

Chapter 2

Mechanisms of dispersion of carbon black agglomerates

Dispersion of carbon black agglomerates in rubber is mainly governed by two mechanisms : erosion and rupture. Due to these mechanisms, the agglomerates size decreases during mixing and a high number of small fragments of carbon black agglomerates are generated. The smaller these fragments and the agglomerates, the better the mechanical and physical properties of the mix. Obviously, it is also required that the agglomerates distribution in the matrix be homogeneous. Both mechanisms are therefore studied in detail to determine the key parameters that influence the efficiency of the dispersion mechanism. This analysis is performed in collaboration with Cemef group and from the information available in literature. Even if most authors consider erosion and rupture as two independent mechanisms, we observe that these mechanisms can occur simultaneously. It is therefore difficult to study separately these mechanisms and to quantify it. Moreover, the decrease of the agglomerates size is influenced by the impregnation of agglomerates by rubber. The effect of this last mechanism on the agglomerates dispersion is also investigated.

2.1 Mechanism of rupture

Rupture is the first dispersion mechanism investigated to explain the decrease of the agglomerates size in a given flow. Bolen and Colwell explained in 1958 that rupture of

carbon black agglomerates is observed only if hydrodynamic forces acting on agglomerates exceed a threshold value (Bolen et al, 1958). This mechanism was also observed by Dizon and Tadmor in 1976 and more recently by Manas-Zloczower et al. in 1988, Rwei et al. in 1990 and Collin et al. in 2004. Threshold value mainly depends on cohesive force of agglomerates that is directly linked to the number of bonds existing between aggregates that compose agglomerates. Different models are developed to evaluate the cohesive stress of agglomerate. Cohesive stress is higher for agglomerates with a high solid volume fraction than for high porosity agglomerates. From these experiments, different authors defined rupture as a discontinuous mechanism characterized by a brutal splitting of agglomerates into several fragments of various sizes. These fragments are considered as new agglomerates if their size is not smaller than $1\mu m$. This mechanism is illustrated in Figure 2.1 where we observe the break-up of one agglomerate in a simple shear flow with a shear rate equal to $6s^{-1}$. Those pictures clearly show the fracture plane and the motion of different fragments after rupture.

In 1962, Rumph proposed that cohesive stress of agglomerates be proportional to the product of mean force between aggregates, that compose agglomerate, and void volume fraction and inversely proportional to the surface of the cross section of these aggregates that compose agglomerate :

$$\tau_{coh} \propto \frac{H(1-\varepsilon)}{2R^2}$$

where H is the mean force between the aggregates, R is the radius of the cross-section of the aggregates and ε is the void volume fraction. This model is defined for low porosity agglomerates and the number of bonds across the fracture section is assumed to be very high and randomly distributed in space. Moreover, this relation is relevant only if the force between aggregates can be represented by a mean force. Other models, close to Rumph model, have been determined by Cheng et al. (1968), Hardley and Parfitt (1985). Soontag and Russel defined in 1987, a model based on the energy of fracture and on the Mises yield criteria. In 1988, Kendall et al. proposed a model for the rupture based on a fracture mechanics approach. Unlikely to Rumph model, Kendall considers that the fracture of agglomerate is not direct. Fracture is like a crack that propagates progressively across agglomerate. According to this approach, Kendall determined a new expression for cohesive stress :

$$\tau_{coh} \propto \frac{kN}{R^2}$$

where k is a constant, N is the number of bonds that have to be broken and R is the radius of the cross section of the fracture plane. If we assume that agglomerate is spherical and that it breaks up in two fragments of same volume, the radius of the cross section is equal to the agglomerates radius. As the number of bonds is proportional to the surface of the fracture plane, this expression can be written as :

