CHAPTER 4

RESULTS AND DISCUSSION

The effects of fillers, calcium carbonate and carbon black, on some mechanical properties of high density polyethylene were studied. The samples of high density polyethylene and high density polyethylene filled with calcium carbonate or carbon black were prepared by a two rolls mill and compression molding. The filled polyethylene compounds were tested for the following properties, tensile strength, elongation, modulus, hardness and Izod impact strength. The microstructures of tensile fracture were observed by means of a scanning electron microscope.

4.1 Some properties of fillers.

The properties of filler that affected the polymer properties are summarized in Table 4.1. Figure 4.1 shows the particle distribution of the fillers, Figures 4.2 a and 4.2 b are the scanning electron micrographs of calcium carbonate 1939 and calcium carbonate 039, respectively, Figure 4.2 c is the scanning electron micrograph of carbonblack.

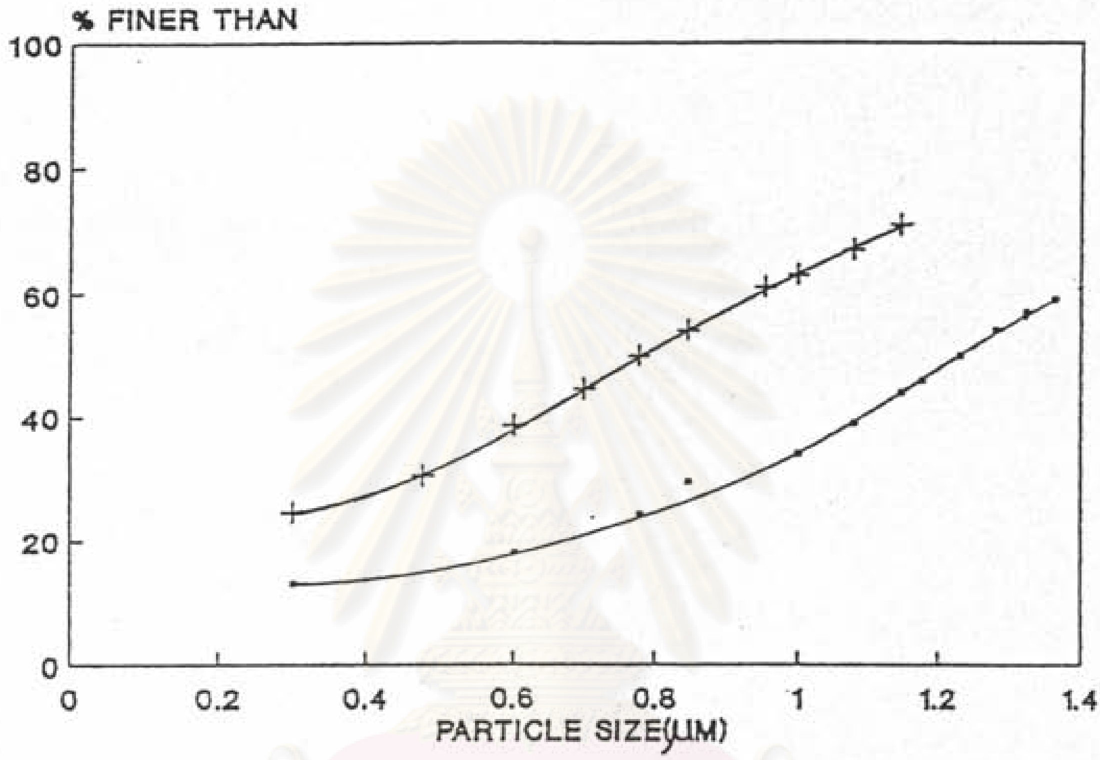
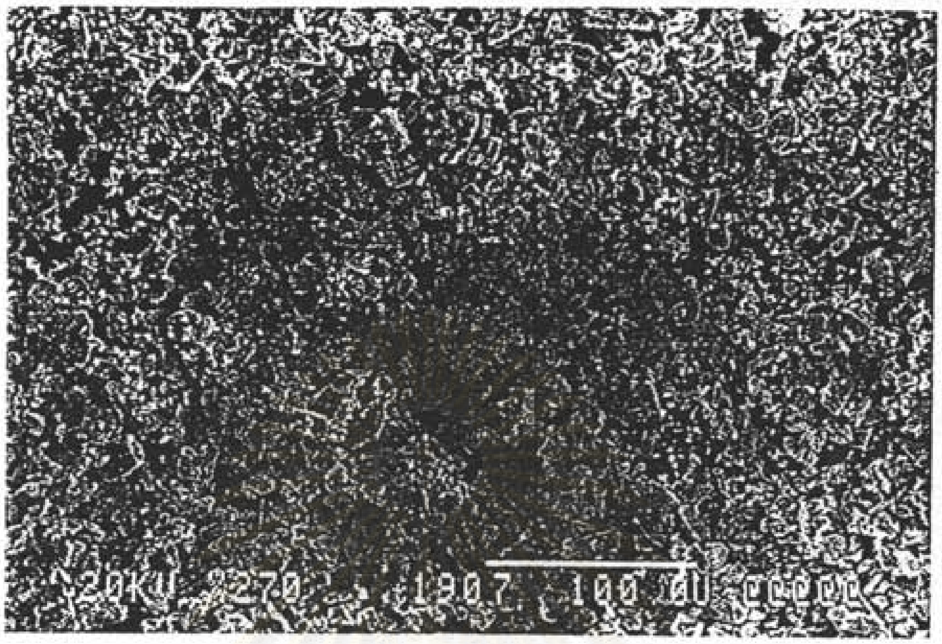


Figure 4.1 Particle size distribution of calcium carbonate.

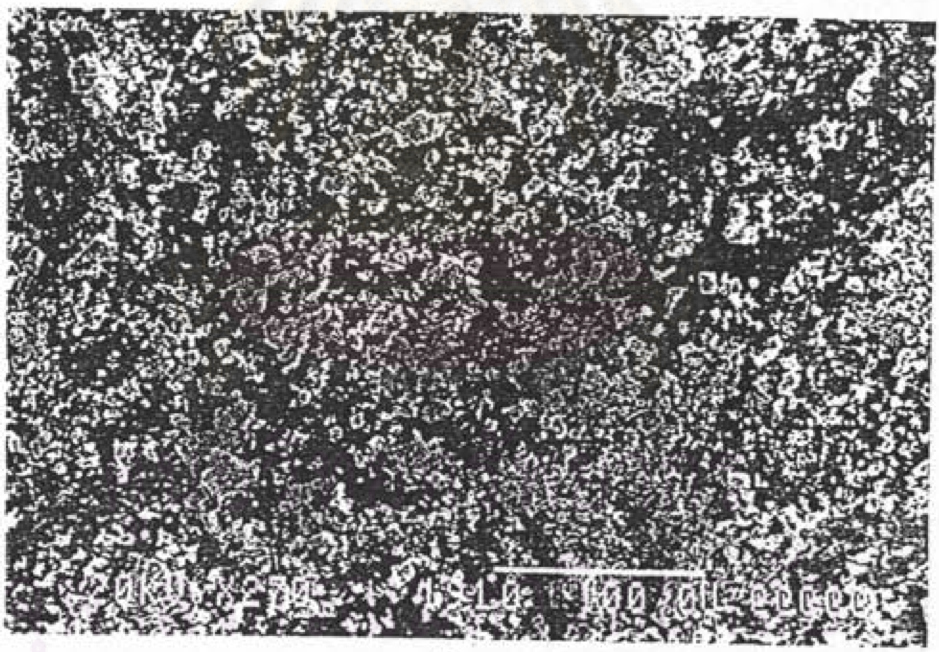
$CaCO_3$ 039 $CaCO_3$ 1939

Table 4.1 Some physical properties of fillers.

Properties	Filler		
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black
Surface area (m^2/g) (BET Method)	1.314	3.670	88.05
Particle size distribution (μm)			
< 3	13	30.5	-
3 - 5	5	12	-
5 - 7	6	8.5	-
7 - 9	5.5	8.5	-
9 - 11	4.5	4	-
11 - 13	5.0	4	-
13 - 15	5.0	(>13)33	-
15 - 17	2	-	-
17 - 19	4	-	-
19 - 21	4	-	-
21 - 23	3	-	-
23 <	43	-	-



a)



b)

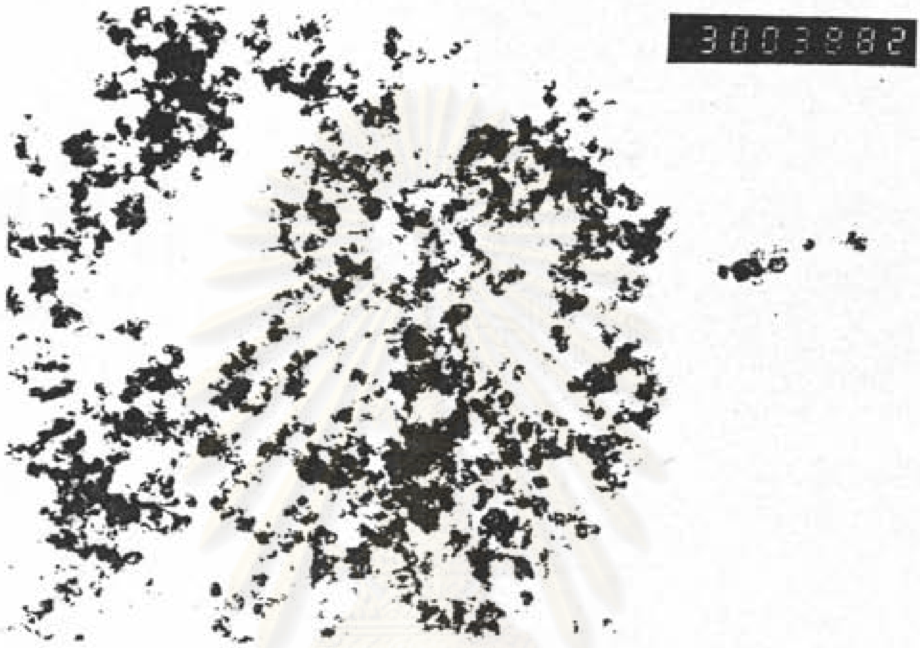
Figure 4.2 Electron micrographs of fillers

(a) calcium carbonate 039,

270x magnification.

