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DÉPARTEMENT DE MÉCANIQUE

MATHEMATICAL MODELLING AND SIMULATION OF DISPERSIVE MIXING.

THÈSE PRÉSENTÉE PAR

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EN VUE DE L'OBTENTION DU GRADE DE
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"Douter de tout ou tout croire sont deux solutions également commodes, qui l’une et l’autre nous dispensent de réfléchir." (Henri Poincaré)

Thanks !

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Contents

Introduction

The simulation of the dispersion of fillers in a flow field is a challenge for industrial and academic researchers. Fillers, as carbon black, are introduced in rubber parts designed to operate under extreme conditions (aerospace, offshore applications, ...) to increase their mechanical resistance. Typically, carbon black fillers are incorporated into rubber to improve the wear of the tires. These fillers improve the rubber properties only if they are thoroughly distributed within the matrix and if they are broken up into sub-micron particles that reinforce the rubber. Unfortunately, all present mixes still contain fillers larger than this size. These fillers can be at the origin of flaws that decrease the lifetime and the reliability of the rubber part. Improving the mixing performance of the batch mixer to blend the fillers with rubber would certainely yield a decrease in the number of these flaws. As a consequence, the rubber consumption and the amount of waste would decrease. One way to improve the quality of the mix consist in increasing the mixing time but this trivial solution is clearly not the most efficient approach in terms of consumption of energy.

Improving the performance of the internal batch mixer requires to understand the effect of the mixer design on the mechanisms that govern the dispersive and the distributive mixing. The dispersive mixing consists in breaking the fillers into the smallest entities that compose it. The distributive mixing aims to homogenizing this mix by distributing the fillers into the matrix. The effects of the rotor design on the mixing can be experimentally evaluated but these techniques are expensive, time consuming and only provide partial information. The numerical simulation is therefore a promising tool to study such a process because it allows for obtaining all the local information at any position in the mixer. Of course, those data are related to a mathematical model that is only an approximation to reality. Nevertheless, several authors have already shown the efficiency of such an approach. Numerical simulation is then used as a virtual laboratory in which a large number of experiments can be performed in a short period of time and at a limited cost.

The objective of this work is to develop a model that will evaluate the dispersive mixing efficiency of different configurations of internal batch mixer by the numerical simulation. This model has to be able to predict the evolution of the fillers size during the mixing by taking into account the main mechanisms that governs the dispersion. The fillers considered here are carbon black agglomerates. As the number of agglomerates in such a mix is very large, we represent them by a distribution that provides the mass density of agglomerates of any size at any point of the mixer chamber. The evolution of this mass density distribution will then be predicted by the model. It is important that this information be easily compared to the information obtained experimentally. Finally, we would like to build a model as a good compromise between simplicity and physical reality.

Our model is developed from the experimental results obtained on the dispersion of carbon black agglomerates in Newtonian and non-Newtonian matrices by the Cemef-Ecoles des Mines de Paris and from the literature. Typically, we distinguish different mechanisms that govern the carbon black dispersion. The contribution of all these mechanisms to the decreasing in agglomerate size is analyzed. The quality of our dispersive model is evaluated by comparing experimental to numerical results. The experimental results are obtained by mixing carbon black agglomerates in styrene-co-butadiene rubber matrix in a Mooney rheometer and by measuring the mass density evolution of agglomerates of each size with a specific optical device. This evolution is then compared to our model prediction.

Finally, this model is used to predict the evolution of a given mass density distribution of carbon black agglomerates in two different mixer configurations. Three-dimensional transient flow of the rubber-carbon black mix in the mixer chamber is calculated with a finite element software dedicated to highly viscous flows: POLYFLOW. This software provides the velocity, pressure and shear rate fields in the whole mixer chamber. The evolution of the mass density distribution is then calculated with our model along the trajectories of a set of material points randomly launched in the mixer chamber. At each trajectory is associated a mass density distribution. The comparison of the evolution of these mass density distributions between both configurations permits to determine which mixers are the most efficient in dispersing carbon black agglomerates. At the same time, the distributive mixing efficiency of both mixers is evaluated by comparing the distribution of a set of material points, initially located between the rotors, in the whole mixer chamber.

The presentation of the state of the art is composed of two chapters. First, we present the internal batch mixer and the evolution of its design from 1880 up to now. Different experimental techniques used to evaluate the mixing efficiency of these mixers are also described. The modification of the property of the rubber matrix by the incorporation of the carbon black agglomerates is investigated and the different experimental devices used in this work to obtain information on the dispersion process are finally presented. In the second chapter, the different mechanisms that govern the evolution of the size of the carbon black agglomerates in a Newtonian or non-Newtonian flows are explained in details.

This thesis has been performed in the frame of an European project called Rotor Project. We have worked in collaboration with seven partners : Michelin, Fluent, Cemef (Ecoles des Mines de Paris), ThyssenKrupp ElastomerTechnic Gmbh, Snecma Propulsion Solide, TUL (Technical University of Lodz) and TechPro. The goal of this project was to design a new rotor with the help of numerical simulation to improve the performance of the actual mixer by 5% without increasing dramatically the energy consumption. Numerical simulations have been used to evaluate the mixing performance of different designs of rotors. A new kind of rotors, which meets the objectives of the project, has been built.

Conferences and publications

Finally, I presented the results of my work at several conferences and in one journal :

- Alsteens, B., Legat, V., Avalosse, Th., Marchal, Th., *Parametric Study of Mixing Efficiency in a Kneading Block Section of Twin-Screw Extruder*, Proceedings of the 60th Annual Conference of the Society of Plastic Eng. (ANTEC), Vol. I, p.194, 2001.

- Alsteens, B., Legat, V., *A Model for the Disagglomeration of Carbon Black in Rubber Matrix*, Proceedings of the 6th Conference Eurheo, p.269, 2002.

- Alsteens, B., Avalosse, Th., Marchand, Y., Slachmuylders, E., *Effect of the full-slip condition along rotors on the mixing efficiency of internal mixers*, Proceedings of the 62th Annual Conference of the Society of Plastic Eng. (ANTEC), p.173, 2003.

- Alsteens, B., Legat, V., *A model for the disagglomeration of Carbon black*, Proceedings of the 6th National Congress on Theoretical an Applied Mechanics, Ghent (Belgium), 123, 2003.

- Alsteens, B., Legat, V., *Modeling the Disagglomeration of Carbon Black in Rubber Mixes*, Proceedings of the Europe/Africa Meeting of Polymer Processing Society (PPS), Athens (Greece), Keynote lecture 109 of the CD PPS Europe-Africa Meeting, 2003.

- Alsteens, B., Legat, V., *Model for the disagglomeration of carbon black agglomerates in batch mixer*, Proceedings of the South America Meeting of Polymer Processing Society (PPS), Florianopolis (Brazil), p.209, 2004.
- Alsteens, B., Legat, V., *Mathematical Models for Erosion and Rupture in Dispersive Mixing*, Proceedings of Int. Conf. of European Rubber Research - Pratical Improvements of the Mixing Process, p. 243, 2005.
- Avalosse, Th., Alsteens, B., Legat, V., *Rotor Shape Design by Numerical Simulation : a New Way to Improve Dispersive and Distributive Mixing in Batch Mixers*, Proceedings of Int. Conf. of European Rubber Research - Pratical Improvements of the Mixing Process, p. 256, 2005.
- Alsteens, B., Legat, V., Avalosse, Th., *Parametric study of the mixing efficiency in a kneading block section of a twin-screw extruder*, International Polymer Processing Journal, Vol XIX, Issue 3, p.207, 2005.

Chapter 1

Reinforcement of rubber by carbon black fillers

Rubber is a common material used in a large scale of applications from simple door tap for automotive applications to complex technical rubber parts for aerospace applications. In tire industry, rubber is the major component of tire tread. Several additives (anti-oxydants, vulcanizating agent, UV stabilizers, lubricants, . . .) and fillers (carbon black, silica) are added to rubber to improve its properties as its wear. Improvement of the rubber properties directly depends on the mixing efficiency of the internal batch mixer used to mix all components.

