CHAPTER III
RESULTS AND DISCUSSIONS

3.1 Pour density and tap density

The results of pour density measurement and the corresponding void fractions are shown in Table 2 The comparison of void fraction in the fuffly blends of carbon black high structure and low structure indicates their structures in a qualitative manner. Small void fraction indicates a compact structure while a larger void fraction yields a more open structure; thus the structures of carbon black blends are ranging from the most compact structure to the most open structure as following:

100%L CB, 20%H CB, 40%H CB, 100%H CB, 60%H CB, 80%H CB

Since void volume depends on structure we may use the specific volume to indicate the structure(Donnet et al, 1976). Small specific volume indicates the compact structure while large specific volume represents the open structure. The results of tap density measurements and the specific volumes are shown in Table 3 giving the degree of structure from the most compact structure to the most open structure as following:

100%L CB, 20%H CB, 40%H CB, 60%H CB, 100%H CB, 80%H CB

Packing characteristics of carbon black blends in 100%L CB and 100%H CB are affected only by low aggregate structure and high aggregate structure respectively while other blends are affected by both aggregate structures. The 80%H CB has the most open agglomerate structure in both loose packing and dense packing. The aggregates of high structure combined with low structure in 80%H CB produce the most irregular structure that is estimated by the least

packing density of the blends. The 100%L CB blend gives the most regular structure with the most dense packing. The result shows that the amount of high aggregate structure which is added to the low aggregate structure alters its dense structure to be a more open structure and even shows greater structure in 80%H CB than the structure of pure high aggregate structure, 100%H CB,.

The results are agreeable when agglomerate structures at pour density and tap density are compared.

Table 2 Pour density and void fraction of carbon black blends

carbon black blends	ρ_{pour} (g/cm^3)	± SD	void fraction	± SD
100%H CB	0.159	0.0016	0.914	0.0009
80%H CB	0.146	0.0006	0.922	0.0003
60%H CB	0.157	0.0017	0.916	0.0009
40%H CB	0.179	0.0019	0.904	0.0010
20%H CB	0.200	0.0010	0.893	0.0005
0%H CB	0.210	0.0013	0.887	0.0007

Table 3 Tap density and specific volume of carbon black blends

carbon black blends	ρ_{tap} (g/cm^3)	± SD	specific volume(cm^3)	± SD
100%H CB	0.219	0.0022	4.57	0.046
80%H CB	0.203	0.0008	4.92	0.021
60%H CB	0.224	0.0035	4.46	0.071
40%H CB	0.257	0.0014	3.90	0.021
20%H CB	0.282	0.0016	3.54	0.021
0%H CB	0.291	0.0026	3.44	0.030

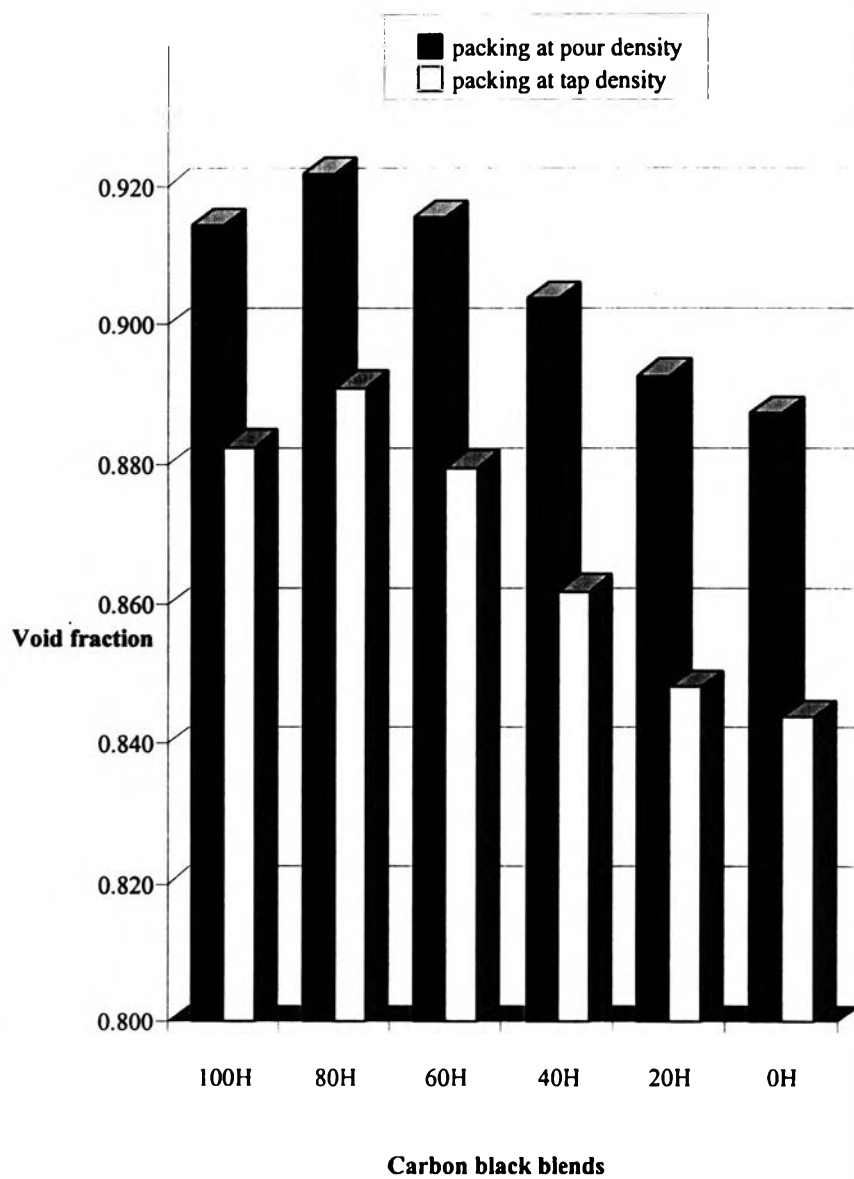Fig. 5 The plot of void fraction against carbon black structures at the packing densities of pour density and tap density.

