

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Agglomerate Density

Agglomerate density of low structure carbon black (0%H), high structure carbon black (100%H), and their blends (20%H, 40%H, 60%H, and 80%H) were measured by pycnometric technique. The value of each condition was found to be in the range 0.20-0.26 g/cm³. In order to study the influence of aggregate structure, agglomerate density of carbon black for each agglomerate blend was taken as the average value of 0.23 g/cm³.

Table 4.1 Agglomerate density of carbon black and blending of carbon black

	Agglomerate Blends					
	0%H	20%H	40%H	60%H	80%H	100%H
Agglomerate Density (g/cm ³)	0.26	0.24	0.22	0.22	0.21	0.20

4.2 Dispersive Mixing Process

Figure 4.1-4.6 represent a power torque curve (plot of torque versus mixing time) obtained from the Brabender mixer for the carbon black mixing with PP while the percentage of carbon black loading in the PP is varied from 5 to 30 %. It was found that the torque curve become steady after

approximately 7 minutes for all conditions. The mixing above 7 minutes in dispersive mixing process is defined as “steady state”. The torque curve shows two peaks corresponding to incorporation and initial stage of dispersion. The first peak represents the torque of PP during the initial stage as a pellet to polymer melt, while the second peak represents the carbon black incorporation within the polypropylene. After the second peak, the process of agglomerate dispersion begins. The torque decreases continuously and eventually reaches a plateau region. Hence, the torque curve occurring after the second peak can be used to evaluate for the dispersion behavior of each carbon black agglomerate blend. Higher loadings of carbon black produced a corresponding increase in the second torque peak. The curves show the same trend for high structure carbon black (100%H) and their blends (20%H, 40%H, 60%H, and 80%H) as shown in Figure 4.2, 4.3, 4.4, 4.5, and 4.6 respectively. It should be noted that the torque values increased gradually as the loading percentage of carbon black increased, suggesting the dispersion behavior of carbon black agglomerate depends on the loading amount and the properties of carbon black.

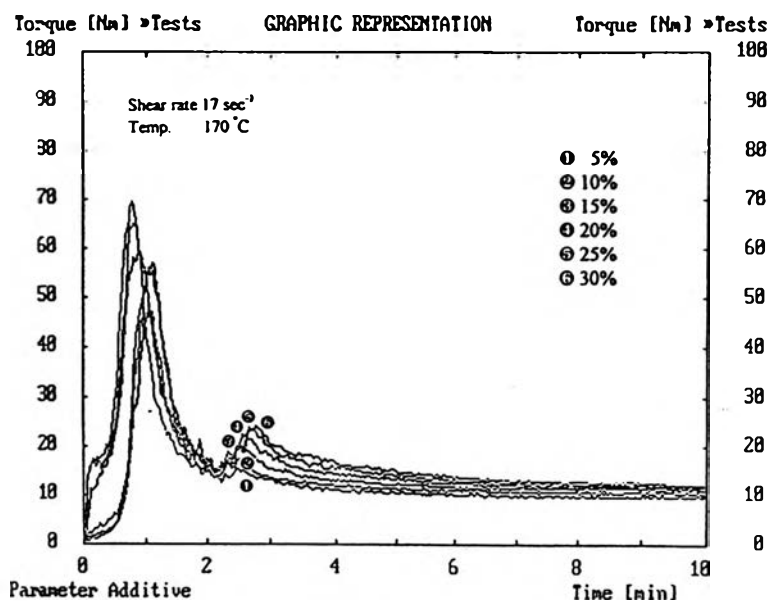


Figure 4.1 Mixing curve of low structure carbon black (0%H) in polypropylene for 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

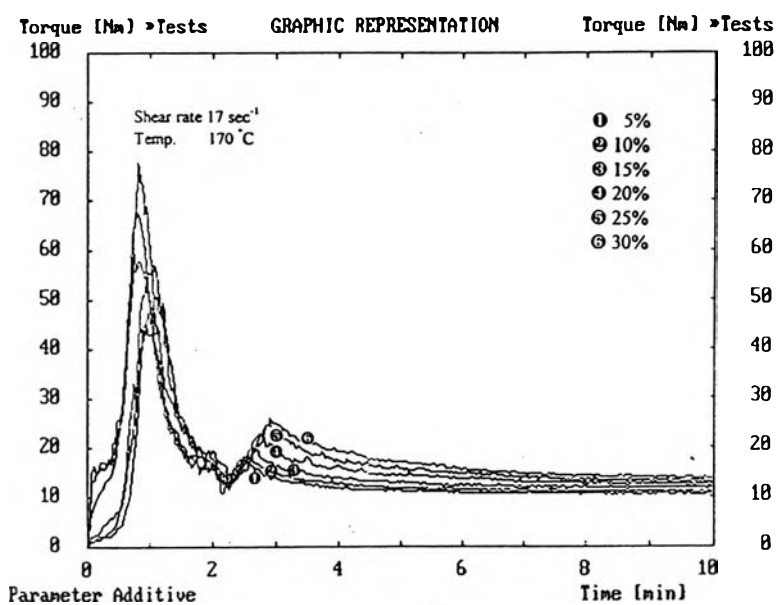


Figure 4.2 Mixing curve of high structure carbon black (100%H) in polypropylene for 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

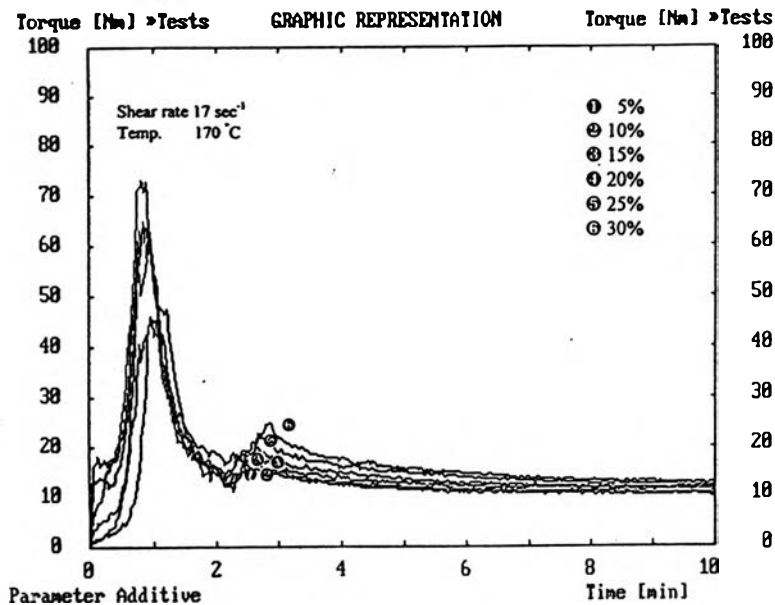


Figure 4.3 Mixing curve of 20% high structure carbon black (20%H) in polypropylene for 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

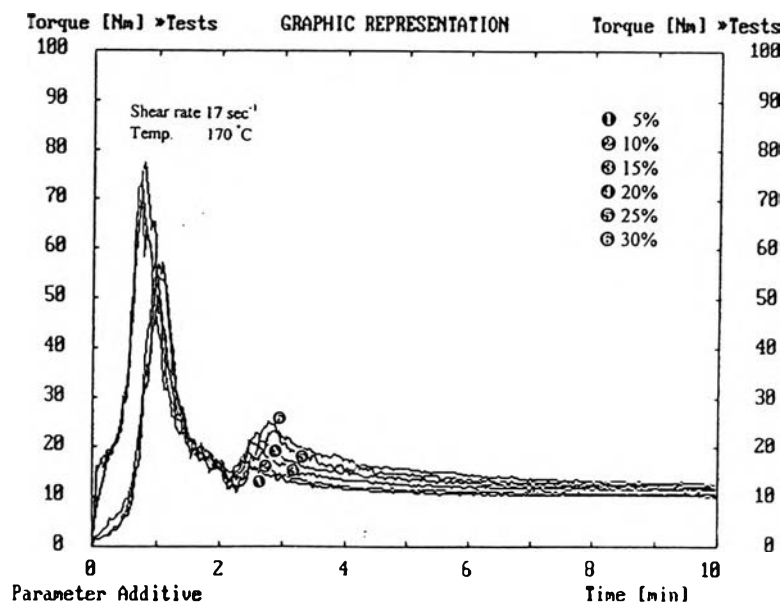


Figure 4.4 Mixing curve of 40% high structure carbon black (40%H) in polypropylene for 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

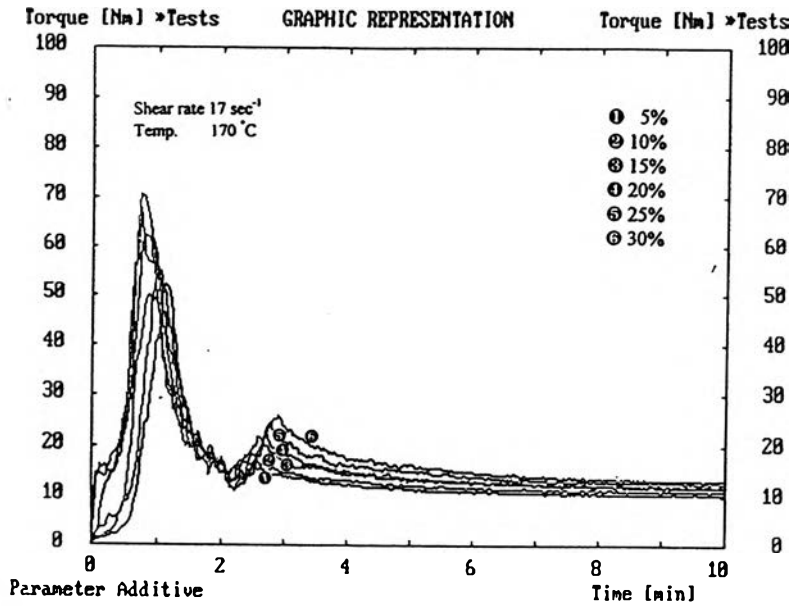


Figure 4.5 Mixing curve of 60% high structure carbon black (60%H) in polypropylene for 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

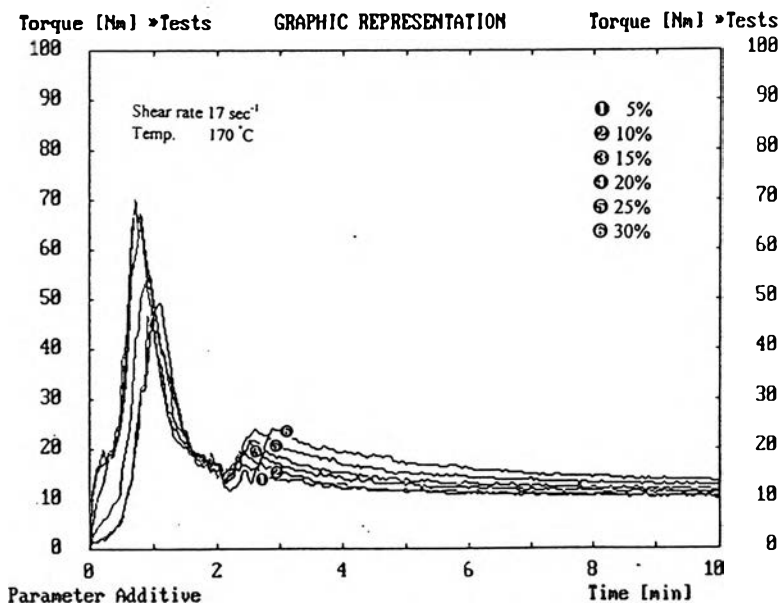


Figure 4.6 Mixing curve for 80% high structure carbon black (80%H) in polypropylene of 5%, 10%, 15%, 20%, 25%, and 30% carbon black loading.