1.1 Internal batch mixer

Internal batch mixers are mainly used to mix products, as rubber or polyvinyl chloride, that are very difficult to pelletize or powder economically. These products cannot be mixed with different additives and fillers in a continuous process as an extruder. Internal batch mixers play a major role in the production of tires or technical rubber parts. In tire sector, internal batch mixers are used in all stages of mixing : mastication, masterbatch mixing (mixing with carbon black) and final mixing. The volume batch is between 240 and 620 liters. In technical rubber part sector, they are used to produce polymer blend of plastic and rubber (car bumpers) and to mix rubber with polymer gels or fillers. The volume batch is here smaller than for tire industry (50 to 200

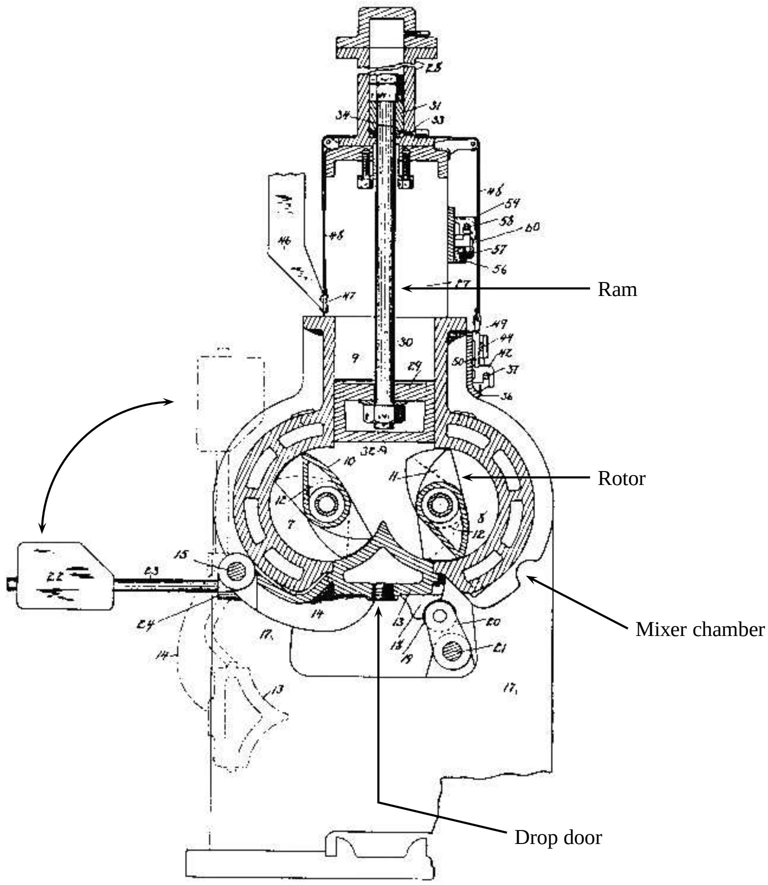
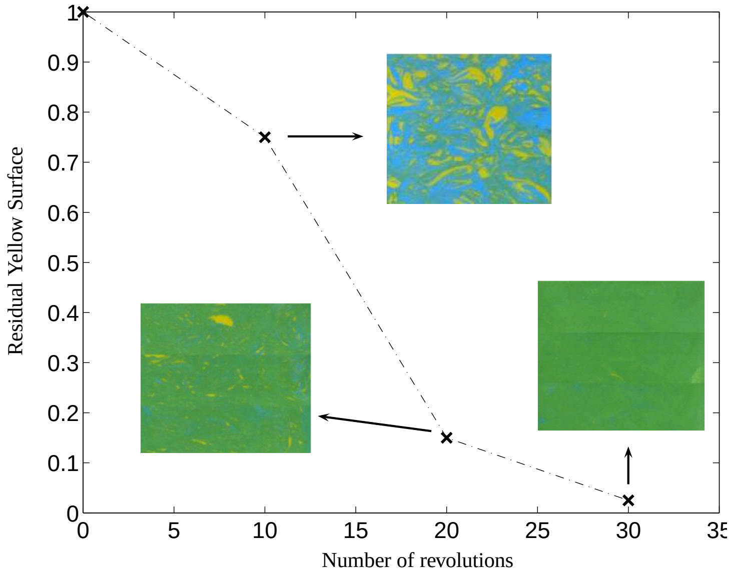


Figure 1.1: Inside view of internal batch mixer where we can see the mixer chamber, the rotors, the drop door and the ram (Drawing extracted from the book "Rubber Processing : Technology - Materials - Principles" (White,1995)).

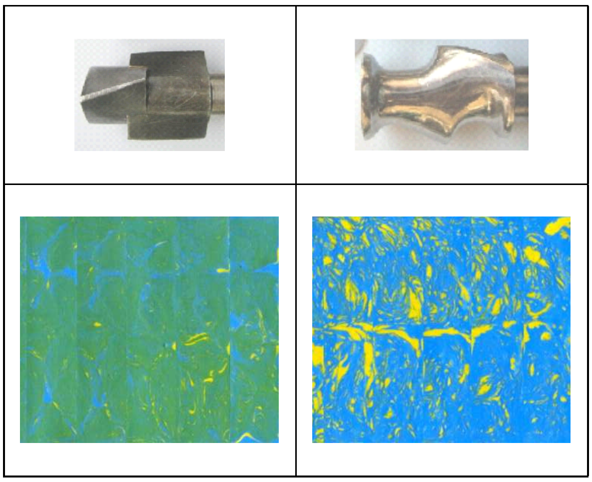
liters). Internal batch mixers are more efficient than continuous mixer to reach a high level of dispersion because the mixing time is longer and the shear stress is higher. As illustrated in Figure 1.1, this mixer is composed of a chamber in which are located two rotors that have a counter-rotating motion. At the start of the mixing, rubber and fillers or additives are pushed in the chamber by the ram located over the chamber. These products are then mixed during a given time and are discharged by the drop door located below the chamber.

Experimental and numerical investigations were performed to understand the effect of the mixer design on its mixing performance. Mixing process has firstly been studied by different static visualization techniques (Manas et al,1994). Information on the flow directions are obtained by curing rubber in mixer chamber. Rubber is then extracted of mixer chamber and unrolled to obtain a sheet of rubber. Main flow directions and stagnation regions are easily identified on this sheet. Stagnation regions are regions in the mixer that do not participate to the mixing. These regions can be filled by air or by one mix component. Mixing efficiency of the mixer is also investigated in mixing two components of different colors. Let us consider a mix with 70% of blue component and 30% of yellow component. Both components are introduced in the mixer, mixed and extracted of the mixer after a given mixing time. This mix is molded in a hexahedral mould and cut in several slices. Each slice is analyzed by a specific device to evaluate the size of yellow zones in the blue component. The smaller these zones, the better the mixing. We can observe in Figure 1.2a that mix becomes green after several revolutions of rotors. The size of yellow zones decreases progressively. In Figure 1.2b, we compare two mixes obtained with two kinds of rotors. Obviously, the second rotor is less efficient to mix both components than the first one. Unfortunately this technique only provides limited information on flow. Finally, the quality of fillers dispersion is measured with optical microscope, electron microscope or electrical conductivity techniques.

For a better understanding of the flow kinematics in mixer chamber, several research groups have worked on the development of on-line flow visualization techniques. Two mains techniques can be distinguished : mounting several sensors in the chamber or placing transparent windows on the mixer. Drawback of these techniques relative to static visualization is the complex modifications of mixers that they involve. In 1978, Freakley and Wan Idris visualize for the first time the distribution of pigmented silicon gums in a polymerics fluids by using specific transparent mixer chamber (Manas et al,1994) (Freakley et al,1978). Min et al. studied the flow of different rubbers and elastomers in internal batch mixer by similar technique (Min et al,1985). These investigations have showed that the flow in mixer dramatically influences the distributive and dispersive mixing efficiency. This flow depends on material considered, on temperature in the mixer chamber, on degree of filling and obviously on rotor and mixer chamber designs. Degree of mixer filling is the ratio between the volume



(a)



(b)

Figure 1.2: (a) Evolution of the residual yellow surface during the mixing of a yellow component (30%) in a blue component (70%). (b) Comparison of the residual yellow surface obtained when we mix these two components with two kinds of rotor during ten revolutions. These experimental results have been obtained by Michelin in a lab mixer.

