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Sample Pages

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Mixing of Rubber Compounds

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# 3

## Mixing Characteristics of Polymers in an Internal Mixer

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In this chapter, the authors try to describe the different principles governing the mixing process. It should be emphasized that in many cases there are also specific requirements and prerequisites for the polymer itself to provide proper mixing results. This chapter shows some examples for the most processed types of polymers used in the rubber industry.

### ■ 3.1 Natural Rubber (NR)

Natural rubber still represents about one third of the polymers used in the rubber industry. In its very basic form it has some very high molecular weight portions and consequently very high viscosity. In this condition it cannot be processed or even mixed. Therefore, it first has to be brought to a certain viscosity level by so called “mastication”.

Mastication more or less means a reduction of the chain length of the polymer. The processor can decide whether to buy already masticated rubber at a defined viscosity or to masticate the raw polymer in house. Quite often RSS1, RSS3, STR20 or SMR 20 rubber types are used. Viscosity tests have shown that over a period of one year the processors have to cope with a wide range of viscosity fluctuations of more than 20 Mooney Units.

The mastication can be driven by high shear forces, thermal degradation or it can be supported by the help of special chemicals (e. g., peptizers). Degradation at high temperatures (above 160 °C) normally inhibits negative effects on the final products properties. Two other properties also have a big influence on the mixing process: one is the effect of crystallization and the other is the high dependency of polymer viscosity on temperature.

As NR is able to crystallize, it shows that a partial crystallization can be initiated after storing in cold areas. For example, this might happen below 15 °C, e.g., during transportation in winter. The decrystallization by thermal effects would

require a range of temperatures above 20 °C over a longer time period (unfreezing a bale of NR takes at least 4 days at 30 °C; a complete pallet might need some weeks!). Of course, partially crystallized NR has other mixing characteristics than non crystallized rubber. To consistently maintain the same quality, decrystallization must be assured. As already mentioned, this is normally done in the storing stage in a warm room.

A more effective approach to mastication is the so called “cold mastication”. Here, a separate mixing step prior to the “usual” mixing procedure can be used. However, this method can lead to uncontrollable high current/power peaks in the mixer and to an inhomogeneous masticated batch.

As already mentioned, the viscosity of NR is highly dependent on temperature. Processors should be aware that if NR is masticated at high temperatures, shear forces could be too low in order to achieve good carbon black (or filler) incorporation and dispersion in the following mixing steps.

As the process of mastication is done in the absence of fillers, the mixer in this case might be underfilled and this in turn could result in less effective mixing. Processors should therefore perform some principal mastication tests before implementing such mixing steps. These can be done after the mastication step is completed and the polymer is dropped and then analysed in terms of homogeneity of viscosity and temperature. Normally, intermeshing mixers are better suited to masticate in a partially filled process than tangential ones.

Usually the mastication process as a first mixing step should be finished in a time frame of 45 seconds ( $\pm 15$ ). Processors should also make sure that the batch has seen enough rotations under the ram (at least 45) before other compound components are added.

It is recommended to use the highest possible rotor speed and a low specific ram force (25 N/cm<sup>2</sup>). At this point in the process, the mixer has a low fill factor. The intake behavior for NR strongly depends on the surface- temperature of rotors and the mixing chamber. The use of higher temperature settings (minimum 40 °C) is recommended. The material behavior is also affected by the rubber temperature. In particular, the storage times of NR compounds between mixing steps have to be constant (minimum and maximum storage time). NR and NR blends exhibit a relaxation effect which has a big impact on the following processing steps.

The mastication effect can be influenced by special chemicals. Zinc oxide can be chosen to achieve faster tack to the surfaces of rotors and mixing chambers. To avoid excessive sticking to metal surfaces, zinc stearate, stearic acid, and sometimes waxes or low viscous polyethylene might be used [1]. If processors masticate natural rubber in a complete mastication step that is supported by aggressive chemicals (e.g., sulphur acid) it is important to use a special mixer design. In addition, the recipe should contain some parts of carbon black when the compound

temperature reaches 130 °C. Above this temperature NR's adhesion to metal parts is higher in comparison to other polymers.