$$\tau_{coh} \propto kR^{m-2}$$

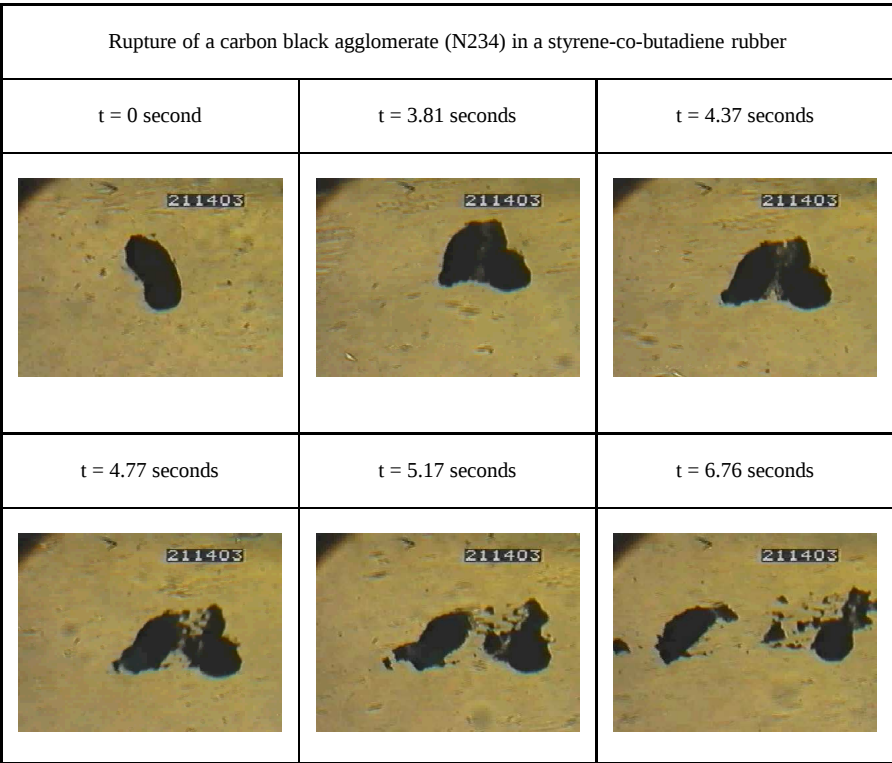


Figure 2.1: Rupture of one carbon black agglomerate in a styrene-co-butadiene rubber (SBR) in a simple shear flow (with the courtesy of Cemef-Ecoles des Mines de Paris). Shear rate is equal to 6 s^{-1} and shear stress is equal to 83900 Pas .

where m lies between 0 and 2. If agglomerate is dense, m is equal to 2 and if agglomerate is porous m is equal to 0. Experimentally, Collin et al. (2004) determined an empirical law in which the critical stress needed to observe rupture, τ_c , decreases when agglomerates size increases. This law reads :

$$\tau_{coh} = a \frac{1}{R} + b$$

where a and b are two parameters and R is the agglomerate size. Finally, we have to mention that all the authors assume that agglomerates break-up in two parts of same volume in these models. But, experiments performed by Collin (2004) show that the rupture of one agglomerate often generates three agglomerates and sometimes four agglomerates of smaller sizes. Such a phenomenon is quite important, because it increases the speed of the dispersion mechanism.

As an illustrative example, we calculate the evolution of one agglomerate, with an initial size radius equal to $100 \mu m$, when it is subjected to successive ruptures. We suppose that all agglomerates break-up in two smaller agglomerates of same volume. The radius of these new agglomerates and the number of agglomerates at each stage of rupture is given by :

$$\begin{cases} n^i = 2 n^{i-1} \\ R^i = \frac{R^{i-1}}{\sqrt[3]{2}} \\ 2 (R^i)^3 = (R^{i-1})^3 \end{cases},$$

where i is the indice of the i^{th} rupture and R is assumed to be the radius of a sphere of same volume than the agglomerates. We illustrate in Figure 2.2 the size evolution of the agglomerates for three different stories. In the first story, agglomerates are broken up in two agglomerates of same size at each rupture and the time needed to break one agglomerate is Δt seconds. In the second story, all agglomerates are broken up in three agglomerates of same size at each rupture but the time required to break agglomerates is now equal to $2\Delta t$. In the third story, we consider that this rupture only required $\frac{4}{3}\Delta t$ instead of $2\Delta t$. It clearly appears that the size evolutions of the agglomerates and their number depend on the number of fragments generated at each rupture and on the time needed to break-up agglomerate. As shown in the second example, break-up of one agglomerate in three fragments is not more efficient than break-up of one agglomerate in two fragments if the time needed for this rupture is longer. In the third example, we assume that rupture of one agglomerate only needs $\frac{4}{3}\Delta t$ and we then obtain the best dispersion of agglomerates at the end of rupture process. This rupture process presents the best compromise between the time for agglomerates rupture and the number of fragments generated by each rupture.