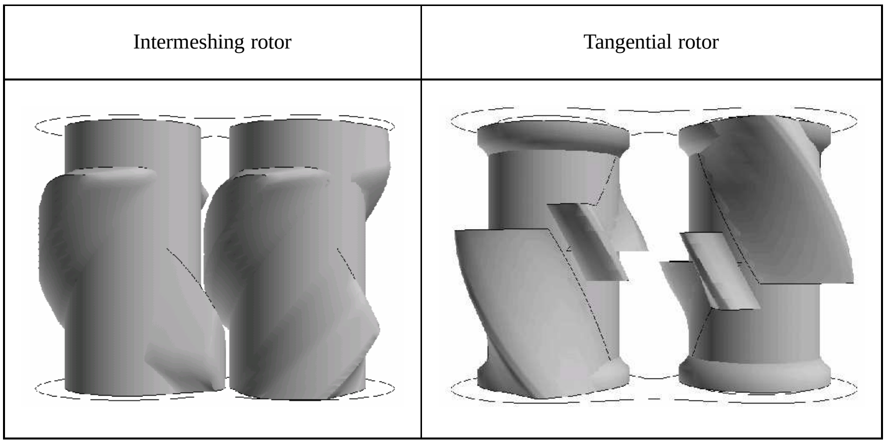
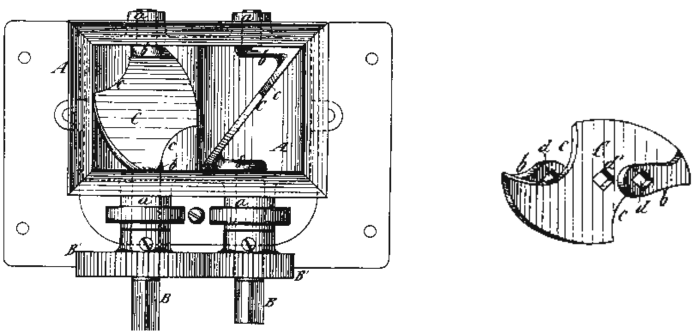


Figure 1.3: Pictures of intermeshing and tangential rotors.

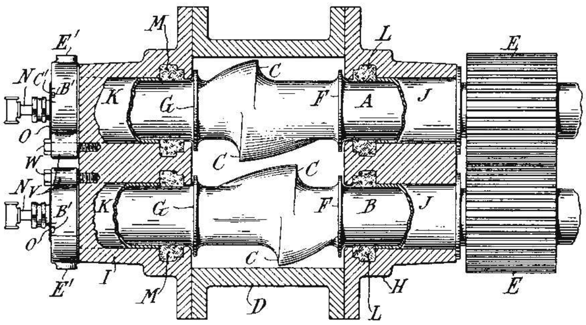
of material introduced in the mixer and the free volume of the mixer chamber. Free volume of the mixer chamber is obtained by subtracting the volume of rotors from the volume of the mixer chamber without rotors. Degree of mixer filling fluctuates between 0.6 and 0.85. It is not constant during the mixing due to the incorporation of fillers or additives into rubber. In 1983, Toki et al. put several sensors on the mixer chamber wall to obtain the pressure evolution in the mixer relative to the rotors position (Manas et al,1994). From this data, they estimated the flow rate along wings. In 1987, Freakley and Patel measured the temperature evolution in the mixing chamber with infrared sensors (Freakley et al,1987).

These visualization techniques are also used to inprove the understanding of the incorporation mechanism of carbon black in rubber (Min et al,1987). At low temperature, rubber is broken in several chunks due to tearing and stretching mechanisms during the mixing. In the same time, a given amount of carbon black can fall between rubber chunks and creates coating of carbon black on chunks. These chunks are compressed and sheared between rotors and walls of the chamber. Carbon black is then progressively incorporated in rubber. At higher temperature, the incorporation mechanism is slightly different because rubber becomes sticky and takes the shape of a continuous sheet that follows rotors motion. In such a case, carbon black is only incorporated in the surface of rubber sheet and not in depth. Distributive mixing is thus less efficient.

Let us now focus on the evolution of rotor design (White,1995). Two kinds of rotor are distinguished : the tangential rotors and the intermeshing rotors (Figure 1.3). Tangential rotors are used in applications where one needs high fill factor, short feed and discharge times and where temperature increase is not an issue. Intermeshing rotors



(a)



(b)

Figure 1.4: (a) Internal batch mixer designed by Pfeiderer in 1880 where rotors are two simple flat wings. (b) Banbury mixer designed by Banbury in 1931. (Drawings extracted from the book "Rubber Processing : Technology - Materials - Principles" (White,1995)).

are used to obtain high shear stress and for applications that need excellent volume to cooling surface ratio. First internal batch mixer with tangential rotors was built in 1876 by Pfeiderer. This mixer, without ram or drop door, is composed of two flat wings as illustrated in Figure 1.4a. In 1913, new generation of mixer is born : *the Banbury mixer*. This mixer, shown in Figure 1.4b, is very similar to mixer used now. It is equipped of a drop door and a ram to introduce rubber in the chamber. Rotor is not a simple flat wing, but a complex three dimensional device composed of two wings. Unrolled view of a two wings rotor and design parameters of the mixer are given in Figure 1.5. Characteristic distances of the mixer chamber are centerline distance (C_L), chamber length (L_{mixer}) and chamber radius (R_{mixer}). The shapes of the drop door and the ram are often complex and cannot be defined by a small number of parameters. Characteristic parameters of the rotor are the minimum and the maximum radius of the rotor (R_{rotor} and R_{wing} respectively), the rotor length (L), the number of wings, the position of these wings and their shapes. Wing position on the rotor is usually defined by three parameters : twist angle (α_1 and α_2), wing length (h_1 or l_1 and h_2 or l_2) and angular position (β_1 and β_2). As for the shape of drop door and ram, the shape of wing flank cannot be defined by a small set of typical distances due to their complexity. Finally, the gap between the wall chamber and the rotor is noted e and usually called clearance zone.

Shape of wings flank can be totally different between two rotors, as illustrated in Figure 1.6a, and can change along wing. All parameters affect axial flow along the wing and the transfer of material between left and right parts of the mixer chamber. The size of the clearance zone, e, also modifies the quality of dispersive mixing and the discharge temperature of mix. If we assume that the flow is incompressible, creeping, isothermal and two-dimensional, a simple calculation based on the usual Navier-Stokes equations provides an analytical expression of the maximum shear rate in the gap :

$$\dot{\gamma}_{max} = \frac{e\Delta P}{2\eta H} + \frac{\omega R_{wing}}{e}$$

where η is the constant viscosity, ΔP $(= p_2 - p_1)$ is the pressure drop across the gap, e is the size of the gap, H is the width of wing tip, R_{wing} is the radius of the rotor at the wing tip and ω is the angular velocity of the rotor. These dimensions are illustrated in Figure 1.6b. Flow in the mixer chamber is also modified by the roughness of surface rotor (Alsteens et al,2003). Transfer of power from rotors to fluid is less efficient when rubber slips along rotors. As a consequence, the rotors efficiency to generate a good distributive mixing decreases and material stretching in the flow is smaller. In 1992, Passoni has designed two wings rotor where all wings are cut in two independent parts. As illustrated in Figure 1.7, this new design modifies the main flow direction and increase the rotor mixing efficiency by a better material stretching between different parts of the wing.