If peptizers are used, which are effective in accelerating the breakdown of rubber and therefore achieving fast mastication, it should be taken into account that sulphur or antioxidants may decrease the mastication effect. Peptizers are designed to saturate the free chain ends, which are produced by shear destructions of the molecular chains. As a result, the mastication effect is quite temperature dependent. If temperatures are low, the speed of the "peptizer reaction" is also low; however, at 120 - 130 °C shear forces in the mixer are getting too small to achieve mechanical degradation, therefore the mastication is also very slow at this temperature level.

As already mentioned, even higher mastication temperatures lead to thermal degradation and should be avoided. A maximum mastication speed can thus be realized in a temperature range from 90 - 110 °C.

Due to its high temperature dependence, the viscosity can drop quite quickly during the incorporation phase of fillers. As a result, NR shows a very pronounced second power maximum (see BIT in Chapter 2) after filler addition. The low viscosity at the end of the mixing cycle and the described high adhesion to metal surfaces can lead to a considerable flow in the direction of the dust stops at the end of the mixing cycle. Also, a penetration of the area between ram and feeding chute is likely to happen under those circumstances. Whenever possible, processors should try to avoid both effects by reducing the ram pressure at the end of the mixing procedure.

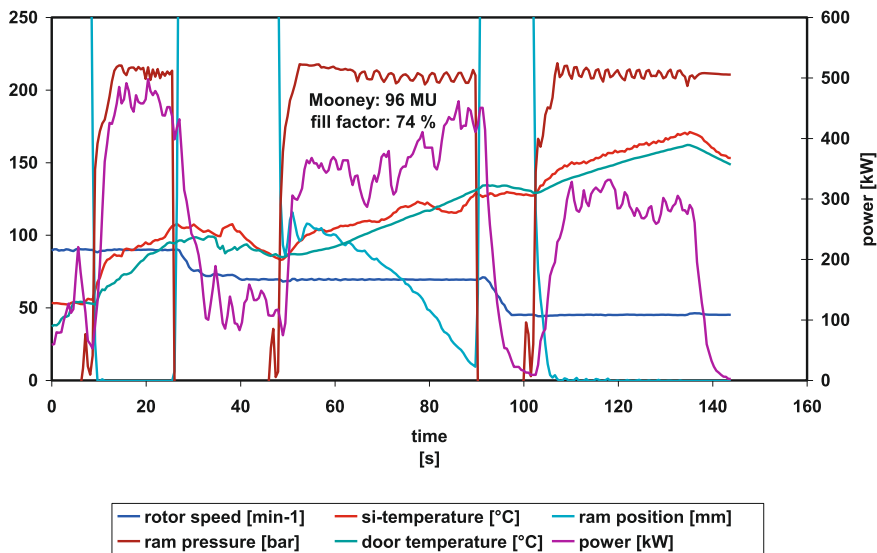
As natural rubber typically exhibits high elasticity, it can produce high pressures at the rotor flights. Consequently, strong ram movement can be seen, when NR is mixed.

A typical mixing process for high viscous NR is shown in Figure 3.1.

In step 1, polymer, zinc oxide, and peptizer are added to the mixer. The mixer (here 45L - intermeshing) is operated at high speed (90 rev/min) to achieve a high mastication effect. As a result, the mastication time itself is cut down to about 25 seconds.

The high temperature increase during this phase of mixing is acceptable because a lot of cold material is added in the following mixing steps and, as a result, the batch temperature is quickly reduced after the addition of the other components.

