Mixing - A STEP BY STEP OPERATION

The second part of the ShibataFenderTeam (SFT) White Paper Series on fender manufacturing follows up on the first part published in the December 2018 issue of World Port Development. Based on the results on rubber compounding shown in the previous paper, the following article focuses on the preparation and blending steps of the raw materials and how they impact the performance of a rubber fender. It is an excerpt of SFT's White Paper.

Marine fender systems are essential when it comes to protecting people, ships, port infrastructure and creating safe berthing operations. The quality of a marine fender is exclusively measured by its performance properties which boil down to three aspects: Safety, Reliability, and Durability. Nevertheless, requirements for each fender system are different, which is why the development of a fender is a unique process from designing and engineering the customised solution to choosing raw materials through to the manufacturing procedures.

Current international standards and guidelines such as PIANC2002, ASTM D2000, EAU 2004, ROM 0.2-90, or BS6349 merely refer to the final physical properties of a marine fender. They do not indicate specifications on the chemical composition, just as there are no industry regulations for mixing and the equipment used in the procedure. Consequently, the quality of a fender and its physical properties are and will remain the defined goal of fender manufacturing.

SFT White Paper Series - PART II
Since mixing is an essential step in the production of rubber products, this part of the SFT White Paper Series focusses on the individual phases of the mixing process and how they impact the performance of a rubber fender. Rubber processing requires thorough incorporation and dispersion of the compounding elements, such as different types of raw rubbers, fillers, and various chemicals. It is vital to pay attention to how these elements come together and make a high-quality fender.

Superior mechanical strength, flexibility, and durability are some of the requirements that play a crucial role in the life of a fender. There is a mutual dependency between all steps of fender manufacturing from choosing the raw materials, balancing out the compound design, up to the accuracy of the mixing process that yield the predefined final product. The development of the compounding recipe and the subsequent mixing process are the most sensitive parts when it comes to fender production.

The following procedure illustrates a two-stage mixing process which by no means claims to be the single pathway to producing a good fender. It does, however, show the correlation of the various steps of the mixing process and the factors to be taken into account for the final quality of a fender. Single-stage mixing in internal mixers is possible, as well as using just one type of internal mixer, although that is not an ideal solution for all rubber compounds.

A. Compounding Ingredients - Fundamental Choices
As discussed in Part I of this series, a well-considered chemical composition of the rubber compound is the cornerstone to a high-quality fender and favourable mixing behaviour. In avoidance of inconsistencies in the product's final properties, the selection of raw rubber is particularly important. The initial condition of natural rubber (NR) as a natural product can vary in viscosity due to varying molecular weight and uneven molecular distribution. NR is sourced in the form of latex from a tree called Hevea brasiliensis.

High consumption and the geographical limitation of this raw material in the 18th century lead to the development of synthetic rubber (SR). The most frequently used synthetic rubber in fender compounds is styrene-butadiene rubber (SBR). Today, it has become standard to blend NR with SR which, due to the various complementary properties of different rubber types, has an enhancing effect on the fender's physical properties like ageing stability, tensile strength and processability. Depending on the composition of the rubber blend, the other compounding ingredients have to be balanced very precisely in order to obtain the optimal features of the final rubber fender.

Additional ingredients to enhance the required physical properties of the fender, as well as the processability of the rubber, are carbon black (CB), natural and synthetic calcium carbonate (CC), process oil, antioxidant and antiozonant to protect the rubber against aging and ozone deterioration as well as sulfur as a vulcanising agent. The chemical interaction and the reciprocal influence between the individual elements must be considered accurately for every rubber composition. As mentioned before, the number of possible formulas is infinite and its composition a matter of precision to the gram.

B. Rubber Mastication - Pivotal Preparation
Natural rubber in its original form possesses a very high molecular weight (which equals high viscosity) and an uneven molecular structure - a condition that complicates homogeneous blending with synthetic rubber as well as uniform dispersion with other ingredients. For this reason, mechanical mastication is conducted prior to the actual mixing process in order to obtain a material surface that is receptive to dispersion of polymer blend and compounding ingredients.

During the mechanical mastication process, the shearing forces of the rotors in an internal mixer break down the rubber's molecular structure, shorten the long molecular chains and produce a parallel alignment of the molecules. The result is a low viscosity rubber with uniform plasticity and flowability - and thus being a raw material with ideal mixing properties and processability.