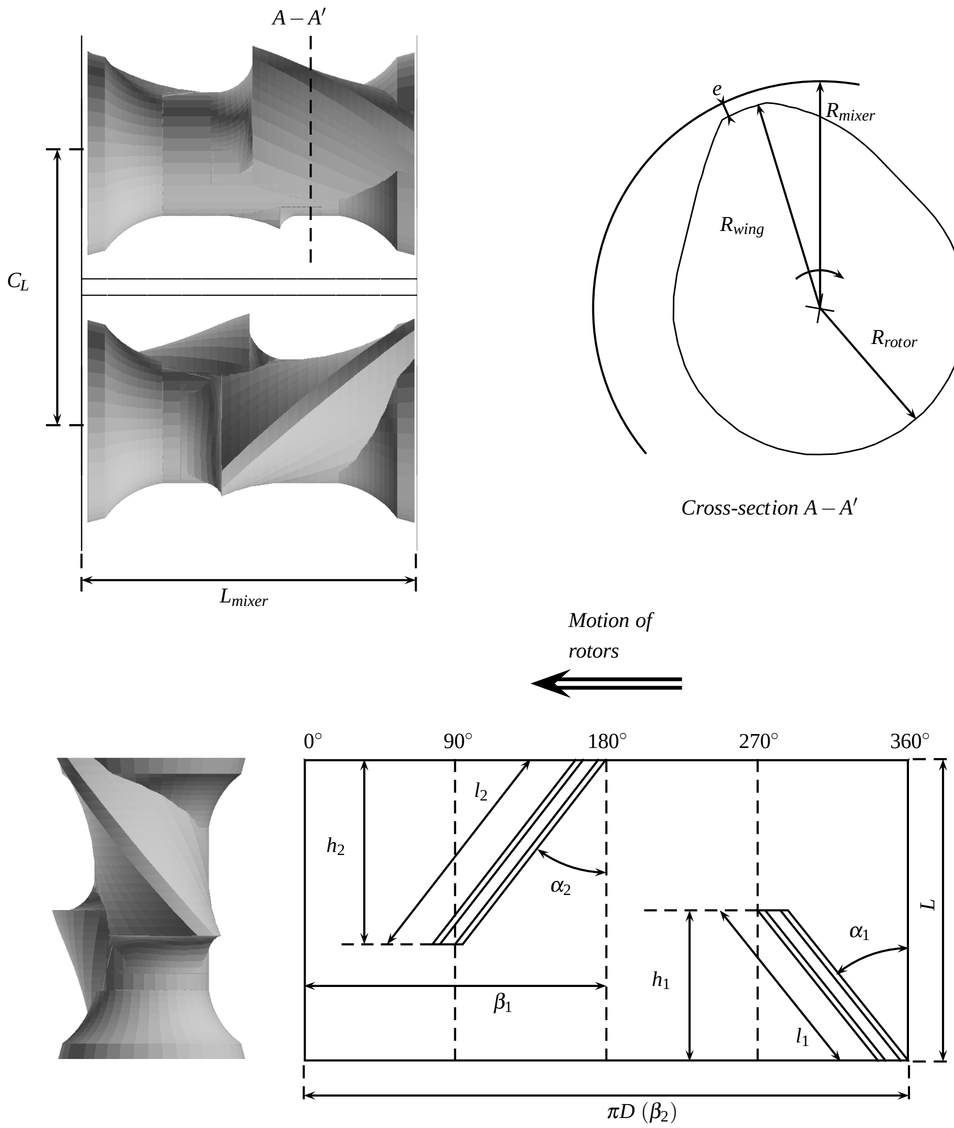


Figure 1.5: Characteristic distances of the mixer chamber and the unrolled view of a two wings rotor with the typical dimensions that define the position of the wings on the rotors.

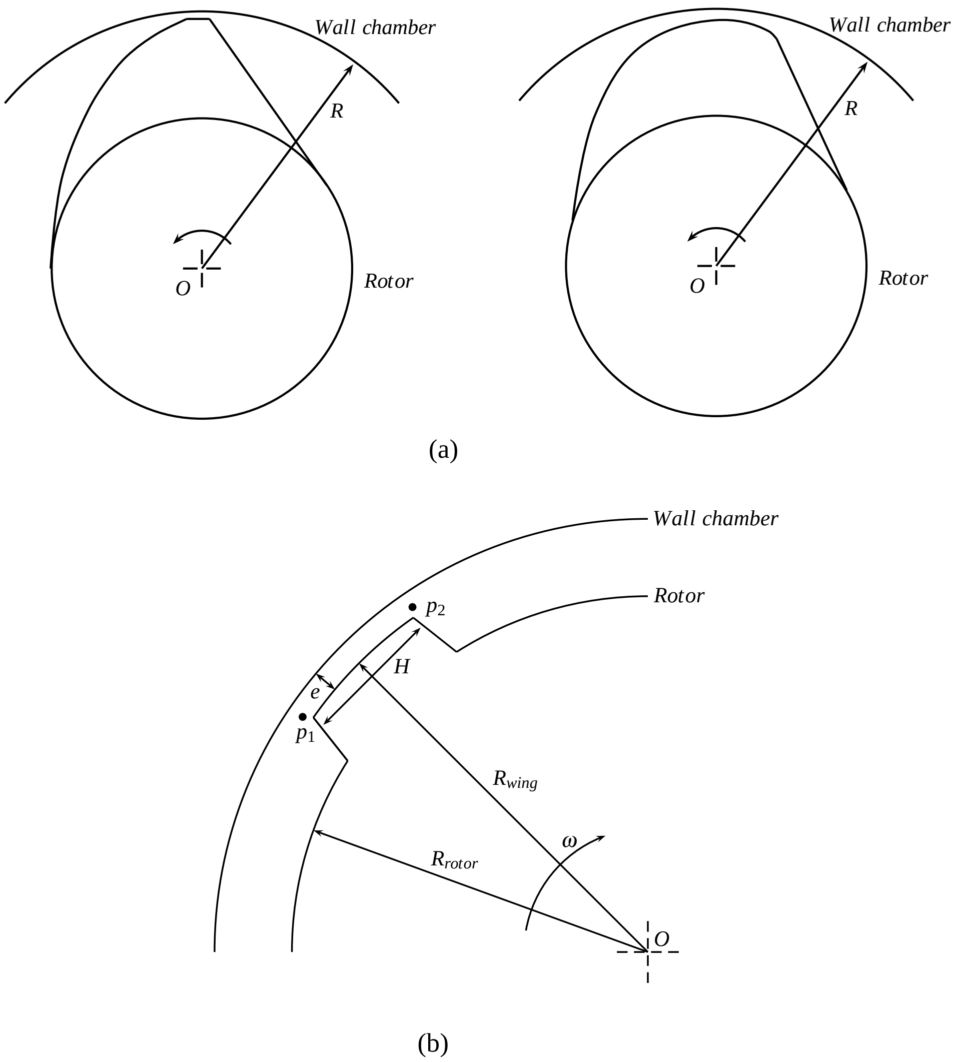


Figure 1.6: (a) Two different cross sections of rotor. (b) Characteristic distances of the rotor considered in the calculation of maximum shear rate.

Concurrently to the development of two wings rotor, several designs of four wings rotor have been imagined as shown in Figure 1.8. Usually, these rotors are composed of two long wings and two short wings. Position of these wings depends on the rotor : short wings can be located at one extremity of the rotor and long wings at the other extremity (Tyzon D.Z. and Comper L.F.) or long wings and short wings can be at the same extremity of the rotor (Nortey N.O.). In the *ZZ*2 rotor, long wings are located in the middle of the rotor and short wings are at its extremities. As for two wings rotor, Passoni proposed in 1992 a rotor where all wings are cut in several parts. In 2000, Inoue et al. have designed a rotor where each wing has a various twist angle. This variation of twist angle is smooth unlikely to the rotor proposed by Regalia and Lonate where wings have two distinct twist angles. Takakura et al. (1996) and Inoue et al. (1997) have also worked on six wings rotors that have a better mixing efficiency than four wings rotors. Rotor of Inoue et al. is particular because the gap along wing is not constant.

Large number of investigations have thus been performed on rotor design to increase their mixing performance. Nevertheless, we have to keep in mind that other parameters as degree of mixer filling, temperature evolution in the mixer, rheological behavior of the mix, velocity of the rotors, . . . affect the flow and therefore rotor mixing efficiency (Freakley et al,1978) (Freakley et al,1987). Unfortunately, mixing efficiency of present batch mixers are not sufficient to well disperse carbon black in rubber. Finally, we have to be careful in the comparison of mixing performance of different kinds of rotor because volume of four or six wings rotor are larger than volume of two wings rotor. The amount of rubber mixes during one step of mixing with this mixer is therefore smaller than with two wings rotor. Even if the mixing efficiency of six wings rotor is higher than the mixing efficiency of two wings rotor, the ratio between the volume of material mixed, the level of dispersion reached and the consumption of energy could be better with two wings rotor.