4.3 Dispersion Rate Constant

From the torque curve as represented in Figure 4.7 (plot of torque versus mixing time), the dispersion rate constant (k) was calculated according to the equation of Cotten (1984),

$$\ln (P_t - P_\infty) / (P_0 - P_\infty) = -kt$$

Where P_t represents the torque at any given time, t , and P_∞ represents the final steady state torque after long mixing times. The rate constant (k) was obtained by graphically fitting the data to give a straight line (plot of $\ln (P_t - P_\infty)$ versus mixing time). P_∞ is defined as the value of P after it has decreased to a certain value, and the difference between P_t and P_∞ is less than 5 percent.

The total change in torque ($P_0 - P_\infty$) is proportional to the initial volume of occluded PP at the second power peak, and ($P_t - P_\infty$) is proportional to the volume of occluded polypropylene at time t . Thus, the constant k represents the rate at which the occluded polypropylene is dispersed, and, therefore, is proportional to the rate at which carbon black is being dispersed. This equation is the integral form of an equation describing a process obeying first order kinetics. It implies that the rate of agglomerate dispersion is proportional to the concentration of agglomerates at any given instant of time.

Figure 4.8 shows dispersion rate constants calculated from power torque curve by using the Cotten equation. %H represents the high structure carbon black blended in the agglomerate system. Comparing the low structure carbon black with the high structure carbon black, it is interesting to note that high structure carbon black shows lower dispersion rate constants than low structure carbon black. This indicates that the high structure carbon black is more difficult to

disperse than the low structure carbon black. This may be due to the morphology of high structure carbon black which are more inter-locked, with more branching. As the percentage of high structure carbon black in the blend increases, the dispersion rate constant is found to decrease. This may be due to the effect of the packing characteristics of high structure carbon black and low structure carbon black on the blending system. It is also interesting to note that when the percentage of carbon black loading is above 25% all conditions show similar values of dispersion rate constants.

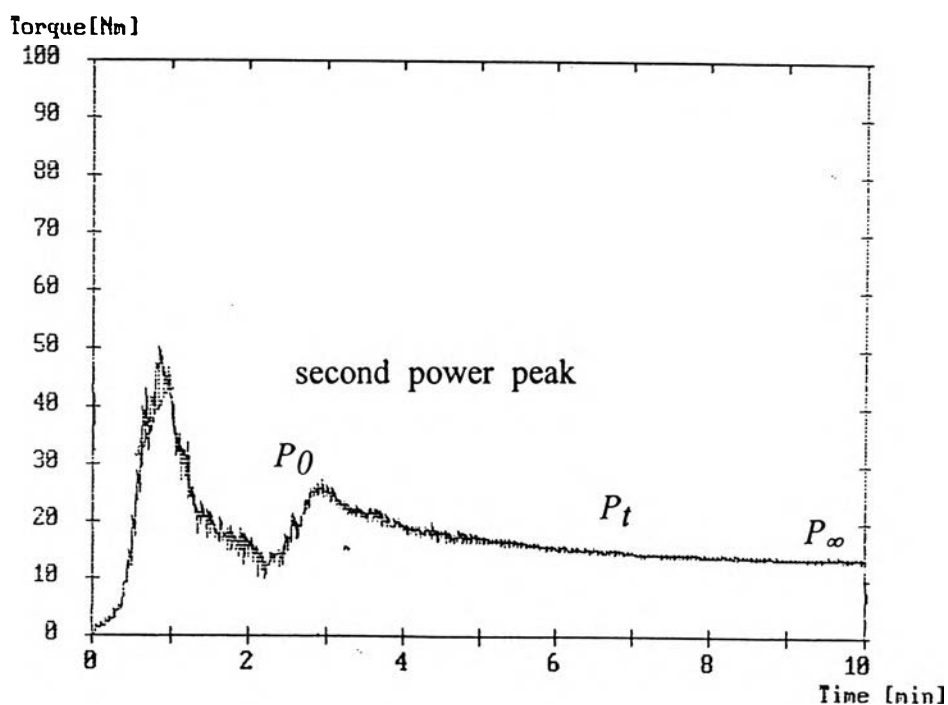


Figure 4.7 Mixing curve of high structure carbon black (100% H) in polypropylene for 30% carbon black loading.

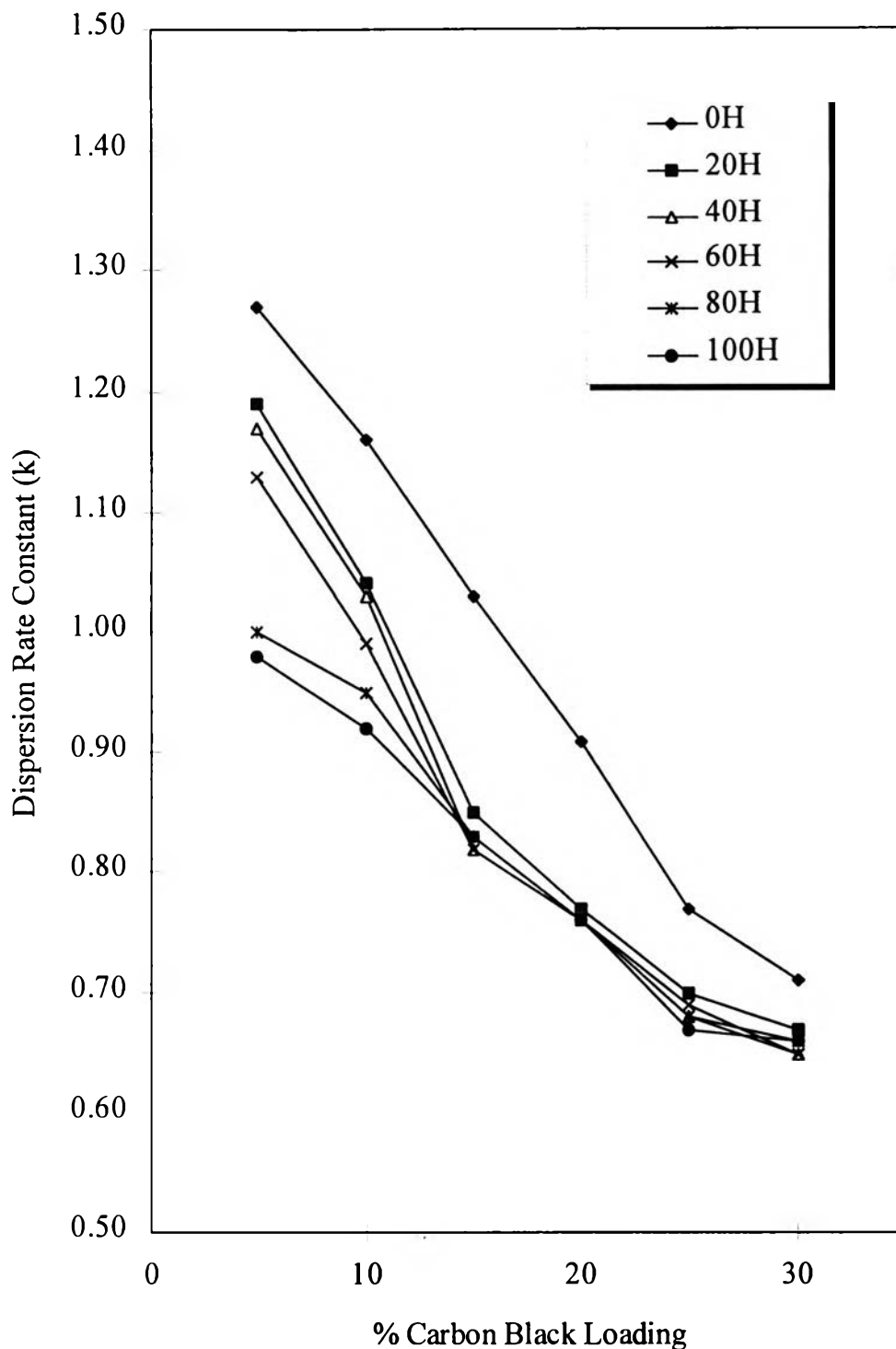


Figure 4.8 Dispersion rate constants of low structure carbon black (0%) high structure carbon black(100%H), and their blends (20%H, 40%H, 60%H, and 80%) as a function of % carbon black loading.

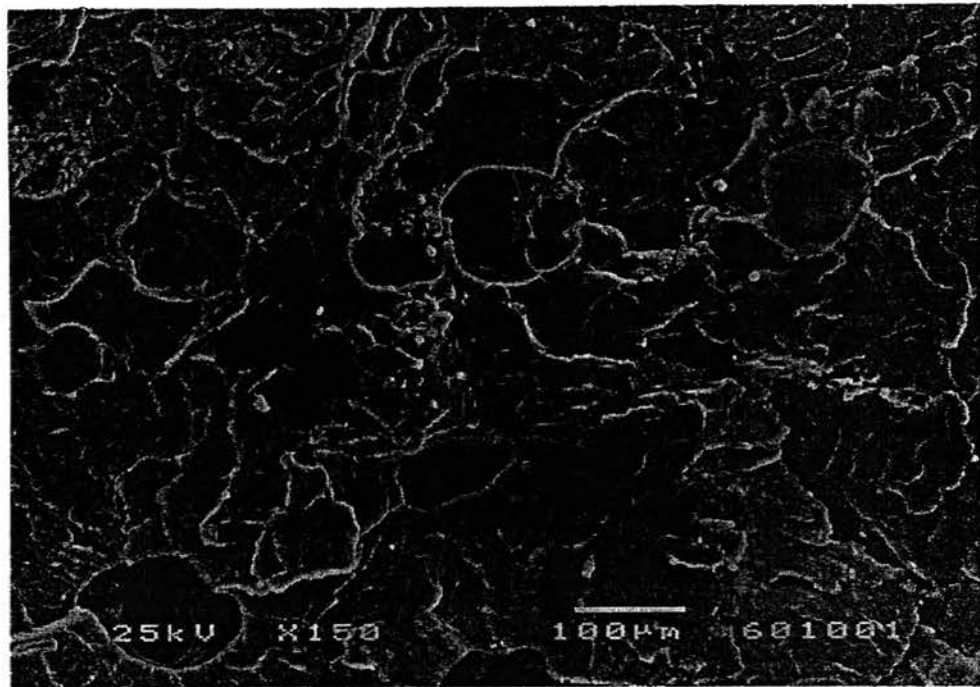
4.4 Size of Agglomerates and Size Distribution

Figure 4.9 shows SEM micrographs of 60% high structure carbon black compounds at 10% carbon black loading, at different mixing times. At 1 minute mixing time (Figure A) large agglomerates of high structure are found in the polypropylene matrix. At 3 minutes mixing time (Figure B) the agglomerate size is decreased drastically. At 5 minutes and 7 minutes mixing times (Figures C and D) the dispersion reached a steady state and the agglomerates of carbon black are dispersed in the polypropylene matrix completely. The size of carbon black agglomerates is small and difficult to detect. Semafore program was applied to analyze the size of agglomerates and their volume fraction as shown in the next section.

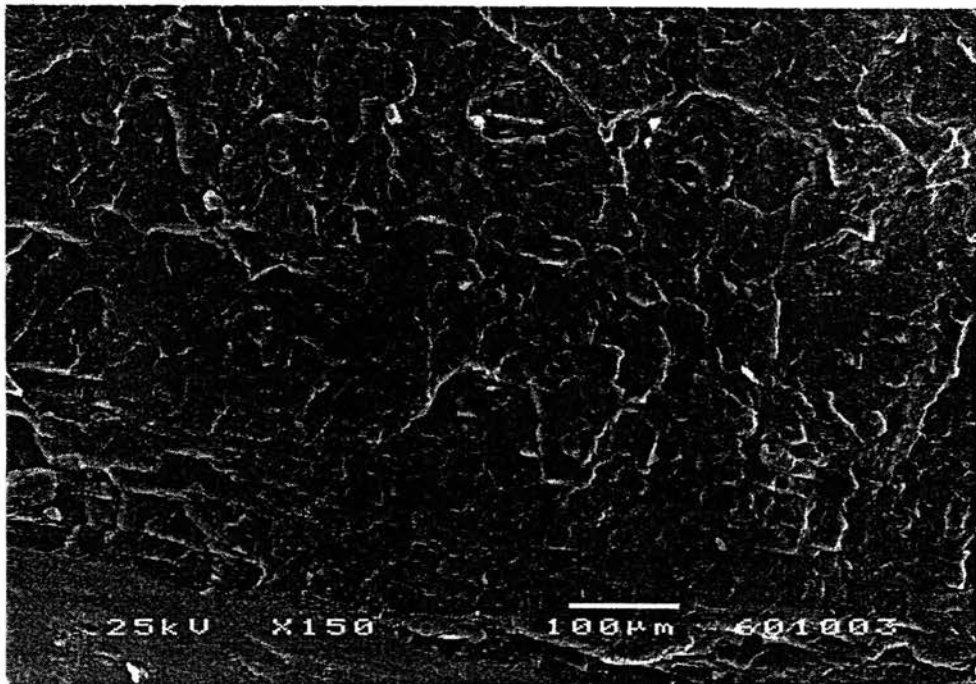
Figure 4.10, and Figure 4.11 are the SEM micrograph of 60% high structure carbon black obtained from 20% carbon black loading, and 30% carbon black loading respectively.

