Chapter 4

Results

4.1 Raw Material Characterization

Figure 4.1 illustrates the particle size distribution of the calcium carbonate powders. It indicates that the average diameter of calcium carbonate particles read out from the cumulative distribution curve at the 50 percent particle content, was 5.57 μm. Scanning electron micrographs of typical calcium carbonate particles is shown in figure 4.2. Figure 4.3 is the photograph of as received high density polyethylene granules. It can be seen that these calcium carbonate particles have roughly spherical in shapes. The agglomerates are also observed.

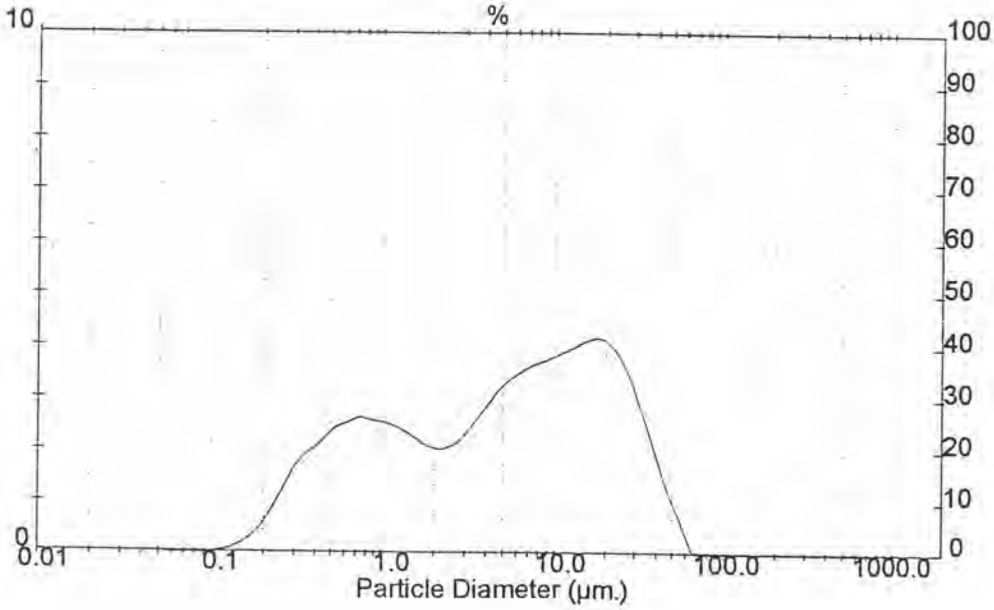

Figure 4.1 Particle size distribution of calcium carbonate particles.

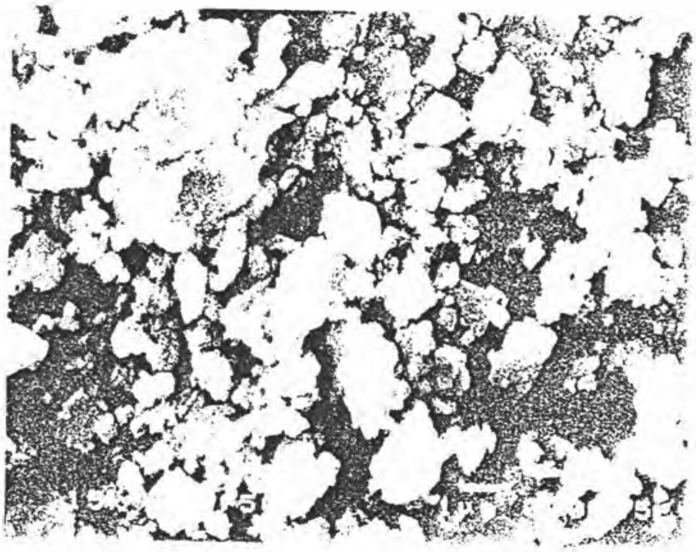

Figure 4.2 Morphology of calcium carbonate particles.

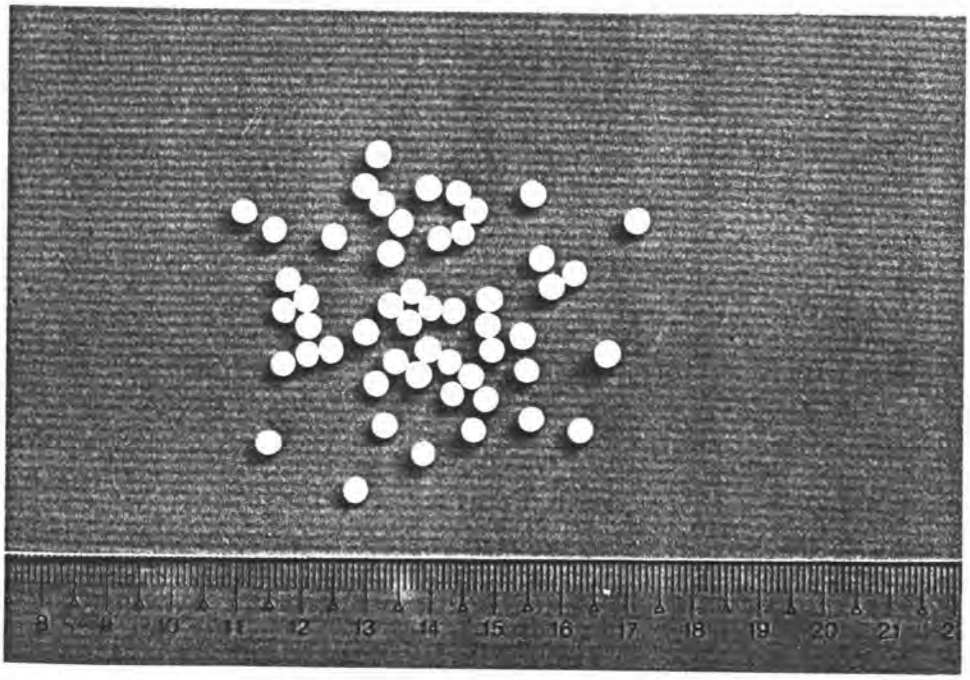

Figure 4.3 Photograph of as received high density polyethylene granules.

4.2 Composite characterization

4.2.1 Dispersion of Fillers

Figures 4.4-4.7 are the scanning electron micrographs of the crynogenic fracture surface of calcium carbonate filled high density polyethylene composites with 0.1, 0.2, 0.3 and 0.4 volume fraction of filler respectively. These micrographs clearly show a good dispersion of calcium carbonate particles in the high density polyethylene matrix without big agglomerates.

4.2.2 Oxidation Determination

The Raman spectra of as received high density polyethylene, of the processed HDPE and of the composites with 0.1, 0.2, 0.3 and 0.4 volume fraction of calcium carbonate are illustrated in figures 4.8-4.13 respectively. The spectra of as received high density polyethylene is found to be similar to that of the processed HDPE and composites. The carbonyl peak (1746 cm^{-1}) caused by the oxidation process of polyethylene matrix is not observed in all materials.

Figure 4.4 Dispersion of $CaCO_3$ particles in 0.1 volume fraction $CaCO_3$ filled HDPE composite.

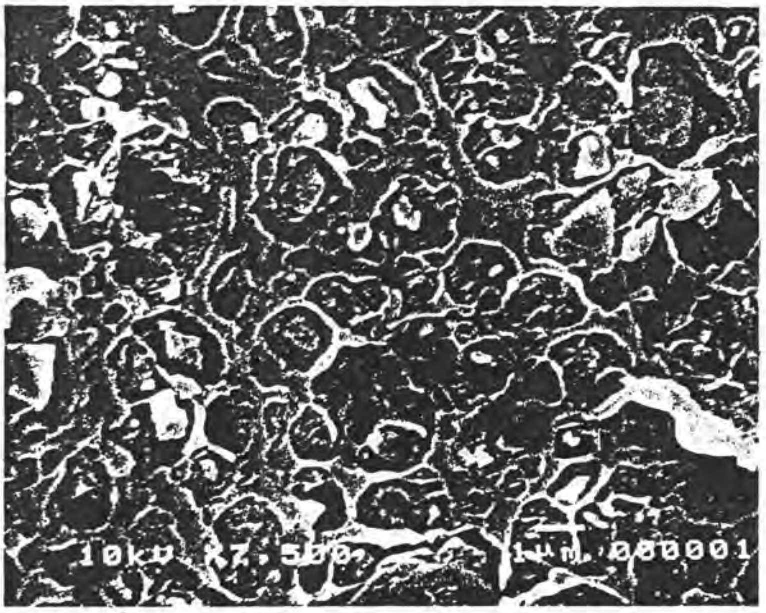

Figure 4.5 Dispersion of $CaCO_3$ particles in 0.2 volume fraction $CaCO_3$ filled HDPE composite.