1.2 Rubber, carbon black and mixing

Natural rubber is an elastic hydrocarbon polymer which occurs as a milky emulsion (known as latex) in the sap of a number of plants. Para rubber tree, Hevea brasiliensis (Euphorbiaceae), has been the major source of latex used for the fabrication of rubber. Today, over half of rubber used is synthetic, but several million tons of natural rubber are still produced annually. Natural rubber needs to be vulcanized to improve its resilience and elasticity. In this work, we focus on one synthetic rubber : the styrene-co-butadiene rubber (SBR). Molecular structure of such an elastomer can be imagined as a big "spaghetti" composed of a large amount of cross-linked polymer chains. The formulation of monomere that composed these chains are given in Figure 1.9. Under

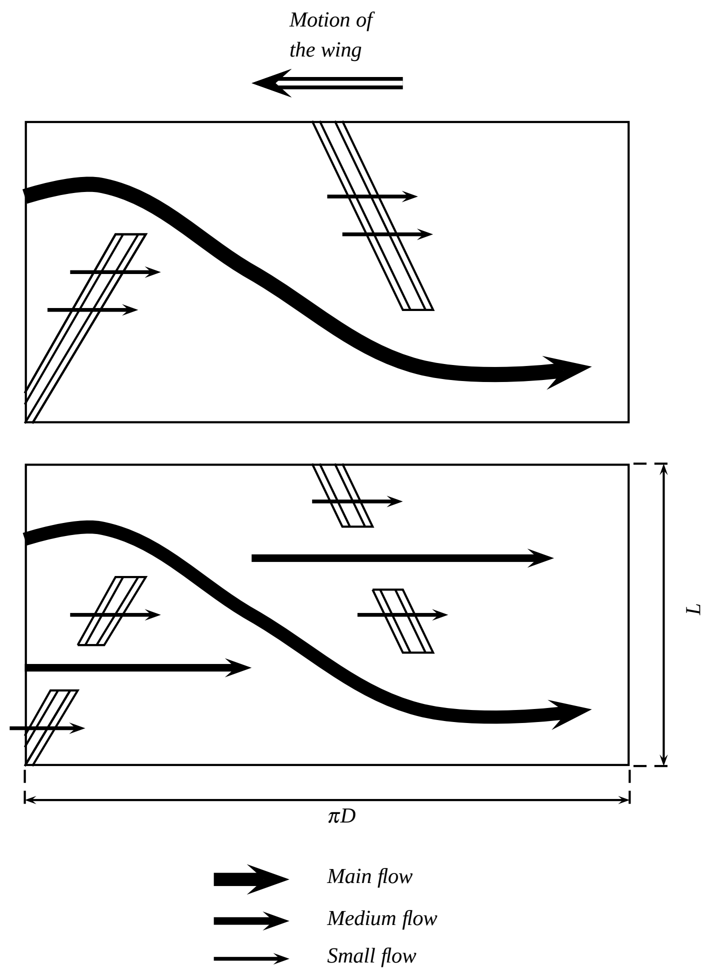


Figure 1.7: Comparison between flows generated by simple two wings rotors and by two wings rotor where all wings are divided in two independent parts.

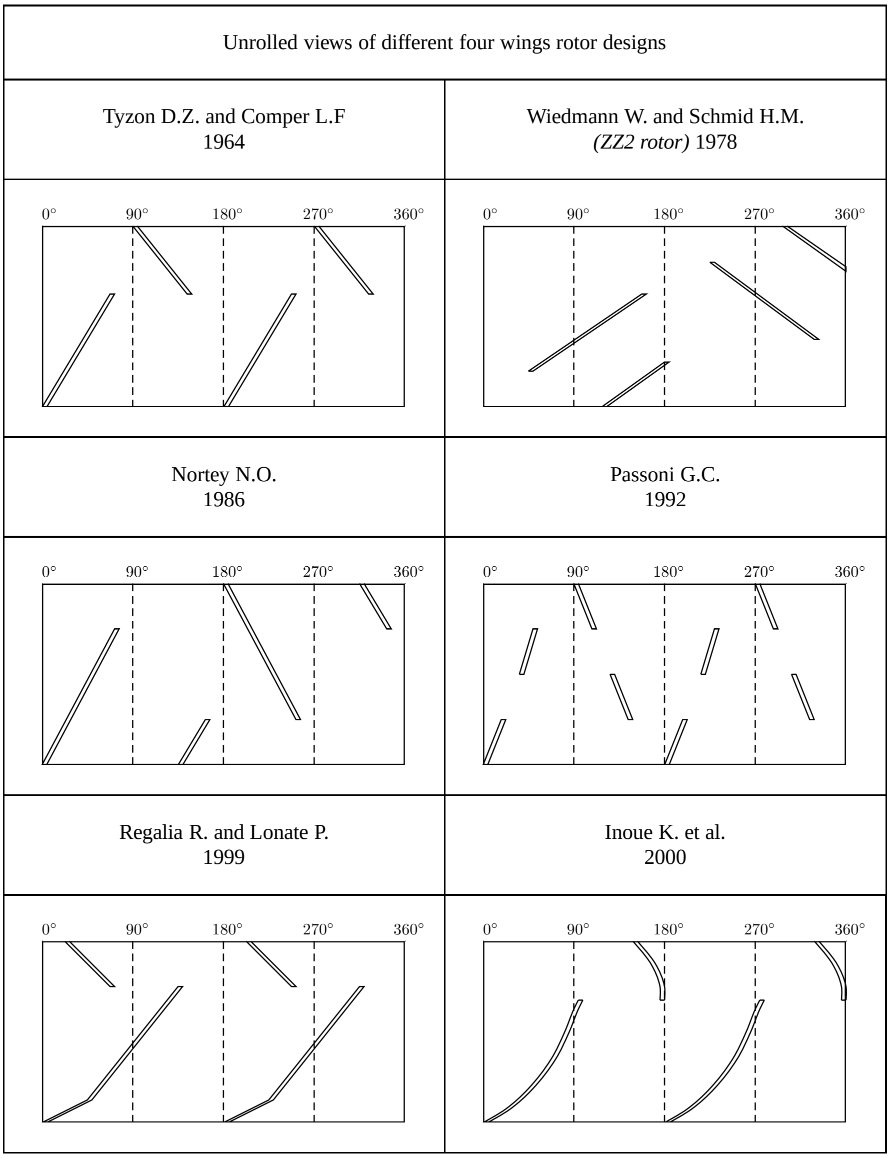


Figure 1.8: Evolution of four wings rotor design since 1964 until now.

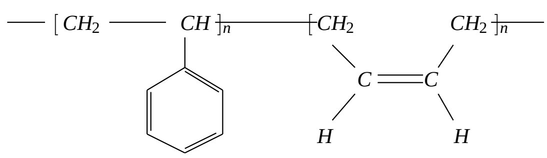


Figure 1.9: Monomere that composes the chains of styrene-co-butadiene rubber.

glass transition temperature T_g ($\approx -58°C$), these polymer chains cannot move and rubber is hard and brittle. Otherwise rubber is elastic. Density and molecular weight of the styrene-co-butadiene rubber are given in Table 1.1. Typical size of the statistical coil of these molecules is around 50 *nm*.

Property of styrene-co-butadiene rubber and butadiene rubber	
Property	styrene-co-butadiene rubber
Density ($\frac{kg}{m^3}$)	938
Molecular weight ($\frac{g}{mol}$)	210000

Table 1.1: Density and molecular weight of styrene-co-butadiene rubber.

