

# 2 Mill Processability

## 2.1 Mastication and mill processability

Mixing of rubber is often preceded by kneading the gum rubber to soften it, a process called mastication. What happens to the rubber in this process may be observed in a mill. During World War II when synthetic rubbers were being developed difficulty in milling was one of the problems that needed to be overcome. In the later years with the introduction of a variety of synthetic rubbers, each rubber was found to show a unique behaviour on the mill. Through experience mill operators learned that there are certain patterns in mill behaviour. Accordingly, they adjusted milling conditions to ease the milling difficulties.

Subsequently, the milling patterns were classified by Tokita and White [1] into four regions of mill processability [1], see Figure 2.1.

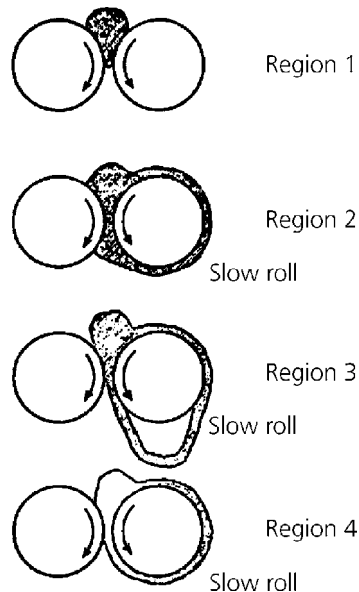


Figure 2.1 Regions of mill behaviour of rubber.

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When a piece of rubber is charged into a mill, if the rubber is too stiff, it slips on the roll and does not go into the mill-gap. If the rubber is forced into the gap, it breaks into pieces, falling down underneath instead of banding around the roll; this is Region I. When the rubber is soft enough it enters the mill-gap easily and forms a band around the roll. When the banded rubber is elastic enough and acts as if squeezing the roll, this is Region II. When the rubber is even softer, it enters the mill-gap, forming a band, but the band does not have the elastic tension; it tends to sag and tear, Region III. Further softening of rubber is accompanied by development of tack, whereby the rubber bands on the roll, however, there is no elastic tension, Region IV. Similar observations have been reported on the behaviour of rubber in the internal mixer [2].

When the behaviour of rubber is in Region I, the operator must scoop up the broken pieces of rubber and recharge them into the mill. This makes the milling operation cumbersome; therefore, the operator makes the mill-gap wide enough so that the rubber goes through without breaking or with a minimum break. The gap is gradually narrowed, while the rubber is passed through the gap repeatedly. Meanwhile the rubber becomes warmer and as a result its behaviour changes to that of Region II. The rubber behaviour in Region II is preferable, not only for mastication, but also for incorporation and dispersion of the reinforcing filler, such as carbon black or silica. In Region III, the operator sometimes pushes rubber against the roll in an attempt to establish a tight band but it is often ineffective. Moreover, the rubber sometimes adheres to the back roll, which is rotating at a somewhat higher speed. There are times when only a part of the rubber goes into the back roll and the rest remains on the front roll.

All in all the handling of rubber is very difficult. The operator tries to avoid Region III behaviour as much as possible. In Region IV there is no problem in the incorporation of the filler but the dispersion is not effective, because the stress transmitted from the machine to the filler agglomerate is not high enough to break it. The tack of the rubber also makes handling difficult.

When the internal mixer is used, the rubber behaviour is not directly observable. However, if the rubber behaviour is in Region I, the rubber breaks down to many pieces. If the filler is added before the rubber is massed, the incorporation becomes difficult. The mixing either takes too long or results in unsatisfactory dispersion. Region II is also the most preferred behaviour with the internal mixer. When the rubber is expected to behave in Region III or IV, the usual practice is to charge the filler first, followed by rubber, i.e., upside-down mixing. In this way a good dispersion of filler may be achieved.

Sometimes rubber and additives are charged together into the internal mixer without masticating the rubber. This is done with relatively soft rubber or with the aid of a 'process oil'. During mastication, NR chains break, resulting in a substantial decrease of

molecular weight. With synthetic rubbers only a small number of the chains usually break. However, some chain breaking does occur, resulting in the generation of free radicals. The free radicals react with other polymer chains to form long branch chains.

