



## Chapter 5

### Discussion

#### Effects of different volume fractions of calcined bone ash reinforced polyethylene

Table 4.1.1 and 4.1.2 demonstrate that the amount of both calcined bone ash and synthetic hydroxyapatite affects the properties of the composite produced under the same method of processing. These effects come from the different properties of the calcined bone ash and the polyethylene matrix. The resulting properties of the composite will be somewhere between the extremes of either the polyethylene matrix or the calcined bone ash alone. Therefore, the volume fraction of filler is very important for producing a change in mechanical behaviour.

By the rule of mixtures the Young's modulus of the composite,  $E_C$ , is

$$E_C = E_{CBA}V_{CBA} + E_{PE}V_{PE} \quad (5.1.1)$$

where  $V$  is the volume fraction of each phase present in the composite. For the components used in this tests, the calcined bone ash has a Young's modulus of  $E_{CBA} \sim 85$  GPa, whereas that of the polyethylene,  $E_{PE}$  is 1 GPa. Since  $E_{CBA} \gg E_{PE}$ ,  $E_{PE}V_{PE}$  in equation 5.1.1 does not alter the value of the Young's modulus of the composite while it increases with increasing the calcined bone ash content.

Table 5.1.1 Estimates of Young's modulus of calcined bone ash reinforced polyethylene composites based on rule of mixtures calculation.

$V_{CBA}$	+	Calculated $E_c$ (GPa)
0		1.0
0.10		9.4
0.20		17.8
0.30		26.2
0.40		34.6
0.50		43.0

The calculated values of  $E_c$  are very different from the experimental data as shown in Table 5.1.1. This observation indicates that method which consider calcined bone ash particles and polyethylene matrix embedded in a homogeneous material does not adequately predict the experimental data. It should be assumed that in such practical cases the formation of discontinuities, defects and small cavities at the interface is possible. Defects induce stress field variation and act as stress concentrators, thus decreasing the Young's modulus in a way that the theory cannot predict.

The experimentally determined Young's modulus of the composites are plotted as a function of the volume fraction of filler in Fig.4.1.5. The Young's modulus increases with increasing the calcined bone ash content. The synthetic hydroxyapatite is smaller particle size than calcined bone ash,

then, there is a tendency of the Young's modulus to increase with decreasing particle size of the filler.

Figure 5.1.1 shows a comparison of the Young's modulus of the composite in the experimental study with the literature data for the same system (Bonfield *et al.*, 1984). It can be seen that, for all the data, the Young's modulus increases with an increase in the filler volume fraction. The experimental data is lower than that of the literature and remains steady at the 0.5 volume fraction. The values provide a more effective reinforcement in the 0.35 to 0.45 range.

The comparison with the previous bone data for a range of volume fractions (Evans *et al.*, 1990) in Fig.5.1.2, the Young's modulus values of natural bone tissue are higher than those of the composite for a given volume fraction. It can be demonstrated that the size, shape and orientations of the hydroxyapatite in bone has the disparity with the analogous composite. In bone, the hydroxyapatite exists in the form of thin plates about 5.0 nm thick and about 40 nm along the c-axis (Glimcher, 1984), whereas the composite has the calcined bone ash of micrometer scale in spherical form. The hydroxyapatite phase of natural bone is arranged within the matrix in a complex hierarchical arrangement. In contrast, SEM micrographs of the composite (Fig.4.3.1 and 4.3.2) show that the arrangement of calcined bone ash particles is the simple dispersion. There is not agglomerate or flocculation of them before binding with the polyethylene matrix.

However, bones of young vertebrates contain more amorphous material, becoming predominantly crystalline with maturity. This change in morphology is associated with changes in the mechanical properties. Thus,

the results of previous studies with the natural bone are not exactly clear according to the sources, positions and test methods. Wainwright *et al.* (1976) suggested that the minimum volume fraction of hydroxyapatite for it to act as a true reinforcement is about 0.35. Since the collagen is the main load-bearer in this fraction. The crystals would then be acting as filler particles stiffening the collagen by restricting its movement under stress.

Effect of strain rate on the Young's modulus values of calcined bone ash reinforced polyethylene can be seen in Fig.4.1.10. Also, this phenomenon is a factor affecting the mechanical values of the natural bone (Cowin, Van Buskirk and Ashman, 1987). As indicated, bone is stiffer and stronger at higher strain rates. These relationships were said to hold for all bone in the skeleton. Conversely, it can be seen that the low crosshead speed causes a higher relative Young's modulus than the high crosshead speed (Fig.5.1.3). The curve of low strain rate shows greatly increase at the low calcined bone ash content and slightly increase at the high about 0.45, while there is a little difference at each calcined bone ash content in the curve of high strain rate.

It should be realized that the low strain rate gives the exactly values for comparison at each volume fraction of filler although the high strain rate contains the data of Young's modulus near that of the bone. It may be the reason that the many previous works in mechanical properties for this composite were tested at the low strain rate.

As the volume fraction of calcined bone ash particles increases, Fig.4.1.6 shows that the tensile strength values slightly decrease at the low calcined bone ash content and remain stable at the about 0.30 volume

fraction. The reason for this phenomenon is not entirely clear, it has so many factors. At the same time the strain to failure decreases as shown in Fig.4.1.7. It can be explained that when the volume fraction increases the number of calcined bone ash particles per unit volume increases, hence, the number of interfaces around which breakage can occur,  $N$ , become larger. Consequently, the flow of large volumes of polyethylene matrix becomes more restricted, deforming to fail when stress applied.

The energy absorbed to the point of failure also decreases because the volume fraction of calcined bone ash and  $N$  increases (Fig.4.1.8) and it requires less energy for the particles and matrix to separate than is required for matrix deformation. In other words there is less polyethylene matrix available for plastic deformation. The toughness signifies its ability to absorb prior to rupture and also decreases for the same reason (Fig.4.1.9).