In the previous cases, we suppose that each kind of rupture generates fragments of same volume. We now consider that break-up of one agglomerate of volume V gener-

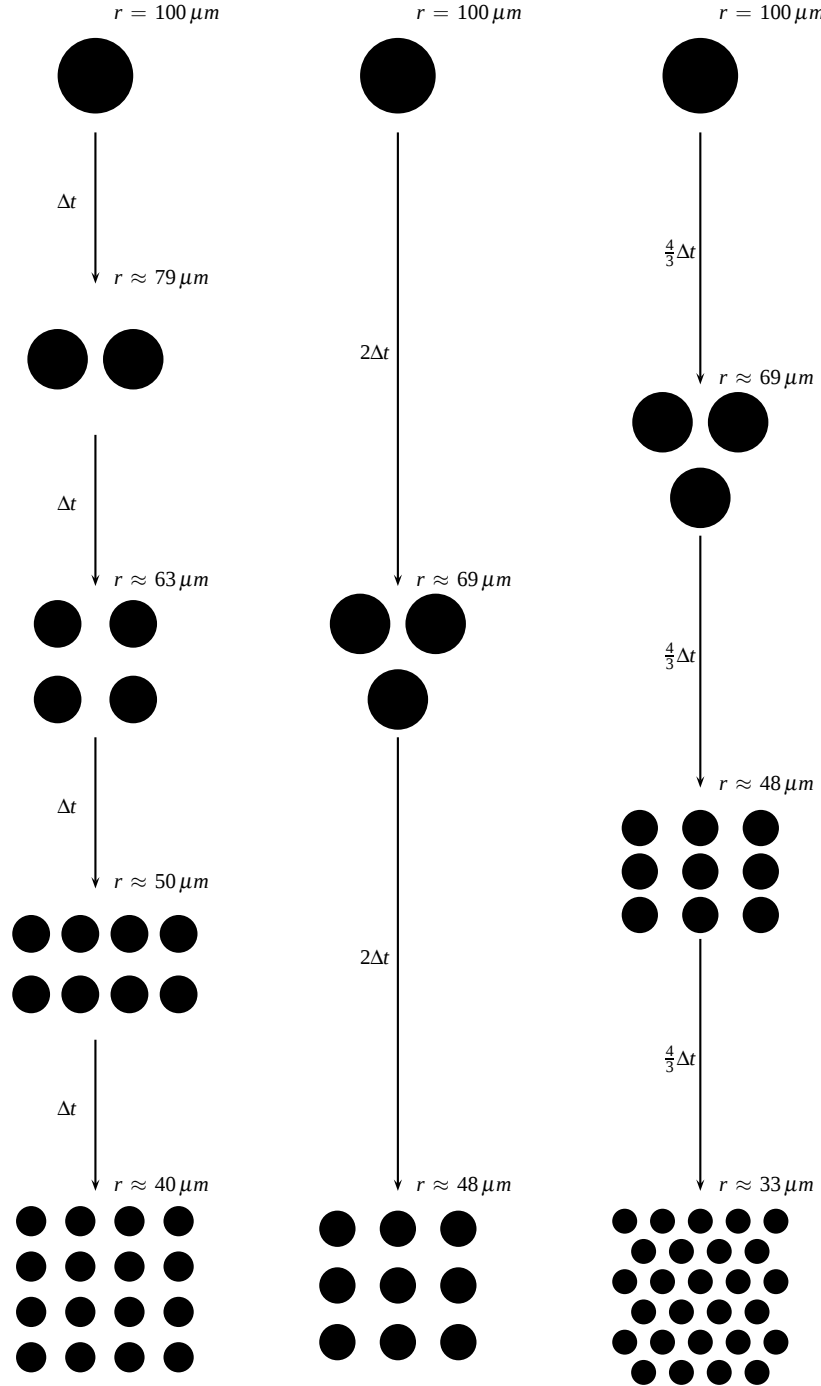


Figure 2.2: Evolutions of the agglomerates size due to the mechanism of rupture during $4\Delta t$ seconds. The number of fragments obtained at the end of rupture process depends on the time needed to observe rupture of one agglomerate and on the number of fragments generated at each rupture.

ates two fragments with a volume of $\frac{3}{4}V$ and $\frac{1}{4}V$ respectively. As illustrated in Figure 2.3, the smallest agglomerates are generated by this scheme of rupture and not when agglomerates are broken up in two agglomerates of same volume. After $2\Delta t$, we obtain four agglomerates of different sizes. Only one agglomerate is bigger than agglomerates obtained in the previous case. Mean agglomerates radius is similar in both case. By assuming that all agglomerates always break-up in two parts of same volume, we then obtain a relevant information on mean agglomerates size. But, we have to keep in mind that larger and smaller agglomerates exist in the mix.