Rubber manufacturers can choose to acquire masticated rubber or to perform in-house mastication (as done at SFT), which provides additional opportunities for quality management and in-batch as well as batch-to-batch uniformity. Mastication is usually done with internal mixers. When using an internal mixer, the natural rubber enters the mixing chamber through the hopper door in block form and is processed by the two heavy steel rotor paddles of the mixer. The masticated rubber is discharged and directly dropped onto a rolling mill, where it is sheeted for further processability (see figure 2). All steps from masticating to finalisation are monitored and documented precisely.

C. Mixing Equipment - Effective Machine Teamwork
The most common mixers in rubber manufacturing are the Banbury and the Kneader (see figure 1), both internal mixers, and the rolling mill. The construction of these two internal mixers is similar in regard to their mechanical characteristics, whereas each machine has its preferences for different procedures, and they can be used complementarily for optimised time and cost efficiency. Both mixers basically consist of counter-rotating pairs of rotors, a mixing chamber, a floating weight (ram), and a feed hopper.

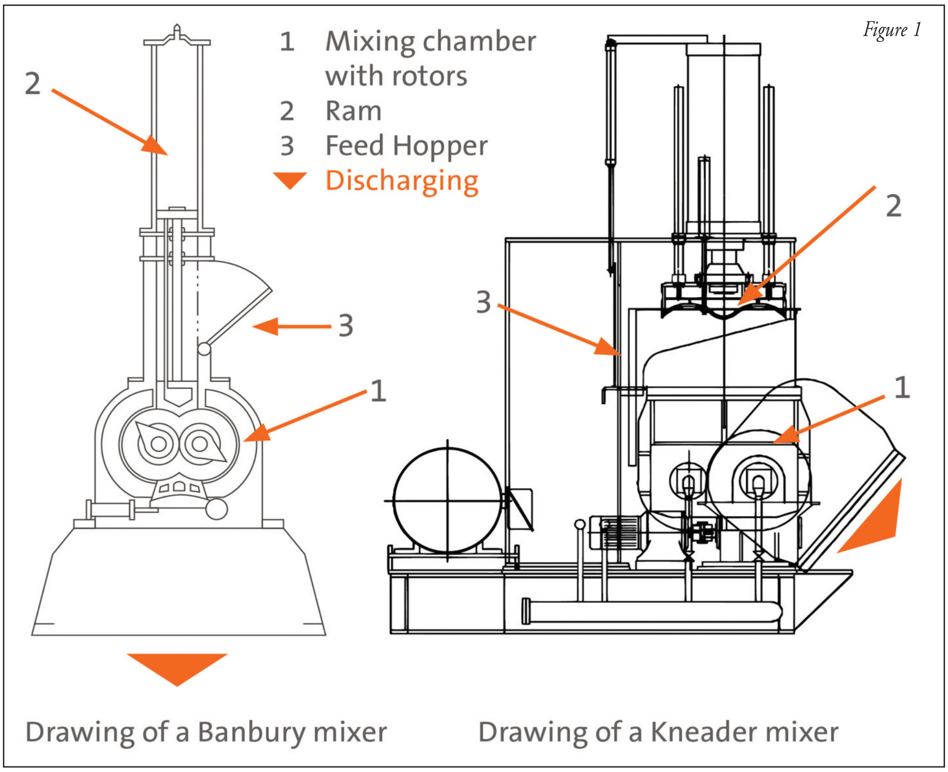

Figure 1

The two mixers have different rubber output mechanisms: the rubber exits the Kneader directly from the mixing chamber, which is tilted backwards in order to discharge the material. The Banbury has a drop door, through which the rubber is dropped onto the rolling mill. Both machines are available in different chamber sizes. Contrary to popular industry belief, a large mixer is not directly linked to a more efficient process or a high quality of the final outcome: with thermally sensitive polymers such as NR and SBR, a certain temperature should not be exceeded during the mixing process. The key advantage of smaller mixers is a more favorable chamber volume to cooling surface ratio.

