CHAPTER I

INTRODUCTION

1.1 Background

The importance of carbon black in the rubber industry is well known. Carbon black is widely used as a filler to enhance the performance of rubber and other polymeric materials. The incorporation of carbon black into rubber gives enhanced modulus, improved fatigue and abrasion resistance, and better overall performance . The degree of dispersion of carbon black into polymer dictates the degree to which material properties are improved.

The structure of carbon black solid can be defined at three levels (high structure, medium structure and low structure). Primary particles (typically 10 to 100 nm. in size) are fused together into aggregates (50 to 500 nm. in size) which are packed into agglomerates (5 μm. or larger in size). It is obvious that there are large voids between the carbon black particles which are filled with air. These voids appear to be indicative of the carbon black structure , the degree of particle aggregation,. Thus carbon black aggregates are described in terms of their "structure". High structure carbon blacks have a more open tentacular morphology while low structure carbon blacks have a more compact configuration. Previous studies have shown that the infiltration of the processing matrix into powder agglomerates affects the dispersion of their clusters(Bohin et al, 1994) and the apparent cohesivity of powder compacts(Howatt et al, 1989). The degree of infiltration of fluid in carbon black agglomerates is affected by packing characteristics, agglomerate structures and the interfacial properties of solid-liquids. The goals of this work

are to study the influence of carbon black aggregate structure (high structure, low structure and their blends) on packing characteristics as well as the effect of interfacial properties between carbon blacks surface and two different fluids, polydimethysiloxane(PDMS) and polybutadiene(PB) on the kinetics of matrix infiltration.

1.2 Theory

1.2.1 Void volume

The void volume in powder carbon black is a measure of structure(Donnet et al, 1976); its determination is an important factor in the assessment of carbon black structure. There are basically two approaches to determine void volume, namely, liquid absorption and specific volume at a given compression.

1.2.2 Liquid adsorption

In the liquid adsorption test, a liquid which wets carbon black very well is incorporated into the void of the black. The amount needed to fill the voids of a given weight of black is then determined . Dibutylphthalate adsorption test (DBPA), an acceptable automatic method, is the volume of dibuthylphthalate that filled the voids in 100g of black. This method requires are adsorptometer. This instrument is basically a torque-measuring electric kneader-mixer. First , a quantity of carbon black is placed in the mixing chamber. The kneader action is started and dibutyphthalate is added dropwisely from an automatic burette. The transition from a free-flowing powder to a semiplastic material at the point of maximum adsorption (the filling of the voids) results in a cut-off in the burette and kneader.

1.2.3 Specific volume(Vs)

The specific volume of carbon black, is generally determined at a specified compression(Donnet et al, 1976). In this study work, the tapping of carbon black 300 times has been performed; the specific volume is the inverse of tapped density(ρ_{tap}).
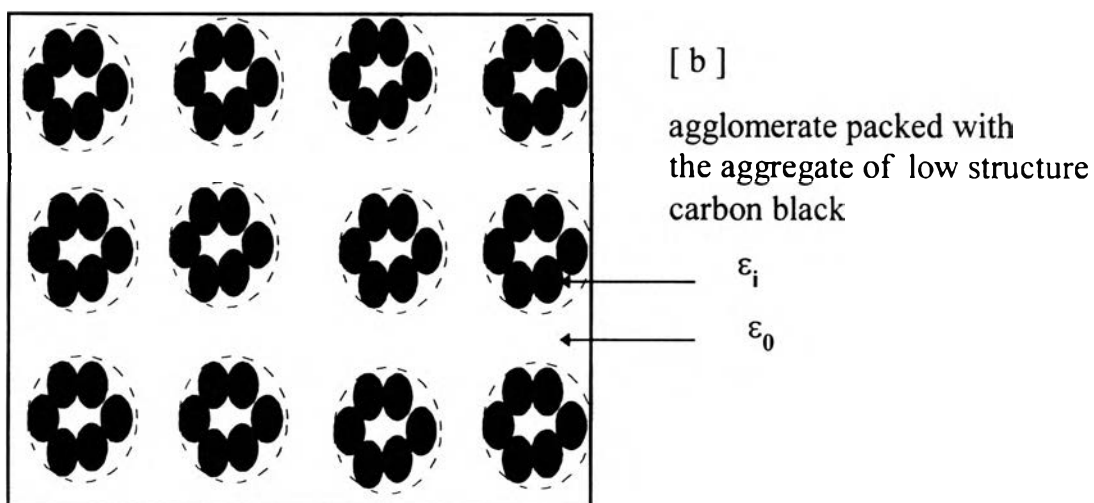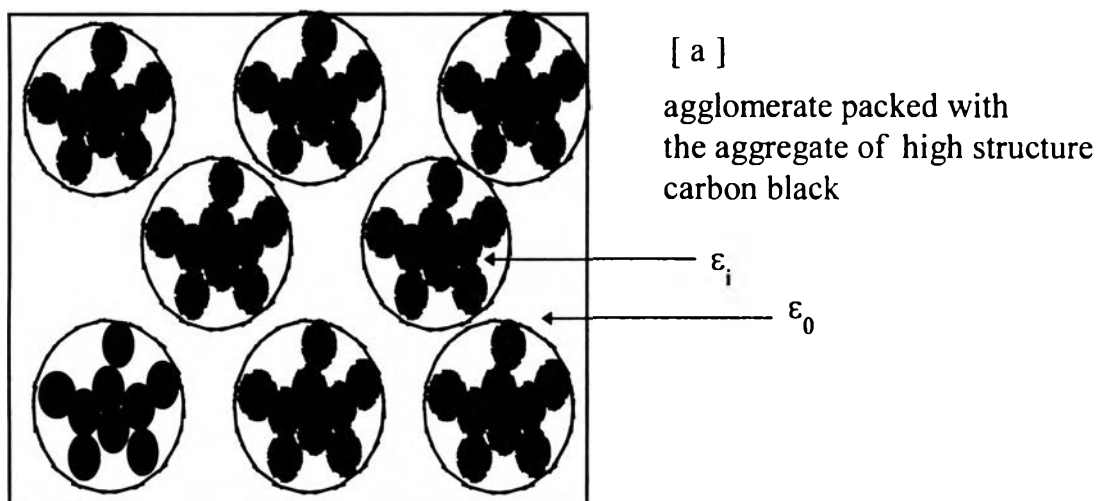
$$V_s = \frac{1}{\rho_{tap}}$$