(b) calcium carbonate 1939,

270x magnification.



c)

Figure 4.2 Electron micrographs of fillers

(c) carbon black, 45,000x magnification.

4.2 Tensile properties measurement

4.2.1 Stress-strain curves at different percents of $CaCO_3$.

Figure 4.3 shows the stress-strain curves of unfilled HDPE. The stress-strain curves of $CaCO_3$-filled-HDPE system are shown in Figures 4.4 and 4.5.

From Figure 4.4, the pattern of stress-strain curves at various percents of $CaCO_3$ 039, are the same. The stress increases and reaches the maximum strength (yield strength) in the range of 25-35 percent elongation. After this range, the stress gradually decreases and some different patterns can be observed. For the filler loading of 2-20 percent, the stress is constant beyond, approximately, the 100 percent elongation. For 2, 10, 20 and 30 percent of filler loading, the higher the percentage of $CaCO_3$ loading, the lower the elongation. Not much difference in maximum stress is observed among different filler loadings, but the yield strength decreases with increasing in percent loading of $CaCO_3$ 039.

For Figure 4.5, the patterns of stress-strain curve of $CaCO_3$ 1939-filled HDPE are very similar to those in Figure 4.4 .But in contrast with the $CaCO_3$ 039 system, the maximum strength increases with increasing the percent loading of $CaCO_3$ 1939.

It should be noted that at 2 percent filler loading for both types of carbonate, the elongation at break reaches approximatly 525 percent.

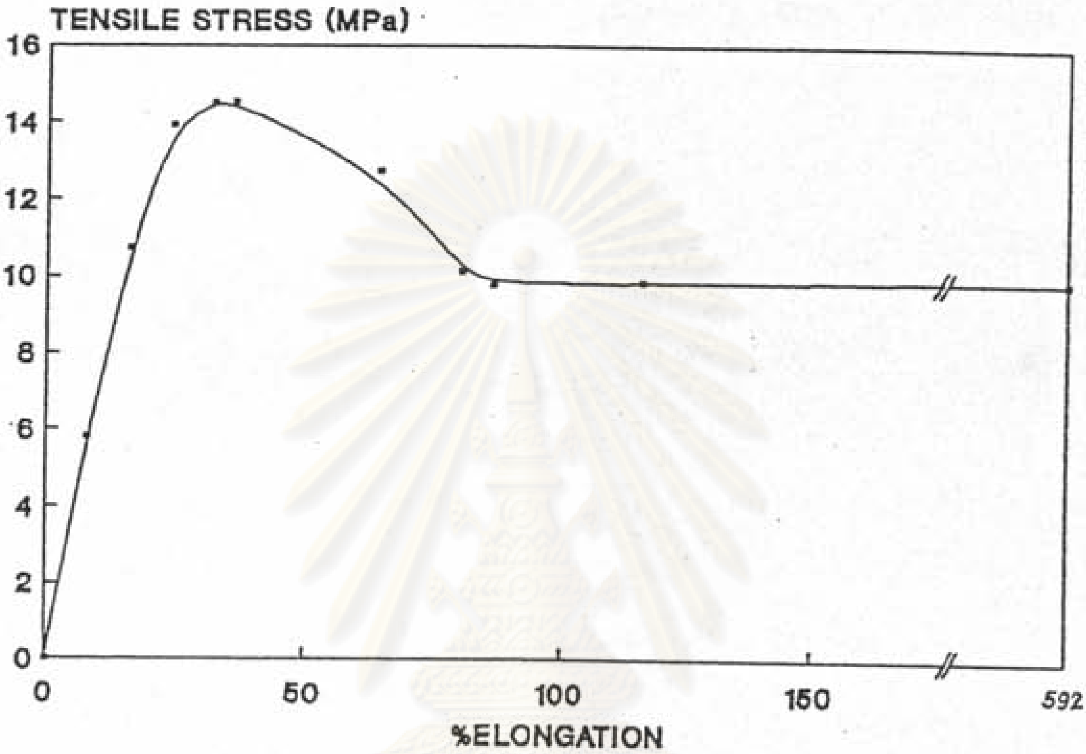


Figure 4.3 Relationship of stress-strain curve of HDPE.

HDPE R-1760

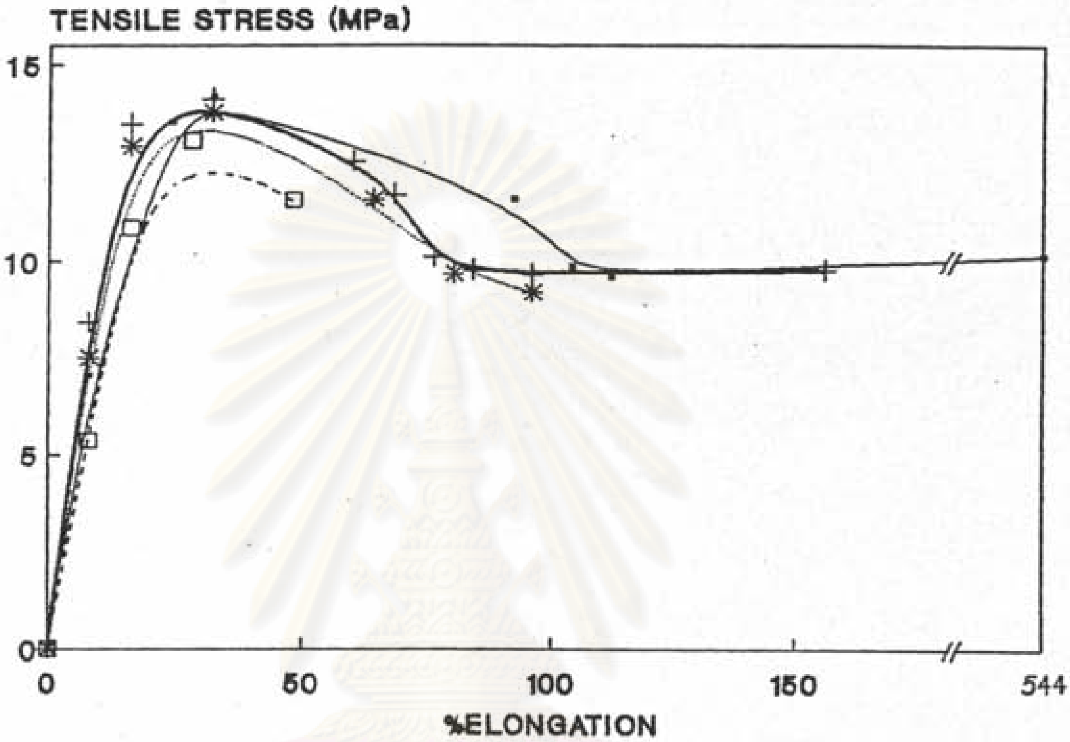


Figure 4.4 Relationship of stress-strain curve at various percents of $CaCO_3$ 039.