Smaller mixing systems have a superior surface-cooling ratio compared to larger systems. The volume increases in the cube, whereas the cooling surface increases in the square. Consequently, the mixing temperature will always be considerably higher in a larger mixer. Furthermore, in larger mixers it takes longer to mix the large batches, which can damage the rubber's molecular structure and can harm the quality of the final compound. The quality decreases with extended mixing time and finally negatively affects the physical properties of the final product. As a matter of fact, a larger mixer is economically beneficial due to its higher output rates, but following the principle of quality as a priority, a middle-sized mixer should be the first choice to put quality over quantity. Despite the similarities of both internal mixers, each machine provides certain benefits that make it more suitable for one production step than another (for a detailed overview see table 1). The Banbury is the superior mixer for masterbatch production with its high-performance engine, adjustable rotor speed, and automated weighing system.

MIXING STEP	INTERNAL MIXERS		ROLLING MILL
	BANBURY	KNEADER	TWO-ROLL MILL
Mastication 01	+ possible but less efficient	+ efficient filling of rubber blocks	+ superior shearing forces – comparatively low productivity
Masterbatch production 02	+ suitable for high viscosity rubbers + adjustable rotor speed + rapid dispersion + sealed chamber + automated weighing + temperature is suitable for chemical dispersion	+ sealed chamber + suitable for colored compound due to lower temperature – lower productivity than Banbury – not suitable for high viscosity rubbers	+ high shear force and very thorough dispersion – comparatively low productivity – raw materials scatter – requires skilled worker – hazardous work environment
Finalization 03	+ possible but less efficient	+ greater cooling effect + easy discharge of material	+/– see above

Table 1: Mixing equipment at a glance

High degrees of dispersion and mixing high viscosity rubber can be achieved within a short time frame. Since the Banbury operates at higher temperatures than the Kneader, it is not the best solution for mastication and finalisation, although it is possible. The higher temperature of the Banbury is compensated by a shorter mixing time. However, there are certain advantages to favour the Kneader over the Banbury.

These are:
- Mastication: ease of loading raw rubber blocks
- Masterbatch production: to produce coloured compounds, like grey compounds, since the mixing temperature needs to be relatively low
- Finalisation: greater cooling effect and the ease of material discharging from mixing chamber

Selecting the right mixer for the respective production step and its correct operation requires a lot of experience; using both mixers can be a huge advantage. The rolling mill consists of two parallel, counter rotating rolls with a gap in between that can be adjusted. The rolling mill can be used for all steps of the mixing process. For the masterbatch production other compounding ingredients are added into the rubber.

The extremely high shearing forces of the rolling mill at a low temperature lead to superior dispersibility of the ingredients, but unlike the internal mixers with their sealed chambers, the rolling mill is an open mechanic system and the raw materials would scatter. This would create a dusty and unsafe production environment, which is a strong argument for the use of internal mixers. Additionally, a longer mixing time reduces the efficiency of the rolling mill and it is therefore most commonly used for sheeting, which will be described in the following section.

D. Sheeting - Creating Uniformity
After each mixing operation (mastication, masterbatch production and finalisation), the rubber is prepared for the next production stage by being sheeted on a rolling mill. The rubber that is dropped into the gap between the milling rolls is once again mixed by the counter rotating rolls and high shear forces. The rubber then wraps around the front roll and is transformed into a sheet by the two milling rolls.

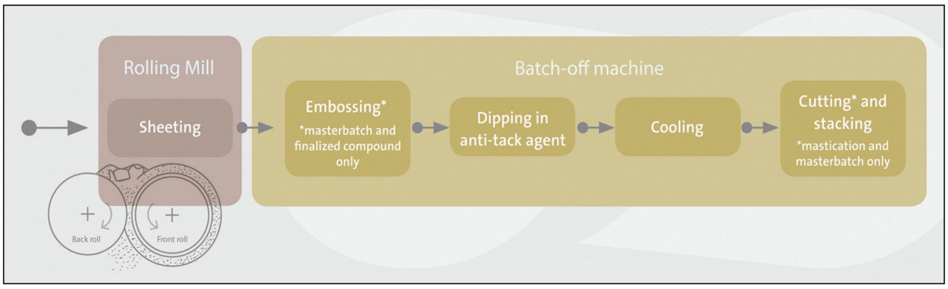

Figure 2: Mixing process - rolling mill and batch-off machine

Next to the rolling mill the batch-off machine is placed. It executes four main steps with a rotary cutter at the end of the line (see figure 2). First, the rubber sheets are embossed with the compound code (masterbatch and finalised compound only) and immersed into a container filled with a diluted anti-tack agent which prevents the uncured rubber sheets from sticking together. The rubber sheets are then transferred to a cooling chamber which quickly decreases their temperature and also helps to dry the anti-tack agent. Finally, the rubber is transferred to the rotary cutter where the sheets are cut into the desired length. The finalised rubber remains uncut and is folded in one piece, in order to improve processability for the following manufacturing process.

