STUDY ON THE CURE CHARACTERISTICS OF SOLID TYRE MIDDLE COMPOUND PREPARED WITH DIFFERENT TECHNICALLY SPECIFIED RUBBER GRADES

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DECLARATION

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ABSTRACT

Cure characteristics of solid tyre middle compounds are critical as it combines the heel and the tread compounds. Also middle compound is subjected to have high heat build-up due to continuous deflection. In this study cure characteristics of solid tyre middle compound were investigated by preparing the middle compounds with different TSR grades. Three different grades of technically specified rubbers TSR-5L, TSR-10 and TSR-20 were used for the study. All the grades were tested for raw properties such as dirt content, ash content, nitrogen content, plasticity, plasticity retention index and viscosity. Molecular weight and molecular weight distribution of TSR grades were also compared by the frequency sweep test using rubber processing analyzer. Solid tyre middle compounds were mixed using laboratory Banbury mixer and laboratory mill machine in controlled laboratory conditions. The effect of raw rubber properties, molecular weight and molecular weight distribution of three different TSR grades on cure characteristics of solid tyre middle compound were evaluated. It can be concluded that the significant effect can be observed on cure characteristics of middle compound against TSR grades. Also molecular weight of TSR can be positively correlated with middle compound M_L value.

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LIST OF ABBREVIATIONS

NR	Natural Rubber
TSR	Technically Specified Rubber
USS	Unsmoked Sheet
MW	Molecular Weight
MWD	Molecular Weight Distribution
TBBS	N-tert-butyl-2-benzothiazole sulphenamide
PVI	Pre vulcanization inhibitor
CTP	4-Chloro-3-[[(3-nitrophenyl)amino]sulfonyl]-benzoic acid
ASTM	American Society for Testing and Materials
Phr	parts per hundred rubber
MDR	Moving Die Rheometer
ODR	Oscillating Disc Rheometer
M_L	Momentum Low (Minimum Torque)
M_H	Momentum High (Maximum Torque)
t_{s2}	Induction Time (Scorch Time)
t_{90}	Optimum Cure Time
RPA	Rubber Processing Analyzer

1. INTRODUCTION

1.1 Background

Solid tyres play a major role in the off-road tyre industry. Mainly there are three categories namely resilient tyres, press on tyres and cured on tyres. Solid tyres have extra-high durability, extremely high grip, and skid prevention. While providing high abrasive resistance, resilient solid tyres also permit heavy loads to be carried at high speeds over a long distance.

The middle compound of solid tires is used to produce the middle section (cushion) of the solid tires which enhance it providing the cushioning effect. Medium hardness, low heat build-up, high elasticity and high resilience are the most desirable characteristics expected from the middle compound of a solid tyre.

Unexpected deviations in the rheological properties of the produced middle compound significantly affect its performance when building solid tires.

Technically Specified Rubber (TSR) is used as the main raw material for producing the middle compound. TSR from different grades may lead to these unexpected deviations in the rheological properties of the middle compound produced. Molecular weights and molecular weight distribution differences on TSR rubber grades affect rheological properties of the middle compounds. When middle compound rheological properties do not meet the specifications, higher compound rejections are accumulated and part of them cannot be reworked due to low scorch safety time. This will lead to scrap the compounds which directly affect the tyre manufacturing plants as well as the environment.

1.2 Research Objectives

The study aims to investigate the effect of molecular weight and molecular weight distribution of TSR grade variations on rheological properties of the middle compound.

Molecular weight and Molecular weight distribution data of different TSR grades are compared using rubber processing analyzer and rheological properties of the middle compounds are tested by producing the laboratory scale compound batches using three different TSR grades. The relationship between the molecular weight and molecular weight distribution of TSR grades against middle compound rheological properties benefits for selecting the most relevant TSR grade to enhance middle compound properties which affect the performance of the solid tyre. Also, compound rejections and reworks can be minimized by understanding the effect of TSR sources on middle compound rheological properties.

1.3 Solid Tyres

Solid tyres are used for off-road vehicles and have high impact and damage resistance. They also have high loading capacity and high stability. Along with being maintenance-free solid tyres are extremely stable and puncture-resistant. They allow for high loading capacity and are economical. Thus, ideal for forklifts, airport vehicles, heavy-duty transport vehicles, side-loading forklifts, platform trucks, and other industrial vehicles.

These tyres prove essential particularly at logistic centres, air and seaports and for industrial applications. Industries where the maintaining of a clean environment is mandatory and prioritised benefit from non-marking versions of solid tyres. Additionally, they are specifically designed for minute floor marking maintaining a clean industrial environment. Referred to as non-pneumatic tyres solid tyres do not compromise of air rather consist of a series of solid rubber and plastic compounds layers attached together via moulding operations. As a result they lead to fewer blowouts.

1.4 Solid Tyre Manufacturing Process

The basic tyre manufacturing process is as below.

1. Compounding and Banbury mixing
2. Milling
3. Extruding and Calendering
4. Component Assembly and Building
5. Curing and Vulcanizing
6. Inspection and Finishing

Resilient solid tyres are the major manufacturing segment in the solid tyre industry and the middle compound of resilient tyres are discussed in this thesis. Hence only resilient solid tyre manufacturing processes are listed here.

1. Inner heel building
2. Heel rolling
3. Bonding layer applying
4. Middle compound rolling
5. Tread compound rolling
6. Green tyre moulding
7. Curing
8. Finishing

The inner heel is the sections which are mounted to rim and heel, bonding, middle tread sections are the other layers consecutively. After curing the green tyre, flashes are removed in the finishing part.

1.5 Rubber Compounding

The art and science of selecting and combining elastomers and additives to obtain intimate mixing is known as compounding. This allows for the development of necessary physical and chemical properties in the attainment of a finished product. The addition of certain chemicals to raw rubber in order to obtain the desired properties is known as rubber compounding or formulation. The chemicals work as crosslinking agents, reinforcements, anti-degradants, and colorants. Long-chain molecules are chemically linked together to form networks, this process is known as formulation. These networks transform the viscous liquid into an elastic solid. This occurs during vulcanization or curing, where the strength increases consequently modulus and hysteresis decrease. The widely used vulcanization agent is sulphur.

Input energy in terms of elastic potential energy in the chains is stored in elastomers. Upon crack growth this energy is released acting as a driving force propagating the fracture. The remaining energy is dissipated via heat through the molecular motion. Due to high crosslink levels a tight network is formed restricting the chain motion stopping the network from dissipating considerable energy causing a brittle fracture at low elongation. An excessive crosslink level is undesirable potentially leading to brittle fracture and limited crosslinks may decrease resistivity to viscous flow failure. Therefore, optimal density range of the crosslinks needs to be defined for practical use.

Reinforcing agents for the rubber compound requiring high specific area act as stress arrestors. Meaning, the particle must be smaller than 1 μm in size. Generally, fillers are carbon black and silica. Primary particle sizes measuring 0.1μm in size are obtained giving the specific area of a few hundred square meters per gram of filler.

1.5.1 Mixing

For rubber compounding two-roll mills have been a common trend since the mid 19th century. Initially, they were also used for mastication of natural rubber in the breakdown of high molecular weight fractions. Mills are used for sheeting off stock from internal mixers or for the heating-up of compounds used in sheet feeding to extruders or calendars.

Consisting of two closely spaced parallel, horizontal rolls made from hard castings the two roll mill is supported by strong bearings in a mill frame. Driven at different speeds the two rolls counter rotate maintaining a friction ratio of 1.05-1.25. The rubber is transported over the top of the roll to the nip area. Travelling through the nip with small adjustable clearance (usually 2–6 mm) the rubber is subjected to high shear stresses. For successful mixing, mill clearances and the amount of stock used should result in a smooth band on one roll being formed. The surface speed of the slow roll is approximately 50 cm/s. The slow speed allows for the operator to cut the band diagonally, folding the cut portion over the remaining band for blending. The hollow mill rolls allow a flow of coolant for temperature control.

Almost always these operations are performed in an internal mixer. Currently the most commonly used internal mixers are Banbury Mixers. Comprised of two rotor blades each counter rotating relative to the other enclosed metal cavity. The rubber, fillers and compounding chemicals are added from a loading chute. Rotor shape, size, and speed determine the mixing shear and the respective mixing time. A large Banbury mixer can produce 500 kg of the finished compound in a matter of minutes. Due to energy being absorbed by the rubber stock, it is plausible that the batch temperature can rise well above 120°C (250°F) prior to being dumped and cooled. The temperature rise resulting from viscous heating of the said rubber compounds means that the compounds must pass through the internal mixer more than once to disperse other compounding ingredients. Batches are typically dumped from an internal mixer onto a mill where they may be additional worked while being cooled. Additionally compounding ingredients are usually added at this point.

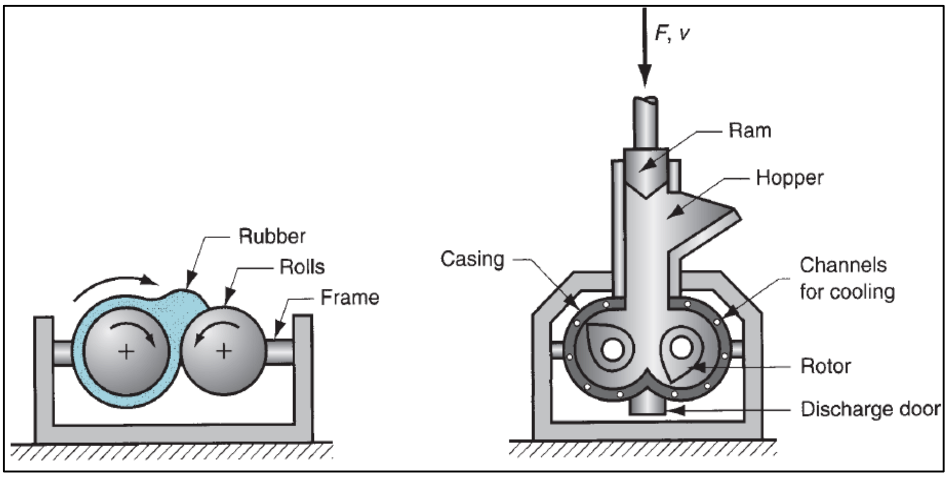

Figure 1-1 Two-roll mill(left) and Internal Mixer(right)

1.5.2 Mastication

Mastication commonly known as “polymer breakdown” is the first step in rubber compounding . Mastication is the process in which a polymer’s receptivity is enhanced. The development of a polymer's viscoelasticity is dependent on its receptivity to the additives. However, most synthetic elastomers minimizes or precludes the need for mastication due to the fact that they are formed with the uniformity in chemistry, viscosity and stability. Although this is generally necessary to provide a uniform mixture prior to further compounding particular for compounds containing a blend of polymers.

By nature rubber is greatly variable with reference to its viscosity from lot to lot. Thus, several lots are required to be blended and masticated to regulate viscosity and physical properties of the compound. By extending, disentangling or severing the polymer chains this breakdown of natural rubber improves viscoelasticity. Breakdown cycles for both natural and synthetic rubber are often facilitated by the inclusion of plasticizers.

1.5.3 Main raw materials used in compounding

The main purpose of adding ingredients into the raw rubber is imparting desired physical properties for production.

A rubber compound generally consists of the following:

1. Rubber
2. Processing aids
3. Vulcanizing agents
4. Accelerators
5. Activators
6. Retarders
7. Antioxidants
8. Fillers
9. Softeners
10. Resins
11. Weather and ozone resistants

1.5.3.1 Rubber

The main part of tyres consists of natural rubber. This rubber is tapped from rubber trees, collected in the form of latex. These trees are grown on plantations world-wide. The colloidal dispersal of solid particles of the polymer polyisoprene and non-rubbers in water is known as latex. Polyisoprene is the chemical substance that comprises of rubber and its content in the emulsion is about 30%. NR is constituted in a milky white fluid that is available as an excretory material in the tree referred to as “Hevea Brasiliensis”. Rubber latex exists as a colloidal system where solid latex particles are suspended in a liquid which is basically water having some dissolved substances. The excessive water in the latex is the main drawback of its use in making industrial products. Further, the presence of proteins in latex acts as a food base for the growth of microorganisms. In view of these problems, latex has to be concentrated to high DRC in order to make it an industrial commodity and to use it in making latex-based products. Most of the non-rubber materials are removed in the process of latex concentration. The latex in concentrated form is required in the manufacture of latex products.

1) Dry rubbers produced out of latex are:
    - Pale crepe (Grading by Visual Inspection)
      1X, 1, 2, 3
    - Latex grades of technically specified rubbers
    - Sole crepe – Used directly as Footwear Soling

2) Dry rubbers produced out of scrap rubber are:
    - TSR-20
    - TSR-50

   Type of Scraps: Fresh cup lumps, old cup lumps, tree lace, shells scrap and earth Scrap

3) Reclaimed Rubber

Reclaim rubber plays an important part in the function of general or specialized compounds especially as a softening agent with natural rubber. Reclaim rubber gives special processing characteristics to specific compounds.

1.5.3.2 Processing Aids

Some of the process aids used in NR compounds in the addition to softeners and resins include stearic acid, zinc, calcium soaps and residues of fatty alcohols. Zinc soaps of unsaturated fatty acids are usually the best process aids. These materials are important in facilitating the dispersion of the fillers in the rubber compound, and they ensure smooth processing. In pure white or pastel colored articles, calcium soaps of saturated fatty acids are preferred. Aromatic oil, naphthenic oil, silane, paraffinic oil and oleic acid are several processing aids.

1.5.3.3 Vulcanizing Agents

These are the chemicals that are required to cross-link the rubber chains into the network that gives the desired physical properties in the final products. The type of rubber determines the cross-linking agent.

Sulphur is the most commonly used agent, entering the reaction with a majority of the unsaturated rubbers to producing vulcanizates. Two forms of Sulphur, rhombic and amorphous (insoluble) are used. They exist as a cyclic (ring) structure composed of eight atoms of Sulphur, S_8. The amorphous form is actually polymeric in nature.

1.5.3.4 Accelerators

Sulphur, by itself, is a slow vulcanizing agent. Large amounts of sulphur with high temperatures and long heating periods obtain an unsatisfactory cross-linking efficiency with substandard strength and aging properties. The vulcanization accelerators are the only machines which give the optimum quality according to current technology. With one universal substance, the multiplicity of vulcanization effects demand cannot be achieved rather a large number of diverse materials are needed. Accelerators can differentiate principally between inorganic and organic vulcanization accelerators.

1.5.3.5 Activators

With organic vulcanization accelerators, it is necessary to use organic or inorganic “activators” to achieve their full potential. ZnO is the most important of these additives. Apart from ZnO in special cases MgO and $Ca(OH)_2$ are used. The activators mentioned improve strength properties of the vulcanizates and reduce vulcanization time. The fatty acids and fatty acid salts provide better processing and improved dispersion of fillers and chemicals. This is important as it affects the total property spectrum of the vulcanizate creating a longer scorch time.

1.5.3.6 Retarders

Vulcanizate specifications often require accelerator systems, which may have inadequate scorch safety. In such cases otherwise when using short vulcanization times or high processing temperatures it is recommended to retard the onset of vulcanization (scorch time) to ensure abundant processing safety. For example, compression moulded articles can flow into the mould cavities.