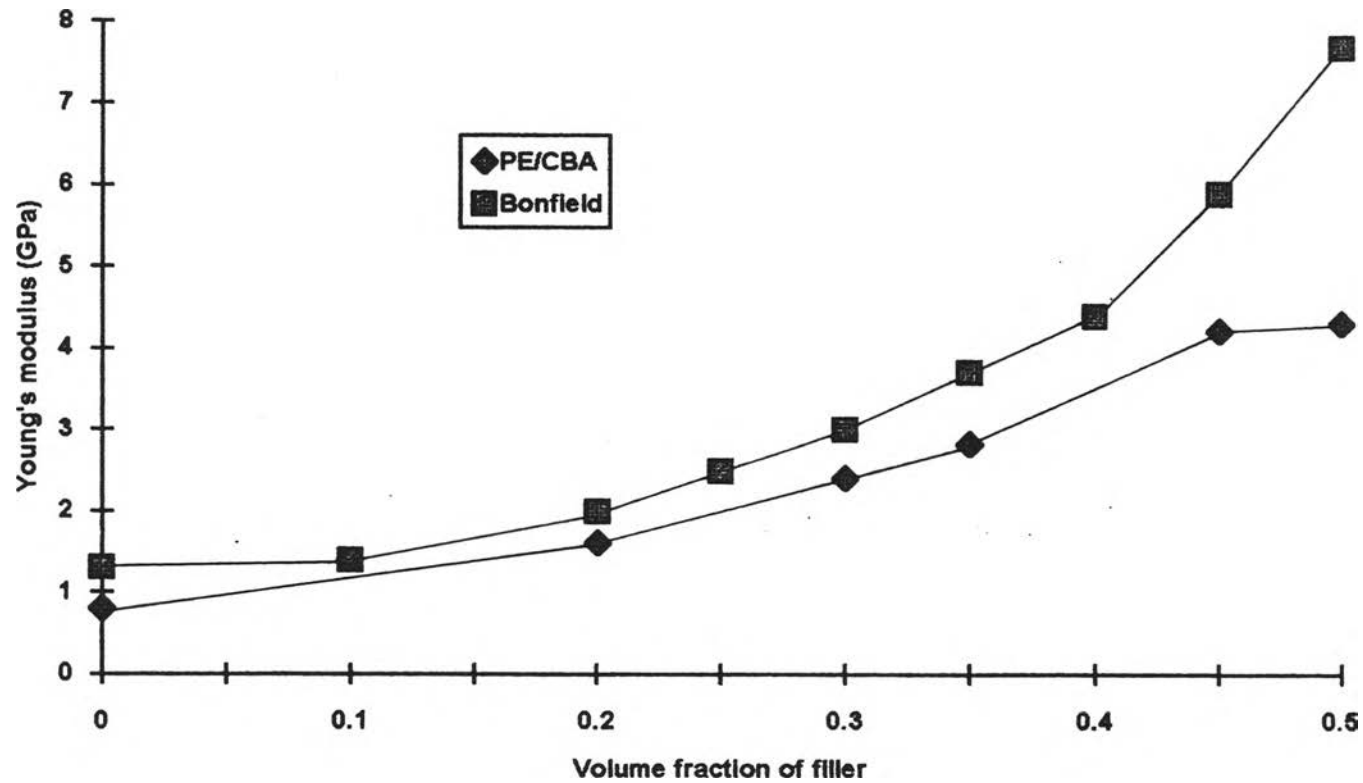


Figure 5.1.1 A comparison of the Young's modulus of the calcined bone ash reinforced polyethylene with the literature data (Bonfield *et al.*, 1984).

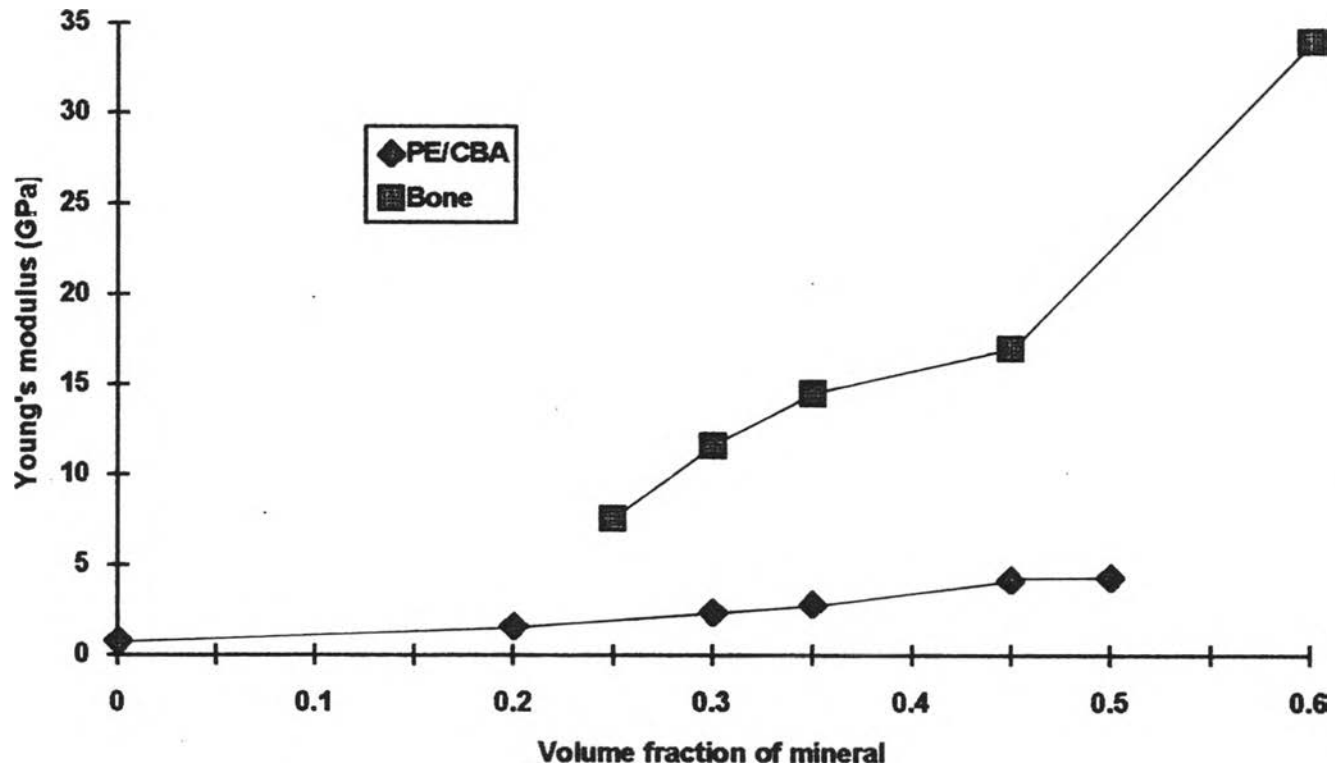


Figure 5.1.2 The relationship between the Young's modulus and mineral volume fraction in the calcined bone ash reinforced polyethylene and in natural bone tissue.

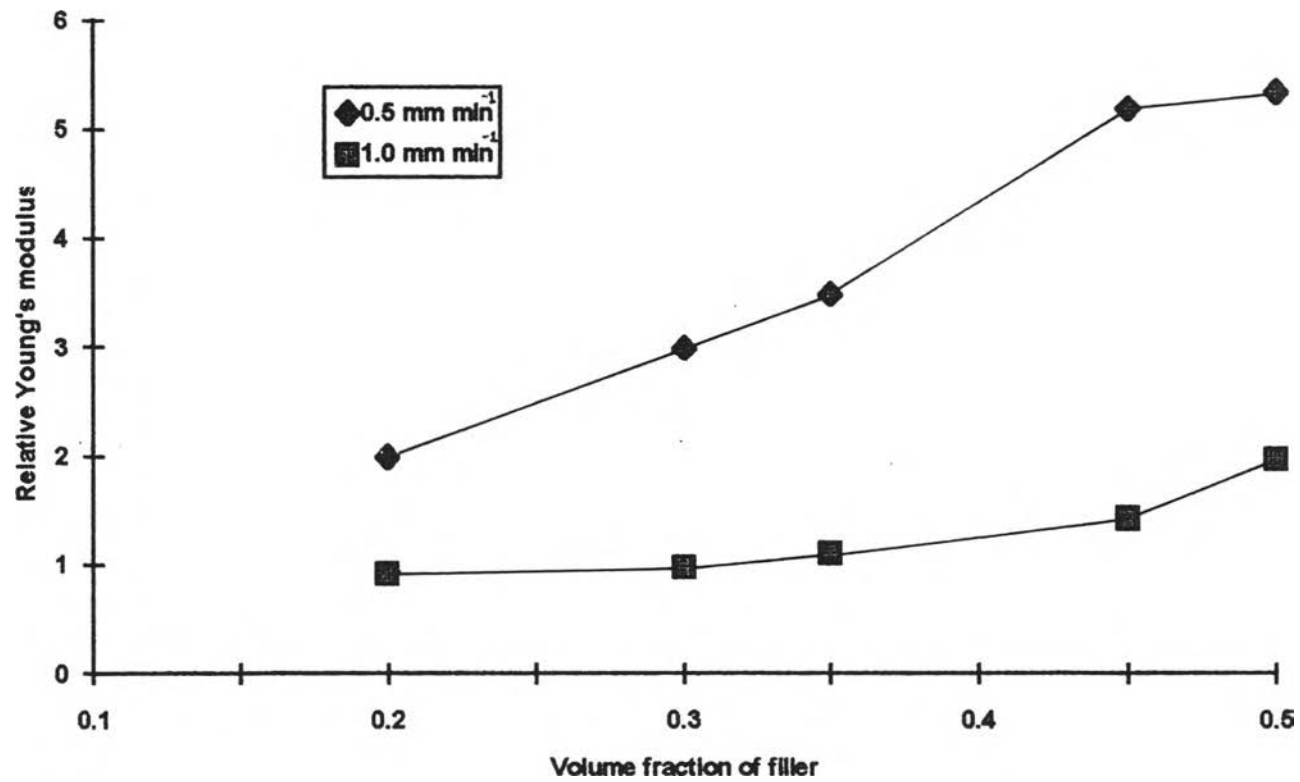


Figure 5.1.3 The difference of the relative Young's modulus ( $E_R$ ) for the two strain rates.



