Processability, Characterisation and Properties of Tyre Retread Compounding Ingredients

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2.1 Introduction

The major requirements for an extruded retread profile intended for retreading (with a view to maintaining consistency) are (i) to be free from porosity, (ii) to be free from blisters and (iii) for the profile to be free from surface imperfections. Uniformity in the shape of the extruded tread section enables proper placing on the buffed contour dimensions of the old tyre that is ready for retreading. The compounding of rubber, its homogeneous mixing, shaping of a tread profile by extrusion, calendering of tread gum and cushion gum sheeting are all steps in the process of achieving a flawless retreading operation.

The most important characteristics required in a retread rubber composition are outstanding adhesion with the old tyre crown, very good tear and cut resistance, and excellent abrasion and ageing resistance after curing. The processing characteristics to achieve efficient bonding of the new tread with the old tyre throughout its length of service, as well as appropriate mechanical properties in the final product and cost-effective economical compounding, must be effectively developed within the factory.

To achieve these aims, a suitable formulation of the rubber compounds, the steps of mixing, extrusion and calendering, and the selection of appropriate ingredients such as reinforcing carbon blacks, precipitated silicas, process aids (PA), accelerator and antidegradant are important decisive factors. Appropriate curing parameters (either cold curing or hot curing) should be followed strictly to achieve the desired properties for the product.

Calendered items required for tyre retreading assembly, such as the tread gum profile and cushion gum sheeting mixes, are processed in a calender machine and have to be of a high quality in terms of lack of porosity, blemish-free, consistent and uniform in thickness. The technology of processing is therefore fundamentally significant for a tyre retreader [1].
In 1864, ink-maker J.K. Wright of Philadelphia (PA, USA) discovered the process of manufacturing carbon black. Improvements in production technology were subsequently developed and, in the early 1900s when the Goodrich Tyre Company started using carbon black, they found that it significantly improved some of the properties of tyre rubber compounds.

Carbon black became widely used after 1915 as a reinforcing agent for the production of automobile tyres, with the effect of increasing both durability and strength. Following the addition of 50 phr (per hundred of rubber) carbon black to rubber compounds, road wear resistance and tensile strength were improved to a great extent. Industrial uses of carbon black today are usually in the form of furnace black and thermal black.

The reinforcing material carbon black, one of the major ingredients in tread rubber compounds, has significant effects. Its impacts include high hardness, extrudability and cure rate. Its effects on mechanical properties such as tensile strength, modulus, tear strength and fatigue are considerable, but it has only a medium impact on resilience and ageing.

On exposure to direct sunlight for a long period a tyre may become increasingly grey. The tyre also deteriorates gradually due to the effect of ultraviolet (UV) light. Carbon black, when incorporated, absorbs UV rays and protects the tyre. An illustration of the different grades of carbon black utilised in tyre retread compounds are discussed in this chapter [2].

Intended for the preparation of rubber-based cement, a high-rubber-content compound mixed with a suitable adhesion promoter such as natural rosin, synthetic resin, swollen and dissolved in a suitable solvent oil, is used in the assembly process for tyre retreading. The specific viscosity is obtained on the way to prepare the vulcanisable cement employed in the construction of retreading. For the purpose of cement preparation, the base rubber needs to be suitably premasticated before incorporating other compounding ingredients in the mixing process.

Rubber cement is essential for retreading assembly. It is prepared in suitable solvent/s and applied with uniform thickness on the ready worn tyre surface to adhere perfectly to the used tyre. In the cold process for retread tyre moulding, as is usually used for car and truck tyres, gum cement preparation is required for fabrication of the precured tread on the used tyres.

Until the mid-1950s, the only antiozonant for rubber compounding available to rubber compounders was wax. Its limited solubility in rubber led to blooming at the surface, and it formed a protective layer that did not allow ozone to permeate, but in dynamic applications the use of wax is ineffective. In 1954, ozone protective
agents for dynamic applications were introduced. It is very important to incorporate antiozonant/antidegradants such as piperidine pentamethylene dithiocarbamate and isopropyl-phenyl-\(p\)-phenylenediamine in tyre tread formulations in order to provide protection against oxygen and ozone attack as well as resistance to surface cracking.

