

Capillary Rheometer: A Practical Rheological Test Instrument for Both Natural and Synthetic Rubbers

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Comparisons related to rheological studies on various types of raw rubber and rubber compound by using the capillary rheometer are still very limited. In this work, rheological testing was performed on both natural rubbers (various Standard Malaysian Rubber grades) and some market available common types of synthetic rubber (styrene butadiene rubber, ethylene propylene diene copolymer, nitrile rubber and isoprene rubber) in order to assess their processability and rheological behaviours. Four different kinds of testing instrument were utilised for comparison purposes, i.e. a capillary rheometer, a Mooney viscometer, a rubber process analyser and an internal mixer (in terms of breakdown index). These tests were based on three different types of rubber formulation, i.e. raw rubber, International Standard Organisation (ISO) gum mix and ISO black mix. Based on the test results, capillary rheometer was identified as the best instrument for processability and rheological behaviours testing (for both natural and synthetic rubbers) due to its ability to perform measurements under the widest regime of true shear rate which had covered all the actual rubber processing conditions.

Keywords: natural rubber; synthetic rubber; rheological property; flow behaviour; processability

The rheological properties of a polymer melt are important in processing but are complicated by a number of factors such as flow rate, pressure and temperature^{1,2}. The rheology of polymer melts is considered to be one of the most important factors in determining the processability of a polymer especially for those which require good flow properties in fabrication and moulding process. It is evident^{2,3} that the flows occurring are complex due to the design of the equipment, the material characteristics and the processing conditions (e.g. pressure and temperature).

In the rubber industry, it is common for rubber technologists to study rheological and processing behaviours of rubber using measurements derived from either Wallace plastimeter or the Mooney viscometer. The Mooney viscometer has been the main viscosity and processability test instrument for over 50 years. However, the use of these two instruments to characterise the complex rheological behaviour of rubbers/rubber compounds especially natural rubber (NR) based ones is not adequate enough. This is due to the fact that these instruments operate

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at fixed shear rates which do not reflect the actual processing condition in rubber industries (e.g. extrusion and injection moulding) where the shear rates vary from 100 s^{-1} to over 10000 s^{-1} ⁴.

Earlier studies also confirmed the inability of low shear rate and single point test to predict the processability of natural rubbers^{5,6}. To date, the best technique used for determination of rheological and flow behaviour of rubbers is by using a capillary rheometer. This instrument can be used to measure rheological properties, e.g. shear stress, shear rate and shear viscosity¹. A number of research on the flow patterns of various polymer melts⁷⁻¹⁴ in the capillary rheometer were reported, but those on comparisons of various rubber compounds (either natural or synthetic based) are still currently very limited.

NR is an elastomer that has long molecular chains. Hence, the entanglement density is very important and high shear forces are needed to permit the flow of this particular material. The long rubber molecular chains will break down into shorter chains when the mechanical breakdown process at low temperature is applied to the rubber material¹⁵. Therefore, shorter molecules are formed with the ruptured chains having free radicals. This results in a decrease in molecular mass and viscosity of the natural rubber¹⁶. Mooney viscosity is the most commonly used parameter of rubber viscosity. Mooney viscosity naturally decreases after mastication process because the constant milling (mechanical process) will break the long rubber chains hence making them shorter. When these chains are reduced in size, less entanglement occurs. This gives a better flow rate and easier processability. By comparison, synthetic rubber (SR) is already composed of short polymer chains; mastication process usually will not further decrease the viscosity of the synthetic rubbers. SRs are mostly obtained by polymerisation of

unsaturated monomers. Co-polymerisation of different monomers allows the resulted material properties to be varied across a wide range and to suit different targeted end applications¹⁷.

The aim of this work was to study the processability and rheological behaviours of both NR and SR based on three types of formulation, *i.e.* the raw rubber, the International Standard Organisation (ISO) gum mix and the ISO black mix. Beside this, it was also intended to investigate the feasibility of capillary rheometer as the most practical rheological testing instrument for both rubbers by comparing to the other three utilised instruments, *i.e.* rubber process analyser (RPA), Mooney viscometer and internal mixer in terms of performance. As a result, four different grades of NR and four types of SR were chosen in this study. The selection of these rubbers was done based on the common grades or types used in the rubber industry and also their availability in the current market. The rheological characteristics reported here were based on the test results of capillary rheometer, RPA, Mooney viscometer as well as internal mixer in terms of Haake breakdown index.

EXPERIMENTAL

Chemicals and Raw Materials

Four common grades of NR were selected, *i.e.* Standard Malaysian Rubber-Light (SMR L), Standard Malaysian Rubber-Constant Viscosity 60 (SMR CV60), Standard Malaysian Rubber-20 (SMR 20), and Standard Malaysian Rubber-20 Constant Viscosity (SMR 20CV). SMR CV60, SMR 20 and SMR 20CV were manufactured by Chip Lam Seng (M) Sdn. Bhd. SMR L was produced by the Malaysian Rubber Board. The four selected types of SR were

styrene butadiene rubber (SBR, grade Nipol 1502, manufactured by Zeon Corporation), ethylene propylene diene copolymer (EPDM, grade Keltan 778Z, manufactured by DSM Elastomer Corporation), nitrile rubber (NBR, grade Krynac 3345F, manufactured by Lanxess Corporation) and polyisoprene rubber (IR, grade SKI-3S, manufactured by NCHZ Sterlitamak Corporation). Both raw NR and SR's average molecular weight (M_w) were determined by using the gel permeation chromatography (GPC, model Waters 2690/5 Separation Module) technique, as shown in *Table 1*. The GPC consisted of three columns; which were SHODEX GPC AT-804S (6000 theoretical plates, 25 cm length), SHODEX GPC AT-805S (6000 theoretical plates, 25 cm length) and SHODEX GPC AT-807S (3300 theoretical plates 25 cm length).

Zinc oxide and stearic acid, common vulcanisation system activators, were added to both ISO gum mix and ISO black mix. Carbon black (Black HAF N330, reinforcing grade) was added as the filler for ISO black mix.