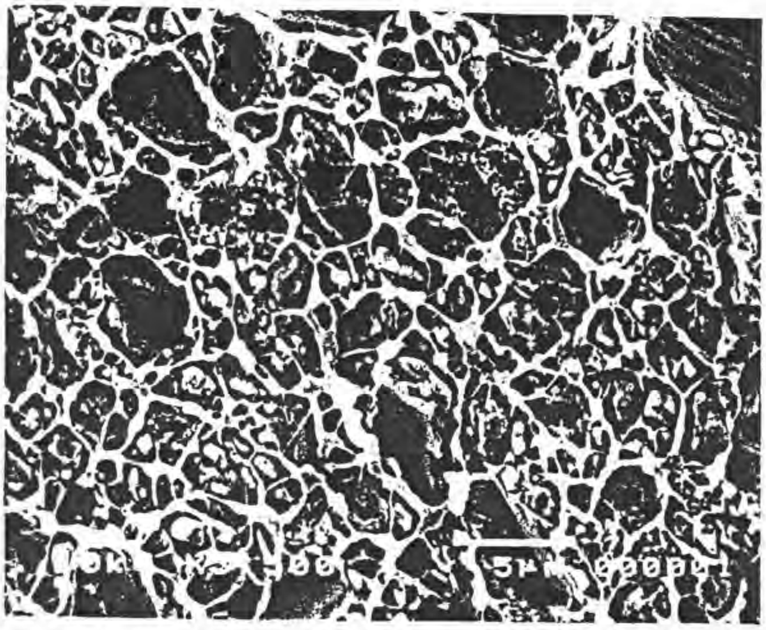

Figure 4.6 Dispersion of $CaCO_3$ particles in 0.3 volume fraction $CaCO_3$ filled HDPE composite.

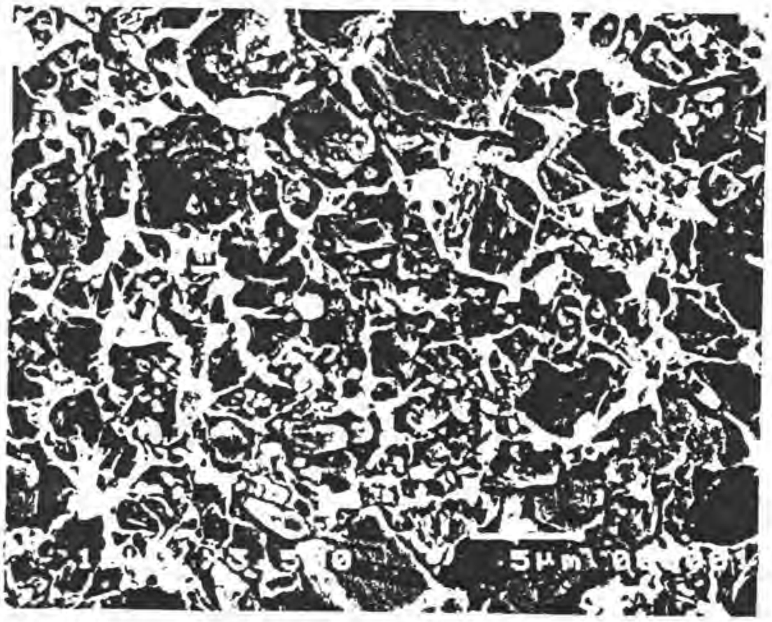

Figure 4.7 Dispersion of $CaCO_3$ particles in 0.4 volume fraction $CaCO_3$ filled HDPE composite.

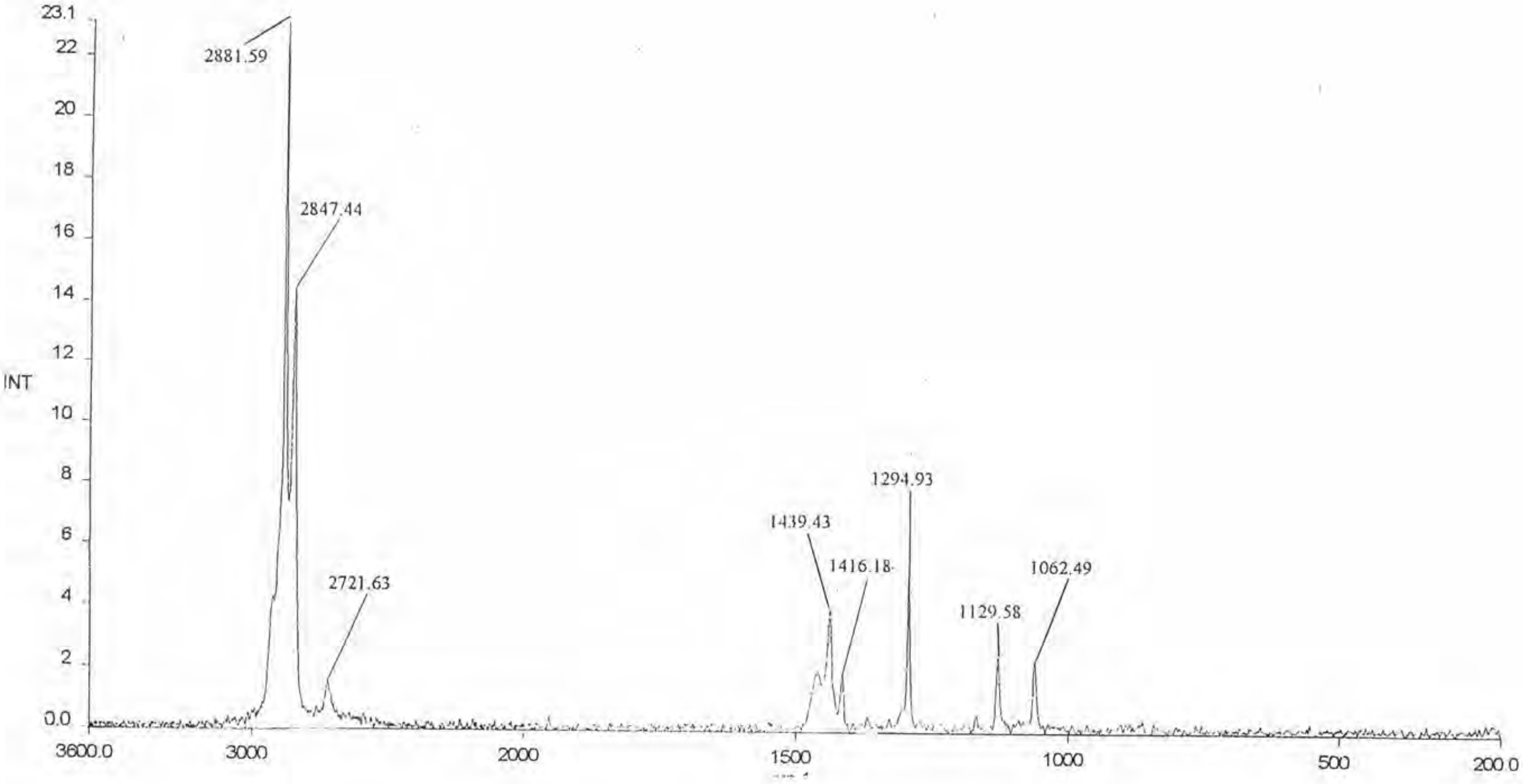

Figure 4.8 Raman spectra of as received high density polyethylene.