3.2 Agglomerate densities

Each carbon black blend is used to make 5 agglomerate densities(aggl 1-5). The results of agglomerate densities of all blends are illustrated in Table 4.

Table 4 Agglomerate densities of all blends

Carbon black	Agglomerate densities(g/cm^3)$\pm$SD				
blends	aggl-1	aggl-2	aggl-3	aggl-4	aggl-5
100%H CB	0.283 ± 0.0111	0.300 ± 0.0141	0.356 ± 0.0304	0.417 ± 0.0271	0.463 ± 0.0227
80%H CB	0.280 ± 0.0078	0.316 ± 0.0260	0.359 ± 0.0237	0.414 ± 0.0253	0.491 ± 0.0395
60%H CB	0.281 ± 0.0085	0.325 ± 0.0104	0.357 ± 0.0119	0.417 ± 0.0426	0.468 ± 0.0273
40%H CB	0.290 ± 0.0085	0.315 ± 0.0101	0.352 ± 0.0298	0.418 ± 0.0173	0.465 ± 0.0296
20%H CB	0.279 ± 0.0117	0.312 ± 0.0176	0.357 ± 0.0132	0.413 ± 0.0065	-
100%L CB	0.291 ± 0.0128	0.323 ± 0.0172	0.351 ± 0.0242	0.412 ± 0.0335	0.476 ± 0.0224

3.3 Polymeric fluid infiltration into agglomerates

The kinetic infiltration model of I. Manas-Zloczower is used to study the sedimentation of agglomerates. Fig 6.,7.,8.,9,10.,11. show the plotting of infiltration function "$2(R/a)^3-3(R/a)^2+1$" against time(s) for agglomerates of 100%H CB, 80%H CB, 60%H CB, 40%H CB, 20%H CB and 100%L CB

respectively. The plots giving straight lines indicate the applicability of the model in all blends and covers agglomerate densities ranging from 0.28 to 0.49 g/cm^3.
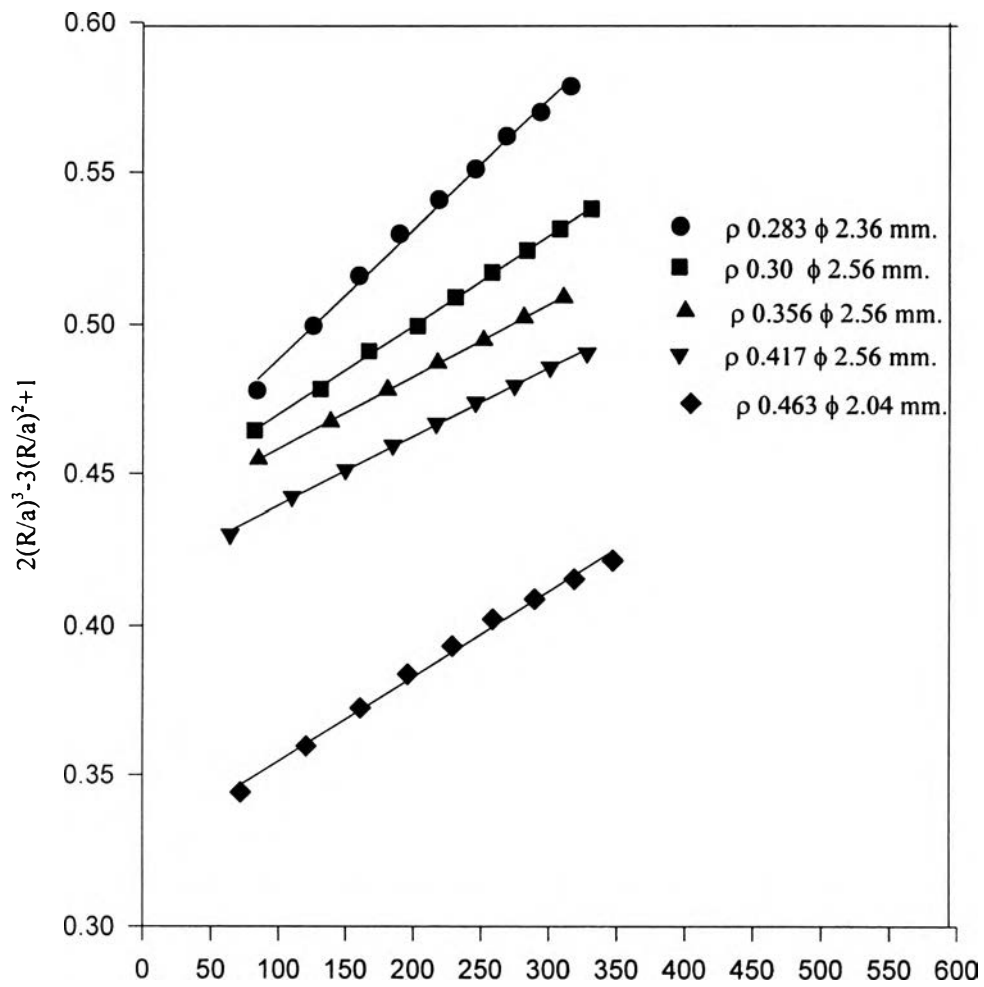