Test Sample Preparation

The study on rheological behaviours was based on three different types of rubber formulation, *i.e.* the raw rubber, the ISO gum mix (without any filler)¹⁸ and the ISO black mix¹⁸. Masterbatches of both natural and synthetic rubbers (without addition of any curatives) were compounded according to the ISO standard formulation¹⁸ (*Table 2*) based on the unit of parts per hundred rubber (p.p.h.r.) for comparison purposes.

About 1 kg of rubber (either NR or SR) was used per mixing. For compounding process, a Banbury internal mixer (BR 1600, 1.6 liter capacity) and a two-roll mill were used to mix and prepare the samples according to ISO recommendations¹⁸. The rubber and chemical ingredients were mixed in the internal mixer with parameter settings: fill factor 0.75, starting temperature 70°C, rotor speed 110 r.p.m. and total mixing time 3 minutes. Each produced masterbatch was subsequently passed through the two-roll mill (a total of 3 passes) and sheet out to about 6 mm thickness.

TABLE 1. AVERAGE MOLECULAR WEIGHTS (M_w)* OF RAW RUBBER
SAMPLE USED IN THIS WORK

Raw Rubber	Average Molecular Weight Value* (M_w) \pm 5000
Natural Rubber	
1. SMR 20CV	1.59×10^6
2. SMR 20	2.41×10^6
3. SMR CV60	2.43×10^6
4. SMR L	2.71×10^6
Synthetic Rubber	
1. NBR	2.71×10^5
2. EPDM	3.11×10^5
3. SBR	6.46×10^5
4. IR	1.73×10^6

*As determined by using 0.0075 g rubber sample (three samples of each rubber) dissolved in 5 mL solvent (tetrahydrofuran) for 24 h at 23°C and filtered (100 meshes and polyvinylidene difluoride syringe filters) to remove gel.

TABLE 2. FORMULATIONS OF RUBBER MIXES

Compound Ingredient	Sample A (Raw Rubber) p.p.h.r.	Sample B (ISO Gum Mix) p.p.h.r.	Sample C (ISO Black Mix) p.p.h.r.
Rubber (NR/SR)100.0	100.0	100.0	
Zinc oxide	-	6.0	5.0
Stearic acid	-	0.5	2.0
Black HAF (N330)	-	-	35.0

For raw rubber samples, each rubber was also passed through the two-roll mill (a total of 6 passes) for mastication purposes before sheeting out to about 6 mm thickness.

Rheological Testing

Capillary Rheometer. The viscosity test was conducted by using a Gottfert Rheograph 75 (piston type) capillary rheometer. In this study, the test temperature was set at 100°C, similar to the temperature setting for the Mooney viscometer and RPA measurement. Two dies were used to conduct this test. The apparent shear rate, was set between the regime of 10 to 2000 s⁻¹ while die ratios were fixed at 10/1 and 20/1 respectively. Both dies had the same diameter of 1 mm but difference in length of 10 mm and 20 mm respectively. Each prepared rubber sample in sheet form was cut into strips of approximately 6 mm × 6 mm × 50 mm in size. The sample was then inserted into the barrel, compressed and packed before the testing was started as shown in *Figure 1*.

The actual viscosity of rubber (η), is given by *Equation 1*:

$$\eta = \left(\frac{\tau}{\dot{\gamma}} \right) \quad \dots 1$$

Where, τ is the true shear stress (in unit Pascal) and $\dot{\gamma}$ is the corrected shear rate (In unit

1/second). For a non-Newtonian material such as rubber, the true shear stress is obtained by using the Bagley correction and the shear rate is corrected by using the Rabinowitch equation¹⁹.

The viscosity test for each rubber sample was done in duplicates in order to calculate the mean value. A chart of log true viscosity versus shear rate was plotted.

Mooney Viscometer. The Mooney viscometer of Alpha Technologies Ltd., was used to determine the Mooney viscosity of the rubber samples. This test is a basic rheological test commonly used to predict the flow behaviour of rubbers. The measurement of a rubber's Mooney viscosity is governed by standard *ISO 289-1*²⁰. This standard specifies the test temperature at 100°C, sample preheating time before the start of shearing of 1 min and shearing duration of 4 minutes. It is conventionally written as 'ML(1+4)100' where 'L' denotes the 'large' rotor used. When a rubber sample undergoes shearing in a Mooney viscometer at 2 r.p.m. (or 1.6 s⁻¹), the torque increases for a few seconds to a maximum value, V_{max} , then decreases rapidly to form a plateau before reaching its end value.

For the Mooney viscosity test, about 25 g weight of each rubber sample was used. The Mooney viscosity test for each rubber sample was done in duplicates in order to calculate the mean value.

