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**Natural Rubber grades, from polymer
characteristics to engineering properties**

(Grades de Caoutchouc Naturel : des caractéristiques
du polymère au propriétés d'ingénierie)

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Natural Rubber grades, from polymer characteristics to engineering properties

This thesis investigates the relationships between the characteristics of Natural Rubber, its processing properties and the mechanical properties of vulcanized specimens by using a selection of representative grades. Spectroscopic, physico-chemical and rheological techniques were used, as well as mechanical testing of vulcanized compounds. Results show that, as such, spectroscopic techniques are not able to reveal significant differences between the various investigated NR grades. However, by using ^{13}C cross-polarization magic angle spinning (CP-MAS) technique, mobile and immobile components can be distinguished, so highlighting differences between grades. Ribbed Smoked Sheet (RSS) grades exhibit the highest gel content, in agreement with molecular weight, Mooney viscosity and complex modulus. Thanks to the very detailed information it provides regarding the nonlinear viscoelastic behavior, Fourier Transform rheometry is shown to clearly distinguish between the various NR grades. For instance all tested samples exhibit a linear region up to around 60% strain but RSS samples exhibit intrinsic non-linearity (i.e. morphology-induced) whilst viscosity stabilized grades show essentially extrinsic non-linearity (i.e. strain-induced), like most simple polymers. Mastication effects on samples of RSS3 and SMR10CV60 were studied and the former were found to require higher mixing energy than the latter. Mooney viscosity and molecular weight decrease with increasing mixing energy. The mastication process appears to destroy the gel content of NR, so that the complex modulus is decreased as well as all strain history sensitivity. Carbon Black filled compounds with field latex grades (STR5L, RSS3 and RSS3E) are found to exhibit higher complex modulus than viscosity stabilized grades (OMNR, STR5CV60 and SMR10CV). Physical properties of cured rubber for the same formula but different rubber samples show no significant difference.

Cette thèse s'intéresse aux relations entre les caractéristiques du Caoutchouc Naturel, ses propriétés de mise en oeuvre et les propriétés mécaniques d'échantillons vulcanisés, en considérant une sélection de grades représentatifs. Des techniques de spectroscopie, physico-chimiques et de rhéologie ont été utilisées, ainsi que des mesures de propriétés mécaniques sur des mélanges vulcanisés. Les résultats montrent que, telles quelles, les techniques spectroscopiques ne révèlent pratiquement aucune différence entre les divers grades étudiés. Cependant, en utilisant une technique de polarisation croisée de l'angle magique de spin ^{13}C , on peut distinguer les composants mobiles et immobiles qui montrent des différences entre les grades. Les grades feuilles fumées (RSS) ont les taux de gel les plus élevés, en accord avec leur masse molaire, leur viscosité Mooney et leur module complexe. Parce qu'elle fournit des informations détaillées sur le comportement viscoélastique non-linéaire, la rhéométrie à Transformée de Fourier se révèle capable de discerner les différents grades étudiés. Par exemple, tous les grades présentent une région linéaire jusqu'à environ 60% de déformation mais les échantillons de RSS montrent une non-linéarité intrinsèque (c.a.d. induite par la structure du matériau) tandis que les grades à viscosité stabilisée sont extrinsèquement non-linéaire (non-linéarité induite par la déformation), comme la plupart des polymères simples. Les effets de mastication ont été étudiés sur des échantillons de RSS3 et de SMR10CV60 et on a trouvé que les premiers requièrent plus d'énergie que les derniers. La viscosité Mooney et la masse molaire décroissent avec l'augmentation de l'énergie de mélangeage. Il apparaît que la mastication détruit le contenu en gel, de sorte que le module complexe diminue, de même que la sensibilité à l'histoire du cisaillement. Les mélanges chargés au noir de carbone avec les grades latex des champs (STR5L, RSS3 et RSS3E) ont des modules complexes plus élevés que les grades à viscosité stabilisée (OMNR, STR5CV60 et SMR10CV). Pour une même formule, mais des grades différents de caoutchouc naturel, les propriétés physiques des caoutchoucs vulcanisés ne montrent aucune différence significative.