## Comparison between theoretical and experimental mechanical properties of calcined bone ash reinforced polyethylene

A large body of literature considers the composite as a two component systems characterized by perfect bonding between spherical inclusion and matrix. The most aim of the theories is to give an exact expression of the effective elastic moduli as a function of the corresponding moduli of the components and of their volume fraction. Fig.5.2.1 shows a comparison of theoretical equations and experimental findings for the Young's modulus. The values of the Young's modulus for calcined bone ash reinforced polyethylene fit the Guth-Smallwood equation well. The other theoretical curves predict too low values except the Thomas and the Mooney equation. Both models work well at low volume fractions but are high for volume fraction greater than 0.30. Hence, it seems that filler agglomeration or flocculation does not occur.

In Fig.5.2.2 the values for calcined bone ash reinforced polyethylene disagree with the Nielsen's and Schragger's models for zero adhesion. The investigation of Svehlova (1982) shows that the higher adhesion of kaolin particles to polyethylene results in the higher relative tensile strength. It should be assumed that the adhesion of the samples is not zero. An estimation of the extent of adhesion at the interface of the two components of the composite is possible by the method of Nicolais and Nicodemo (1974)

$$\frac{\sigma_c}{\sigma_p} = 1 - K\phi_f^{2/3} \quad (5.2.1)$$

where  $K$  is a parameter whose value is indicative of the extent of adhesion. For these data the composites fit very well with Eq.5.2.1 with  $K = 0.40$  (as shown by predicted curve in Fig.5.2.2). The SEM micrographs (Fig.4.4.1 to 4.4.7) reveal that the calcined bone ash and polyethylene do not bond chemically because no strands of polyethylene are attached to the calcined bone ash particles, otherwise the bonding in this relied on the mechanical coupling created by the shrinkage of the matrix around the particles during cooling after processing.

Nielsen's model for perfect adhesion predicts lower values for  $\mathcal{E}_R$  (Fig.5.2.3) than found in experimental values up to a filler content of  $\phi_f = 0.20$ . At higher filler contents the calculated values are too high. It seems that the break on the composite curve is not due to agglomeration of particles, considering the results of relative Young's modulus and the appearance of the fracture surfaces. It may be assumed that the 0.30 volume fraction of calcined bone ash is not able to undergo larger deformation.

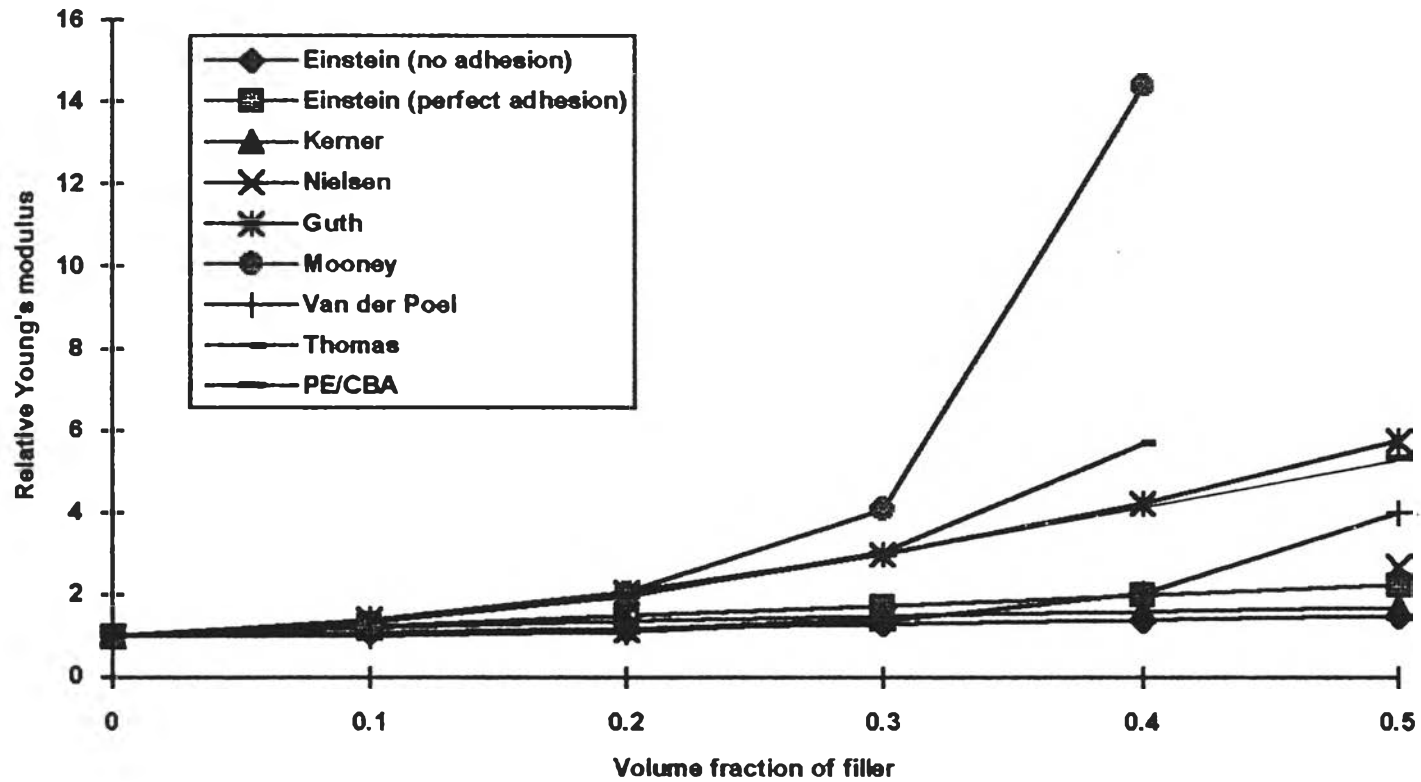


Figure 5.2.1 Comparison of theoretical models and experimental data of the relative Young's modulus against volume fraction.

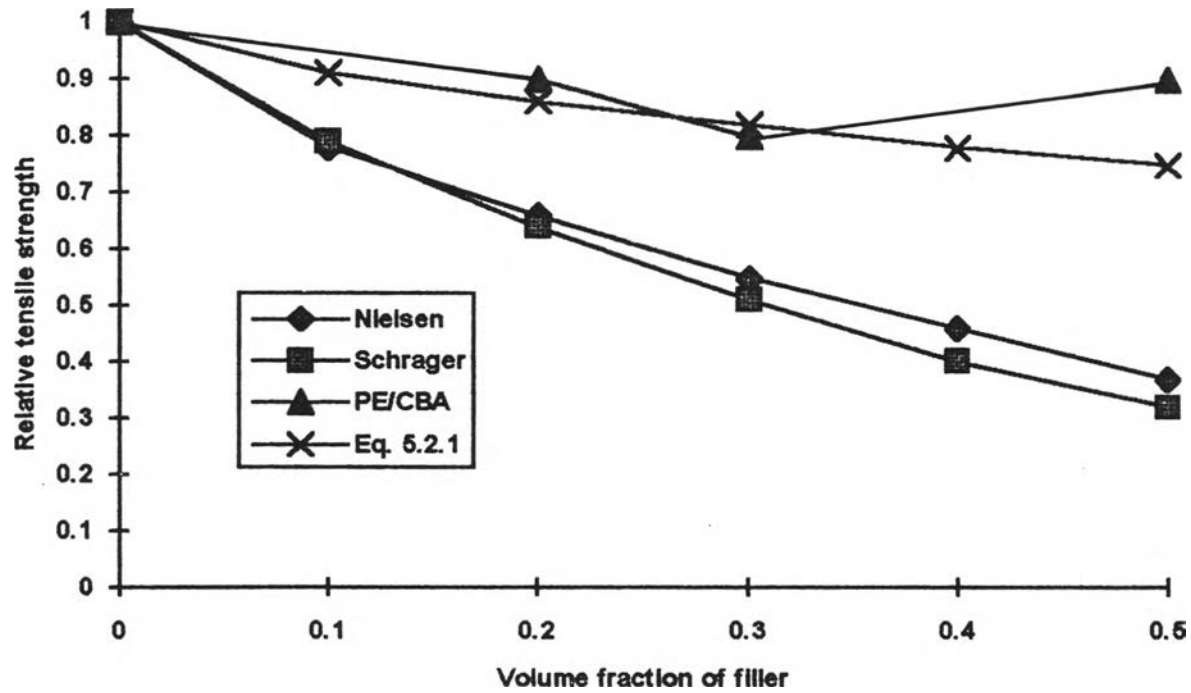


Figure 5.2.2 Comparison of theoretical models and experimental data of the relative tensile strength against volume fraction.