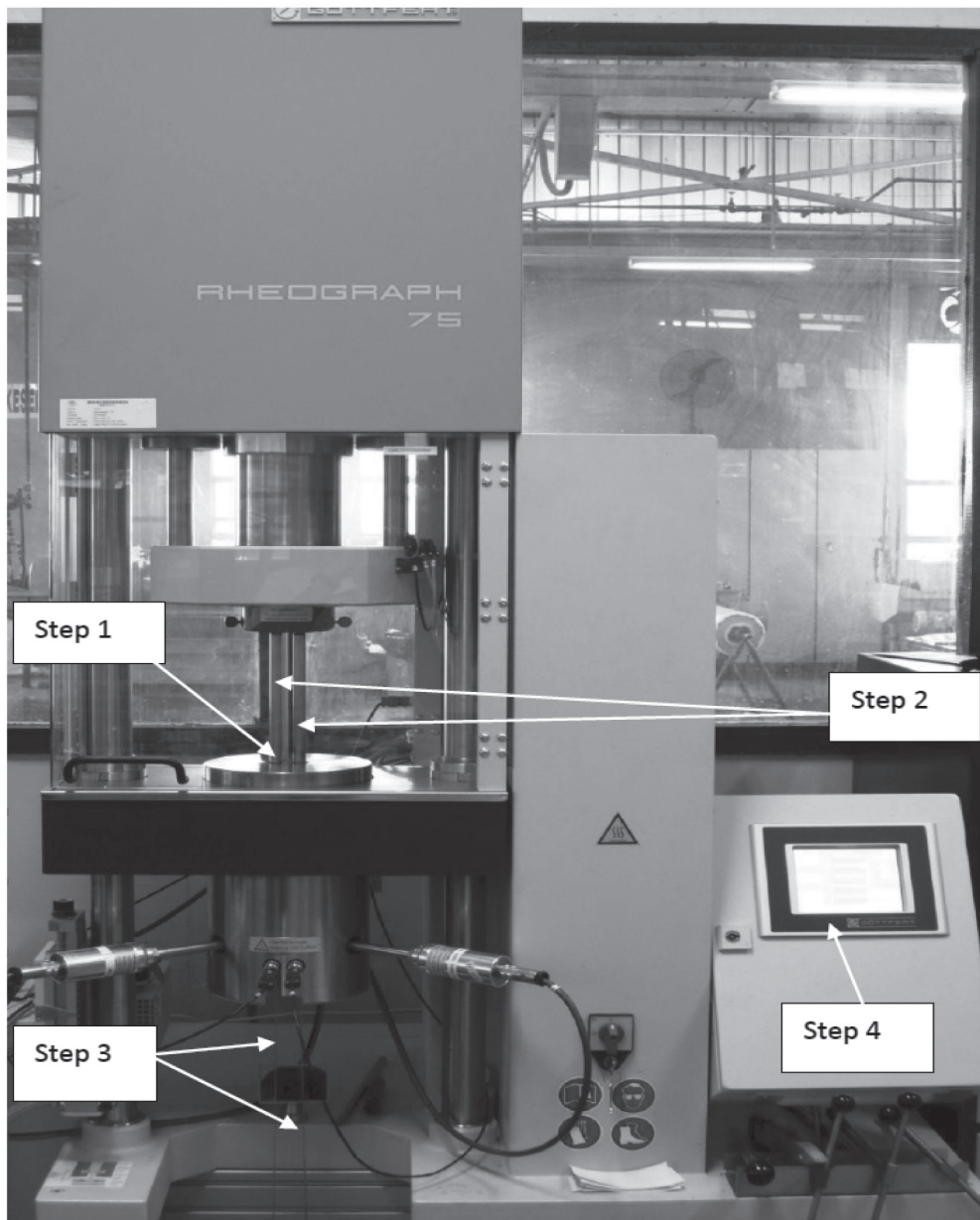


Figure 1. Sequences of viscosity test by using a capillary rheometer.

- Step 1: Rubber samples in strip form were inserted and packed in through the barrel top opening.
Step 2: Two pistons simultaneously compressed the rubber samples downward.
Step 3: Extrudate rubbers flowed out from both of the capillary dies.
Step 4: Data recorded by the computer system.

Rubber Process Analyser (RPA). The processability test was performed by using a rubber process analyser (RPA 2000) of Alpha Technologies Ltd. The RPA subtest adopted was as follows: frequency was set between 6 to 1500 cycles per minute (c.p.m.), while strain and temperature were fixed at 1° (or 14%) and 100°C respectively. For the RPA test, about 10 g of rubber sample per test was used. The test for each sample was done in duplicates in order to calculate the mean value. Processability of rubber was based on tan delta value measurement and calculated by using *Equation 2*.

$$\text{Tan delta} = \left(\frac{G''}{G'} \right) \quad \dots 2$$

Where; G'' is the viscous (or loss) modulus and G' is the elastic (or storage) modulus. All these values were recorded and calculated automatically by the instrument.

Internal Mixer (Breakdown Indices-BI). An internal mixer (Haake RheoDrive 16) was used in order to carry out the BI test for both raw NR and SR samples. The BI was used to characterise the efficiency of mastication. It was estimated as the quotient of the relative reduction of the rubber's Mooney viscosity following mastication and the corresponding quantity of energy consumed.

The higher the BI value, the greater the rubber chains breakdown by the shearing action of an internal mixer. The result of this test was only valid to the raw rubber sample because the BI value was only influenced by the mastication process during sample preparation. The mixing temperature, rotor speed and time were fixed at 100°C, 45 rounds per minute (r.p.m.) and 10 min respectively for each test. The breakdown index test for each raw rubber sample was done in duplicates in order to calculate the mean value. The

calculation of BI of a rubber is given by *Equation 3*:

$$BI = \left(\frac{Vi - Vf \times 10000}{Vi \times Wu} \right) \quad \dots 3$$

Where, Vi is Mooney viscosity before mastication, Vf is the Mooney viscosity after mastication and Wu is the unit work in MJ/m³.

RESULTS AND DISCUSSION

Viscosity Determination by using Capillary Rheometer

The viscosity test was conducted by using the capillary rheometer in order to study the rheological behaviour of rubber when increasing actual shear rate. Viscosity is a measure of the resistance of a fluid which is being deformed by shear stress. Low viscosity values indicate good processability and vice versa. The obtained results of capillary rheometer test are presented in *Figures 2–7*.

Based on the viscosity test results of raw NR as shown in *Figure 2*, it was observed that SMR 20CV possessed the lowest viscosity if compared to other NR grades as its viscosity curve lay below those of other NR grades for the entire shear rate regime tested. The SMR CV60 viscosity curve was slightly lower than SMR L and SMR 20 but both of these two grades showed comparable flow behaviour at high shear rate range as their curves overlapped. As for the raw rubber of SR, the viscosity curves in *Figure 5* showed that IR possessed the lowest viscosity followed by EPDM, SBR and NBR.

