# Chapter 5

# Discussion

## 5.1 Composite characterization

The processing stages employed in this work which consist of premixing, compounding, powderising and compression moulding can give the calcium carbonate filled high density polyethylene composites with a good dispersion of calcium carbonate without big agglomerate as shown in figures 4.4-4.7. The micrographs show that even at very high loading of calcium carbonate (40 vol-%), the dispersion is still good. It can be explained that in the compounding process, because of the high torque characteristic of the processing screws, the Betol co-rotating twin screw extruder used in this study can generate the high shear force to disperse calcium carbonate particles in highly viscous high density polyethylene melts effectively. Moreover, it can be assumed that the enhanced dispersion of calcium carbonate also achieved by changing the composite pellets into the form of powders before processing by the compression moulding. In composite system when heat and pressure is applied, the polymer acts as the mobile phase. The polymer in powder form can tranfer heat and flow easier than in pellets form because of higher surface area.

In addition to a good dispersion of calcium carbonate in the high density polyethylene matrix, the preservation of calcium carbonate content in the composites after processing is also required. Because the properties of composites depend upon the fraction of two phases.

By the rule of mixtures the calculated density values of the composites, $\rho_c$ is defined by :

$$\rho_c = \rho_m V_m + \rho_f V_f \tag{5.1}$$

where V is volume fraction of each phase and subscripts m and f represent the matrix and filler phase respectively.

From figure 5.1, it appears that the agreement between the experimental results and the calculated values is very good. This means the satisfactory ratio of calcium carbonate in the composites after processing is obtained. Moreover, the real amount of calcium carbonate in the composites obtained from the thermogravimetric analysis as shown in figure 5.2 also support density measurement results. However, it can be seen that the experimentally determined volume fraction are slightly less than the calculated values, though not significant. This caused by many factors such as the loss of filler during processing, technical error during the measurement and the skin effect, excess polymer at the surface of the composite sheet caused by the mobility of polymer to the walls of mold during compression moulding.

In order to prepare the composites with high filler loading, higher processing temperature is necessary for good mobility of the melt to achieve a good dispersion of calcium carbonate because of the higher viscosity. Consequently, the oxidation of high density polyethylene matrix may occur which can cause the deterioration of properties of the composites. From Raman spectra of the calcium carbonate filled high density polyethylene composites with various volume fraction of calcium carbonate as shown in figures 4.8-4.13, it can be observed that the spectrums of all composites do not show a peak at 1746 $cm^{-1}$ which corresponds to the $>C=O$ stretching of the carbonyl group caused by the oxidation of high density polyethylene matrix. Therefore, it can be said that there is no oxidation of high density polyethylene matrix during the compounding of calcium carbonate filled high density polyethylene composites.
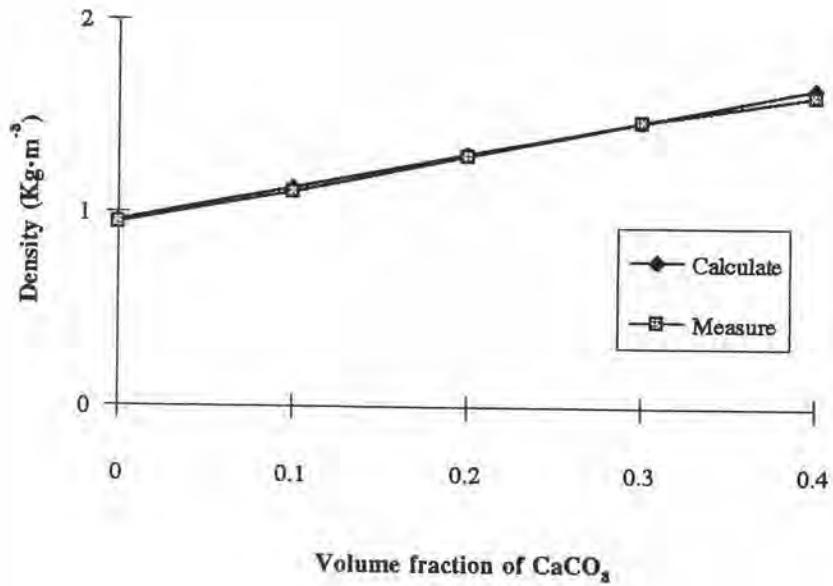
Figure 5.1 A comparison of calculated and measured densities of $CaCO_3$ filled HDPE composites with various filler volume fraction.
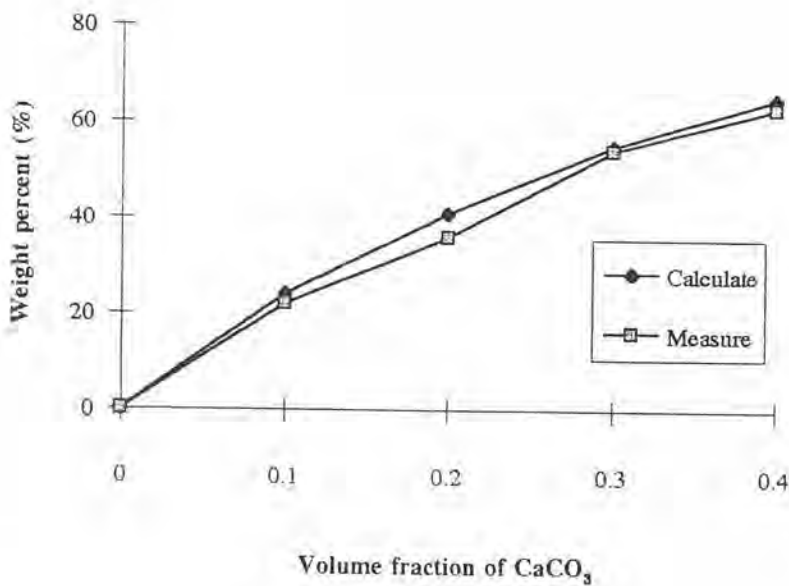


Figure 5.2 A comparison of calculated and measured weight percent of $CaCO_3$ filled HDPE composites with various filler volume fraction.

## 5.2 The effect of calcium carbonate volume fraction on the tensile properties of the composites.

Generally, tensile testing is a technique frequently used to determine the mechanical properties of the materials, especially for polymer because many mechanical information of the polymer can be obtained in this test mode.

Table 4.3 shows the tensile results of calcium carbonate filled high density polyethylene composites with various volume fraction of calcium carbonate. It is obvious that Young's modulus of the composites increase with increasing calcium carbonate content. However, the increase in Young's modulus was accompanied by the deterioration of tensile strength and ductility of the composites, figures 5.3-5.7. The increase in Young's modulus of composite with filler content is mainly due to the much more rigid of calcium carbonate than the polyethylene matrix which result in the higher Young's modulus of the composite. The explaination for the significant increase in Young's modulus with the filler content is also based on the assumption of a special morphology of the polymer matrix around calcium carbonate particles suggested by Vollenberg and Heikens (1989). The changes in morphology is associated with the changes in Young's modulus of the composites. During cooling the composites from processing temperature to room temperature, calcium carbonate particles can act as initiation sites of the solidification process. The polymer matrix adjacent to the embedded particles contract because of a more favorable orientation of the molecules than the polymer matrix in the bulk, then a zone with higher density having a higher modulus will be formed around the

filler particles. Therefore, when the filler content is increased, there are a great number of initiation sites for contraction process, hence, the increase in Young's modulus of the composites. Figure 5.3 shows that the Young's modulus of calcium carbonate filled high density polyethylene composites increases non-linearly with the filler content, attaining a value about 170 percent higher than that of the unfilled high density polyethylene at 0.4 volume fraction of calcium carbonate. The increase in flexural modulus and compressive modulus of the composite with filler content can be explained by the same reason.