Fundamentally it should be contemplated if vulcanization retarder is really necessary. The choice of vulcanization accelerators make it possible to achieve a retarded vulcanization start (longer scorch time) since with a number of accelerators vulcanization is slower to start. For example, MBTS and sulphonamides accelerators. Furthermore, retarded vulcanization can be obtained by the proper combination of accelerators (primary – and secondary accelerators) by for example combining a fast vulcanization accelerator with a slow one that does not act synergist ties.

1.5.3.7 Antioxidants

Aging is a term applied when addressing the change in the property of materials that occur when kept in long-term storage without the effect of chemicals leading to corrosion and partial or complete degradation. These changes are usually observed in the form of rotting, softening, degradation, embrittlement, fatigue processes, and static crack formation.

1.5.3.8 Fillers

The fillers are categorised as either carbon blacks or light-coloured fillers. The chemical composition of light-coloured fillers is primary basis for categorisation. For example, one can list colloidal silica, calcium and aluminum silicate, alumina gel, kaolin, silica, talcum, chalk (calcium carbonate), metal oxide, like zinc oxide and metal carbonates.

Different degrees of activity are present with each class of fillers. Unlike chalk which is categorised as an inactive filler, most carbon blacks, colloidal silica, and most small particle size silicates belong to the high-and medium activity fillers.

1.5.3.9 Softeners

A great number of different materials serve, the most important ones being mineral oils. These oils include a wide range of products, from paraffinic to aromatic. Vegetable and animal oils are also important softeners or process aids, to include wool grease, fish oil, pine tar, and soya oil. NR requires a lesser amount of softener than most SR’s. Synthetic softeners, which are commonly used with CR or NBR, play only a minor role in NR compounding. When selecting softeners for NR, the potential of blooming or migration has to be considered.

1.5.3.10 Resins

While it is important to add resins to compounds from most SRs, so that they can be fabricated, this is not generally necessary with NR compounds. If an exceptionally good building tack is required, such as compounds for fabricating of textiles, it is advantageous to add rosin, tar, or other tackifiers to NR compounds. Those tackifiers which were specially developed for SRs are little relevance in the compounding of NR.

1.5.3.11 Weather and Ozone resistance

Even after vulcanization has taken place double bonds are still prevalent in the NR polymer chain. As a result it has insufficient weather and ozone resistance, this is especially seen in light-coloured vulcanizates. This can be improved, if carbon black is added to the compound, or especially, if paraffine, microcrystalline waxes, or certain enol ethers are added. Nevertheless, the ozone and weather resistance of NR vulcanizate cannot compete with the excellent performance of vulcanizates of saturated rubber.

1.6 Vulcanization of Rubbers

When considering rubber technologies vulcanization (curing, cross-linking) is an extremely significant process. Here via consecutive and parallel changes of chemical and physical nature, rubber is changed to its final product, vulcanizate. Vulcanization essentially is the creation of cross-links between rubber macromolecules. This then creates a three-dimensional network of a rubber matrix. The vulcanizate network comprises of physical bonds such as polar, hydrogen or dispersed powers between individual macromolecules or their snarls. These bonds were created at preparation or during the processing of the respective rubber compounds. Other ingredients being used in rubber compounds are either in their original form or have been chemically changed being either connected, dispersed or soluble. Vulcanization agents comprise of peroxides, sulphur, resins, metal oxides, and quinones these are used in the formation of cross-links between rubber macromolecules. Various types of radiation can potentially cause curing. Where due to the sufficient energy from the radiation the generation of macromolecules often forms radicals. This interaction is what causes the formation of cross-links. In addition, microwaves or ultrasound can cause spontaneous curing. Whereas, in the majority of rubbers where vulcanisation is almost a necessity in thermoplastics is not required.

1.6.1 Vulcanizate Properties

Vulcanization causes rubber molecules to be linked by crosslinks. For vulcanized rubber, the value of fatigue life, tear strength and toughness are increased with minor amounts of crosslinking. Then, they decrease with further crosslinking.

Hysteresis and permanent set decrease with increasing crosslink density. Elastic recovery and stiffness increase with crosslink density.

The type of crosslinks affects properties. Polysulfidic networks give larger tensile strength and larger strain at break. Polysulfidic networks are also more flexible than monosulfide ones. 10 Monosulfidic networks have better heat stability than polysulfides ones [1].

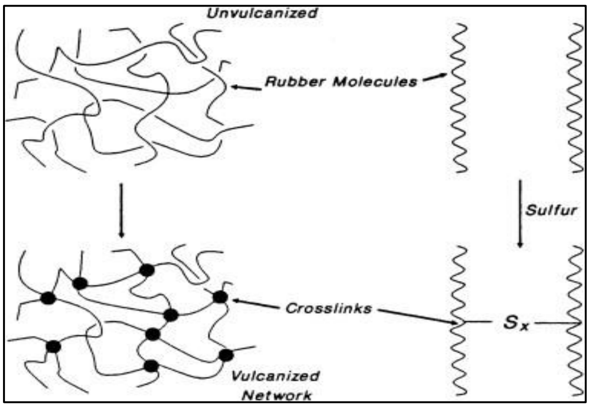

Figure 1-2 Rubber chain crosslinking

In brief, as per the figure 2, vulcanized rubber molecules are linked with sulphur crosslinks which gives rigidity into the polymer network.

1.6.2 Characterization of the Vulcanization Process

The moving die rheometer (MDR) is one type of cure meter used to measure the state of crosslinking. A test piece is put into a sealed test cavity under positive pressure and maintained at a specified temperature. A rotor, fixed in the test piece oscillates through a small rotary amplitude. Stiffness increases when crosslinks form.

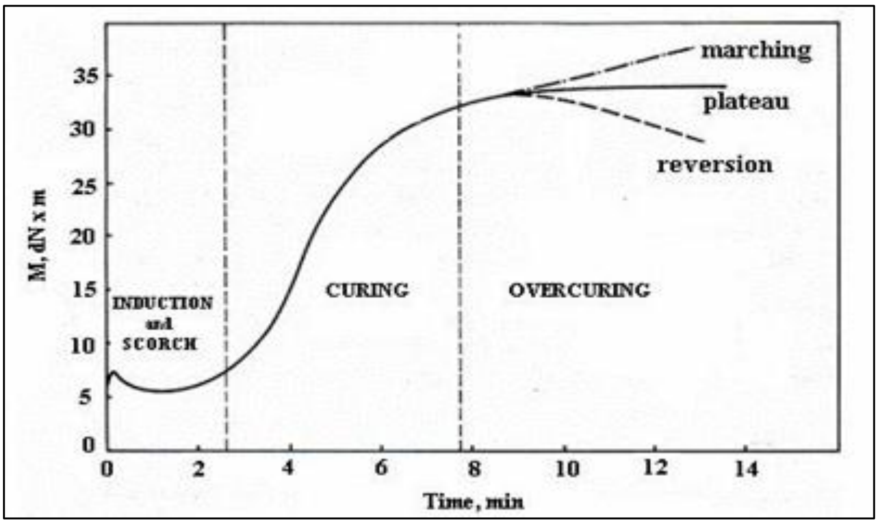

Figure 1-3 Moving die rheometer curve

In figure 3 torque against time gives a cure curve. At the beginning of the vulcanization, torque decreases due to decreased viscosity. Torque decrease until cross-linking begins. In the end, three situations could occur; marching, plateau, and reversion due to post vulcanization effects. Four main measurements are widely used in the industry mentioned below:

1. Minimum torque value (ML)
2. Maximum torque value (MH)
3. Scorch safety time (Ts2)
4. 90% curing completion time (T90)

1.7 Technically Specified Rubber (TSR)

Technically specified rubbers are produced as blocks and normally wrapped in polythene sheets. TSR block rubber undergo a series of unit operations during production, these steps vary slightly depending on whether the feed-stock is either field latex or field coagula. Steps involved in production include bulking, coagulation, dewatering, size reduction, drying, baling and pelletizing. TSR is categorized according to dirt content, ash content, volatile matter, nitrogen content, color, plasticity, plasticity retention index and viscosity level. Technical properties are defined for the relevant categories and they can be used for the applications based on pre-determined characteristics [2].

TSR CV, TSR-L, TSR-5L, TSR-10, TSR-20 and TSR-50 are the main grades of TSR. TSR-CV is the constant viscosity technically specified rubber type which is produced using high-quality latex and has limited defined viscosity range. The storage hardening effect of this TSR type is minimum comparing to other grades. TSR-L is the lighter color grade in TSR which is also been manufactured by high-quality latex.

TSR-10 is produced using cup lumps and unsmoked sheet (USS) rubbers together with cup lumps are used to produce TSR-20. The main source for TSR-5L is field latex. For each grade series of size reductions there is a following washing step, preceding this is the use of shredder machines. Then bale molds filled with small particles are dried in ovens at 110-130 ^{0}C for 4-5 hours. Cooling and cutting are the final steps of the TSR production lines.

1.8 TSR Testing

Raw technically specified rubbers can be tested for their raw properties to get technical information on the material.

1.8.1 Dirt Content

Dirt content is the measure of insoluble impurities retained on a 45 µm mesh such as wood bark, sand and earth particles. Dirt content is expressed as a percentage.

% Dirt content = $(m_1 / m_o) \times 100$

Where m_o- weight of the test portion in grams

m_1- weight of the dirt in grams

1.8.2 Ash Content

Ash content is the measure of rubber soluble impurities, mainly inorganic matter after incinerated at 550^{0}C in a muffle furnace.

% Ash content $= ((m_2-m_1) / m_o)$ x100

Where; m_o - weight of test portion in grams

m_1- weight of empty crucible in grams

m_2- weight of ash + crucible in grams

1.8.3 Initial Plasticity Number (P_o)

Initial Wallace Plasticity is a measure of the plasticity of the rubber which indirectly gives the estimation of the polymer molecular chain length or molecular weight.

A rubber pellet is compressed between two circular platens which are maintained at a temperature of 100^oC

P_o is the median value of the thickness of three test pieces at the end of compression period expressed in hundredths of a millimeter

1.8.4 Plasticity Retention Index (PRI)

The plasticity retention index is a measure of the resistance of raw NR to thermal oxidation. This is based on the retention of the plasticity of the rubber after oven aged for 30 min at 140± 0.2 ^{0}C.

PRI = [Plasticity after ageing (P_{30})/ Plasticity before ageing (P_0)] X 100

1.8.5 Nitrogen Content

Nitrogen is determined by the semi-micro Kjeldahl method. This is the estimation of protein content with minor amounts of non-protein N containing constituents and indicates as the percentage of nitrogen content.

1.8.6 Viscosity

Mooney viscometer measures the shearing viscosity of Rubber. The shearing action is given by a metal disk rotating in a cylindrical chamber filled with rubber under pressure. The resistance of the rubber to the shearing action develops a thrust in the vertical shaft and presses against and deflects a u-spring The deflection is indicated on the display.

1.9 Rubber Molecular Weight and Molecular Weight Distribution

Rubber is a polymer having long-chain molecules that have repeating units of the molecular segment. For the rubber elastomers

1. The molecules must be able to rotate freely about the bonds joining neighbouring units and molecular units very long (chain-molecules).

2. Due to chemical bonding or to mechanical entanglements the molecules must be connected in a three-dimensional network.

3. Intermolecular interactions should be very low.

Natural rubber is an hydrocarbon meaning it consists solely of carbon and hydrogen with an empirical formula of C_5H_8 and its double bond makes it an unsaturated hydrocarbon. Isoprene is the repeating unit of natural rubber where one double bond unit exist for each C_5H_8 group. NR has a high average molecular weight. It is a straight-chain polymer structure which almost all (90-95%) the isoprene have the cis-1,4 configuration. 1, 4 structure means that carbon atoms 1 and 4 are joined in forming the chain [3].

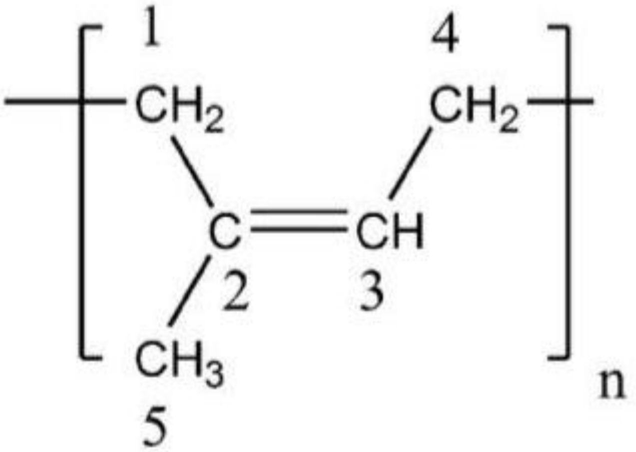

Figure 1-5 Cis 1,4 Polyisoprene

There are many polymer parameters linked with molecular weight. The length of the polymer chain affects the viscous and elastic modulus of the polymer. Viscous modulus measures the resistance when polymer chains flow past each other. For longer molecules, the high viscous modulus is there due to high resistance.

The breadth of the molecular weight distribution can be measured by comparing the number average, weight average, and z average molecular weight. If these three molecular weights are apart from each other, molecular weight distribution is broad and vice versa [4].

1.10 Rubber Processing Analyzer (RPA)

Rubber process analyzer is an instrument providing standard cure curves with additional enhancements and testing capabilities such as frequency sweep, temperature sweep and strain sweeps. RPA testing modes provide information on polymer molecular weights, molecular weight distribution and branching for chemical composition aspects. Also, it gives information on mechanical properties under thermoforming, extrusion, blow moulding and damping, filler recovery, cured rubber network structures are the end-use properties. Hence RPA can be considered as raw polymer tester, processability tester, advanced cure meter, and dynamic mechanical analyser. Temperature, strain, and frequency can be programmed as required in RPA according to the required test method which cannot be done in moving die rheometers [5].

1.11 Moving Die Rheometer

Moving die rheometer is the currently used curing properties measuring test equipment in the rubber industry as the oscillating disc rheometer’s technology is essentially obsolete. MDR measures the material response to specified deformation, this is done at a continual frequency as a function of time and temperature. It typically reports viscoelastic properties of elastic torque. A sample of a compound is placed in between the bi-conical dies where the lower die oscillating at 5 degrees at a frequency of 100 rpm. Due to the applied pressure and temperature chemical reactions cause crosslinking of the samples which give the rigidity. Then the responsive oscillation given by the upper die is changed accordingly and the measured torque value is graphed against time is called a cure curve [5].

2. LITERATURE REVIEW

Studies have been done on natural rubbers on molecular weight and molecular weight distribution using rubber processing analysers. Molecular weight and molecular weight distribution of natural rubber has been differentiated with milling processes and molecular properties have been analysed by GPC-Gel Permeation Chromatography. Assessed by RPA tests of strain sweep, frequency sweep, and stress relaxation, this data has been correlated with dynamic and rheological properties. This research revealed that molecular properties measured from GPC are directly linked with the MW/MWD data given by PRA. When increasing the milling time MW/MWD of NR decreases and this is evident through the cross over points analysis of elastic modulus and viscous modulus in RPA results [6].

Variations on compound rheological properties have been studied on natural rubber compounds when changing carbon black and silica ratio. This study finds the direct correlation on compound rheological properties against filler ratio blended [7]. Also, other studies have found that have analysed the effect of rubber mixing process on the curing features of natural rubber. It concludes that mixing temperature, filler loading and mixing steps influence compound rheological properties [8]. However effect of natural rubber molecular weight and molecular weight distribution are not considered in these studies.