The SEM micrographs show that at 30% carbon black loading, a higher the agglomerates in PP can be observed more significantly than that of 29% and 10% % carbon black loading.

A



B



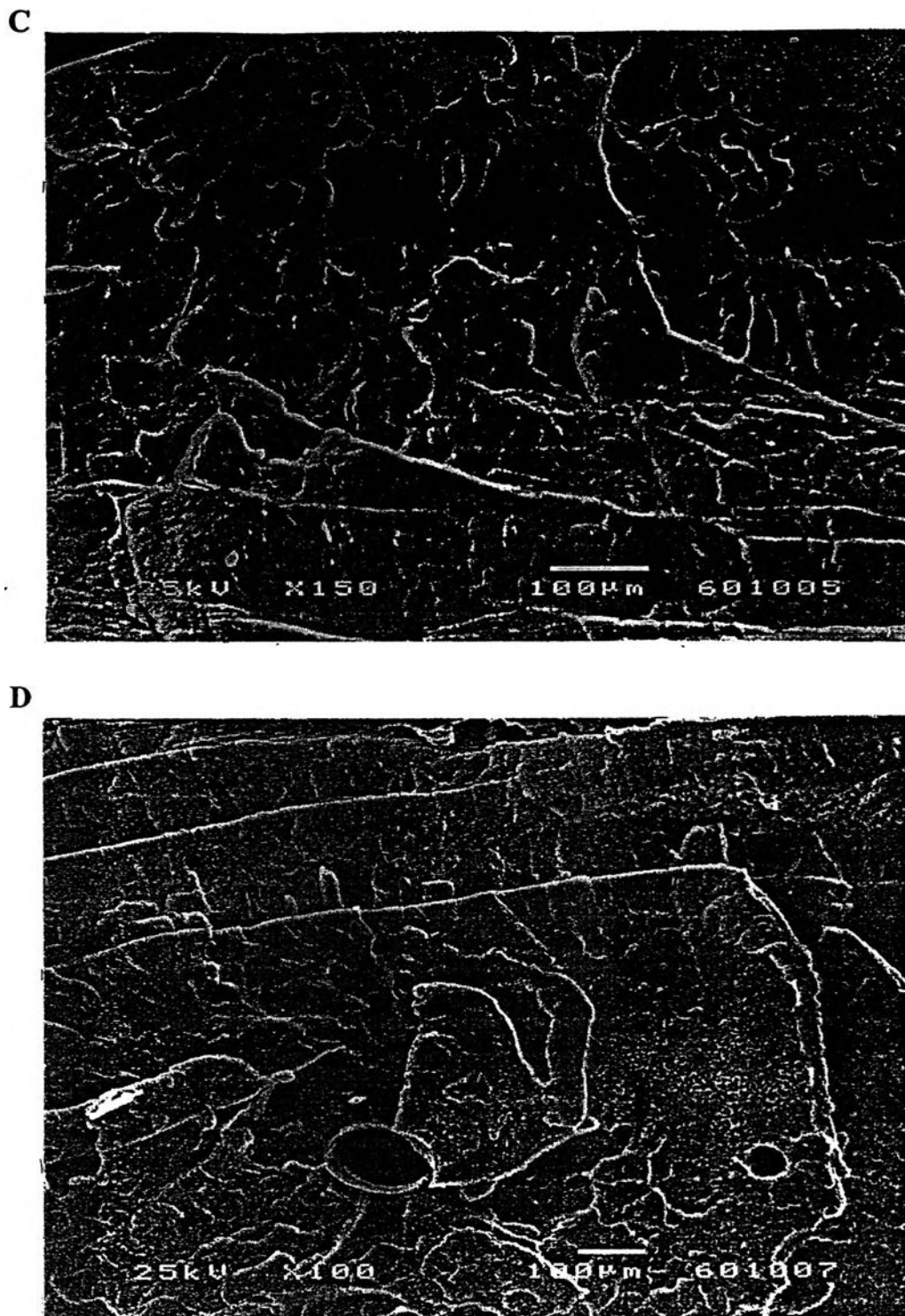
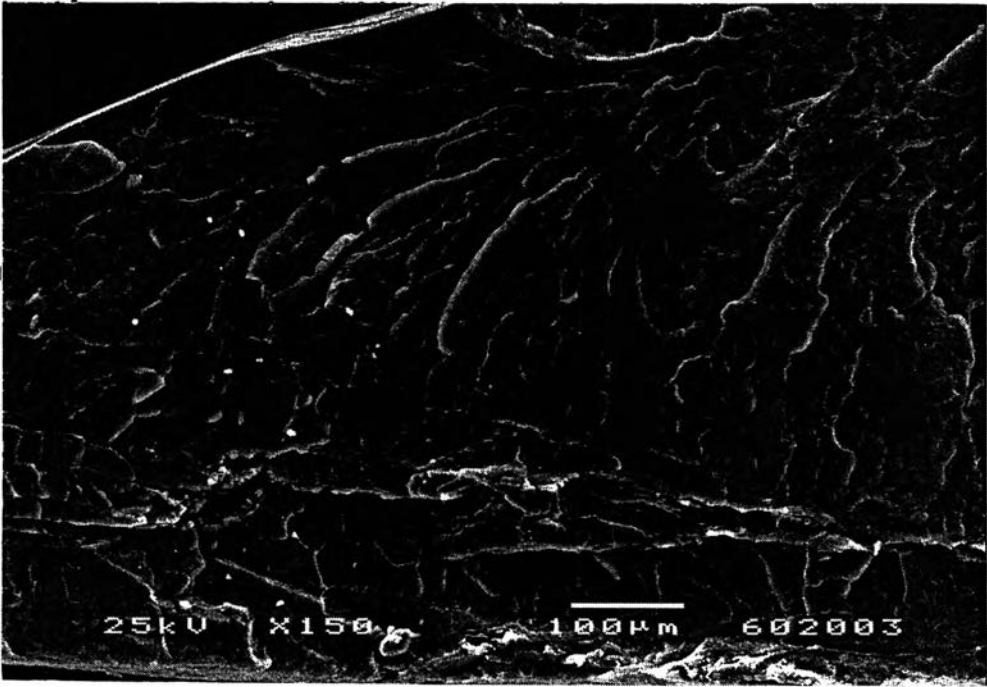
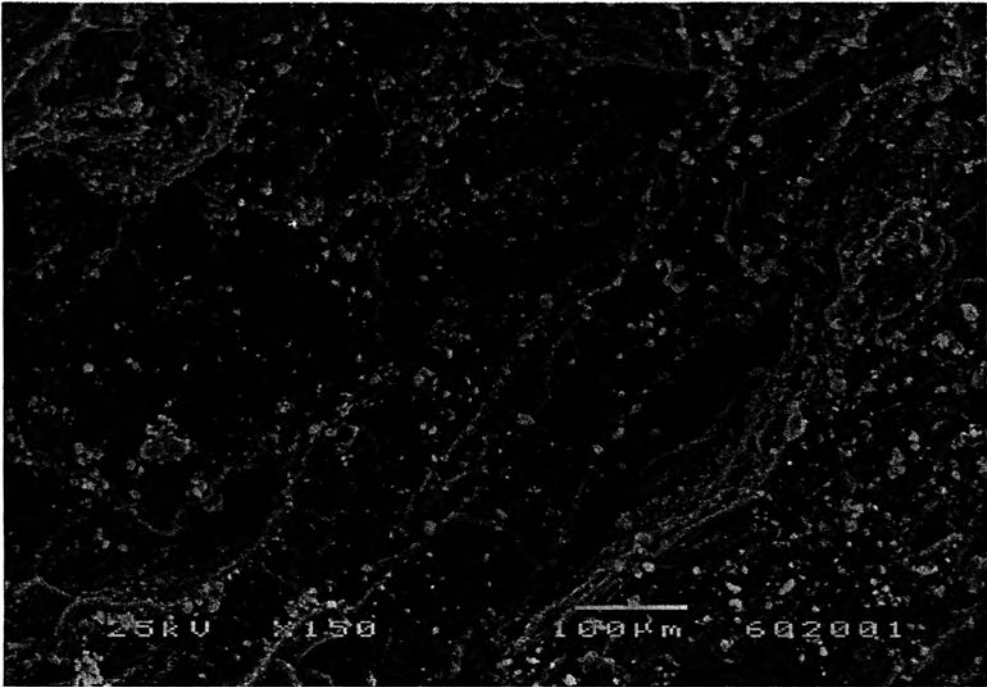
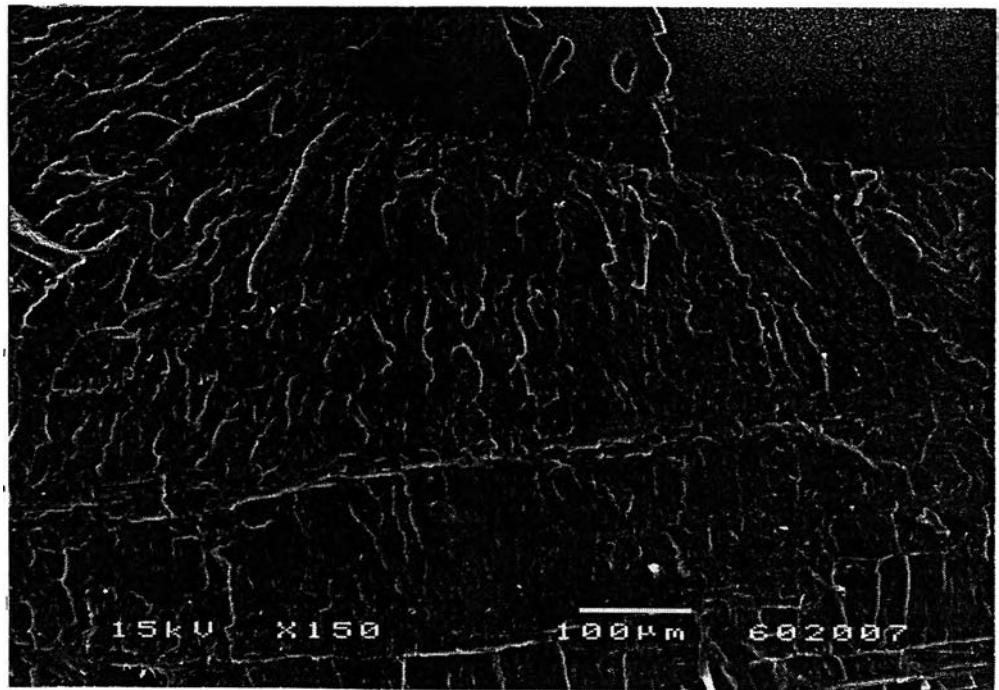
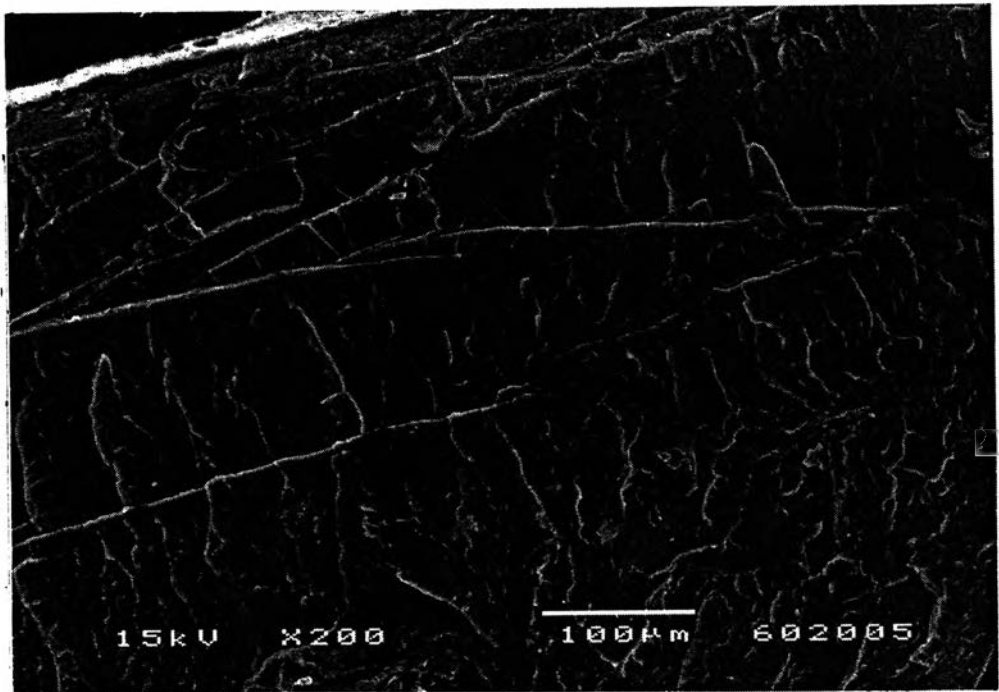
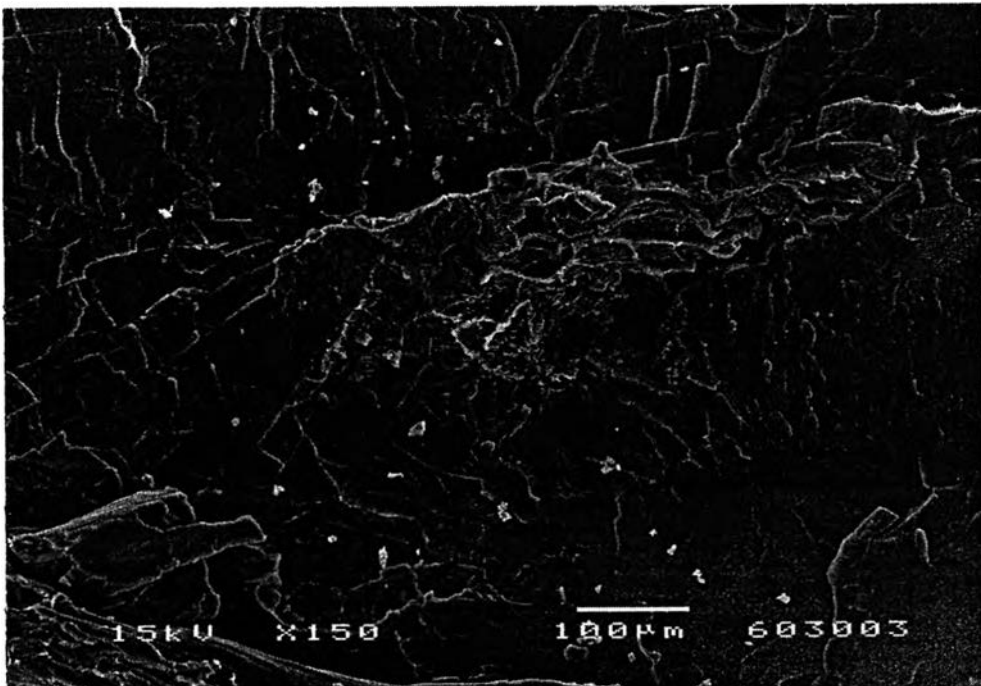
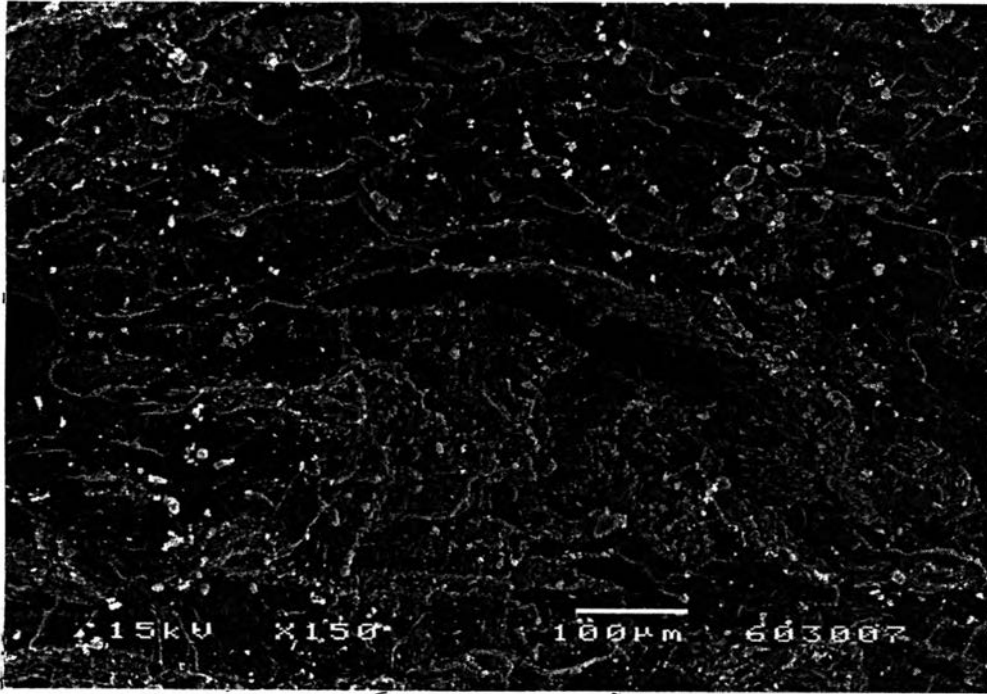
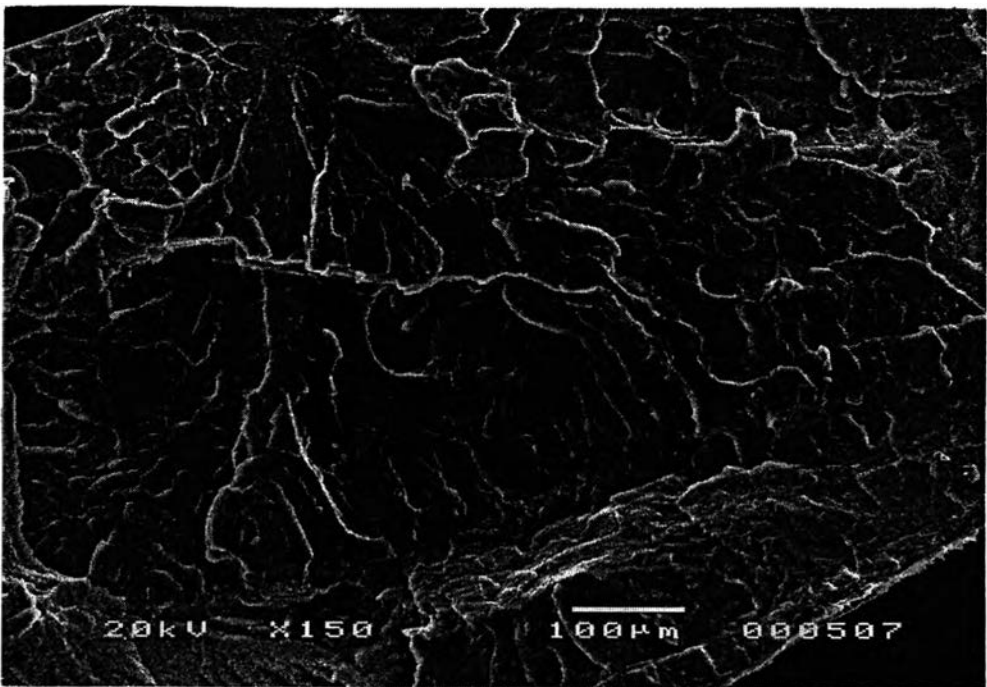
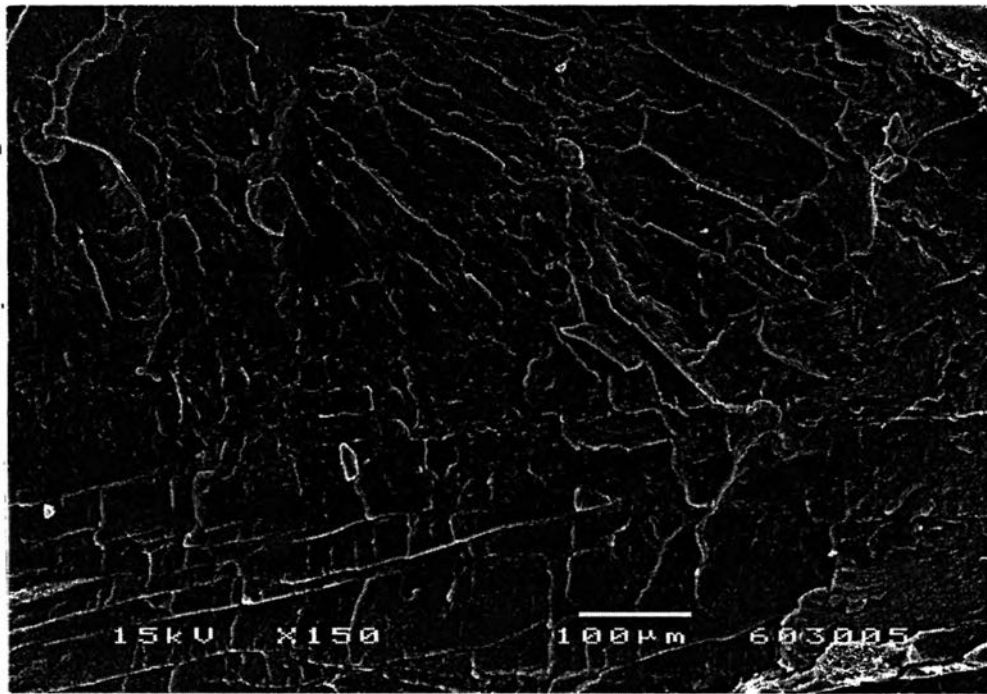