Carbon black is one of the most reinforcing fillers for rubber. It is generally obtained by oil furnace process. In this process, a spray of aromatic liquid hydrocarbon feedstock is heated and injected into combustion zone of specific furnace. Aromatic liquid is decomposed to form carbon black. Hot smoke, in which are located carbon black particles, is cooled by passing through heat exchangers and direct water sprays. Filter is finally used to separate black from gaz stream (Manas et al,1994). Different entities are distinguished during this process. Initial droplets of liquid have a size around 2*nm* to 20*nm*. During this process, the droplets progressively generate solid particles that fuse to obtain aggregates with a size around 50*nm* as illustrated in Figure 1.10. A new entity called agglomerate is then obtained by the grouping of aggregates. Typical size of an agglomerate is between $1\mu m$ to $200\mu m$ and its cohesion is mainly due to Van der Waals force existing between aggregates. We can remark that agglomerates size of

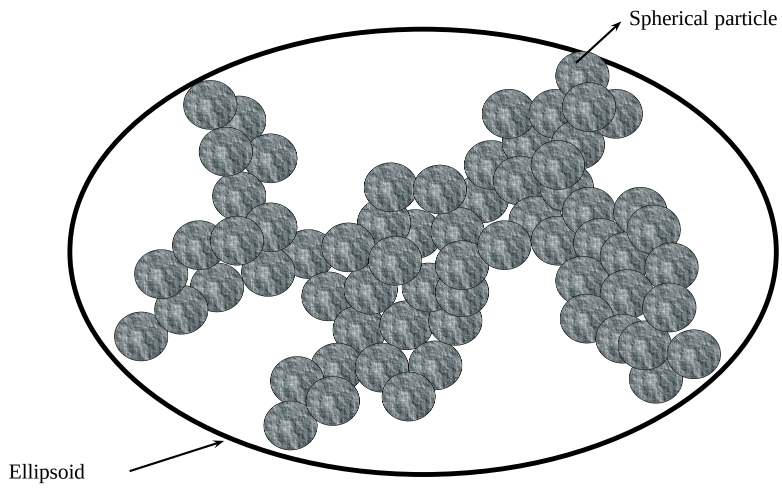


Figure 1.10: Aggregate structure and ellipsoid that represents the effective volume filled by aggregates.

carbon black is larger than statistical coil size of rubber. Pellets of carbon black, with a size around $0.3 - 1mm$, are finally created from these agglomerates with the help of pelletizers. Density of pellets is around $1950\frac{kg}{m^3}$.

Typically, the mixing of rubber with carbon black fillers can be divided in two main steps: incorporation and dispersion. In a first step, the carbon black pellets are incorporated in the rubber matrix and broken up in agglomerates of various sizes. In a second step, these agglomerates are mixed with rubber and their sizes decrease progressively. Two different mixing are distinguished during this second step : distributive and dispersive mixing. On one hand, distributive mixing consists of creating a flow kinematics that provides uniform concentration of agglomerates in rubber. Efficiency of the flow to mix agglomerates with rubber directly depends on the design of the mixer chambers, on the rotors and on the operating conditions. One of the criteria to obtain a good distributive mixing is to create a flow that does not present stagnation zones and in which the exchange of material between the left and right parts of the mixer chambers is high. On the other hand, the dispersive mixing consists of breaking agglomerates into particles of the smallest size as possible. Smaller these particles, better the effect of the carbon black on the rubber properties. The smallest particles obtained by dispersion are the aggregates. Both dispersive and distributive mixing can be achieved simultaneously, as in internal batch mixer, or in several steps. Bad dispersion or/and bad distribution of the carbon black agglomerates implies an irregular wear of the rubber part and some flaws that can cause failure.

Each aggregate of carbon black has unique shape and specific morphology. Major properties of aggregates are specific surface area and bulkiness or "structure" (Manas et al,1994). Specific surface area of aggregate is obtained by dividing its surface area by its weight. Surface area of aggregate is evaluated with a technique based on absorption of iodine by aggregates (ASTM). Bulkiness is the ratio between effective volume of aggregate (the volume of the ellipsoid that contains the whole aggregate) to its true volume that can be measured by immersion in a liquid. Nomenclature, called *ASTM*, is defined to rank different kinds of carbon black. For instance, all reinforcing carbon black used in tire treads and other applications requiring abrasion resistance are noted *Nabc* where the letter *N* denotes curing characteristic in sulfur-accelerator, number *a* indicates the range of surface area and the last two number *bc* are arbitrary. Interactions between rubber and carbon black depend on specific surface area, bulkiness and loading, but also on chemical interactions between polymer chains and rubber. We summarize in Table 1.2, the effect of these properties on styrene-co-butadiene rubber. We observe that carbon black with high surface area increases abrasion resistance, tensile strength, elastic modulus, viscosity and hardness of rubber but their incorporation and dispersion time in the rubber is longer. Incorporation time is the time needed by carbon black to be included within rubber matrix. Moreover hysteresis (the conversion of mechanical energy to heat) increases with surface area. Carbon black with a high bulkiness also increases abrasion resistance, hardness, viscosity and elastic modulus but slightly decreases tensile strength. Unlikely to specific surface area, increase of bulkiness implies a decrease of incorporation and dispersion time. Hysteresis of styrene-co-butadiene rubber is not affected by bulkiness. Finally, loading increase does not affect dispersion time, but increases incorporation time, hardness, elastic modulus, tensile strength, viscosity, hysteresis and abrasion resistance.

At the microscopic scale, interactions between aggregates and molecules of rubber create a network (Leblanc,1996) (Manas et al,1994). Three areas of elastomer can be distinguished around aggregates. First area is a thin layer of elastomer located around aggregates and strongly bound to aggregates. It approximatively represents 3% of the total mass of elastomer. Cotten et al. have observed that the amount of bound rubber increases with the time of mixing (Cotten,1984). Second layer, that represents 10% to 20% of the total mass of elastomer, is observed around aggregates. This layer is weakly bound to aggregates and is connected to other aggregates by small

Effect of surface Area, bulkiness and loading on the properties of the styrene-co-butadiene rubber			
Rubber Property	Higher surface area	Higher bulkiness	Higher loading
Processability			
Incorporation time	Slight increase	Decrease	Increase
Dispersion time	Increase	Decrease	Not important
Viscosity	Increase	Increase	Increase
Vulcanizate properties			
Hardness	Slight increase	Increase	Increase
Elastic Modulus	Increase a low strain amplitude	Increase	Increase
Hysteresis	Increase	Not important	Increase
Tensile strength	Increase	Slight decrease	Reaches maximum
Abrasion resistance	Increase	Increase at high severity	Reaches maximum

Table 1.2: Effect of surface area, bulkiness and loading on properties of styrene-co-butadiene rubber (Table extracted from the book "Mixing and Compounding of Polymer" (Manas et al,1994)).

filaments as illustrated in Figure 1.11. Carbon black with high surface area and bulkiness makes also stronger inter-aggregate associations and generates larger amount of bound rubber. These filaments create a network between aggregates that makes harder the motion of rubber molecule. The last area is the free rubber surrounding aggregates. Network is also at the origin of the increase of rubber slipping along the wall of the mixer chamber. This effect becomes important when mass fraction of carbon black exceeds 10% or 20%. Rubber close to the mixer wall is then dragged by the network motion.

Finally, shear thinning behavior of these two elastomers is also affected by reinforcing fillers as illustrated in Figure 1.12 for styrene-co-butadiene rubber. Higher the loading of carbon black, higher the shear viscosity. Moreover, Cotten and Thiel have shown

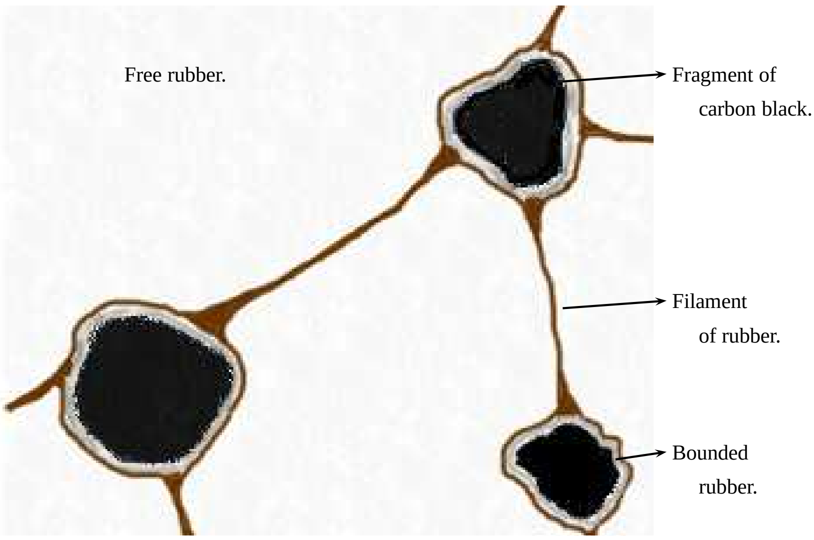


Figure 1.11: Network created by the interaction between carbon black aggregates and rubber (Picture drawed from the pictures found in the book "Rhélogie des élastomères et mise en forme des polymères." (Leblanc,1996)).