MW and MWD of natural rubber varies according to the manufacturing process as well as the age of the rubber tree, climate, soil type and clones [3]. In a study, three types of natural rubber molecular variations have been discussed and have analyzed using RPA. Variation of curing characteristics of natural rubbers that have the same viscosity range can be observed through RPA analysis. Those variations directly impact to the properties of the compound and the properties of final products [9]. Another study done on molecular weight and molecular weight distribution of natural rubber against the age/clone of the rubber tree reveals that there is a great variation on MW/MWD based on rubber tree age/clones.

A study has been done on originate from different places of natural rubber sources taken from Malaysia and Vietnam on carbon black filled natural rubber composites.

Differences in Mooney viscosity values of natural rubber grades have been discussed there in link with molecular chain lengths of natural rubber. When it comes to industrial productions mastication step variations are there due to the variations of natural rubber molecules in different NR sources. Also, natural rubber molecular differences affect the cure characteristics of the composites such as scorch time(ts2) and cure time (t90). It concludes that higher molecular chains affect the viscosity of NR directly and different origins of natural rubber affect the cure characteristics with no influence on mechanical and physical properties [10]. Also, cure and tear properties study on epoxidized natural rubber(ENR) and standard Malaysian natural rubber(SMR) blends reveals the influence on rubber blend ratios on cure properties of the compound [11].

Natural rubber taken from rubber trees have very high molecular weights and molecular weight distribution. Climate, soil, age of the tree and clones affect these molecular variations. Though the commercial lots on natural rubber mixed with different clonal lattices molecular weight and weight distribution are there due to processing and storage changes. Natural rubber compound rheological property variations are discussed in the aspects of seasonal, clonal and manufacturing methods [12]. The drying process in manufacturing is directly affecting the rheological variations of natural rubber commercial products. This has been studied in and concluded with the viscosity data of raw natural rubbers [13]. Dirt content is there when producing natural rubbers using cup lumps. As discussed in the introduction different TSR grades having different dirt contents. A study which was done using standard Malaysian natural rubber (SMR 20 CV) conclude that dirt content affects the property variations [14] Dirt content directly affect the physical properties of the compounds and performances of finished products and not on the compound rheological properties [2].

3. MATERIALS AND METHODOLOGY

3.1 Research Plan

The test plan on this research was done to find the cure characteristics of solid tyre middle compound prepared using three different technically specified rubber grades. Solid tyre middle compound was taken for the study which used a high amount of technically specified rubber. Commercial grade rubbers and chemicals were used for the testing. Three grades of technically specified rubber types were used for the study; TSR-5L, TSR-10, and TSR-20. Molecular weights and molecular weight distributions were compared among those grades using rubber processing analyser. All the TSR grades were tested for raw rubber properties and solid tyre middle compounds were mixed using a laboratory internal mixer machine by keeping the other materials and process parameters in the same conditions. Those batches were tested for rheological properties using a moving die rheometer.

3.2 Materials

3.2.1 Technically Specified Rubber

Three types of technically specified rubber grades TSR-5L, TSR-10, TSR-20 were used for the study. All the grades were taken from commercial lots supplied by Thai Hua Rubber Public Company, Thailand. The commercial brand was standard Thai rubber (STR).

3.2.2 Carbon Black N-330

Reinforcing filler, Carbon black N330 was taken from a commercial lot supplied by Jiangxi black cat Singapore PTE, LTD, Singapore.

3.2.3 Carbon Black N-550

Reinforcing filler, Carbon black N-550 was taken by a commercial lot supplied by Himadri Speciality Chemical LTD, India.

3.2.4 Calcium Carbonate

Non-reinforcing filler, Calcium carbonate was taken from a commercial lot supplied by Lanmic Exports Pvt, Ltd, Sri Lanka.

3.2.5 Stearic Acid

Organic activator, Stearic acid was taken from a commercial lot supplied by Palm-Oleo SDN, BHD, Malaysia.

3.2.6 Zinc Oxide

Inorganic activator, Zinc oxide 99.5% was taken a commercial lot supplied by Rubamin Limited, India.

3.2.7 IPPD

Anti-degradant, IPPD was taken from a commercial lot supplied by Shandong Sunshine Chemical Limited, China.

3.2.8 6PPD

Anti-degradant, 6PPD was taken from a commercial lot supplied by Shandong Sunshine Chemical Limited, China.

3.2.9 TMQ

Anti-degradant, TMQ was taken from a commercial lot supplied by Huangyan Zhedong Rubber company. China.

3.2.10 Sulphur

Vulcanizing agent, Sulphur was taken from a commercial lot supplied by Mivon Chemical limited, India.

3.2.11 TBBS

Accelerator, TBBS was taken from a commercial lot supplied by Shandong Sunshine Chemical Limited, China.

3.2.12 CTP

Pre vulcanization inhibitor, CTP was taken from a commercial lot supplied by Multiform Chemicals Pvt, Ltd, Sri Lanka.

3.3 TSR Testing

Five bales from TSR-5L were selected from the same manufacturing lot and subjected to bale cutting. Fresh pieces in plate forms were taken from inside of all the five bales. The sample volume was around 10 cm^3. The same method was followed for TSR-10 and TSR-20 bales. 15 raw TSR samples from three different grades were taken for the testing. All the samples were conditioned for 12 hours in laboratory conditions before analysing in RPA. Five samples from each grade were sent to Rubber Research Institute, Rathmalana for raw rubber testing including dirt content, ash content, initial plasticity number (Po), plasticity retention number (PRI), nitrogen content and viscosity.

3.3.1 Rubber Processing Analyser (RPA)

Alpha 2000 rubber processing analyser was used to compare molecular weight and molecular weight distribution among three different technically specified rubber grades mentioned above. The isothermal frequency sweep test method was followed for all the 15 TSR samples. The temperature was set to 100 ^{0}C, strain was set to 10% and frequency set values are from 0.05 Hz to 20 Hz.

3.4 Compounding

Both master batch and final batch mixing were done on a laboratory scale using Farrel Banbury laboratory mixer and laboratory mill machine. A common recipe was used for the compounding which is used for solid tyre middle. The compound recipe given in Table 3-1 was used for master batch mixing according to the mixing cycle given in Table 3-2. The fill factor was 0.6 and the rotor speed was 110 rpm.

Table 3-1 Master batch compound recipe

MATERIAL	**PHR**
TSR-20	100
CARBON BLACK N-330	10
CARBON BLACK N-550	15
CALCIUM CARBONATE	20
STEARIC ACID	2
ZINC OXIDE 99.5%	5
IPPD	0.75
6PPD	0.75
TMQ	0.5

Table 3-2 Master batch mixing cycle

Time /(Sec)	Description
0	Rubber
+30	CBN330+N550+CaCO3+Stearic Acid+ZnO+6PPD+IPPD+TMQ
+30	Ram Sweep-1
+40	Ram Sweep-2
+(30-60)	Dumping 145 ± 5 ºC

The first step was rubber mastication for 30 seconds and all the other materials were added after the first step. The first ram sweep was done after 30 seconds of adding the above materials. Second ram sweep done after 40 seconds from first ram sweep. The dumping temperature was 145 ºC. Just after the dumping step compound lump was milled in the laboratory by a two roll mill machine to get the compound in sheet forms.

Five laboratory-scale master batches were mixed using TSR-5L and the same number of master batches were produced using TSR-10 and TSR-20. All the 15 master batches were subjected to final mixing after 24 hours maturation time.

Final mixing was done in Farrel laboratory Banbury mixer according to the recipe given in table 3-3 and mixing cycle given in table 3-4

Table 3-3 Final batch compound recipe

Material	**PHR**
Master Batch	154
Sulphur	1.8
MBS	1
TBBS	1
CTP	0.5

Table 3-4 Final batch mixing cycle

Time (Sec)	Description
0	Master batch compound
+30	Sulphur+ MBS+ TBBS+ CTP
+(45-60)	Dumping 95 ± 5 ºC

After the 30 seconds of adding master batch compounds, all the final mixing chemicals were added into the laboratory mixer. The final mixed batch was dumped at 95 ºC. The dump batch was subjected to two roll milling to get the compound batch in sheet form. 15 final batches were produced as five batches from each TSR type.

3.5 Compound Testing

All the final mixed batches from three different TSR grades were tested for curing characteristics using moving die rheometers. Before each test compound samples were conditioned for one hour in the laboratory conditions where the temperature was 23±1 ºC and relative humidity was 50±5 %.

3.5.1 Moving Die Rheometer

All the 15 samples were tested for moving die rheometer according to ASTM D5289-19. All the test compound samples were prepared by cutting the compound samples in Montech MDR Volumetric Cutter. Montech MDR 3000 was used for the compound rheological testing. The test temperature was 170 ºC and the test time was 250 seconds. The lower die oscillation angle was 0.5 degree and the lower die oscillation frequency was 100 cpm.

4. RESULTS AND DISCUSSION

Raw technically specified rubber properties of three different grades and cure properties of middle compounds are discussed in this section.

4.1 Results of technically specified rubber

TSR test results on dirt content, ash content, plasticity number, plasticity retention index, nitrogen content, and viscosity are discussed here. Also, molecular weight and molecular weight distribution variations among the different TSR grades are discussed.

4.1.1 Dirt Content

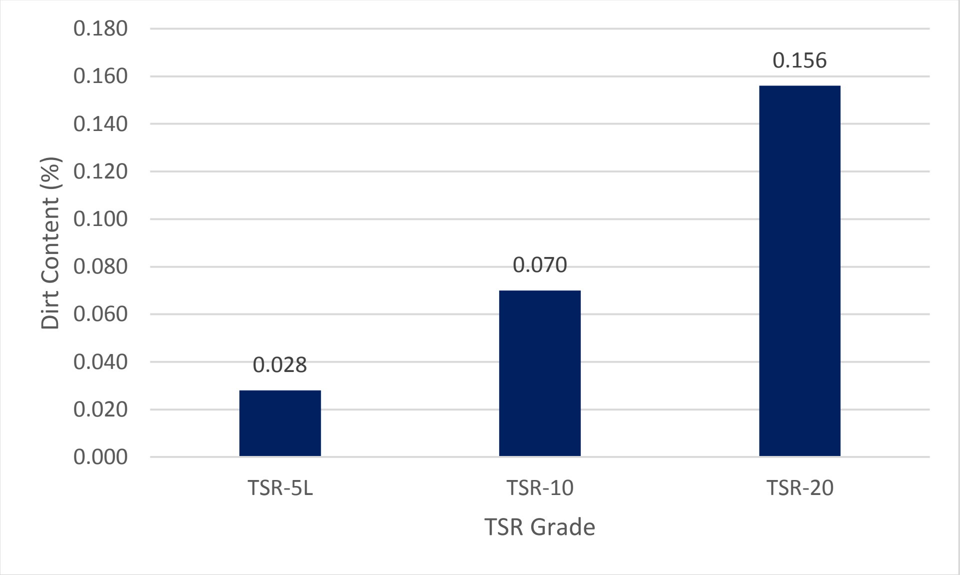

Figure 4-1 Dirt Content(%) of TSR Grades

As indicated in Figure 4-1, TSR-20 is the TSR grade consists of the highest amount of dirt content. This is due to the impurities of the source used for TSR manufacturing. As the cup lump coagulum is used for TSR-20 manufacturing where the field latex is used to produce TSR-5L. Even cup lumps are passed through several steps of washing. Dirt is remanent due to insufficient washing. Dirt content of TSR-5L is at a minimum since it is produced using latex. TSR-10 has medium dirt content as both cup lumps and unsmoked rubber sheets are used to produce TSR-10.

4.1.2 Ash Content

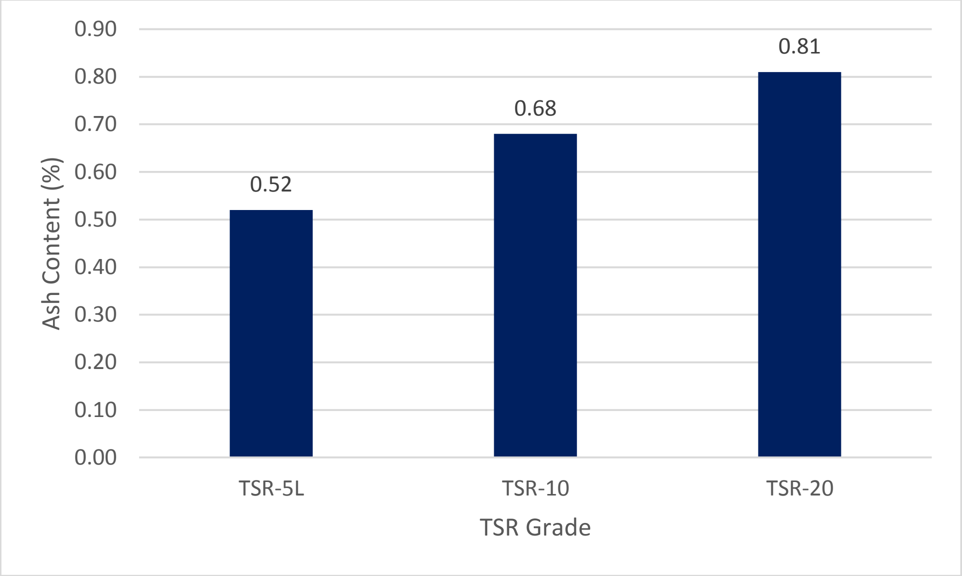

Figure 4-2 Ash Content(%) of TSR Grades

When tested the TSR grades for ash content, TSR-20 has the highest amount of ash content as given in Figure 4-2. This is due to high inorganic and organic impurities. Non-rubber part of latex is high in TSR-20 raw rubbers.

4.1.3 Plasticity Number (Po)

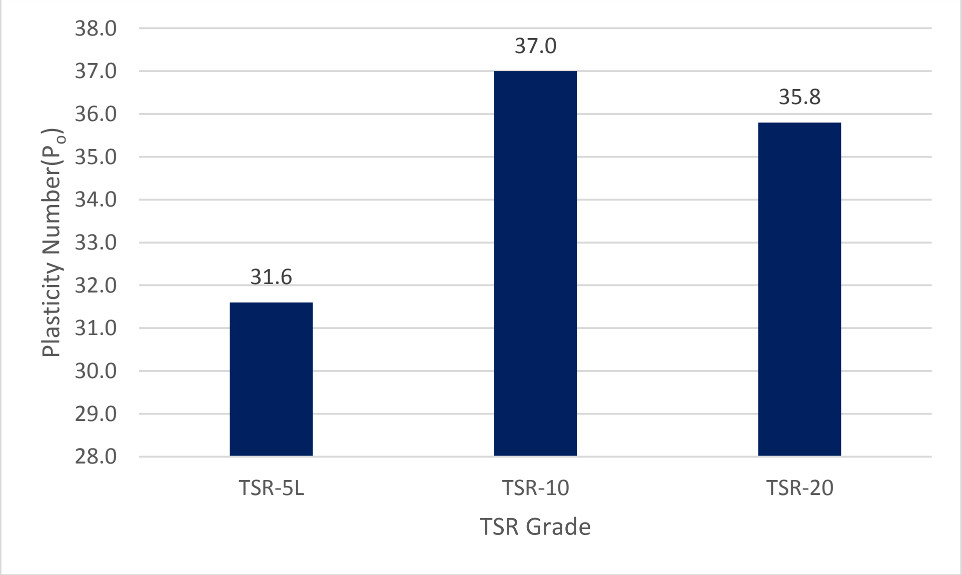

Figure 4-3 Plasticity Number(P_o) of TSR Grades

The highest Po value is for TSR-10 and the minimum value is for TSR-5L sample as indicated in Figure 4-3. P_o indicating hardness or softness of the raw rubber. Clonal effects, maturation, storage hardening, drying temperatures and molecular weight affect the P_o value. Also P_o is generally positively correlated with the viscosity of rubber [15].