In case of the tensile strength of calcium carbonate filled high density polyethylene composites, it appears that tensile strength values slightly decrease with increasing the filler content, about 35 percent lesser than that of unfilled high density polyethylene at 40 percent volume fraction of calcium carbonate. It can be noticed that the improvement of the Young's modulus is much more dominant than the reduction in tensile strength of the composites. The reason for the reduction of tensile strength of the composite is that the mechanical bond is only formed at the interface of calcium carbonate particles and polyethylene matrix. This is caused by the different in the coefficients of thermal expansion which result in thermally induced stress. Whenever the applied stress exceeds the frictional force between phase, debonding occurs and stress can not transfer through the filler particles then the majority load bearer is the polymer matrix.

In additional filler can act as stress concentrator, a large flaw exists within this area. This phenomenon also results in the decreasing in the tensile strength of the composites as shown in figure 5.4. In 1992, Fu and Wang found similar result in un-modified polypropylene-calcium carbonate composites.

Figure 5.7 shows that the energy absorbed to the point of failure greatly decreases as filler content increases. The reason is that when volume fraction of calcium carbonate increase, it requires less energy for calcium carbonate particles and polyethylene matrix to separate than is required for the fracture in the matrix. In addition it can be assumed that the sharply decrease in strain at break with filler content caused by the coalescence of holes around the calcium carbonate particles when the tension force is applied. This leads to a reduction of the plastic zone and transition from ductile to brittle fracture behavior of the composites when the filler content is increased. Figure 5.8 reveals the brittle-ductile transition of the composites occurs at 0.2 volume fraction of filler.

The scanning electron micrograph of the tensile fractured surface of composites are shown in figures 5.9-5.12. It effectively reveals the interfacial state of the composites. It can be seen that there are nacked, released particles of calcium carbonate between the polyethylene fibrils caused by the large plastic deformation of the polymer matrix during tensile testing. These micrographs indicate that the adhesion strength at the interface is lower than that of polyethylene matrix so the fracture preceeded along the interface and no strands of polyethylene are attached to the calcium carbonate particles. Moreover, the micrographs further

show that the fracture behavior of composites can be divided into 2 types, ductile and brittle. the ductile failure show the extensive polyethylene fibrils around calcium carbonate, figures 5.9 and 5.10, whereas limited fibrils were seen in case of 0.30 and 0.40 filler volume fraction composites, figures 5.11 and 5.12.
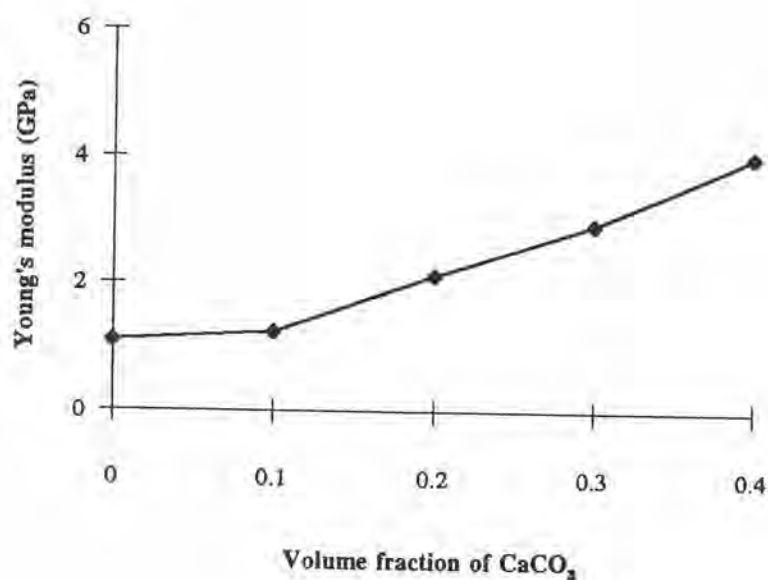


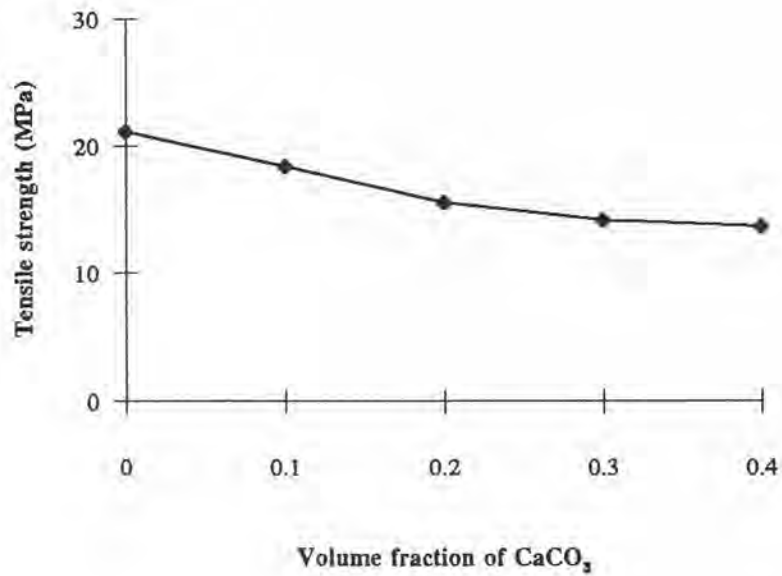Figure 5.3 Young's modulus of $CaCO_3$ filled HDPE composites versus volume fraction of $CaCO_3$.

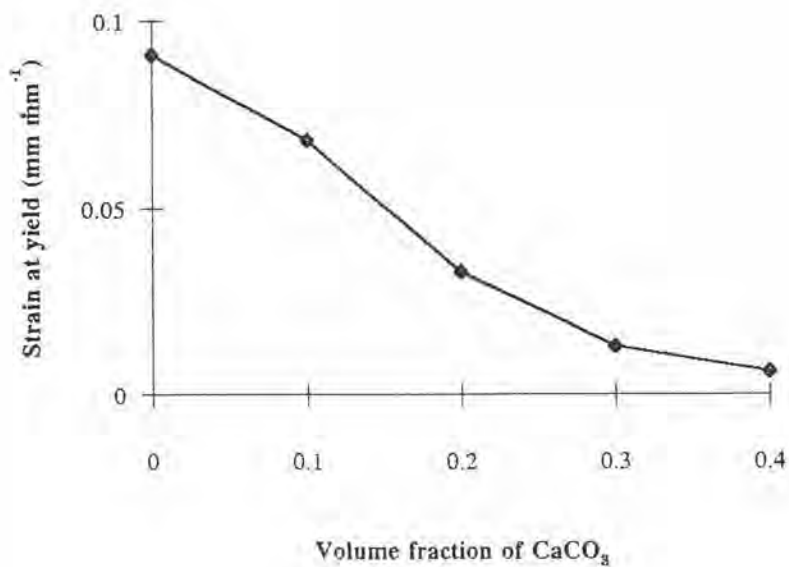Figure 5.4   Tensile strength of CaCO₃ filled HDPE composites versus volume
fraction of CaCO₃.