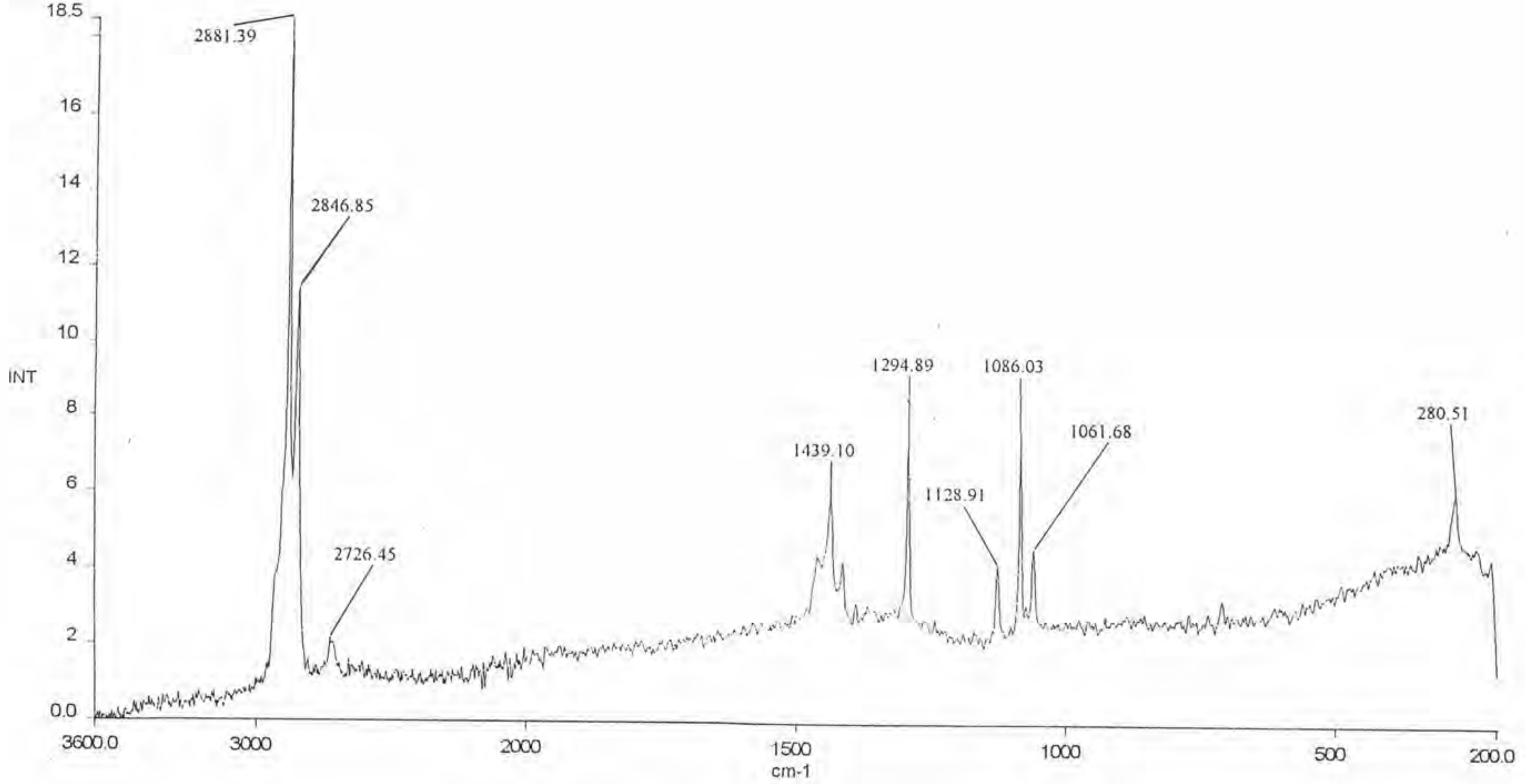

Figure 4.9 Raman spectra of processed high density polyethylene.

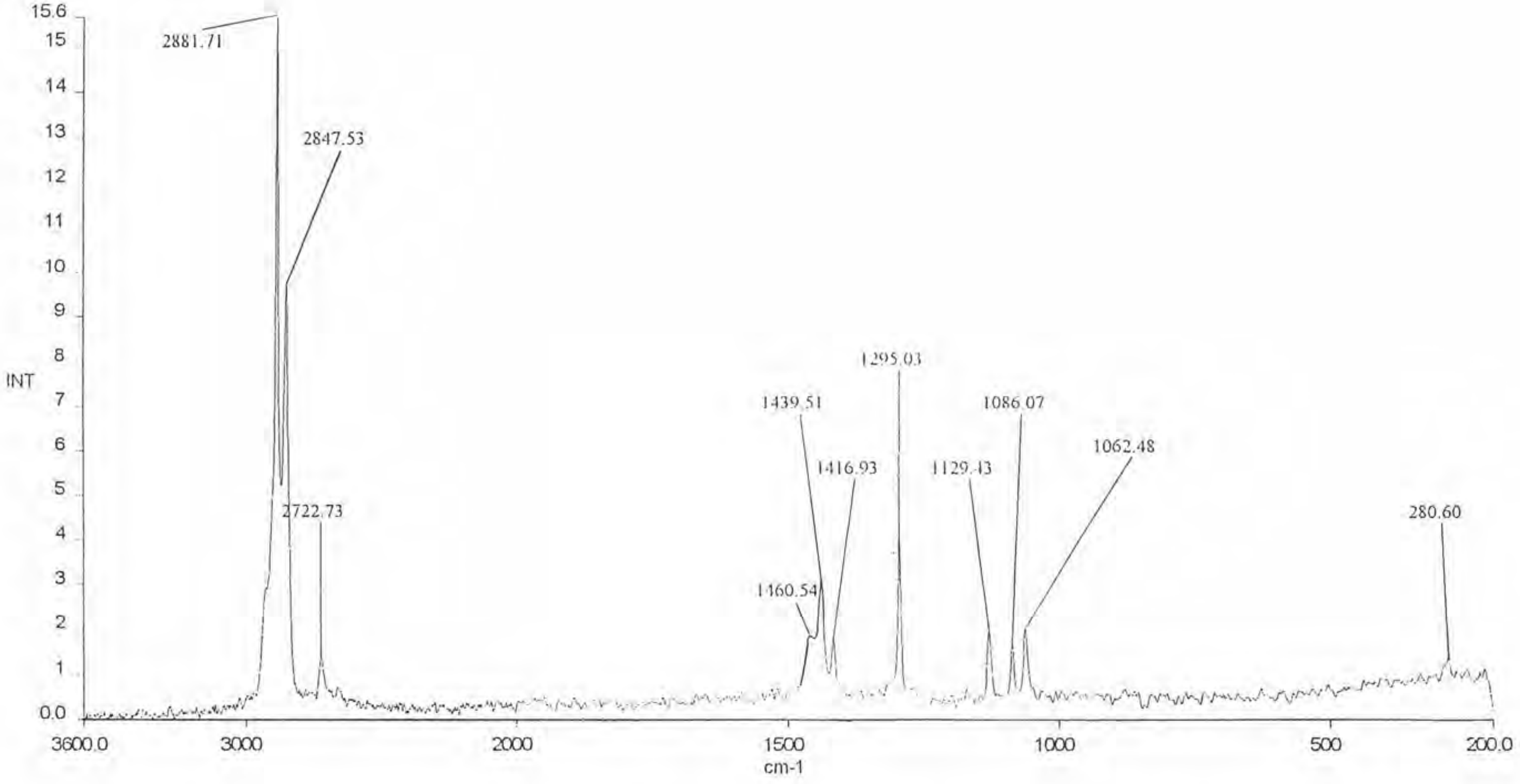

Figure 4.10 Raman spectra of 0.1 volume fraction $CaCO_3$ filled HDPE composite.

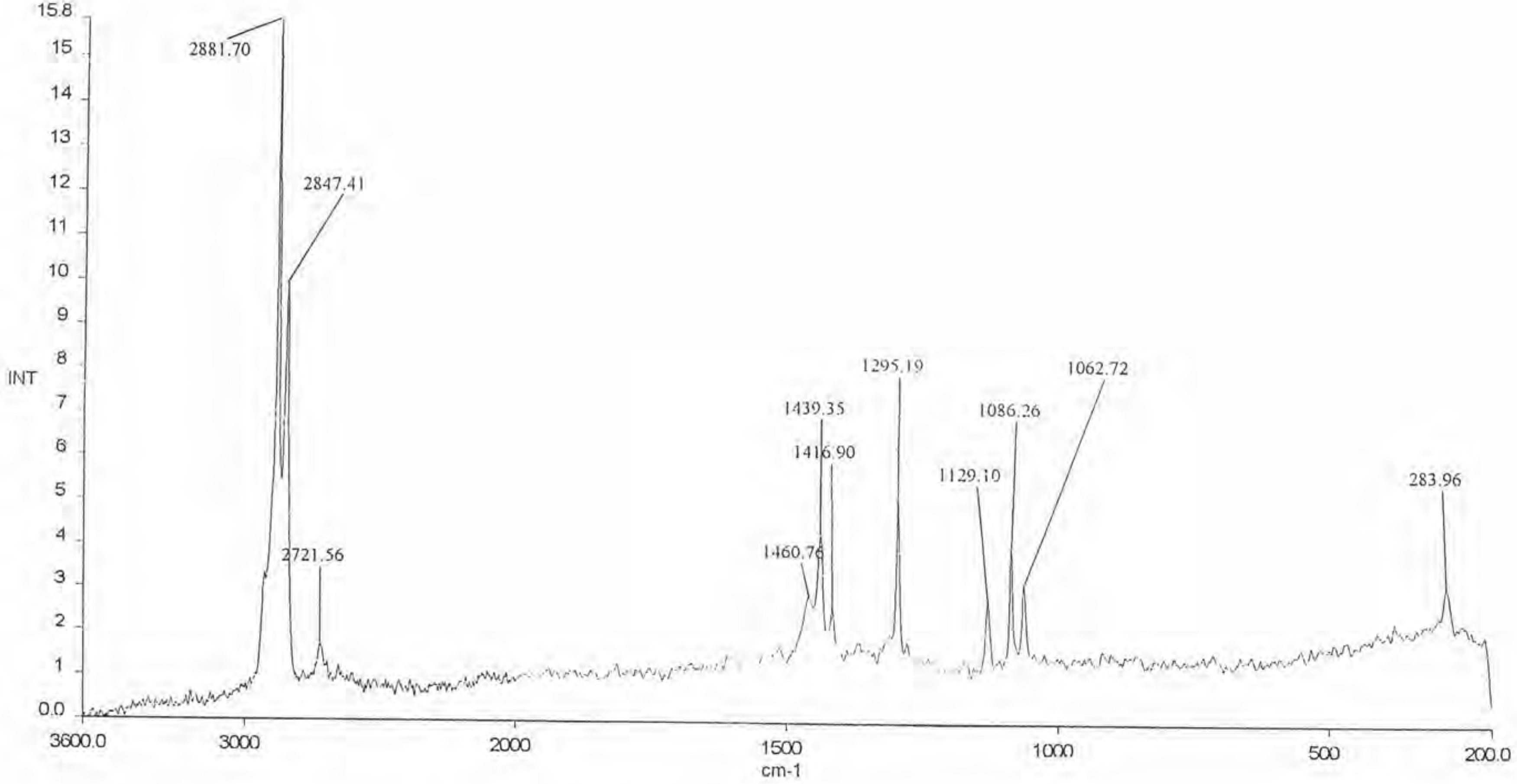

Figure 4.11 Raman spectra of 0.2 volume fraction $CaCO_3$ filled HDPE composite.