E. Masterbatch - All about the Additives
The two-stage mixing process starts with the production of the masterbatch: a crucial step in the mixing process, preferrably operated with the Banbury (see figure 3). This is where all compounding ingredients except for the vulcanising agent are mixed. Special attention has to be paid on the sequence of ingredient addition and the subsequent mixing times.

In a first step, masticated natural rubber (NR) is mixed with synthetic rubber (styrene-butadiene rubber, SBR) to create a uniform rubber blend. Due to the natural rubber's properties obtained through mastication, the rubber blend can be optimally mixed with all the fillers and chemicals required for the desired physical properties. Carbon black and process oil are added in a second step and after the set mixing time, fillers and chemicals are released into the chamber. After every addition of an ingredient, the hopper door is closed again and the material is pressed into the chamber by the ram, where it is then mixed under accurate surveillance of temperature development and rotation forces. There are several parameters that have to be monitored accurately in this operation. For a start, the automated weighing system and the auto mixing process controller of the Banbury prevent human errors regarding the chemical composition of the compound and the mixing settings. If the mixing is insufficient at this stage, carbon black is not dispersed homogeneously which negatively affects the final compound. Mixing has to be conducted at a relatively high temperature in order to melt the chemicals for sufficient dispersion. Whereas with too high temperatures, the rubber becomes too soft and sufficient shearing forces cannot be generated, which subsequently leads to poorer ingredient dispersion. Besides, NR & SBR do not have a high

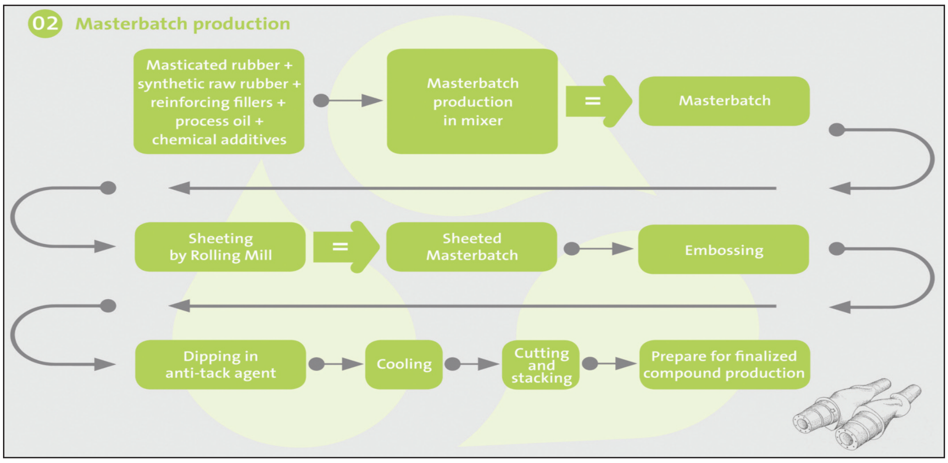

Figure 3: Masterbatch production - detailed steps

temperature resistance so too high temperatures will negatively impact the physical properties of the compound. This fine temperature balance calls for close monitoring of the mixing speed and time. Furthermore, the Banbury is equipped with a highly efficient cooling system which helps to control the temperature throughout the procedure. The masterbatch is then once again processed by the rolling mill and the batch-off machine and will be stored for a cooling period before it is further processed.

F. Finalisation - A Pinch of Sulfur

In the second step of the mixing process, being the finalisation, the masterbatch is mixed with sulfur in preparation for the manufacturing and curing process which will be addressed in the forthcoming part III of the White Paper Series (see figure 4). Sulfur is the most common vulcanising agent for rubber fenders. It is used in combination with other chemicals that accelerate vulcanisation and prevent scorching such as zinc oxide, stearic acid, and others. While this step is important for effective cross-linking of the rubber's polymer chains (vulcanisation), the addition and the thorough mixing of sulfur enhances the final hardness of the rubber and elasticity properties.