Figure 5.5   Strain at yield of CaCO₃ filled HDPE composites versus volume
fraction of CaCO₃.
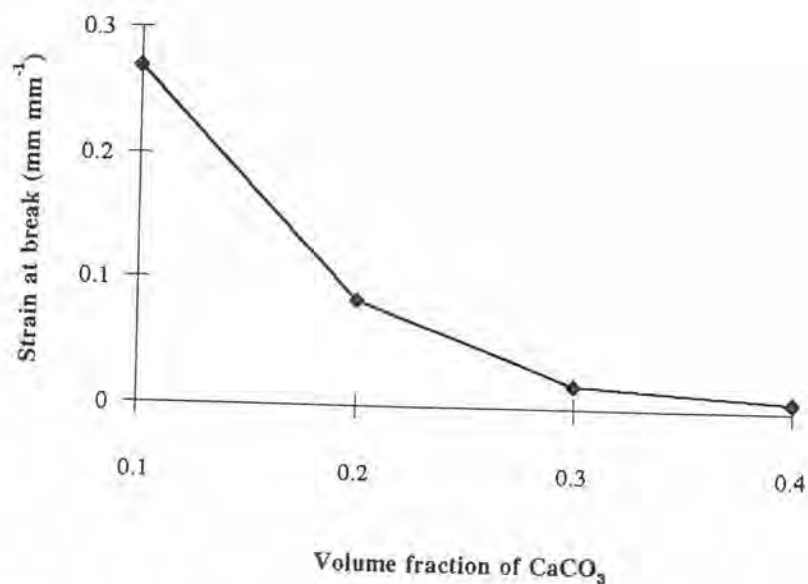
Figure 5.6   Strain at break of $CaCO_3$ filled HDPE composites versus volume
fraction of $CaCO_3$.
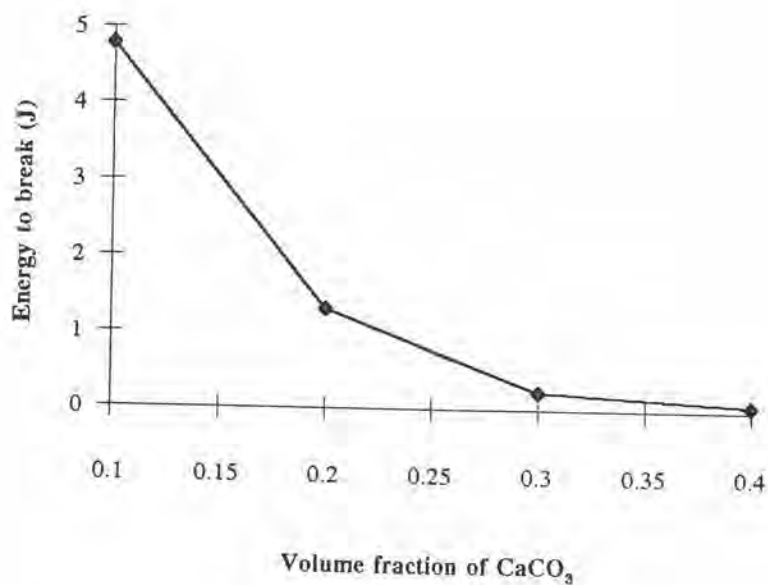


Figure 5.7   Energy to break of $CaCO_3$ filled HDPE composites versus volume
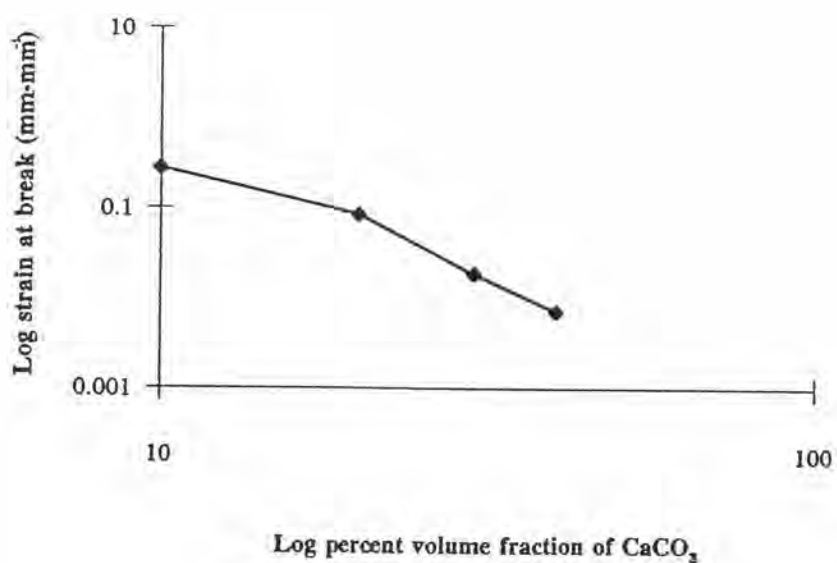fraction of $CaCO_3$.

Figure 5.8   Tensile strain at break are plotted against the volume fraction of CaCO₃
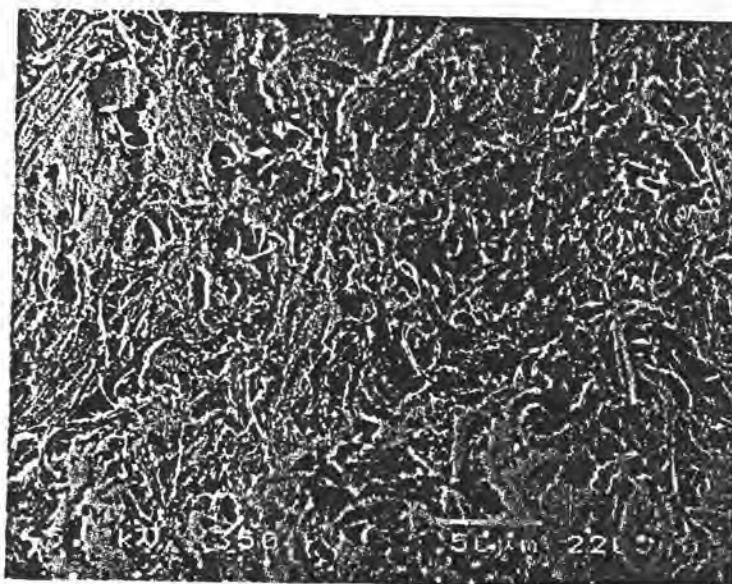
in logarithm scale.



Figure 5.9   SEM micrograph of tensile fractured surface of HDPE filled with 0.1
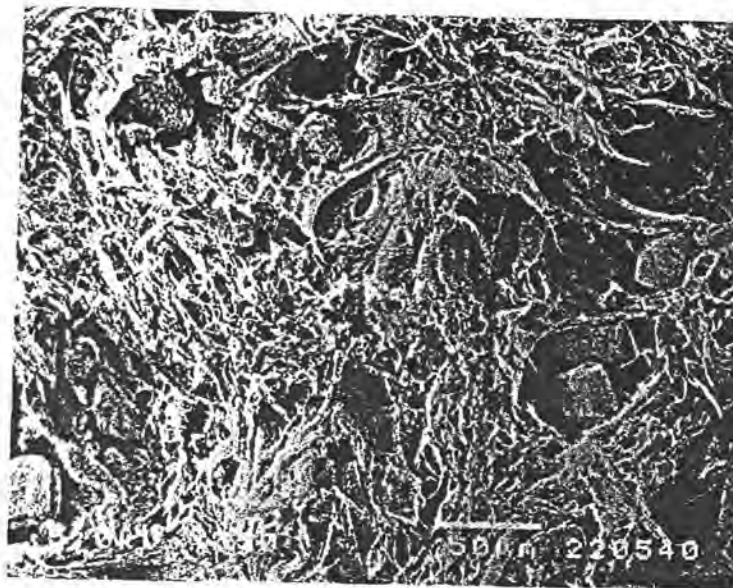
volume fraction of CaCO₃.

