensitive to fiber content. The flexural strength and modulus were apparently not improved by the incorporation of polyethylene fibers in the acrylic cement, probably because of the presence of voids, the poor mixing practice and the weakness of the fiber/matrix interfacial bond.

Another recent reinforcing phase material was aramid fibers. Wright and Trent(76), using Kevlar fibers as Kevlar 29-EI Dupont obtained results for the ultimate tensile strength, and also fracture toughness of bone cement. Although Kevlar fibers were not developed for medical use, implantation studies with dogs have shown that bone cement of tibia sufficiently biocompatible for safe surgical used. They found that by mixing with up to 7 % by weight of these fibers increased for ultimate tensile strength from about 30 to over 40 MPa while additional increased in fracture toughness of between 1.5 to 3.3 MPa. Fracture surfaces from both tensile and fracture toughness specimens were examined under an scanning electron microscopes. Upon examination the aramid fibers appeared unwetted by polymethylmethacrylate cement. Fiber protruded from surfaced of both types of specimen but they oriented more normal to the fracture surface in the tensile specimens. The increase in strength with 7 % addition of

aramid fibers was approximately a third of that found with additions of 2 % by volume of carbon fiber, the increase in modulus of elasticity in 2 % aramid fibers was 11 % greater than that obtained by 1 % of carbon fibers. Strengths of carbon reinforcement could possibly be reached equal by using a greater percentage of aramid fibers, but such large additions made mixing the cement more difficult. More important than this, large increasing in strength might not be necessary to eliminate the problems of cement breakdown. Even if such strength increases were achievable, they might be undesirable in that the associated increase in stiffness could affect the transmission of load from a prosthesis to the surrounding bone.

Murakami, A. *et al.*(77) (Himeji Institute of Technology, Japan and QueenMary College, University of London, U.K.) have been developed hydroxyapatite fiber reinforced bone cement composites and investigated ranging from 2-8 % by weight fraction in bone cement. There were demonstrated that hydroxyapatite reinforcement provided an increase in fracture toughness and creep resistance with reductions in exothermic temperature and in unreacted monomer content. This study offered considerable potential for addressing the major problems on current orthopaedic practice. In addition, Weinans, H. *et al.*(78) studied the effects of a fibrous membrane between cement and bone in a femoral total hip replacement. The study involved the problem of modeling this fibrous membrane in finite-element analyses, and its global consequences for the load-transfer mechanism and its resulting stress patterns. The results showed that the load transfer mechanism from stem to bone changes drastically when membrane was present. These effects were predominantly caused by

tensite loosening and slip at the interface, and were entranced by the nonlinear membrane characteristics, therefore, could not be described satisfactory with linear elastic models. Most important, the fibrous tissue interposition caused excessive stress concentrations in bone and cement, and relatively high relative displacements between these materials.

Previous approaches to enhancing the mechanical properties of bone cement have been directed towards improving existing PMMA rather than developing a new cement because of the time and expense required in finding a substitute and obtaining approval from federal regulatory agencies such as Department of Health and Social Service (DHSS) of the United Kingdom and Foods and Drugs Agency (FDA) of the United States of America. These attempted modifications, which have concentrated on improving the strength and stiffness mainly as a consequence of fiber reinforcement(79,72,74, 76,80) have been shown to adversely affect the distribution of load from the metal stem to the surrounding bone(74). For this reason, the lower strengthening efficiency in a particulate composite allows a better mechanical match with the surrounding materials(24,81).