Cracking of tread rubber during service is largely a result of the effects of oxygen on high flexing of the tyre. Ozone is particularly active in producing this detrimental effect. An antioxidant added into the tread rubber formulation in combination with a suitable antiozonant will safeguard the tread from attack from oxygen and ozone, resulting in the intensification of flexing, as discussed in this chapter [3].

Tyres may be attacked by microorganisms, fungi and some bacteria. These infiltrate the rubber and weaken its double bonds, in particular when the tyre is used in marsh/wetlands for long periods, ultimately damaging the tread. Accordingly, for such applications it is necessary to protect the tread compound by using special additives, as also discussed in this chapter [4].

2.2 Processability

Rubbers are highly viscous, so it is necessary to reduce the molecular weight (MW) and viscosity of elastomers to facilitate processing of rubber compounds. Decreasing the viscosity and increasing the plasticity of the elastomers used for tyre retreading applications can be achieved by mechanical milling, either using open two-roll rubber mills or internal mixers (the Banbury mill). This initial process is necessary to incorporate reinforcing fillers, PA and other powdery compounding ingredients into a homogeneous mix of the desired plasticity for use in retreading processes for various types of tyre of different designs.

Processability is critical to the properties required in compounding to produce an ultimate product. Each compounding ingredient should be dispersed in the rubber matrix consistently and it should have uniform rheological properties in order to provide the desired attributes in the end product. On preparation of the rubber mix, a highly viscous material behaves as a non-Newtonian liquid.

The initial mastication of natural rubber (NR) can be performed in an open two-roll rubber mill or in an internal mixer. Repetitive mechanical deformation in the presence of atmospheric oxygen causes a reduction in the MW of the rubber, and it becomes increasingly plastic. At this stage, rubber compounding ingredients can be incorporated with further mixing. Synthetic rubbers such as styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), ethylene propylene diene monomer (EPDM) and chloroprene rubber (CR) can be treated like NR during the mixing operation [3].
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To speed up the mastication process, chemical peptising agents such as pentachlorothiophenol (Renacit VII), together with dispersing additives and zinc-2-benzamidothiophenate (Pepton 65), in dosages of 0.2–0.5 phr will assist in breaking down rubbers at a lower operating temperature. Higher proportions may be necessary for synthetic rubbers. The mill temperature during mastication of NR should be maintained at about 70 °C, and for synthetic rubbers 130 °C may be necessary to reduce the mastication time effectively.

Lowering the viscosity with peptisation will facilitate the incorporation of a high proportion of fillers and other compounding ingredients during mixing. This can assist with flow properties during the extrusion of tread profile and in the calendering of tread/cushion gum strips, and all through the process of moulding. Appropriate peptisation of the rubber, particularly high-viscosity NR, will help in blending with other synthetic elastomers, which are available in different viscosity levels (even lower viscosities, e.g., general purpose synthetic rubbers).

The advantages of correctly peptising rubbers during compounding are as follows:

• Improvement in blending of elastomers
• Faster incorporation of fillers and other compounding ingredients
• Decreased processing temperature
• Facilitated processing of extrusion/calendering/moulding
• Increased building tack of tread and other components
• Reduced batch-to-batch variation of mixed stocks
• Reduced time of mixing
• Reduced cost

Plots depicting the effects of peptisation on NR (without and with peptiser) are presented in Figure 2.1 [5].
The addition of homogenising agents (Struktol 40MS/60MS) into tread formulations will promote the homogeneity of elastomer blending, smoothen the incorporation of compounding constituents during the mixing process, and also help minimise batch-to-batch variations in mixed stocks. These agents are composed of a mixture of aromatic hydrocarbon resins and display good compatibility that facilitates the blending of rubbers. The usual effective dosage for NR is 4–5 phr, and this gives satisfactory results in general purpose synthetic rubber blends such as NR, SBR and PBR. For special purpose synthetic rubber blends such as CR or EPDM, a higher proportion of 7–8 phr is necessary to achieve optimum processing effects.