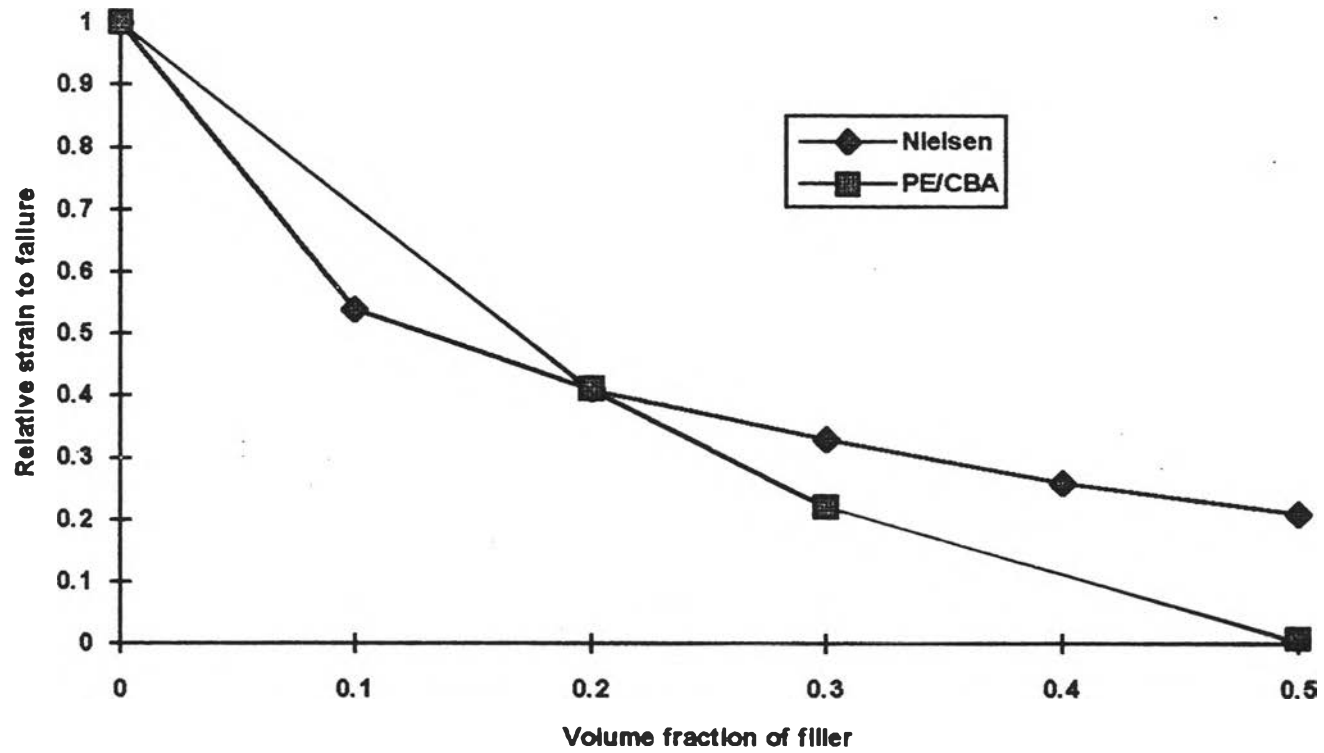


Figure 5.2.3 Variation in the relative strain to failure of theoretical model and experimental data.

### The relationship between hardness and Young's modulus of materials

Biological hard materials such as bones are often difficult to test mechanically because they come in small pieces and awkward shapes. One possible method of estimating those mechanical properties would be to infer them from properties that can be tested on small specimens.

The work of Evans *et al.* (1990) was the first to show clearly the relationship between Young's modulus and hardness. An analogue for bone in which the mineral content range is similar to the bone specimens was also investigated for comparison purposes. In this study, regression analysis was used in order to find a function which gave the best fit of the data for each variable and each material. Table 5.3.1 summarizes the results of this analysis.

Table 5.3.1 Equations relating microhardness (*VHN*) to mineral volume fraction ( $\phi_f$ ) and Young's modulus (*E*) for bone and the calcined bone ash reinforced polyethylene composite.  $R^2$  is the coefficient of determination.

Bone		Composite	
Equation	$R^2$	Equation	$R^2$
$VHN = 717 (\phi_f)^{3.6} + 19.5$	0.87	$VHN = 75.6 (\phi_f)^{3.0} + 5.8$	0.99
$VHN = 0.104 (E)^{2.0} + 17.5$	0.96	$VHN = 1.24 (E)^{1.2} + 4.25$	0.99

Fig.5.3.1 shows the relationship between microhardness and mineral volume fraction for bone (Evans *et al.*, 1990). It can be seen that 87% of the variance in the data is explained by modeling the relationship as a power function with an exponent of 3.6. In the composite (Fig.5.3.2) the fit is even better with 99% of the variance. The value of 3.6 for bone shows a relationship very different from the linear and probably reflects the wider range of the variance assessed in this study.

In fact, for a given volume fraction, the hardness of the natural tissue is higher than that of the composite because of the different size and distribution of the mineral component and the way in which it is bound to the matrix. In bone, a direct physical bond between the collagen and apatite accounts for the tensile stiffness of bone and that provides a large part of the resistance to indentation. In contrast, SEM micrographs of fracture surface of the composite found no residual polyethylene on the calcined bone ash particles. This is further evidence that chemical bonding does not occur between filler and matrix. Therefore, the major resistance to the penetration of the indenter comes from a frictional force as the calcined bone ash particles are forced to move through the polyethylene matrix under the indenting load.

Fig.5.3.3 and 5.3.4 show the relationship between microhardness and Young's modulus for bone and the composite respectively. For bone, microhardness is related to Young's modulus by a square function, whereas in the composite the relationship is closer to a linear one. In both cases, a very good fit to the data is obtained with 96% and 99% of the variance explained for the bone and composite respectively.

The theory of hardness testing suggests that it is related to the yield strength of the material, rather than the Young's modulus, since the indent is formed as a result of plastic flow in the material. Consideration of the ideal strength of a material, however, shows that strength is theoretically related to the modulus divided by ten (Kelly and Macmillan, 1986). Thus, the correlation observed in this study between modulus and hardness would be expected in an ideal solid.

The strength of the relationships shown in this study suggests that microhardness could be used as an indicator of Young's modulus in bone specimens that do not easily lend themselves to normal testing procedures.

In Fig.5.3.5 the relationship between microhardness and mineral volume fraction is shown for both the natural bone tissue and the composite. This demonstrates more clearly the large differences in *VHN* that exist between the two materials. In all cases, the hardness of bone is higher than that of the composite, which shows that factors other than the ratio of the two phases present must be influencing the relationship as alluded in the previous episodes. The same can not be said for the relationship between *VHN* and Young's modulus (Fig.5.3.6). It can be found that in some regions the relationship appears to be accepted.