For the ISO gum mix of NR as shown in *Figure 3*, the lowest trend in viscosity was observed for SMR 20CV based mix. Both SMR CV60 and SMR L based mixes exhibited the highest viscosity by possessing almost

indistinguishable curves. As for ISO gum Mix of SR (Figure 6), the trend in viscosity indicated that IR based mix had the lowest viscosity followed by EPDM, SBR and NBR based mixes. For the ISO black mix of NR (Figure 4), the SMR 20CV based mix also showed the lowest viscosity curve for the entire shear rate regime studied if compared to other NR grades. SMR CV60 based mix showed the highest viscosity only at high shear rate regime (above 1000 s^{-1}) due to its high molecular weight (Table 1) where higher energy level was expected to shorten their molecular chains. As for the ISO black mix of SR (Figure 7), similar trend in the viscosities was observed as for its raw and ISO gum mix.

Mooney Viscosity Determination by using Mooney Viscometer

The Mooney viscosity, ML(1+4)100 results of NR and SR are summarised in Figures 8 and 9 respectively. For raw NR, the results showed that the SMR 20 possess the highest viscosity followed by SMR L, SMR CV60 and SMR 20CV. It is expected that SMR 20, produced from matured-field coagulated cup lumps showed higher viscosity than SMR L produced from fresh latex. SMR CV60 and SMR 20CV are both constant viscosity grades with the Mooney viscosities specified at $60 + 5$ and $65 + 5$ respectively. As shown in Figure 9, EPDM exhibited the highest raw rubber Mooney viscosity followed by IR, SBR and NBR.

For ISO gum mix of NR grades (Figure 8), a significant drop in the Mooney viscosity values was observed if compared to the raw rubber ones. The SMR L based ISO gum mix showed the highest viscosity followed by SMR 20, SMR CV60 and SMR 20CV based ones. A decrease in Mooney viscosity value of NR based ISO gum mix was due to

the mastication process performed during the preparation of masterbatch samples. Whereas for SRs based ISO gum mixes with the exception for IR, see Figure 9, the Mooney viscosity values were generally higher if compared to their raw rubbers. The EPDM based ISO gum mix showed the highest Mooney viscosity value followed by SBR, IR and NBR based ones. This phenomenon indicated that the Mooney viscosity of IR based ISO gum mix was affected by the mastication process during the mixing of the rubber. Polyisoprene has the most similar basic chemical structure if compared to the *Hevea brasiliensis* natural rubber.

As for the NR based ISO black mixes, their Mooney viscosities were higher if compared to their ISO gum mixes. The SMR L based ISO black mix also exhibited the highest viscosity value followed by SMR 20, SMR CV60 and SMR 20CV based ones. Similarly for the SR based ISO black mixes, higher Mooney viscosities were observed if compared to their ISO gum mixes. The EPDM based ISO black mix possessed the highest viscosity followed by SBR, NBR and IR based ones. These results showed that the addition of carbon black filler did increase the Mooney viscosity of both NR and SR. This was due to carbon black being the reinforcing filler, which could enhance the mechanical strength of rubber.

For NR, the Mooney viscosity result of SMR 20CV was in agreement with those obtained from the capillary rheometer, which showed that it had the lowest Mooney viscosity value if compared to other NR grades. However, the Mooney viscosity results for SR were not in agreement with the results as obtained from the capillary rheometer. It is proposed that the SRs in general have lower molecular weights compared to the NRs (Table 1). They were also less sensitive to the action of mastication, by using a two-roll mill, for their molecular chains shortening and homogenisation purposes

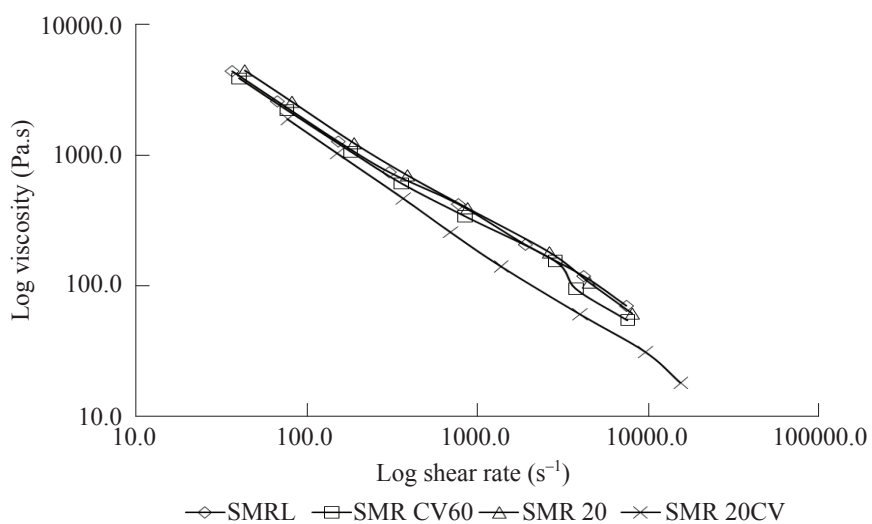


Figure 2. Actual viscosity of raw natural rubbers as determined by using a capillary rheometer.

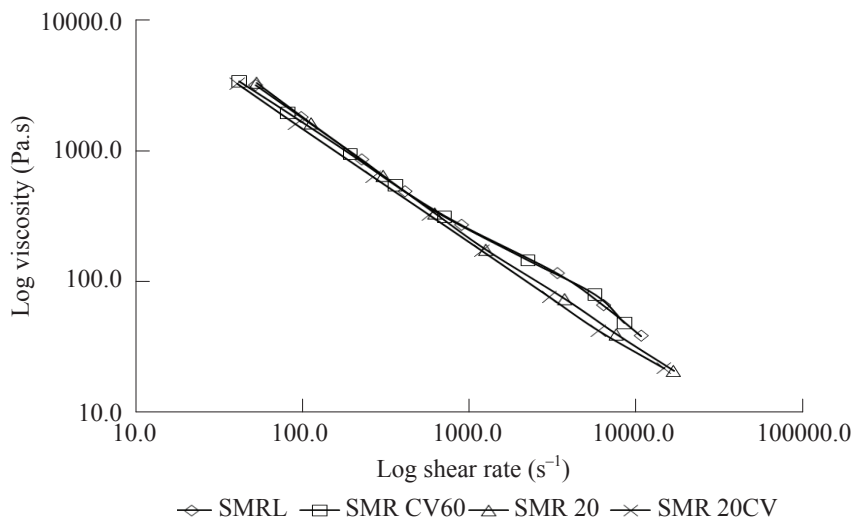


Figure 3. Actual viscosity of natural rubber based ISO gum mixes as determined by using a capillary rheometer.