As a result of the excellent wetting properties of compatibilisers, fillers can be incorporated more quickly and dispersed more evenly during mixing. They also increase the green strength of compounds and improve green tack, which helps in the construction of retread as a result of superior homogeneity. Flow properties are also improved, which facilitates curing.

The following benefits arise incorporating homogenising agents into retread rubber compounds:

- Improved homogeneity of stocks/reduced nerve
- Better batch compactness
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- Smoothness of compounds
- Improved processing (e.g., extrusion and calendering)
- Better dispersion of fillers in compounds
- Increased building tack
- Uniformity in processing behaviour

A plot of viscosity reduction versus temperature on peptisation of NR is shown in Figure 2.2.

![Figure 2.2 Peptisation of NR viscosity reduction versus temperature. Reproduced with permission from Rubber Handbook – Schill + Seilacher, Struktol, Stow, OH, USA, 2004, p.30. ©Struktol and Schill + Seilacher [5]](image)

The incorporation of some PAs (e.g., petroleum-based process oils, plasticisers, resins, factices and zinc salts of unsaturated fatty-acids, internal lubricants, waxes, tackifying resins, and pine tars) considerably improves processing behaviour, including mill mixing and extrusion and calendering operations in natural/synthetic rubber-based stocks.

The utilisation of zinc soaps of higher fatty-acids in mixes may assist in avoiding the problem of sticking to the mill during mixing, and is effective in the extrusion of tread profile and calendering of tread/cushion gum sheeting. They can also aid in the dispersion of fillers, and will improve the flow behaviour of mixes while moulding the tyre, leading to a better finish of the retread [5].
To promote the tack of rubber compounds, resins such as coumarone–indene resins (CI resin), petroleum resins, phenolic resins and wood rosin are added, as well as to improve processing, incorporate dry fillers during mixing and facilitate extrusion/calendering operations.

The essential results of these actions in the processing of rubber compounds for use in tyre retreading applications are:

- Appropriate viscosity (to improve flow properties)
- Adequate green strength on handling
- Control of shrinkage
- Appropriate tack (to impart adhesion with the old tyre substrate during assembly)

The benefits of using a silane coupling agent (Struktol SCA 98/SCA 985) in tread rubber compositions where a high proportion of reinforcing silica filler is incorporated arise from coupling of the silica fillers to the elastomer backbone, thus improving the reinforcing potential. The following properties of the tread compound at the time of processing and in cured tyre tread are improved:

- Rate of incorporation of fillers (faster)
- Dispersibility of ingredients (improved)
- Viscosity of the rubber compound (reduced)
- Modulus of the compound (enhanced)
- Abrasion resistance property (increased)
- Rolling resistance (improved)
- Hysteresis (lowered)

Petroleum oils of aromatic type with a low aniline point improve the processing of NR-based compounds, helping in the dispersion of powdered fillers and maintaining the viscosity of the mixes for further processing. These oils act as an extender to rubber mixes; aromatic oils are suitable extenders for NR and general purpose synthetic rubber blends, and naphthenic/paraffinic oils are suitable for EPDM blends with NR [1].

In terms of the effect of oil extender/plasticisers in retread rubber mixes, the following advantages can be achieved:
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- Lower compound viscosity
- Faster incorporation of fillers
- Reduced generation of heat during mixing
- Improved flow properties during processing
- Increased building tack
- Lower compound hardness
- Greater elongation
- Enhanced flex life

Because NR has a high degree of unsaturation in its polymer chain, there is a tendency towards premature curing or ‘scorching’ of NR-based compound during processing in the extruder or calender. This processing problem is also observed for some synthetic rubber mixes when reinforcing carbon blacks are added in a high proportion to the rubber compounds, when accelerators are added in a high dosage or when processed at higher temperatures. The ‘heat history’ of processed mixes from the stage of mixing and including the temperature of storing the compounds influences this kind of phenomenon.