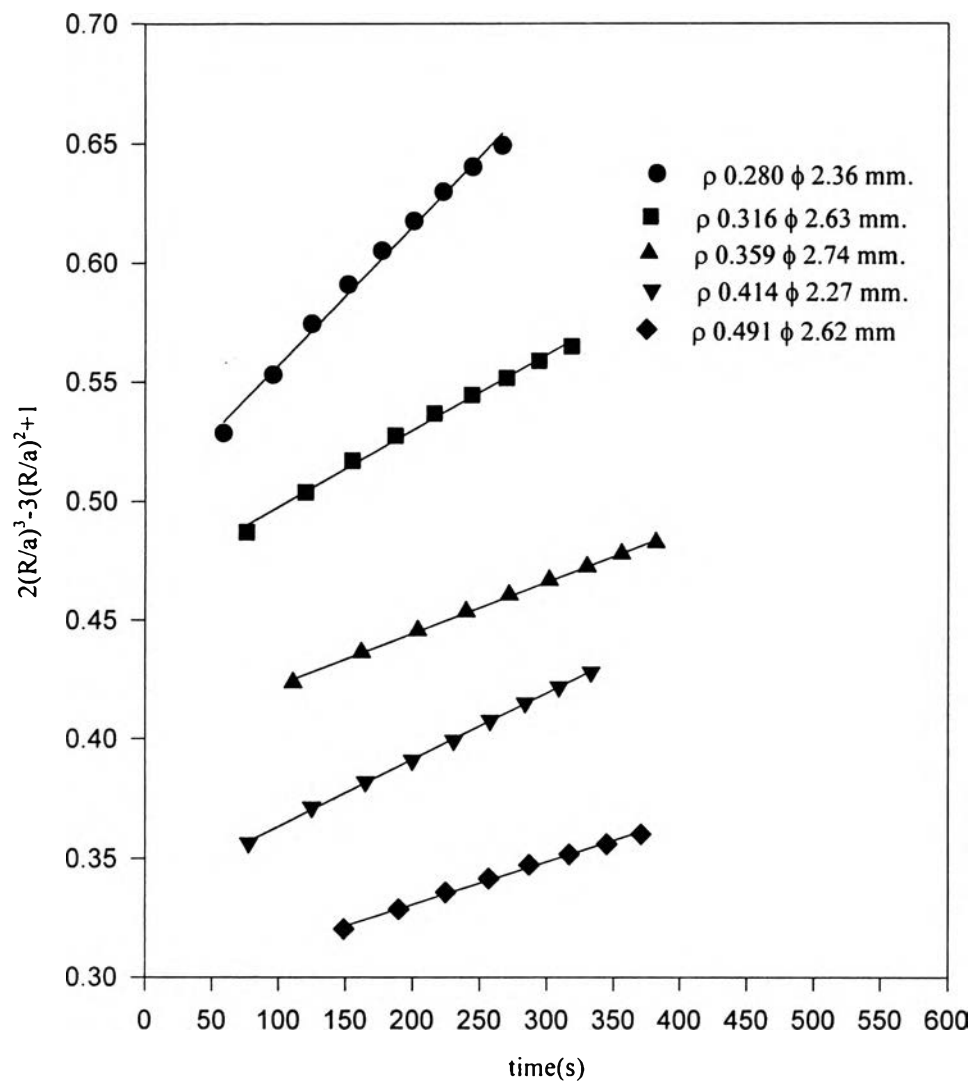Fig. 6 Infiltration of PDMS in the agglomerate of 100%H CB.