4.1.4 Plasticity Retention Index (PRI)

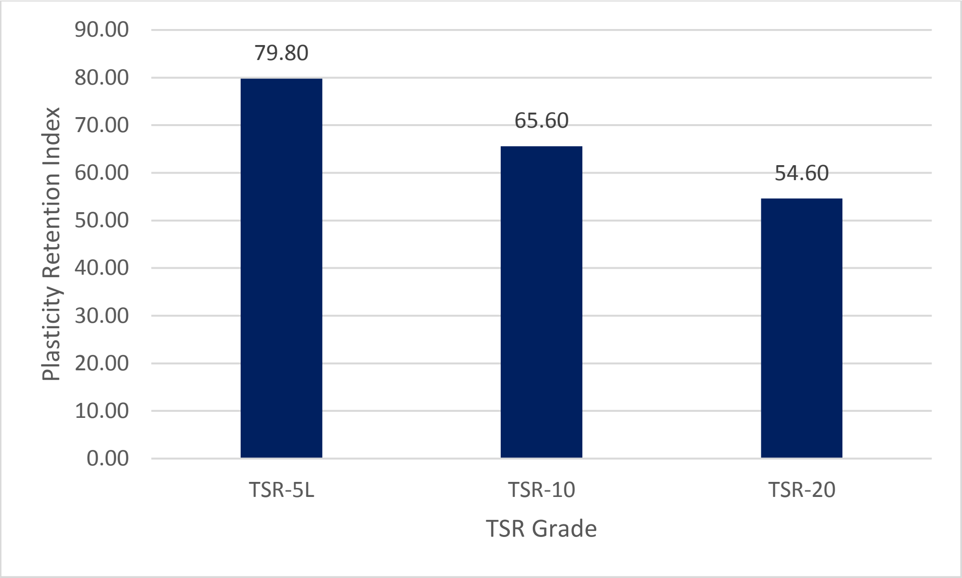

Figure 4-4 Plasticity Retention Index(PRI) of TSR Grades

As shown in Figure 4-4, plasticity retention time is highest in TSR-5L and lowest in TSR-20. PRI indicates the resistance to oxidation and due to the use of old cup lumps that were exposed to sunlight for a long time PRI is lowest in TSR-20 grade. In addition to that many factors mentioned in the chapter 2, also affect the PRI.

4.1.5 Nitrogen Content

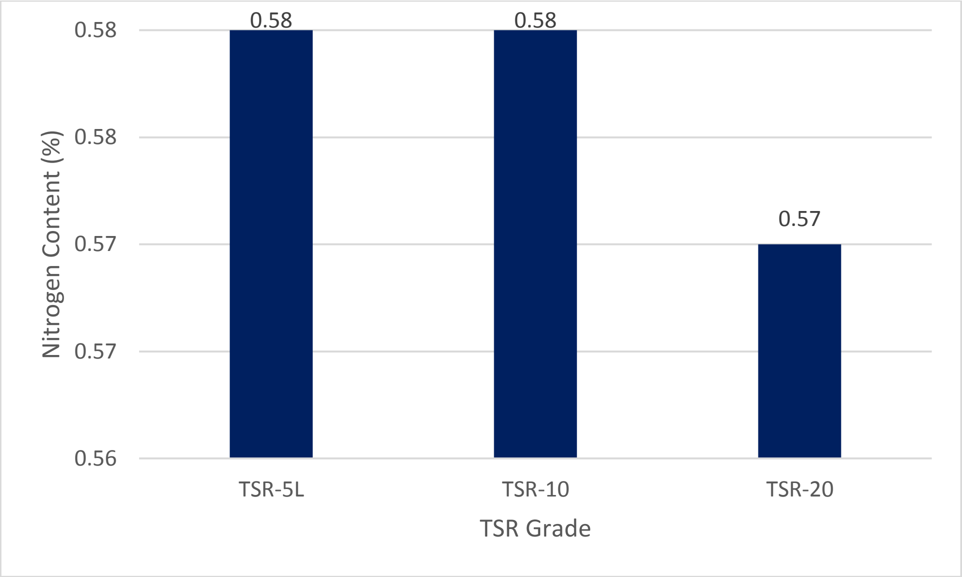

Figure 4-5 Nitrogen Content(%) of TSR Grades

The Nitrogen content is almost the same in all the TSR grades and bit lower in TSR-20 grade as given in Figure 4-5. Nitrogen content gives the estimation of protein content in the rubber and it depends on the raw rubbers sources.

4.1.6 Viscosity

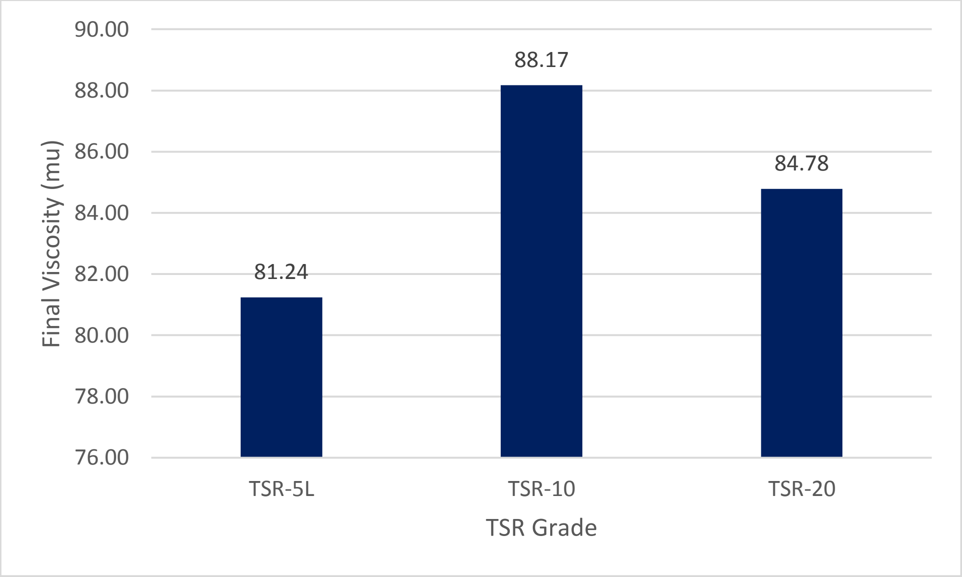

Figure 4-6 TSR Viscosity(mu) of TSR Grades

As given in Figure 4-6, TSR-10 gives the maximum viscosity value comparatively. This may be due to the use of a high amount of unsmoked sheet rubbers for the TSR-10 manufacturing process. Also, the same kind of behaviour is observed in Figure 4-3, which proves the relationship between P_o and the viscosity.

4.1.7 Loss Modulus (G”) of TSR

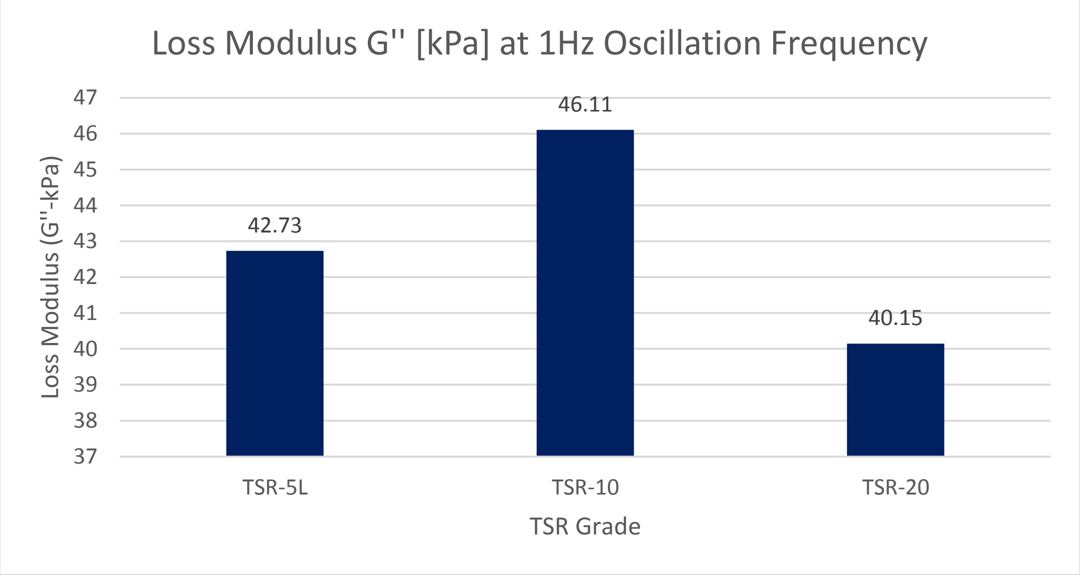

Figure 4-7 Loss Modulus at 1Hz oscillation frequency

In Figure 4-7, G”-Loss modulus (Viscous Modulus) is compared among TSR grades at 1 cpm oscillation frequency in rubber processing analyzer. TSR-10 grade gives the maximum loss modulus 46.11 kPa and TSR-20 grade gives the lowest loss modulus 40.15 kPa. There are many parameters that change with molecular weight. The length of the polymer chain affects the viscous and elastic modulus. The viscous modulus (Loss modulus) measures the resistance when polymer chains flow pass each other. The longer chains give greater resistance and then viscous modulus (Loss modulus) is high. Hence molecular weights of the TSR grades are MW TSR-10 > MW TSR-5L > MW TSR-20 [16].

4.1.8 TSR phase angle (tan δ) vs oscillation frequency

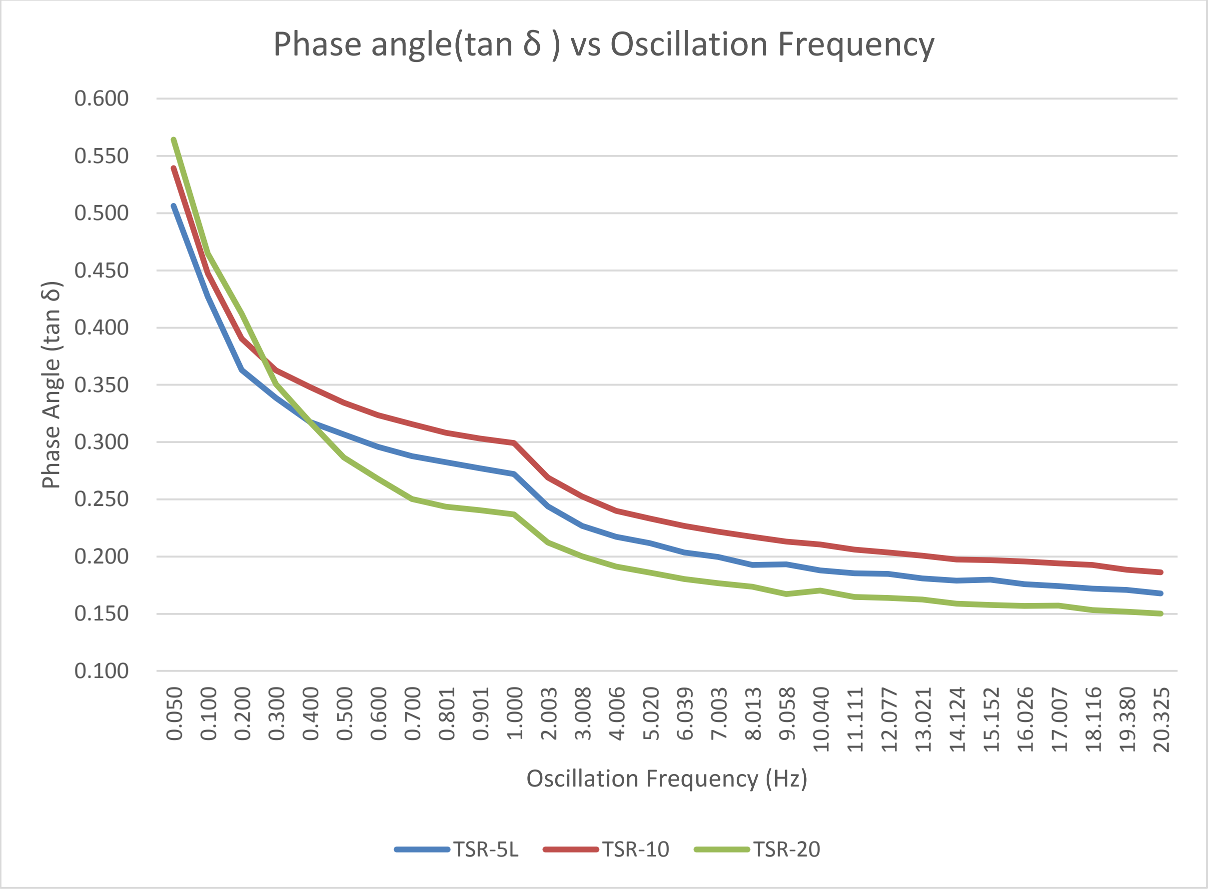

Figure 4-8 Phase angle vs oscillation frequency

In Figure 4-8, phase angle (tan δ) of three TSR grades are plotted against oscillation frequency. TSR-5 and TSR-10 indicate the same pattern while TSR-20 is found to give a greater phase angle at lower frequencies and lower phase angle for higher frequencies. The breadth of the molecular weight distribution can be analytically measured by comparing the number average, weight average, and z average molecular weights. When these three values are apart a lot, molecular weight distribution is high. Molecular weight distribution can be assessed by a rubber processing analyzer by comparing the polymer rheology at different frequencies. At low frequency, the low molecular weight chains will have fewer entangles and easy followability. Hence lower viscous modulus can be observed. If two polymers are being compared, broader molecular weight distribution will cause reduced modulus loss at lower frequencies and increased modulus loss at high frequencies [16].

When comparing three TSR grades, TSR-20 has the highest molecular weight distribution and this may be due to collecting cup lumps from different sources and subjected to many granulation processes during the manufacturing stage.

4.2 Cure characteristics of solid tyre middle compounds

All the 15 middle compound batches produced using three TSR grades, were tested for rheological properties using moving die rheometer. All the rheometer curves are attached in the annexure.