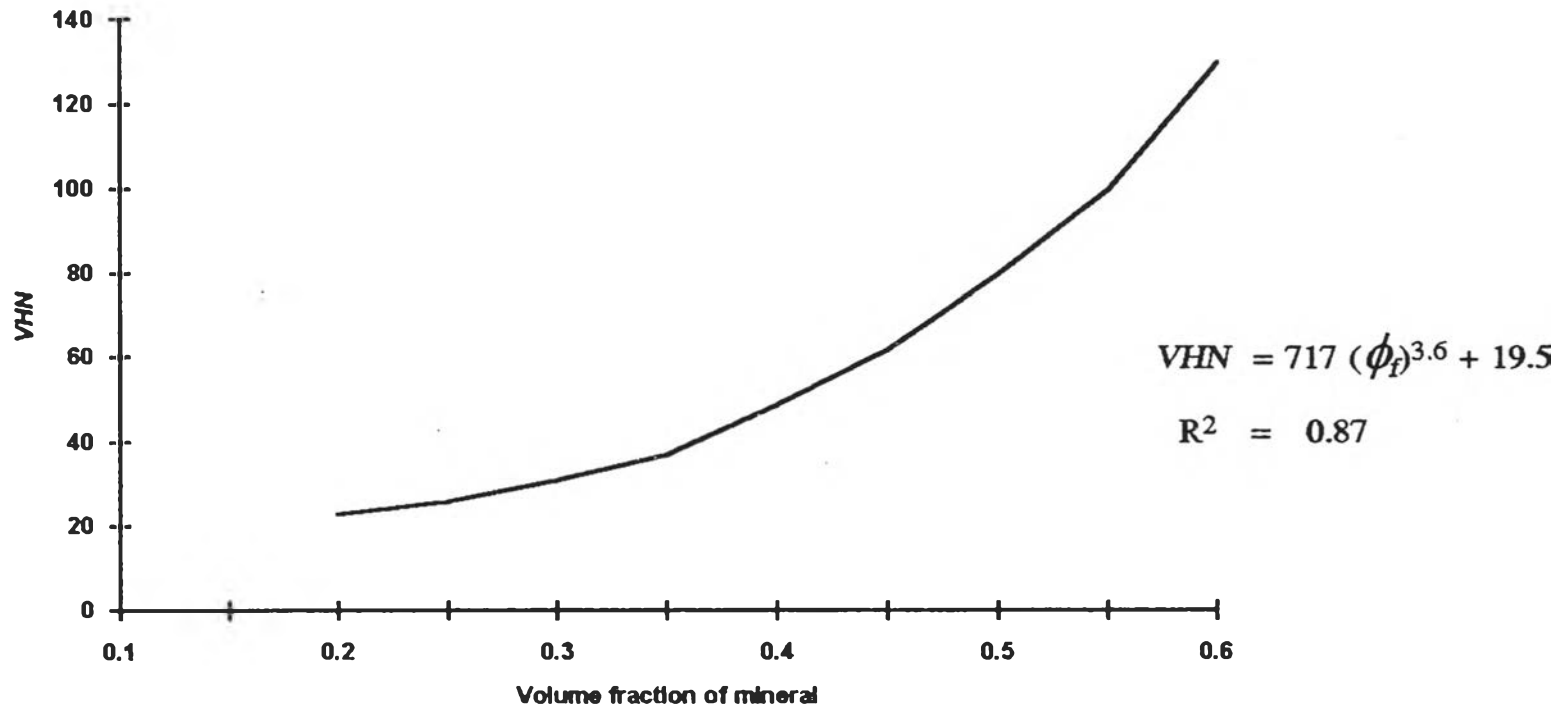


Figure 5.3.1 The relationship between microhardness and mineral volume fraction in natural bone tissue (from Evans *et al.*, 1990).

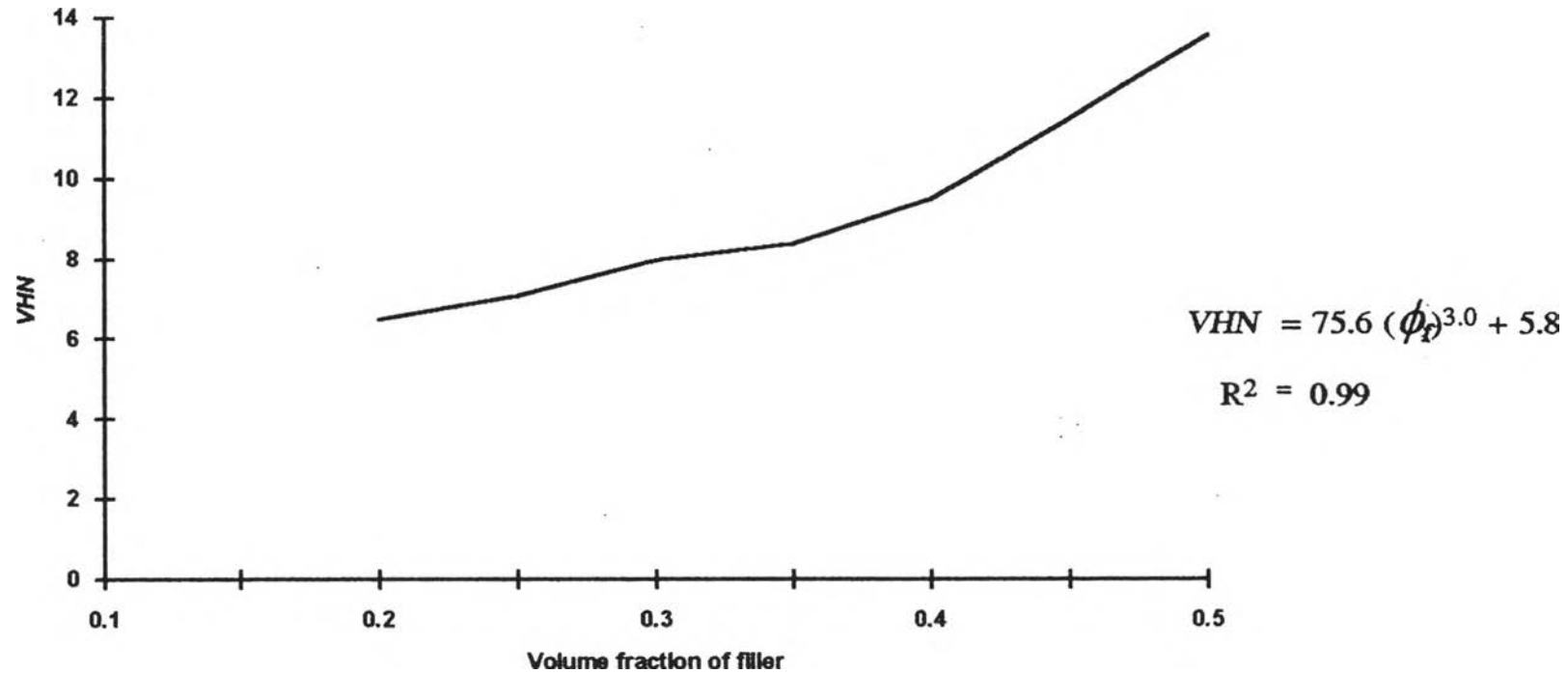


Figure 5.3.2 The relationship between microhardness and volume fraction of filler in the calcined bone ash reinforced polyethylene composite.