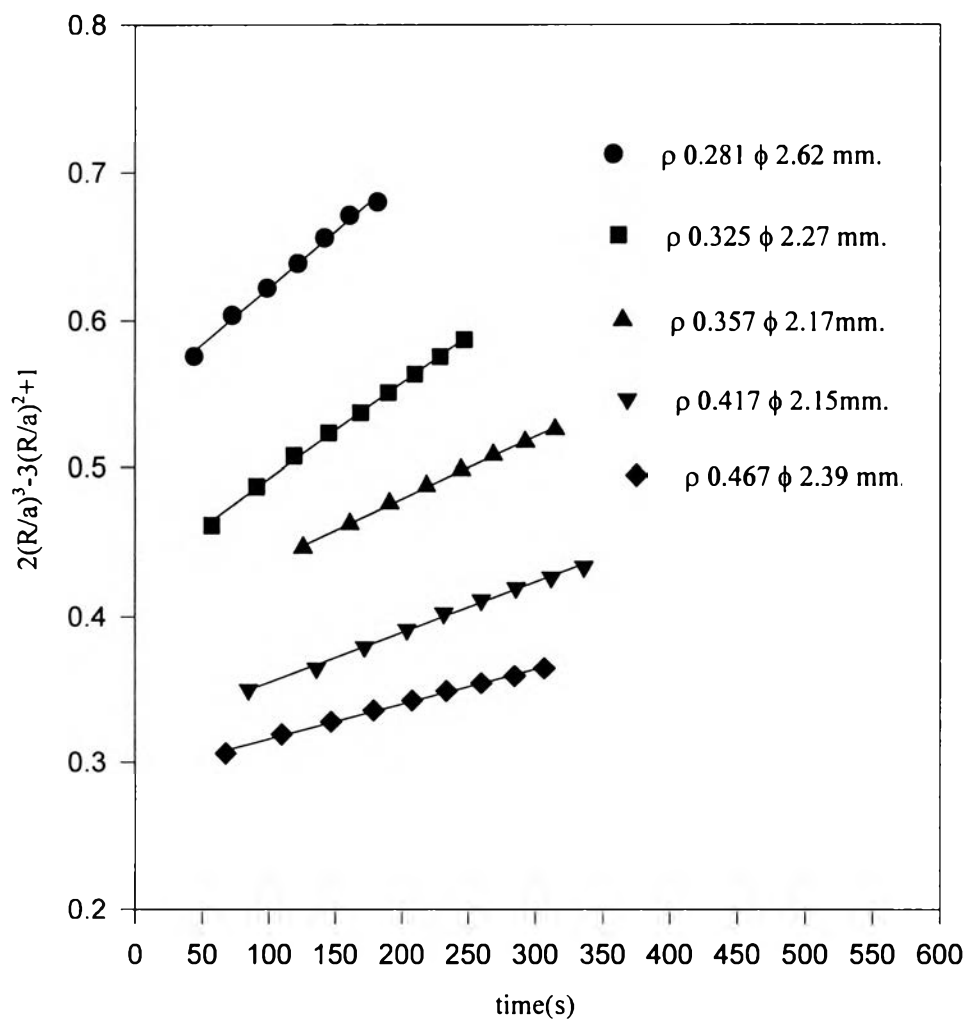Fig. 7 Infiltration of PDMS in the agglomerate of 80%H CB.

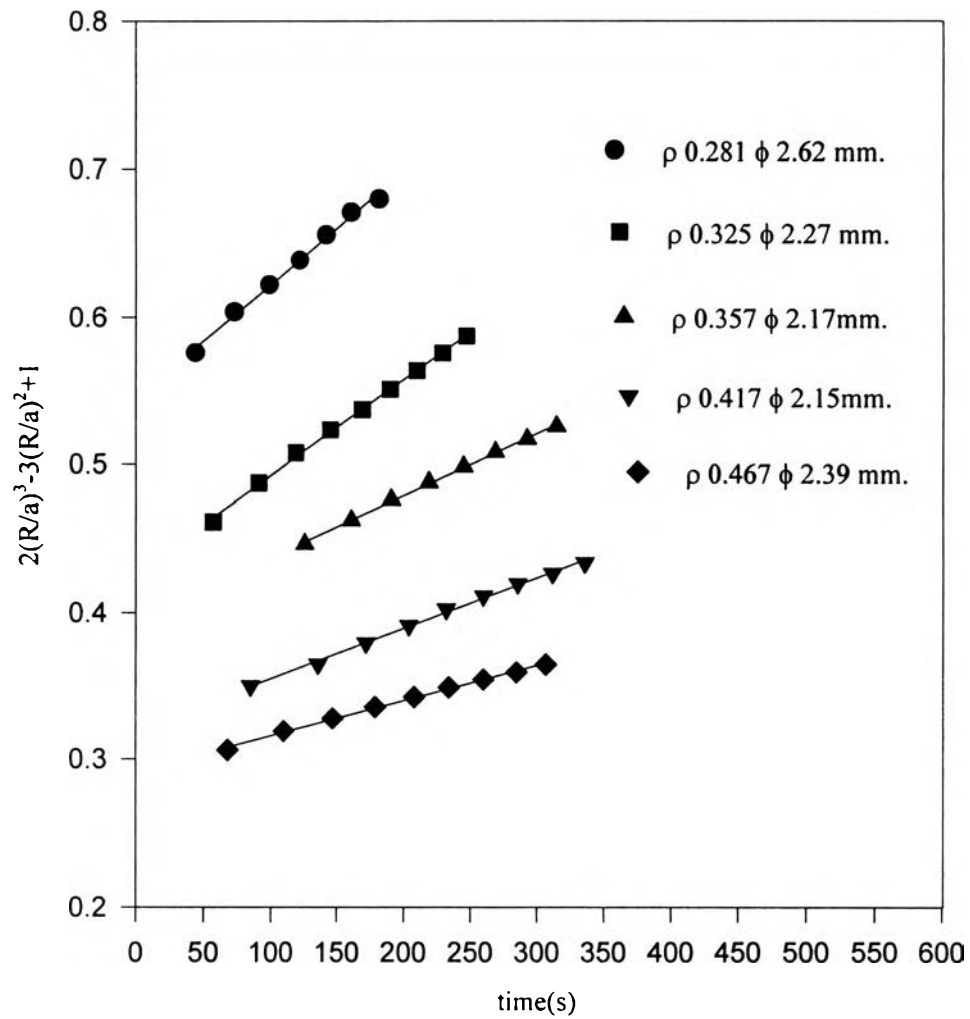Fig. 8 Infiltration of PDMS in the agglomerate of 60%H CB.