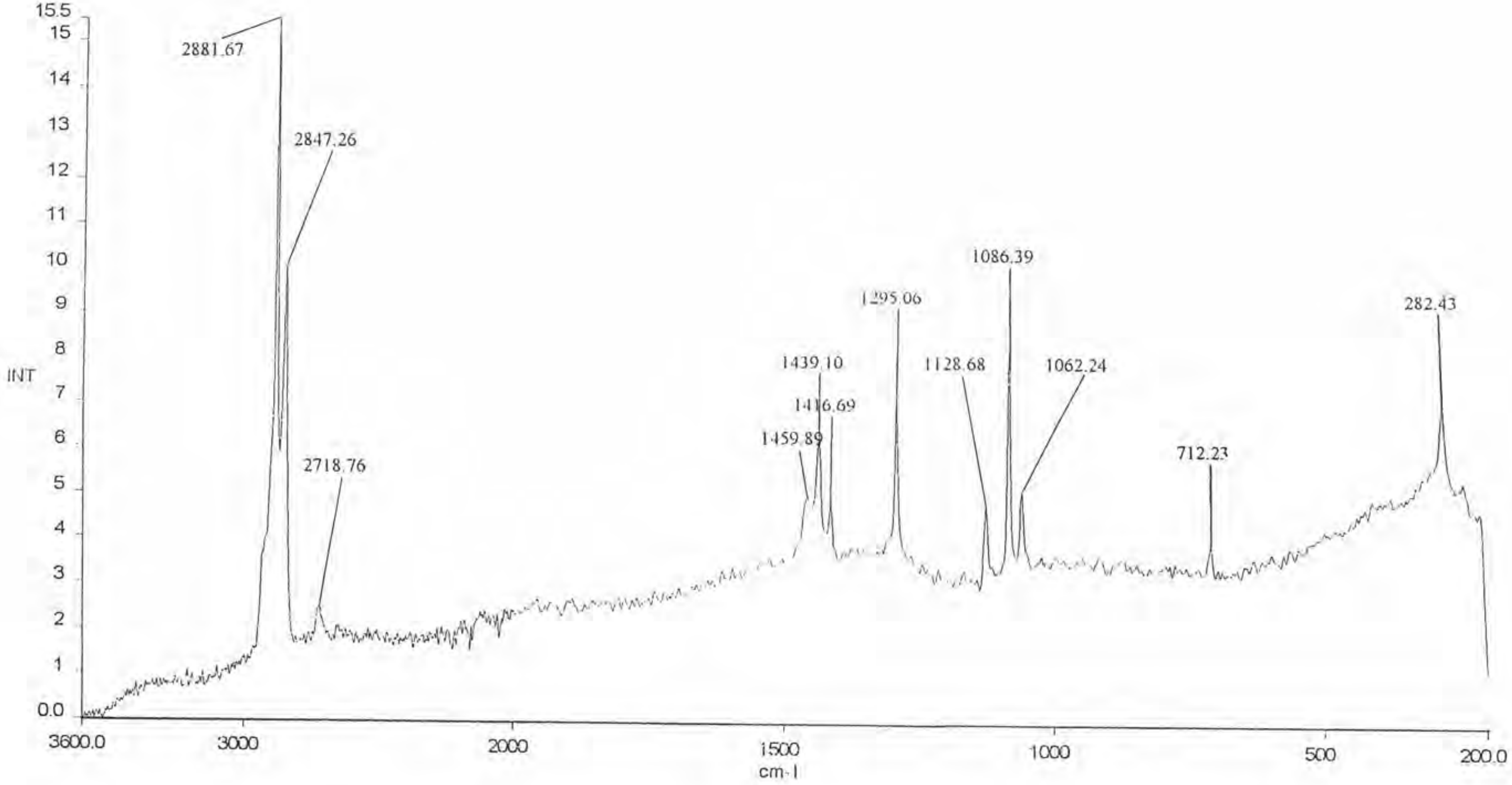

Figure 4.12 Raman spectra of 0.3 volume fraction $CaCO_3$ filled HDPE composite.

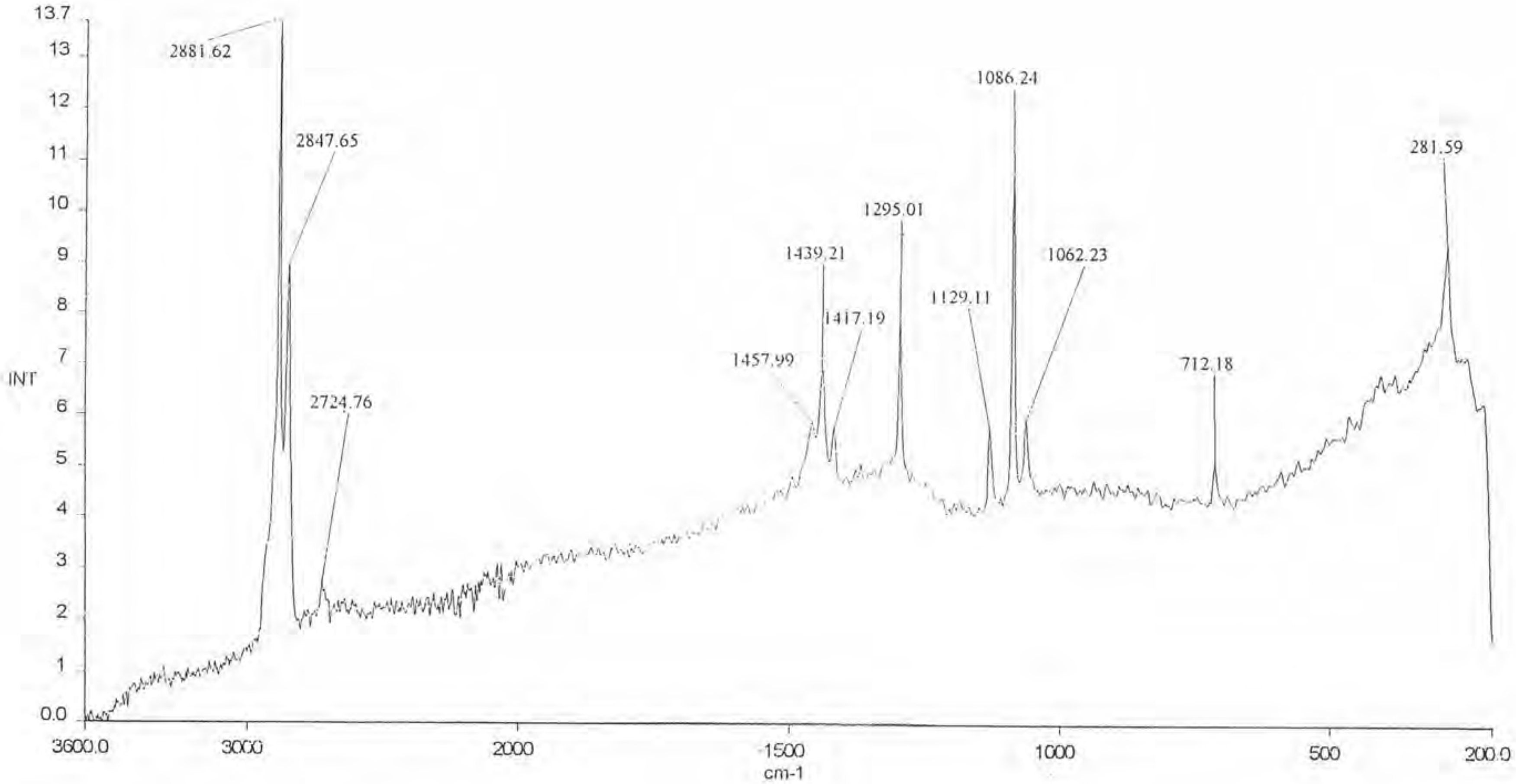

Figure 4.13 Raman spectra of 0.4 volume fraction $CaCO_3$ filled HDPE composite.

