In marine fenders, the rubber component is critical in developing the characteristics of the system. However, there is generally a limited understanding of rubber compound quality and its impact on fender performance. The role of ingredient selection, mixing and the manufacturing process is poorly understood.

FORMULATING BEST PRACTICE

PIANC’s “Guidelines for the design of fender systems, 2002” highlighted the importance of Velocity Factor (VF) and Temperature Factor (TF) in the design and selection of fenders, and provides direction for reporting and calculating both.

It is exceptionally difficult to conduct tests at actual berthing velocities due to the wide range of different fenders and the lack of testing facilities. Fenders are therefore usually tested at 2-8mm/s compression speed, which is drastically lower than a ship’s actual berthing speed. To compensate for this, VF is applied to low speed test results to simulate a real life berthing.

The performance of a fender is directly proportional to the fender’s rubber stiffness, which scales according to the temperature. Fenders are usually tested at 23 ±5 °C. However, in the real world, they can be exposed to a much broader range of temperatures. To simulate performance in real world situations, TF is applied.

Both VF and TF are highly sensitive to the chemical composition (formulation) of different kinds of rubber compounds. Ingredient selection and rubber compound formulation are also very important factors in determining the efficiency – the ratio of energy absorption and reaction force – of a particular fender.

Rubber formulation also has a direct impact on the fatigue life of a fender. The American Society for Testing and Materials (ASTM) defines fatigue life as, ‘the number of stress cycles of a specified character that a specimen sustains before failure of a specified nature occurs’. For marine fenders, the fatigue life defines the longevity of the fender, or the number of fatigue cycles it can withstand before failure.

Until recently, understanding chemical composition in rubber fenders was not practiced in the fender industry due to a lack of suitable tests and specifications.

However, after undertaking comprehensive research on the impact of formulation on fender performance, Trelleborg Marine Systems introduced new specifications for stakeholders to evaluate quantitatively and qualitatively the chemical composition of a given fender, using the Thermo-Gravimetric Analysis, or TGA test.

The TGA test has been well received by the industry. Other high quality manufacturers have followed suit and, currently, the trend in the industry leans towards consultants building requirements for TGA testing into specifications.

This is important, because the TGA test determines whether fenders have been produced using a technically superior rubber formulation, one that includes little or no recycled rubber and only reinforcing fillers, like carbon black. Reinforcing fillers improve the mechanical properties of rubber, whereas non-reinforcing fillers, such as calcium carbonate might damage a fender’s mechanical properties.

The rubber and filler used are critical: 70-80% of a typical fender’s rubber formulation consists of raw rubber (natural or synthetic) and carbon black, while the remaining 20-30% consists of ten to fifteen other small ingredients. Raw rubbers, carbon black and these other ingredients are then converted to a rubber compound through a mixing process.

Although the TGA test ensures a superior formulation, relying on this test alone is not sufficient to guarantee the rubber compound’s quality, or the consistency of finished products. These parameters rely on a superior mixing process.

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### INGREDIENTS

<table>
<thead>
<tr>
<th>INGREDIENTS</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Rubber (Polymer)</td>
<td>40-45</td>
</tr>
<tr>
<td>Filler (Reinforcing)</td>
<td>30-40</td>
</tr>
<tr>
<td>Oil (Functional Additives)</td>
<td>20-10</td>
</tr>
<tr>
<td>Others (S + ACC etc)</td>
<td>10-5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
A superior formulation, confirmed by TGA test, when converted to a rubber compound can still be of poor quality due to an inferior mixing process. This can ultimately produce an inferior fender, incapable of absorbing the correct amount of energy.

Trelleborg has a long history in polymer engineering, and through ongoing research in rubber compound mixing, has proven the importance of the mixing and manufacturing process in producing a superior rubber compound, and subsequently, a superior rubber fender.

To break carbon black down to aggregate level and ensure a uniform distribution throughout the rubber matrix, rubber and carbon black must undergo the following major steps inside a mixer:

**Incorporation of carbon black:** When carbon black is mixed with the rubber, the carbon black agglomerates get encapsulated by the rubber in a process called wetting or incorporation.

**Distribution of carbon black:** The rubber then penetrates into the void space of the carbon black agglomerates. As the rubber penetrates through the narrow channels between the agglomerates, bound rubber is formed. The bound rubber helps in breaking agglomerates to aggregates.

**Dispersion of carbon black:** Dispersion is a slow erosion phase in which agglomerates are downsized to aggregate level, as a result of stress generated through the mixing process.

The percentage of carbon black dispersion in the final compound is what controls the quality of the end product. Poor dispersion can lead to damaging effects such as reduced product life, poor performance, poor appearance, poor processing characteristics, or even poor product uniformity.

To achieve a high and uniform carbon black dispersion, operators must ensure close control over the mixing process and the machinery used in this process must be in mint condition.

This paper will provide insight into the importance of the mixing process, equipment used to manufacture rubber compounds, the impact of both on the performance and lifecycle of a fender.