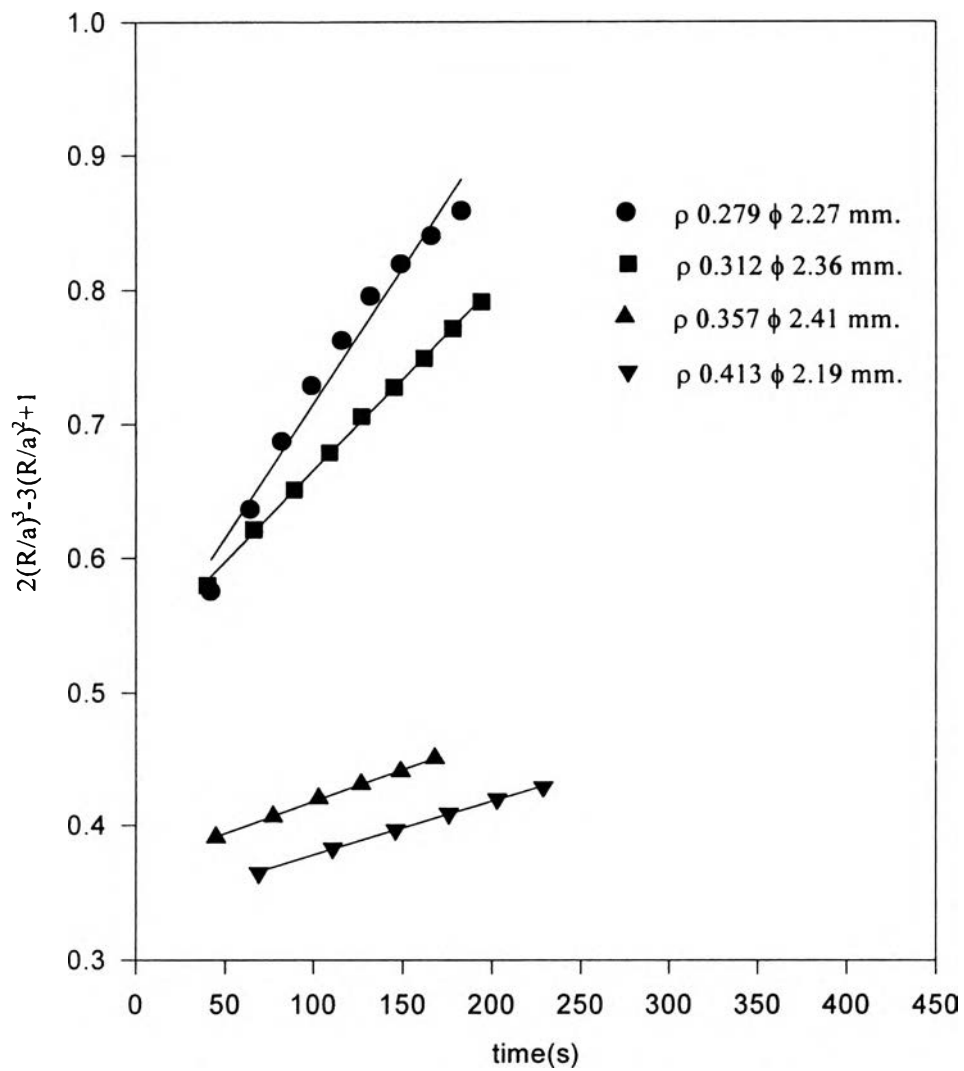Fig. 9 Infiltration of PDMS in the agglomerate of 40%H CB.