Figure 4.9 Scanning electron micrographs of 60% high structure carbon black (60%H) in polypropylene at 10% carbon black loading. A :at 1 minute mixing time, B :at 3 minutes mixing time, C :at 5 minutes mixing time, and D :at 7 minutes mixing time.









4.5 Agglomerate Size Analysis

Figures 4.12-4.17 show fragment volume fraction distributions at 10% carbon black loading, at different mixing times for high structure carbon black, low structure carbon black and the blending. When mixing reached the steady state, the agglomerate size tends to be small. The size of agglomerates of low structure carbon black is smaller than that of high structure at steady state conditions. This suggests that the rate of erosion in low structure carbon black is greater than that in the high structure carbon black. Therefore, it can be concluded that low structure carbon black can be more easily dispersed than high structure carbon black (at similar agglomerate density blends).

Figures 4.18-4.23 and Figures 4.24-4.29 show size distributions at various mixing times (1, 3, 5, and 7 minutes) at 20%, and 30% carbon black loading for high structure carbon black, low structure carbon black and the blending. When the mixing reaches a steady state, the agglomerate becomes smaller. The distributions at steady state when using the same shear rate (17 sec^{-1} , according to the experimental) showed the mean agglomerate size to decrease from the 80%H to 60%H, 40%H, and 20%H, respectively. This may be due to the differences in packing characteristics and cohesivity of carbon black agglomerates made of high and low structure aggregates.