2.3.4.2 Particulate Reinforcement

Since bone cement has a poor properties and a shrinkage after polymerization, gap between constituents can occurred. Certain problems associate with loosening of orthopedic devices may arise from the dissimilarity between the properties of conventional synthetic material. Metal fixation has a higher modulus than the cortical

bone and consequently causes the bone to be loaded abnormally and resorbed. Such dissimilar modulus, with the associated differential strain characteristics, also make it difficult to create a stable interface between tissue and implant. Although one solution to loosening has been to attempt to create a biological bone between the implant material and bone (using bioactive materials), it should be possible, to produce a material with a similar stiffness to cortical bone. So, particulated reinforcement should be a properties of biod diametrical an occurrence bone ingrowth, which other papers found that using hydroxyapatite could(82,83). By directly measuring tensile strength of the interface between hydroxyapatite and bone(84), using several electron microscopy techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning-transmission electron microscopy (STEM), etc. were studied(85,86) and this experimentals were both *in vivo*(87) and *in vitro* in animals and in man(88).

Bone attachment to 2 classes of hydroxyapatite coated polymer was evaluated mechanically and histologically. Coated and uncoated implants of both types were implanted in the distal femurs of rabbits for four and twelve weeks. these results found that hydroxyapatite coatings significantly improved the bond strength between polymers and bone by allowing direct bone apposition and some mechanical interlocking with the bone(89). At present, the biological performance of macroporous and dense hydroxyapatite after implantation in the rat middle ear was evaluated during an induced *Staphylococcus aureus* middle ear infection. The results obtained so far suggest that hydroxyapatite was highly suitable for middle ear

for middle ear implantation(90). In addition, hydroxyapatite was the major inorganic component of human matrix which has long been suggested as a possible bone substitute. It was a different from many other biomaterials, characterized by excellent osteoconductive ability through its appropriate pore structure, direct contact with bone tissue without any intervening connective tissue, mechanical strength sufficient to withstand physiological loads *in vivo*, and nontoxicity(91).

While some other authors have concentrated on fiber reinforcement, others have studied a particulate reinforcement with various inclusions such as carbon spheres, inorganic bone particles, sugar, and tricalcium phosphate in bone cement. All particulates have been used primarily to improve mechanical properties and in some could a promote ingrowth of living bone into the cement at the bone/cement interface with varying degrees of success. The most promising results were found using inorganic bone as hydroxyapatite. Park *et al.*(92) showed that by mixing hydroxyapatite particle with cement, and found that fatigue cracks propagation rates decreased and the bone/cement interfacial shear strength increased. These finding have also been backed by the findings of Castaldini *et al.*(93) who alloyed bone cement in varying percentages about 2 to 12.5 % with hydroxyapatite with the aim of optimising the physio-mechanical performance of the composites. They performed creep tests on rectangular bar specimens and showed that cements alloyed with hydroxyapatite attain the stationary stage of creep sooner and fracture stress varies with the hydroxyapatite concentration producing a maximum of about 69 MPa with a hydroxyapatite content of about 2.6 %. Young's modulus was also seen to increase from 2.6 to 3.5 GPa.

The same authors undertook to obtain measurements of Young's modulus for the filled cement as an indirect measure of the strength. They introduced in the polymer a second phase made up by crystalline hydroxyapatite, showed significant difference between the pure polymer and the composite. This differences was partly due to hydroxyapatite having a higher Young's modulus than PMMA and also partly due to the action of hydroxyapatite as a condensation factor for the porosity present in the dough during the polymerization process which mechanical properties of hydroxyapatite shows in Table 2.8. In addition, having to improve the physico-biological characteristic of PMMA normally employed in prosthetic surgery(94), hydroxyapatite was alloyed in varying percentages about 2.0 to 12.5. From the tests carried out, it was determined that the best value of hydroxyapatite was almost 3 %, which brought about a significant increase in flexural strength.

Table 2.8 The mechanical properties of of typical bioactive materials(95)

Material	Ultimate tensile strength (MPa)	Toughness (MNm ^{-3/2})
45-D-5 Bioglass	42	ND
Hydroxyapatite	190	0.9

Note : ND, no data.