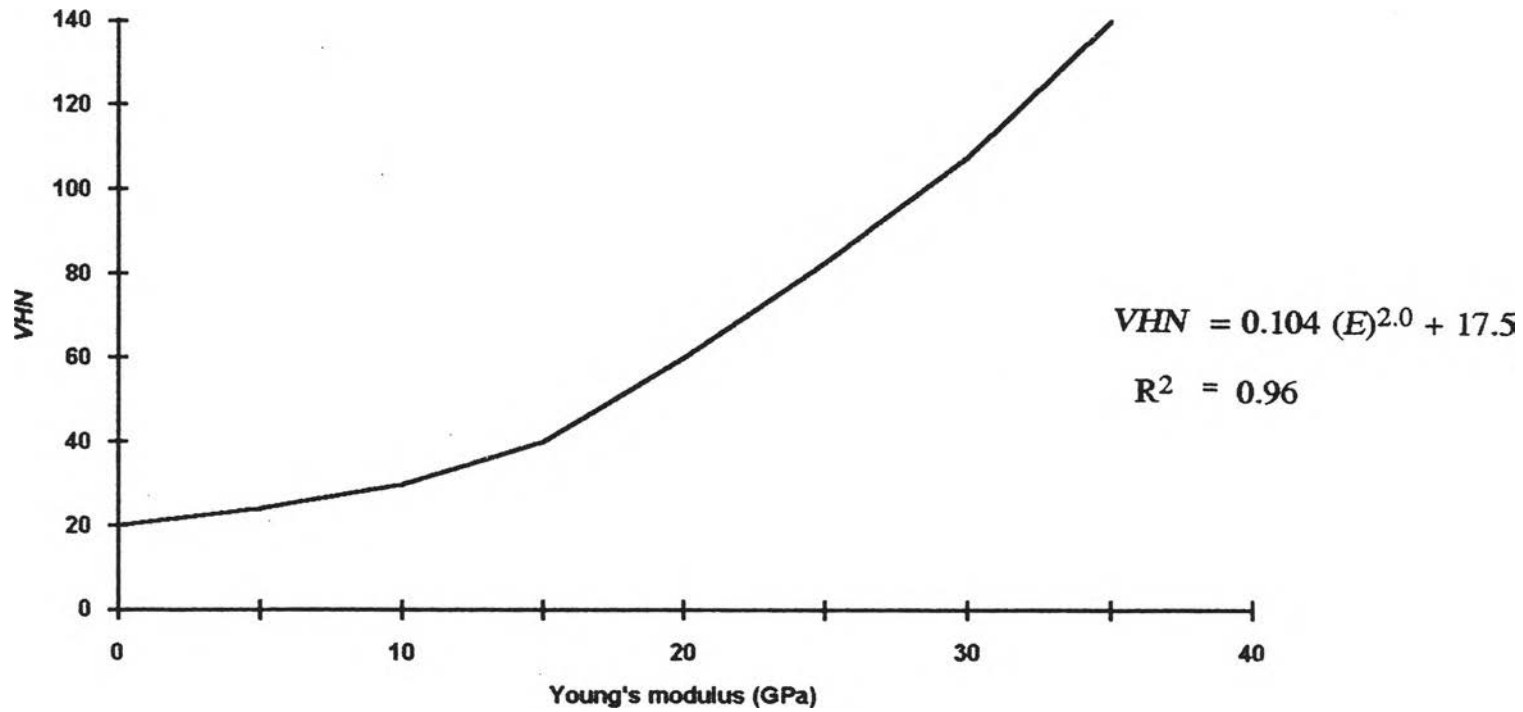


Figure 5.3.3 The relationship between microhardness and Young's modulus in natural bone tissue (from Evans *et al.*, 1990).

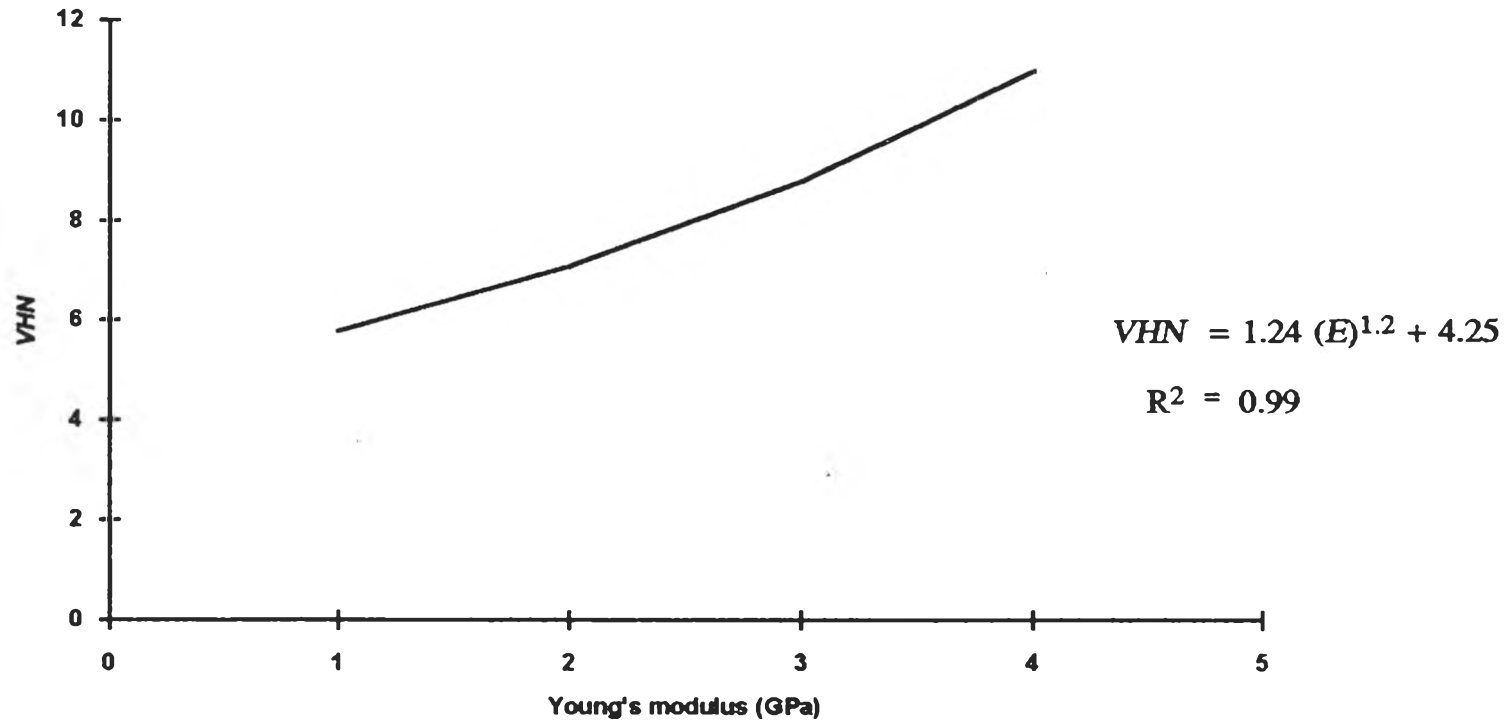


Figure 5.3.4 The relationship between microhardness and Young's modulus in the calcined bone ash reinforced polyethylene composite.