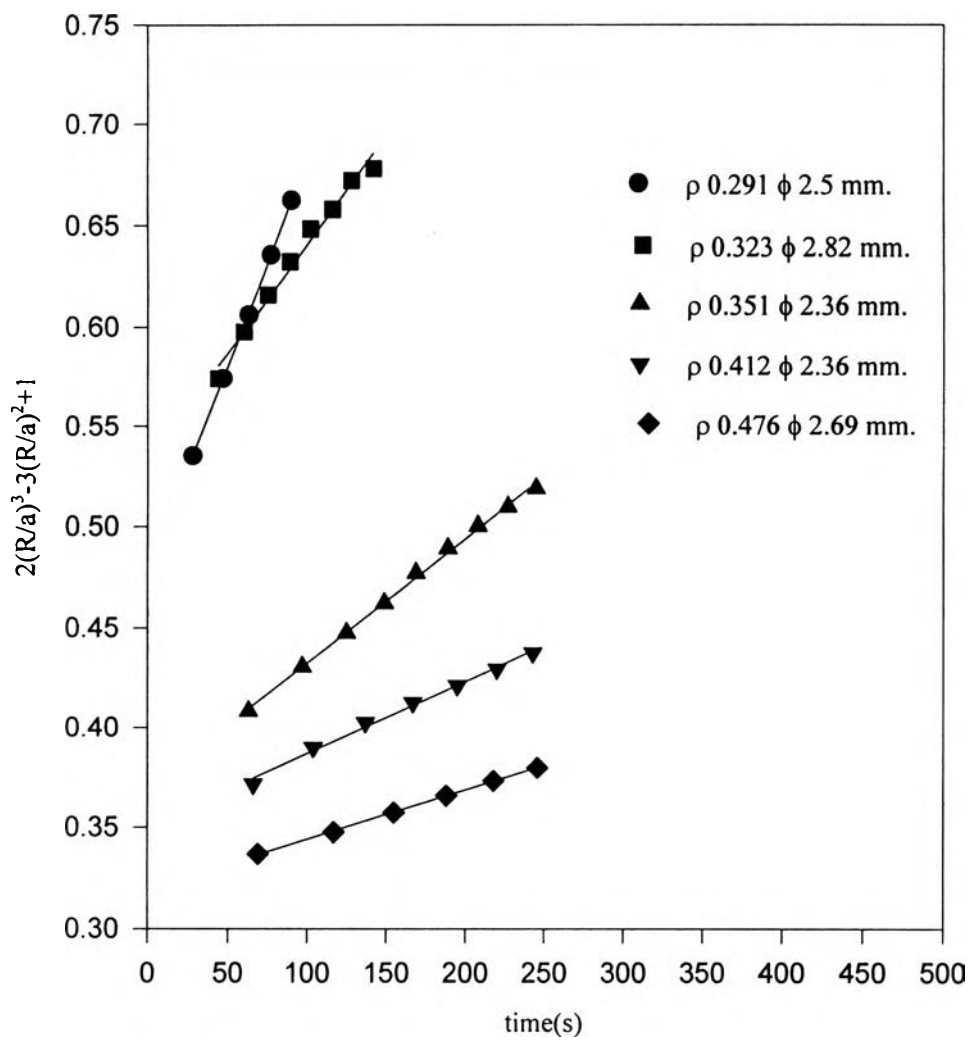Fig. 10 Infiltration of PDMS in the agglomerate of 20%H CB.

Fig. 11 Infiltration of PDMS in the agglomerate of 100%L CB.

3.4 Effect of void inside aggregate(ϵ_i) and void between aggregate(ϵ_o) on the infiltration of fluid in agglomerates

Both ϵ_i and ϵ_o in agglomerates of 100%H CB and 100%L CB can be calculated by using Medalia equation and the related equation described above. The results are shown in Table 5 and Table 6. High structure carbon black has a more open structure with more voids present inside the aggregates(as reflected by higher DBPA numbers) and less voids present between the aggregates, at the comparable agglomerate densities. Low structure carbon black has a more compact configuration . Thus the voids between the aggregates in low structure is greater than in high structure. Usually the voids between the aggregates are more accessible than the voids inside the aggregates. So we predict that the fluid will access to a larger extent agglomerates of low structure carbon black than of high structure carbon black at comparable agglomerate densities. Therefore the corresponding hydraulic radius(R_h) is larger in low structure than in high structure. The experimental results(Fig. 12) agree with this hypothesis in that the R_h of 100%L CB is always larger than the R_h of 100%H CB at comparable agglomerate densities.

Table 5 ϵ_i and ϵ_o in agglomerates of 100%H CB

Agglomerate density(g/cm^3)	ϵ_I	ϵ_o
0.283	0.19	0.66
0.300	0.2	0.64
0.357	0.24	0.57
0.417	0.28	0.50
0.463	0.31	0.44

Table 6 ε_i and ε_o in agglomerates of 100%L CB

Agglomerate density(g/cm^3)	ε_i	ε_o
0.291	0.10	0.74
0.323	0.11	0.72
0.351	0.12	0.69
0.412	0.14	0.64
0.476	0.16	0.58

3.5 Hydraulic radius(R_h) and the packing characteristic

Fluid infiltrates in carbon black by accessing into its voids. Carbon black agglomerates with loose packing and more voids can be penetrated more than carbon black agglomerates with dense packing and less voids. The study of the effect of ε_i and ε_o indicates that fluid is more accessible in ε_o than in ε_i. Thus the size of R_h can be correlated with agglomerate structures and their packing characteristics. Large R_h represents more compact structure and larger ε_o. Small R_h represents more open structure and smaller ε_o. The results of measuring t_{max} and calculating R_h are shown in Fig.12.

At packing densities 0.28-0.33 g/cm^3 , 100% L CB can be arranged to pack for the most compact structure because of the largest R_h while 100%H CB has the most open structure indicated by smallest R_h. Structures of all blends can be categorized from the most open structure to the most compact structure as well as values of ε_o from the least voids to the more voids in the following order.

100%H CB, 80%H CB, 60%H CB, 40%H CB, 20%H CB, 100%L CB

At packing densities 0.35-0.42 g/cm^3, 80%H CB gives the most open structure while 100%L CB still has the most close structure and the categories of structures for all blends ranging from open structure to close structure are in the following order.