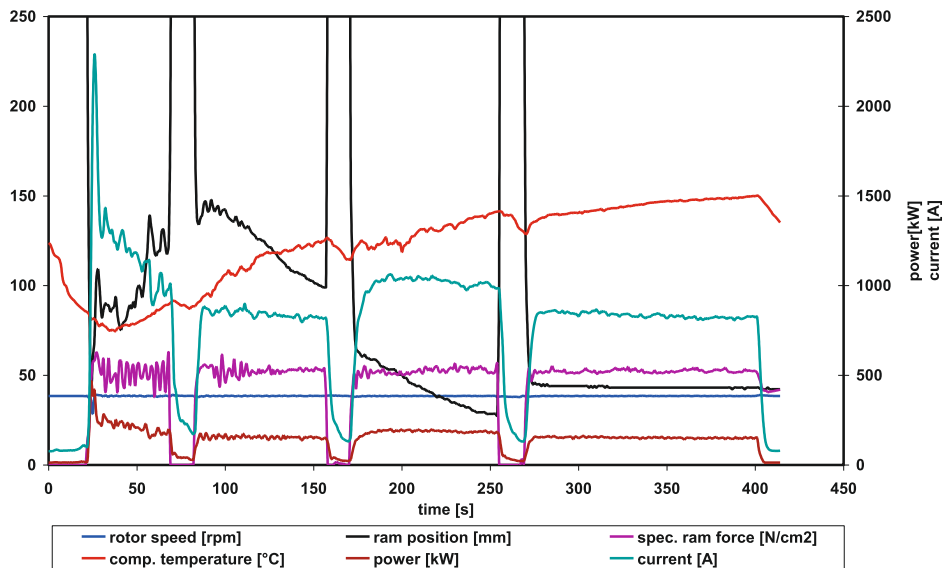
During the addition of fillers the speed is reduced to about 70 rev/min in order to guarantee a high power input. After the ram has reached its end position, the curing chemicals are added. In order to distribute these chemicals properly, the speed is once again reduced (to 45 rev/min). If the mixing conditions are kept constant, the viscosity level of the compound can be estimated on the basis of temperature and torque values (proportional to the amperes of the motor).



**Figure 3.1** Mixing curve (fingerprint) for a NR masterbatch (NR 96 ME ML (1 + 4, 100 °C))

The high viscosity of NR allows to “overfill” the mixer to a certain level. It means that even when the ram is still about 10 to 25 mm away from its end position, an effective mixing at the ram bottom takes place.

Figure 3.2 also shows a typical low viscous NR mixing procedure. It can be seen that after the second ram lift the ram is not able to reach its final position, because



**Figure 3.2** Fingerprint for a low viscous NR masterbatch

the low viscous compound is pressed into the gap between ram and chute in the last phases of mixing. The ram gets “jammed” in the chute and the compound in the mixing chamber is not affected by any ram pressure. Consequences of such “bad practice” are (at least) bad dispersion and potentially the long-term destruction of the walls of the feeding chute.

Depending on the height of the “jammed” ram, the temperature sensor is not able to monitor the proper compound temperature (bad flow around the sensor). In this case, the best option would be to lower the ram more slowly than normal (e.g., using a ram position control system). This phenomenon often occurs when mixing a second stage or a final stage of NR or NR blended compounds. Quite often processors are using the maximum ram pressure for all mixing steps. It is generally accepted that there is a correlation between ram pressure, shear force, and filler dispersion. As long as the BIT has not been reached, using the maximum available rotor speed and maximum ram pressure would be best. After dispersion is accomplished (as indicated by power or current peaks), the ram pressure can be lowered to a certain level in order to maximize lifetime of the mixer components and more importantly, to minimize problems such as a “jammed” ram. Usually the ram should “dance or oscillate” around its final position in the final mixing steps in all mixing stages.

NR is normally delivered in the form of bales. The mixing procedure is sensitive to the size of the dosed NR-lumps to the mixer (see also chapter two).

## ■ 3.2 Ethylene Propylene Diene Rubber (EPDM)

EPDM is often processed in the form of polymer blends. Due to the strong polyolefin base (especially when the ethylene content is high) EPDM are able to crystallize to a certain extent. To achieve specific final product properties, amorphous and crystalline types are often blended. As also shown in Chapter 6, fillers can have a tendency to move into a specific polymer. Due to this fact, often rather extended areas of unfilled and undispersed polymers can be found in these compounds because:

1. Crystallization of some areas of the “crystalline polymer”. As the crystallization already takes place at room temperature and is only very slowly reversible, the dosing temperature should be at least above 15 °C. Since crystallinity tends to increase with a decrease in temperature, it is appropriate to provide adequate storage time under sufficient warmth (hot room as for NR) to minimize dispersion problems. Some processors use a special milling process before they add the crystalline EPDM types to the mixer. If the processors have to work with a

wider temperature range regarding the raw polymer, it is recommended to add the crystalline type together with the filler to achieve the highest possible shear and also to destroy the crystalline parts (polymer lumps).