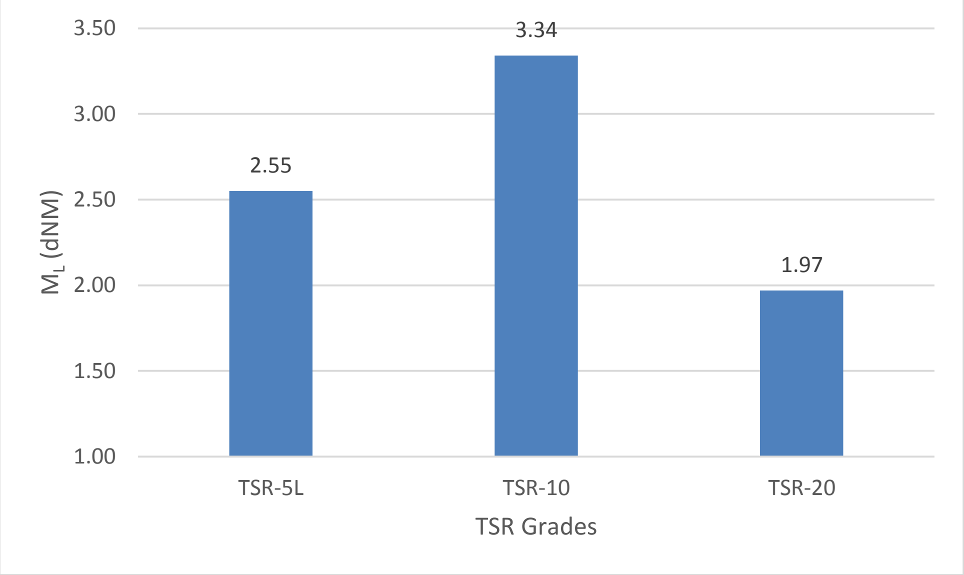

Figure 4-9 Middle Compound M_L (dNm)

Figure 4-9 illustrates the M_L-minimum torque value of the solid tyre middle compounds produced using three different TSR grades. M_L value is highest in TSR-10 grade and lowest in TSR-20 grade. This behaviour is directly linked with loss modulus data given in Figure 4-7. Hence rubber molecular weight affects the M_L values of the middle compound [14]. The lowest torque value of the compound means that the compound has minimum stiffness comparatively. M_L value of the compound directly effects for the mixing process and energy required for the mixing. It directly links with the processability of the compounds in the downstream processes in tyre manufacturing process. Specially for the extrusion processes lower M_L compounds are preferred due to easy processability.

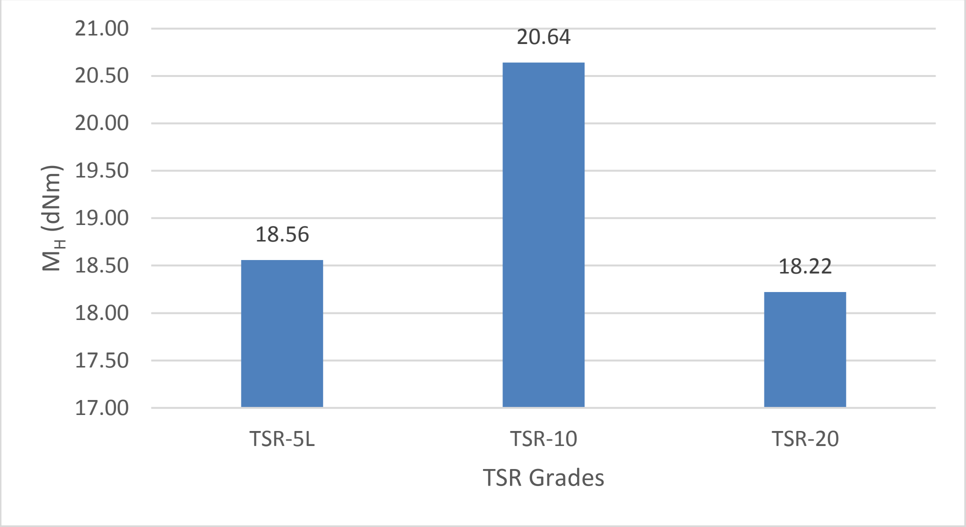

Figure 4-10 Middle Compound M_H (dNm)

Compound maximum torque value is high in TSR-10 as given in Figure 4-10. M_H is high due to high cross-linking density of polymer network. Due to high molecular weight, polymer chains are long and number of sulphur crosslinks are higher among polymer chains which increase the cross-link density. As TSR-10 is produced using unsmoked sheets high M_H values are observed. M_H is positively correlate with hardness values of the compounds. Hence due to usage of raw TSR grades, different M_H properties are observed in the compounds.

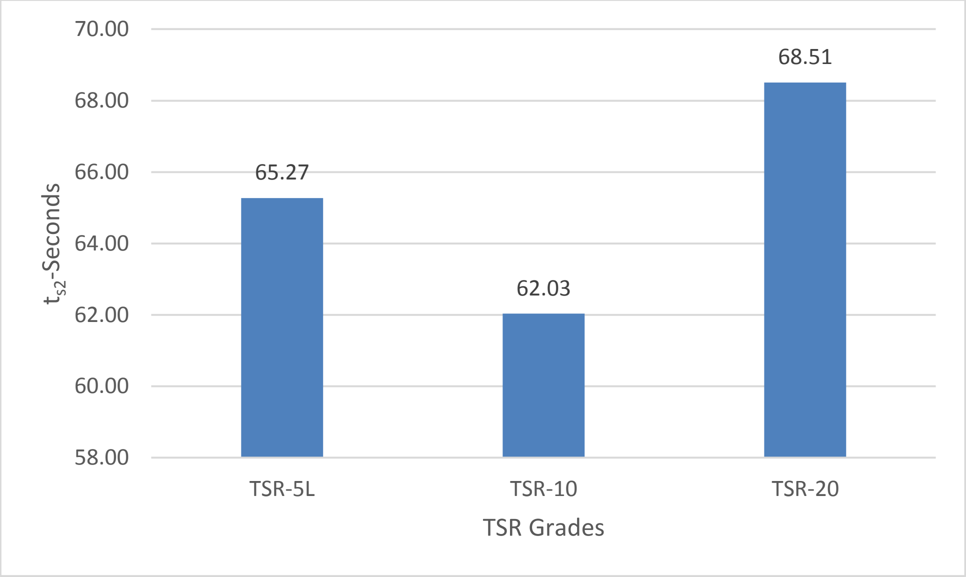

Figure 4-11 Middle Compound t_{s2} (Seconds)

Scorch time of the compound is the lowest in TSR-10 grade as indicated in Figure 4-11. Due to higher molecular weight and high viscosity t_{s2} becomes low in the TSR-10 grade compound. When mixing the compounds in the mixer heat generation is high due to high viscosity and longer polymer chains. Due to the high heat generation vulcanization process is accelerated and scorch safety time becomes low. This is a main parameter which affects the tyre manufacturing process as scorch safety time is the processing time of the compound without getting scorched. Milling, green tyre building and moulding should be completed within scorch safety time. According to the TSR grade used for the compounding, different t_{s2} values were observed.

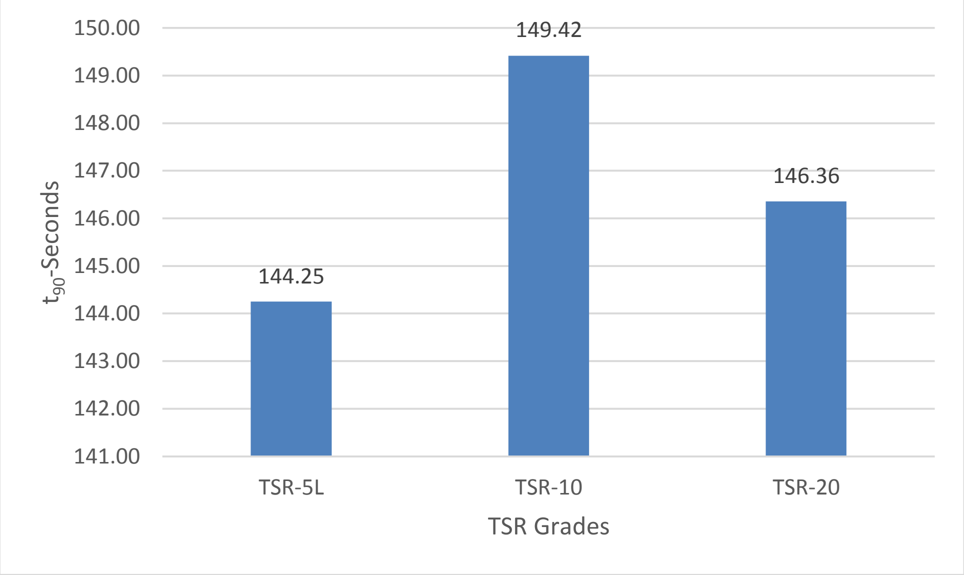

Figure 4-12 Middle Compound t_{90} (Seconds)

t_{90} is higher in TSR-10 compounds comparatively and t_{90} is directly linked with the chemical reactions and cure rate during the vulcanization process. As due to longer molecular chains of TSR-10, time taken to complete the crosslinking will be high. t_{90} is the time taken to complete 90% of vulcanization process, which decides the demoulding time of tyre when curing. As observed in Figure 4-12, different t_{90} values observed when using different TSR grades for compounding.

5. CONCLUSIONS AND RECOMMENDATIONS

When evaluating technical properties of technically specified rubber grades, variations can be observed among the different grades. As per the observations made in the experiments these factors affect the compound mixing process and compound properties directly. By identifying the differences of TSR grades, many advantages can be gained by using only the most relevant TSR grade for compounding. TSR-10 has the highest molecular weight and TSR-20 has the highest molecular weight distribution. The highest ML is observed for the middle compound prepared with TSR-10 grade. Hence according to the experiment results it can be concluded that molecular weight is positively correlated to the ML value. In addition as assessed in this experiment, for higher molecular weights of TSR, high viscosity and high initial plasticity values are observed, experimentally supporting the conclusion that the higher molecular weights of TSR contributes to high viscosity and high initial plasticity.

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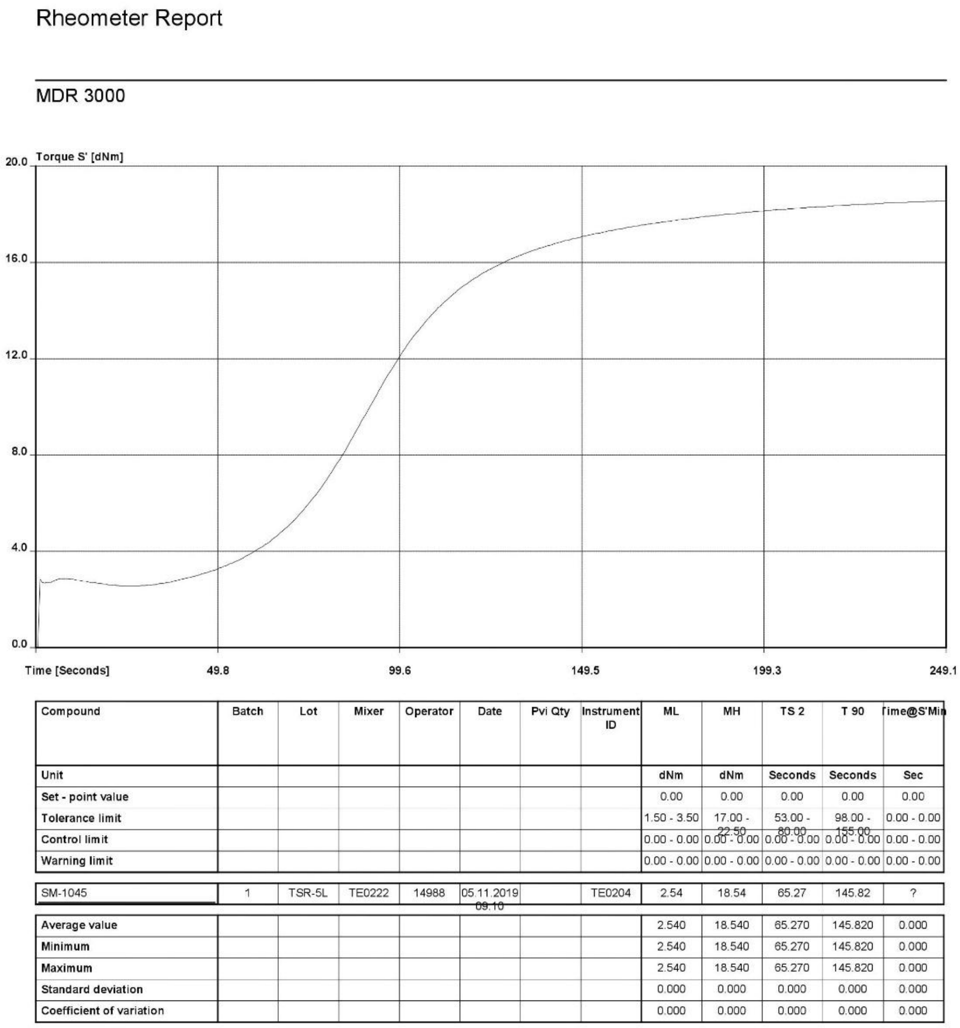
ANNEXURE

Moving Die Rheometer test data for solid tyre middle compounds produced using three technically specified rubber types TSR-5L, TSR-10 and TSR-20 have been attached from page number 37. The reports were automatically generated through Moncontrol software when the tests were conducted using Montech MDR 3000 test machine.

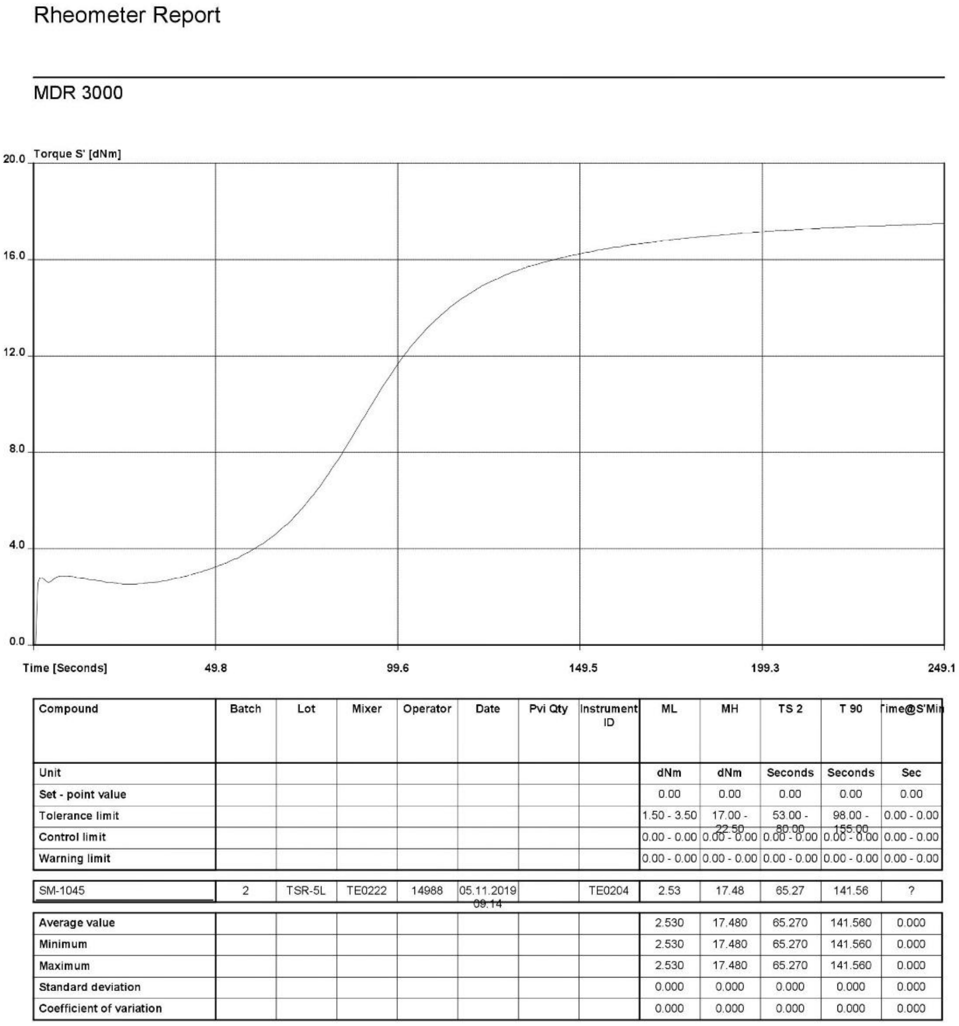


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	1	TSR-5L	TE0222	14988	05.11.2019 09:10		TE0204	2.54	18.54	65.27	145.82	?
Average value								2.540	18.540	65.270	145.820	0.000
Minimum								2.540	18.540	65.270	145.820	0.000
Maximum								2.540	18.540	65.270	145.820	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