NR, in general, has a very high MW and mastication is used to bring its molecular weight down to a more easily processible range. Traditionally, the MW level expressed as a Mooney index of 50 was considered to be the easiest processing level. This is the reason why the standard grade, E-SBR 1500 (copolymer of styrene and butadiene prepared by emulsion polymerisation) was made to a Mooney index of 50. The E-SBR, as is well-known, was the first synthetic rubber designed to be a substitute for NR.

## **2.2 Interpretation of mill processability**

In section 2.1 the behaviour of rubber on the mill was explained with respect to four typical behaviours, i.e., four regions of processability. With some rubbers, milling starts from Region I, finishing at Region II, and other rubbers remain at Region II throughout milling. Starting from Region II, sometimes rubbers go to Region III or Region IV. Nevertheless, the four regions of behaviour are common to all rubbers; therefore, it provides a means of systematic classification. The scientific explanation for the four regions of processability behaviour is as follows.

In Region I, the rubber is too stiff which means that the modulus is too high. If the rubber is forced into the mill-gap, it breaks into pieces because the strain at break is not large. In Region II, rubber has an ideal softness; that is, the modulus is lower than that in Region I. The rubber does not break and makes a tight band around the roll because its strain at break is large. In both Regions I and II the elasticity is the controlling factor.

But, what is elasticity in this context? The high elasticity does not necessarily mean a high modulus. It is related to the extensibility and more importantly to the ability of the rubber to recover from deformation. Although elasticity controls Region I and II, the temperature of the rubber increases as the milling continues. This is due to the internal friction, which is the viscous contribution. Therefore, both viscosity and elasticity are recognised to be the contributing factors. Thus, the subject of viscoelasticity is introduced into mixing of rubber.

When a certain amount of mechanical energy is imparted to rubber a part of the energy is stored as elastic energy and other part is dissipated as heat. A part of the energy converted to heat is lost. Only the elastic energy is effective for recovering from deformation. When the elasticity is controlling Region I and Region II behaviour, it means the ratio of stored energy to dissipated energy is high.

In Region IV, the modulus is lower than in Region II; the elasticity becomes low, giving a large permanent deformation. It is a fluid state, which is manifested as tackiness. In Region IV viscosity is the controlling factor.

Region III is the border between Region II and IV where elasticity and viscosity compete with each other for the control of the overall behaviour. Rubber on the mill is not uniform; when it is taken out as a sheet, it is wavy and has non-uniform thickness. In Region III the overall behaviour comes from Region II in some areas and Region IV in other areas. Region II and IV co-exist like a mosaic pattern. The areas where viscosity dominates lack tension and therefore, the rubber sags. The areas of high elasticity pull apart the viscous, weak areas, which deform permanently and tear.

Summarising the discussion up to this point, the state of rubber during roll-milling may be classified using modulus, strain at break and a ratio of elastic to viscous energy. The modulus and the viscoelastic ratio are subjects concerning deformation and flow, i.e., rheology. The strain at break is related to a large deformation and failure. Thus, a bridge is built between the hands-on experience of roll-milling and scientific methodology.

The increase of the temperature resulting from the milling of rubber tends to change the behaviour of rubber in the direction from Region I towards Region IV. Instead of the viscous heat generation, the machine or rubber may be externally heated to bring about the same change. This indicates that temperature is an important (dynamic) state variable.

When a rubber has a milling problem in Region I, the mill-gap is made wider in the beginning and gradually the gap is made narrower. When the roll speed is kept constant, a wider gap makes the deformation rate lower. The wider gap also gives a smaller deformation. However, the rubber behaviour needs to be considered from a dynamic (time-dependent) view point; therefore, deformation rate is selected rather than deformation itself as a variable. In general, when the gap is made wider, the rubber behaviour changes in a direction from Region I towards Region II; the reverse change can also occur. Therefore, the deformation rate is also a dynamic-state variable. Increasing temperature and decreasing deformation rate changes the rubber behaviour in the same direction: that is, there is a correspondence between temperature and deformation rate. Under the lower deformation rate, deformation takes a longer time. Therefore, the above correspondence may also be called time-temperature correspondence. However, at this stage of the discussion the correspondence principle remains to be qualitative. It must be differentiated from the quantitative definition of viscoelasticity [3].