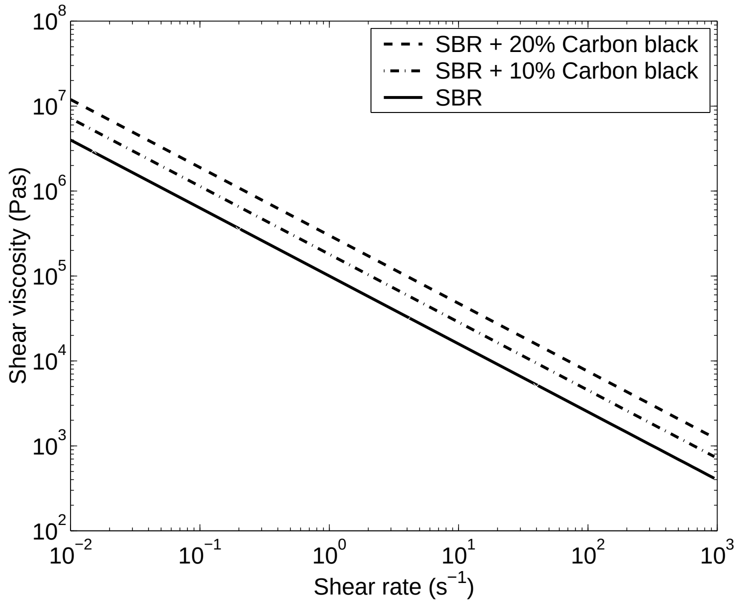


Figure 1.12: Evolution of the shear viscosity of the styrene-co-butadiene rubber (SBR) as a function of the volume fraction of carbon black (N220) (Data from the book "Rhélogie des élastomères et mise en forme des polymères." (Leblanc,1996)).

that the elongational viscosity increases with the increase of loading and bulkiness of carbon black (Cotten et al,1978). For the same level of loading, carbon black with a higher surface area also increases viscosity.

Different authors (Guth et al,1938) (Smit et al,1970) (Pliskin et al,1972) (White et al,1974) have tried to determine law that would provide the evolution of viscosity with the carbon black volume fraction in the matrix. All laws are empirical and their use is limited to the experimental conditions in which they have been determined. Moreover, they are only relevant for Newtonian flows. In consequence, they cannot be used in our application because mix rubber-carbon black presents a non-Newtonian behavior in the area of high shear rate as the gap in the mixer chamber. A review of these different laws is presented in Table 1.3.

This description of the interaction between carbon black and rubber has allowed us to understand that improvement of mechanical and physical properties of a given rubber depends on the kind of carbon black and on the level of dispersion of carbon black in the rubber matrix. Smaller the entities of carbon black, better the rubber reinforce-

Authors	Viscosity laws	Domains of application
Einstein theroy.	$\eta_{mix} = \eta_{poly}\,(1 + 2.5\phi)$	Relevant only for spherical loading in Newtonian flow.
Guth, Gold and Simha law (Guth et al,1938).	$\eta_{mix} = \eta_{poly}\,(1 + 2.5\phi + 2.5\phi^2)$	Relevant only for carbon black with a weak bulkiness in Newtonian flow.
Smith and van der Vegt law (Smit et al,1970).	$\eta_{mix} = \eta_{poly}\,(1 + f\phi)^3$	Relevant only for non reinforcing carbon black with a weak bulkiness in Newtonian flow.
Pliskin and Tokita law (Pliskin et al,1972).	$\eta_{mix} = \eta_{poly}\,(1 + \phi_{eff})^N$	Relevant only for Newtonian flow.
White and Crowder law (White et al,1974).	$\eta_{mix} = \eta_{poly}\,(1 + a_1\, f\phi + a_2\, f^2\phi^2)$	Relevant only for Newtonian flow.
Symbols :	η_{poly} is the Newtonian viscosity of polymer, η_{mix} is the viscosity of polymer-carbon black compound, ϕ is the volume fraction of carbon black, ϕ_{eff} is the volume fraction of carbon black plus the volume fraction of the bounded rubber, f is a shape factor for the asymmetry of the fillers, N is a parameter depending of the filler orientation, a_1 and a_2 are two empirical constants that depend on the studied system.	

Table 1.3: Several relations have been proposed by different authors to model the effect of the volume fraction of carbon black on rubber viscosity as a function of the matrix and carbon black considered.

ment by the creation of a large network. Mixing efficiency of internal batch mixer is therefore a key point of this process.

1.3 Experimental analysis

In this work, two experimental devices are used to evaluate and understand the dispersions mechanisms. Firstly, the evolution of a single agglomerate in simple shear flow is observed with a camera put on a microscope. These experiments are led by the Cemef group. With this device, it is possible to observe on-line the agglomerate dispersion and to measure its size evolution in time. Secondly, we evaluate in Michelin facilities, with the help of Véronique Collin, the state of dispersion of agglomerates contains in a rubber matrix after its mixing in a Mooney rheometer with a device called *dispergrader*.

Optical device used by Cemef group to observe dispersion mechanisms is composed of two transparent plates that have an opposite rotation; the velocity of the upper and lower plates determining the shear rate amplitude. Diameter of the plates and gap between both plates are equal to $40mm$ and $0.5mm$ respectively. Larger the velocity, larger the shear rate. Matrix with low concentration of carbon black agglomerates is introduced between these two plates and heated at $140^{\circ}C$. The evolution of agglomerates in the flow are observed with a microscope and recorded with the help of a camera located under the lower plate as illustrated in Figure 1.13. If the agglomerate is located at the half distance of the plates, it has only a rotating motion on itself. Otherwise the agglomerate rotates and moves with the flow and can leave the field of view of the camera. In such a case, the upper and lower plates velocities are adapted to limit the agglomerate motion. Evolution of the agglomerate size during the experiment is measured from the picture of this film with the help of specific software. The film is finally analyzed in detail to understand how and when the erosion and rupture mechanims occur. Those experiments are repeated with different kinds of carbon black agglomerates or silica in different matrices (Newtonian fluid or polymer). From these observations, law that provides the size evolution of a single agglomerate in a Newtonian or rubber matrix as a function of shear rate and time of mixing is identified. The different pictures that we use to illustrate the dispersion mechanisms in the next chapter are extracted from films obtained with this device by the Cemef group. More information on the experimental conditions of these experiments are available in Collin (Collin,2004).

Such a device is efficient to observe on-line evolution of single agglomerate in matrix but this does not provide information on the dispersion state of all agglomerates in

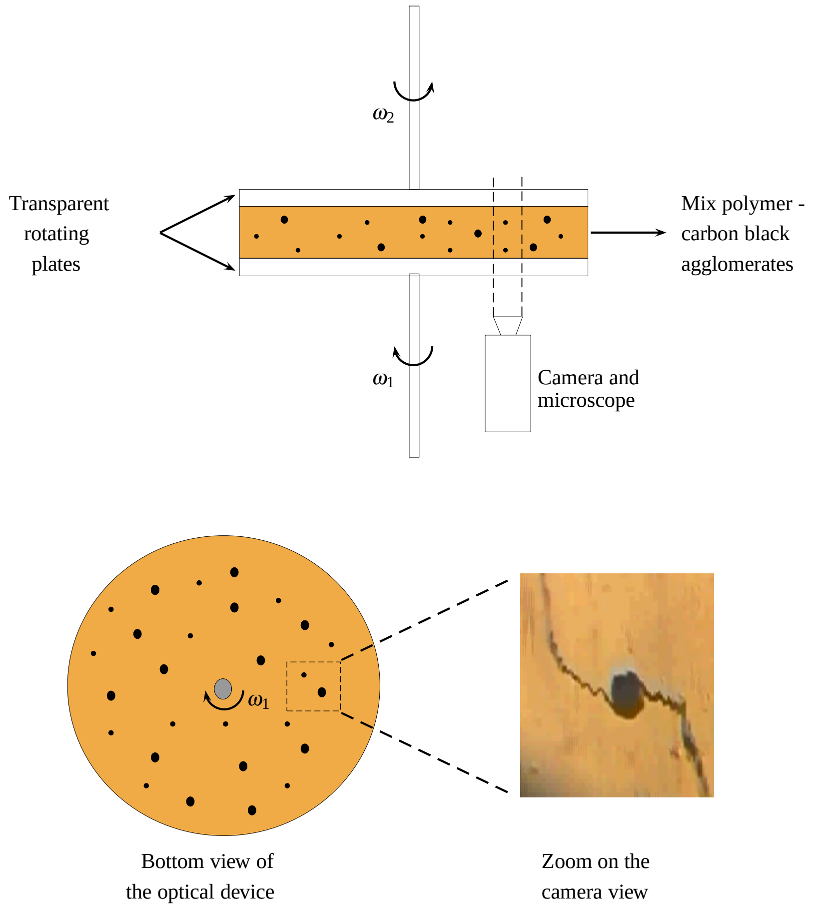


Figure 1.13: Optical device used by Cemef group to study the kinetic of erosion and rupture.