—■— $CaCO_3$ 039, 2%   —+— $CaCO_3$ 039, 10%

·✳· $CaCO_3$ 039, 20%   --□-- $CaCO_3$ 039, 30%

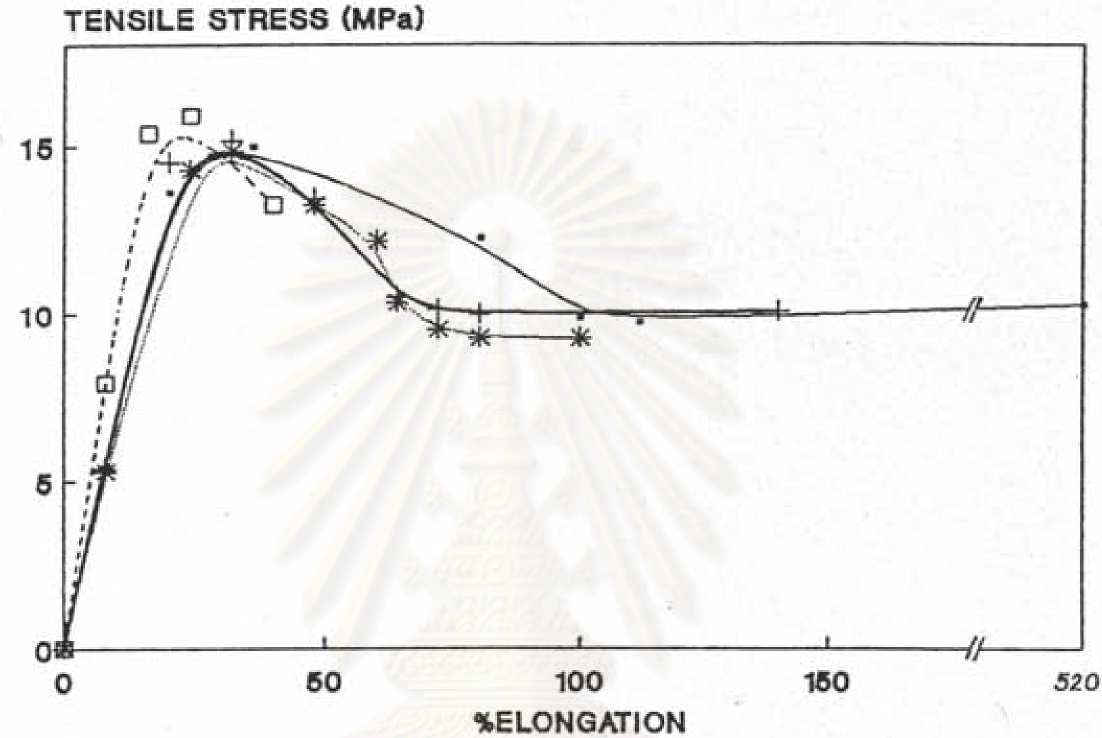


Figure 4.5 Relationship of stress-strain curve at various percents of $CaCO_3$ 1939.

—■— $CaCO_3$ 1939, 2% —+— $CaCO_3$ 1939, 10%

.✱. $CaCO_3$ 1939, 20% --□-- $CaCO_3$ 1939, 30%

4.2.2 Stress - strain curves at different percents of carbon black.

Stress-strain curves of carbon black-filled HDPE system are shown in Figure 4.6 in which the stress-strain behavior is similar to the $CaCO_3$ 1939-filled HDPE system. The higher the percent loading, the higher the maximum stress values but the lower the elongation at break. For this system, the maximum possible quantity of carbon black incorporated into high density polyethylene is 30 percent. The test specimen of 40 percent carbon black loading cannot successfully be formed because the prepared plaque is cracked by itself after opening the mold.

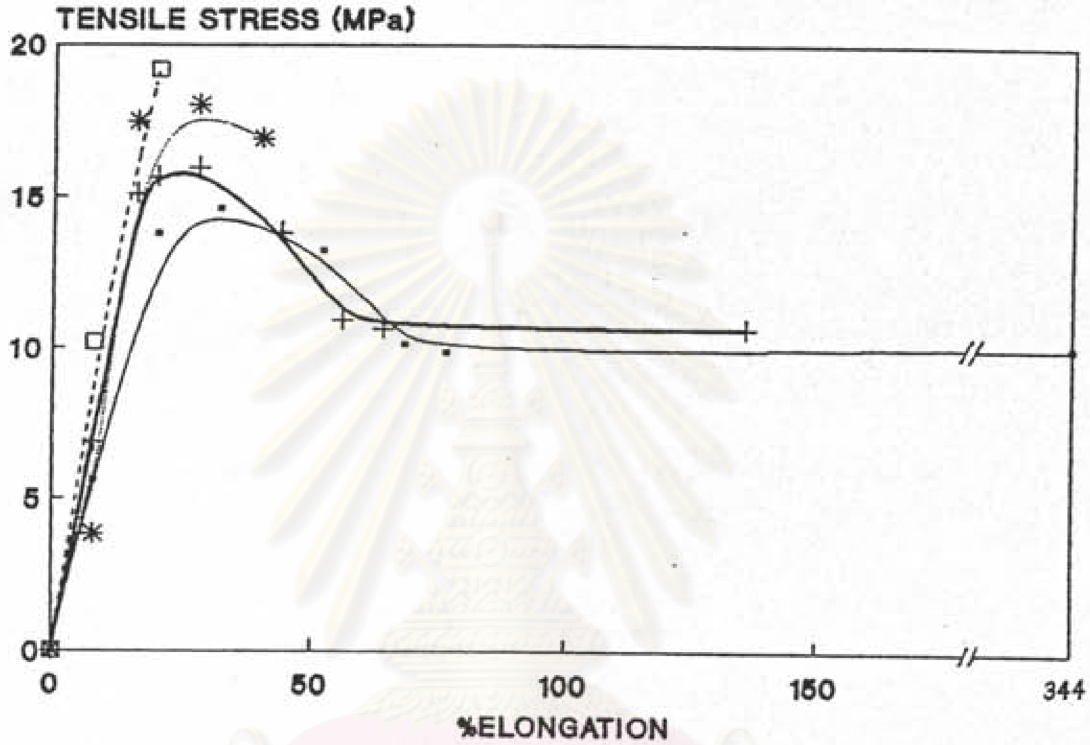


Figure 4.6 Relationship of stress-strain curve at various percents of carbon black.

carbon black, 2% carbon black, 10%

carbon black, 20% carbon black, 30%

4.2.3 Stress - strain curves at different percent of glass fiber.

To compare fibrous reinforcement filler with particle filler, the mechanicle properties of glass fiber-filled HDPE were also studied. The data of the fiber e.g. type of glass, size of fiber, surface treatment and treatment method are not available since the compound is supplied in a form of filled pellet. Figure 4.7 shows the stress-strain curve of glass-fiber filled HDPE at 10 % and 20% loading. To compare with particle filler, at the same percent loading in high density polyethylene (10 and 20 percent), the tensile stress and elongation of glass fiber-filled HDPE are higher than those of particle-filled HDPE. However, the stress-strain behavior is similar to other systems.

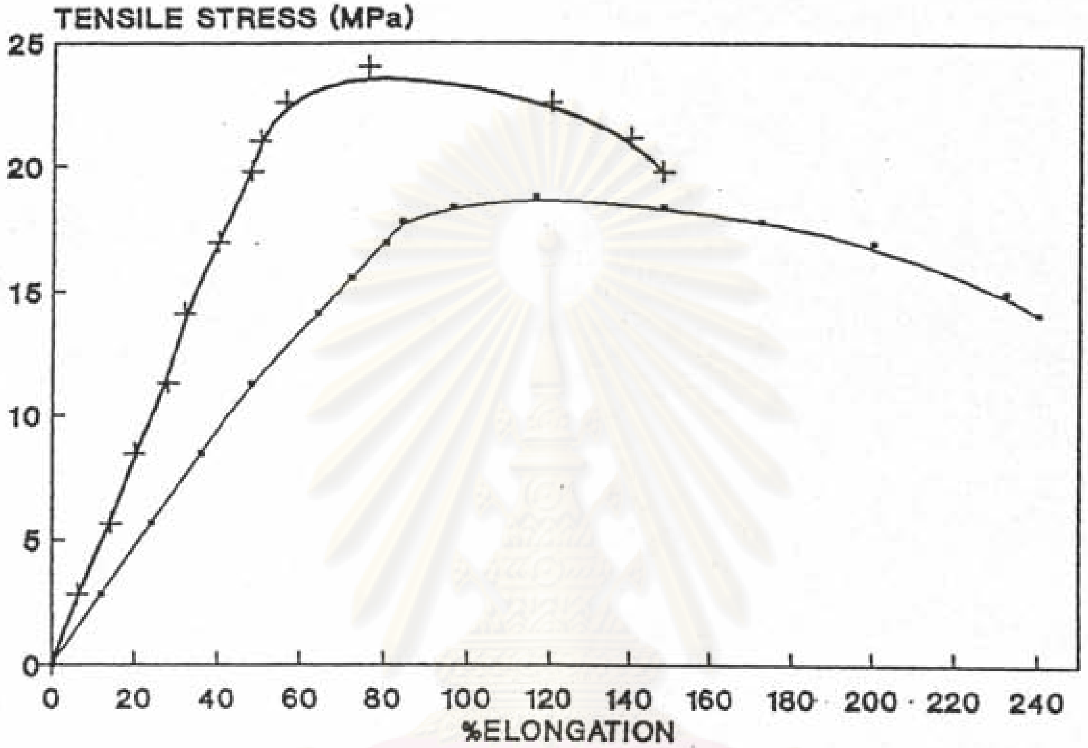


Figure 4.7 Relationship of stress-strain curve at various percents of glass fiber.

—■— glass fiber, 10% —+— glass fiber, 20%

4.3 Effect of filler on mechanical properties of high density polyethylene

4.3.1 Tensile strength

Figure 4.8 and Table 4.2 illustrate the effect of filler type on tensile strength at various filler loadings. For all types of filler, except the calcium carbonate 039 tensile strength increases with increasing in filler loading. The glass fiber filled HDPE shows the best properties improvement since it shows the highest slope in this system. The properties improvement changes with the type of filler. For carbon black filler, the properties of filled HDPE changes moderately. But the properties of $CaCO_3$ filled HDPE changes very little.