4.2.3 Density Measurement

The density values of calcium carbonate filled high density polyethylene composites are tabulated in table 4.1. The results indicate that the densities of composite are closed to the calculated data for the same volume fraction of calcium carbonate.

Table 4.1 Density measurement results of the $CaCO_3$ filled HDPE composites with various filler volume fraction.

Volume fraction of $CaCO_3$	Density ($kg{\cdot}m^{-3}$)	
	Calculated	Measured
0.0	0.96	0.95 ± 0.01
0.1	1.13	1.11 ± 0.00
0.2	1.31	1.30 ± 0.01
0.3	1.48	1.48 ± 0.01
0.4	1.65	1.62 ± 0.00

4.2.4 Thermogravimetric Analysis (TGA)

The weight percent of calcium carbonate in the composites at various volume fractions of fillers are listed in table 4.2, in comparison with those from calculations. The results show that the calcium carbonate content in the composites is closed to calculated data for the same volume fraction of filler. The TGA curves of each volume fraction of the composites are shown in the Appendix.

Table 4.2 Thermogravimetric analysis results of $CaCO_3$ filled HDPE composites with various filler volume fraction.

Volume fraction of $CaCO_3$	$CaCO_3$ weight percent	
	Calculated	Measured
0.0	0	0
0.1	24	22
0.2	41	36
0.3	55	54
0.4	65	63

4.3 Mechanical Testing Results

4.3.1 Tensile Testing

The typical stress-strain curves of the composites with various filler volume fraction are summarized in figures 4.14 and 4.15. The unfilled high density polyethylene specimens do not break at the specific strain limit and show necking with extensive drawing as shown in figure 4.16. For the composite specimens with 0.1 and 0.2 filler volume fraction, necking with drawing are also observed but only limited. In contrast, the composites with 0.3 and 0.4 volume fraction of calcium carbonate fracture in brittle manner. After breaking, the fracture specimens of each composition were visually examined. It can be seen in figures 4.17-4.20 that the fracture area of the composites containing filler less than 0.2 volume fraction failed in a ductile manner with fibril formation whereas the higher filler volume fraction failed in brittle mode with limited fibril or none.

The tensile properties of calcium carbonate filled high density polyethylene composites are tabulated in table 4.3. It shows that the Young's modulus of calcium carbonate filled high density polyethylene composites are much higher than that of unfilled high density polyethylene. Increasing filler volume fraction results in the increase in modulus. On the other hand, there is a decrease in the tensile strength and ductility at the same time.

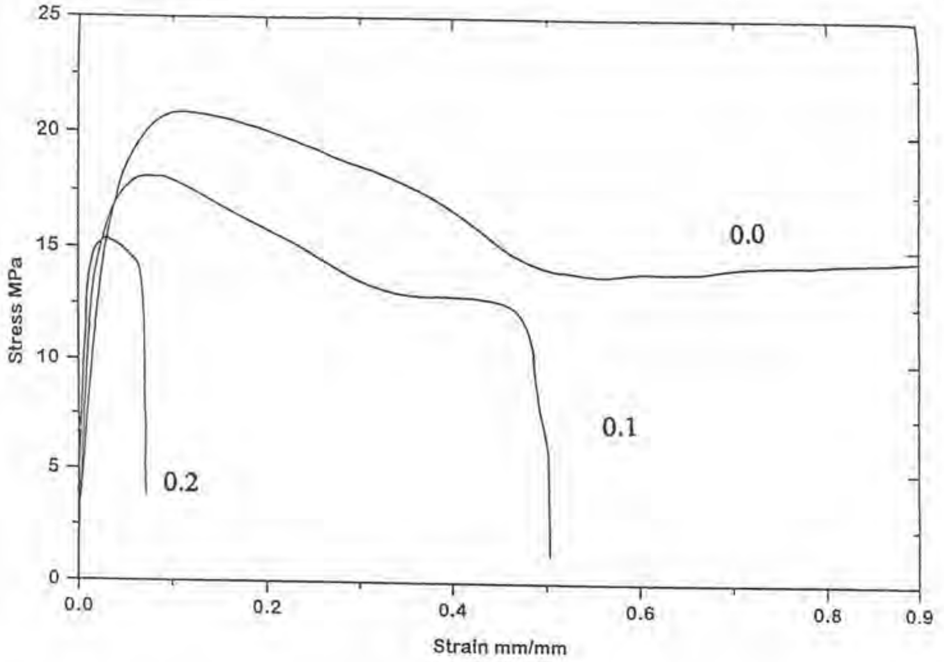

Figure 4.14 Typical tensile stress-strain curves of $CaCO_3$ filled HDPE composites at 0.0, 0.1 and 0.2 filler volume fraction.

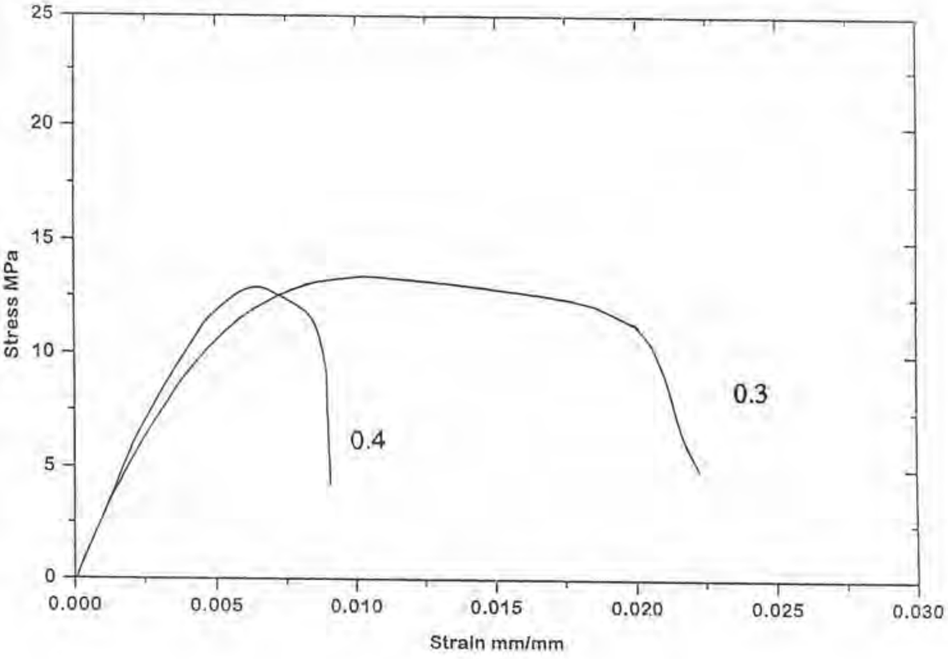

Figure 4.15 Typical tensile stress-strain curves of $CaCO_3$ filled HDPE composite at 0.3 and 0.4 filler volume fraction.

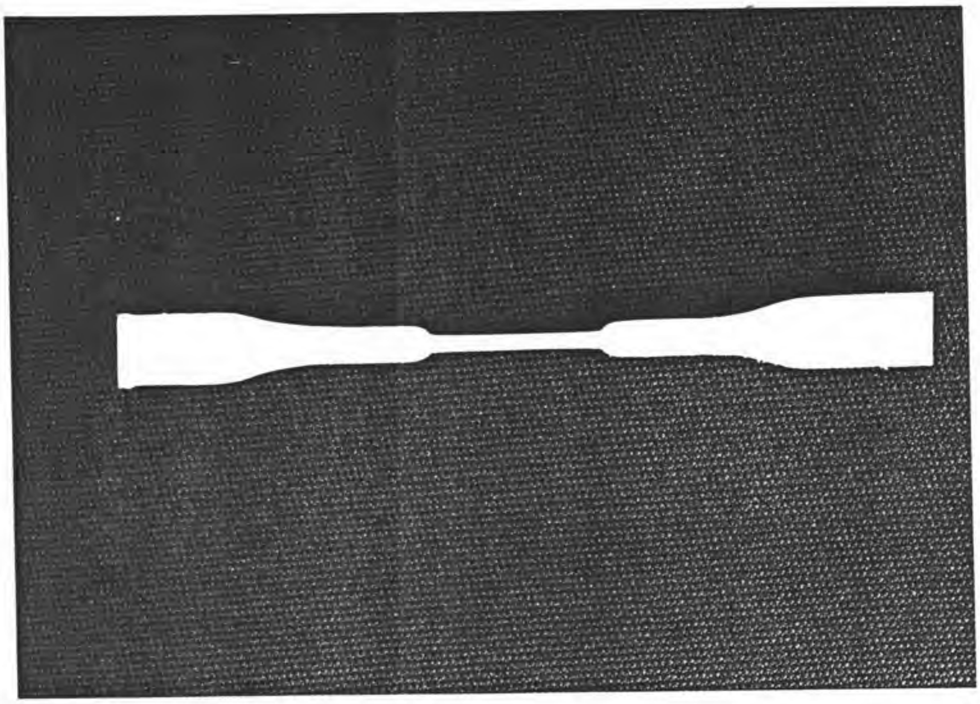

Figure 4.16 Tensile specimen of unfilled HDPE after testing.