Those different examples allow us to observe that rupture is a quite complex mechanism. Unfortunately, information available in literature on the dependence of the fragments size on the characteristic of the flow, on the internal structure of carbon black and on the shape of the agglomerates is scarce. No kinetic law, that provides the evolution of the agglomerates size in time as a function of shear stress or shear rate due to rupture mechanism, is available. Due to this lack of information, it will be difficult to determine a rupture model that would be quantitatively and qualitatively correct.

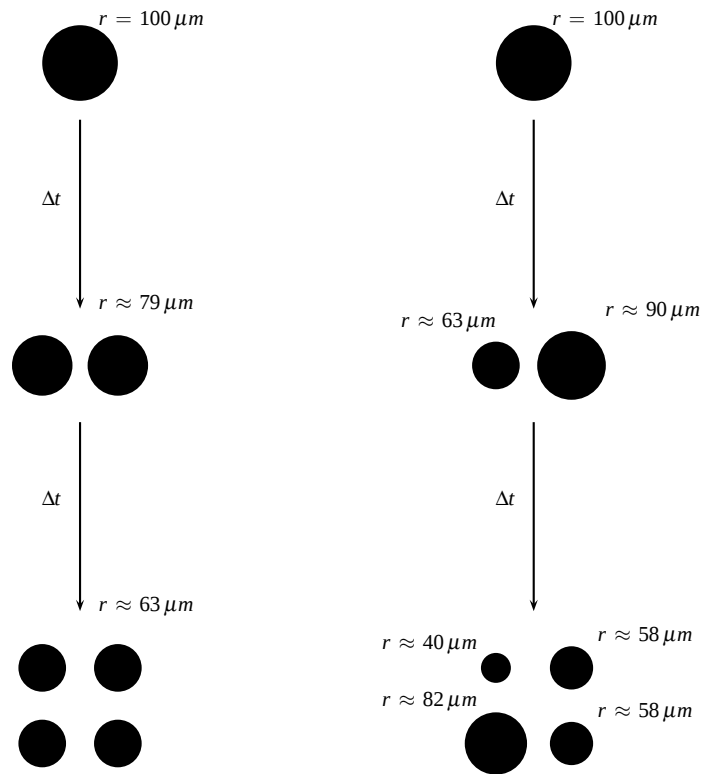


Figure 2.3: Influence of the fragments size generated by rupture mechanism on the agglomerates dispersion. In the second example (on the right), we assume that all agglomerates are broken up in two fragments of variable size. In the first example (on the left), all the fragments have the same size.

2.2 Mechanism of erosion

Erosion is the second dispersion mechanism investigated to explain the variation of agglomerates size. This mechanism is characterized by the detachment of a large number of small fragments (probably aggregates) from the outer surface of agglomerate (Rwei et al,1990). Erosion is observed for lower hydrodynamics forces than rupture and is very slow. In 1985, Shiga and Furuta proposed the "*onion peeling*" mechanism to explain erosion. In this mechanism, aggregates are either individually or collectively scraped from the agglomerate surface as illustrated in Figure 2.4. At each crossing of one agglomerate through a zone of high shear rate, a given amount of material ΔM is drawn from agglomerate. This amount of material is proportional to hydrodynamic stress σ_h acting on the agglomerate surface, to the square of the agglomerate size R and to the time t :

$$\Delta M \propto \sigma_h R^2 t.$$

More recently, second erosion mechanism called "*ribbon peeling*" has been proposed to explain erosion (Collin et al,2004). In this mechanism, fragments are eroded from the agglomerate surface and generate a ribbon of carbon black as illustrated in Figure 2.4. Such a ribbon is assumed to be infiltrated by rubber.

Erosion of carbon black agglomerate	
"Onion peeling" mechanism in a BR elastomer ($\dot{\gamma} = 6s^{-1}$)	"Ribbon peeling" mechanism in a EPDM elastomer ($\dot{\gamma} = 10$)
	

Figure 2.4: Onion peeling and ribbon peeling mechanisms for carbon black agglomerate in a simple shear flow of an ethylene-propylene-diene matrix (EPDM) and a butadiene rubber (BR) respectively (with the courtesy of Cemef-Ecoles des Mines de Paris).