There have many discrepancies found in the effect of filler on tensile strength on the other literature and theory. Some show the improvement of these properties (9,16) but some reduced (8,14,15). These may be, due to, there have many conditions that affect the properties. Filler affects tensile properties according to their packing characteristics, size, and interfacial bonding. The maximum volumetric packing fraction of a filler, P_f, reflects the size distribution and the shapes of the particles. At P_f, the filler particles of a composite are separated by at least the thickness of matrix sufficient to uniformly coat them. The spaces between particles are assumed to be filled with matrix and no voids or air bubbles are present. Under these conditions, for a given system, the matrix volume is at a minimum and acts as individual segments or pockets to support a tensile load. When a tensile load is applied, these matrix segments stretch and pull away from the particles, resulting in the very low strength and elongations of highly filled composites. At the other extreme, a specimen of matrix is not restricted in its ability to stretch and to support a load and therefore would be expected to provide greater strength. Now, if two fillers having singnificantly differing P_f values are compared well below P_f and at the *same* filler volume in the same matrix, the one having the higher P_f will have larger spaces between particles, larger segments of matrix to support the load, and therefore will provide a higher value of tensile strength. Large particles cause greater stress concentrations in the matrix than small ones. All other conditions being equal, smaller average particle sizes provide higher strengths. Under conditions where the particles have been treated with bonding or coupling agents, the matrix is severely restricted by interfacial bonding, so tensile strength is improved.

From Figure 4.2, the particle size of $CaCO_3$ 039 is larger than the $CaCO_3$ 1939. This may answer why the strength of $CaCO_3$ 039 cannot compete with $CaCO_3$ 1939.

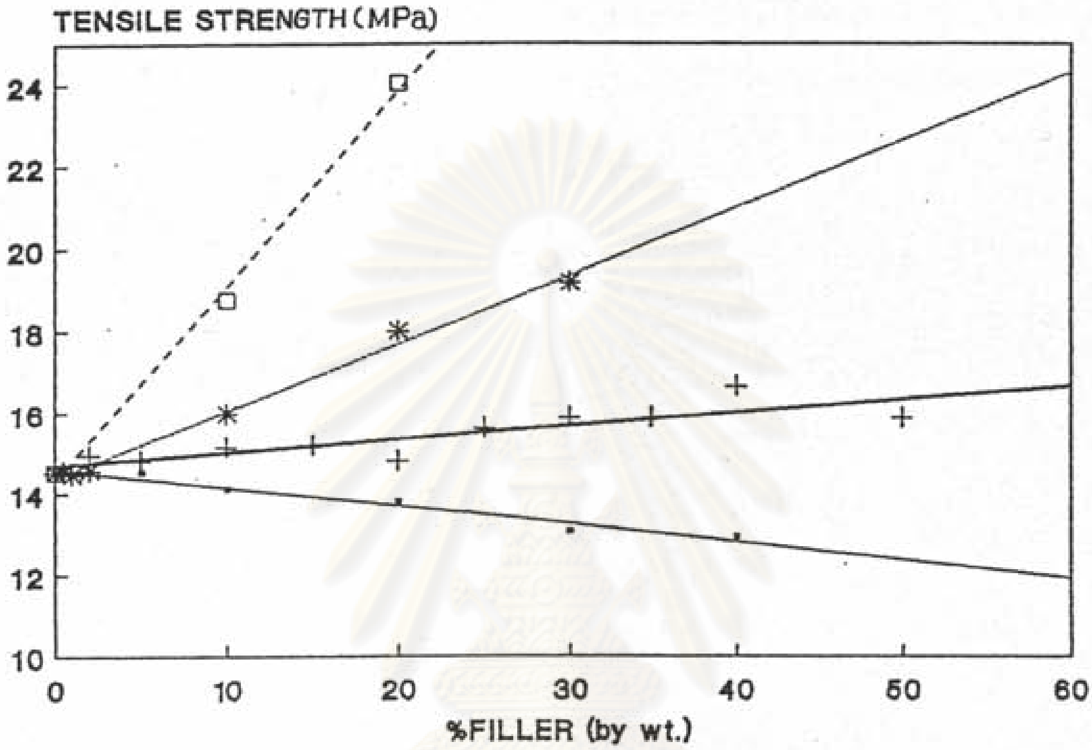


Figure 4.8 Effect of fillers on tensile strength at various percents of fillers.

--□-- glass fiber · ✳ · carbon black

—■— $CaCO_3$ 039 —+— $CaCO_3$ 1939

Table 4.2 Effect of fillers on tensile strength at various percents of fillers.

% filler	Tensile strength (MPa)			
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black	glass fiber
0	14.51	14.51	14.51	14.51
0.5	-	-	14.54	-
1.0	-	-	14.45	-
2.0	-	14.97	14.57	-
5.0	14.51	14.81	-	-
10.0	14.21	15.15	15.96	18.77
15.0	-	15.19	-	-
20.0	13.78	14.82	18.00	24.03
25.0	-	15.60	-	-
30.0	13.05	15.88	19.18	-
35.0	-	15.86	-	-
40.0	12.92	16.64	-	-
50.0	-	15.85	-	-

4.3.2 Elongation

The effect of filler on elongation is illustrated in Figure 4.9 and Table 4.3. Figure 4.9 shows the rapid reduction in elongation for a range of filler from 0 to 10 percent and all filler filled systems. Both calcium carbonates and carbon black filler have a similar pattern of decrease in elongation. The glass fiber shows a higher elongation than other fillers at the same filler fraction because of the better adhesion of polymer-fiber interface than the particle filler. Therefore the polymer matrix of glass fiber filled HDPE can then produce an apparent strength improvement and greater tenacity, resulting in a higher ultimate elongation. For the particle system, the interfacial bond may exceed the matrix strength, the matrix has fewer freedoms to draw around the particles, and a lower elongation. Conversely, very weak interfacial bonding causes almost immediate separation of the matrix from the particles and cavitation begins at a low elongation.

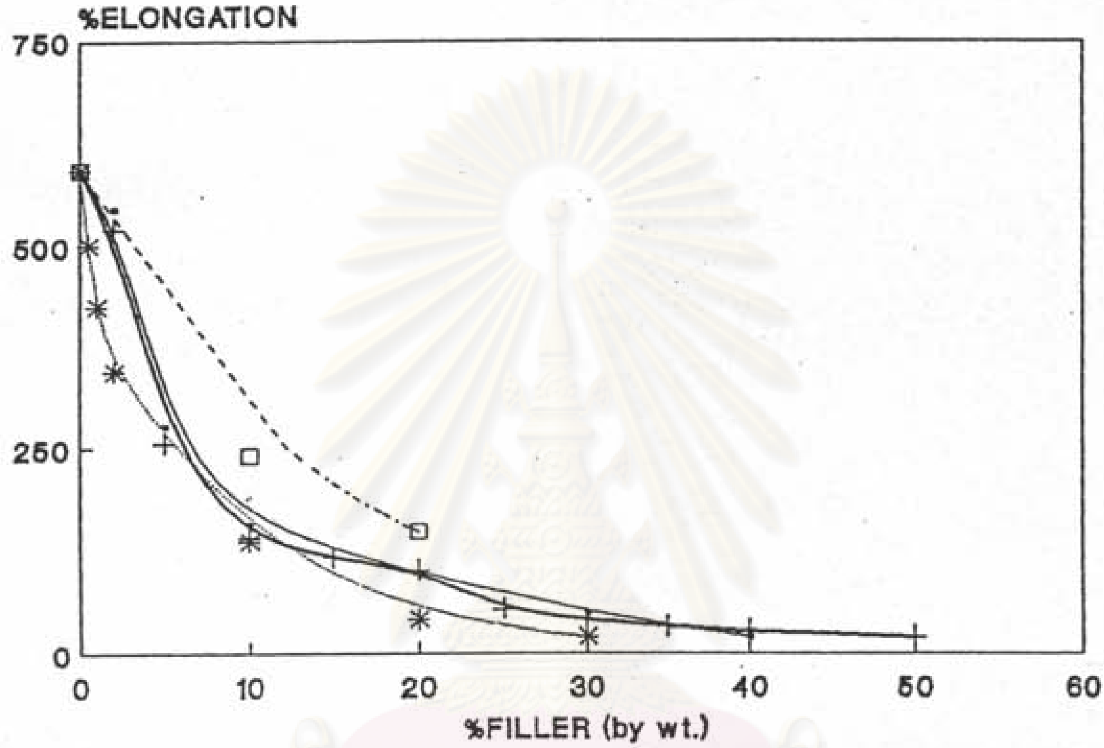


Figure 4.9 Effect of fillers on elongation at various percents of fillers.

--□-- glass fiber · ✳ · · carbon black

—■— $CaCO_3$ 039 —+— $CaCO_3$ 1939

Table 4.3 Effect of fillers on elongation at various percents of fillers.