**THE MIXING PROCESS**

A high quality compound is one where the carbon black is broken down and distributed uniformly throughout the rubber matrix. Carbon black is supplied to manufacturers in the form of granules. These granules can be broken down into smaller and smaller fragments: granule to agglomerate to aggregate to nanoparticle.

Ideally, carbon black should be broken down into nanoparticles and distributed into the rubber matrix. However, it requires an extremely advanced mixing machine to break it down to aggregate level, the bare minimum to ensure an intimate dispersion within the rubber matrix.

The percentage of carbon black dispersion in the final compound is what controls the quality of the end product. Poor dispersion can lead to damaging effects such as reduced product life, poor performance, poor appearance, poor processing characteristics, or even poor product uniformity.

To achieve a high and uniform carbon black dispersion, operators must ensure close control over the mixing process and the machinery used in this process must be in mint condition.
There are a number of machinery related parameters that affect the carbon black dispersion of the final mix. These include ram pressure, rotor speed and design, fill factor, coolant temperature, mixing sequence, time and the number of passes through the mixer.

**Ram pressure**: The pressure applied to the ram during mixing must be monitored to ensure that materials in the mixer engage rapidly with the rotors. This will also prevent any subsequent up thrust of the batch.

**Rotor speed and design**: Rotor speeds must be adjusted to achieve dispersion more quickly.

**Fill factor**: The fill factor must be adjusted to meet a particular mixture’s specifications. If the fill factor is too high, parts of the batch may escape, resulting in non-homogeneity and non-uniformity of the mix. Having a fill factor too low will result in the formation of voids in the rubber mass behind the rotor wings.

**Coolant temperature**: The mixing temperature must be controlled to a specific level, depending on the type of compound. During mixing, if the mixing chamber is not cooled adequately, there may be a rapid increase in temperature, causing the rubber chains to break into small fragments. This may have a negative impact on the rubber compound’s mechanical properties.

**Mixing sequence**: The order in which new ingredients are added to the mixture is another important factor. The sequence should be adjusted based on the type of rubber, carbon and oil used.

**Number of passes**: The number of times a rubber compound repeats the mixing process influences the quality of carbon black dispersion. For compounds containing large quantities of reinforcing fillers, a three stage mixing sequence is commonly used. The maturation time between the successive stages of mixing also influences the percentage of carbon black dispersion of the final mix. Simply having one stage in the mixing process produces poor carbon black dispersion.
In the past, two roll mills were used to mix rubber with carbon black. However, this is extremely time consuming and not viable in today's commercial manufacturing. When large quantities need to be mixed efficiently, there is one superior machine available to manufacturers: the Internal Mixer (or Banbury mixer).

The Kneader is a small mixer used by some fender manufacturers to cut the costs of the mixing process. Most of the critical mixing parameters are poorly controlled in the Kneader. Kneader manufacturers have a limited understanding of the importance of the mixing process on product performance and these machines are usually used to mix rubber compounds for non-critical products.

The Internal Mixer is a large enclosed chamber equipped with two precisely designed rotors, connected to a strong motor with a power of over 1200KW. The compound production is a batch process whereby the rubber, carbon black and other ingredients are introduced into the mixer. The powerful rotation of the two rotors is what causes shearing of the raw rubbers, fillers and other ingredients inside the chamber.

This shearing causes an intimate mixing of the carbon black and other chemicals into the rubber matrix through the incorporation, distribution and dispersion process, in a short time frame.

The Internal Mixer requires a large operational area, over several stories. The top story contains storage and measuring equipment to feed precise quantities of ingredients into the mixing chamber (which is accommodated on the middle level). Before the mixing process starts, the bottom door of the chamber is closed. Once the rubber, carbon black and other ingredients have been added, the ram lowers to form a sealed chamber.

Once the chamber is totally sealed, the mixing process begins. Inside the chamber, the tearing and shearing of the rubber takes place. To mitigate this exothermic process, the sophisticated cooling system of the Internal Mixer precisely controls the temperature to meet the process requirements. Once mixed, the batch is dropped onto a two roll mill situated below the mixer, which produces the sheets of rubber compounds.

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<table>
<thead>
<tr>
<th>PARAMETERS</th>
<th>INTERNAL MIXER</th>
<th>KNEADER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ram pressure</td>
<td>Controlled</td>
<td>Lack of fine control</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>Variable for efficient mixing (20-60 rpm)</td>
<td>Fixed (30 rpm)</td>
</tr>
<tr>
<td>Rotor design</td>
<td>Sophisticated to improve dispersion</td>
<td>Simple</td>
</tr>
<tr>
<td>Coolant temperature</td>
<td>Controlled</td>
<td>Lack of precise controlled unit</td>
</tr>
<tr>
<td>Mixing time</td>
<td>2-5 mins</td>
<td>8-20 mins</td>
</tr>
<tr>
<td>Mixing sequence + weighing system of rubber + chemicals</td>
<td>Controlled and automatic</td>
<td>Manual and difficult to control</td>
</tr>
<tr>
<td>Mixing room environment</td>
<td>Clean</td>
<td>Dusty and dirty</td>
</tr>
<tr>
<td>Operation cost</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Initial investment</td>
<td>Millions</td>
<td>Thousands</td>
</tr>
<tr>
<td>Batch size</td>
<td>Big (200 kg/batch)</td>
<td>Small (50-75 kg/batch)</td>
</tr>
</tbody>
</table>
The Internal Mixer is equipped with an automatic ingredient weighing system, which removes the possibility for human error and variation in batch production. The rotors used are also specially designed for the effective tearing and shearing of rubber.