Figure 5.10   SEM micrograph of tensile fractured surface of HDPE filled with 0.2
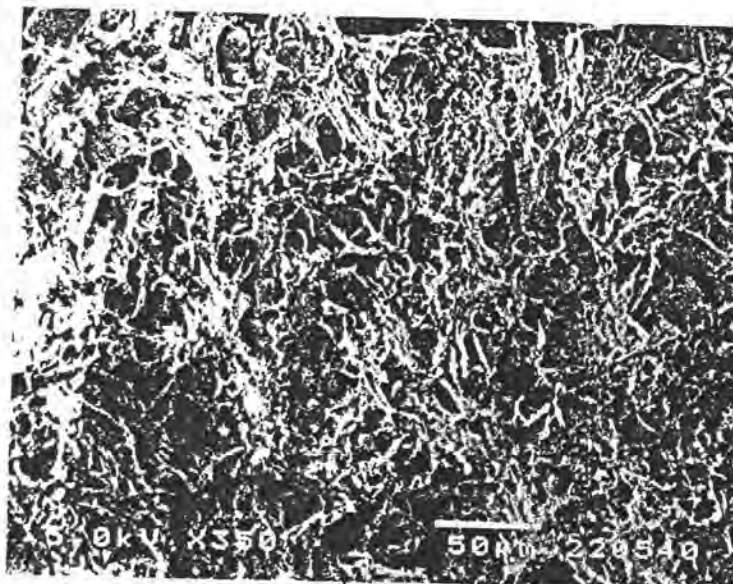
volume fraction of $CaCO_3$.



Figure 5.11   SEM micrograph of tensile fractured surface of HDPE filled with 0.3

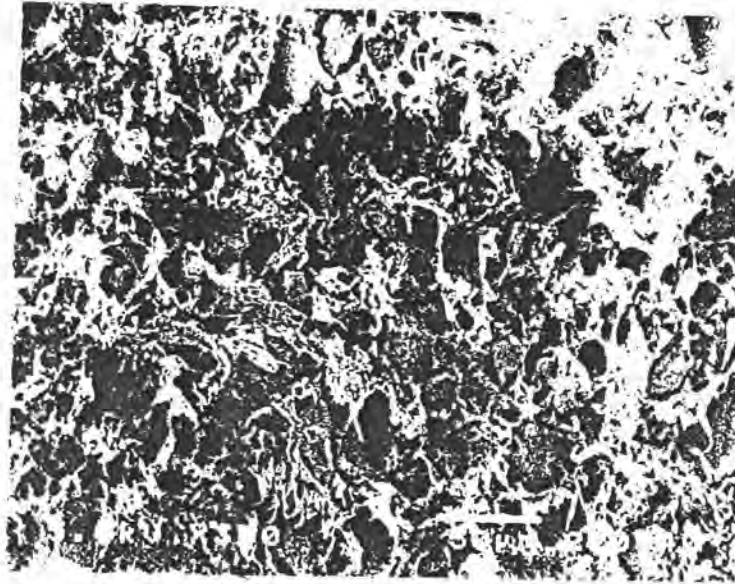volume fraction of $CaCO_3$.

Figure 5.12   SEM micrograph of tensile fractured surface of HDPE filled with 0.4

volume fraction of CaCO$_3$.

There are many theories and equations derived to describe the elastic

behavior of the composite.  Each equation prove useful for particular composite

system.   For Einstein's, Sato and Furukawa's, Van der Poel's and Kerner's

equations, they considered the surface interaction between filler and a matrix.

Einstein's equation can be used only for the system with low concentration of filler

with no interaction between filler particles.   Sato and Furukawa's equation was

derived to the intermediate case of relatively poor adhesion.  Kerner's equation is

applicable for the system containing nearly sphearical particles being much more

rigid than the polymer matrix and having some adhesion between two phases.

However, the other parameters are taken into account in the case of Nielsen's,

Guth's and Thomas's  equations such as the influence of the shape anisotropy of

the filler particles, filler size and the interaction of fillers. Figure 5.13 shows a comparison of tensile modulus of calcium carbonate filled high density polyethylene composites in this experimental study with various theoretical predictions. It shows that the experimentally determined tensile modulus agrees well only with the prediction of Kerner's equation. This agreement indicates that there is some adhesion at the interface of composite in this study.

The comparison of experimental tensile strength of calcium carbonate filled high density polyethylene composites with the theoritical prediction is shown in figure 5.14. The experimental values disagree with all models for poor adhesion between filler and polymer matrix. The experimental curve runs parallel to theoritical curves, but are higher. It can be assumed that there is some adhesion at the interface of calcium carbonate and polyethylene matrix. The reason for this disagreement is that for poor adhesion, stress can not tranfer through the filler particles because of the dewetting between filler particles and polyethylene matrix so the majority of bearer is the polyethylene matrix. On the other hand, if there is some adhesion at the interface and the applied stress is not higher than the adhesion strength, stress can transfer through the filler particle resulting in higher tensile strength.
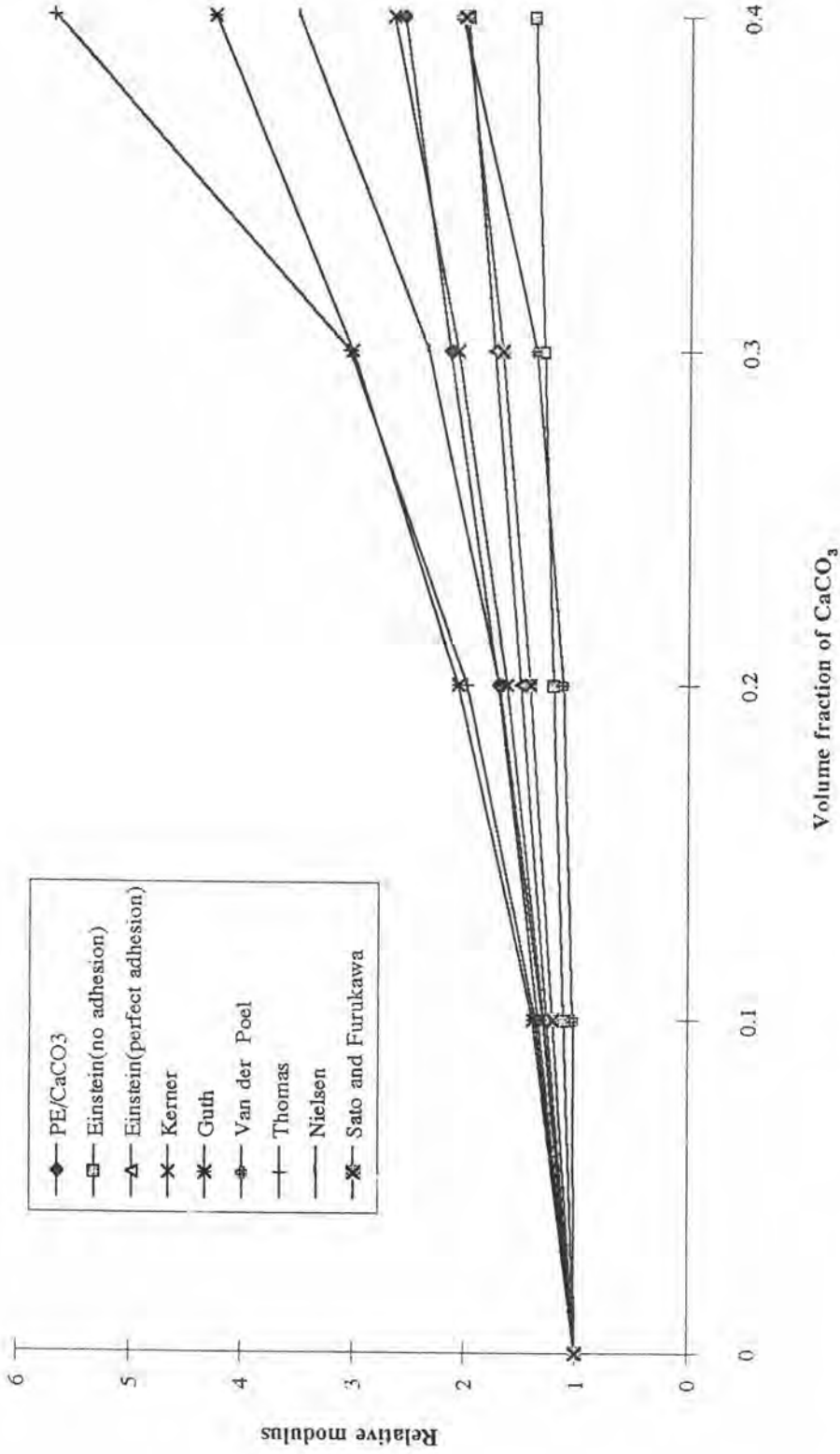
Figure 5.13 Comparison of theoretical models and experimental data of the relative Young's modulus against volume fraction
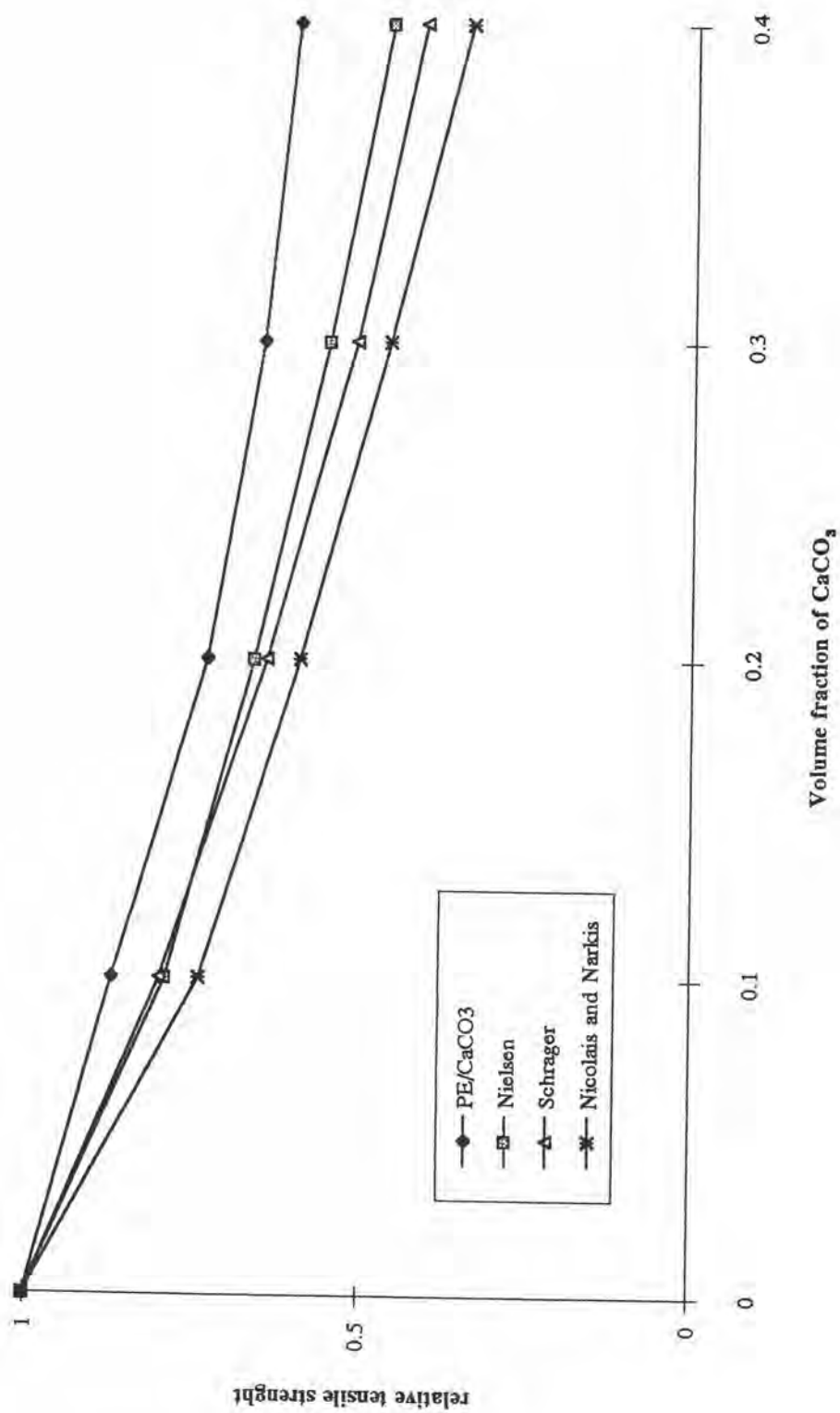
Figure 5.14 Comparison of theoretical models and experimental data of the relative tensile strength against volume fraction