To extend the scorch time to a safe level for the processing temperature of rubber mixes, chemical rubber retarders such as cyclohexylthiopthalimide, nitrosodiphenylamine and benzoic acid are added in dosages of 0.1–0.3 phr. These can extend the level of operational safety while processing unvulcanised compounds [3].

### 2.3 Requirement of Mechanical Properties

Carbon black is used in rubber compounds to augment mechanical properties such as tensile strength, modulus, abrasion and tear resistance. Selection of the proper grade of carbon black to achieve these specific physical characteristics for tread applications is described in Table 2.1.
### Table 2.1 Types of carbon black used for tyre retreading formulations

<table>
<thead>
<tr>
<th>Type of carbon black</th>
<th>ASTM designation</th>
<th>Particle size (millimicron)</th>
<th>Surface area (m²/gm)</th>
<th>Oil absorption (cm³/g)</th>
<th>Dibutyl phthalate absorption number (cm³/100 g)</th>
<th>Iodine absorption (g/kg)</th>
<th>Pour density (kg/m³)</th>
<th>Heat loss (% maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF</td>
<td>N110</td>
<td>20–25</td>
<td>110–120</td>
<td>1.50</td>
<td>113</td>
<td>145</td>
<td>370</td>
<td>3.0</td>
</tr>
<tr>
<td>ISAF</td>
<td>N220</td>
<td>24–33</td>
<td>100</td>
<td>1.35</td>
<td>114</td>
<td>121</td>
<td>344.43</td>
<td>3.0</td>
</tr>
<tr>
<td>HAF</td>
<td>N330</td>
<td>28–36</td>
<td>65–70</td>
<td>1.30</td>
<td>105</td>
<td>82</td>
<td>376.4</td>
<td>2.5</td>
</tr>
<tr>
<td>FEF</td>
<td>N550</td>
<td>40–55</td>
<td>40</td>
<td>1.35</td>
<td>121</td>
<td>43</td>
<td>360.4</td>
<td>1.5</td>
</tr>
<tr>
<td>SRF</td>
<td>N762</td>
<td>61–100</td>
<td>33</td>
<td>0.7</td>
<td>65</td>
<td>27</td>
<td>350</td>
<td>1.5</td>
</tr>
<tr>
<td>GPF</td>
<td>N660</td>
<td>49–60</td>
<td>36</td>
<td>1.1</td>
<td>90</td>
<td>36</td>
<td>440</td>
<td>1.0</td>
</tr>
<tr>
<td>MT</td>
<td>N990</td>
<td>250–350</td>
<td>10</td>
<td>–</td>
<td>43</td>
<td>6–12</td>
<td>640.8</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**ASTM:** American Society for Testing and Materials  
**FEF:** Fast extrusion furnace  
**GPF:** General purpose furnace  
**HAF:** High abrasion furnace  
**ISAF:** Intermediate Super Abrasion Furnace  
**MT:** Medium thermal  
**SAF:** Super Abrasion Furnace  
**SRF:** Semi-reinforcing furnace
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The physical properties are improved because the carbon black aggregates create physical and chemical bonds with the rubber that give the requisite tensile strength, tear strength, abrasion resistance and flex fatigue resistance [6].

The reinforcing filler precipitated silica provides higher reinforcement properties in polar elastomers like CR, and in NR/PBR/SBR blended stocks reinforcement may improve on using silane coupling agent along with the silica. Non-black reinforcing fillers can be included in compounding; for example, coupling agents in mixes improve coupling to the elastomer backbone. They can increase the modulus of the compound, improve abrasion resistance, give low hysteresis and improve rolling resistance.

Fine-particle silica can also contribute to improving properties such as tear, cut and chip resistance, and also lowers the heat build-up characteristics during high tyre flexing conditions. An average silica surface area of about 152 g/m² is acceptable for these purposes [7].

NR exhibits good abrasion and tear resistance characteristics, and the incorporation of reinforcing carbon blacks into compounds of NR further improves these characteristics, as well as the tensile properties.