When the mill processability is in Region II, it is within the time-temperature window, which defines the rubbery state. The Region I is the border (transition) between the

rubbery and glassy state. The Region IV is the flow state outside of the window. The Region III is at the border between rubbery and flow state.

Although most of mixing of rubber has been done with a tangential mixer, some rubbers like EPDM may be more advantageously mixed with an intermeshing mixer. If a relatively stiff rubber such as E-SBR or NBR is charged into an intermeshing mixer, the rubber tends to behave like Region I in the mill because the gap is narrow. The problem may be overcome by prewarming the rotors. EPDM softens easily and is not likely to give the behaviour of Region I. The basic difference between EPM and NBR in viscoelastic characteristics is described in Chapter 6.

So far the discussion has covered traditional rubber processing for making tyres, belts, and other industrial products. However, the recent trend of using new materials such as thermoplastic elastomers and polymer blends should also be noted. Also, non-traditional formulations have been developed, for example, for rollers in office printers and belts for money changers. Sound-proofing and vibration-damping are another area, which bring new formulations. For these new areas, the criteria of the mill processability may or may not be valid. When polymers of widely varied glass transition temperature ( $T_g$ ) are blended, grafted or block-polymerised, the time-temperature correspondence discussed earlier, becomes very complicated. Therefore, interpretations of the mill behaviour must be properly modified. Even when the four regions of the mill processability appear applicable, subsequent handling of material may require fresh thinking. More discussion on this topic will be given in Chapter 14.

### **2.3 Science of mill processability**

When the mill behaviour can be related to the fundamental properties of rubber, the mill-operator's experience can be interpreted in a scientific manner. When a piece of rubber is subjected to tensile testing, its modulus and the strain at break can be evaluated. The test may be performed at different temperatures and with different deformation rates, in order to include all ranges of temperature and deformation rates encountered in the mixer. An example of tensile stress-strain data is shown in Figure 2.2 for a sample of NBR [4].

A high speed tensile tester was used to match the deformation rates in the internal mixer.

This type of experiment has been a subject of scientific investigation for some time. The failure behaviour is presented as a locus of breaking strength and the breaking strain, i.e., failure envelope [5]. Examples of the failure envelopes are shown in Figure 2.3a for four different grades of NBR [4].

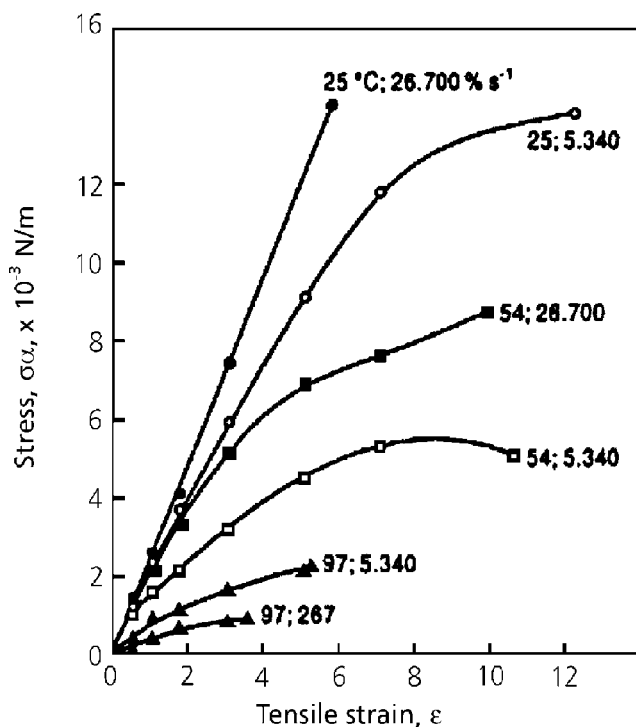


Figure 2.2 Tensile stress-strain data of NBR.

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The stress,  $\sigma$ , based on the undeformed cross-section is converted to that based on the deformed cross-section with a use of the extension ratio,  $\alpha$ . The value plotted in the figure,  $\sigma_{\infty}$  is therefore the true stress.