Experimental investigations of erosion mechanism allow to determine different kinetic laws to predict the evolution of the agglomerates size. Distinction is made between cohesive and cohesiveless agglomerates. If the agglomerates are cohesive, shear stress acting on agglomerates has to exceed a threshold value to observe erosion. Otherwise, erosion is observed for any value of shear stress. In 1975, Kao and Mason proposed a law, valid for cohesiveless agglomerates, in which the variation of agglomerate volume is proportional to shear stress acting at a given point of the agglomerate surface. Eroded volume is independent of the initial size of agglomerate. Erosion of small agglomerates is therefore faster than erosion of large agglomerates. Powell and Mason defined in 1982 a kinetic law where the decrease of the agglomerate size is proportional to the fragments size removal from its surface. This law is valid for cohesiveless agglomerates. In 1991, Rwei et al. proposed an exponential law for the size evolution of cohesive agglomerates with shear rate. More recently, Bohin and al. (1996) and Scurati and al. (2002) defined two different models where the variation of the agglomerate size is proportional to the difference between its cohesive strength and hydrodynamic forces. As cohesive and hydrodynamic forces depend on the agglomerate size, these laws predict that the evolution of the agglomerate size is proportional to the square of its size. In the law of Scurati et al., such a result is obtained when fractal dimension, d_f , of the agglomerate is equal to 3. This value of d_f is associated to agglomerate that presents a uniform structure. These different laws are given in Table.2.1.

Evolution of the size of one agglomerate, with a initial size of $100\mu m$, predicted by these different laws are compared in Figure 2.5. The parameters of the laws have been chosen to obtain the same final radius with each law after the same dimensionless time given by the product $\dot{\gamma}t$. We observe that the law of Kao and Mason predicts an increase of the rate of erosion with the decrease of the agglomerate size. While Rwei et al., Bohin et al. and Scurati et al. defined a law where the rate of erosion decreases when the agglomerate size decreases. Finally, a linear evolution of the radius is given by the law of Powell and Mason. These laws do not provide the same evolution of the agglomerate size because the couple "agglomerates - matrix" used in experiments to determine those laws are different. Kao and Mason studied the evolution of polymethylmethacrylate sphere in a silicon oil (10 Pas^{-1}), while Powell and Mason used a polystyrene sphere. Rwei and al. used cohesive agglomerates in a PDMS oil with a viscosity between 30 to 600 Pas^{-1} and Bohin et al. observed the behavior of high porosity silica in a matrix of polydimethylsiloxane (PDMS) with a viscosity between 30 to 60 Pas^{-1} . Finally, Scurati et al. investigated the behavior of cohesive silica in the same matrix of PDMS.

In 2004, Collin et al. determined experimentally a kinetic law, derived from the kinetic law of Kao and Mason, to predict the evolution of cohesive carbon black agglomerates in styrene butadiene rubber. They show erosion is only observed if shear stress exceeds

kinetic law for erosion mechanism		
Kao and Mason (1975)	$\frac{dR}{dt} = -\frac{k\dot{\gamma}}{3R^2}$	k is a material constant.
Powell and Mason (1982)	$\frac{dR}{dt} = -kb\eta\dot{\gamma}$	k is a material constant, η is the viscosity, b is the size of the eroded fragment.
Rwei et al. (1991)	$\frac{dR}{dt} = Rk\dot{\gamma}$	k is a material constant.
Bohin et al. (1996)	$\frac{dR}{dt} = K(\beta F_H - F_{coh})$ where $F_H = \frac{5\eta\dot{\gamma}R^2}{2}$	F_H is the hydrodynamics force, F_{coh} is the cohesive force, K is a factor related to agglomerate structure, β is the fraction of hydrodynamics force that bears on the fragment.
Scurati et al. (2002)	$\frac{dR}{dt} = \frac{-k\pi\sin^2\Psi_0\dot{\gamma}\sigma_c}{\left\{ \frac{5\lambda\eta\dot{\gamma}R^2}{\sigma_c} - R^{d_f-1} \right\}}$ $= -K_1R^2 \quad \text{if } d_f = 3$	k is material constant, σ_c is cohesive stress, λ characterized the kind of flow considered, R_0 is the initial radius, d_f is the fractal dimension of agglomerate (equal to 3 for uniform structure and less than 3 for nonuniform structure) η is the viscosity, Ψ_0 is the size of spherical gap to be detached.