In comparison with NR, SBR exhibit better crack initiation and abrasion resistance characteristics than NR. PBR can provide excellent abrasion resistance when blended with NR in tyre tread compositions [8]. Because PBR shows higher abrasion resistance when blended with NR, the addition of some percentage of this rubber into mixes based on NR, SBR and CR can enhance this property noticeably. Because NR, being a non-polar rubber, can blend easily with other non-polar rubbers, it can contribute its excellent properties of tear and abrasion resistance to blends [9].

The small particle size and high surface area of carbon black helps to increase the mechanical properties of rubbers. To obtain extruded tread and calendered gum materials with dimensional stability and to achieve surface perfection, proper dispersion of blacks into mixes is essential.

The use of dual-phase fillers such as a blend of carbon black and silica in NR-based tread compounds for heavy-duty truck tyres and off-the-road (OTR) tyres on the whole can provide improved performance due to the high elastomer–filler interaction and low filler–filler interaction. In comparison with silica alone, the carbon–silica dual filler can contribute considerably to the improvement of tearing strength and abrasion resistance. Further improvement can be achieved by the addition of a small dosage of coupling agent into the tread formulation [e.g., bis(3-triethoxysilylpropyl tetrasulfane) (Struktol SCA 98)] [10].
Some resins (e.g., coumarone resin, petroleum and phenolic resins), when added in the right proportion (about 4–5 phr), can contribute to improving tear resistance. Excellent levels of properties such as abrasion resistance are achievable for EPDM, similar to those for NR, when blended with NR and PBR.

Proper curing of the elastomer plays an essential role in determining abrasion resistance, and it may deteriorate if the crosslinking is not adequate [11].

### 2.4 Perceptions of Reinforcement in Rubber Compounding

Mixes used for tyre retreading applications can include fillers of the reinforcing type to improve the properties of the end products as well as some inert fillers to reduce the cost of the compounds. Fillers improve the properties of the elastomer by enhancing mechanical properties such as abrasion resistance and fatigue life.

Different reinforcing fillers are incorporated into rubber compounds to enhance mechanical properties such as modulus, tensile strength and wear resistance. The most commonly used are carbon black and silica. Reinforcing fillers in retreading formulations are significant in enabling demanding performance requirements to be met, in particular in relation to resistance to wear. They impart a degree of strengthening to the rubber network, leading to considerable enhancement in tensile strength, modulus and resistance to abrasion, as well as an increase in endurance. Such improvements are significant because strength is improved throughout the tread, particularly in its footprint region, thereby improving road grip and decreasing the stopping distance of articulated vehicles, for example, and contributing to road safety for passenger vehicles [7].

Reinforcing fillers achieve these properties by ensuring a high number of chemical linkages within the elastomer network. Non-reinforcing fillers, however, do not form chemical links with the elastomer and so do not provide any considerable improvement in this regard.

While designing a product and analysing the service properties of a critical item such as tyre tread, it is imperative to understand the effect of filler in the rubber composite. In elastomer formulations the distribution of particle sizes is important, as this affects the mechanical properties and therefore the performance of the ultimate product [12].

Fillers impart distinctiveness to a rubber compound as a result of their particle characteristics, including size, surface area, surface activity and shape. A summary of strength and stiffness of SBR with and without reinforcing filler is shown in Figure 2.3.
Commercially available rubber grades of carbon black have particle sizes ranging from 10 to 500 nm. The larger the particle size, the smaller the reinforcement property. Surface activity affects the compatibility of the filler with the rubber and the ability of the rubber to integrate with the filler. Properties depend on the dispersibility of the carbon black in mixes, and this usually depends on the size of particle, hardness of the pellets and structure.

The reinforcement of rubber compounds, in particular the interaction of filler and rubber, should be examined in order to improve vulcanisate mechanical properties, including tensile strength, tear resistance, abrasion resistance and modulus. Incorporating fine-particle fillers into rubber mixes improves the physical characteristics of the cured product as a result of these rubber/filler interactions. Reinforcing fillers provide a large degree of strengthening of the rubber network by providing a high number of chemical links with the polymer network [13]. A graphical representation of the tensile strengths of different rubbers is presented in Chapter 1 (Figure 1.1).