## 5.3 The effect of testing mode

In addition to tensile testing, compressive and flexural test can be used to determine the mechanical properties of the materials, though, not widely used. In case of flexural and compressive stress-strain curves, yield point is not well defined, so the stress and strain at yield are necessary to be obtained from offset yield point. This is done by specifying a point on the stress-strain curve where the curve departs from linearity by a specified percentage elongation or extension, using 0.2 percent strain in this study. The results show that the type of testing does not influence on the modulus of the composite for the same volume fraction of filler. On the other hand, stress at yield and strain at yield of the composites depend on the type of testing. For the sake of comparison, tensile yield values are taken as offset values as for the other modes. In figures 5.15 and 5.16, the comparison of the stress at yield and strain at yield of the composites among three different mode of testing is shown respectively. It can be noticed that at the same volume fraction of calcium carbonate, stress at yield and strain at yield measured from the compressive test are higher than that from flexural and tensile test.

This phenomenon caused by the different stress fields that are applied resulting in the different molecular process in the specimens during testing. In tensile testing, the applied force tends to open the cracks and flaw in the composite specimens so the failure occurred easily. In contrast, compression test tends to close the cracks rather than open them. In case of flexural test, both of tension and compression occur on the specimen, the outer part of the specimen is under tension

and the inner part is under compression, so it shows the intermediate values between that from tension and compression test. This trend is further illucidated if the apparent tensile yield values is taken for comparison instead of offset yield values, figure 5.4 versus figure 5.15. In figure 5.4, the tensile yield stress decreases with increasing filler content whereas flexural and compressive yield stress, figure 5.15, increase. This is again obviously due to the debonding phenomenon. This is also reflected in the theoretical prediction of mechanical behavior of the composites. Different testing mode displays different behavior of composites though containing similar filler content. This will add the further complication in predicting generalized equation of the particulate composite.
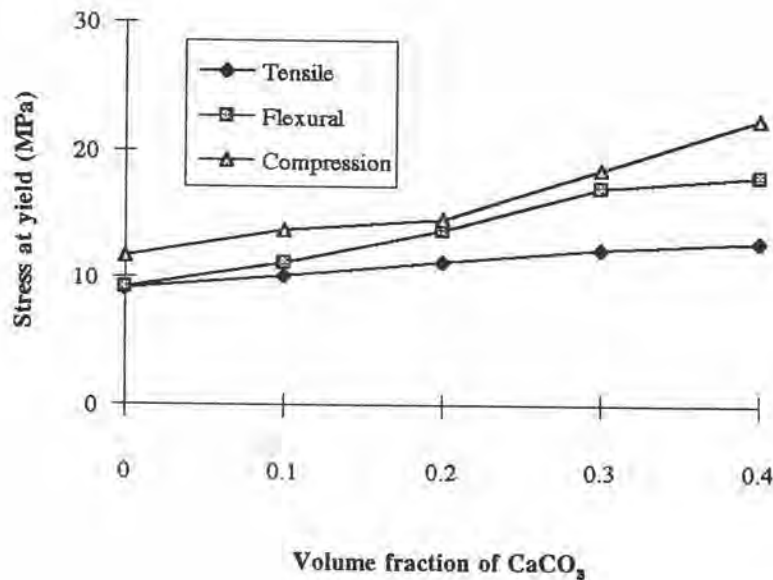