Table 2.1: Different kinetic laws are presented in the literature to predict the size evolution of the agglomerates due to erosion. The material constant k has not the same value in all the laws.

a critical value τ_c . Moreover, erosion rate increases with shear stress. The value of τ_c is independent of the initial size of the agglomerates but depends on the structure of the carbon black agglomerate. The kinetic law reads :

$$\frac{dR}{dt} = \begin{cases} -\frac{\alpha(\tau - \tau_c)\dot{\gamma}}{3R^2} & \text{if } \tau > \tau_c, \\ 0 & \text{if } \tau \leq \tau_c. \end{cases} \quad (2.1)$$

where R is the characteristic size of the agglomerate, t the time, α is a material constant, τ is the shear stress, τ_c is the critical shear stress and $\dot{\gamma}$ is the shear rate. If τ is lower than τ_c , agglomerates are not eroded. We give in Table 2.2 the couple of values (α, τ_c) for different kinds of carbon black agglomerates in a styrene-co-butadiene rubber. Collin et al. also show that erosion rate of agglomerates increases with the concentration of carbon black agglomerates in the matrix. Moreover, they observe that erosion rate is higher when the number of agglomerates in rubber increases or when the volume of each agglomerate is higher even if the mass concentration of carbon black is kept constant. The presence of the other agglomerates in the vicinity of one agglomerate modifies the shear stress acting on this agglomerate. Obviously, this observation is independent of the kinetic law considered.

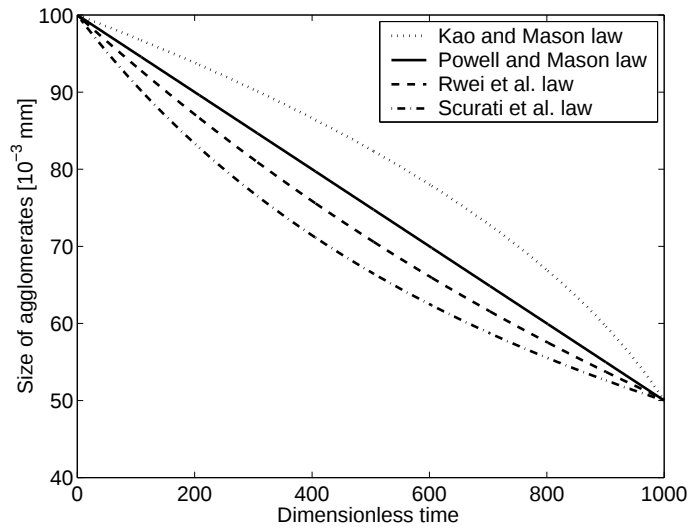


Figure 2.5: Evolution of the radius of an agglomerate vs. the dimensionless time ($\dot{\gamma}t$) predicted by different kinetic laws. The value of the material constants of the kinetic laws have been chosen to obtain the same radius after a dimensionless time equal to 1000.

Parameters of the erosion kinetic law proposed by Collin et al.		
Kind of carbon black	$\alpha (\mu m^3 Pa^{-1})$	$\tau_c (Pa)$
N234	$1.8e^{-5}$	71000
N347	$2.0e^{-5}$	65000
N326	$1.3e^{-5}$	72000

Table 2.2: Value of the different parameters of the kinetic law proposed by Collin et al. for the erosion mechanism of three kinds of agglomerate in styrene-co-butadiene rubber.

2.3 Infiltration of the agglomerates by rubber

Due to their porosity, the agglomerates can be totally or partially infiltrated by the matrix. Level of infiltration directly affects the cohesive stress of agglomerate and therefore erosion and rupture mechanisms. In 1994, Bohin et al. studied the infiltration of silica agglomerates by silicone polymers (Bohin et al,1994). They used silica agglomerates because the optical properties of this kind of agglomerate make easier the observation of the infiltration of silicone. Silica agglomerates become transparent with the infiltration of the silicone as illustrated in Figure 2.6. Phase contrast microscopy was the technique used to distinguish non-wetted and wetted regions of agglomerates (Stein et al,1969). Experiments of Bohin et al. show that the infiltration of the agglomerate by a Newtonian fluid is a gradual and homogeneous process. Such a process reinforces the link between silica aggregates if agglomerate is totally penetrated. Otherwise, agglomerate is weakened by the partial infiltration of the matrix. Li et al. (1994) explain this effect by a reorganisation of the structure at the periphery of agglomerate surface due to the infiltration. This reorganisation decreases the agglomerate strength. Yamada et al. (1994 and 1998) propose a model to explain this behavior. This model is based on two typical distances : the depth at which matrix is infiltrated in the agglomerate δ and the depth at which shear rate field is transmitted within agglomerate L_p . If δ is larger than L_p , the infiltration of agglomerate by matrix increases the agglomerate strength. If δ is smaller than L_p , matrix only reinforces a small part of agglomerate. Eroded fragments have then the size of the infiltrated layer of agglomerate. They are bigger than typical fragments eroded without infiltration of the matrix.