80%H CB, 100%H CB, 60%H CB, 40%H CB, 20%H CB, 100%L CB

The different packing characteristics of carbon black blends at different overall packing densities are due to the influence of both low aggregate structure and high aggregate structure in the blends and has been mentioned earlier. In this experiment, packing densities are controlled to give comparable agglomerate densities. The results show that for loose agglomerates (agglomerate densities 0.28-0.33 g/cm^3)of carbon black blends, packing characteristics show little difference by comparison with dense agglomerates (agglomerate densities 0.35-0.42 g/cm^3).

At a packing density about 0.47 g/cm^3, the R_h of all blends show little difference except that the R_h for 100%H CB is smaller.

In application, packing characteristics and the corresponding agglomerate structure will affect matrix penetration inside the cluster during dispersion(Drakopoulou et al, 1993). This in turn will affect agglomerate dispersibility. In general, matrix penetration inside the agglomerate retards the dispersion process due to an increase in agglomerate cohesivity through the formation of liquid bridges between aggregates and primary particles(Howatt et al, 1989).
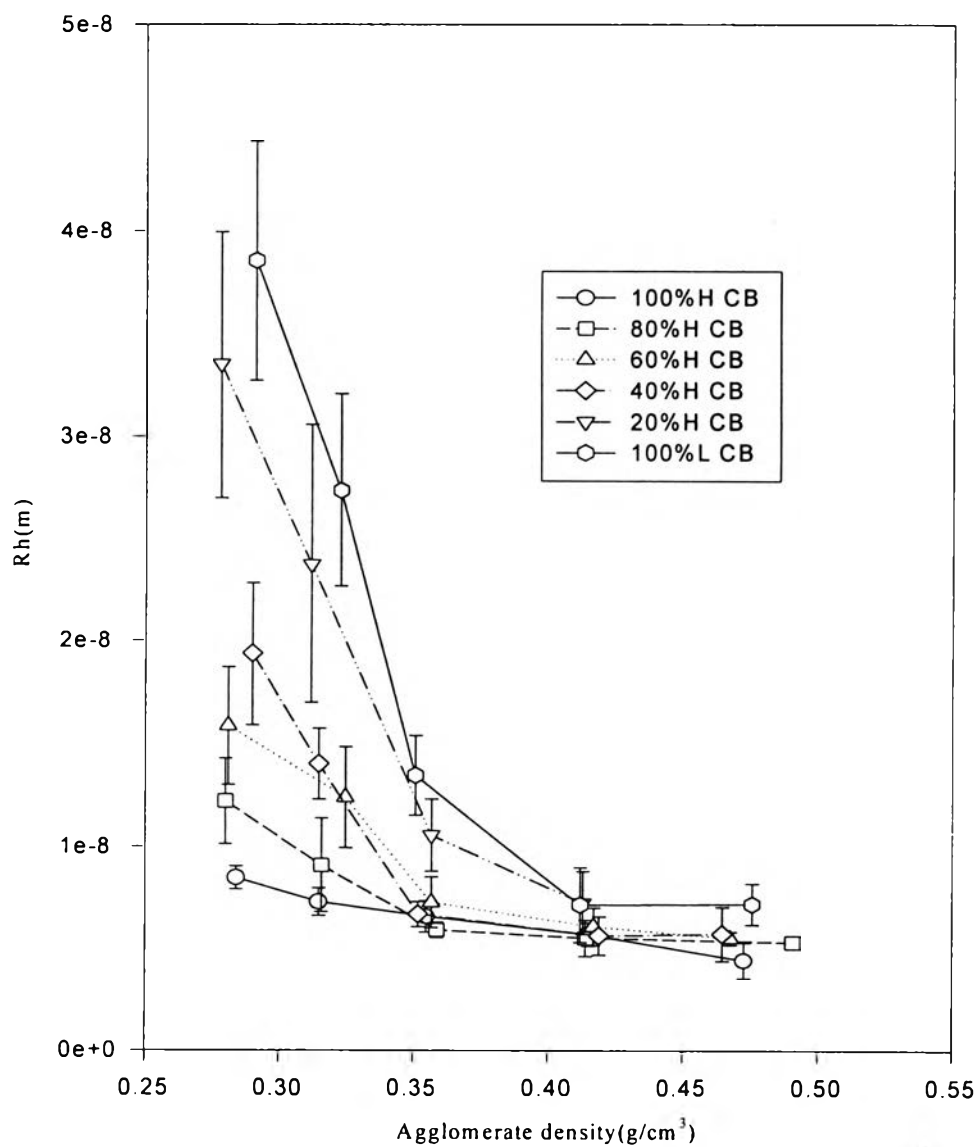
Fig. 12   Hydraulic radius of agglomerates prepared from high structure carbon black, low structure carbon black and their blends versus the agglomerate densities.

3.6 Interfacial properties between carbon black and polydimethysiloxane, carbon black and polybutadiene

R_h of the same agglomerate density when infiltrated by PDMS and PB are illustrated in Table 7. R_h of the same agglomerate density in PDMS are generally larger than in PB.

By taking the R_h in Table 7 and taking agglomerate diameter as 2 mm. and the equation (11), t_{max} of the same agglomerate density and the same diameter are computed as shown in Table 8. D_p is the mean aggregate size and is constant for a given carbon black blends; thus the ratio of cosine of contact angle of PDMS and cosine of contact angle of PB is calculated by using equation (12).

$$\frac{\cos \theta_{PDMS}}{\cos \theta_{PB}} = \frac{\mu_{PDMS}\gamma_{PB}t_{max\ in\ PB}}{\mu_{PB}\gamma_{PDMS}t_{max\ in\ PDMS}}$$

Table 8 shows $\cos \theta_{PDMS}/\cos \theta_{PB}$ in the range of 1.3-2.0. It means that PDMS can wet more the carbon black surface than PB.