Figure 5.15 The variation of stress at yield of $CaCO_3$ filled HDPE composites as a function of $CaCO_3$ volume fraction and testing mode.
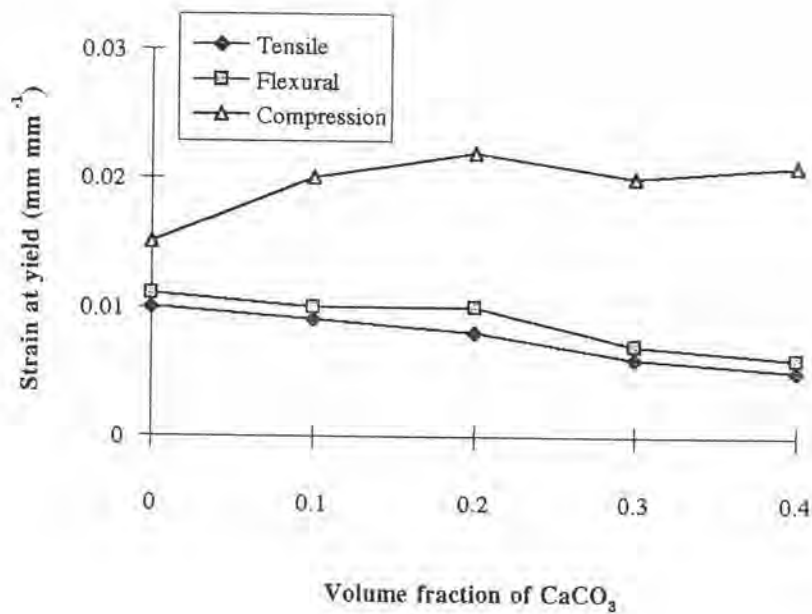
Figure 5.16 The variation of strain at yield of CaCO₃ filled HDPE as a function of

CaCO₃ volume fraction and testing mode.

## 5.4 The influence of annealing

Crystallinity of annealed unfilled and filled high density polyethylene is equivalent to the ratio of specific heat of fusion of the polyethylene and that of 100% crystalline polyethylene (277 $kJ \cdot kg^{-1}$) obtained from tables. The variation of heat of fusion, melting temperature and degree of crystallinity of the unfilled high density polyethylene as a function of annealing temperature is shown in figures 5.17-5.19 respectively. It indicates that annealed unfilled high density polyethylene gives better thermal properties than non-annealed one, and the improvement is more obvious at higher annealing temperature up to 140 °C. Then it slightly decreases and is followed by annealing temperature independence. During

processing, polymer molecules are constrained by external stress and short cooling time so the unfavorable crystalline region occurs. In heat treatment, the applied heat energy causes the mobility of the polymer molecules and then different structural changes occurs depending on the annealing temperature. The results from figures 5.17 to 5.19 can be explained by using the assumption of El-kindi and Schreiber (1992) as mentioned in section 2.6. At low annealing temperature, energy causes the small mobility of molecules in the amorphous region which can result in the elimination of defect, impurity and the formation of new crystallite. As annealing temperature increase the order region of the polymer becoming more populated and result in the increasing in melting temperature.

The result shows that the maximum increase occurs at melting temperature in the range of 135-140 °C. It can be explained that at this temperature region, the energy is high enough to cause the rearrangement of fold chain in crystalline lamellae, the lamellae thickening process is occured. Then the bigger crystallite with higher density are formed. The evidence for the lamellae thickening of the crystalline can be investigated in differential thermograms as shown in Appendix. It can be assumed that the width of a broad peak corresponds to the melting of crystals with varying lamellae thickness. As the lamellae thickness increase, the width decreases. Beyond the temperature of 140 °C, the melting temperature of the sample decreases because the melting and recrystallize of polymer molecule occurs. The newly formed crystals may not as thick as the previous ones. The results show that the optimum heat treatment condition is at 135 °C, making the crytallinity,

crystallite size and other crystalline parameters of high density polyethylene approach "optimization".

The effect of heat treatment on the mechanical properties of unfilled high density polyethylene is investigated in the term of tensile modulus, tensile strength and tensile strain at yield. Figures 5.20-5.22 represent the variation of these properties as a function of annealing temperature. From figures 5.20 and 5.21, The modulus and tensile strength of the samples show the same trend as that of thermal properties. It can be noted that the improvement of the modulus and tensile strength can relate to the enhancement in degree of crystallinity and morphology of crytalline materials. The modulus increase with crytallinity because the crystallites in the amorphous region can act as cross-links by tying segments of many molecules together. In addition, they also behave as rigid filler in an amorphous matrix giving the reinforcing effect on the materials. In case of tensile strength, it can be assumed that after heat treatment the defect and tie molecule in the amorphous region which is the weak point and cause lower strength are reduced so the tensile strength is increased.

In this study, the annealing condition for composite was done at the temperature of 120 and 135 °C for 1 hour to investigate the effect of annealing on the properties of calcium carbonate filled high density polyethylene composites. These conditions were chosen from the trend observed in unfilled polyethylene. From figures 5.23 to 5.25, the Young's modulus, tensile strength and strain at break of the composites are plotted as a function of annealing temperature and volume

fraction of filler. The curves indicate that the annealed composites have higher Young's modulus and tensile strength than non-annealed ones for the same filler content and the improvement increases with increasing annealing temperature. However, the strain at break does not show the annealing temperature dependence. Moreover, the curve shows that the increasing Young's modulus of the composites annealed at 120 and 135°C compared to that of non-annealed are quite constant along with increasing of filler content. This is found to be true for tensile strength of the composites with filler volume fraction from 0.1 to 0.4 as well. The increasing tensile strength of unfilled HDPE annealed at the same temperatures are higher than that of the composites. It means that the addition of filler is influence on the increasing tensile strength but not for Young's modulus. However, it can be assumed that the constant increasing of tensile strength and Young's modulus of the composites along with the increasing filler cantent after annealing treatment causes by the structural changes in the polymer matrix phase, not in filler. That means the annealing only affects the polyethylene matrix phase.

The thermal properties results of the composites with various volume fraction of filler annealing at 120 and 135°C can confirm this assumption. In figures 5.26 and 5.27, the melting temperature and heat of fusion of the composites with various volume fraction of filler are plotted as a function of annealing temperature and volume fraction of filler. The curves show that at the same annealing condition, the melting temperature and heat of fusion of the composites do not depend on the filler content.
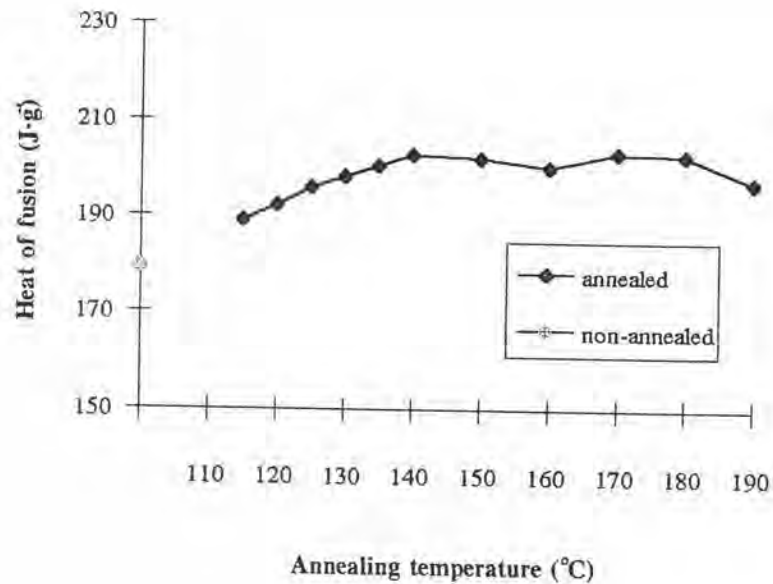
Figure 5.17 The variation of heat of fusion of unfilled HDPE as a function of annealing temperature.
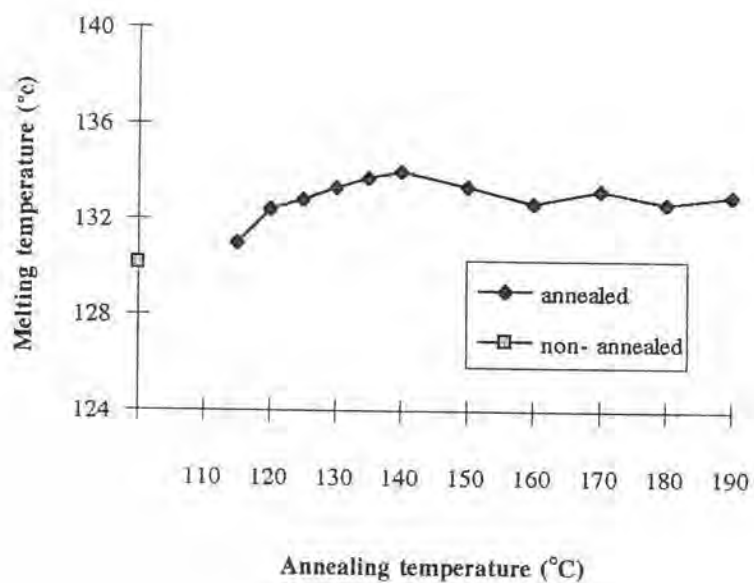