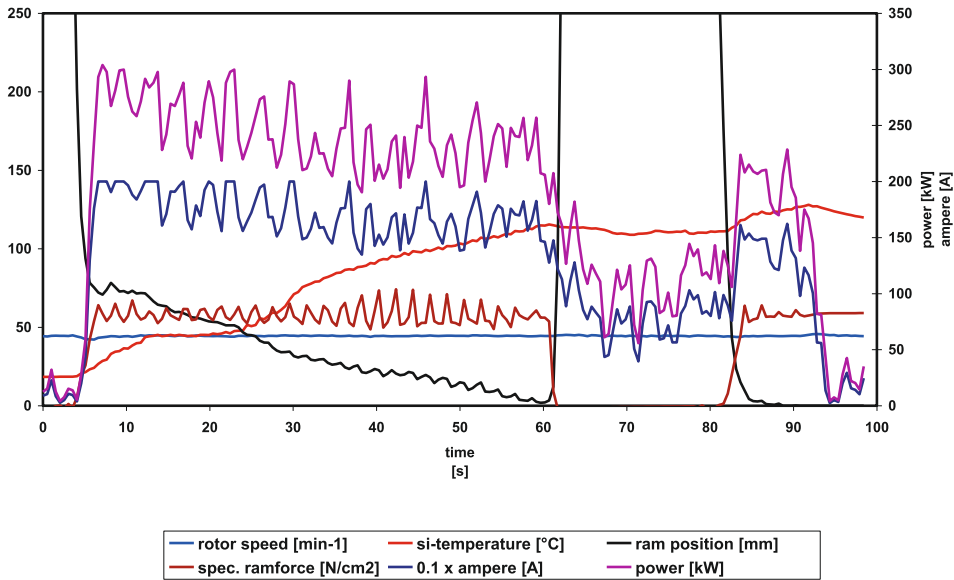
2. Filler transport into only one phase of the polymer blend. This can be avoided by a good “pre-blending” technique of the respective polymers before filler dosing. At the end of this mixing phase a good and desirable level of dispersion of the different polymers within each other must be achieved, in which the domain sizes should be as small as possible. Processors should therefore evaluate the quality of this preblending step by dropping the polymers after the completion of the preblending phase using a visual inspection. However, as EPDM recipes have often a high filler content, it may be difficult to preblend effectively because the mixer is underfilled during this phase of mixing.
3. High viscosity differences between crystalline and amorphous polymer. These effects can make it very complicated to disperse the high viscous polymer in a low viscous matrix. In such a case, processors should try to create shear forces as high as possible at the beginning of mixing. To this end and in some instances, it may be desirable or necessary to load the compounding ingredients in one shot using “upside-down” (rubber put in last, after fillers, oil, and so forth)<sup>1</sup>. Under such conditions, the mixer is highly filled at the very beginning of the mixing cycle (but effect 2 has also to be taken into account!). Also, higher rotor speeds can help to achieve better polymer dispersion. A challenge is mixing compounds with a high polymer viscosity but with a low batch viscosity at the end of the mixing cycle. Sometimes, the best way to process these different polymers is the addition of the soft amorphous polymer later in the mixing cycle, even after the BIT.

Another unique effect of EPDM recipes is the effect of “black scorch”. This means that at the end of the mixing cycle the compound viscosity starts to increase which results in a steady increase in the power demand of the mixer or a separate power peak. In further processing, scorched particles and surface defects can be found. To get “black scorch” no curatives, but rather EPDM and carbon black are necessary. In [2] this effect was investigated and it was shown that it is more pronounced for high ENB contents and high structured carbon blacks. It seems that bonding between the reactive surface areas on the carbon black side and some reactive ends on the polymer is responsible for this phenomenon.

The effect of black scorch can be suppressed by the addition of a very small amount of sulphur (about 0.1 phr) prior to filler incorporation. Figure 3.3 shows a typical one-stage mixing cycle for a recipe for technical rubber goods. At the beginning of the cycle, all compounding ingredients are loaded “Up-Side Down” into the machine. It can be seen that the power input is quite high, even at the start of the

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<sup>1</sup> This means to dose the fillers first and the polymer(s) afterwards



**Figure 3.3** Up-side down mixing cycle for an EPDM compound

cycle. Thus, good polymer as well as good filler dispersion could be achieved. After a final ram venting, the compound was dropped at a total cycle time of only 95 seconds.