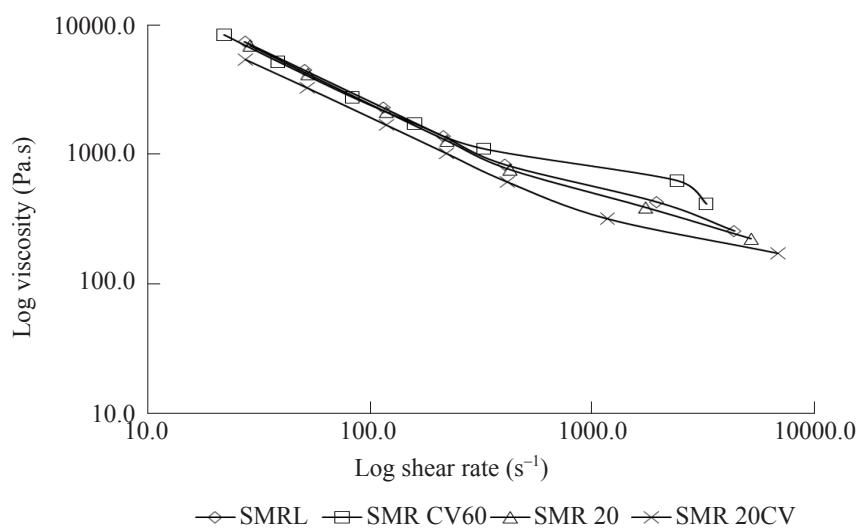


Figure 4. Actual viscosity of natural rubber based ISO black mixes as determined by using a capillary rheometer.

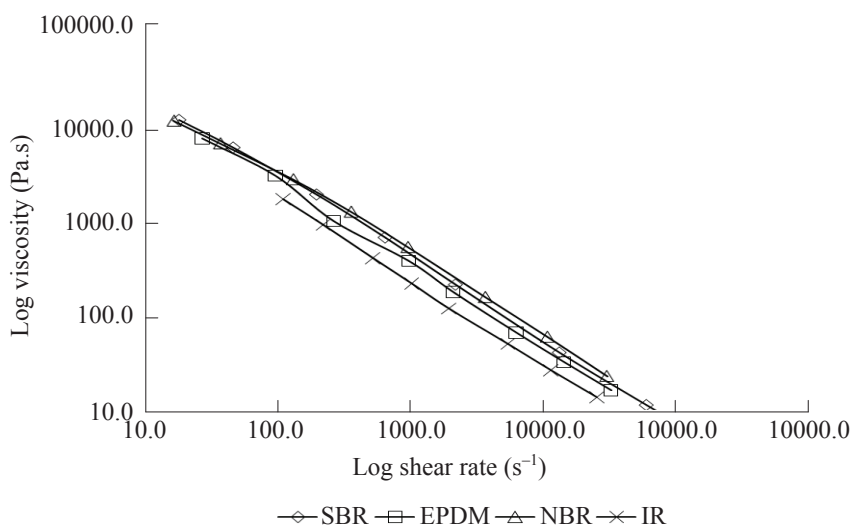


Figure 5. Actual viscosity of raw synthetic rubbers as determined by using a capillary rheometer.

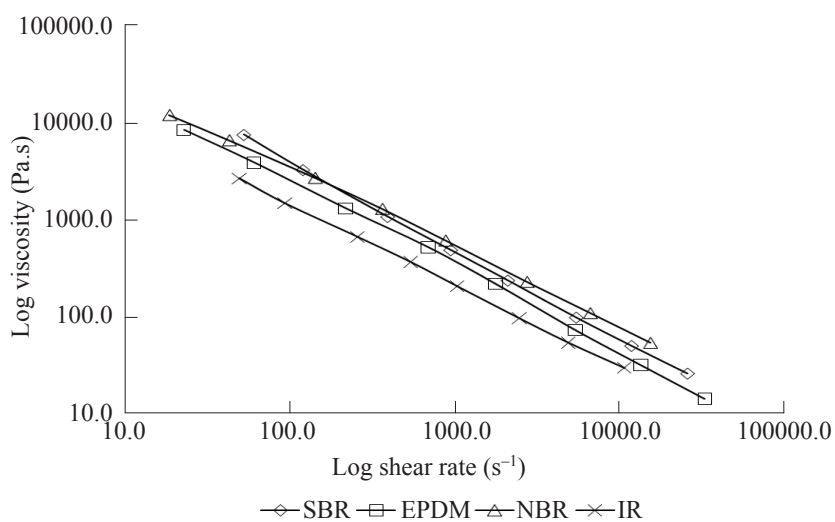


Figure 6. Actual viscosity of synthetic rubber based ISO gum mixes as determined by using a capillary rheometer.