The hydroxyapatite reinforced high molecular weight polyethylene(96-98) was a development which sought to address biocompatibility as well as the mechanical requirements. The mechanical properties data for the hydroxyapatite reinforced polyethylene system demonstrated that an increase in modulus with volume fraction was achieved at the expense of a decrease in elongation to fracture toughness. Consequently an appropriate balance between stiffness and fracture toughness could be achieved, so as to obtain approximate modulus matching, with a superior fracture toughness as compare with cortical bone. In particular, the incorporation of the hydroxyapatite phase in a polymer matrix produced a significantly higher fracture toughness than would be obtained for hydroxyapatite by itself. The processing of such a composite was difficult, and the choice of compounding and moulding methods was important to minimize polymer degradation.

2.3.5. Polymer Replacement Bone Cement

Weightman *et al.*(2) have tried by using a new more ductile bone cement. The new bone cement consisted of PEMA containing 1.5 % by weight of benzoyl peroxide and n-butyl methacrylate containing with 2.5 % by volume of N,N-dimethyl-p-toluidine. Unfortunately, the new bone cement was observed to have a Young's modulus of elasticity approximately half of the commercial PMMA bone cement and to have a ductility about 5 to 10 times greater. This was suggested unlikely to be significance since the materials lower Young's modulus would reduce the stress to which it was subjected and

its greatly increased ductility means that it had to be strained far more than polymethylmethacrylate before it cracked.

However, Behiri *et al.*(7) found that both Young's modulus and yield stress of the PEMA bone cement reinforced with 0-40 % hydroxyapatite increased from 702-1417 MPa and 18-22.69 MPa, respectively. Moreover, strain to failure of the system was found to remarkable decrease from 50-10.8 %.

2.3.6 Compatibility Enhancement with Silane Coupling Agent

A coupling agent is primarily a material that provides a water resistant bond between an organic polymer and an inorganic substrate. Modification of the interface material produced other changes in composites that are very desirable. Surface treatment of a mineral may improve wetout with a polymer, as well as dispersion of fillers in liquid polymers. The treatment protects the mineral against cleavage and may even heal flaws in the surface. The polymer layer may be strengthened by interface modification that promotes alignment of polymer segments and interdiffuses with the polymer, possibly forming interpenetrating polymer networks (IPN'S)(99), as shown in Figure 2.4. Surface modification may overcome inhibition of polymer cure by mineral surfaces. A silane treatment on a metal oxide surface stabilizers the oxide against recrystallization into a weak oxide form. All these factors may be important in determining total practical adhesion, but the test of a true coupling agent is whether it promotes retention of

adhesion under wet conditions. Their use results in improved bonding and upgraded mechanical and electrical properties.

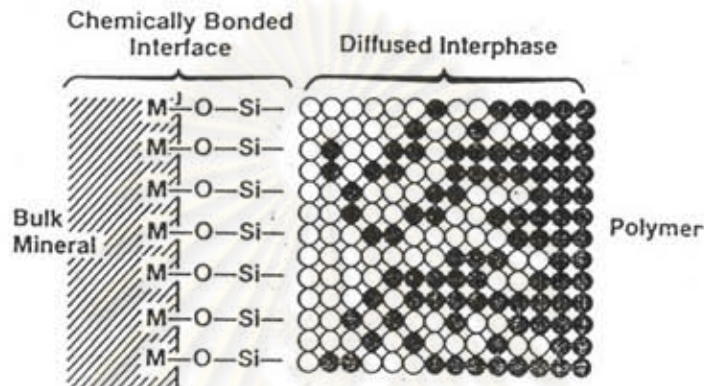


Figure 2.4 Bonding through silanes by interdiffusion: open circles indicate of regions of coupling agent ; solid circles.