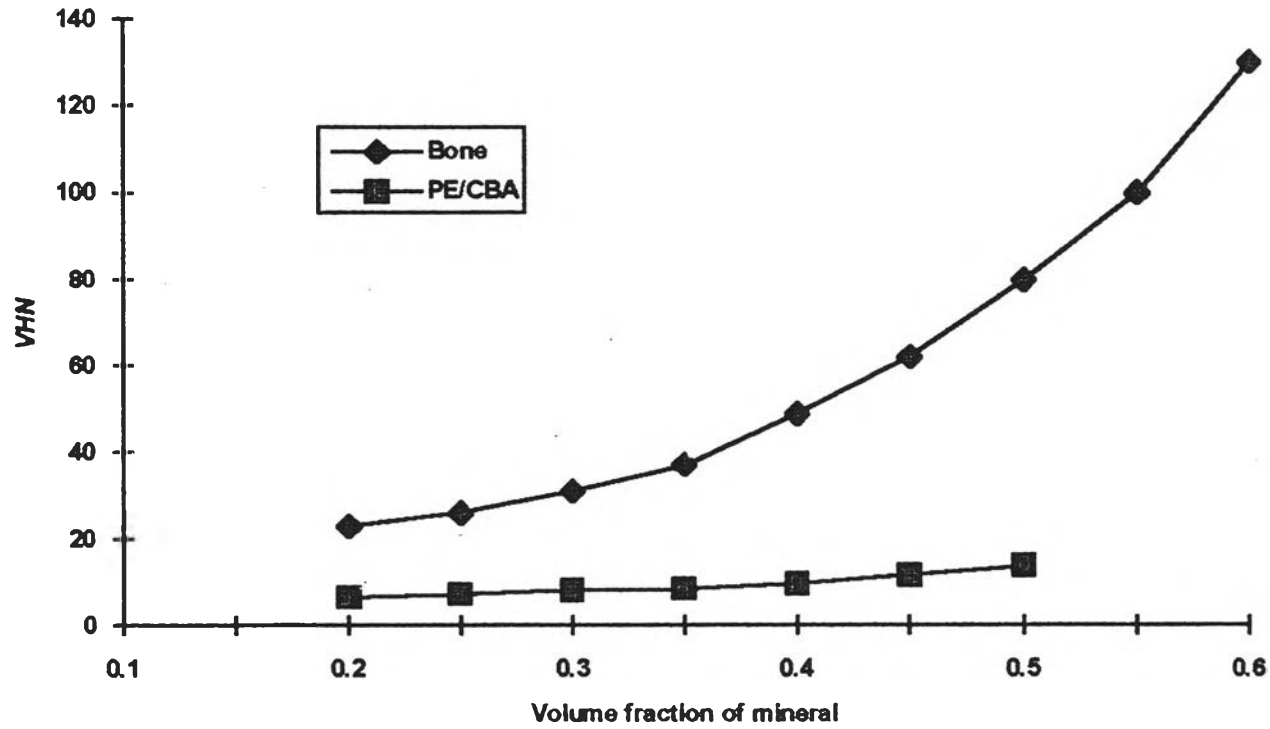


Figure 5.3.5 The relationship between microhardness and mineral volume fraction for both natural bone tissue and the calcined bone ash reinforced polyethylene composite.

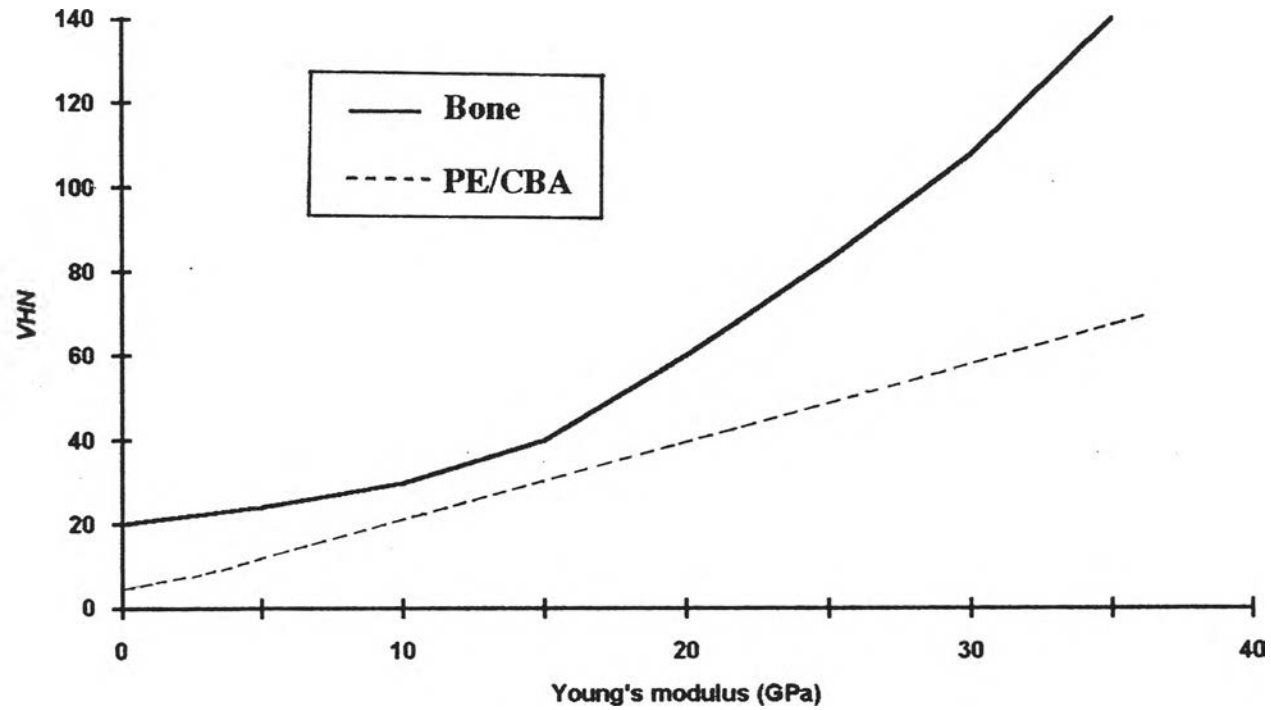
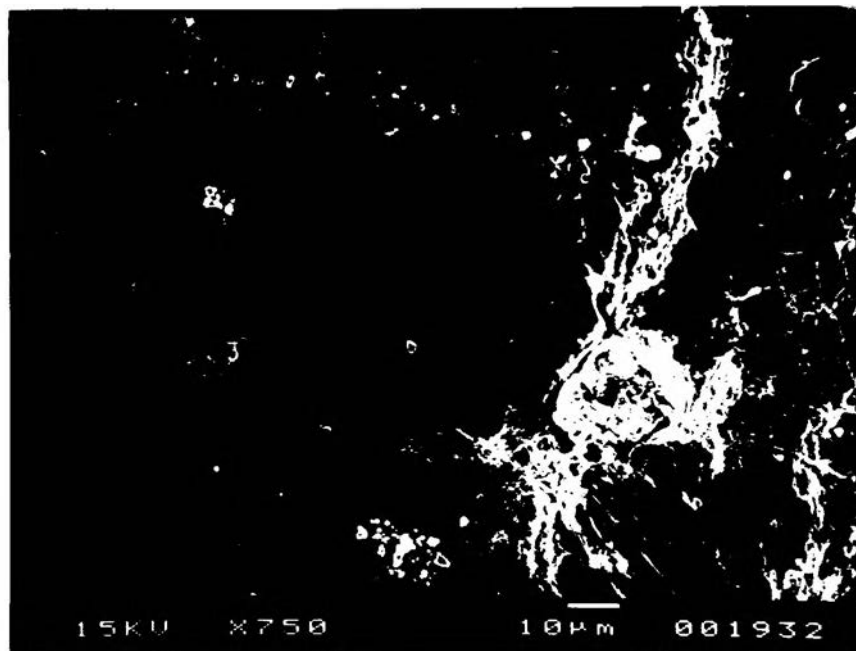


Figure 5.3.6 The relationship between microhardness and Young's modulus for both natural bone tissue and the calcined bone ash reinforced polyethylene composite.