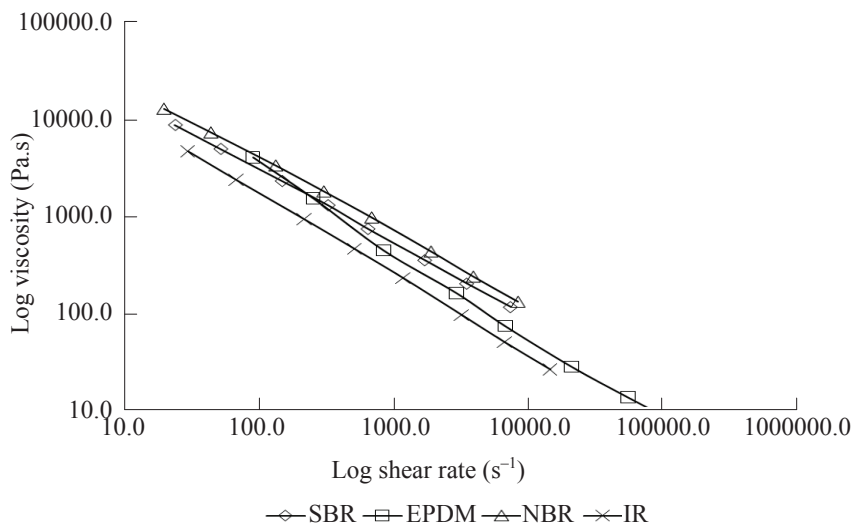


Figure 7. Actual viscosity of synthetic rubber based ISO black mixes as determined by using a capillary rheometer.

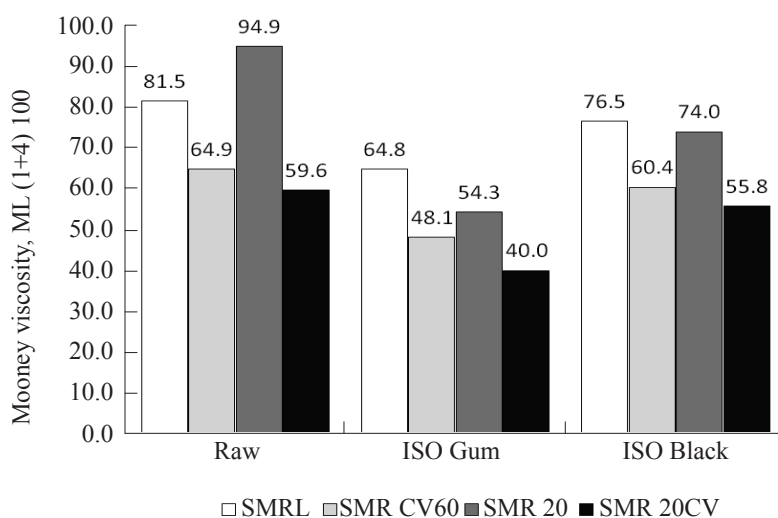


Figure 8. Mooney viscosities of raw natural rubbers, their ISO gum mixes and ISO black mixes.

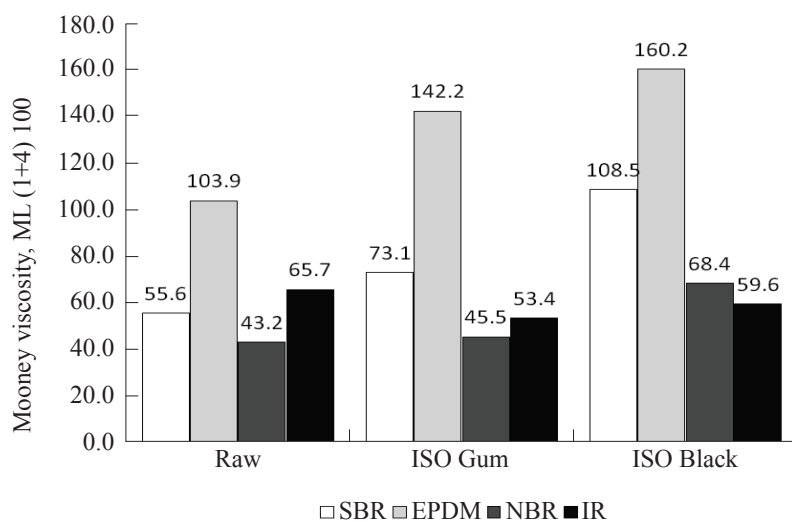


Figure 9. Mooney viscosities of raw synthetic rubbers, their ISO gum mixes and ISO black mixes.

which were in contrast with NRs. The Mooney viscosity measurement was performed at a fixed and low shear rate (*i.e.* about 1.6 s^{-1}), which was definitely not adequate to shorten the SR molecular chains. The measurement at such a low shear rate also could not reflect the actual rubber processing conditions.

Tan Delta Determination by using Rubber Process Analyser (RPA)

The processability of a rubber can also be assessed from the result of tan delta property as obtained from the RPA test. The higher the tan delta value, the better the processability of the rubber and *vice versa*. In the RPA test, the values and trend of tan delta with variation in the applied frequency cycle per minute (c.p.m.) was studied. Although the frequency was set from 6 to 1500 c.p.m., the actual shear rates involved during the testing were still very low (*i.e.* below 25 s^{-1}). This is the limitation for using the RPA instrument.

The RPA test results are summarised in *Figures 10-15*. As shown by the RPA test results of raw NRs (*Figure 10*), SMR 20CV showed the highest tan delta followed by SMR CV60, SMR 20 and SMR L. For the raw SRs (*Figure 13*), NBR showed the highest tan delta followed by SBR, EPDM and IR. For the NR based ISO gum mixes (*Figure 11*), the SMR 20CV based ISO gum mix exhibited the highest tan delta followed by SMR CV60, SMR 20 and SMR L based ones. The tan delta values of the ISO gum mixes were slightly higher if compared to their raw rubbers due to the mastication process performed during the preparation of their masterbatch samples. For the SR based ISO gum mixes (*Figure 14*), the trend of tan delta curves was similar to their raw rubbers with NBR based ISO gum mix showing the highest tan delta values followed by SBR, EPDM and IR based ones. However, the tan delta values of both raw SR and SR

based ISO gum mixes were comparable. For the NR based ISO black mixes (*Figure 12*), the SMR 20CV based ISO black mix again showed the highest tan delta values if compared to the other NR grades. For the SR based ISO black mixes (*Figure 15*), it was observed that NBR based ISO black mix showed the highest tan delta values if compared to the other SR types.