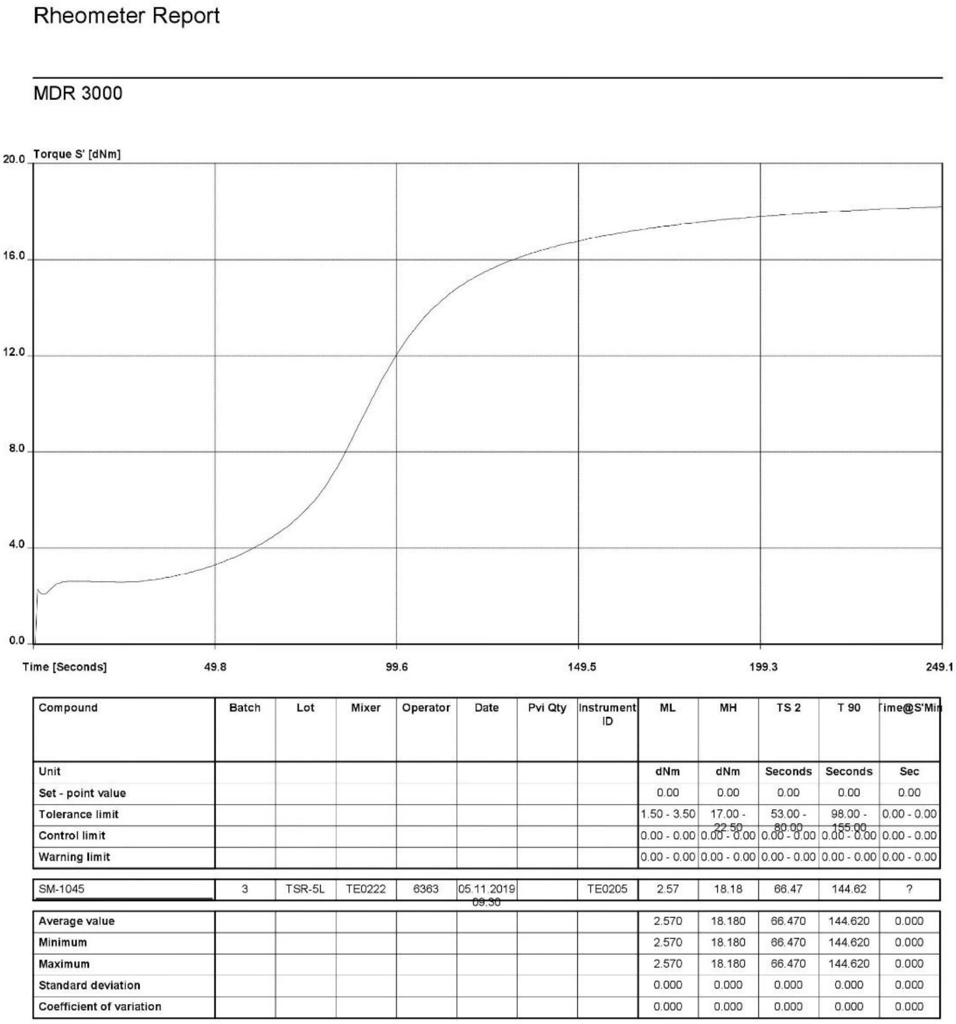
Figure A. 2 MDR test data for middle compound batch-1 (TSR-5L)


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Mi
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	2	TSR-5L	TE0222	14988	05.11.2019 09:14		TE0204	2.53	17.48	65.27	141.56	?
Average value								2.530	17.480	65.270	141.560	0.000
Minimum								2.530	17.480	65.270	141.560	0.000
Maximum								2.530	17.480	65.270	141.560	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 3 MDR test data for middle compound batch-2 (TSR-5L)

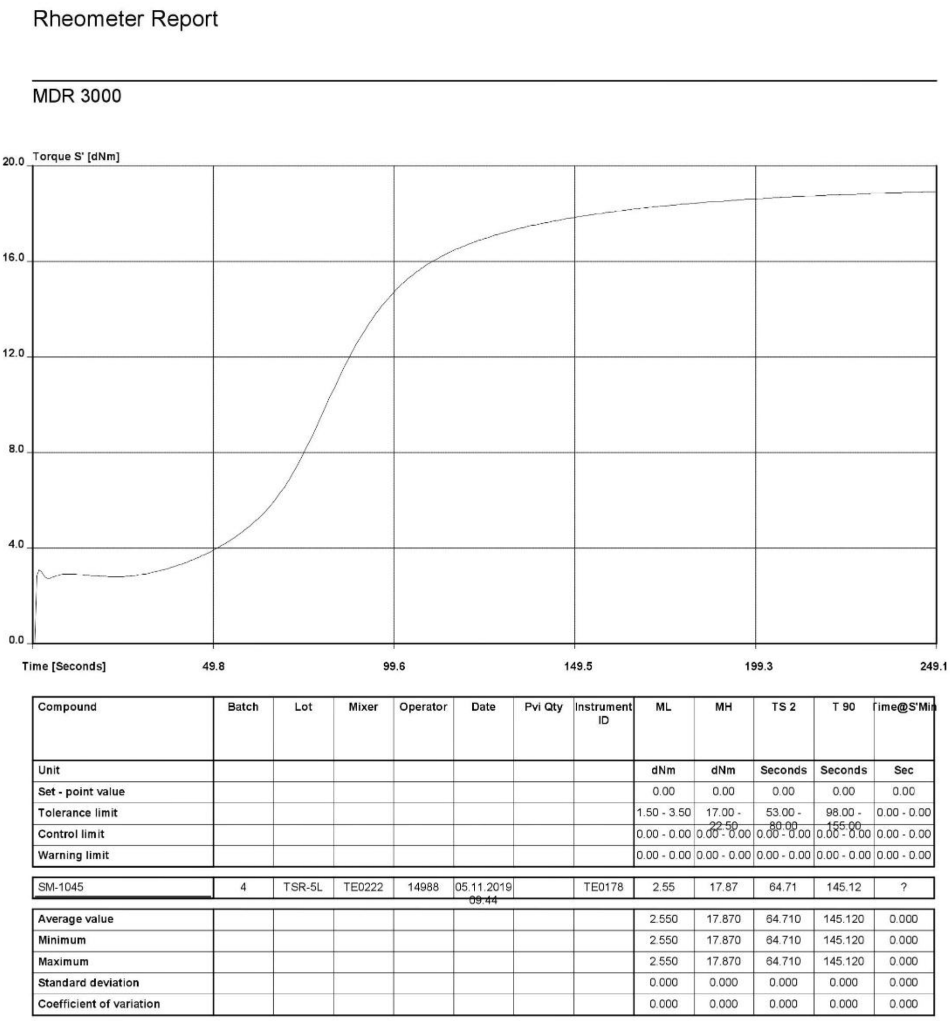


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	ime@S'Mi
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	3	TSR-5L	TE0222	6363	05.11.2019 09:30		TE0205	2.57	18.18	66.47	144.62	?
Average value								2.570	18.180	66.470	144.620	0.000
Minimum								2.570	18.180	66.470	144.620	0.000
Maximum								2.570	18.180	66.470	144.620	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 4 MDR test data for middle compound batch-3 (TSR-5L)

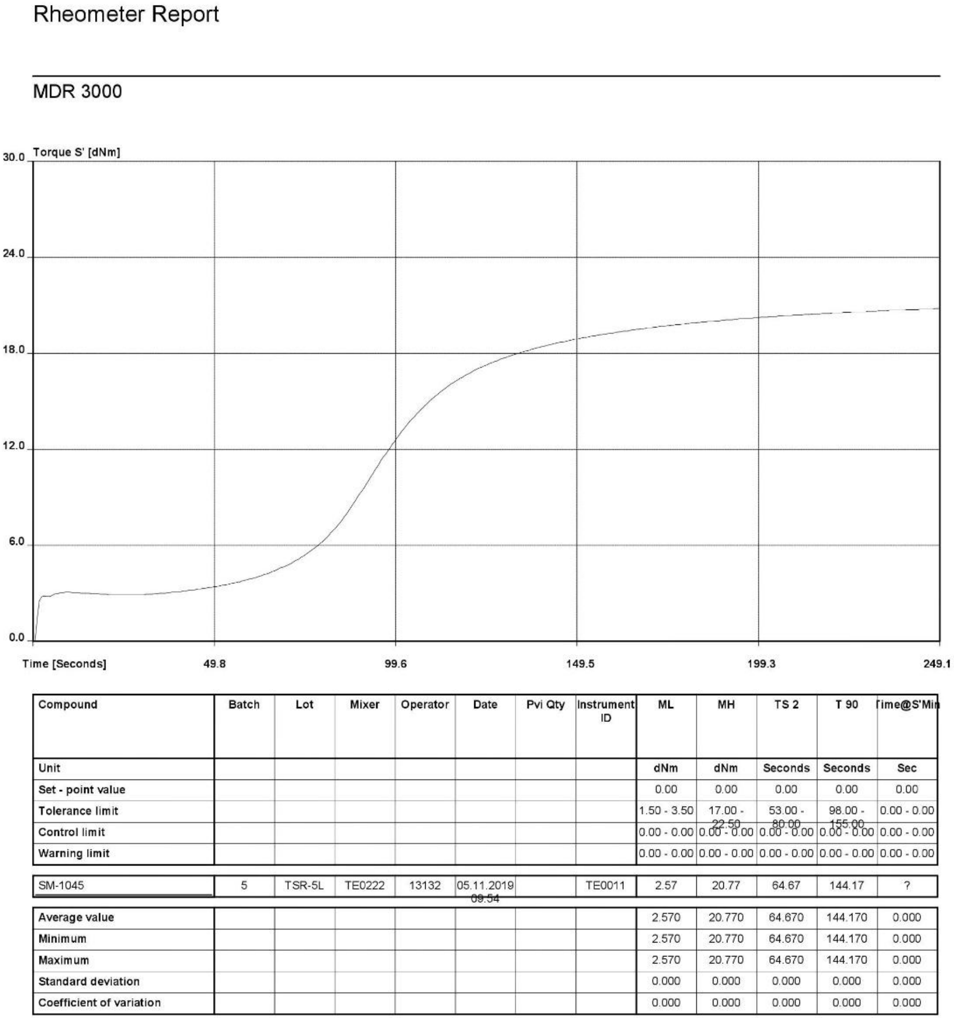


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	4	TSR-5L	TE0222	14988	05.11.2019 09:44		TE0178	2.55	17.87	64.71	145.12	?
Average value								2.550	17.870	64.710	145.120	0.000
Minimum								2.550	17.870	64.710	145.120	0.000
Maximum								2.550	17.870	64.710	145.120	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

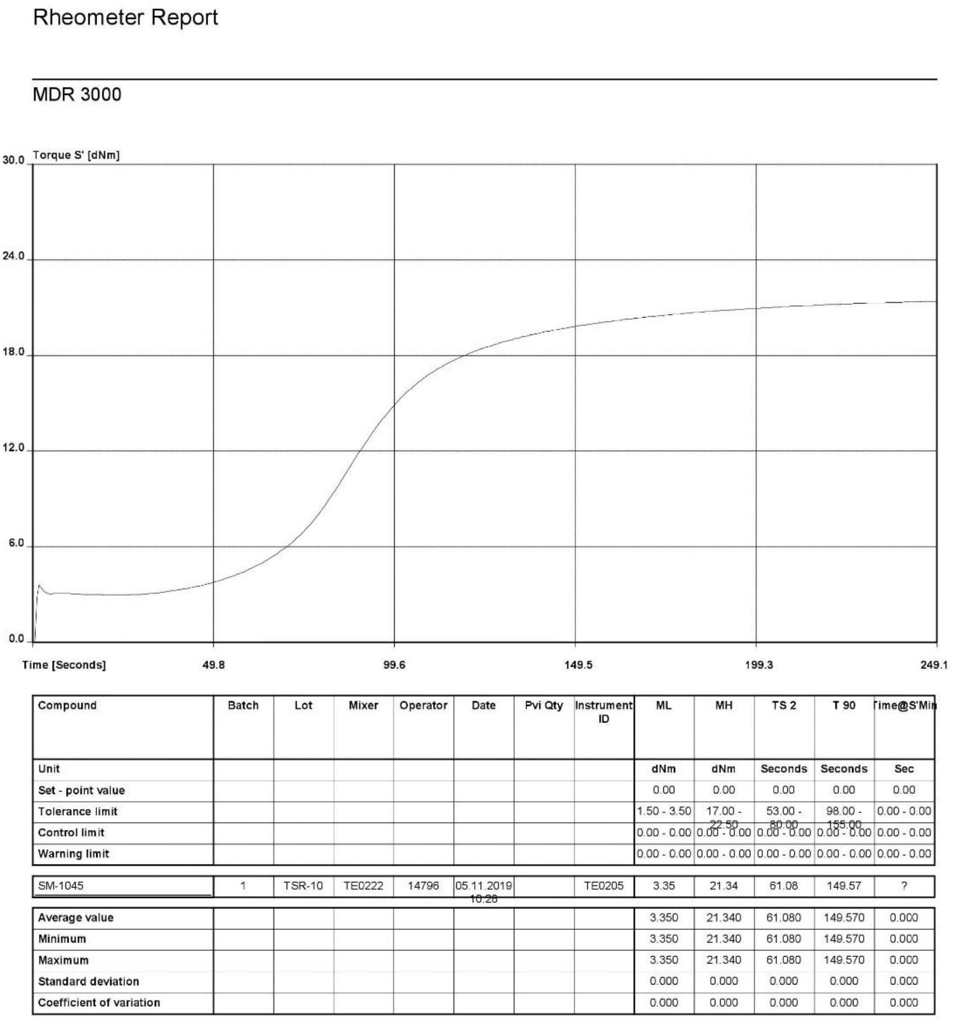
Figure A. 5 MDR test data for middle compound batch-4 (TSR-5L)


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	5	TSR-5L	TE0222	13132	05.11.2019 09:54		TE0011	2.57	20.77	64.67	144.17	?
Average value								2.570	20.770	64.670	144.170	0.000
Minimum								2.570	20.770	64.670	144.170	0.000
Maximum								2.570	20.770	64.670	144.170	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 6 MDR test data for middle compound batch-5 (TSR-5L)