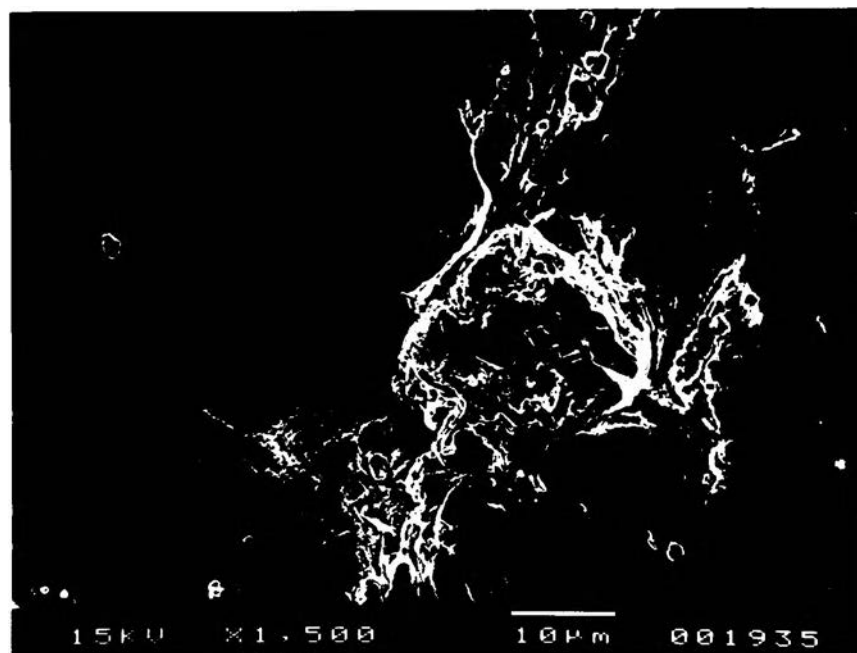
## Fractography

From the SEM micrographs of fracture surfaces reveal voids around the calcined bone ash particles and strands of stretched polyethylene thinning continuously towards their ends. This indicates that the polyethylene is plastically deformed and stretched away from the parts of the calcined bone ash particles which lie perpendicular to the applied stress, as shown in Fig.5.4.1. In Fig.5.4.1(a) the lower magnification micrograph of a distinct form of microfailure is seen and is denoted as craze. The craze is characterized by a void-fibril structure with dominant dimension, perpendicular to the applied stress. Associated with the craze is seen large dewetted calcined bone ash particle. The mode is seen more clearly in Fig.5.4.1(b), the fibrillated nature of the craze is more distinctly revealed. Fully dewetted particle is evident in the midsection of the craze.

A possible explanation for crazing in filled thermoplastics is discussed by Chacko *et al.* (1983) and Friedrich and Karsch (1981) and this is shown in Fig.5.4.2 (a), (b) and (c). Only a small amount of plastic strain is needed for the first step of damage. With further plastic strain the voids usually grow in the stress direction, forming dimple-like holes around the particles (step II). Subsequently, the stress concentrations would shift to the equatorial region since the void is nonreinforcing. A profile of the void would accelerate the formation of craze (step III).



(a)



(b)

Figure 5.4.1 SEM images of a single calcined bone ash particle during tensile test.



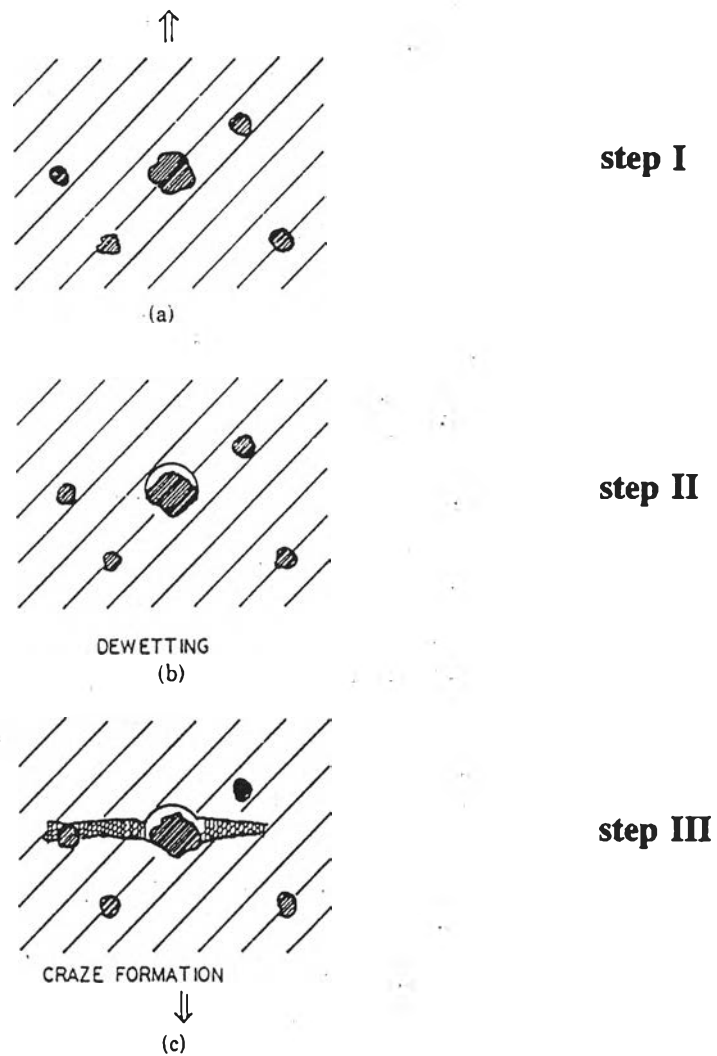


Figure 5.4.2 Schematic for proposed craze formation process in filled polyethylene : (a) initial configuration; (b) dewetted particle; (c) craze formation normal to the stress direction (from Chacko, Farris and Karasz, 1983).

The strain levels in Fig.5.4.2 (b), (c) are continuously reduced with increasing filler fraction. This will lead to a transition from a more ductile mode of failure to brittle fracture behaviour. In the ductile mode (Fig.4.4.1 to 4.4.3), the polyethylene matrix is not restricted in its ability to stretch and to support a load and therefore would be expected to provide greater strength. In the brittle mode (Fig.4.4.4 and 4.4.5), the coalescence of holes, which is the dominant mechanism of crack formation and fracture, will occur even before the ultimate dimple length is reached.

It can be explained that when mechanical energy is supplied to the polyethylene matrix, it will attempt to absorb at least some of the energy by deforming. If enough energy is supplied the polyethylene matrix will fracture, consuming some of the available energy in breaking the atomic or molecular bonds and disentangling molecular chains in polymers. In practice fracture starts from a flaw, which the stress is concentrated, and propagates across the matrix. Griffith's theory postulates that as the crack grows it absorb energy to form the new fracture surfaces and simultaneously releases energy from the broken bonds at the tip of the crack. If the energy absorption is greater than the energy release, the crack stops (unless external energy is supplied to it). Conversely if the energy release is larger than the energy absorption the crack continues to propagate. Increasing the rate of energy release causes the crack to propagate faster. Hence, the fracture surface energy, which is the energy needed to open the crack unit area, may be calculated.

When the calcined bone ash volume fractions are low, all the mechanisms of void formation, dimple growth and plastic deformation of the

polyethylene matrix can become effective in front of a crack, so a large plastic zone can be expected. It is the ductile mode of failure. In the case of higher the calcined bone ash fractions the polyethylene matrix is not able to develop its resistance to crack growth because so much energy release is obtained. In addition the maximum amount of strain at break is reduced by the coalescence of holes around the particles. This leads to a reduction of the plastic zone and a transition from ductile to brittle fracture behaviour.

In the case of bone, there are many points of crack tip instability in fracture propagation because bone is a nonhomogeneous, anisotropic and nonlinearly viscoelastic material. The discontinuous structure of bone such as blood vessels, lamellae, osteons is formed as the weak cross-links between them. When a fiber breaks, there is a discrete drop in the stress at the crack tip and each fiber fails catastrophically because there is nothing to allow any changes in the stress. Hence, the discontinuous structure of bone leads to its discontinuous type of fracture, increasing the robustness of bone rather than increase its tendency for brittle fracture (Paiekarski, 1970).

By comparison, the calcined bone ash reinforced polyethylene is isotropic material because there is continuously bound through the polyethylene matrix due to inter-molecular forces. Then, at the tip of a propagating crack material can take up much of the stress by deforming plastically for some distance ahead of the crack tip. When material at the crack tip breaks, the stress is zero, and immediately ahead, the yield stress will be reached by material some distance in front of the crack tip. The reason of this continuity is the inter-molecular attraction of polyethylene matrix, causing plastic deformation. Piekarski (1970) found that no bone has

been stretched or drawn out into thin strands in the same way as the polyethylene.