For NR, the tan delta results from RPA measurements were again echoing the results obtained from the capillary rheometer which showed that SMR 20CV had the lowest viscosity values among all four NR grades tested. However, the tan delta results for SR were not in agreement with the results as obtained from the capillary rheometer. It is again likely due to the lower molecular weights of SR if compared to the NR (*Table 1*). SRs were also less sensitive to the action of mastication. At the same time, RPA could only perform rheological measurements at the regime of very low shear rates (below 25 s^{-1}); which shared the same limitation as for the Mooney viscometer.

Breakdown Indices (BI) Determination by using Internal Mixer

To further characterise and study the processability of rubbers, the breakdown index (BI) test was performed. The higher the BI values, the better the processability of a rubber and *vice versa*. The BI test results of both raw NR and raw SR are summarised in *Tables 3* and *4* respectively.

As observed from BI test results of raw NR samples (*Table 3*), raw SMR 20CV showed the highest BI value followed by raw SMR 20, SMR CV60 and SMR L. This result again showed that the raw SMR 20CV had the best processing behaviour if compared to other NR grades. For raw SR samples as shown in

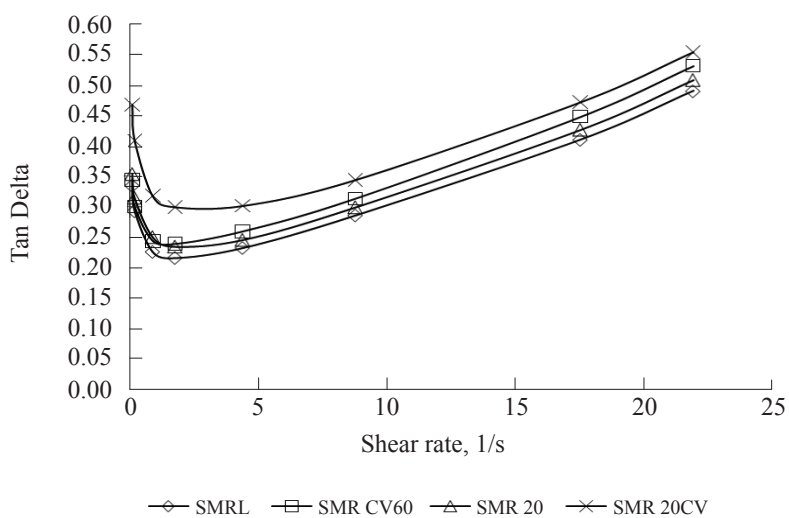


Figure 10. Tan delta of raw natural rubbers.

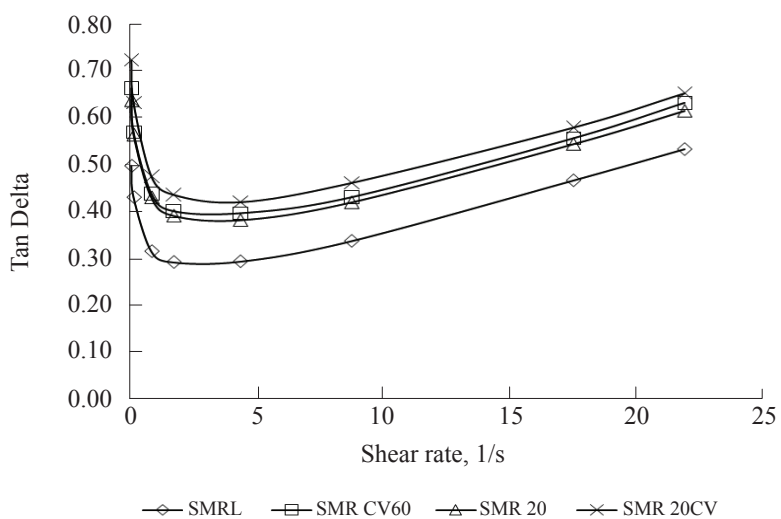


Figure 11. Tan delta of natural rubber based ISO gum mixes.

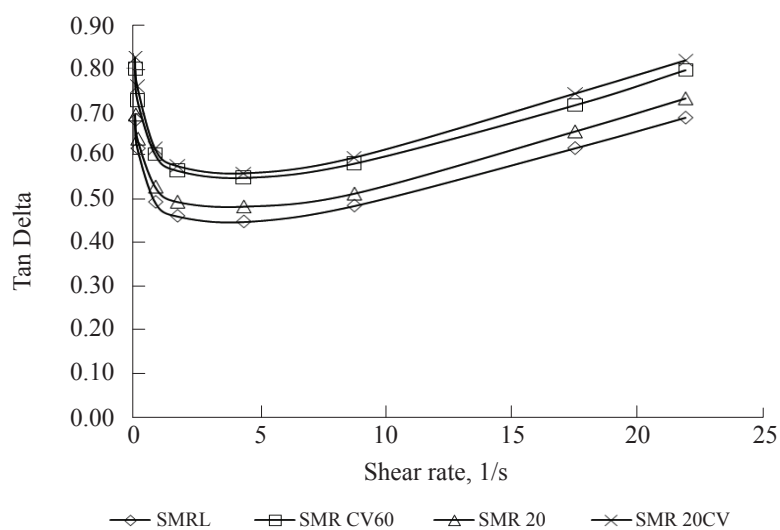


Figure 12. Tan delta of natural rubber based ISO black mixes.