Kinetic law of the infiltration process of agglomerate by a newtonian fluid was deter-

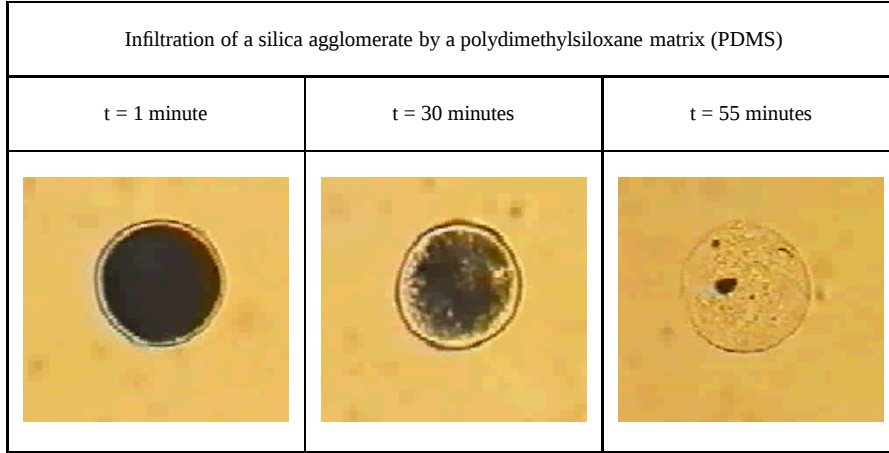


Figure 2.6: Infiltration of a silica agglomerate by a matrix (with the courtesy of Cemef-Ecoles des Mines de Paris). Agglomerate becomes transparent due to the modification of its optical properties by the infiltration of the polydimethylsiloxane (PDMS).

mined by Bohin et al. (Bohin et al,1994). This kinetic law reads :

$$2 \left(\frac{R}{R_0} \right)^3 - 3 \left(\frac{R}{R_0} \right)^2 + 1 = \frac{36 D_p \varepsilon^2 \gamma_v \cos \theta}{150 \eta R_0^2 (1 - \varepsilon)} t$$

where R is the radius of the non-wetted core of the agglomerate, R_0 is the radius of the agglomerate, D_p is the mean aggregate size, ε is the porosity, γ_v is the liquid vapor surface tension, η is the viscosity and θ is the contact angle. This law is based on the equation of Blake-Kozeny (Bird et al,1960) that allows to calculate the superficial velocity of a fluid into a packed bed of porosity ε in laminar regime. The time to obtain a total infiltration of fluid into agglomerate is obtained when $R = 0$,

$$t_{max} = \frac{150 \eta R_0^2 (1 - \varepsilon)}{36 D_p \varepsilon^2 \gamma_v \cos \theta}$$

It clearly appears that the speed of the infiltration process increases with the increase of porosity, of mean aggregate size and of liquid vapor tension surface of the fluid. Smaller viscosity makes also easier the infiltration of agglomerate by the fluid. We illustrate in Figure 2.7 the evolution of the radius of the non-wetted core of the agglomerate. The ratio $\frac{R}{R_0}$ decreases exponentially with the dimensionless time $\frac{t}{t_{max}}$.

More recently, the effect of the infiltration of the agglomerate by an elastomer matrix was studied (Astruc et al,2004) (Collin,2004). Astruc et al. investigate the infiltration

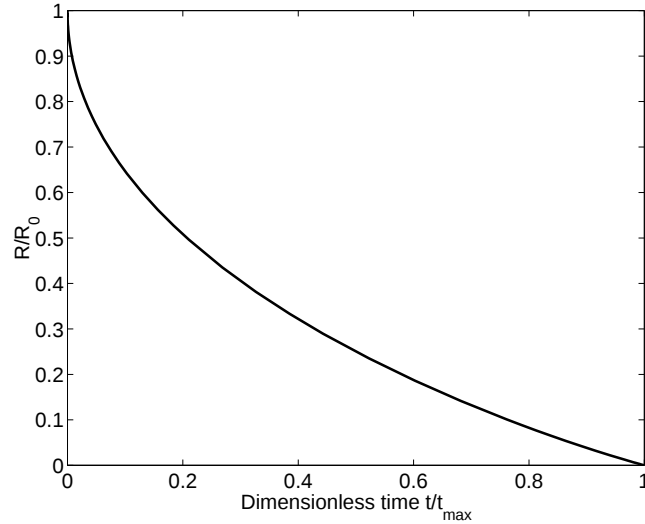


Figure 2.7: Evolution of the ratio between the radius of the non-wetted core of the agglomerate (R) and its initial size (R_0) vs. the dimensionless time of infiltration of the matrix in the agglomerate.