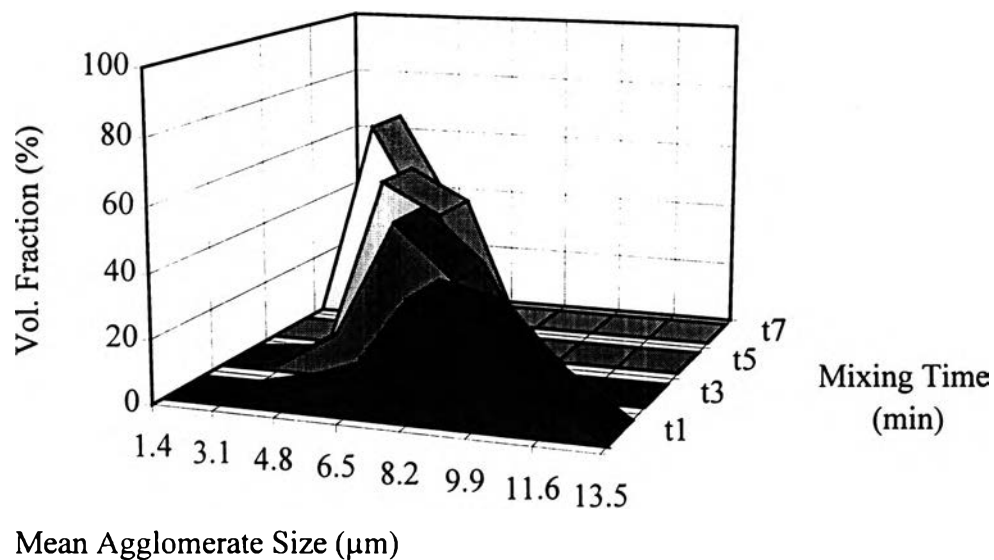


Figure 4.12 Volume fraction distribution of eroded fragments obtained from low structure carbon black (0%H) at 10% carbon black loading.

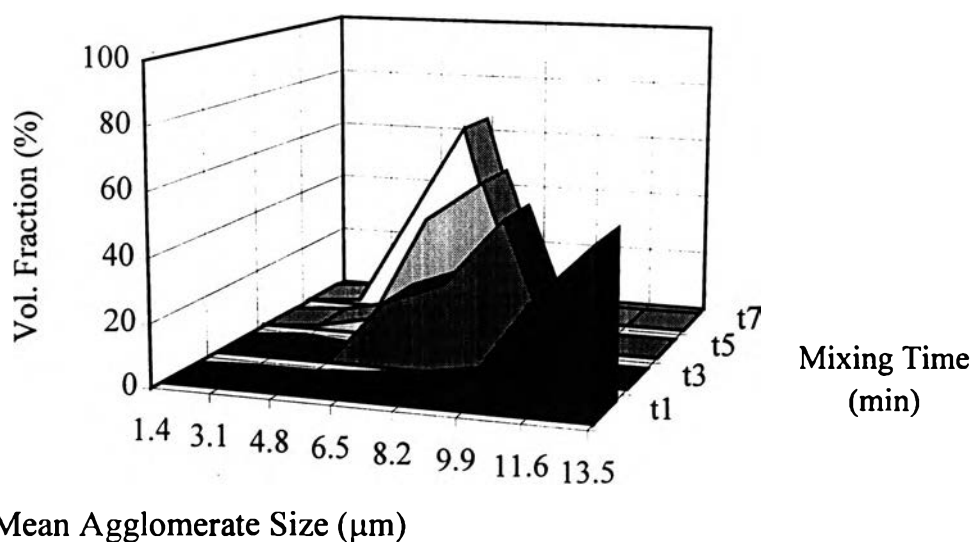


Figure 4.13 Volume fraction distribution of eroded fragments obtained from high structure carbon black (100%H) at 10% carbon black loading.

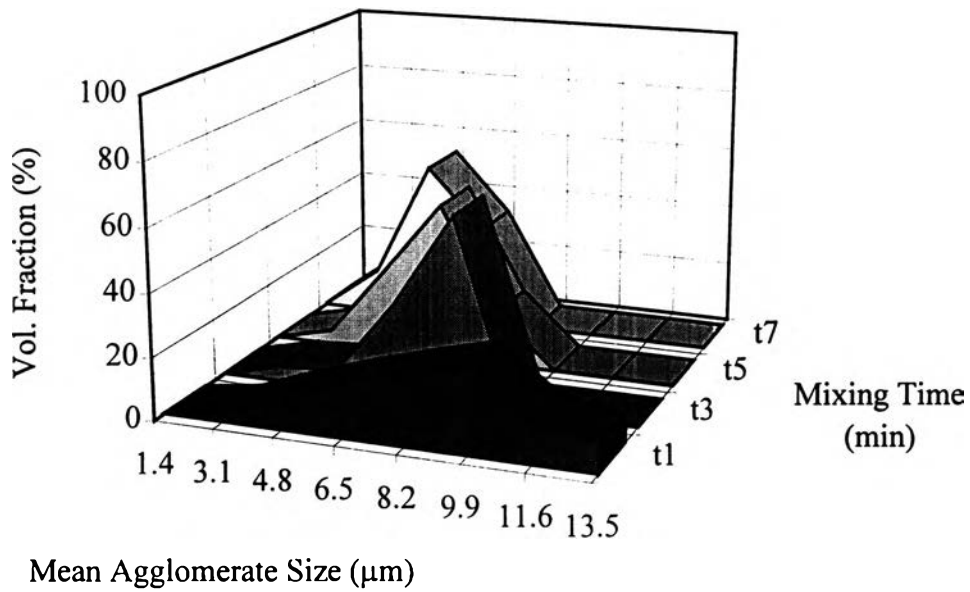


Figure 4.14 Volume fraction distribution of eroded fragments obtained from 20% high structure carbon black (20%H) at 10% carbon black loading.

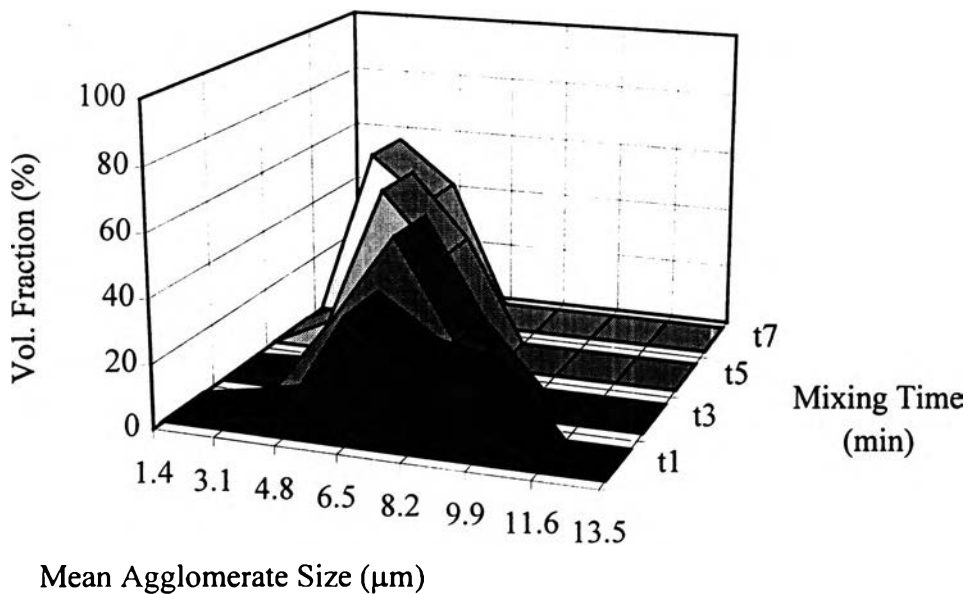


Figure 4.15 Volume fraction distribution of eroded fragments obtained from 40% high structure carbon black (40%H) at 10% carbon black loading.

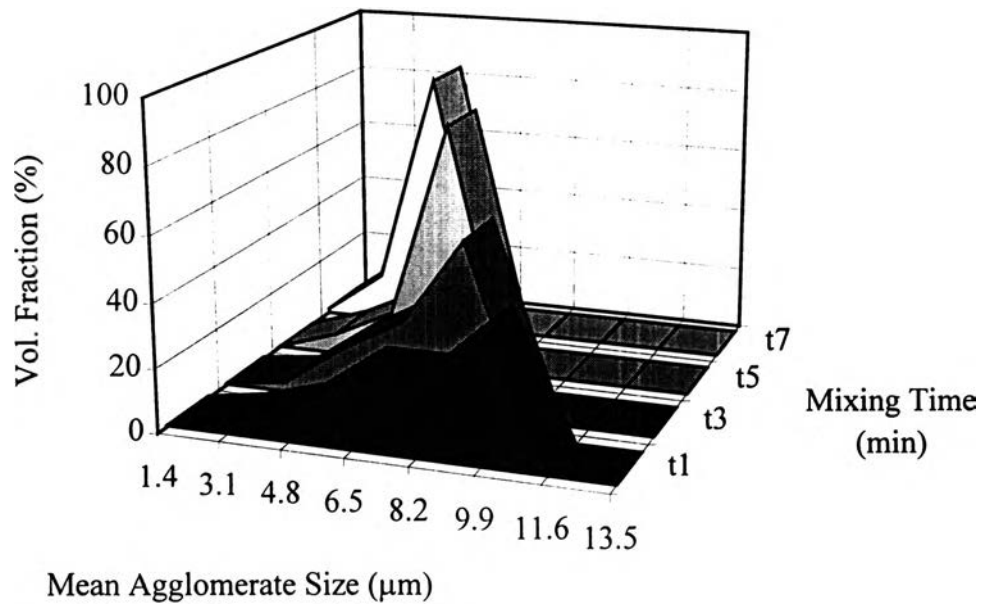


Figure 4.16 Volume fraction distribution of eroded fragments obtained from 60% high structure carbon black (60%H) at 10% carbon black loading.

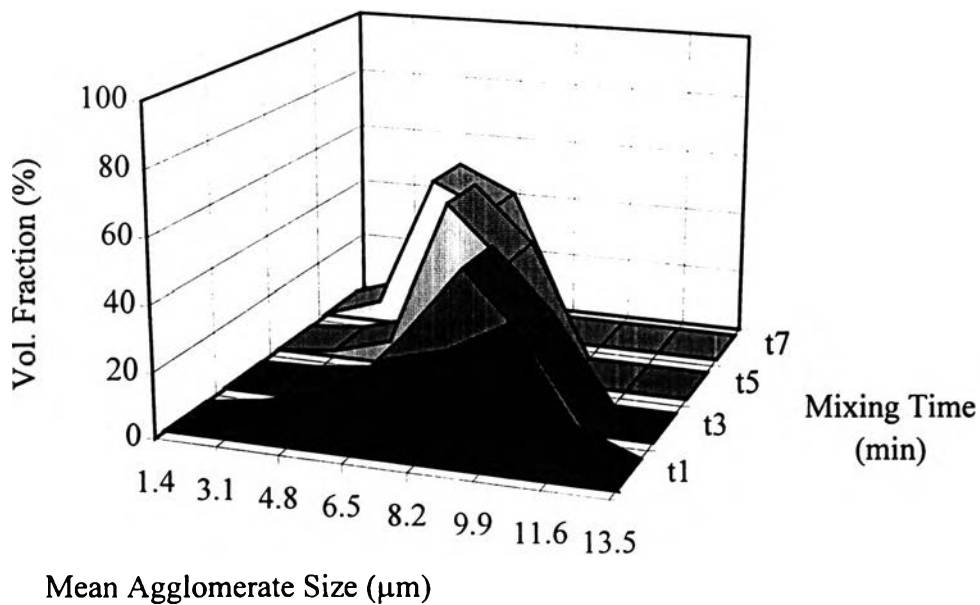


Figure 4.17 Volume fraction distribution of eroded fragments obtained from 80% high structure carbon black (80%H) at 10% carbon black loading.

