Evaluation of rubber processing in unvulcanised rubber

H. Kondo
Chemicals Evaluation and Research Institute, Japan

INTRODUCTION

Rubber processing technology could be described as an integrated production system technology based on information about the structure, rheology, mechanical properties and thermal ageing behaviour of the polymers used. If such a system is to be operated without problems under optimum conditions, it is vital to go beyond the long-standing approach of intuition and experience specific to rubber, and define the processing conditions at the mixing stage, vulcanising stage, etc, quantitatively. The processing of rubber materials can be broadly divided into the sequence: (1) reception of raw materials ® (2) compounding ® (3) mixing ® (4) inspection of mix ® (5) extrusion/calendering ® (6) vulcanising ® (7) finishing/inspection. Rather than functioning in isolation, however, the steps in this sequence interact with one another. For instance, the viscosity of the unvulcanised compound in mastication of the rubber stock and mixing the compound will be considered. From observations on unvulcanised rubber in an open roll, deformation behaviour can be broadly divided into the four regimes shown in Figure 1. In the mixing step, free end groups increase as milling proceeds, owing to temperature rise in the mixed compound, disentanglement of polymer entanglements, and scission of molecular chains; polymer viscoelasticity changes and behaviour shifts from regime 1 to regime 4.

MILLING BEHAVIOUR ON OPEN ROLLS [1, 2]

The deformation behaviour of the rubber compound in mastication of the rubber stock and mixing the compound will be considered. From observations on unvulcanised rubber in an open roll, deformation behaviour can be broadly divided into the four regimes shown in Figure 1. In the mixing step, free end groups increase as milling proceeds, owing to temperature rise in the mixed compound, disentanglement of polymer entanglements, and scission of molecular chains; polymer viscoelasticity changes and behaviour shifts from regime 1 to regime 4.

Regime 1

Directly after charging to the rolls, the polymer is relaxed in a highly entangled state and fed into the nip by friction with the roll, whereupon mixing commences. The mixed compound passes between the rolls for an extremely short time, less than 1 second; when the rubber temperature is low and deformation is imparted only briefly, therefore, the rubber under deformation cannot conform to the roll geometry and recoils, exhibiting elastic behaviour.

Figure 1. Milling behaviour on open rolls
Regime 2

Mixed compound emerging from the nip forms a band wrapped around the front roll, leaving a bank over the roll nip. In this state part of the compound in the bank exchanges with part of the compound feeding through in the band and mixing proceeds in the radial direction from the band surface towards the roll surface; at the same time, dispersion of the filler, etc., is in progress. As it passes through the nip, the mixed compound undergoes a rise in temperature under shear heating followed by molecular chain scission, and fluidity increases, resulting in regime 2. In this regime the mixed compound is stretched by the rolls; since the compound retains its elastic properties, restitutional force maintains the wrapped state on the rolls. Since roll wrapping is related to the tensile stress in the compound, a suitable method of evaluation is to measure green strength. The stress-strain curve when roll wrap is satisfactory indicates a state where stress rises, albeit slightly.

The bank formed between the two rolls is a site of exchange between the bank and the band wrapped on the roll. Under continuous shear and compression in the roll nip, the filler and other compounding agents are progressively broken up and comminuted and make contact with the fresh rubber surface exposed as the rubber compound stretches. The compounding agents are thereupon taken up through elastic recovery of the rubber compound. Natural rubber has chemical crosslinks as well as polymer entanglements, making a mastication step necessary in order to break the network chains and create a flowable state.

Regime 3

Instead of wrapping to the roll, the mixed compound that has passed through the roll nip sags in bag fashion (“bagging” - also called “fundoshi” in the factory) with the result that no rotary motion occurs in the bank. In this state, without shear of rubber versus rubber, almost no dispersion of compounding agents or mixing can proceed. With progression from regime 2, the polymer undergoes scission, green strength diminishes, and elongation falls. The rubber also suffers a marked decline in elasticity, exhibiting plastic rheology; after passage of the compound through the nip, therefore, the rate of contraction falls below the speed of the roll surface, the tendency for roll wrapping decreases, and bagging occurs. Furthermore, since the elongation at break decreases, splits develop in parts of the compound.