Generally, silane coupling agents can be represented by the formula $YRSiX_3$, where X represents a hydrolyzable group as typically alkoxy and Y is a functional organic group such as amino, methacryloxy, epoxy, etc. For R typically is a small aliphatic linkage, $-(CH_2)_n-$, that serves to attach the functional organic group to silicon (Si). Silane coupling agents provides chemical bond between organic polymer and mineral surfaces. Methoxy silanes $[-Si(OH)_3]$ may react directly with hydroxyl groups on a mineral surface to form oxane bonds. The silane may also be prehydrolyzed to form silanetriols, which condenses with surface hydroxyl groups and with each other to form an organosilicone bonds surface. The fiberglass industry invariably applies

silanes from aqueous solution to deposit about 0.5 % by weight of siloxane on the fibers, as shown in Figure 2.5.

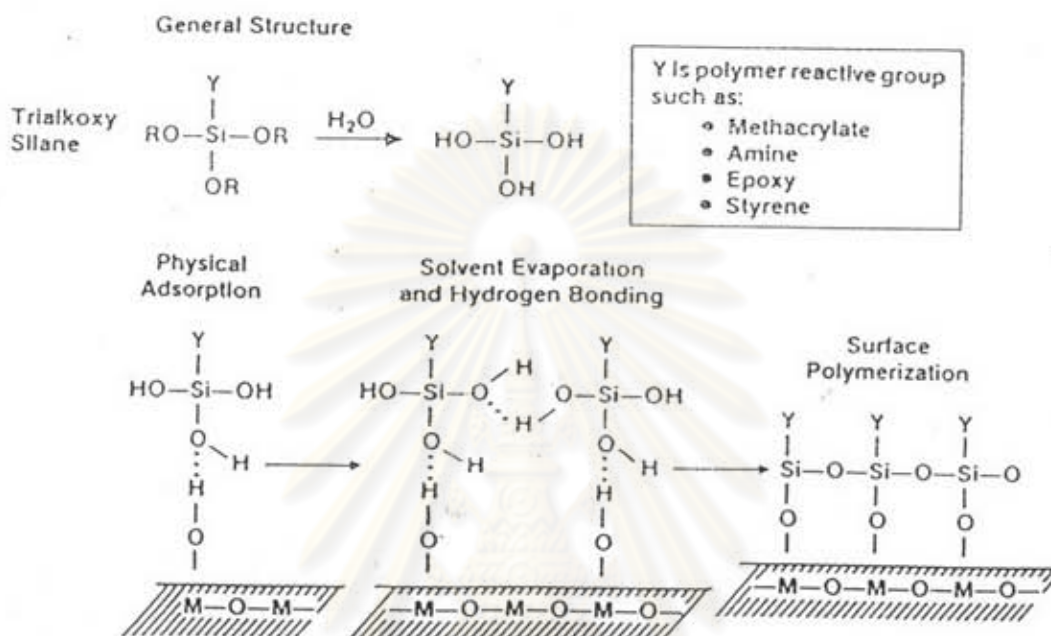


Figure 2.5 Monolayer model for bonding in mineral-polymer composites.

Coupling agents may be added to resins to obtain unprimed adhesion to mineral surfaces. Silanes may be formulated into primers by partial hydrolysis or by modification with polymer precursors. Primers on massive mineral surfaces are related to coupling agents applied to fiberglass or particulate minerals but are often applied in much thicker layers.

Organofunctional silanes are used in mineral filled thermoplastic polymers, desirable improvements in composite processing and strength properties were observed(100). Moreover, some of investigators (Bonar Polymers Ltd.) showed recently that

superior mechanical properties were obtained when filler alloyed in the bone cement alloyed with hydroxyapatite pretreated with organofunctional silane to the one encapsulated in PMMA beads should show desirable improvements in mechanical properties. At the same investigation(101), applying a silane coupling agents to treat the surface of inorganic filler enhanced to improve the mechanical, thermal, and electrical properties, as well as decreased mold shrinkage and color difference of the composites. Behiri *et al.*(7) also found that introduction of a silane coupling agent (3-trimethoxysilylpropyl methacrylate) to the surface of hydroxyapatite further enhanced the properties of the hydroxyapatite reinforced PEMA bone cement.



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