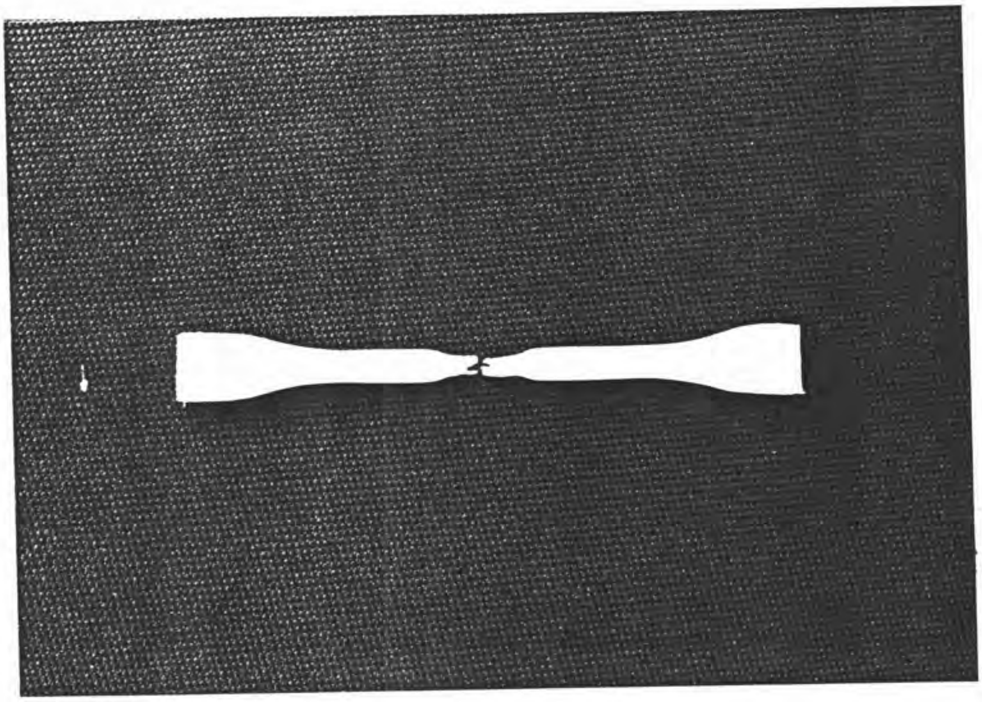

Figure 4.17 Tensile fractured specimen of $CaCO_3$ filled HDPE composites with 0.1filler volume fraction.

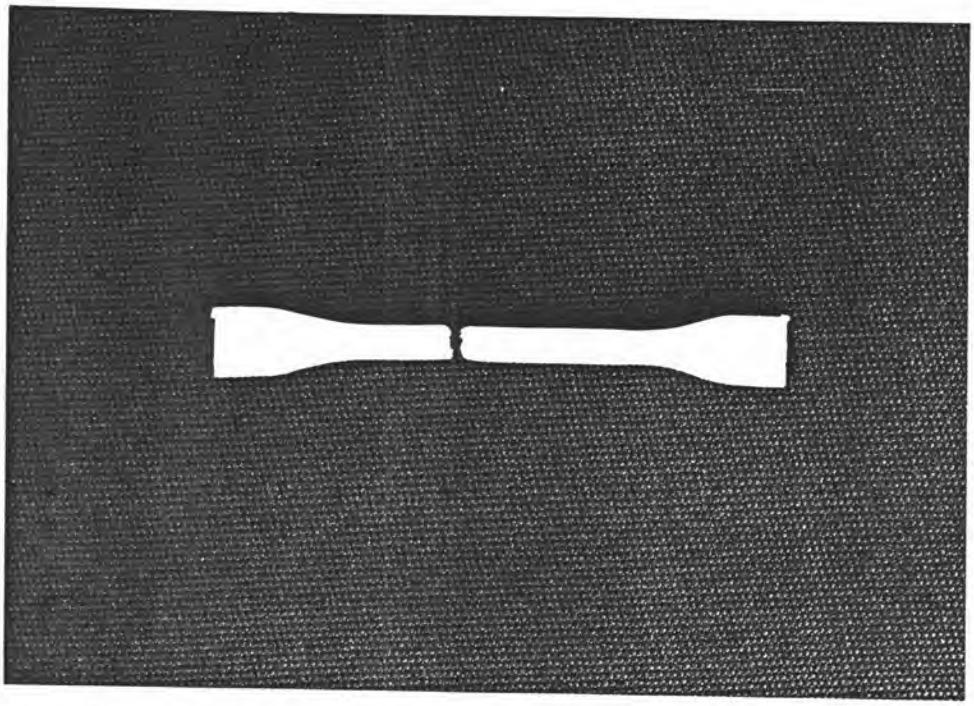

Figure 4.18 Tensile fractured specimen of $CaCO_3$ filled HDPE composites with 0.2 filler volume fraction.

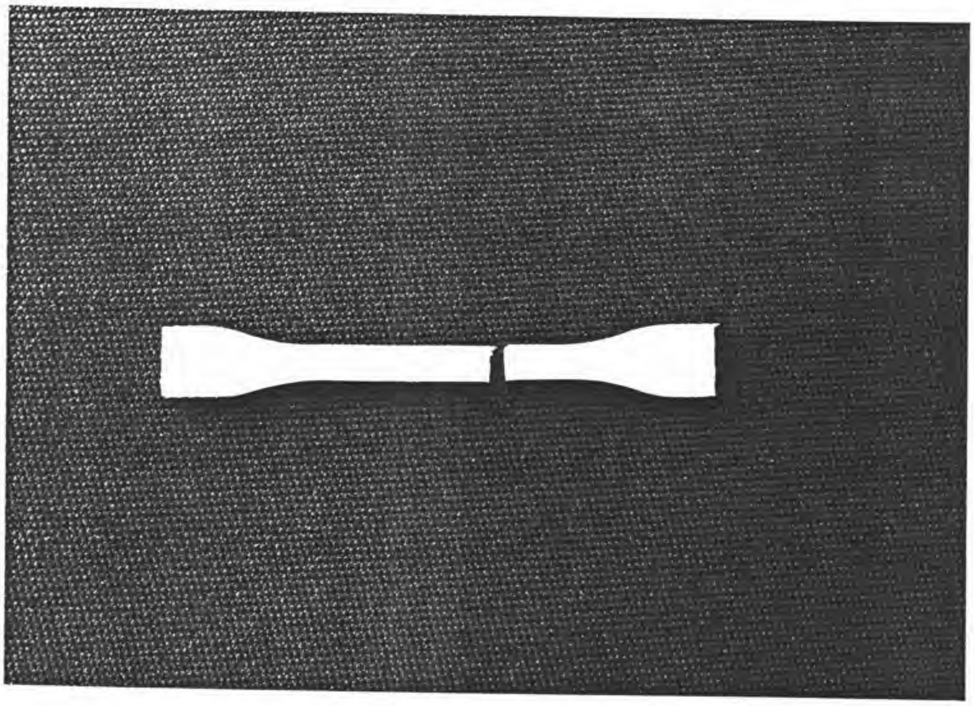

Figure 4.19 Tensile fractured specimen of $CaCO_3$ filled HDPE composites with 0.3 filler volume fraction.