Regime 4

The wrapped compound cannot detach from the roll, making it difficult to carry out the cutting and rolled batch endwise pass operations important for distributing and dispersing the compounding chemicals; a state thus arises where mixing by exchange of mixed compound between band and bank is inefficient. Under regime 4, the temperature of the mixed compound rises and molecular chain scission continues unbroken with passage of mixing time. Viscous motion of the compound becomes dominant and the stress-strain curve in green strength determination no longer rises, the compound exhibiting viscous rheology instead. Owing to marked adhesion to the roll, the feed back of compound in the bank that developed in regime 2 becomes difficult and dispersion or mixing of compounding agents ceases. Another result is difficult sheet off, impacting on the subsequent processing steps.

Hence, for effective mixing to proceed, it is vital that the mixed compound on the roll maintains its regime 2 status and continues to form a firmly wound band.

KNEADING BEHAVIOUR IN AN INTERNAL MIXER [3]

Unlike open rolls, the Banbury mixer and pressure kneader forms of internal mixer do not allow direct observation of the rubber during mixing. The state of mixing is generally inferred from a torque (power) versus mixing time curve of the kind shown in Figure 2, and the final decision often has to rely on the operator’s experience.

Comminution (fine division)

This refers to the process whereby the large masses of rubber stock charged from the hopper are broken down to a size suitable for uptake of compounding agents. Under mechanical shearing and stretching forces, the rubber stock charged to the internal mixer becomes finely divided, with increase in surface area and simultaneous mechanical scission of the rubber molecules. Torque rises...
directly after charging to the internal mixer as the large masses are broken down.

**Uptake (incorporation)**

The early stage of mixing directly after carbon black has been charged is marked by a sudden rise in torque owing to (1) increase in apparent packed volume due to entry of bulky powder to the chamber, (2) intake into the space between rotors directly beneath the ram, and (3) stretching, compression and tearing in the tip clearance between the rotor blade and internal wall of the chamber, and a first peak appears.

**Dispersive comminution (dispersion)**

This describes the process whereby particulate compounding agents, etc., taken up into the interior of the rubber stock by shearing and stretching are dispersed and comminuted. Shearing deformation and stretching deformation produce successive fresh rubber surfaces where the particulate compounding agents are taken up. With uptake of carbon black into the rubber, the exposed rubber surfaces cling together, creating large rubber masses. As the rubber masses increase in size, the torque rises again and exhibits a maximum when the mixed compound has formed an integral mass. This point marks the BIT (black incorporation time). The carbon black taken up into the rubber continues to disperse thereafter, the torque gradually decreases and the curve gently falls away. The dispersion of carbon black is essentially complete at the inflection point on the curve.

**Mixing and homogenisation (simple mixing)**

Here the compounding agents incorporated are uniformly mixed: the dispersed and comminuted compounding agents undergo repeated shear and stretching deformation, mixing with the thoroughly kneaded rubber to form a homogeneous compound.

**METHODS OF EVALUATING PROCESSABILITY**

In view of how the compounding agents are incorporated and dispersed in the rubber stock during mixing, the chief aims in the evaluation of mixing are (1) to evaluate the flow and viscoelasticity of the unvulcanised rubber, and (2) to evaluate dispersion of the compounding agents, particularly the fillers such as carbon black. The indices used in evaluating the flow of unvulcanised rubber are the Mooney viscosity and the melt viscosity by capillary rheometer. The Mooney viscosity represents the viscosity in the low shear rate range but it is quick and easy to measure and is therefore much used for processability evaluation in the factory. The capillary rheometer allows melt viscosity to be measured at the shear rate during extrusion, etc, and is therefore also used in process control applications. The degree of dispersion of carbon black can be determined by directly counting undispersed agglomerates by light microscope as in ASTM D2663 "Standard Test Methods for Carbon Black - Dispersion in Rubber"; other methods of evaluating the dispersion of compounding agents include evaluation with the electrical conductivity of the mixed batch, and evaluation of the roughness of the cut surface.