matrix. To obtain such information, we should measure the size of each agglomerate before and after mixing. It is unimaginable to make such a measure because mix rubber-carbon black contains too many agglomerates. As example, a volume of 1 mm^3 of typical mix rubber - carbon black contains roughly 2000 agglomerates with size of 50 μm if the mass fraction of carbon black in rubber is equal to 20%. Second device, the *dispergrader*, is therefore used to obtain this information. This device does not allow to visualize the evolution of each agglomerate during mixing. But, it measures the state of dispersion of a set of agglomerates in any sample of rubber-carbon black extracted from any mix rubber-carbon black. By repeating this measure on several samples of rubber-carbon black at different times of mixing, we obtain information on the evolution of the dispersion state of agglomerates during mixing. This device is used by industrials to evaluate the dispersion state of fillers as carbon black in rubber matrix in order to determine mixing efficiency of their mixing process. In this work, the *dispergrader* is used to measure the dispersion state of a mix carbon black agglomerates -rubber after different times of mixing in a Mooney rheometer. Such an evolution is compared to the prediction of our model to evaluate its quality. The Mooney rheometer is composed of one chamber in which a conical rotor is put. The rotation of the rotor in this chamber creates simple shear flow.

Basically, three techniques are used to evaluate the dispersion state of a mix : electrical, mechanical and optical techniques. Electrical method links the dispersion state to the material conductance, but this method is not relevant because mix rubber-carbon black agglomerates is not considered as conductive. Mechanical method uses a micro stylus to measure surface roughness of sample. Higher the roughness, lower the dispersion of carbon black agglomerate. The drawback of this technique is that the sample preparation is time consuming. Finally, optical method has two options, transmitted light and reflected light. Transmitted light method is costly, involving the use of an electron microscope, while reflected light method is faster, easier and less expensive. This last technique is used in the *dispergrader* to evaluate the dispersion state of mix rubber-carbon black.

To do this measure, a given amount of rubber-carbon black is taken in the mix and is cut in several slices. The dimensions of the slices are around $3mm \times 2mm \times 1mm$. The cutting-out of the rubber sample in several slices is a very critical step. If it is not carefully executed, a small layer of carbon black can be dragged on the whole side of the slice and no accurate measure can be performed on this slice. One solution to avoid this problem is to refrigerate the sample to make it harder. The bending of the sample during the cutting-out is therefore less important. Each slice of rubber is then put in front of an aperture located on the *dispergrader* through which a light is emitted onto the sample. The angle between the incident light and the sample is around 30 degrees. If the light hits an agglomerate, the light is reflected into a camera put in the *dispergrader*. Otherwise, the light is reflected away. Typical pictures obtained on the camera is illustrated in Figure 1.14. All black spots represents the section of carbon black agglomerates. Smaller these spots, better the mixing. The size and the surface of each black spot is measured and represents the state of dispersion. Two histograms are built from this data : one histogram that represents the cumulative surface associated at each class of size of agglomerates (the sum of the area of all agglomerates that are ranked in the same class of size) and a second histogram that provides the number of agglomerates in each class (Figure 1.15). This measure is repeated on several slices cut in the same sample of rubber in order to evaluate the quality of the measure. If the results are totally different between all slices, this indicates that either

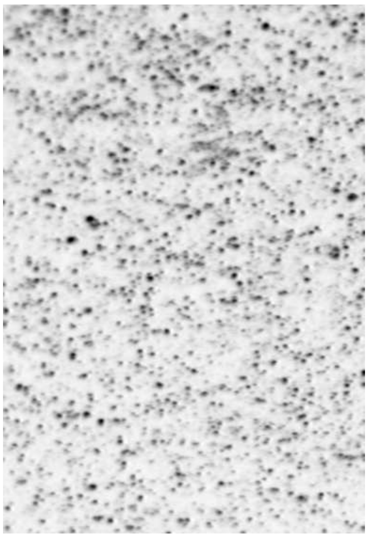
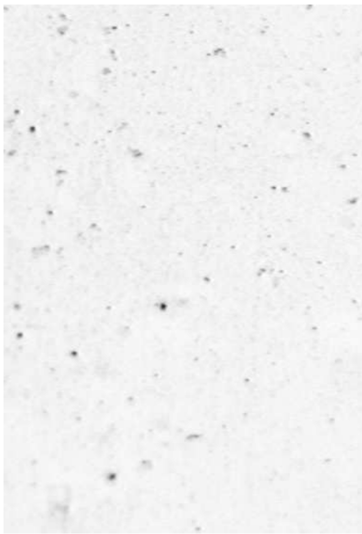
Bad dispersion $\dot{\gamma} = 2.5s^{-1}$ Mixing time = 2 minutes	Good dispersion $\dot{\gamma} = 10s^{-1}$ Mixing time = 12 minutes
	

Figure 1.14: Pictures of the state of dispersion of carbon black agglomerates in a rubber matrix after the mixing of the rubber and the carbon black in a Mooney rheometer.

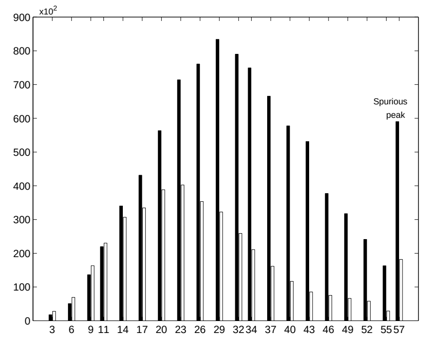
the measure is not well performed or the distribution of the carbon black agglomerates in the rubber matrix is very bad. It is also important to note that the *dispergrader* is only able to distinguish agglomerates with typical size (diameter) between $3\mu m$ and $57\mu m$. All agglomerates with size larger than $57\mu m$ are considered as agglomerates with size of $57\mu m$ and this generates the "spurious peak" observed in cumulative surface histograms. While agglomerates with size smaller than $3\mu m$ are not detected by the optical device.

Finally, we can do this measure after different times of mixing to obtain the time evolution of the state of dispersion of carbon black agglomerates during the mixing. As this measure is destructive, we have to consider a new rubber-carbon black mix at each measure. In such an approach, we assume that the inital state of dispersion of carbon black agglomerates is identical in each sample extracted from the same rubber-carbon black mix.

Histogram of the number of agglomerates and of the cumulative surface provided by the Dispergrader

Cumulative surface vs. agglomerate diameter. (μm^2)

Mixing time = 0 min.
Mixing time = 8 min.



Number of agglomerate vs. agglomerate diameter (μm).

Mixing time = 0 min.
Mixing time = 8 min.

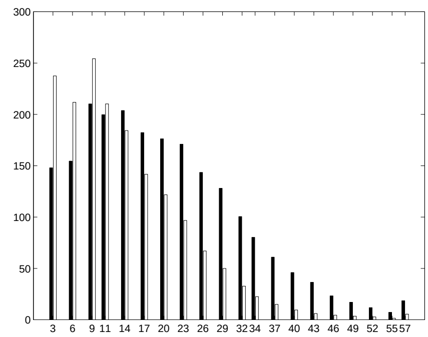


Figure 1.15: Histograms provided by *dispergrader* from the analysis of sample of carbon black agglomerate-rubber matrix. This sample is extracted from rubber matrix mixed with carbon black agglomerates in simple shear flow with shear rate of $2.5 s^{-1}$.