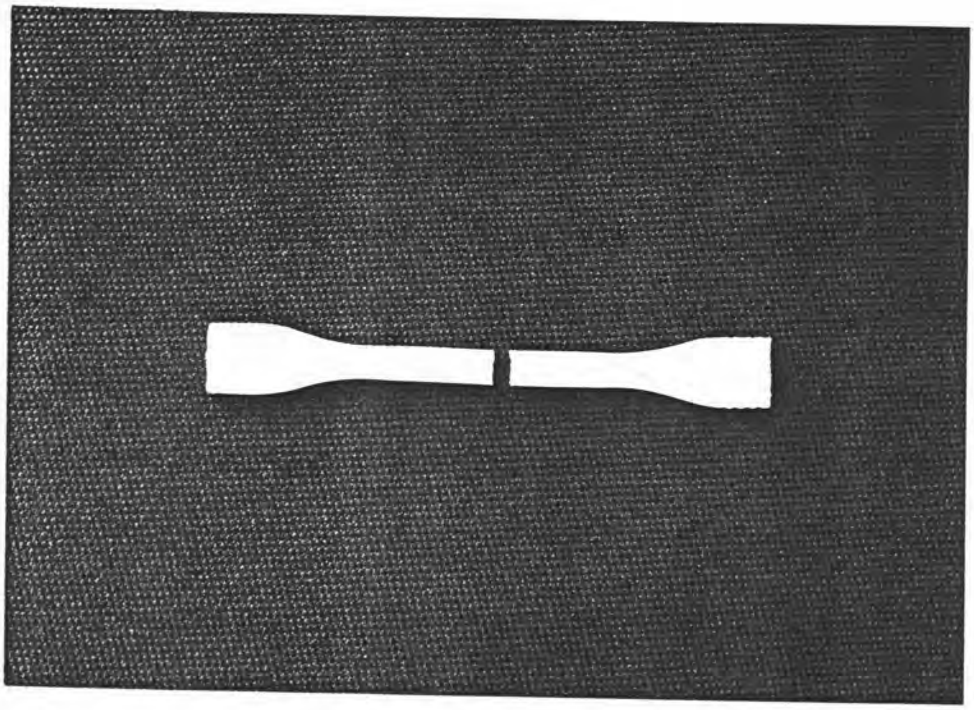

Figure 4.20 Tensile fractured specimen of $CaCO_3$ filled HDPE composites with 0.4 filler volume fraction.

Table 4.3 The tensile properties of $CaCO_3$ filled HDPE composites with various filler volume fraction.

Volume fraction of $CaCO_3$	Young's modulus (GPa)	Tensile strength (MPa)	Strain at yield (mm mm^{-1})	Strain at break (mm mm^{-1})	Energy to break (J)
0.0	1.10 ± 0.02	21.09 ± 0.35	0.091 ± 0.002	> 2.000	N.C.
0.1	1.24 ± 0.08	18.35 ± 0.35	0.068 ± 0.005	0.269 ± 0.050	4.78 ± 0.87
0.2	2.13 ± 0.26	15.50 ± 0.15	0.033 ± 0.004	0.084 ± 0.017	1.31 ± 0.29
0.3	2.94 ± 0.06	14.16 ± 0.72	0.013 ± 0.002	0.018 ± 0.007	0.23 ± 0.11
0.4	4.02 ± 0.27	13.61 ± 0.43	0.006 ± 0.000	0.007 ± 0.000	0.07 ± 0.02

4.3.2 Flexural Testing

The flexural properties of calcium carbonate filled high density polyethylene composites with various volume fraction of calcium carbonate are listed in table 4.4. Due to fact that all composites did not break in the test except 0.4 filler volume fraction specimen, the yield values are used instead for comparison. The results indicate that flexural modulus and flexural stress at yield of the composites increases with increasing calcium carbonate content. On the other hand, flexural strain at yield sharply decreases at 0.2 volume fraction of filler. The typical flexural stress-strain curve of the composite with 0.4 filler volume fraction is shown in figure 4.21.

Table 4.4 Flexural properties of $CaCO_3$ filled HDPE composites.

Volume fraction of $CaCO_3$	Flexural modulus (GPa)	Stress at yield (MPa)	Strain at yield (mm mm^{-1})
0.0	1.06 ± 0.08	9.19 ± 0.68	0.011 ± 0.001
0.1	1.30 ± 0.06	11.16 ± 0.54	0.010 ± 0.001
0.2	2.21 ± 0.04	13.72 ± 0.51	0.010 ± 0.000
0.3	2.91 ± 0.29	17.09 ± 0.28	0.007 ± 0.002
0.4	3.96 ± 0.23	18.04 ± 0.32	0.006 ± 0.001

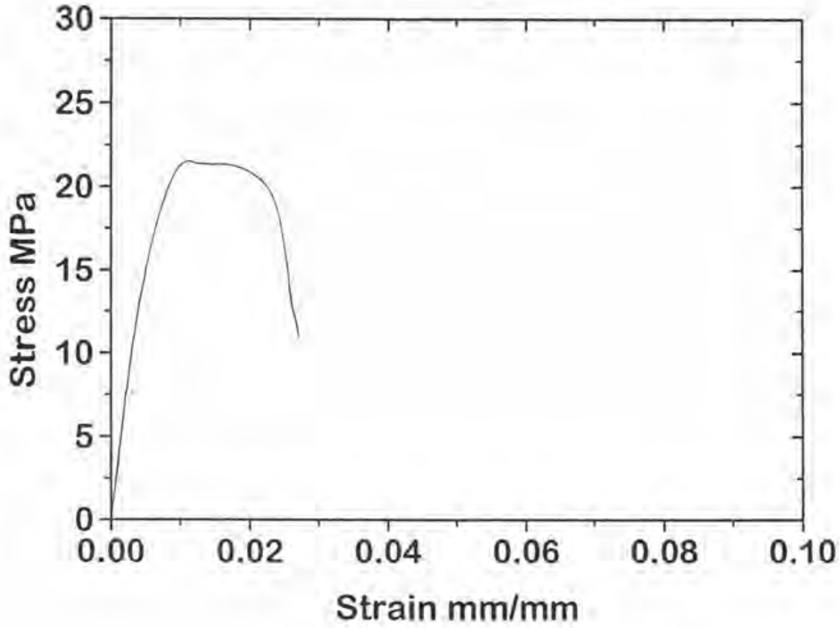

Figure 4.21 The flexural stress-strain curve of the composite with 0.4 filler volume fraction.

4.3.3 Compressive Testing

The compressive properties of calcium carbonate filled high density polyethylene composites with various filler volume fraction are shown in table 4.5. The results indicate that compressive modulus and compressive stress at yield increase with the increasing calcium carbonate volume fraction. The compressive strain at yield is independent of the filler content. The typical compressive stress-strain curves obtained from compressive modulus and compressive strength measurements of the composite with 0.4 filler volume fraction are shown in figures 4.22 and 4.23 respectively.

Table 4.5 The compressive properties of $CaCO_3$ filled HDPE composites with various filler volume fraction.

Volume fraction of $CaCO_3$	Compressive modulus (GPa)	Stress at yield (MPa)	Strain at yield (mm mm^{-1})
0.0	0.92 ± 0.10	11.64 ± 0.50	0.015 ± 0.001
0.1	1.22 ± 0.02	13.68 ± 0.58	0.020 ± 0.001
0.2	2.18 ± 0.11	14.61 ± 0.54	0.022 ± 0.003
0.3	2.87 ± 0.10	18.49 ± 1.97	0.020 ± 0.002
0.4	4.09 ± 0.02	22.50 ± 2.19	0.021 ± 0.004

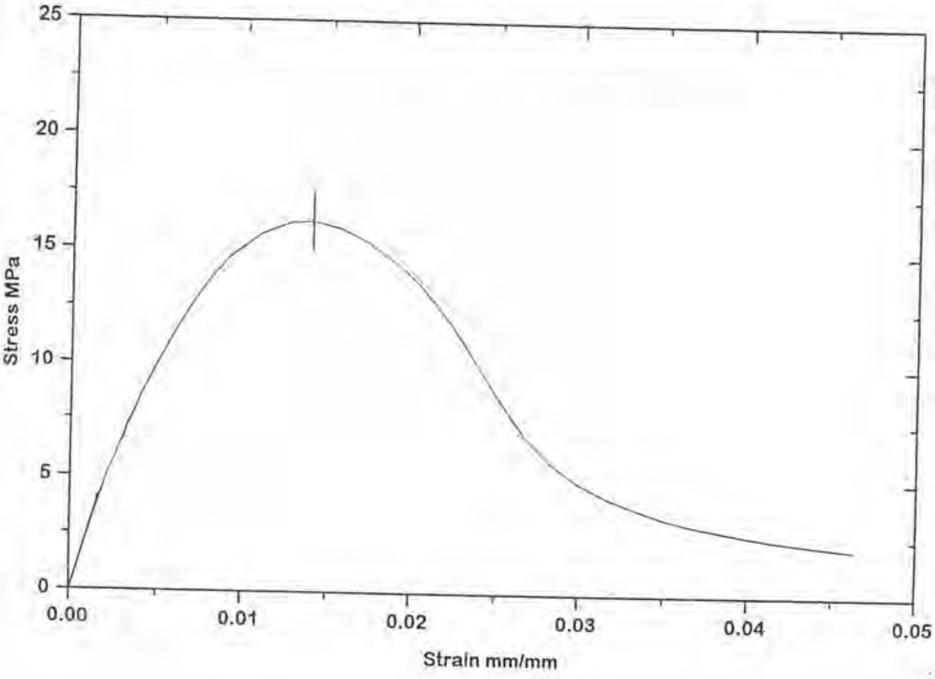

Figure 4.22 The typical compressive stress-strain curve for compressive modulus measurement of the composite with 0.4 filler volume fraction.