**Viscosity measurement**

The viscosity data from evaluation of unvulcanised rubber commonly appertain to forming processes, as in roll processing, extrusion and press forming. From the compounding standpoint, viscosity varies markedly with polymer grade, the compounding agents such as carbon black and plasticiser, and the compound recipe. A two-fold approach is used in evaluating the flow of unvulcanised rubber: one is to detect the stress when the sample is subjected to deformation at different rates, chiefly by means of viscometry. The viscometer may be of the rotary type or extrusion type, the former represented by the Mooney viscometer and the latter by the capillary rheometer. The other approach is to measure the change in deformation with time under constant load, typically with a plasticity meter or plastometer. The parallel plate instrument is simple to operate and is currently used in the quality control of natural rubber and silicone rubber; it is generally known as the rapid plastometer. Although Mooney viscosity is widely recognised, the industry has in recent years been keen to make use of CAE (computer aided engineering), and there is great demand for viscosity data from capillary measurements. Figure 3 shows the relation between method of evaluation and the shear rate imposed on unvulcanised rubber during forming. The fluidity of the unvulcanised rubber in different forming steps differs greatly at the rate of shear imparted in processing the rubber. At low shear rate polymer melts generally show Newtonian flow, with viscosity virtually independent of shear rate. At high shear rate, however, they exhibit non-Newtonian flow, viscosity decreasing as shear rate increases. Polymers A and B show little difference in the shear range of Mooney measurement and have almost the same Mooney viscosities. However, when viscosity is determined over a wider range of shear rate with a capillary rheometer, A and B have different viscosities, affecting polymer flow.

Different manufacturing processes apply different rates of shear to the unvulcanised rubber. In other words, while processability tends to be evaluated at factory level with Mooney viscosity data alone because of
the convenience of measurement, viscosity data at the shear rates applied are required for the specific means of processing.

**Measurement of Mooney viscosity**

In determining Mooney viscosity, 100 Mooney is taken as the torque per 83 N.m when a rotor milled with grooves is rotated at 2 rpm in a die cavity at 100°C. The mean shear rate of the rotor is 1.25 s⁻¹. Other viscometer types recently used have a variable speed rotor or measure the rubber relaxation behaviour from the decay in torque when the rotor is stopped suddenly during viscosity measurement. The usual Mooney viscosity curve shows a sharp rise in torque directly after measurement, with a gradual decline once torque has peaked. In other words, a stress develops straight after deformation and then decreases as flow commences. This phenomenon is the result of scission of carbon-polymer and carbon-carbon linkages in response to the initial shear stress, thereby initiating flow, and can be viewed as thixotropic behaviour. The mode of deformation in measurement of Mooney viscosity is thus shear, which would be the same mode of deformation as when the Payne effect is manifested. The following four points should be borne in mind when measuring Mooney viscosity: (1) the shear rate distribution and stress distribution are uneven, and averaging must hence be used in converting Mooney viscosity data to shear stress-shear rate data; (2) the sample temperature distribution at the start of testing is uneven since the rotor in the sample chamber is not amenable to direct heating control; (3) the torque data include the rotational friction generated in the seal part of the rotor shaft; and (4) rotor management impacts on Mooney viscosity. Thus, evaluation procedures using Mooney viscosity data, containing as they do such indeterminate errors, need to allow for the above points when the results are being analysed.

**Capillary rheometer measurements**

The capillary rheometer has pressure sensors located at two or more points on the side wall of a cylindrical die and determines viscosity from the pressure gradient in the rubber as it passes through the die, using the die dimensions and shear rate. The shear rate can be varied from 10² to 10⁵ s⁻¹ by adjustment of the rate of extrusion from the die; the viscometer thus covers a wide range of shear rate. The JIS specification appears in the group dealing with the evaluation of plastics, and a specification for rubber materials is laid down in ASTM D 5099 “Standard Test Methods for Rubber - Measurement of Processing Properties Using Capillary Rheometry”. Measurements on rubber require attention to the conditioning time between sample loading and the start of measurement. Moreover, since a large pressure loss arises with rubber, a Bagley correction is necessary. To make the Bagley correction, the test pressure is measured as a function of apparent shear rate in two or more dies of different L/D ratio; the test pressure is then plotted as a function of L/D at the apparent shear rate (a Bagley plot) [6], where L is the capillary length, and D is the capillary diameter. The slope of the plot is four times the true shear stress, and the intercept corresponds to the pressure loss at the die entrance and exit. Change in properties at the ripening point in unvulcanised rubber may be identified as a point for attention common to all viscosity measurements. Figure 4 shows the changes in Mooney viscosity and bound rubber content when unvulcanised carbon-compounded
SBR (styrene butadiene rubber) was ripened at 23°C x 50% RH for a maximum of 21 days [7]. There is a tendency for Mooney viscosity and bound rubber content to increase with increase in ripening time. The results for unvulcanised rubber properties also vary depending on whether measurements are made some days after mixing or the material is remixed before measurement; caution is therefore required in processability evaluation and compounding investigation.