Since void volume depends on carbon black structures, we may use the specific volume as an indicator of carbon black agglomerate structures.
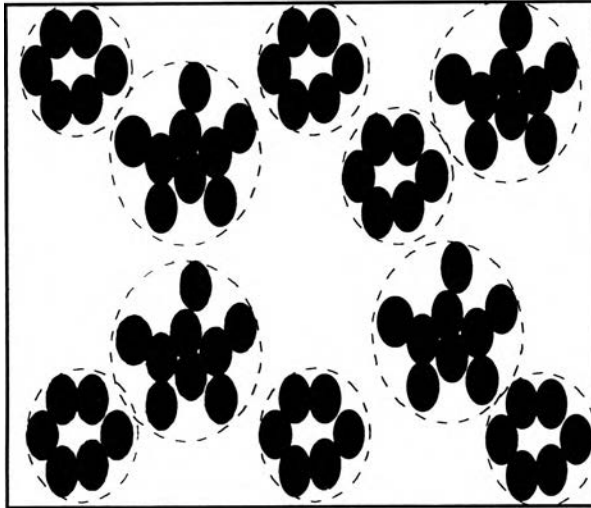
1.2.4 Pour density (ρ_{pour})

Pour density is the apparent density of powder carbon black given by the weight per bulk volume of powder. Thus the following relation holds among the void fraction(ε), the particle density (ρ_p) and the pour density (Shinohara et al).

$$\rho_{pour} = \rho_p \left(1 - \varepsilon \right)$$

1.2.5 Packing of carbon black aggregate structures

[a]

agglomerate packed with
the aggregate of high structure
carbon black

ε_i

ε_0

[b]

agglomerate packed with
the aggregate of low structure
carbon black

ε_i

ε_0

[c]

agglomerate packed with
the mixture aggregate of
50% high structure and
50% low structure

Fig. 1 Agglomerate structures   at   the   comparable agglomerate density prepared from   the carbon black aggregate structure of [a] high structure, [b]low structure and [c] the mixture of high and low structure.

Primary particles of carbon black are fused together in aggregates(Drakopoulouet al, 1993).   The voids between particles inside aggregates are defined as ε_i . Aggregates are packed and form agglomerates. The voids between aggregates are defined as ε_0 . The void fraction (ε) of an agglomerate is the summation of ε_0 and ε_i. The calculation of ε_0 and ε_i can be computed by using the following equations(Yamada et al) :

$$\varepsilon = \varepsilon_0 + \varepsilon_i$$

$$\varepsilon_0 = 1 - \phi_{(aggl)} / \phi_{(aggr)}$$

where: $\phi_{(aggl)}$: solid volume fraction of agglomerate.

$\phi_{(aggr)}$: solid volume fraction of aggregate.

Medalia Equation (Drakopoulouet al, 1993)

$$\phi_{(aggr)} = 1.46 / (1+0.02139 \text{ X DBPA})$$

From Fig.1 the agglomerate structure of high structure black (a) has a more open structure than the agglomerate structure of low structure black(b). The more open structure has more pores inside the aggregates (as reflected by the higher DBPA) and less pores between the aggregates, at comparable agglomerate densities. Low structure carbon blacks have a more compact configuration (Fig.1 b).

1.2.6 Sedimentation of carbon black agglomerates in polymeric fluids

Bohin, Feke and Manas-Zloczower(Bohin et al, 1995) describe the motion of agglomerates in viscous fluids by using transient buoyancy measurements.

The motion of the agglomerates is given by Newton's law.

$$\frac{d\left(m_p v_p\right)}{dt} = m_p g - F_f \qquad (1)$$

m_p = buoyant mass of the agglomerate.

v_p = vertical velocity.

g = the acceleration of gravity.