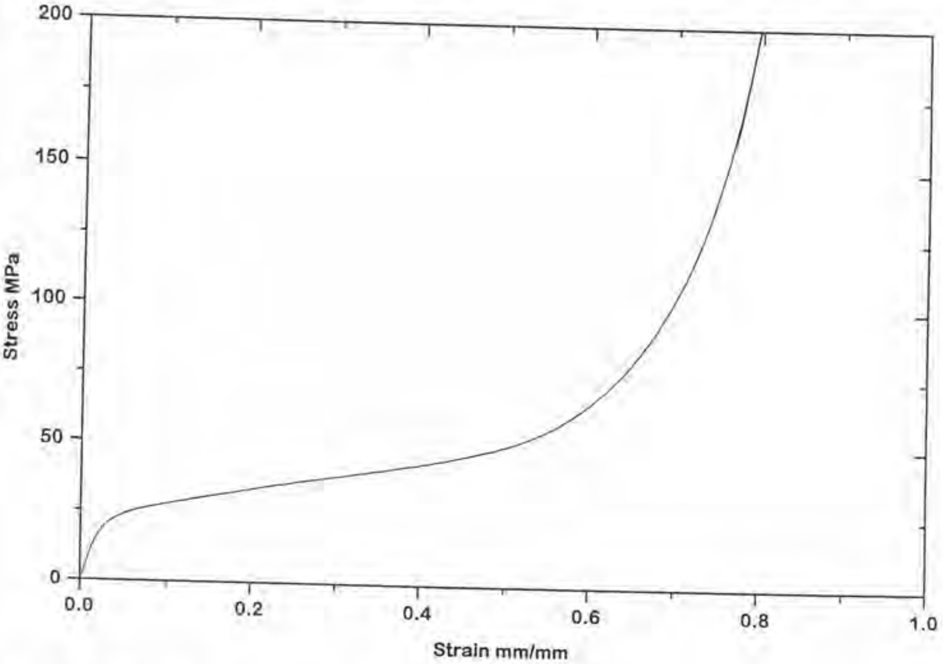

Figure 4.23 The typical compressive stress-strain curve for compressive strength measurement of the composite with 0.4 filler volume fraction.

4.4 Influence of annealing

4.4.1 Mechanical testing results

The data listed in table 4.6 shows tensile properties of high density polyethylene annealed at various temperatures for 1 hour. It can be seen that Young's modulus tends to increase with an increasing annealing temperature and reachs a maximum value at an annealing temperature of 135-140 °C, amounting to 1.59 GPa, 37 percent greater than that of non-annealed high density polyethylene (1.16 GPa). Tensile strength was also found to increase up to an annealing temperature of 135-140 °C, the maximum value is 25.89 MPa. However, tensile strain at yield did not change much with annealing treatment.

The values for tensile properties of calcium carbonate filled high density polyethylene composites with various volume fraction of calcium carbonate annealed at 120 and 135 °C for 1 hour are reported in tables 4.7 and 4.8 respectively. The results show that calcium carbonate filled high density polyethylene composites annealed at 135 °C and 120 °C have a higher Young's modulus and tensile strength than that of non-annealed composites. Moreover, Young's modulus and tensile strength of the composites annealed at 135 °C are higher than that of the composites annealed at 120 °C for the same volume fraction of calcium carbonate. On the other hand, tensile strain at berak of the composites do not show the dependence of annealing temperature.

Table 4.6 Tensile properties of unfilled HDPE annealed at various temperature for 1 hour.

Annealing temperature (°C)	Young's modulus (GPa)	Tensile strength (MPa)	Strain at yield (mm·mm^{-1})
non-annealed	1.10 ± 0.02	21.09 ± 0.35	0.091 ± 0.002
115	1.10 ± 0.03	20.73 ± 0.19	0.109 ± 0.005
120	1.26 ± 0.13	22.31 ± 0.35	0.099 ± 0.002
125	1.28 ± 0.04	22.64 ± 0.26	0.100 ± 0.012
130	1.46 ± 0.09	24.11 ± 0.15	0.082 ± 0.003
135	1.59 ± 0.03	25.38 ± 0.16	0.088 ± 0.003
140	1.57 ± 0.09	25.89 ± 0.46	0.075 ± 0.004
150	1.45 ± 0.05	24.11 ± 0.28	0.084 ± 0.005
160	1.43 ± 0.04	24.01 ± 0.40	0.083 ± 0.003
170	1.39 ± 0.05	23.96 ± 0.51	0.095 ± 0.007
180	1.40 ± 0.03	24.01± 0.42	0.092 ± 0.004
190	1.39 ± 0.05	24.23 ± 0.37	0.089 ± 0.006

Table 4.7 Tensile properties of $CaCO_3$ filled HDPE composites annealed at 120 °C for 1 hour.

Volume fraction of $CaCO_3$	Young's modulus (GPa)	Tensile strength (MPa)	Strain at yield (mm mm^{-1})	Strain at break (mm mm^{-1})	Energy to break (J)
0.0	1.26 ± 0.04	22.31 ± 0.17	0.099 ± 0.002	>2.000	N.C.
0.1	1.50 ± 0.03	19.08 ± 0.25	0.075 ± 0.007	0.316 ± 0.075	5.85 ± 1.30
0.2	2.33 ± 0.11	16.20 ± 0.44	0.036 ± 0.005	0.100 ± 0.037	1.61 ± 0.61
0.3	3.25 ± 0.27	14.38 ± 0.77	0.012 ± 0.001	0.015 ± 0.004	0.19 ± 0.07
0.4	4.26 ± 0.16	14.10 ± 0.38	0.006 ± 0.000	0.007 ± 0.001	0.07 ± 0.01

Table 4.8 Tensile properties of $CaCO_3$ filled HDPE composites annealed at 135 °C for 1 hour.

Volume fraction of $CaCO_3$	Young's modulus (GPa)	Tensile strength (MPa)	Strain at yield (mm mm^{-1})	Strain at break (mm mm^{-1})	Energy to break (J)
0.0	1.59 ± 0.03	25.38 ± 0.16	0.088 ± 0.004	>2.000	N.C.
0.1	1.67 ± 0.18	20.33 ± 0.18	0.067 ± 0.003	0.275 ± 0.087	5.47 ± 1.79
0.2	2.53 ± 0.33	17.31 ± 0.07	0.027 ± 0.001	0.051 ± 0.013	0.89 ± 0.25
0.3	3.49 ± 0.13	15.81 ± 0.91	0.010 ± 0.001	0.010 ± 0.000	0.13 ± 0.01
0.4	4.40 ± 0.05	15.02 ± 0.15	0.005 ± 0.000	0.006 ± 0.001	0.06 ± 0.01

4.4.2 Thermal testing

Heat of fusion, melting temperature and degree of crystallinity for non-annealed and annealed high density polyethylene obtained from differential scanning calorimetry measurement are listed in table 4.9. Thermal properties of calcium carbonate filled high density polyethylene composites with various volume fraction of calcium carbonate annealed at 120 and 135 °C are shown in table 4.10 and 4.11 respectively. Thermograms for all of filled and unfilled high density polyethylene annealing at various temperature are shown in Appendix.

The results indicate that in the case of unfilled high density polyethylene annealed at various temperatures, heat of fusion, melting temperature and degree of crystallinity gradually increase with annealing temperature until 140 °C, then it slightly decrease and appear to be independent of annealing temperature. Thermal properties of calcium carbonate filled high density polyethylene composites do not show the filler concentration dependence.

Table 4.9 Thermal properties of unfilled HDPE annealed at various temperature for 1 hour.

Annealing temperature (°C)	Heat of fusion ($J{\cdot}g^{-1}$)	Melting temperature (°C)	Degree of crystallinity (%)
non-annealed	179.11	130.13	64.66
115	189.18	130.96	68.30
120	192.26	132.37	69.41
125	195.88	132.82	70.71
130	198.11	133.28	71.52
135	200.47	133.73	72.37
140	202.64	134.00	73.16
150	202.15	133.33	72.98
160	200.12	132.67	72.97
170	203.15	133.20	73.34
180	202.65	132.67	73.16
190	197.13	133.00	71.17

Table 4.10 Thermal properties of $CaCO_3$ filled HDPE composites with various filler volume fraction annealed at 120 °C.

Volume fraction of $CaCO_3$	Heat of fusion ($J{\cdot}g^{-1}$)	Melting temperature (°C)	Degree of crystallinity (%)
0.0	192.26	132.37	69.41
0.1	193.52	130.20	69.86
0.2	186.18	129.47	67.21
0.3	194.97	128.80	70.39
0.4	197.76	128.67	71.39

Table 4.11 Thermal properties of $CaCO_3$ filled HDPE composites with various filler volume fraction annealed at 135 °C.

Volume fraction of $CaCO_3$	Heat of fusion ($J{\cdot}g^{-1}$)	Melting temperature (°C)	Degree of crystallinity (%)
0.0	200.47	133.73	72.37
0.1	197.43	130.74	71.27
0.2	198.24	133.14	71.57
0.3	204.50	131.67	73.83
0.4	207.86	132.14	75.04