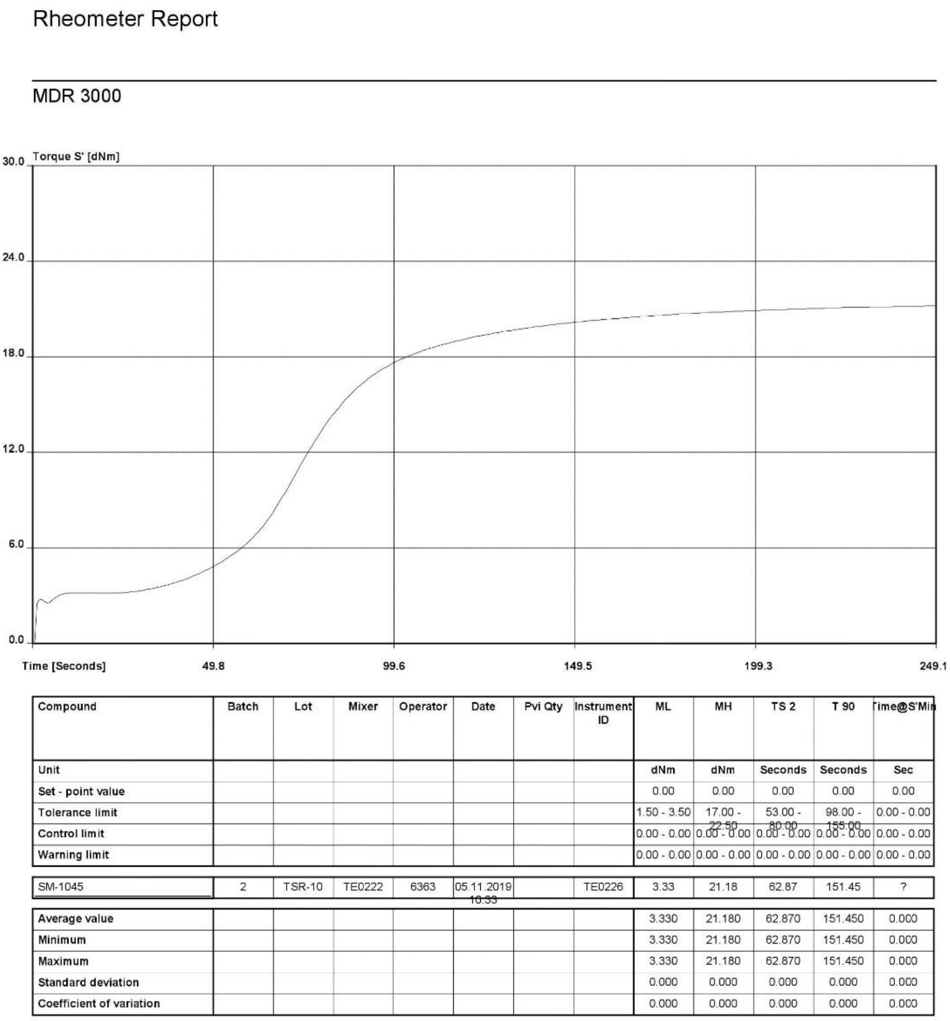


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	1	TSR-10	TE0222	14796	05.11.2019 10:28		TE0205	3.35	21.34	61.08	149.57	?
Average value								3.350	21.340	61.080	149.570	0.000
Minimum								3.350	21.340	61.080	149.570	0.000
Maximum								3.350	21.340	61.080	149.570	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 7 MDR test data for middle compound batch-1 (TSR-10)

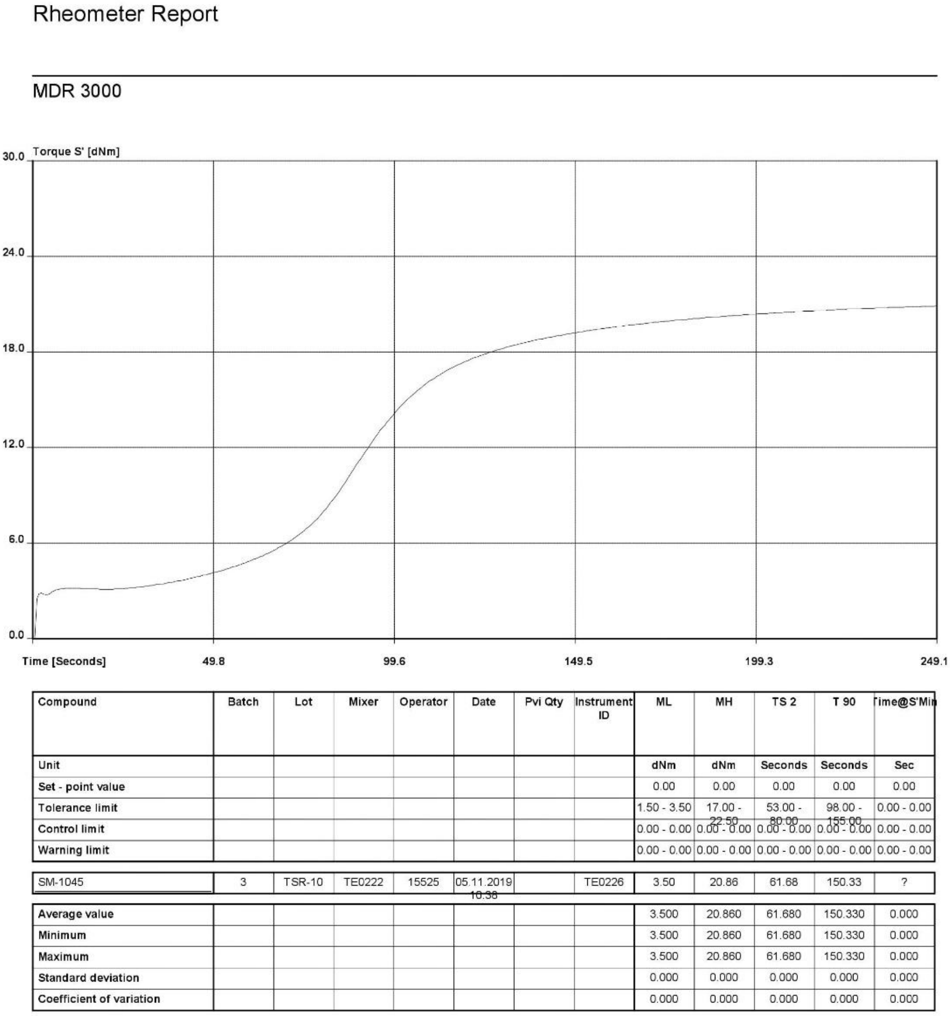


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	2	TSR-10	TE0222	6363	05.11.2019 10.33		TE0226	3.33	21.18	62.87	151.45	?
Average value								3.330	21.180	62.870	151.450	0.000
Minimum								3.330	21.180	62.870	151.450	0.000
Maximum								3.330	21.180	62.870	151.450	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 8 MDR test data for middle compound batch-2 (TSR-10)

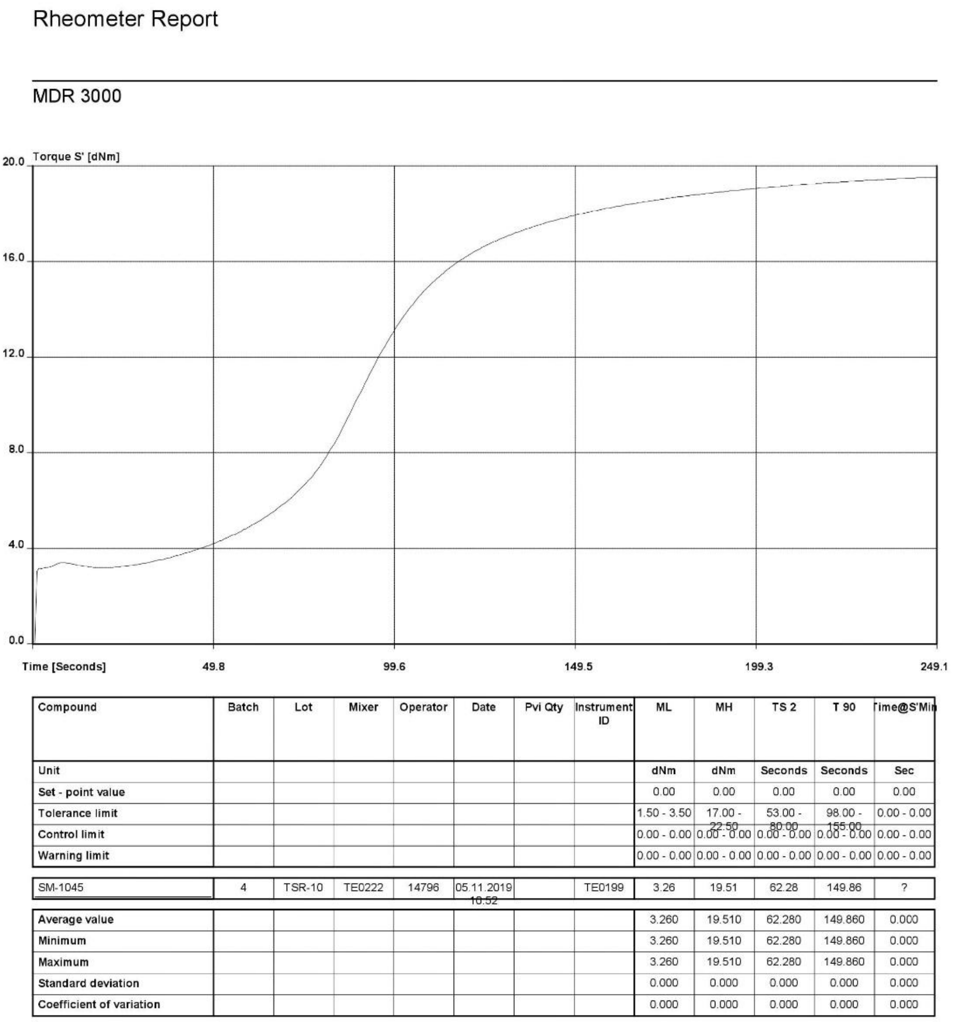


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	3	TSR-10	TE0222	15525	05.11.2019 10:38		TE0226	3.50	20.86	61.68	150.33	?
Average value								3.500	20.860	61.680	150.330	0.000
Minimum								3.500	20.860	61.680	150.330	0.000
Maximum								3.500	20.860	61.680	150.330	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 9 MDR test data for middle compound batch-3 (TSR-10)

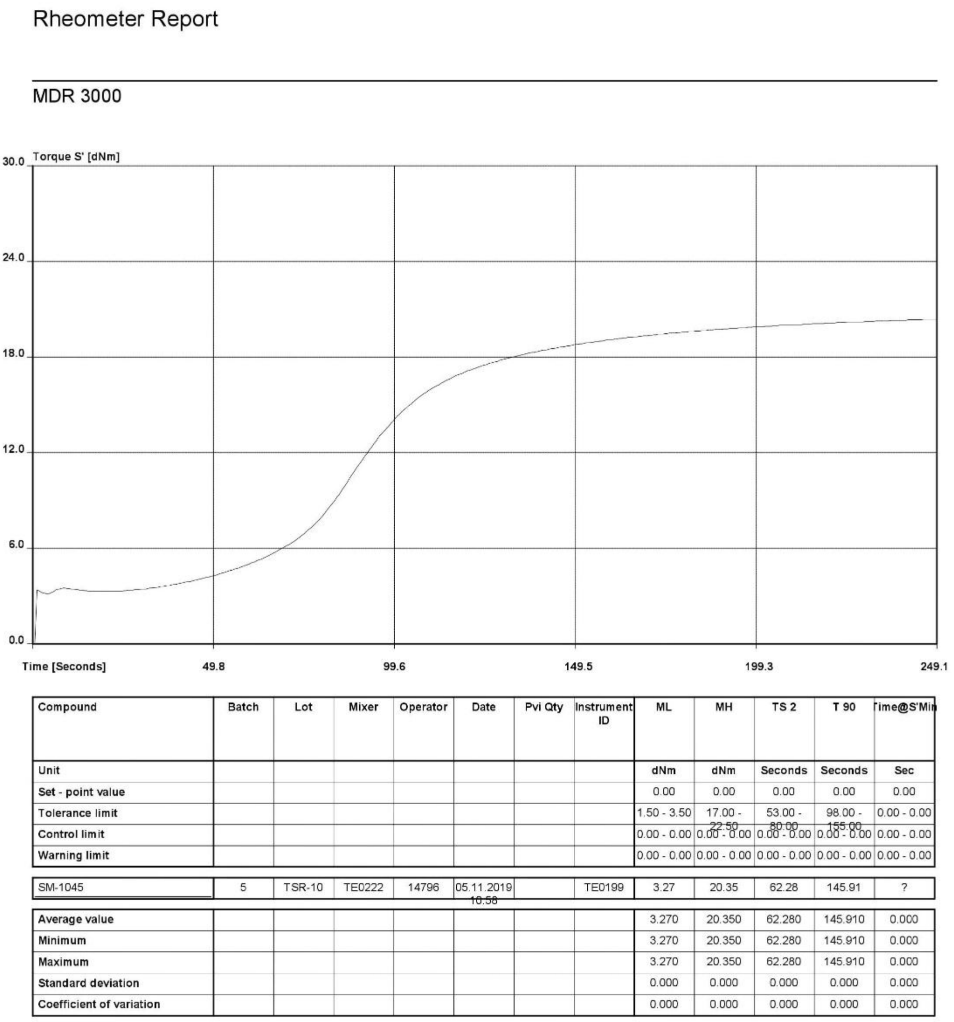


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Mi
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	4	TSR-10	TE0222	14796	05.11.2019 10.52		TE0199	3.26	19.51	62.28	149.86	?
Average value								3.260	19.510	62.280	149.860	0.000
Minimum								3.260	19.510	62.280	149.860	0.000
Maximum								3.260	19.510	62.280	149.860	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 10 MDR test data for middle compound batch-4 (TSR-10)

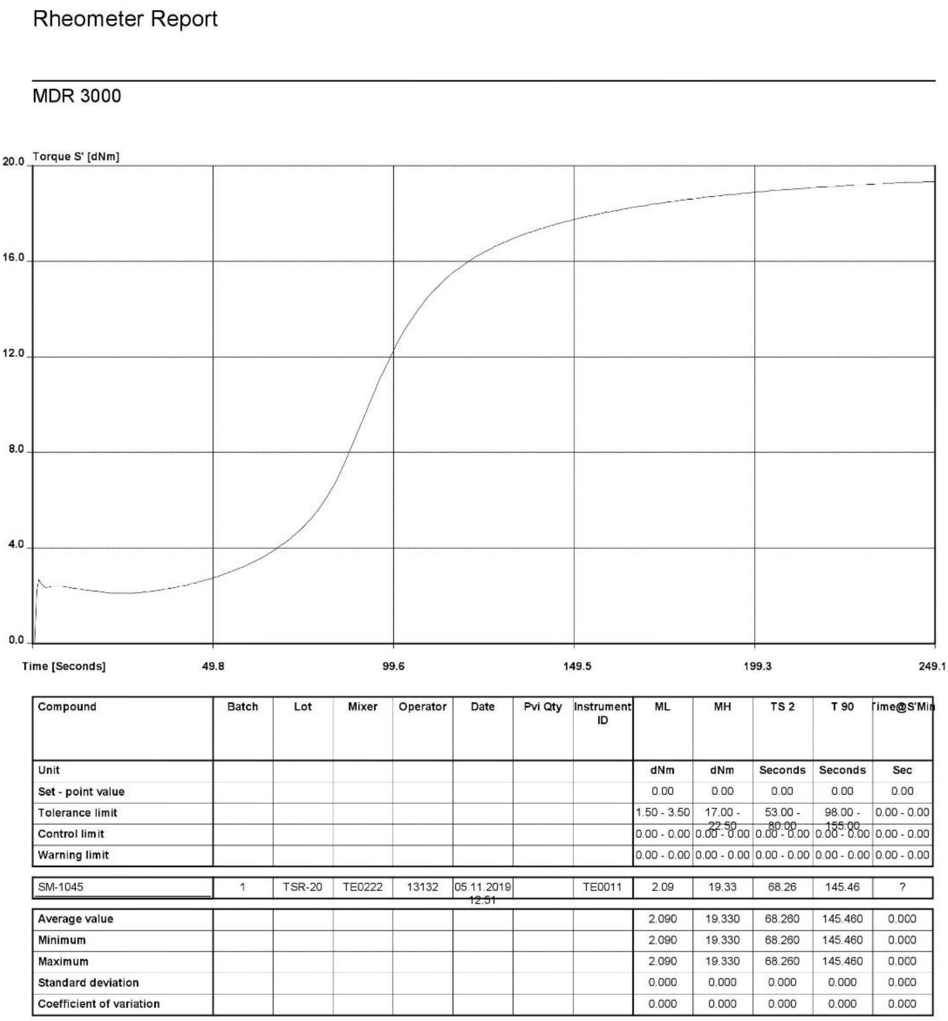


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	ime@S'Mi
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	5	TSR-10	TE0222	14796	05.11.2019 10:58		TE0199	3.27	20.35	62.28	145.91	?
Average value								3.270	20.350	62.280	145.910	0.000
Minimum								3.270	20.350	62.280	145.910	0.000
Maximum								3.270	20.350	62.280	145.910	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 11 MDR test data for middle compound batch-5 (TSR-10)