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Appendix :

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Characterizing gum natural rubber samples through advanced techniques

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1. Introduction

1.1 Natural Rubber world context and technology

In 2009, the global world rubber consumption was approximately 21.8 million metric tons of which 9.6 million metric tons were Natural Rubber (NR) and the remaining were synthetics [1]. Natural rubber is therefore among the most important elastomers used in manufacturing highly technical products such as tires and conveyor belts, as well as various goods, including household, engineering, medical, and commercial appliances. When compared to synthetics however, production specifications of NR remain relatively poor since only the so-called technically specified grades (TSR) are characterized with respect to basic rubber test techniques, such as the Mooney viscosity, the Wallace Plasticity (P_0) and the Plasticity Retention Index (PRI) [2]. Other well-known grades, such as Ribbed Smoked Sheets (RSS) are classified with respect to visual inspection only [3].

NR is obtained by tapping the bark of the *Hevea Brasiliensis* tree. Processing factories receive Natural Rubber in two forms, either field coagula (dry rubber) or field latex (concentrated latex). Dry rubber is then processed into Ribbed Smoked Sheet (RSS), Air Dried Sheet (ADS), Technically Specified Natural Rubber (TSR), some of regular and constant viscosity (CV) grades, and others. Constant viscosity NR grades are produced by adding hydroxylamine (salt) either to the NR latex before the coagulation process or by spraying to the freshly coagulated material, in order to minimize the storage-hardening phenomenon, whose origin is currently assigned to the formation of (natural) crosslinks on storage. Natural Rubber is normally used when high elasticity related properties are desired, such fatigue and tear resistance. However, NR presents some disadvantages over synthetic rubbers due to properties inconsistency inherent to any natural products. The progressive hardening that occurs in NR upon long-term storage leads to an increase in plasticity number and Mooney viscosity. RSS are made from intentionally coagulated whole field latex and are classified through visual evaluation. To establish acceptable grades for commercial purposes, the International Rubber Quality and Packing Conference has prepared a description for grading, with details given in the so-called Green Book [3]. The International Standards Organization (ISO) first published a technical specification (ISO 2000) for Natural Rubber in 1964 [2]. Based on these specifications, Malaysia introduced a national standard Malaysian Rubber (SMR) scheme in 1965, and since then, all the natural rubber producing countries have started producing and marketing technically specified rubbers based on the ISO 2000 scheme. This resulted in the introduction of further national standards in addition to Standard Malaysian Rubber (SMR), i.e. Standard Thai Rubber (STR), Standard Indonesian Rubber (SIR), Standard Sri Lanka Rubber (SSR), Standard Vietnam Rubber (SVR), Indian Standard Natural Rubber (ISNR), etc. The claimed advantages of Technically Specified Rubbers over the conventional ribbed smoked sheet and crepe grades are a guaranteed conformity to certain technical specifications as defined by the national schemes or by ISO 2000. These commercial TSR rubbers are produced according to a carefully controlled procedure. Among the specified and limited properties are the dirt, the ash and the nitrogen content, the initial plasticity P_0 , the plasticity retention index (PRI) and the Mooney viscosity [2].

These properties are considered important for an efficient processing of NR. The most important property of NR for its use in products manufacturing plants is viscosity [4]. Viscosity is a function of the elastomer's molecular weight (MW), its molecular weight distribution (MWD) and the amount of other materials present in the polymer, such as low molecular weight resin, fatty acids and other natural products, generally referred as "non-rubber components". Viscosity impacts the initial mixing of the rubber with other compounding ingredients and the subsequent processing steps of the compounded materials in order to elaborate the final manufactured (i.e. vulcanized) products [5]. For technical grades classification only simple rheology related properties are tested: initial plasticity (P_0) and plasticity retention index (PRI) as measured with a parallel plate plastimeter (i.e. a complex radial flow situation from axial compression); the Mooney rheometer provides a single torque reading value, at best a single point reading of shear viscosity.