% filler	% Elongation			
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black	glass fiber
0	592.0	592.0	592.0	592.0
0.5	-	-	500.0	-
1.0	-	-	424.0	-
2.0	544.0	520.0	344.0	-
5.0	276.0	256.0	-	-
10.0	156.0	140.0	136.0	240.0
15.0	-	116.0	-	-
20.0	96.0	100.0	40.0	148.0
25.0	-	52.0	-	-
30.0	48.0	40.0	20.0	-
35.0	-	32.0	-	-
40.0	20.0	27.2	-	-
50.0	-	20.0	-	-

4.3.3 Modulus

The most pronounced effect on mechanical properties of adding a rigid filler to a polymer system is the modulus. Incorporating calcium carbonate or carbon black into high density polyethylene sinificantly increases tensile modulus while reducing elongation. From Figure 4.10 and Table 4.4, carbon black gives the most stiffening and also the greatest reduction in ductility. These properties change may be due to that a typical effect of the higher surface area of carbon black gives a much more polymer-filler interface than the others. The modulus of HDPE at a small percentage of carbon black loading may be the same as the higher loading for the other filler. Both two types of calcium carbonate give the same pattern of improvement, but with higher modulus in the $CaCO_3$ 1939-filled HDPE; the reason could be the same as the improvement of tensile strength discussed earlier. For the glass fiber, the improvement pattern in modulus is the same as the carbon black, due to that the "wet" fiber in the polymer shows better adhesion and then the composite can re-orient when it exposes to stress. At the same stress applied, the glass fiber filled high density polyethylene yields a higher elongation which results in lower modulus than carbon black.

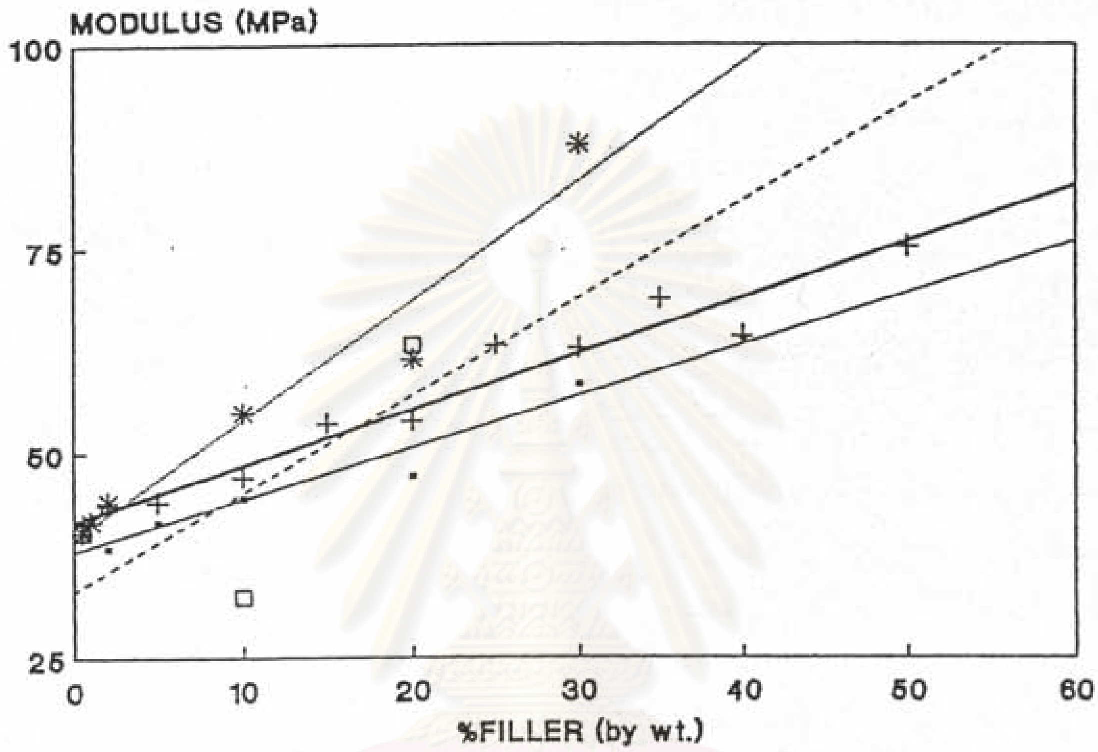


Figure 4.10 Effect of fillers on modulus at various percents of fillers.

--□-- glass fiber   ..✳.. carbon black

—■— $CaCO_3$ 039   —+— $CaCO_3$ 1939

Table 4.4 Effect of fillers on modulus at various percents of fillers.

% filler	Yield Modulus (MPa)			
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black	glass fiber
0	40.32	40.32	40.32	40.32
0.5	-	-	40.32	-
1.0	-	-	41.58	-
2.0	38.35	43.70	43.93	-
5.0	41.52	43.94	-	-
10.0	44.42	47.00	54.87	32.36
15.0	-	53.59	-	-
20.0	47.13	53.93	61.53	63.24
25.0	-	63.10	-	-
30.0	58.33	62.79	87.68	-
35.0	-	68.33	-	-
40.0	64.10	64.26	-	-
50.0	-	75.26	-	-

4.3.4 Notched Izod impact strength

The effects of filler on Izod impact strength are summarized in Figure 4.11 and Table 4.5. Both calcium carbonate fillers give the same pattern of reduction in Izod impact strength. The impact values decrease rapidly in the filler ranging from 0 to 5 percent and gradually decrease further beyond this range. The impact strength of carbon black-filled gives a declining curve continuously with increasing in filler loading.

Fundamentally, impact strength is proportional to the area beneath the stress-strain curve at relatively high testing speeds. It has been established that its inclusions in a matrix act as stress concentrators. Such inclusions must differ substantially from the matrix in ductility. Thus, crystallites, voids, particles, fibers, notches, and crack all act as stress concentrators. Considering only the case of particulate fillers, it is apparent that the matrix will tend to improve impact strength. Impact modifiers are generally of this class. Most commonly used fillers are rigid, very high modulus materials with vitually no elongation, and therefore embrittle the composite. This statement must be qualified according to two factors; if a filler contributes improved cohesive strength to a composite compared to that of the matrix, and if the filler particles distribute the impact stress over a larger area perpendicular to the force of impact, then an improvement in impact strength will result. Improvement is usually limited to low filler concentrations and very fine particle size fillers. Again, the packing fraction of the fillers is an important determinant. Poorly packing fillers occupy larger volumes, and therefore, contribute greater number of stress concentrators; or to view the composite as a whole, they more effectively reduce the continuity of the matrix. Since the matrix must absorb the shock of impact, those filler having high packing fractions will tend to reduce impact strength much less at the same filler volume.

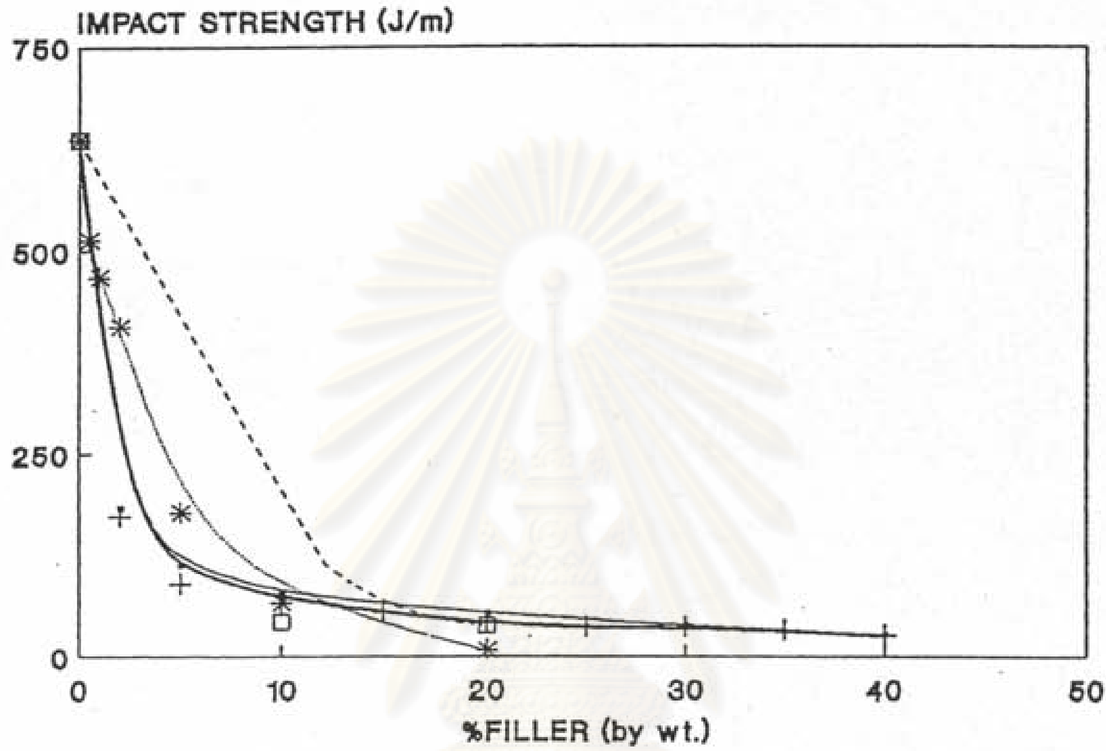


Figure 4.11 Effect of fillers on Izod impact strength at various percents of fillers.