F_f = friction force.

From Stokes' law the friction force is given by

$$F_f = 6\pi\mu_f a v_p \qquad (2)$$

a = the agglomerate radius.

μ_f = the viscosity of fluid.

From Eq.(1) and Eq(2) and the assumption of pseudo steady state yields:

$$v_p = \frac{m_p g}{6\pi\mu_f a} \qquad (3)$$

The measure of v_p directly yields m_p which is related to the degree of matrix infiltration.
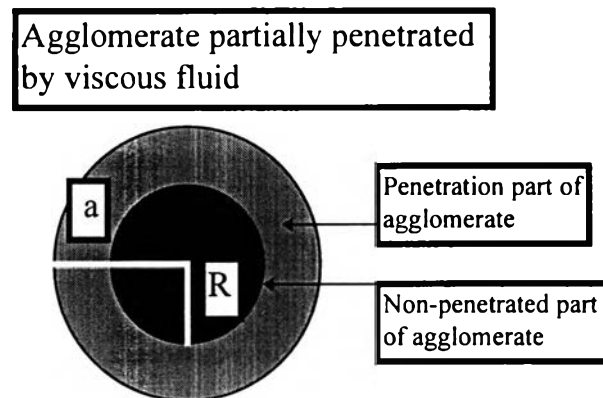

Fig. 2 Schematic diagram of a partially infiltrated agglomerate.

We assume a spherical agglomerate (radius a), and a spherical symmetric infiltration (to radius R) of matrix fluid. The buoyant mass of agglomerate is given by

$$m_p = \frac{4}{3}\pi\left[R^3\rho_s + (a^3 - R^3)\rho_w - a^3\rho_f \right] \qquad (4)$$

where : ρ_S = The density of unweted part of agglomerate.

ρ_W = The density of wetted part of agglomerate.

ρ_f = The density of fluid.

For an agglomerate with fillable porosity ε.

$$\rho_W = \rho_f\,\varepsilon + \rho_S \qquad (5)$$

Substitution of Eq. (4) into Eq(3) yields

$$v_z = \frac{2a^2 g}{9\mu_f}\left[(\rho_s - \rho_w)\left(\frac{R}{a}\right)^3 + (\rho_w - \rho_f) \right] \qquad (6)$$

At the start of infiltration, R=a and the initial sedimentation speed , v_z^0 , is

$$v_z^0 = \frac{2a^2 g}{9\mu_f}(\rho_s - \rho_f) \qquad (7)$$

The ultimate sedimentation speed, v_z^∞, is

$$v_z^\infty = \frac{2a^2 g}{9\mu_f}(\rho_w - \rho_f) \qquad (8)$$

Combining Eqs (6), (7) and (8) yields the degree of penetrated fluid (R/a).

$$\left(\frac{R}{a}\right) = \left(\frac{v_z - v_z^{\infty}}{v_z^0 - v_z^{\infty}}\right)^{1/3} \tag{9}$$

So, the observation of v_z^0, v_z^{∞} and v_z can determine the degree of penetration . However measuring of v_z^0 is difficult due to the immediate infiltration of matrix; the value of v_z^0 in this study was computed by using Eq.(7) instead. The kinetics of polymeric fluids infiltration into agglomerate can be described by using I. Manas-Zloczower model (Bohin et al, 1994).

$$2\left(\frac{R}{a}\right)^3 - 3\left(\frac{R}{a}\right)^2 + 1 = \frac{t}{t_{max}} \tag{10}$$

t_{max}, the time at which infiltration stop(R=0) is

$$t_{max} = \frac{25a^2 \mu_f}{36\varepsilon R_h \gamma_{lv} \cos\theta} \tag{11}$$

$$t_{max} = \frac{150a^2 \mu_f (1 - \varepsilon)}{36\varepsilon^2 D_p \gamma_{lv} \cos\theta} \tag{12}$$

where γ_{lv} is liquid-vapor surface tension of fluid.

θ is contact angle of liquid-solid.

R_h is hydraulic radius of the fluid path through the agglomerate[$R_h = \varepsilon D_p/6(1-\varepsilon)$](Bohin et al, 1994).

D_p is the mean aggregate size.

Usually the fluid is more accessible in the voids between aggregates than the voids inside aggregates. Thus, R_h mainly implies the size of pores between aggregates rather than the voids inside aggregates for an agglomerate. As a result of R_h representing the voids between aggregates and elucidating the packing characteristics of the agglomerates, agglomerate structures can be described in a qualitative manner.

1.2.7 Interfacial properties of solid-liquid

The capabilities of fluids to move in carbon black depend on the interfacial properties of carbon black surface and the liquids. R_h reflects not only the packing characteristics of the agglomerate, but also is related to the characteristics of the fluid infiltrating the agglomerates, for example some pores might be accessible to one fluid, but not to another fluid.

1.3 Objectives

- To study the packing characteristics and the corresponding agglomerate structures of high structure , low structure carbon black and their blends.
- To investigate the average effective pore size in agglomerates.
- To study the interfacial properties between carbon black and PDMS , carbon black and PB.