1.2 Nonlinear viscoelastic characterization

Most rubber processing operations occur at a high rate of strain, and therefore it is essentially the non-linear viscoelastic response of rubber materials that is of interest. Not all instruments or test techniques allow the non-linear viscoelastic domain to be investigated and, when specific harmonic testing methods are concerned, only a few rheometers, with a closed test cavity, e.g. the Rubber Process Analyzer RPA® 2000 (Alpha Technology, now a division of Dynisco) proved to provide accurate and reproducible results. Such instruments are an evolution of the rotorless vulcameter that was invented in the early 1970's as a replacement of the oscillating disk rheometer, developed in the 1960's. Closed cavity torsional dynamic testes are true rheometers of industrial origin; they were designed to give access to viscoelastic information on uncured and on cured rubber samples, essentially through adequate combinations of strain, frequency and temperature sweep tests. The operation principle was studied in details and demonstrated by numerical simulation [6]. Commercial instruments are robust machines, designed to be used on the factory floor and therefore meeting all the requirements for safe handling, but they operate only with respect to an expected linear response of the material. In other words, a sinusoidal strain deformation of controlled magnitude is applied on the material, whose stress (or torque) response is taken as strictly proportional to the strain. Strain sweep tests are thus preliminary to any other ones so that the strain (deformation angle) limit for a linear response of the material is detected. Indeed in the linear viscoelastic region, the complex modulus is constant but starts to be strain dependent in the nonlinear region. Generally a linear viscoelastic response is observed up to a few 10% strain with most pure, unfilled elastomers. In principle tests made above this strain limit have no validity in terms of material science but their results can be considered as "apparent" material properties, and used for comparison purposes. A suitable modification of commercial closed cavity torsional dynamic rheometers lead however to what is called **Fourier Transform rheometry**, an advanced technique that allows **both** the linear and the non-linear viscoelastic domains to be accurately investigated [7].

1.3 Scope and objectives of the work

Although many researches have been made to study the linear and non-linear viscoelastic response of polymers by using Fourier Transform rheometry [8-11], only a small number was devoted to studying Natural Rubber [12,13]. Especially no deep study was ever made to consider different NR grades, from the gum rubber up to the vulcanized sample. The objectives of this thesis work were to study the relationships between the characteristics of gum rubber, the processing properties (i.e. mixing and compounding) and the mechanical properties of vulcanized specimens, by using a selection of various NR grades. The experimental work was performed either in Le Mans or in Vitry/Seine. Spectroscopy experiments were first performed during a one year stay in the UCO2M laboratory (Prof. J.F. Pilard) of the Université du Maine, Le Mans; rheological experiments were performed during the subsequent three years in the Polymer Rheology and Processing laboratory of the Université P. & M. Curie -Paris 6 (Prof. J.L. Leblanc).

After this introduction, the report is arranged in two sections:

Section 2 is an extended description of all the experimental techniques that were used in performing the study: the analysis of gum rubber samples by using Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR), Raman Spectroscopy, and gel content assessment, as well as rheological testing with the Mooney viscometer and a Rubber Process Analyzer modified for Fourier Transform rheometry (hereafter referred as RPA-FT).

Section 3 reports and discusses all the results obtained in the course of the work: first all the analytical and rheological results on the gum rubber samples, then a study of mastication effects on samples of RSS3 and SMR10CV60, with respect to gel content and RPA-FT results, and eventually an investigation on the compounding aspects of selected NR samples, as well as their mechanical properties.

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2. Natural Rubber: test materials and test techniques