--□-- glass fiber
·✳· carbon black
—■— $CaCO_3$ 039
—+— $CaCO_3$ 1939

Table 4.5 Effect of fillers on Izod impact strength at various percents of fillers.

% filler	Impact strength (J/m)			
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black	glass fiber
0	636.00	636.00	636.00	636.00
0.5	-	-	512.99	-
1.0	-	-	467.47	-
2.0	183.00	173.00	460.55	-
5.0	113.43	90.67	178.00	-
10.0	78.00	-	66.77	42.77
15.0	-	54.75	-	-
20.0	53.22	42.00	8.60	38.73
25.0	-	35.70	-	-
30.0	38.50	36.25	-	-
35.0	-	32.50	-	-
40.0	27.67	26.00	-	-
50.0	-	-	-	-

4.3.5 Hardness

Figure 4.12 and Table 4.6 illustrate the effect of filler on hardness of high density polyethylene. The calcium carbonate system can improve the hardness of HDPE. At the same loading, the hardness of glass fiber-filled HDPE is higher than those of carbon black-filled HDPE and $CaCO_3$-filled HDPE. From this study, the filler which increases the moduli of composites generally will increase the hardness values of composites. Also, hardness is a function of the relative packing fraction of the filler and its true modulus. Other factors which influence hardness of filled systems are degree of dispersion, interfacial bonding, shear degradation of the polymer by the filler during processing, distribution of filler due to sample preparation, disruption or improvement in crystallite bonding, filler adsoprtion of stabilizers, processing aids or other additives, and probably many more.

4.4 <u>Comparison of filler types</u>.

The properties of high density polyethylene filled with calcium carbonate, carbon balck and glass fiber at 10%, 20%, and 30% loading are summarized in Table 4.7

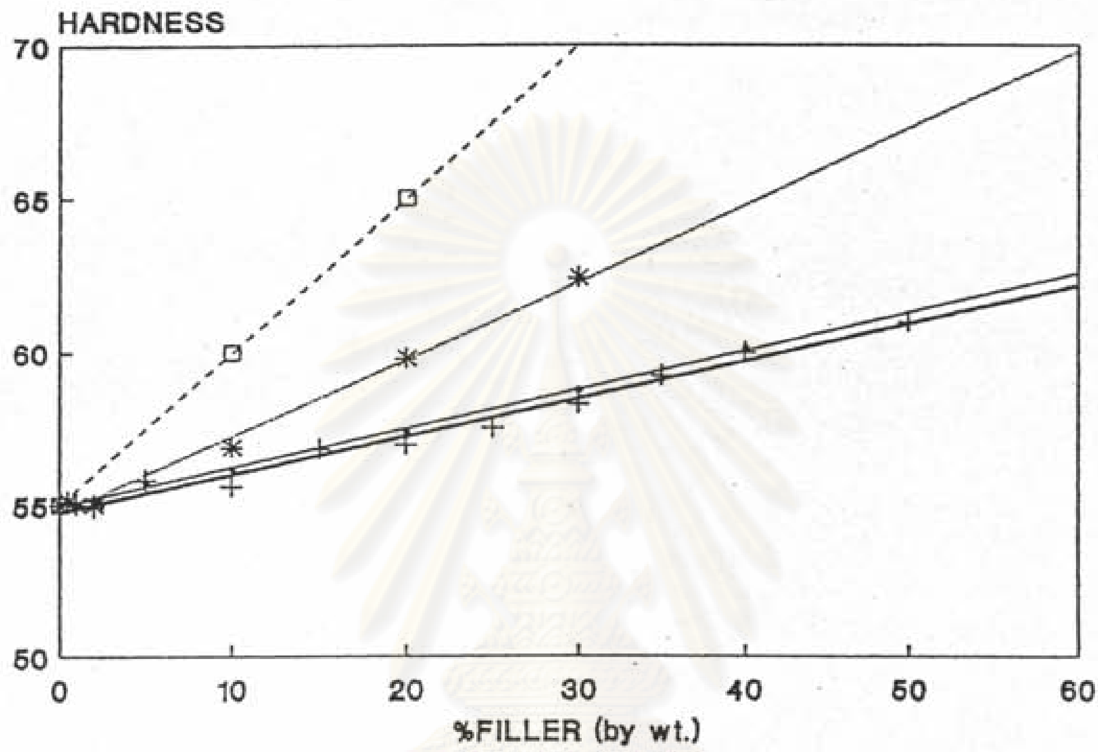


Figure 4.12 Effect of fillers on hardness at various percents of fillers.

--□-- glass fiber . * . carbon black

—■— $CaCO_3$ 039 —+— $CaCO_3$ 1939

Table 4.6 Effect of fillers on hardness at various percents of fillers.

% filler	Hardness			
	$CaCO_3$ 039	$CaCO_3$ 1939	carbon black	glass fiber
0	55.00	55.00	55.00	55.00
0.5	-	-	55.11	-
1.0	-	-	55.00	-
2.0	55.17	54.92	55.00	-
5.0	55.73	55.80	-	-
10.0	56.17	55.60	56.89	60.00
15.0	-	56.81	-	-
20.0	57.40	56.95	59.78	65.00
25.0	-	57.50	-	-
30.0	58.75	58.30	62.40	-
35.0	-	59.20	-	-
40.0	60.11	60.00	-	-
50.0	-	61.00	-	-

Table 4.7 Summary of mechanical properties of unfilled and filled HDPE.

Properties	no Filler	$CaCO_3$ 039			$CaCO_3$ 1939			carbon black			glass fiber		
		10%	20%	30%	10%	20%	30%	10%	20%	30%	10%	20%	30%
Tensile strength (MPa)	14.52	14.12	13.79	13.06	15.15	14.82	15.88	15.97	18.00	19.18	18.77	24.03	-
Elongation (%)	592.0	156.0	96.0	48.0	140.0	100.0	40.0	136.00	40.00	20.00	240.0	148.0	-
Modulus (MPa)	40.32	44.43	47.13	58.33	47.00	53.93	62.79	54.87	61.53	87.68	32.36	63.24	-
Hardness	55.00	56.17	57.40	58.75	55.60	56.95	58.30	56.89	59.78	62.40	60.00	65.00	-
Izod Impact (J/m)	636.0	78.00	53.22	38.50	-	42.00	36.25	66.77	8.60	-	42.77	38.73	-

4.5 Scanning electron micrographs

After testing the tensile properties, the fracture surface of the samples was subject to a Scanning Electron Microscope. Figures 4.13 to 4.18 are the electron micrographs of HDPE filled with calcium carbonate at various percents. From these figures, it shows the difference in particle size of the filler. Both types of calcium carbonate do not seem to have any polymer-filler-interface bonding. The particles, especially the large size of calcium carbonate 039, have no "wetting" with polymer metrix. The figures also show the holes which have been occupied by the filler and it represents the ease in losing the large particles out of the matrix than do the smaller ones. So the calcium carbonate 039 exhibits the lower tensile strength than calcium carbonate 1939; and at a higher percentage of loading, the carbonate 039-filled HDPE system will illustrate a lowering in tensile strength than a lower percentage of loading.

Figure 4.19 illustrates the carbon black-filled HDPE system. The figure shows only a lower percentage of loading because the particles of carbon black are too small to be observed with the same magnification used in the carbonate system, so the higher percentage of loading gives the same pattern with the lower one. Because of the extreme small particle size of carbon blacks and its properties, it will readily and easily disperse in the polymer, and will give the higher mechanical properties than the calcium carbonate.

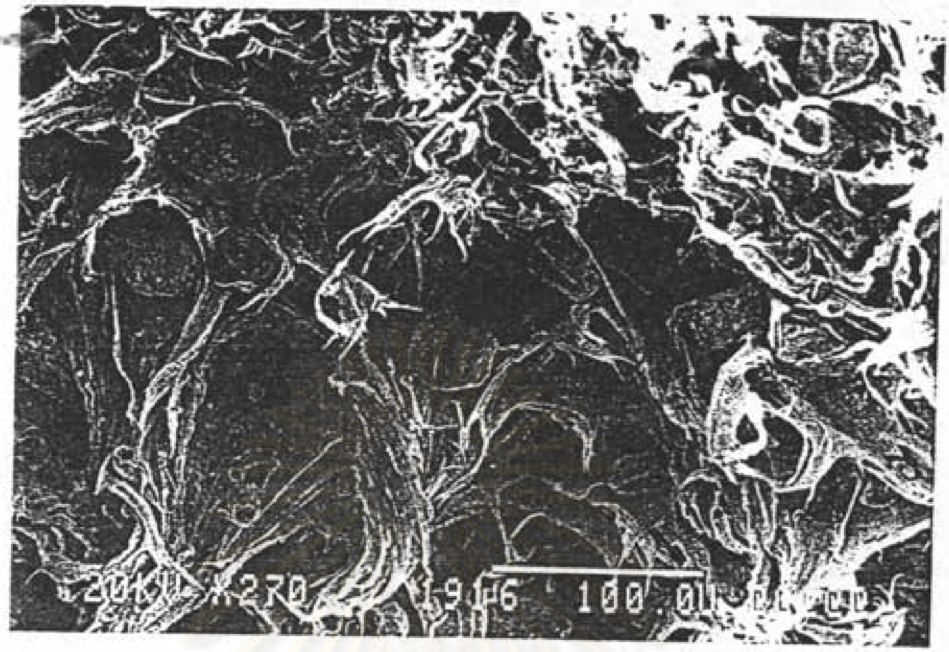


Figure 4.13 Scanning electron micrograph of the fracture surface of HDPE filled with 30% $CaCO_3$ 039. 270x magnification.