of silica agglomerates by styrene-co-butadiene rubber (SBR). Unlike to Newtonian matrix, the infiltration of the rubber matrix into the silica agglomerate is not homogeneous and does not start directly when matrix is in contact with agglomerate. Latent time before infiltration is observed and noted t_l . This latent time is equal to 17 hours with styrene-co-butadiene rubber. Moreover, it appears that the size of the wetted core of the agglomerate tends to a plateau for long time of infiltration. New time of infiltration $t_{infiltr}$, that corresponds to the time between the start of the infiltration t_r and the start of the plateau, is defined. Those different times are illustrated in Figure 2.8. kinetic law for the infiltration mechanism defined by Bohin et al. does not allow to correctly predict all the process of infiltration with elastomer matrix. This law does not reproduce the latent time before infiltration and the start of the plateau. Nevertheless, if we replace the time t by the ratio $\frac{t-t_l}{t_{infiltr}}$, the kinetic law well predicts the kinetic of infiltration between the times t_l and $t_{infiltr}$. We give in Table 2.3, the value of those different times for an agglomerate of $45\mu m$ penetrated by a styrene-co-butadiene rubber.

Different studies of the infiltration mechanism allows us to conclude that silica or carbon black agglomerates can be penetrated by rubber matrix and this modifies the

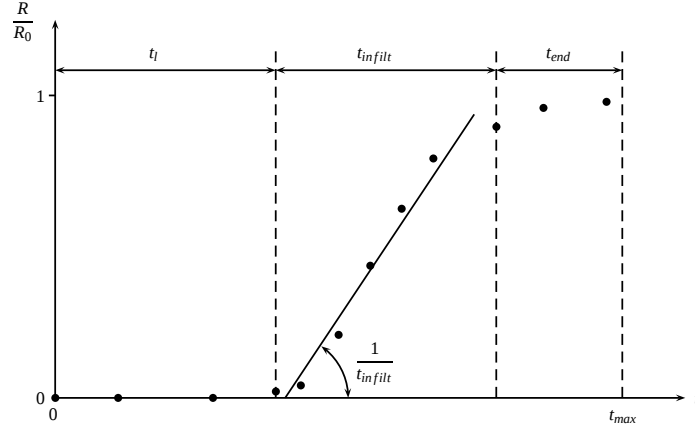


Figure 2.8: Latent time (t_l), infiltration time ($t_{infiltr}$) and maximum time (t_{max}) for the infiltration of agglomerates by a rubber matrix. Circle marks are the experimental data and solid line is the evolution of the infiltration predicted by the kinetic law of Bohin et al.

agglomerate cohesion. But it also appears that infiltration is a slow mechanism with respect to the typical mixing time. Only very small agglomerates are affected by this mechanism during mixing. It therefore seems relevant to neglect this effect in the modeling approach of the dispersive mixing of carbon black agglomerate in internal batch mixers.

In conclusion, the study of those different mechanisms show us the key parameters that influence the evolution of the size of the agglomerates. In our modelling approach, we will only focus on both mechanisms : erosion and rupture. Impregnation of carbon black by rubber matrix is neglected because this process is very slow. Erosion rate of a given agglomerate depends on its structure, on its surface area and on the characteristic of the flow. The choice of the appropriate kinetic law to predict the evolution of the agglomerates size is therefore not a trivial task. Rupture mechanism is only observed if the stress acting on agglomerate exceeds a critical value that only depends on the size of the agglomerate and not on its bulkiness or on its surface area (Collin,2004). These observations are used to build a new model to predict the size evolution of a distribution of agglomerates in complex flows.

Latent time and penetration time for the styrene-co-butadiene into silica agglomerate.	
Times	SBR matrix
Latent time t_r Penetration time $t_{infiltr}$	$\approx 17h$ $\approx 27h$

Table 2.3: Value of the latent time and penetration time of the styrene-co-butadiene into a silica agglomerate of $45\mu m$ (data obtained by Cemef group (Collin,2004)).