As mentioned in section 2.2, the characteristic mill behaviour can be defined on the basis of modulus and strain at break. Therefore, a new failure envelope is proposed as a locus of the modulus at break and the strain at break [4], see Figure 2.3b.

The upper part of the figure corresponds to the lower temperature or a higher rate of deformation; the modulus is high and the breaking strain is small, Region I. Either by increasing temperature or decreasing the rate of deformation, the behaviour moves downward in the figure, showing the lower modulus and the larger strain at break, Region II. Passing downward through this region in the figure, the strain at break becomes smaller, Region III. The bottom part of the figure represents Region IV, where the temperature is even higher or the deformation rate is lower. Whether the breaking strain becomes larger or not, cannot be ascertained, because at Region IV the specimen tends to elongate non-uniformly.

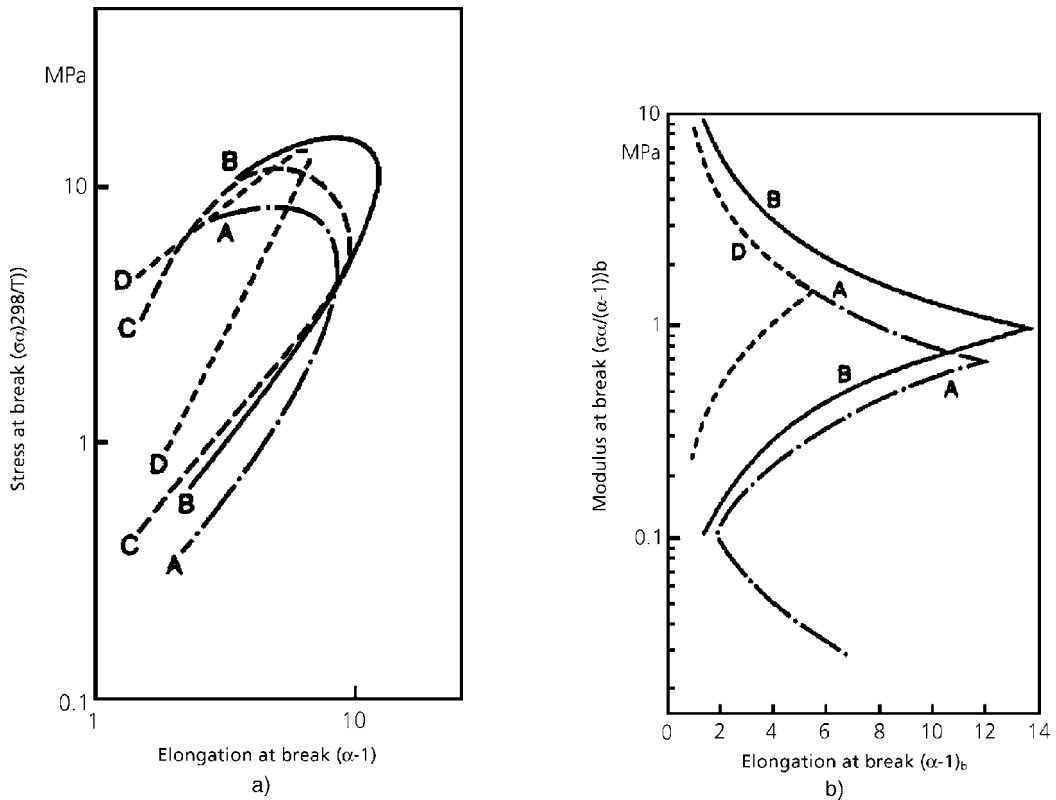


Figure 2.3 Failure envelopes of butadiene-acrylonitrile copolymer, samples A, B, C and D.  
 a) locus of breaking strength and breaking strain  
 b) locus of modulus at break and elongation at break

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In this figure, samples A and B show Region II behaviour, indicated here with large strain at break; these are easy to mill. Sample D does not deform as much as samples A and B. Also, at the maximum strain at break, the modulus is high. Sample D tends to give Region I behaviour. Although not shown in Figure 2.3b, the behaviour of sample C is similar to those of A and B.

Because the mill behaviour and the results of the tensile test are shown to be related, the tensile test results may be used for the characterisation of processability for a given rubber. This aspect will be expanded in Chapter 6.