The reinforcing fillers used in tread rubber compounds are essential to achieving the desired performance requirements. Tread compounds have demanding requirements regarding resistance to wear. They should also have the durability that allows their use at high-speeds over a long period, as well as the effect of lowering fuel consumption, as far as possible [14].

The following are essential factors that intensify the reinforcement of elastomer properties:
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- Size of the particles or specific surface area (in combination with loading, determine the effective contact environment of the filler and polymer network)

- Structure of the filler particles, and to an extent their aggregation (affect the physical interaction between filler and rubber)

- Type of filler surface and intensity of the interaction between rubber and filler (contribute to restricting motion of the rubber molecular chain while under stress)

Thus, surface activity is a dominant factor in filler–filler and filler–rubber interactions [15].

The reinforcement of high abrasion furnace (HAF) carbon black per hundred of rubber (phr), and with aromatic process oil is illustrated in Figure 2.4.

![Figure 2.4 Reinforcement of HAF black with process oil](image)

**2.4.1 Reinforcing Carbon Blacks**

The physical properties of tensile strength, flexing, abrasion and tear resistance of NR are usually high. The incorporation of reinforcing carbon blacks, such as SAF, ISAF and HAF, in tread mixes will further enhance the tensile strength, abrasion and tear resistance of this elastomer. The characteristics of different carbon blacks used in tyre retreading compounding are displayed in Table 2.1.

In general, carbon blacks are graded according to their surface area parameter: (i) semi-reinforcing (<45 g/m²) and (ii) reinforcing (65–140 g/m²). Pneumatic tyre retread made from NR or using a blend of different rubbers is typically reinforced with carbon...
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black as a major reinforcing filler [12]. The properties of different grades of carbon black in NR-based mixes are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Grade of carbon black</th>
<th>Hardness (Shore A)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus at 300% (MPa)</th>
<th>Elongation at break (%)</th>
<th>Rebound resilience (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 65</td>
<td>25.6</td>
<td>12</td>
<td>500</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>ISAF 61</td>
<td>25</td>
<td>12.2</td>
<td>520</td>
<td>60.5</td>
<td></td>
</tr>
<tr>
<td>HAF 60</td>
<td>24.8</td>
<td>11</td>
<td>510</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>FEF 58</td>
<td>22.4</td>
<td>13.5</td>
<td>480</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>SRF 57</td>
<td>21.8</td>
<td>11.8</td>
<td>490</td>
<td>71.6</td>
<td></td>
</tr>
<tr>
<td>GPF 55</td>
<td>19.5</td>
<td>11.5</td>
<td>530</td>
<td>72.5</td>
<td></td>
</tr>
<tr>
<td>MT 49</td>
<td>20</td>
<td>4.5</td>
<td>620</td>
<td>84</td>
<td></td>
</tr>
</tbody>
</table>

Base recipe: NR (RSS 1X), 100; zinc oxide, 5; stearic acid, 2; carbon black, 50; process oil, 3; cyclohexyl benzthiazole sulfenamide, 1; and sulfur, 2.5

For mixes of tread gum or cushion gum compounds, the preferred grade of carbon black is FEF, as this provides improved calendering properties compared with the next choice of SRF. Furnace blacks such as SRF/GPF grades are suitable variety for the compounds utilise in repair mixes and for rubber cement compositions [13].

2.5 Reinforcing Silica, Silicates and Carbonates for Tyre Retread

Silicas such as fumed silica and precipitated silica enhance the tear strength of rubber compounds due to their small particle size and complex aggregate structure. To achieve the highest degree of reinforcement in tread mixes, it is essential to select the appropriate grade and proportion. Precipitated silica is added to compound formulations together with carbon black to improve properties such as flex cracking and cut growth resistance.

Major improvements in rubber properties are achievable by using reinforcing fillers with particle sizes of 10–100 nm in rubber mixes. Equitable improvements in physical properties can be obtained with fillers such as calcium and aluminium silicates and activated/precipitated calcium carbonate. These partially reinforcing fillers can be used in tread gums, repair compounds, cushion gums or in cement recipes [16].