After sulfur has been added, an increase in temperature must be avoided in order to prevent premature vulcanisation. The Kneader is the preferred mixing device for finalisation because unlike the Banbury, the Kneader does not easily exceed the vulcanisation-critical temperature. The finalised compound is processed on the rolling mill and batch-off machine and is then stored in one folded piece without being cut, which facilitates the further manufacturing process (Part III of the White Paper Series).

The following step of fender production, manufacturing and curing, relies on the exact determination of scorch time, optimum curing time as well as minimum and maximum torque. These parameters can vary between different compound batches which is why testing and determining these parameters is extremely important regarding the high quality of fender products. For this purpose, a specimen of the finalised compound is placed onto a Curemeter which determines all relevant data based on a special software in order to schedule the ideal curing parameters individually for each compound. In this way, consistent quality can be reassessed each compound batch. The same test specimen is used to test the physical properties of the compound. Doing both tests at this stage of the fender production, allows for an early quality assessment.

Conclusion

From what we have learned so far in Part I and Part II of this White Paper Series, the road from designing the compound for a rubber fender with the desired physical properties to a mixing procedure that adheres to the highest quality standards is a complex one. Rubber compounds for rubber fenders must have superior mechanical strength, flexibility, and durability with a healthy cost-performance ratio. Rubber fender compounds can by no means be generalised for the entire industry. We are not exaggerating when we say that balancing raw materials is a necessity for compound design and an integral part of our experience. There are infinite combinations of rubber compositions and they all depend on the type and amount of raw rubbers and compounding agents used in the formulation. We at SFT firmly believe that the expertise in the fields of compound designing, mixing, production and testing are the key to safety, reliability, and durability of a fender.

However, the best formulation of the compound and the highest quality raw materials may not result in a durable rubber fender when inappropriate mixing techniques are involved, or the wrong equipment is used. Both, the Banbury and the Kneader are reliable and efficient solutions to mixing high-quality compounds and it can even be beneficial to operate both. The approach to achieving this quality may vary depending on the required physical properties of the final product but has in most cases emerged through a long history of experience with the materials and the processes involved. Ultimately, the consistency of a multi-layered process such as customised rubber mixing depends to a great extent on the operational control over every production step, a solid concept of quality management and once again the manufacturer's experience. WPD

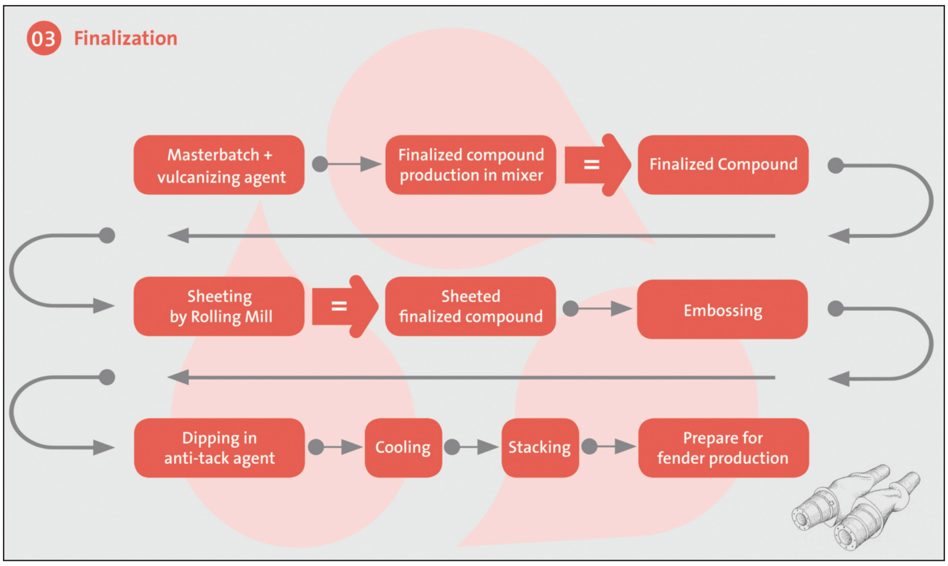

Figure 4: Finalisation - detailed steps