Mixing in a mill or an internal mixer involves both small and large deformations. The modulus at break is only one point in the large deformation. Therefore, the evaluation of modulus over the range from small to large deformation is required in order to fully explain the mixing behaviour.

Samples A and B are 'gel-free' grades and sometimes called easy processing grades. Method of the gel determination is given in ASTM D3616-95 [6] and sometimes as much as a few percent of gel may be found by this method without giving processing difficulty. A difference between A and B is their MW level. A lower MW rubber, A, was made using a MW modifier, which also suppressed the branch formation.

Sample D was made in such a way that it contained approximately 70% of macrogel. Although this material presents mixing difficulties, it is made for special applications. For example, it accepts a higher amount of reinforcing filler, e.g., carbon black, compared to samples A and B. It also provides a higher 'green-strength' (resistance to sagging), when a sheet of uncrosslinked compound is held up. When high gel-content latex is coagulated, dried and compressed into a bale, the multi-branched gels appear to form a complex network of entanglement. This entanglement is different from that formed by linear molecules. The entangled gel-network makes the bale appear as if it were permanently crosslinked. This type of gel is sometimes called a 'macrogel', because of its appearance. In reality, however, each gel molecule is microscopic in size, because it was formed in an emulsion particle.

The macrogel is different from crosslinked latex particles prepared with use of a difunctional comonomer; the latter is sometimes called, 'microgel', which contains crosslinked network chains and some branches. The rubber containing a significant amount of macrogel tends to behave as Region I at the beginning of milling. In the open mill an operator can make an adjustment of mill gap and thereby the milling operation may be controlled. With an internal mixer, however, the behaviour of rubber is not directly observable. Therefore, it is important to know the characteristics of a rubber before mixing. Otherwise, the results of mixing may be unsatisfactory and the compound may have to be remilled. How much macrogel is allowed in a gum rubber in order to avoid the mixing problem, depends upon the mixing conditions and formulation. For example, the mixer may be prewarmed or a process oil may be added.

Sample C contains 50% of microgel, and the other 50% is the same as sample B. Its mill behaviour is very similar to samples A and B. All grades of NBR exhibit either Region I or Region II of mill behaviour except for a specially made grade having a very low MW, which may show Region III or IV behaviour. The E-SBRs behave in a similar way.

On the other hand rubbers made through anionic polymerisation tend to go into Region III and IV. These rubbers have a very narrow MW distribution and no branches unless

the rubber is manufactured to have them by design. The reason for the mill behaviour is the absence of the high MW tail of the distribution. If the distribution is not extended to the high MW tail, even though the distribution is not necessarily narrow, the rubbers still tend to go into Region III and IV. This trend is accentuated if the average MW is low or there are no longer branches.

ACM is made through emulsion polymerisation, in much the same way as NBR is. There is a chain transfer mechanism, resulting in long branches and macrogel. Yet, this rubber tends to go to Region III or IV. The reason lies in its chain structure. The 73% of its MW is in the pendent group and therefore, it is a fat and short chain. Even when the MW is high, it acts like an equivalent of the low MW NBR.

*Cis*-1,4-butadiene rubbers (*cis*-1,4-BR) tend to go into Regions III and IV, even though they are very long and thin molecules, 100% of their MW being in the main chain. This is because their  $T_g$ , is very low, -112 ~ -120 °C. The normal milling temperature lies at the upper border of the time-temperature window.

In general the question of which region of mill processability a given rubber goes into, is related to its time-temperature window. Temperature-wise it is the processing temperature range compared to the  $T_g$  of a given rubber. Time-wise it is related to a 'mobility' of a given molecular segment at the shorter times and the mobility of the whole molecule at the longer times. The shorter-time border of the window is independent of the MW and the longer-time border is dependent. In the latter, therefore, the higher the MW the wider the window time-wise. Instead of the term 'mobility', the term 'relaxation-time' is used in science and its definition is given in Chapter 6.

The low MW tail of the molecular weight distribution is usually not a concern in rubber processing. The rubber is manufactured not to have this fraction, because it weakens the finished products.

MQ made through a condensation reaction is an exception. Because of the inherent nature of the reaction, there are low MW fractions, as discussed in Chapter 1.

## References

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