Figure 5.18 The variation of melting temperature of unfilled HDPE as a function of annealing temperature.
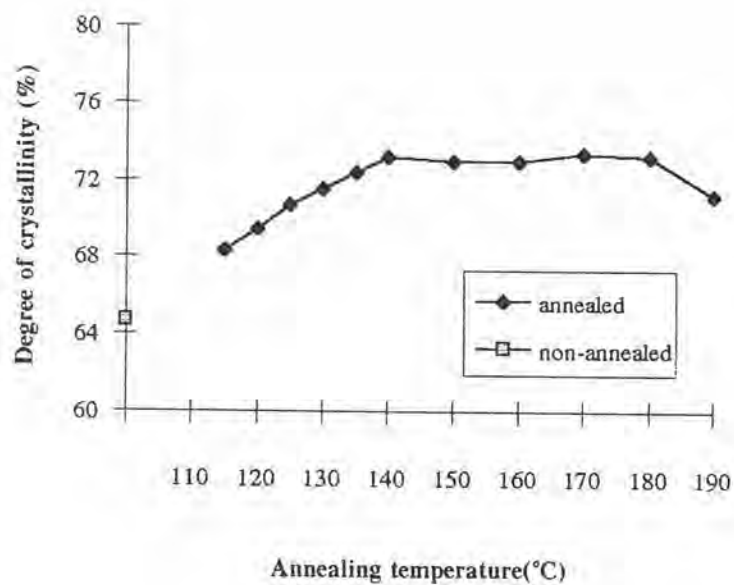
Figure 5.19 The variation of degree of crystallinity of unfilled HDPE as a function of annealing temperature.
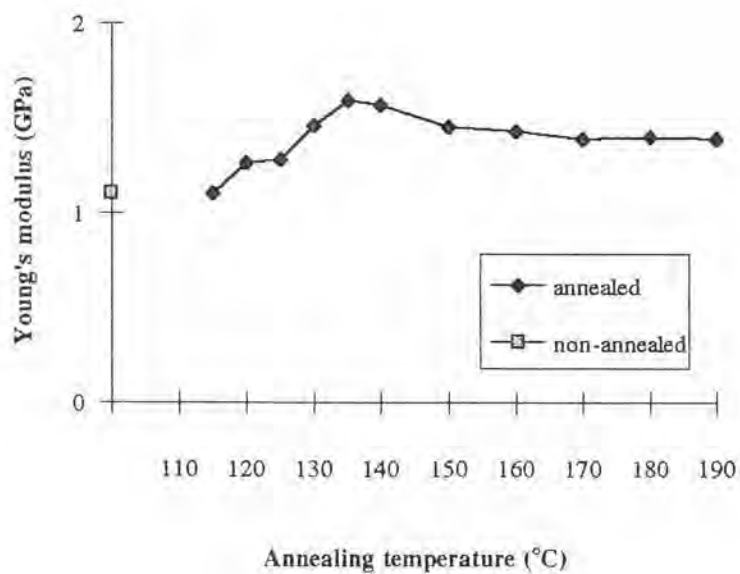


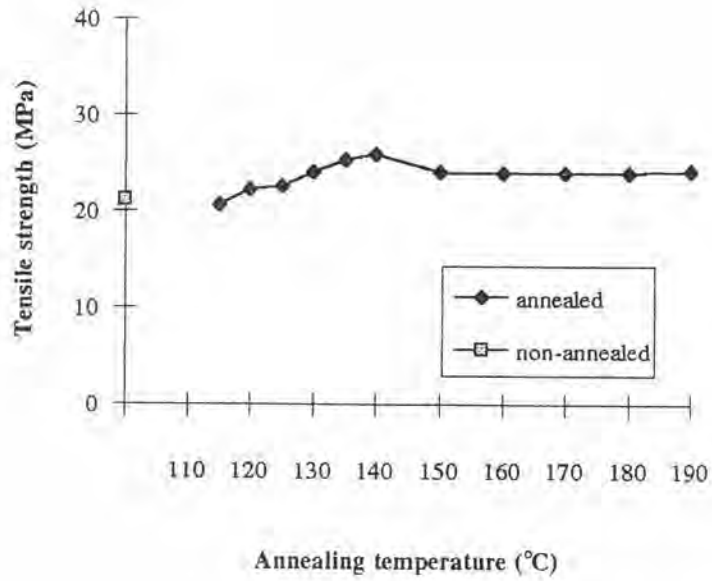Figure 5.20 Young's modulus of annealed unfilled HDPE versus annealing temperature.

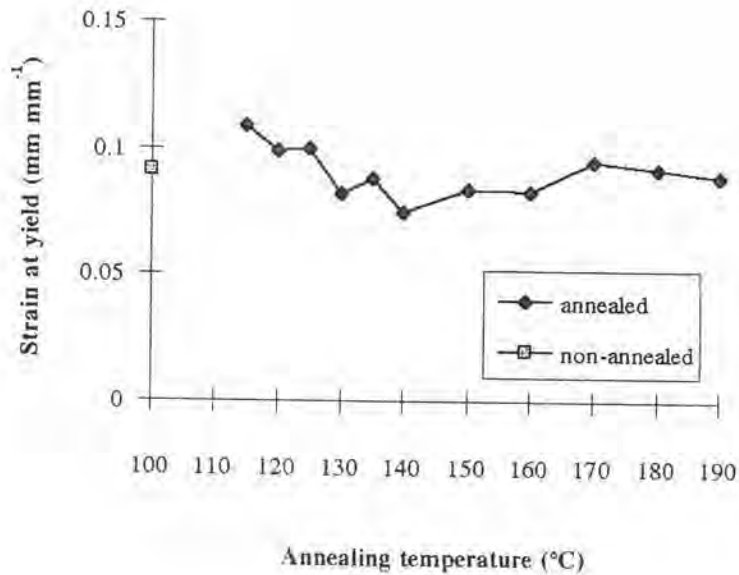Figure 5.21  Tensile strength of annealed unfilled HDPE versus annealing

temperature.