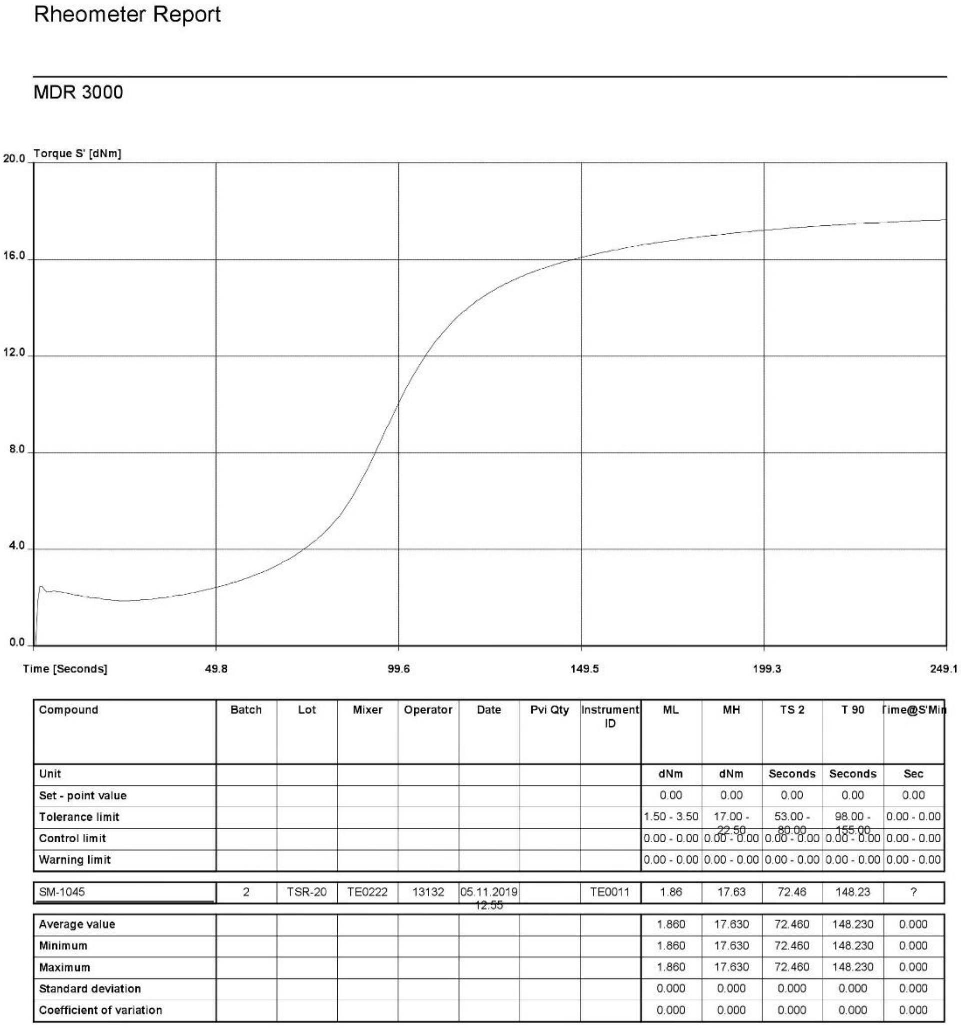


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	1	TSR-20	TE0222	13132	05.11.2019 12:51		TE0011	2.09	19.33	68.26	145.46	?
Average value								2.090	19.330	68.260	145.460	0.000
Minimum								2.090	19.330	68.260	145.460	0.000
Maximum								2.090	19.330	68.260	145.460	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 12 MDR test data for middle compound batch-1 (TSR-20)

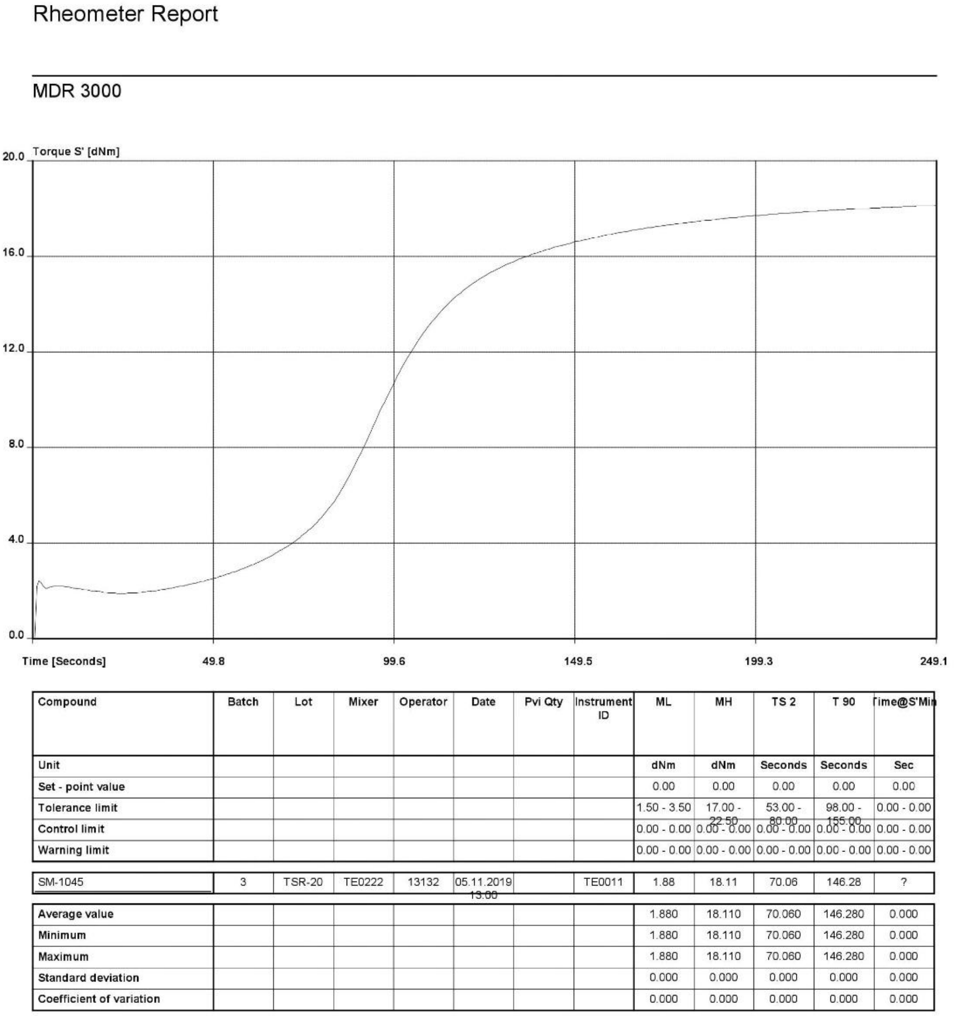


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	ime@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	2	TSR-20	TE0222	13132	05.11.2019 12:55		TE0011	1.86	17.63	72.46	148.23	?
Average value								1.860	17.630	72.460	148.230	0.000
Minimum								1.860	17.630	72.460	148.230	0.000
Maximum								1.860	17.630	72.460	148.230	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 13 MDR test data for middle compound batch-2 (TSR-20)

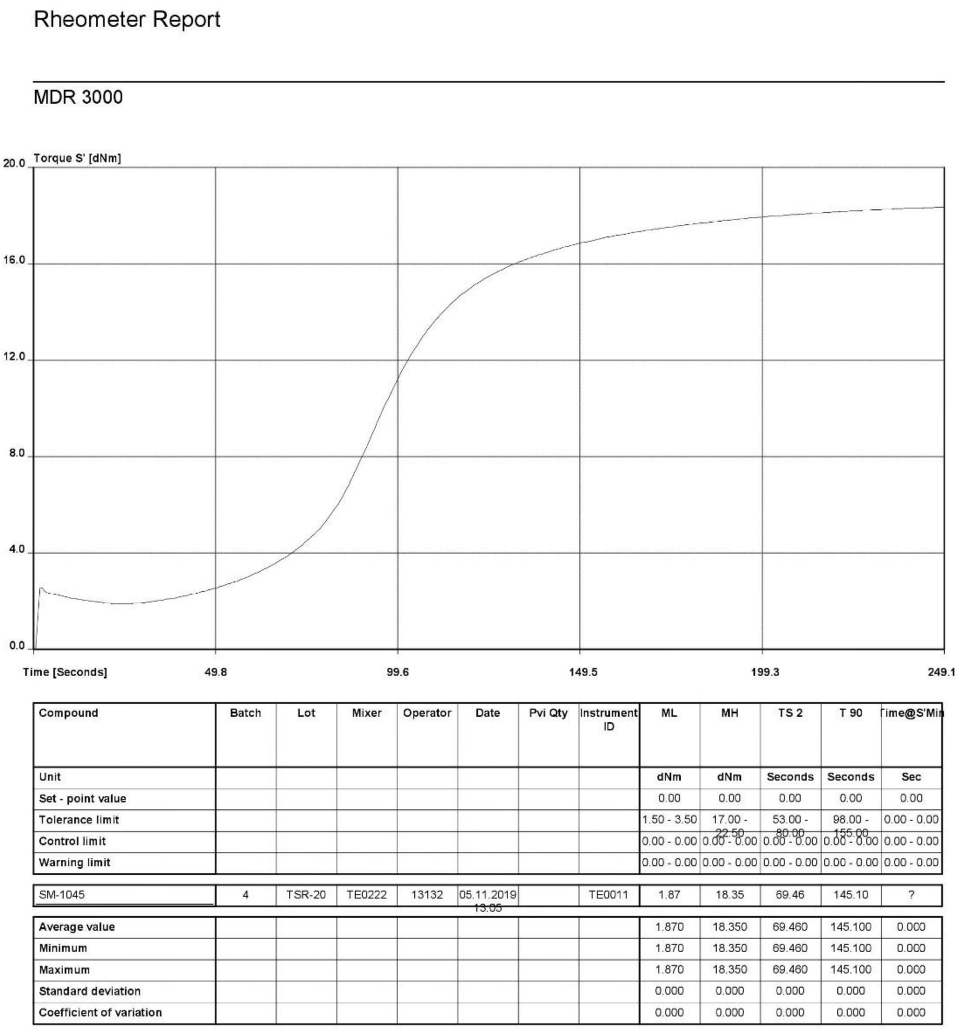


Rheometer Report

MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	3	TSR-20	TE0222	13132	05.11.2019 13:00		TE0011	1.88	18.11	70.06	146.28	?
Average value								1.880	18.110	70.060	146.280	0.000
Minimum								1.880	18.110	70.060	146.280	0.000
Maximum								1.880	18.110	70.060	146.280	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 14 MDR test data for middle compound batch-3 (TSR-20)



Rheometer Report

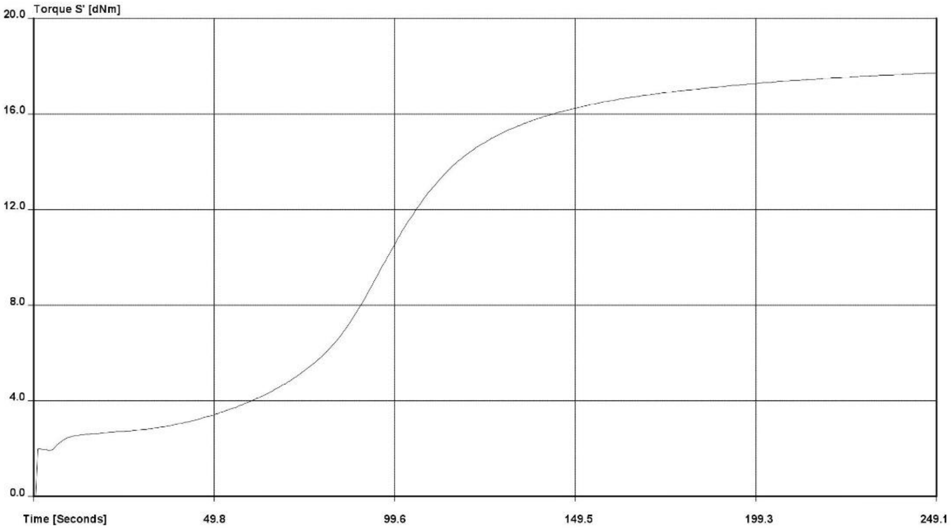
MDR 3000

Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90	Time@S'Min
Unit								dNm	dNm	Seconds	Seconds	Sec
Set - point value								0.00	0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00	0.00 - 0.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	4	TSR-20	TE0222	13132	05.11.2019 13:05		TE0011	1.87	18.35	69.46	145.10	?
Average value								1.870	18.350	69.460	145.100	0.000
Minimum								1.870	18.350	69.460	145.100	0.000
Maximum								1.870	18.350	69.460	145.100	0.000
Standard deviation								0.000	0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000	0.000

Figure A. 15 MDR test data for middle compound batch-4 (TSR-20)

Rheometer Report

MDR 3000



Compound	Batch	Lot	Mixer	Operator	Date	Pvi Qty	Instrument ID	ML	MH	TS 2	T 90
Unit								**dNm**	**dNm**	**Seconds**	**Seconds**
Set - point value								0.00	0.00	0.00	0.00
Tolerance limit								1.50 - 3.50	17.00 - 22.50	53.00 - 80.00	98.00 - 155.00
Control limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
Warning limit								0.00 - 0.00	0.00 - 0.00	0.00 - 0.00	0.00 - 0.00
SM-1045	5	TSR-20	TE0222	147969	05.11.2019 13.15		TE0205	2.15	17.70	62.28	146.75
Average value								2.150	17.700	62.280	146.750
Minimum								2.150	17.700	62.280	146.750
Maximum								2.150	17.700	62.280	146.750
Standard deviation								0.000	0.000	0.000	0.000
Coefficient of variation								0.000	0.000	0.000	0.000

Figure A. 16 MDR test data for middle compound batch-5 (TSR-20)