**Evaluation of carbon black dispersion**

Dispersion of carbon black greatly affects not only the processability and properties of the unvulcanised rubber but also the properties of the vulcanisate. Dispersion of carbon black at the site of production is not simply a matter of macro- and micro-dispersion, and within-batch and between-batch variation must be taken into account. A rapid method of evaluation is therefore required in the factory. The chief methods of evaluating the level of dispersion of carbon black are listed in Table 1.

**ASTM D2663 “Standard Methods for Carbon Black - Dispersion in Rubber”, method B**

Evaluation by light microscope as typified by ASTM D2663 Method B is an excellent way of quantifying visualised images. The size of carbon black amenable to observation by light microscope is several µm or larger, affording an index of macrodispersion. Advances in image analysis hardware have now greatly reduced the time taken for measurements. However, as the field of observation is several mm across, information can only be obtained over an extremely limited area.

Steps that must be taken to ascertain within-batch uniformity of dispersion, therefore, include increasing the sampling frequency and number of fields of observation in the sample. Figure 5 shows the results from a comparison of the level of dispersion of carbon by ASTM D2663 Method B for NBR (nitrile rubber) of the same recipe mixed at room temperature with an 8 inch open roll and 2.5 L pressure kneader, respectively [8]. Comparison of the pressure kneader and roll in respect of agglomerate distribution shows there is little difference in distribution profile. The mean agglomerate size is 11.1 µm for the pressure kneader and 9.0 µm for the roll. Despite the roll and kneader compounding carbon black at the same recipe loading, the roll gives fewer agglomerates than the kneader at all agglomerate sizes. This is because more agglomerate particles of nm order undetectable by the ASTM test method arise in roll mixing. As shown in Table 1, the ASTM method uses a light microscope to evaluate the number of carbon agglomerates as macrodispersion, but it must be remembered that agglomerate particles of nm order are not counted in the histogram obtained, the method simply evaluating dispersion of µm order.

**Electrical conductivity**

The electrical conductivity method measures microdispersion, i.e. the carbon network. As microdispersion progresses, contact between aggregates diminishes, and

<table>
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<tr>
<th>Method of evaluation</th>
<th>Level of dispersion</th>
<th>Characteristic features</th>
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<tr>
<td>ASTM</td>
<td>Macro</td>
<td>Evaluates dispersion by rating with a light microscope</td>
<td>Vulcanised</td>
</tr>
<tr>
<td>Electron microscope (TEM)</td>
<td>Micro</td>
<td>Examines ultrathin sections from an ultramicrotome</td>
<td>Vulcanised</td>
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<tr>
<td>Atomic force microscope</td>
<td>Micro</td>
<td>Measures phase image of specimen surface</td>
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<tr>
<td>Small angle X-ray scattering</td>
<td>Micro</td>
<td>Analyses angular dependence of scattering intensity</td>
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<tr>
<td>Electroconductivity</td>
<td>Micro</td>
<td>Enables evaluation for carbon blacks at equal loading</td>
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<td>Mixing torque</td>
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<td>Micro</td>
<td>Evaluates dispersion from the Payne effect</td>
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![Figure 5. Carbon black agglomerate distribution from different mixing processes](image-url)
conductivity falls. The method is effective when scaling up a mixer, for example, but is unsuited to comparative evaluation of dispersibility in different compounds; furthermore, since conductivity is dependent on carbon loading, comparative evaluations cannot be made unless the recipe remains the same. Again, measurements on high structure or high filler recipes are impossible with commercial instruments because the conductivity exceeds the observable range. The procedure for measuring volume resistivity is straightforward but, on closer inspection, factors other than dispersion of carbon black, such as temperature, the pressure on the sample, sample thickness and the state of the surface have a subtle effect, serving as sources of variability.