The Kneader is much smaller and lacks the technological sophistication of the Internal Mixer. A Kneader is unable to generate the required shearing force needed for sufficiently uniform carbon black dispersion. The mixing process takes longer, and there is very little operator control.

The machine doesn’t have the technology to automatically weigh different ingredients; the operator has very little control over the temperature, and length of the mixing cycle. Due to poor temperature control and an extended mixing time, the rubber’s molecular chains are often broken, which degrades the characteristics of the final compounds.

Improvements are being incorporated into Kneader technology; however, low cost fender suppliers are still relying on the old Kneader mixers because of the huge investments needed to replace them.

### MEASURING SUCCESS: THE IMPACT OF CARBON BLACK DISPERSION ON FENDER PERFORMANCE

Hardness is the current industry practice for judging the energy absorption capacity and reaction force of a rubber fender. The hardness of a fender can easily be measured by a handheld instrument called a Durometer. However, this method of measuring a fender’s performance is too simplistic and largely inaccurate. The current market perception is that softer fenders will have a lower energy absorption capacity and harder fenders will have higher energy absorption ability, but it is easy to increase the hardness of a rubber fender by using non-reinforcing white fillers and recycled rubber.

Modulus (stiffness) is the slope of the stress/strain graph during tensile strength measurement of a cured rubber sample. Having a higher modulus of a rubber compound indicates a higher energy absorption capacity of a fender. Therefore, as a more robust alternative, Trelleborg suggests that the industry starts to measure modulus, rather than hardness.

An example of this can be seen in the table above: a superior compound with no recycled rubber, and an inferior one with a high percentage of recycled rubber mixed in two different Internal Mixers. Although the hardness values of the compounds are similar, there is a greater difference in the modulus values. Evidently, measuring only hardness will provide a false impression of fender performance.

Modulus of rubber compounds and the fatigue life of fenders are dependent on carbon black dispersion, when all other factors remain constant. Therefore, it’s vital that the industry evaluates the mixing process and measures the uniformity of carbon black dispersion in the samples of rubber compounds and fenders.

The ASTM has a well-established method to test carbon black dispersion in fenders and rubber compounds, which requires only a small sample. A machine called a Dispergrader can be used to evaluate carbon black dispersion in the samples. It measures both the size of the carbon black particles and the uniformity of dispersion. The Dispergrader then provides a percentage rating, allowing engineers to understand the homogeneity of the final mix.
The following table illustrates the dispersion ratings and the compound modulus of one compound mixed in two Internal Mixers and a Kneader.

<table>
<thead>
<tr>
<th></th>
<th>Internal Mixer 1</th>
<th>Internal Mixer 2</th>
<th>Kneader</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion rating (%)</td>
<td>79</td>
<td>81</td>
<td>54</td>
</tr>
<tr>
<td>Compound modulus (Mpa)</td>
<td>8.0</td>
<td>8.1</td>
<td>7.2</td>
</tr>
</tbody>
</table>

The fatigue life (lifecycle) of a fender also changes significantly depending on the mixer used. Trelleborg tested an inferior rubber formulation and a superior rubber formulation. Both were mixed using the Internal Mixer and the Kneader. The graph below shows just how much of an impact the mixing equipment has on the fatigue life of compounds.

For the superior formulation, the fatigue life is reduced by approximately 10 kilocycles. The inferior formulation reveals even more drastic results, with the fatigue life of the compound mixed using the Internal Mixer being almost double that of the Kneader.

**Impact of carbon black dispersion on compound modulus**

CONCLUSION

It is proven by experiment and supported by theory that compound modulus (stiffness) is the determining factor of a fender’s performance. Keeping all other factors constant, the modulus of rubber compounds is affected by carbon black dispersion. Mixing equipment and mixing procedure not only has impact on the compound modulus, but also the fatigue life of fenders.

It’s essential that designers, operators and owners of port infrastructure begin to educate themselves on the importance of rubber compound composition, carbon black dispersion and modulus of rubber fenders. All these factors need to be taken into account during the design and procurement process. Long overdue is the appropriate application of rubber technology principles and standards in fender systems, using the same intensity as those applied in steel fabrication.

It’s important that the industry works towards a deeper understanding of the impact of the manufacturing process while ensuring that the mixing quality does not impact product performance.

Port owners, operators, contractors and consultants need comprehensive specifications/testing methods covering ingredient selection, mixing procedure and production process to stipulate the performance of finished products.
Trelleborg is a world leader in engineered polymer solutions that seal, damp and protect critical applications in demanding environments. Its innovative solutions accelerate performance for customers in a sustainable way.

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