Figure 5.22  Tensile strain at yield of annealed unfilled HDPE versus annealing
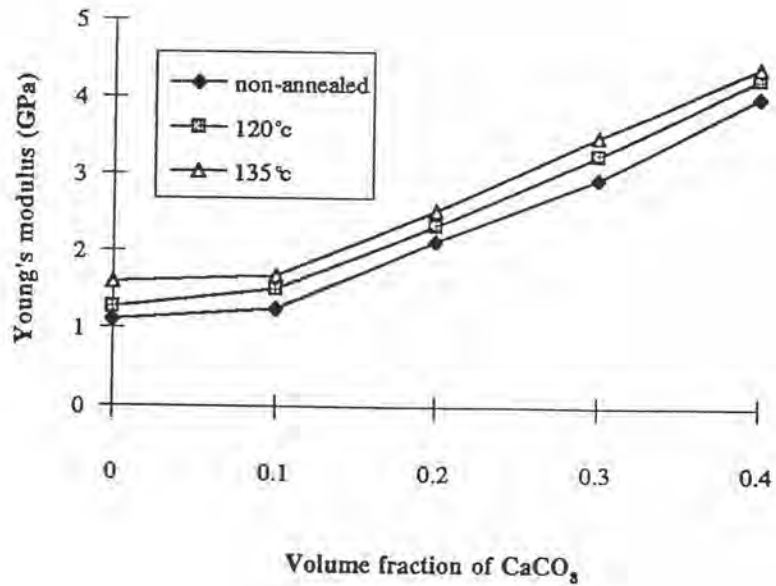
temperature.

Figure 5.23 Young's modulus of annealed CaCO₃ filled HDPE composites as a function of annealing temperature and volume fraction of CaCO₃.
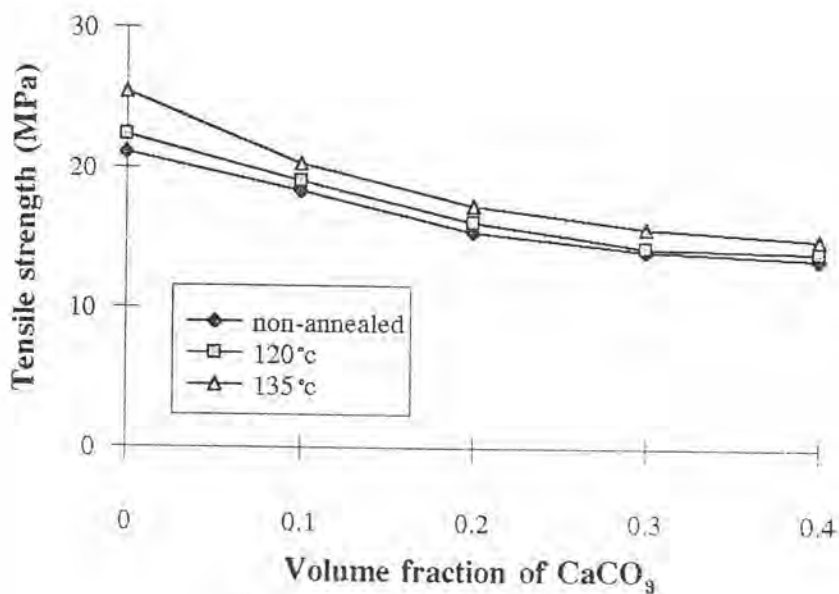


Figure 5.24 Tensile strength of annealed CaCO₃ filled HDPE composites as a function of annealing temperature and volume fraction of CaCO₃.

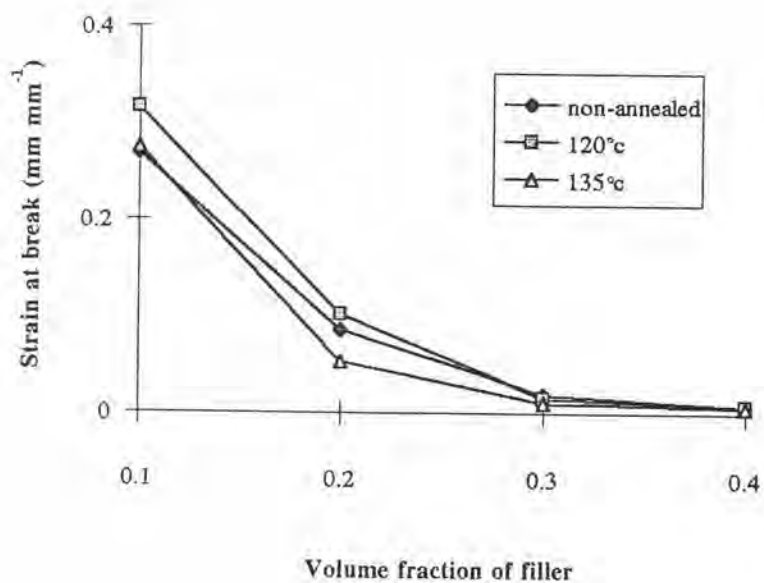Figure 5.25    Strain at break of annealed CaCO$_3$ filled HDPE composites as a

function of annealing temperature and volume fraction of CaCO$_3$.
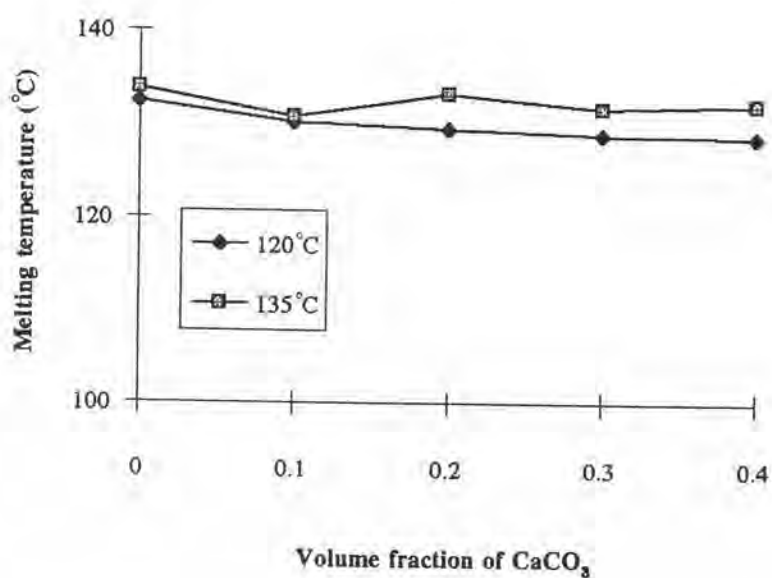


Figure 5.26    Melting temperature of annealed CaCO$_3$ filled HDPE composites as

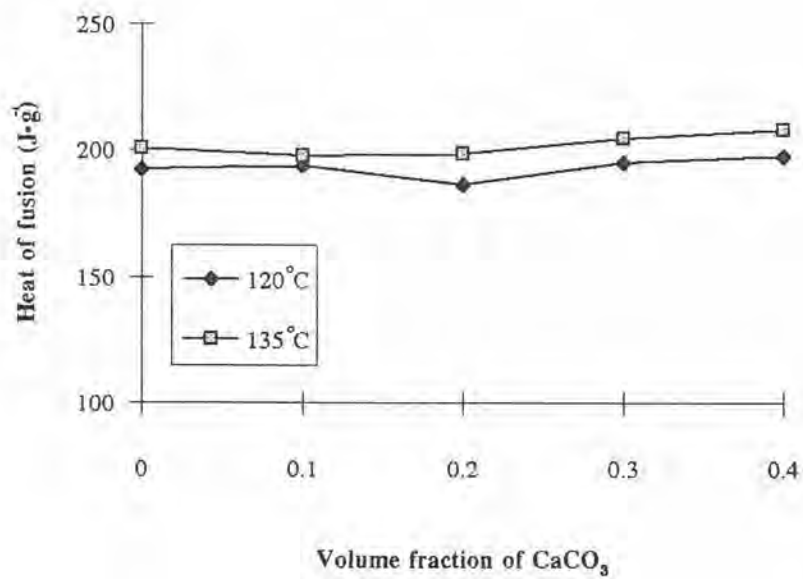a function of annealing temperature and volume fraction of CaCO$_3$.

Figure 5.27 Heat of fusion of annealed CaCO₃ filled HDPE composites as a

function of annealing temperature and volume fraction of CaCO₃.