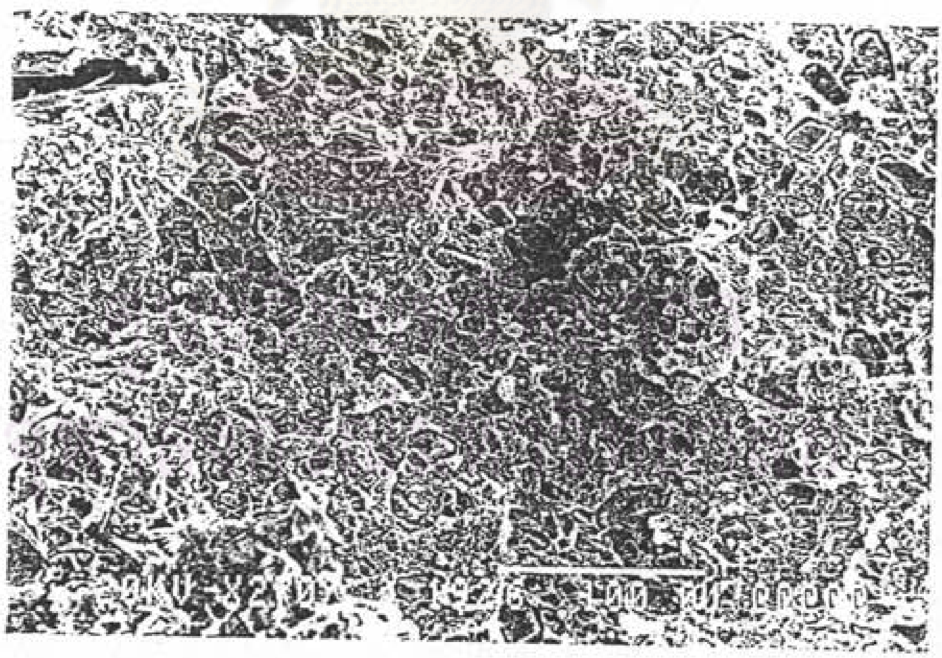


Figure 4.14 Scanning electron micrograph of the fracture surface of HDPE filled with 30% $CaCO_3$ 1939, 270x magnification.

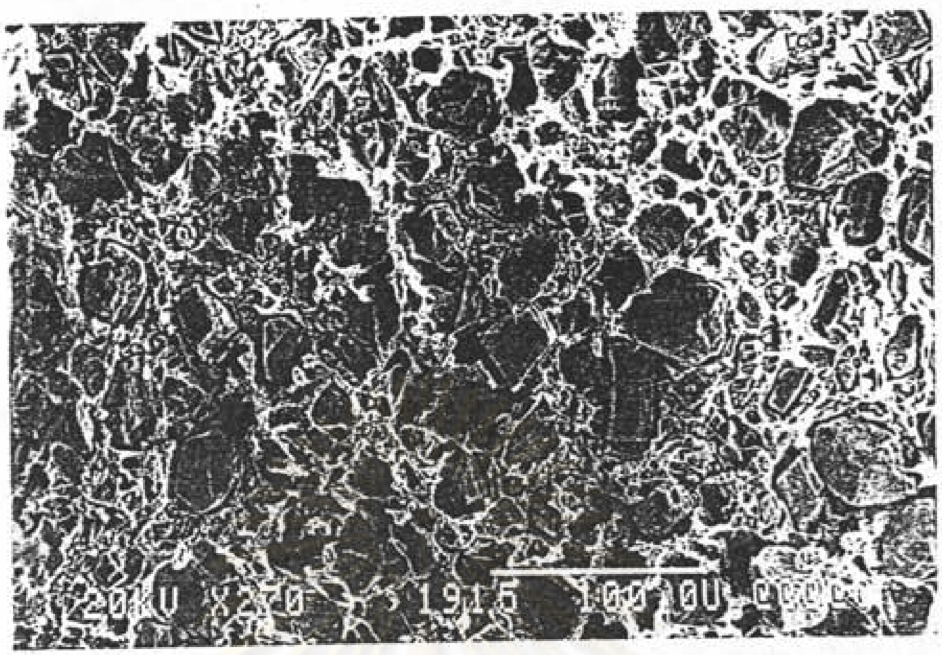


Figure 4.15 Scanning electron micrograph of the fracture surface of HDPE filled with 40% $CaCO_3$ 039, 270x magnification.

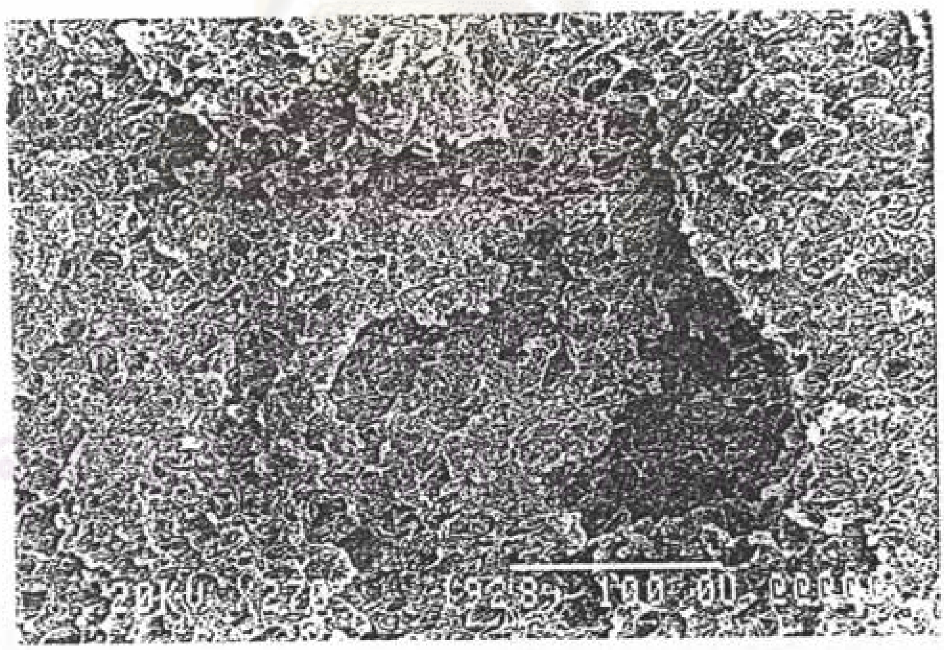


Figure 4.16 Scanning electron micrograph of the fracture surface of HDPE filled with 40% $CaCO_3$ 1939, 270x magnification.

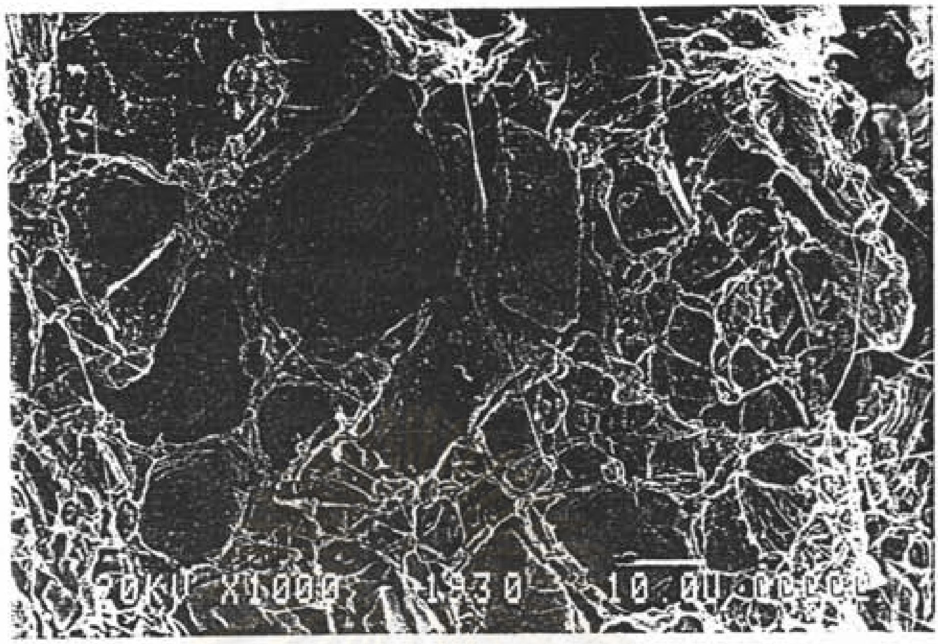


Figure 4.17 Scanning electron micrograph of the fracture surface of HDPE filled with 40% $CaCO_3$ 039, 1000x magnification.