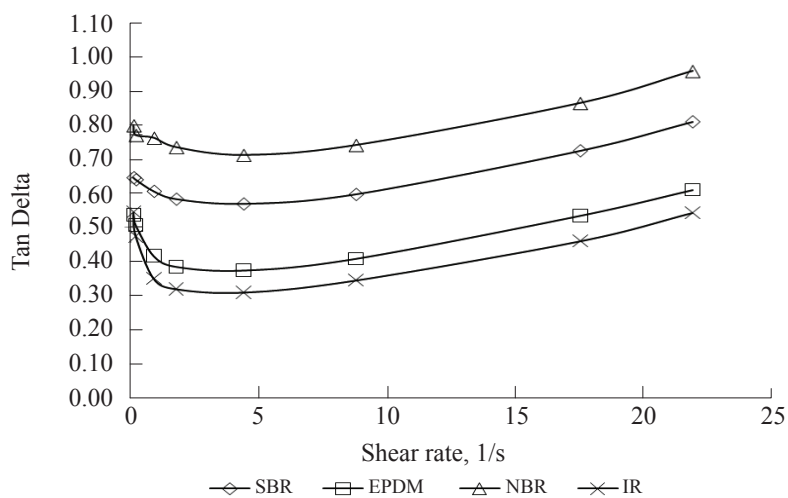


Figure 13. Tan delta of raw synthetic rubbers.

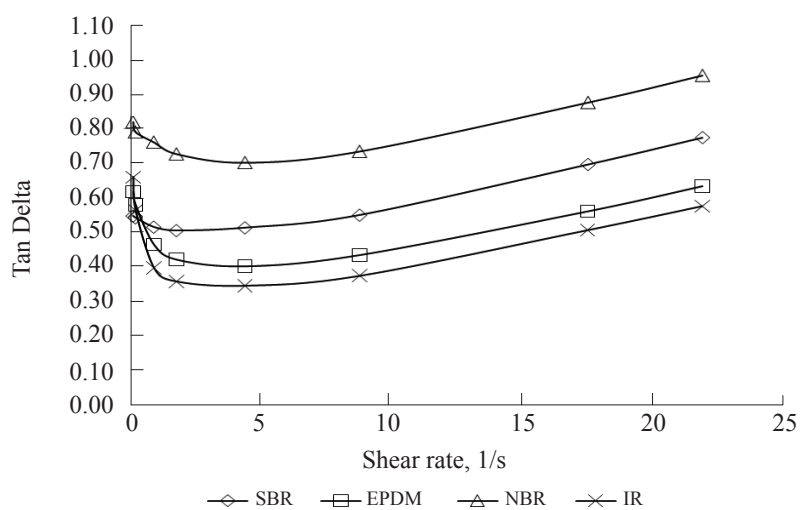


Figure 14. Tan delta of synthetic rubber based ISO gum mixes.

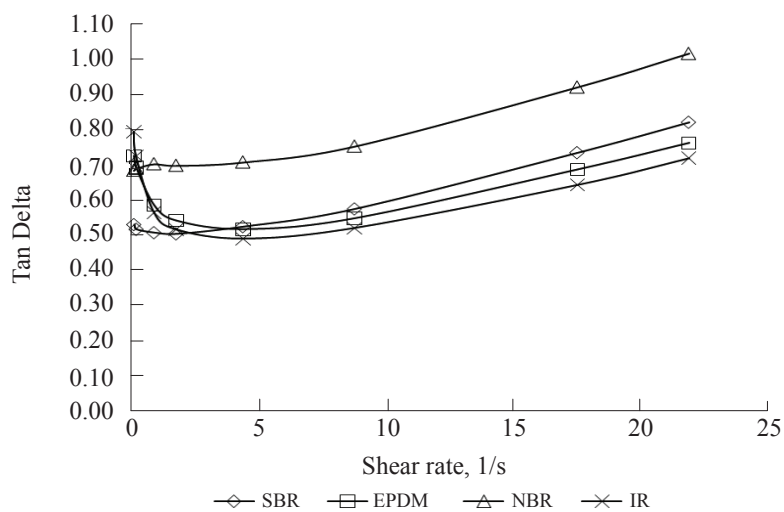


Figure 15. Tan delta of synthetic rubber based ISO black mixes.

TABLE 3. HAAKE BREAKDOWN INDICES (BI) OF RAW NATURAL RUBBERS

Grades of Rubber	Breakdown Indices (BI)
SMR L	1.40
SMR CV60	1.96
SMR 20	3.41
SMR 20CV	3.63

TABLE 4. HAAKE BREAKDOWN INDICES (BI) OF RAW SYNTHETIC RUBBERS

Types of Rubber	Breakdown Indices (BI)
EPDM	-2.90
SBR	0.60
NBR	0.81
IR	7.09

Table 4, IR exhibited the highest BI value followed by NBR, SBR and EPDM. Very low BI values were recorded for the NBR, SBR and EPDM, with negative values for the EPDM. Low BI values indicated that these synthetic rubbers were less influenced by the mastication process. Final viscosity of raw EPDM at room temperature increased after the mastication process, and thus created its negative BI value. It is proposed that this phenomenon could be attributed to the realignment and enhanced entanglement of EPDM's molecular chains after being cooled down.

Both raw NR and raw SR Haake BI test results were in agreement with the results as obtained by using the capillary rheometer. However, the Haake BI test is only suitable for raw rubber sample as explained earlier.

CONCLUSION

For the case of natural rubbers, test results of both Mooney viscometer and RPA were echoing those results obtained from the capillary rheometer. However, the test

results of synthetic rubbers were not in agreement with the ones as obtained from the capillary rheometer. It was likely due to the lower range of molecular weight of SRs if compared to natural rubber. Synthetic rubbers were also less sensitive to the action of mastication during sample preparation. Both Mooney viscometer and RPA shared the same limitation that could only perform measurement at very low shear rates, *i.e.* 1.6 s^{-1} and below 25 s^{-1} respectively, which were definitely not adequate to shorten the rubber molecular chains. At the same time, BI test was only valid for the raw rubber samples because the BI value was only influenced by the mastication process during sample preparation.

It was proven that capillary rheometer is the most practical instrument for processability and rheological behaviours testing for both NR and SR, compared with Mooney viscometer, RPA and internal mixer. This was due to its ability to perform measurements under the widest regime of true shear rates, approximately $10\text{-}100000 \text{ s}^{-1}$, which had also covered all the actual rubber processing conditions

(e.g. in an extruder or injection moulding machine).

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