Table 7 R_h of the same agglomerate density when infiltration matrix are PDMS and PB

carbon black blends	agglomerate density(g/cm^3)	R_h in PDMS X 10^{-9}m.	R_h in PB X 10^{-9}m
100%L	0.351	13.8	10.3
20%H	0.357	10.5	5.18
40%H	0.352	6.77	4.59
60%H	0.357	7.32	4.68
80%H	0.359	5.95	4.37
100%H	0.356	6.63	4.35

Table 8 t_{max} of agglomerate diameter 2 mm. when sedimentation in PDMS and PB, cos θ_{PDMS} is the wet contact angle of PDMS on CB surface, cos θ_{PB} is the wet contact angle of PB on CB surface

carbon black blends	agglomerate density(g/cm³)	t_{max} in PDMS(s)	t_{max} in PB (s)	cos θ_{PDMS} / cos θ_{PB}
100%L	0.351	1115	3981	1.3
20%H	0.357	1472	7948	2.0
40%H	0.352	2275	8939	1.5
60%H	0.357	2111	8797	1.6
80%H	0.359	2600	9433	1.4
100%H	0.356	2329	9458	1.5

Fig.13 shows the molecular structure of PDMS and PB. PDMS has a more linear structure than PB which has a bulky structure. PDMS is flexible and rotation of siloxane chains is fairly free about the Si-O axis, especially with small substituents(methyl) on the silicone atom . Rotation is also free about Si-C axis. The movement of butadiene chain is hard to perform compared with the movement of siloxane chain, because of the bulky structure, consisting of π-bonds in the chain. PB is an organic compound which has less polarity than PDMS with inorganic Si atoms showing strong polarity. Carbon blacks in this study have pH around 10 , so the interaction with polar liquids will be better than with non-polar fluids. As a result of freedom of motion and its polarity and its better wetting , the penetration of PDMS to agglomerate is greater than the penetration of PB , although the molecular weight of PDMS is much greater than the molecular weight of PB.
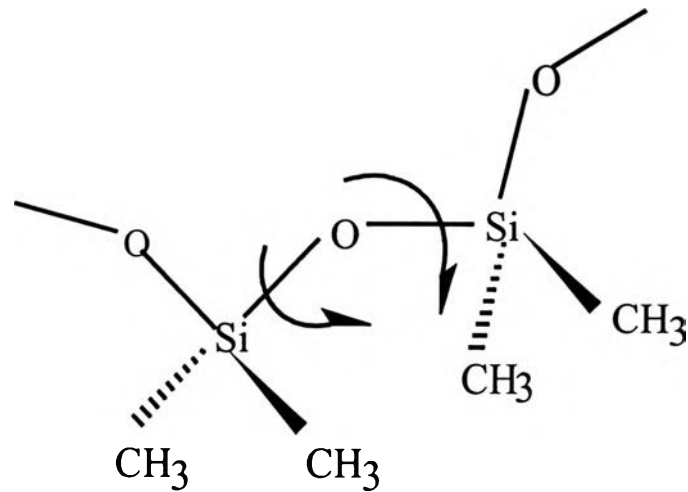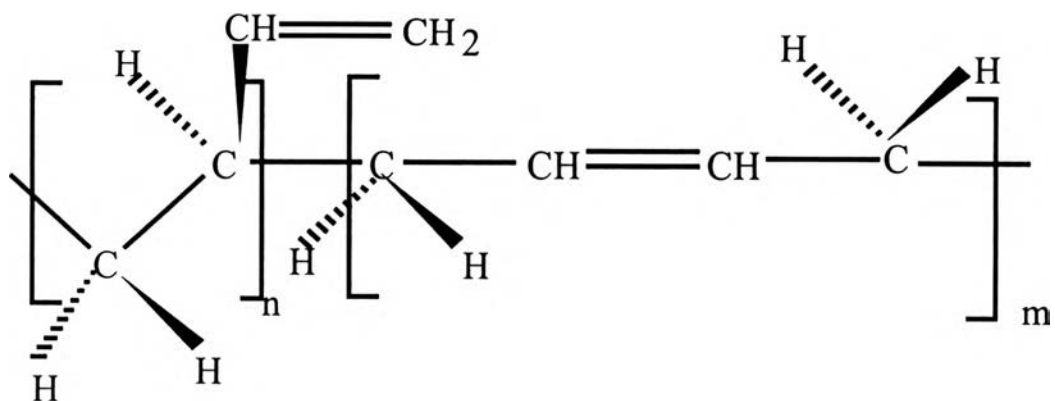
Polydimethysiloxane (PDMS) MW. 17,000

Si-O-Si $=143^{O}$

C-Si-C $=112^{O}$

O-Si-O $=110^{O}$

1,2 Polybutadiene(PB) MW. 1,400

C-C-C $=105^{O}$

Fig.13 The molecular structure of Polydimethysiloxane (PDMS) and 1,2 Polybutadiene(PB)