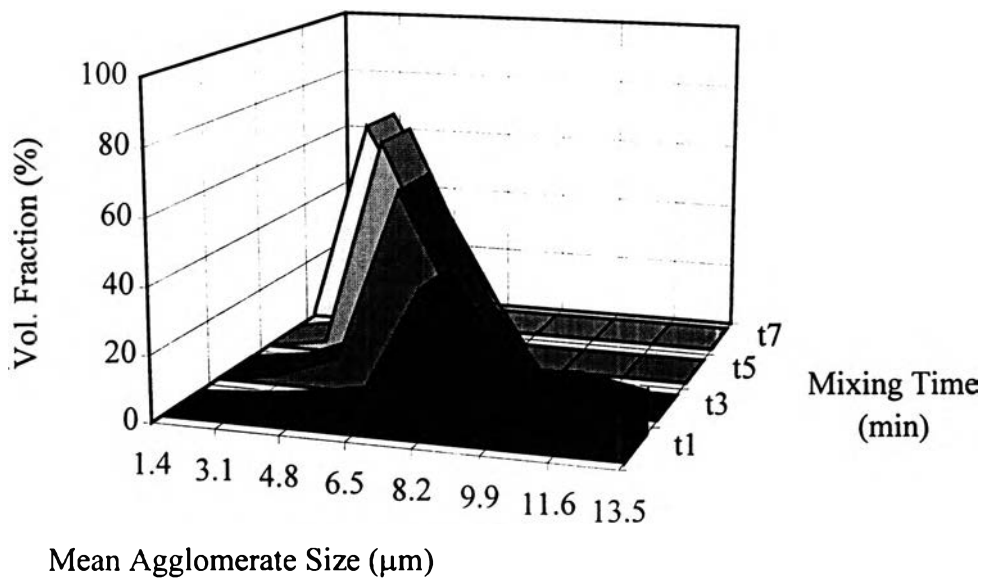


Figure 4.18 Volume fraction distribution of eroded fragments obtained from low structure carbon black (0%H) at 20% carbon black loading.

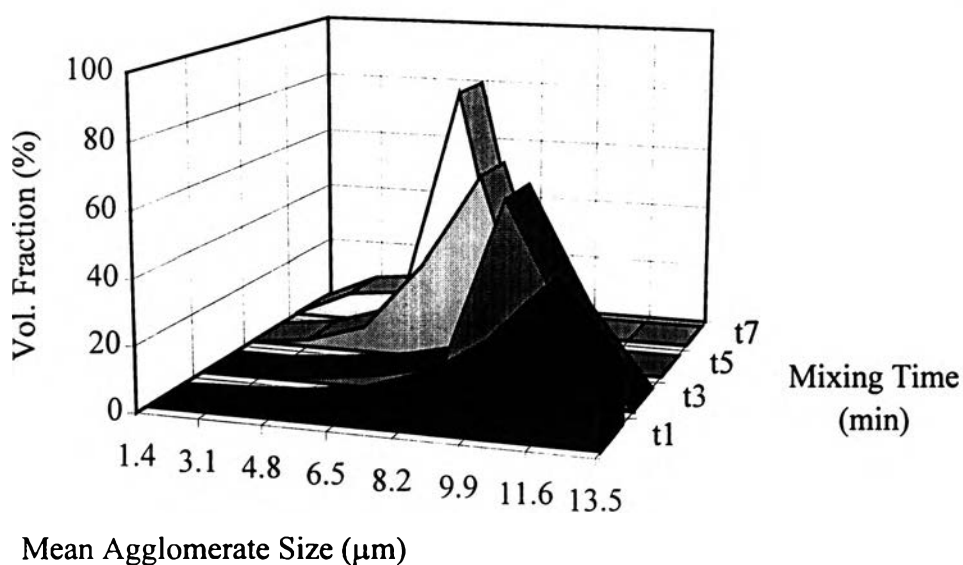


Figure 4.19 Volume fraction distribution of eroded fragments obtained from high structure carbon black (100%H) at 20% carbon black loading.

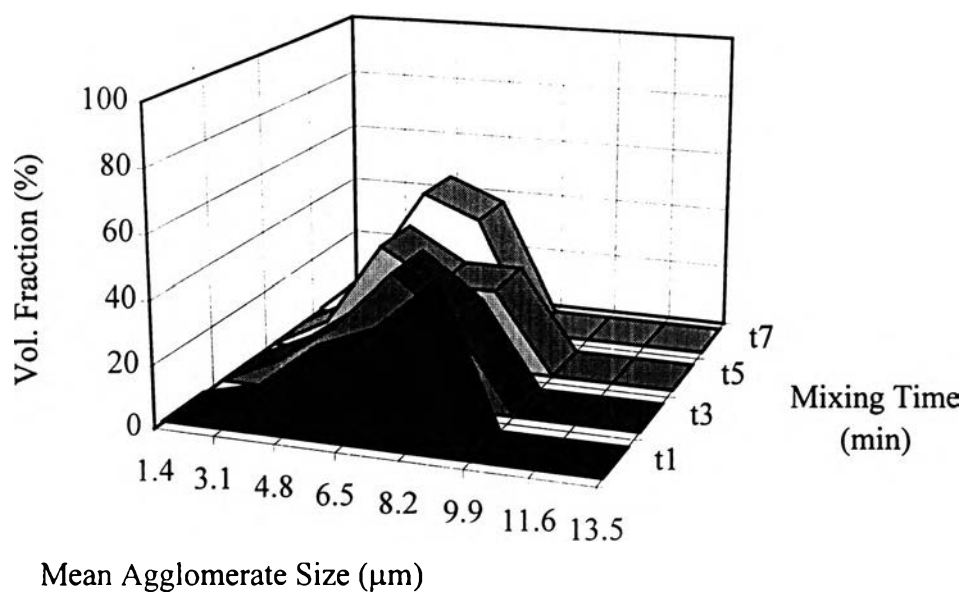


Figure 4.20 Volume fraction distribution of eroded fragments obtained from 20% high structure carbon black (20%H) at 20% carbon black loading.

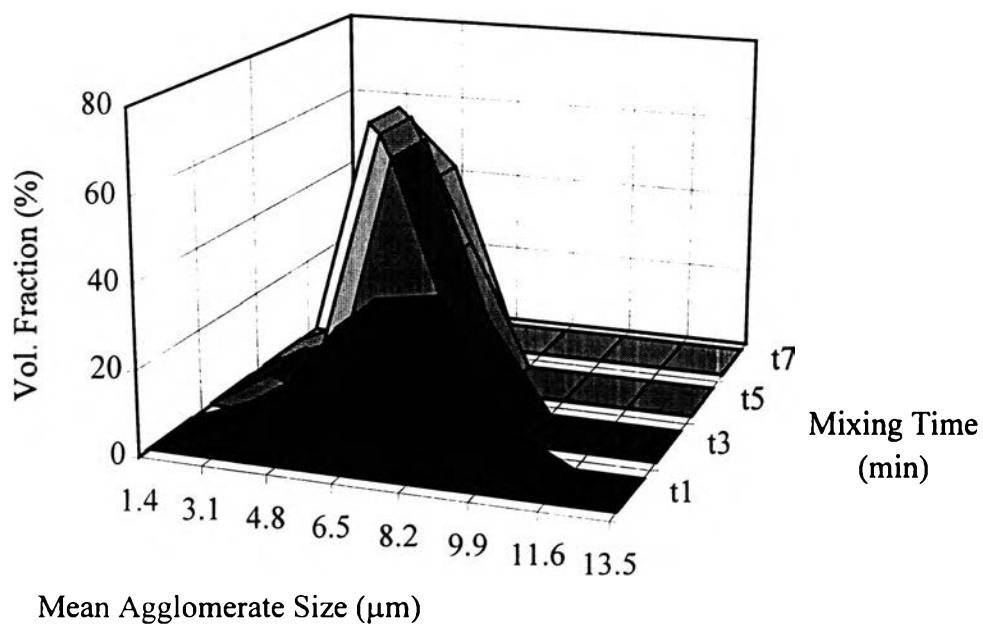


Figure 4.21 Volume fraction distribution of eroded fragments obtained from 40% high structure carbon black (40%H) at 20% carbon black loading.

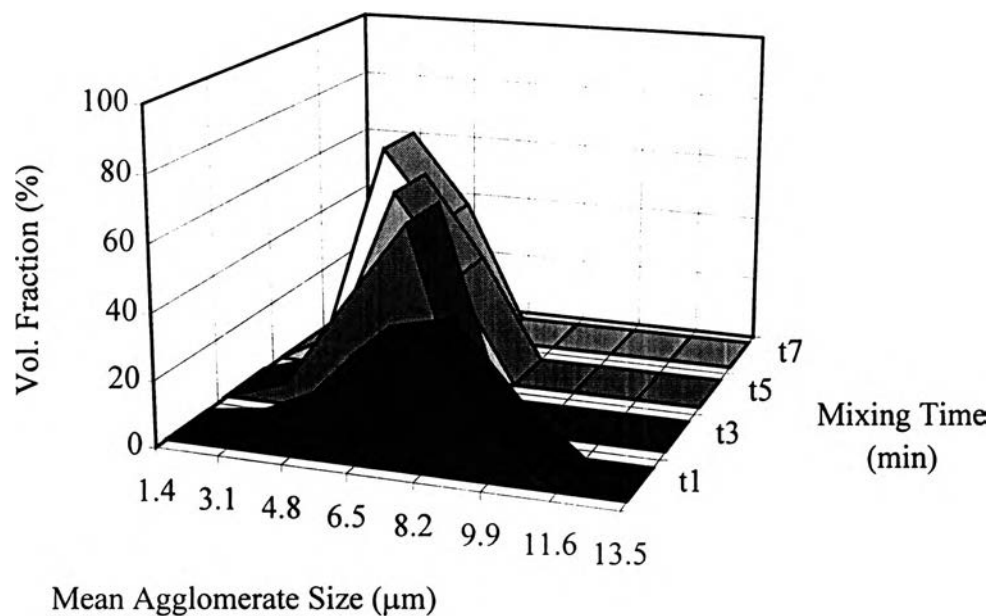


Figure 4.22 Volume fraction distribution of eroded fragments obtained from 60% high structure carbon black (60%H) at 20% carbon black loading.

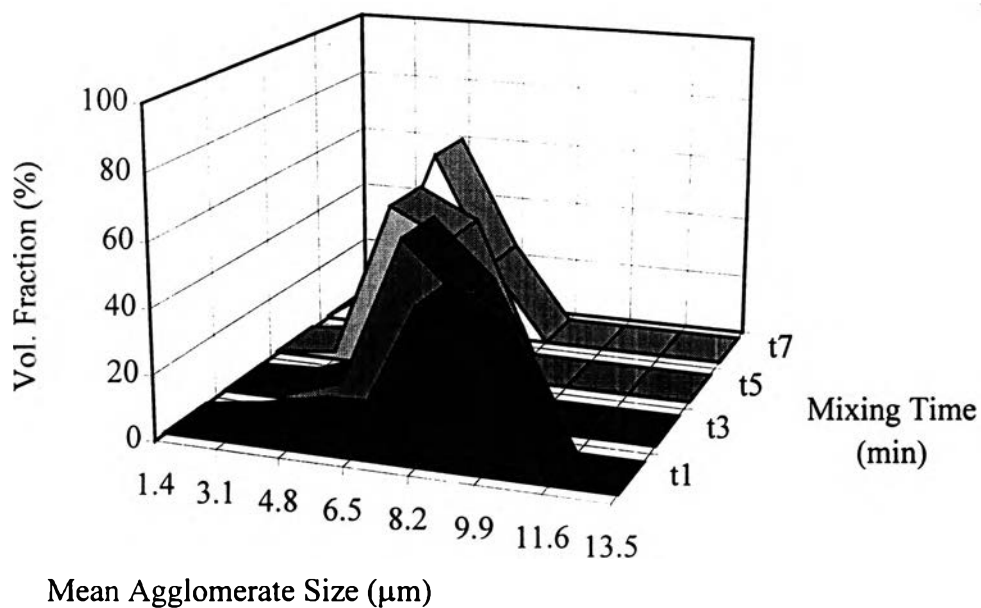


Figure 4.23 Volume fraction distribution of eroded fragments obtained from 80% high structure carbon black (80%H) at 20% carbon black loading.