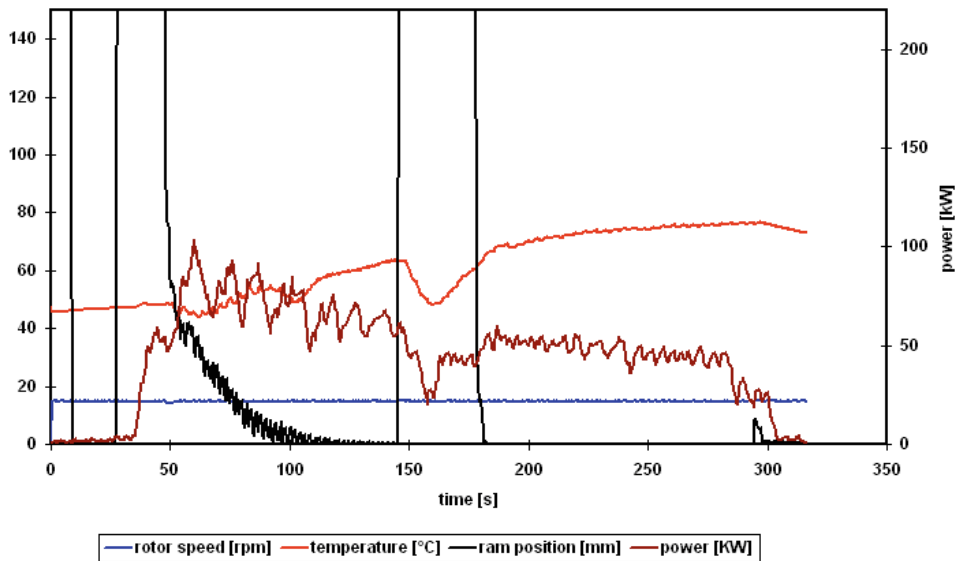
EPDM can be supplied in bale, granule and powder form. A special feature is a “friable bale”. These bales can be disintegrated by small forces and lead to a quick “crumbling” of the material. Antitack agents are used to keep bales in a “friable” form and to prevent the adherence of granules. If particle sizes are small at the beginning of the cycle, it is important to achieve a quick power input (in general: higher fill factors, high speeds, “up-side-down”, and so forth).

EPDM compounds are able to absorb a high content of oil in a short time. This is especially true if the compound temperature is elevated ( $> 80^{\circ}\text{C}$ ). As already explained in Chapter 2, the carbon black itself can also absorb a high amount of oil. To achieve this, it ought not to be completely incorporated at the time of oil injection.

Processors have the possibility to either buy oil extended polymers or to incorporate the oils (free oils) during the mixing cycle.

The best way to incorporate oils is to use a torque related oil injection system. Additionally, to prevent the low viscous compound from creeping up into the feeding chute, the compound temperature should be kept constant after the oil was injected. A controlled setback of the ram in this phase (e. g., by a ram position control) would be more recommendable.





**Figure 3.4** Power curve for an ultra low viscous EPDM compound

Figure 3.4 shows an example of a really soft compound. The viscosity of 7 Mooney Units was measured at ML 1+4 (120 °C). Compounds like this have to be mixed cold and the temperature settings are another main key for a good processing. The drop temperature was at 70 °C and the TCU set the rotors at 35 °C and the chamber at 45 °C. These compounds tend to stick to the rotors and to the rest of the mixing chamber. It is essential for a good quality that the mixer is completely emptied after the compound is dropped.

### ■ 3.3 Chloroprene Rubber (CR)

In principle, CR is able to react in a cyclic reaction. There are both sulphur and mercaptan modified types on the market, of which the latter are mostly used. Both exhibit a slow variation of their viscosity during storage and are able to crystallize. and their recipes contain slow, medium or fast crystallization rate types. As the “cyclization” goes on during the processing chain, temperatures should be kept as low as possible. In the mixer temperatures higher than 130 °C must be avoided and it is even recommended to stay below 110 °C.

CR is usually delivered in chips, which are approx. 75 mm long and contain anti-tackifiers to prevent the chips from sticking to each other and to guarantee quick power input into the compound.