**Dynamic viscoelasticity**

The dynamic viscoelasticity method applies a sinusoidal strain to the rubber specimen and measures the resulting stress. Strain dependence of the dynamic storage modulus \(G'\) would be expected to manifest with increase in strain, as the linkages between aggregates break down, i.e. as the carbon network structure disintegrates: 

\[G_0 - G_\infty = \Delta G'\]

then indicates the amount of carbon network in the polymer, providing an index of microdispersion. \(G_0\) is the dynamic storage modulus of the carbon black filled rubber and \(G_\infty\) is the dynamic storage modulus under high strain when the carbon network structure has been completely broken down, and is larger than in the pure gum. This means that microdispersion is better the smaller the strain dependence of the dynamic storage modulus. When measuring \(G'\), care is needed with security of contact between the jig and sample for both uncured rubber and cured rubber; slip occurs more easily the higher the strain range, causing variability.

**Measurement of green strength**

Green strength can be measured as an evaluation of the processability during mixing and operability in transport of the mixed compound to the next processing step. Test specifications are prescribed in ISO 9026 “Raw Rubber or Unvulcanized Compounds. Determination of Green Strength” and ASTM D6746 “Standard Test Method for Determination of Green Strength and Stress Relaxation of Raw Rubber or Unvulcanized Compounds”. As shown in Figure 6, the dumbbell test pieces of ISO 9026 have a bulging grip section; rather than gripping the dumbbell, the jig is latched onto the bulge, avoiding breakage at the chuck. In ASTM D6746 the dumbbell shape test piece, taken from 2 mm thick unvulcanised sheet, is gripped with an air chuck and is therefore prone to failure at the grip when the clamping pressure is too great. In Japan the No. 1 dumbbell specified in JIS K6251 is commonly used, but it can be difficult to exclude air when fabricating the test piece, and the air retained within the test piece greatly affects the stress-strain curve. Since unvulcanised rubber readily undergoes plastic deformation, the use of a camera extensometer offers higher reproducibility than a contact type strain gauge.

**Evaluation of extrudability**

A method for extrudability is prescribed in ASTM D2230, which entails Garvey die measurement of extrudate geometry and evaluates die swell. The former evaluation uses a Garvey die and the latter a round die. The Garvey die test uses a die of fixed shape and size to determine extrudability, allocating a four point score to each of four items (giving a full score of 16 points): (1) the sharpness of the extrudate edges, (2) continuity, with unbroken edges, (3) smooth gloss on the surface skin, (4) the porosity in the cross-section. Although measurements can be made with a laboratory size screw extruder, it is desirable that 

\[L'/D' \leq 5\]

and the length from the screw tip to the die is within the range 1-2 times \(D'\), where \(L'\) is the screw length and \(D'\) is the outer diameter of the screw. Measurements are often made without recourse to a breaker plate. Care should be taken when making measurements to charge a warmed up sample and ensure no force is applied that would deform the extrudate during the test or in storage.

**CONCLUSIONS**

The processing of rubber is an advanced technology in which mechanical shearing and stretching forces are applied to the rubber stock while plasticity is imparted and various compounding agents including filler are added, simultaneously generating chemical and physical
changes to obtain the desired mixture. Furthermore, there are diverse ways of processing rubber products, and the deformation and temperatures experienced by the unvulcanised rubber differ greatly in each case. However, compared with the analysis of vulcanisates and evaluation of their properties, there is little processability evaluation of unvulcanised rubber, and there are at present a limited number of standards. In this context, selection of evaluation methods that reflect the deformation of the unvulcanised rubber during processing, and the establishment of measurement conditions such as temperature and rate of deformation, are important for quantifying and objectifying the processing technology hitherto managed with empirical knowledge and for improving the productivity and technology of rubber manufacture.

REFERENCES