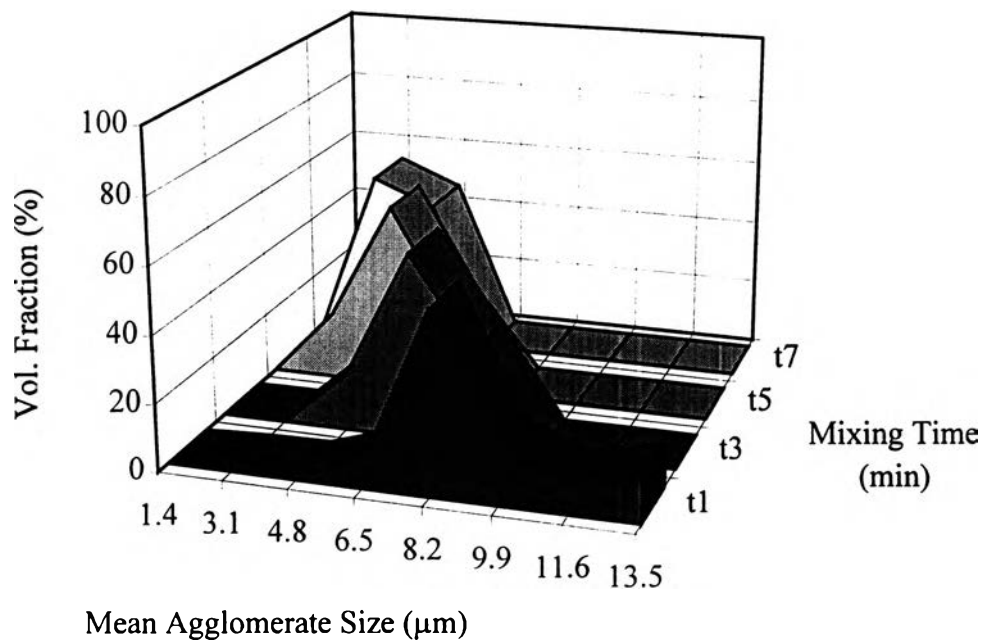


Figure 4.24 Volume fraction distribution of eroded fragments obtained from low structure carbon black (0%H) at 30% carbon black loading.

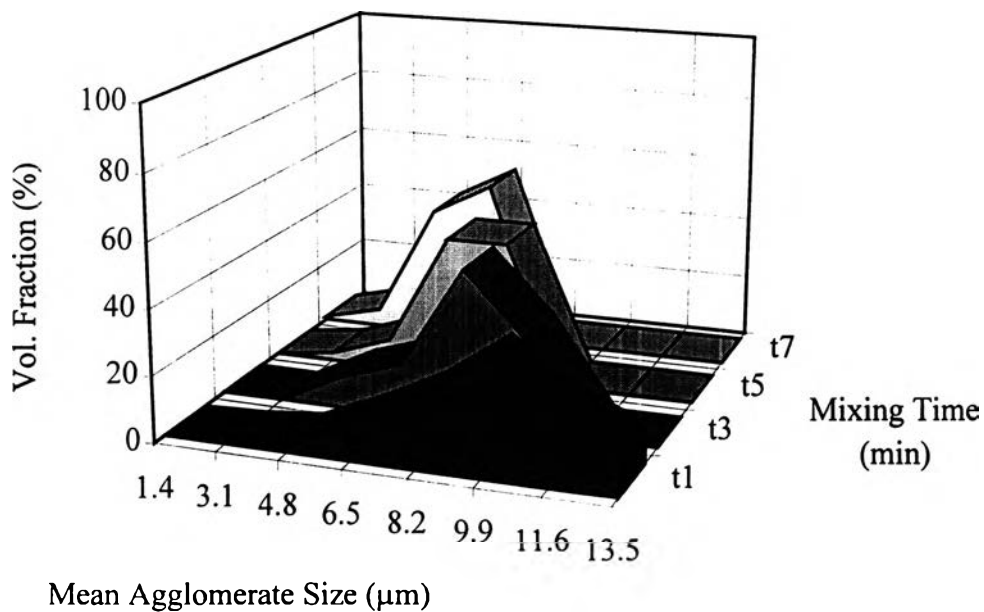


Figure 4.25 Volume fraction distribution of eroded fragments obtained from high structure carbon black (100%H) at 30% carbon black loading.

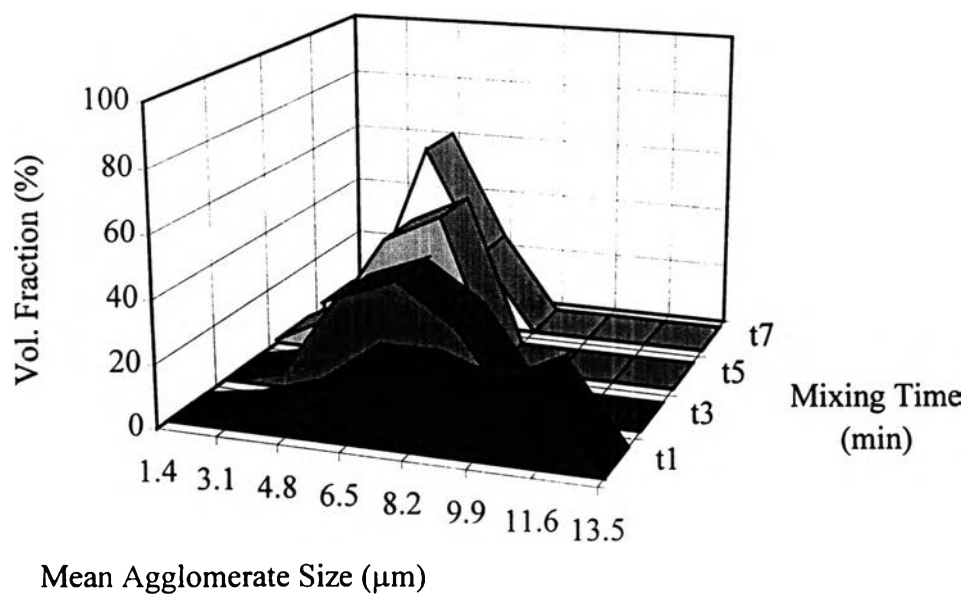


Figure 4.26 Volume fraction distribution of eroded fragments obtained from 20% high structure carbon black (20%H) at 30% carbon black loading.

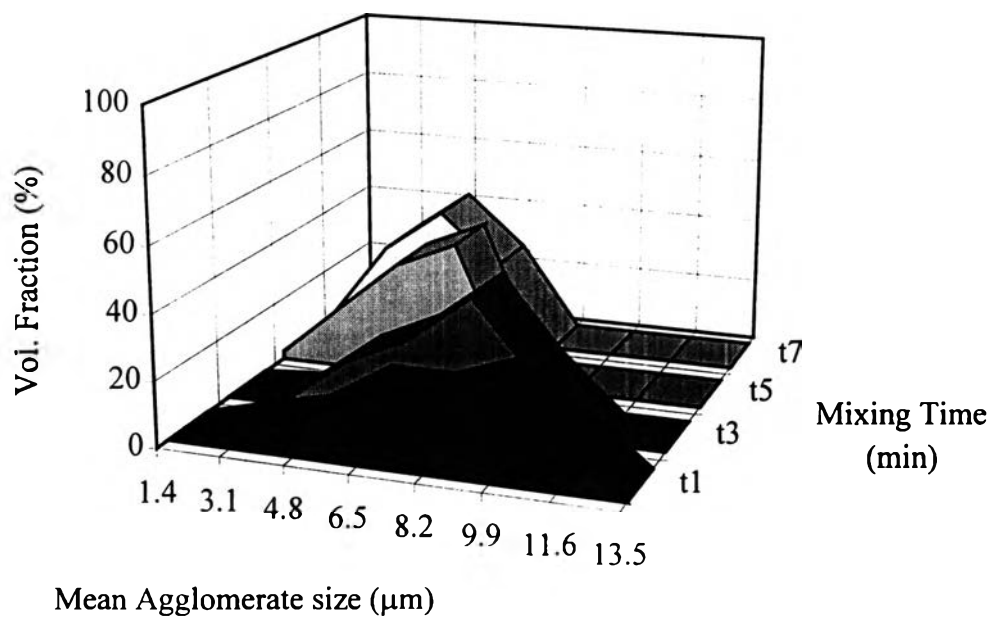


Figure 4.27 Volume fraction distribution of eroded fragments obtained from 40% high structure carbon black (40%H) at 30% carbon black loading.

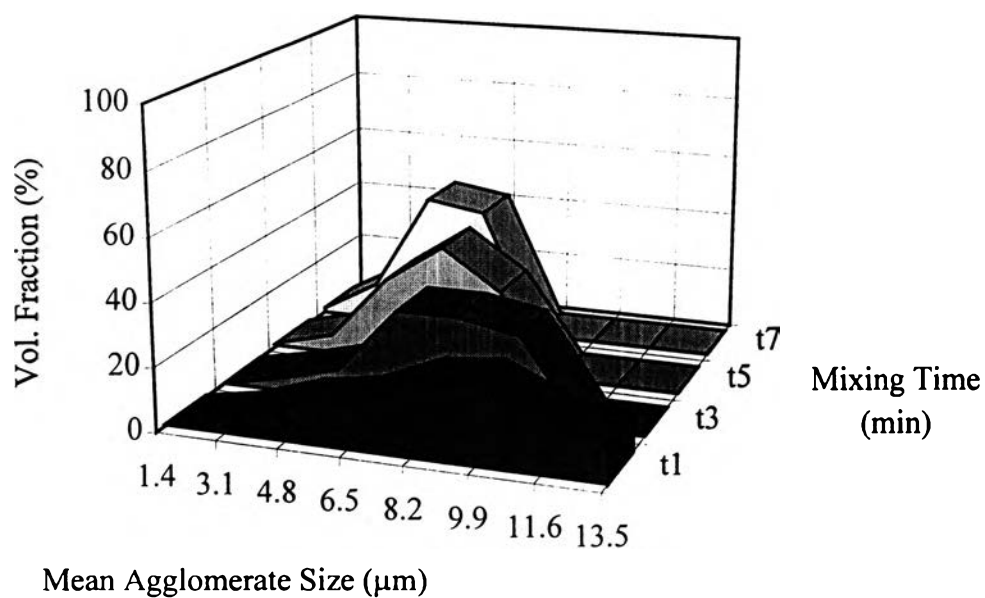


Figure 4.28 Volume fraction distribution of eroded fragments obtained from 60% high structure carbon black (60%H) at 30% carbon black loading.

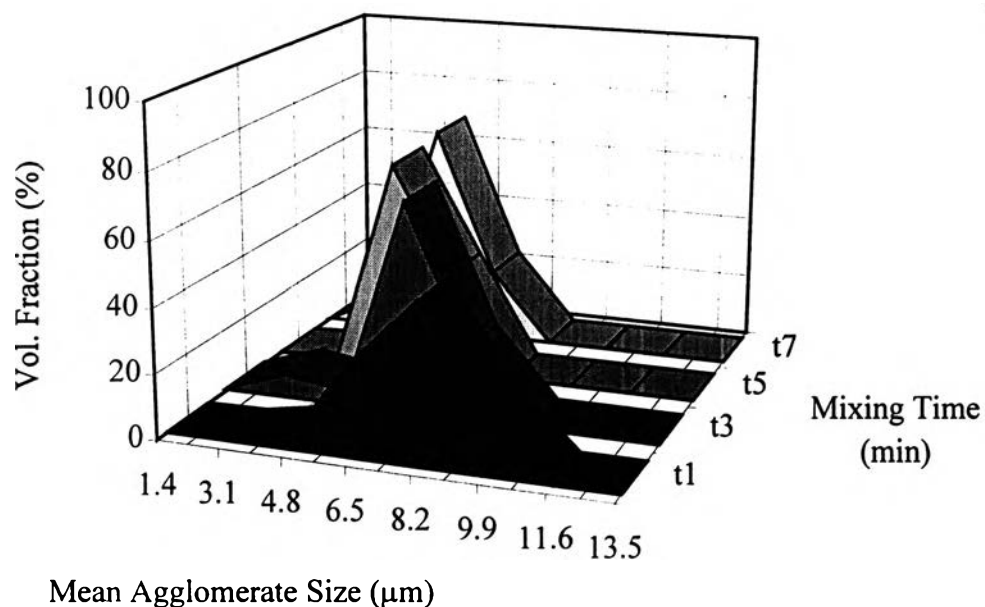


Figure 4.29 Volume fraction distribution of eroded fragments obtained from 80% high structure carbon black (80%H) at 30% carbon black loading.