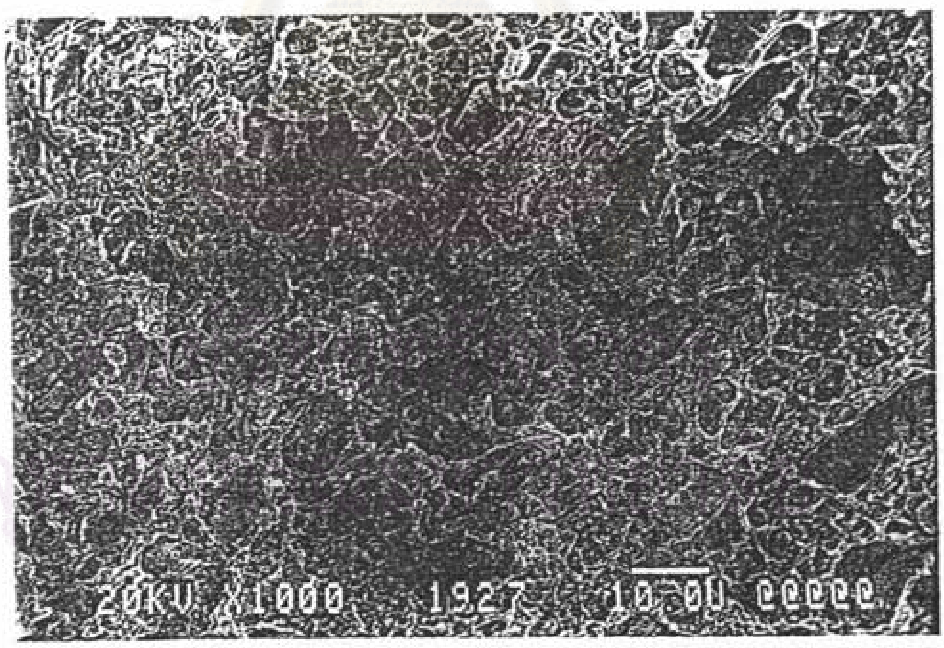


Figure 4.18 Scanning electron micrograph of the fracture surface of HDPE filled with 40% $CaCO_3$ 1939, 1000x magnification.

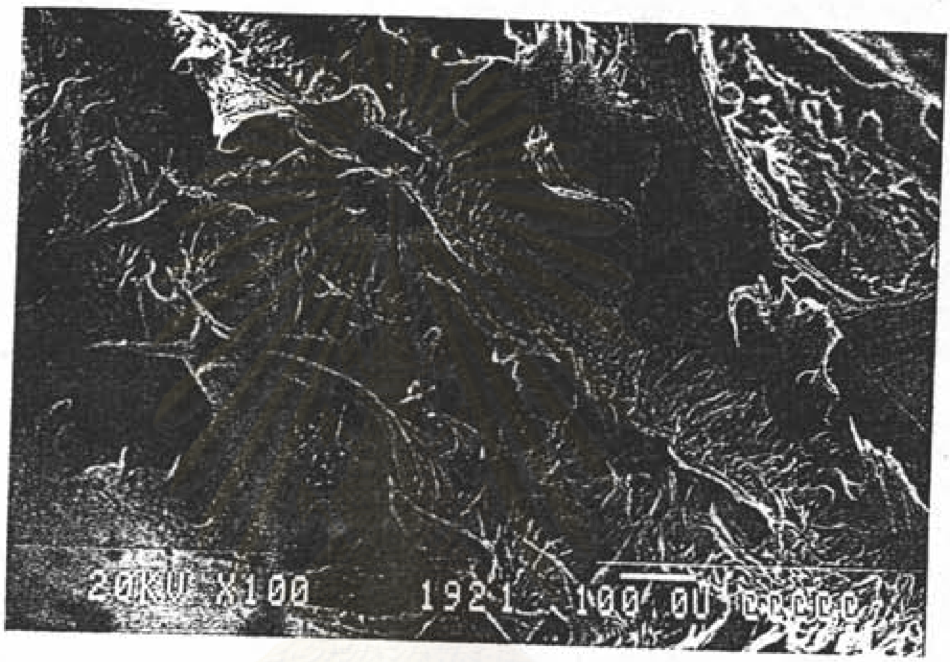


Figure 4.19 Scanning electron micrograph of the fracture surface of HDPE filled with 2% carbon black, 100x magnification.

Figure 4.20 to 4.21 represent the electron micrographs of the glass fiber-filled HDPE. It shows more coatings on the fibre with polymer than the particle system and this is the answer for the higher mechanical properties of glass fiber-filled HDPE than the other particulate systems.

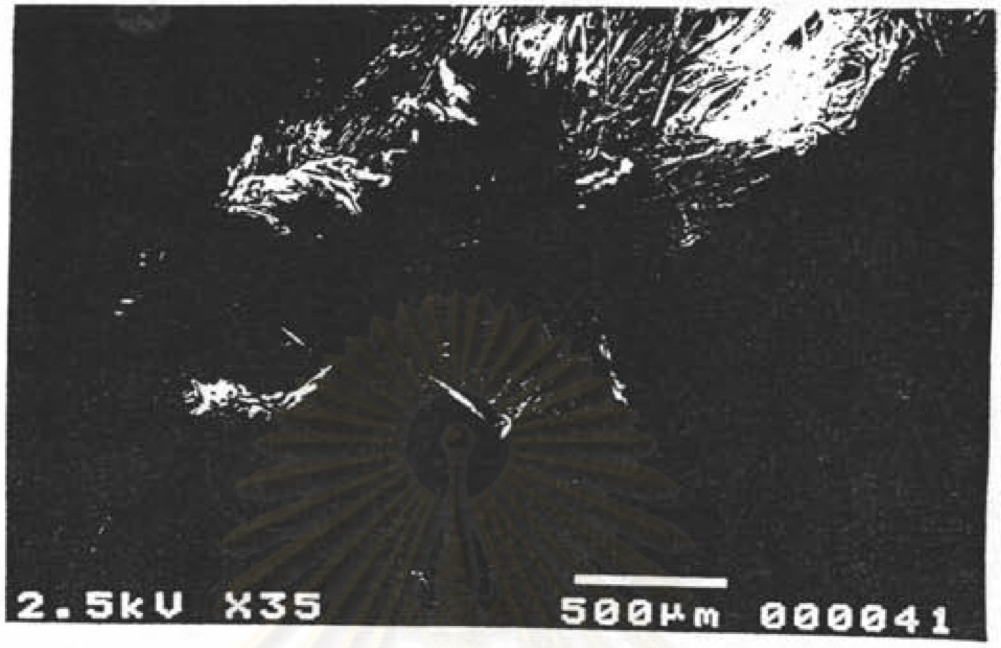


Figure 4.20 Scanning electron micrograph of the fracture surface of HDPE filled with 10% glass fiber, 35x magnification.

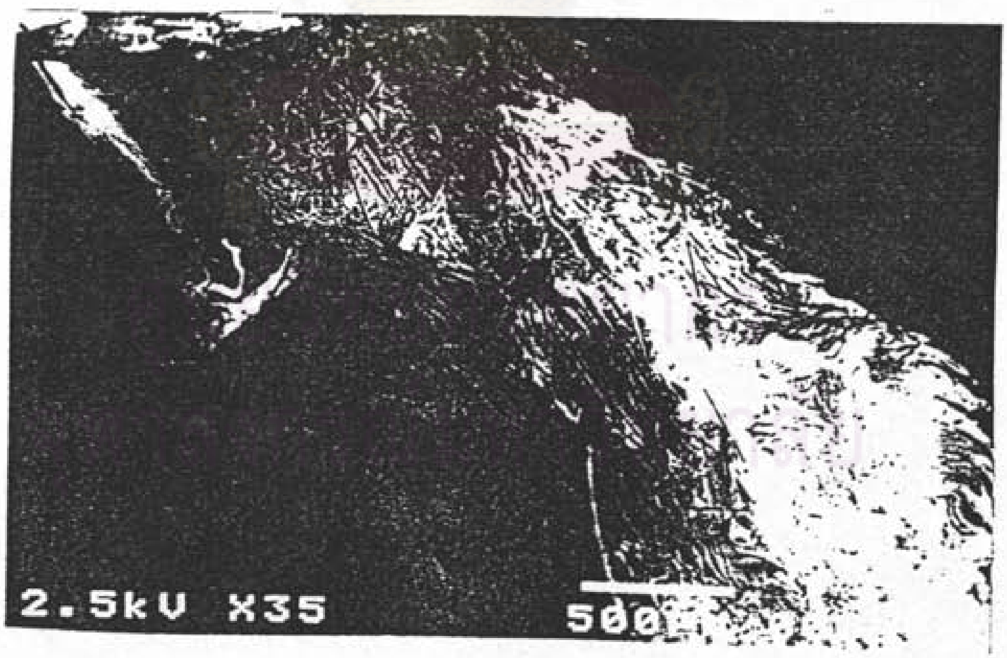


Figure 4.21 Scanning electron micrograph of the fracture surface of HDPE filled with 20% glass fiber, 35x magnification.

These figures show the uniform distribution of the fillers. However, it looks like very little or even no adhesion between the filler and the polymer except those of glass fiber, in which much more polymer coating on fiber surface is evidenced.