4.6 Dynamic Mechanical Analysis

Dynamic mechanical tests measure the response or deformation of a material to periodic or varying forces. Generally, both the applied force and the resulting deformation vary sinusoidally with time. With this study, the effect of carbon black networks which are dispersed in PP matrices can be evaluated for the strength by study the strain amplitude and shear modulus relationship. Generally, at a certain temperature, as the strain amplitude increase polymer matrices will be affected directly and the network of carbon black will break down. The change of dynamic shear modulus is related to the strength of carbon black network. However, the strength of carbon network in PP is concerned with the network of carbon black aggregate itself together with the carbon black dispersion behavior. Thus, it is to the interest to study the influence of carbon aggregate structure on agglomerate dispersion behavior by means of dynamic mechanical analysis.

Figure 4.30 shows the relationship between shear modulus and strain amplitude. According to Payne effect [Kraus (1984)], the shear modulus decreases with increasing the strain amplitude. It can be concluded that the strain amplitude causes a breaking down of the carbon black aggregate network and the strength of polypropylene matrices is decreased gradually. The differences of shear moduli at different shear times reveals that the performance of the carbon black network supported on the polypropylene matrices.

It should be noted that in the case of high structure carbon black, (100%H in Figure 4.30), dynamic shear modulus and the decrease of shear modulus (G') are in the order of 1, 3, 5 and 7 minutes respectively. The decrease of G' implies that the strength of polypropylene structure is supported by the carbon black aggregate. It is found that the 1 minute shear time

condition gives the highest shear modulus compared to other conditions. This maybe due to the poor dispersion performance of high structure of carbon black in polypropylene. In the case of short shear times the agglomerates of carbon black aggregates are compacted locally on the matrices of polypropylene which provides the strength of polypropylene. When the shear time increases, the agglomerates of carbon black aggregates are broken down, which makes the polypropylene matrices becomes weaker and the response to the strain amplitude is more significant. Thus, 1 minute of shear time for high structure carbon black shows a very high value of G' (compared to other cases) owing to the carbon black aggregate supporting the matrices locally.

However, in the case of low structure carbon black (0%H in Figure 4.30), the results are completely different. It is found that the dynamic shear modulus and G' are decreased from 7, 5, 3 and 1 minute. With reference to dispersion rate constant study, it is found that the dispersion of low structure carbon black in polypropylene is better than that of high structure carbon black. Hence, it can be expected that the polypropylene with low structure carbon black will be strengthened by the uniform dispersion of the carbon black on the matrices. In the case of longer mixing times or shear times (e.g. 7 minutes), the dynamic shear modulus value and the decrease of G' is less than in other cases. This can be explained that in the case of the longer mixing time the low structure carbon black is dispersed thoroughly, thus, the matrices of polypropylene are stronger than the cases of shorter mixing times.

Figure 4.31 shows the relationship of shear modulus and strain amplitude in the cases of blending of low structure carbon black and high structure carbon black. In all cases, the shear moduli decreases as the strain amplitude is increased. This suggests that the carbon black network is broken down as seen in the case of high structure carbon black or low structure carbon black in Figure 4.30. It should be noted that 20% high structure carbon black

shows the highest initial G' and that the decrease of G' is less than in other cases. It can be concluded that the 20% high structure carbon black blending system provides the optimum dispersion behavior of carbon black on polypropylene network. For the dispersion of carbon black, it can be expected that there will be an optimum ratio of high:low structure carbon blacks that will produce a well dispersed PP/carbon black system.

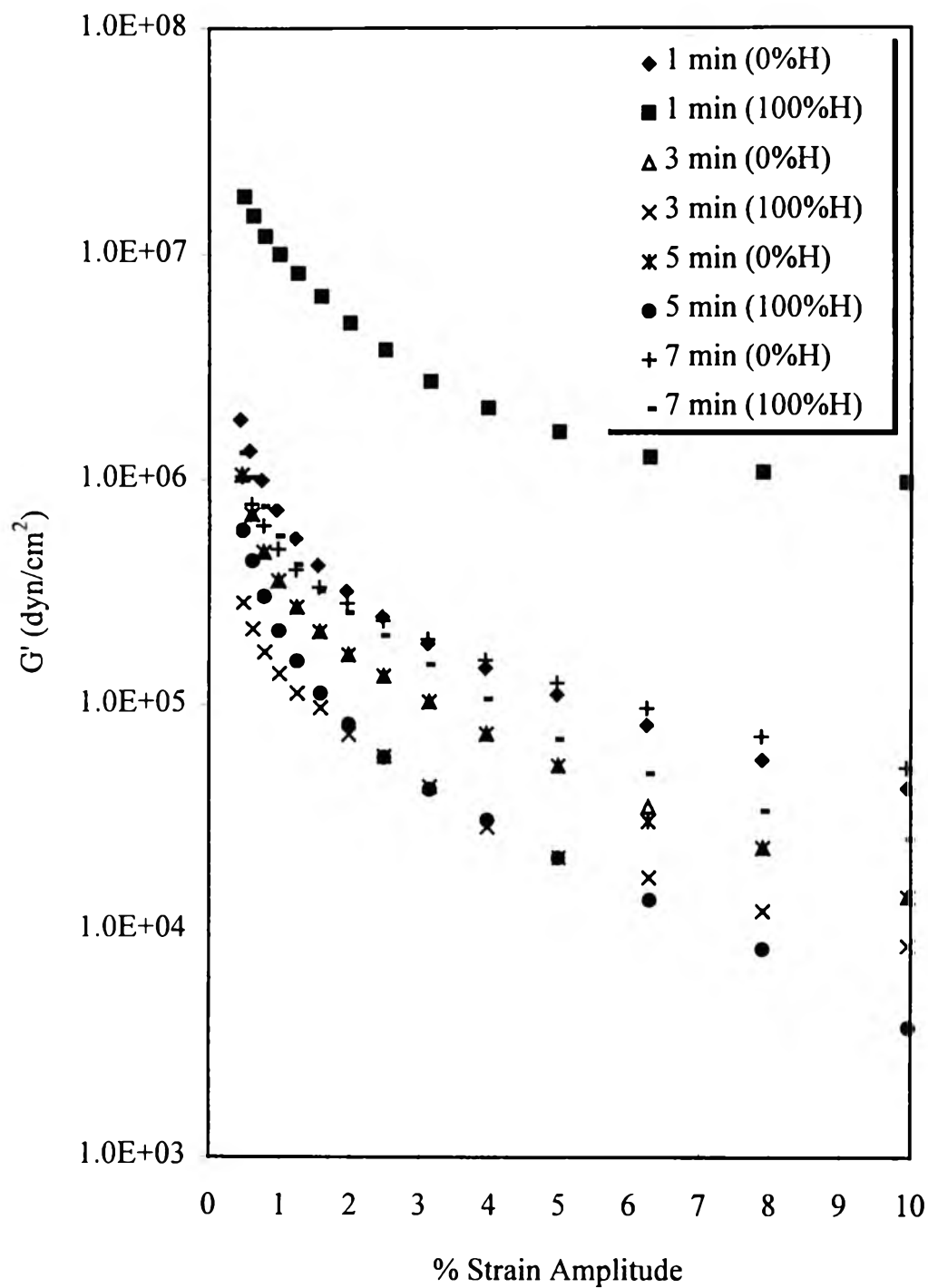


Figure 4.30 Dynamic shear modulus versus % strain amplitude at 30% carbon black loading for low structure carbon black (0%H) and high structure carbon black (100%H).

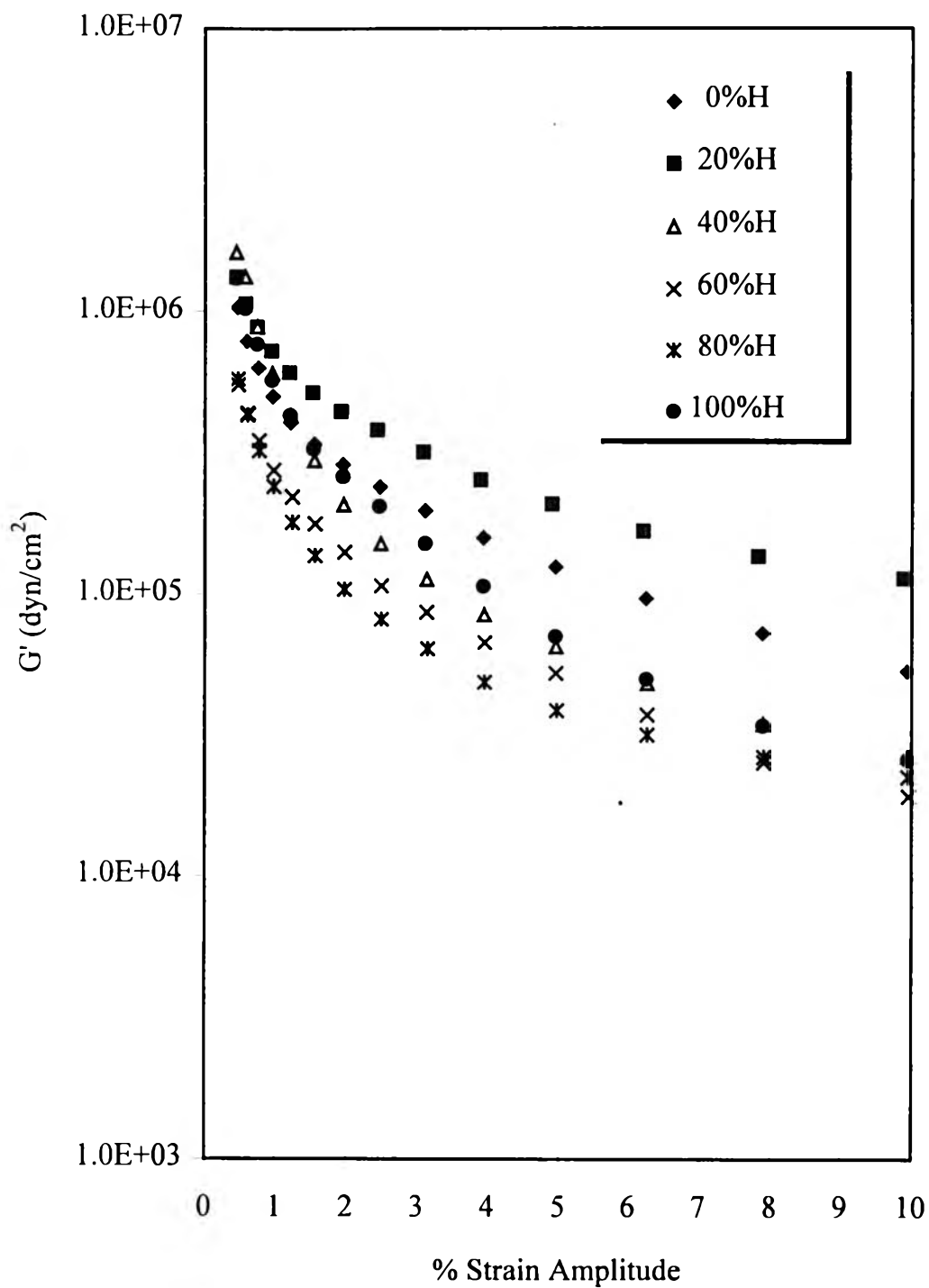


Figure 4.31 Dynamic shear modulus versus % strain amplitude at 30% carbon black loading at 7 minutes of shear time.