Natural Rubber (NR) is a high molecular weight hydrocarbon polymer obtained from plants of the euphorbia family (around 6000 plants). Among the rubber producing plant species, the Brazilian rubber tree named *Hevea Brasiliensis* is at present the only commercial source, due to the high rubber content and exceptional quality of the latex obtained by repeatedly wounding its bark. Hevea rubber is typically high *cis*-1,4 polyisoprene with a very wide range of molecular weight (MW) and molecular weight distribution (MWD). In 2009, the six leading producers Thailand, Indonesia, Malaysia, India, Vietnam and China accounted for roughly 90% of world NR production. Combined output in Thailand, Indonesia and Malaysia alone represented around 70% of the global output. Table 2.1 shows world NR and synthetic rubber productions in 2005-2009. Table 2.2 shows world NR production in 2005-2009. For dry rubber, freshly tapped latex and field coagulum can be made into various rubber categories by different processing methods. Various types of dry NR are produced in the world, i.e., Ribbed Smoked Sheet (RSS), Air Dried Sheet (ADS), Technically Specified Natural Rubber (TSR) with some of them regular and constant viscosity (CV) grades, Crepe (Pale and Brown) and others. Figure 2.1 shows Thai NR production by type in 2009. Traditionally, NR has been made into sheets whose quality was visually inspected. The traditional methods of processing into sheet rubbers are still widely used, especially by smallholdings.

Table 2.1 World NR and synthetic rubbers productions in 2005-2009; unit '000 tons [1]

Year	Natural Rubber	Synthetic rubbers	Total
2005	8904	12136	21040
2006	9791	12690	22481
2007	9801	13430	23231
2008	10031	12784	22815
2009	9602	12168	21770

Table 2.2 World NR production in 2005-2009; unit '000 tons [1]

Year	Thailand	Indonesia	Malaysia	India	Vietnam	China	Other	Total
2005	2937	2271	1126	772	482	510	806	8904
2006	3137	2637	1284	853	555	533	792	9791
2007	3056	2755	1200	811	606	590	783	9801
2008	3090	2751	1072	881	660	560	1017	10031
2009	3164	2535	856	817	724	630	954	9602

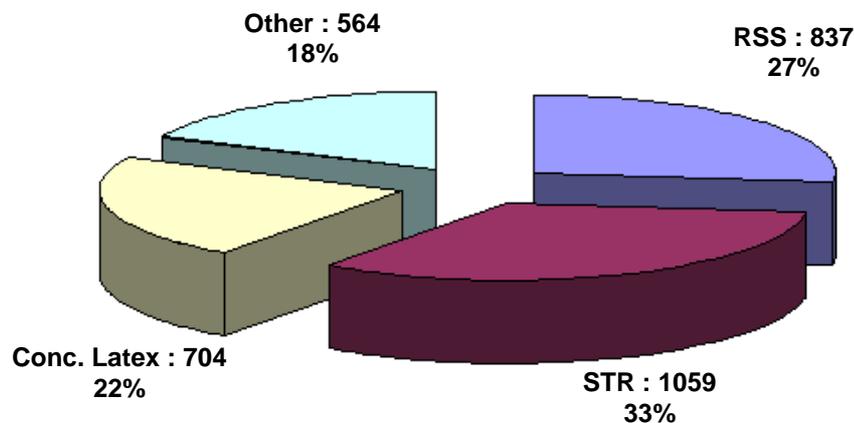


Figure 2.1 Thai NR production by type in 2009; unit ‘000 tons

2.1 Natural Rubber; general description

2.1.1 RSS (Ribbed Smoked Sheets)

NR in sheet forms is the oldest and the most popular type. Being the simplest and easiest to produce on a small scale, smallholder's rubber in most of the countries are processed and marketed as sheet rubber. Two types of sheet rubbers are produced and commercialized in the international market, namely the Ribbed Smoked Sheets (RSS) and the Air Dried Sheets (ADS). Between these two types, Ribbed Smoked Sheet is the most popular and is available for volume consumption. RSS are used in various industries due to their variety in the requirements on cleanliness and tear strength of the sheets. There are five major grades: RSS1 to RSS5. The difference in the grades is the result of the preparation of the coagulated field latex during the production of the unsmoked sheets. The sheets are selected and smoked at a controlled timing and temperature window to ensure that they are properly smoked without causing negative impact on the rubber properties.

2.1.2 RSS (Ribbed Smoked Sheets) Process

Latex from various sources (i.e.; trees) is initially collected and blended in a large latex bulking and blending tank. This blending operation is important to ensure the production of uniform and consistent rubber. The fresh latex is diluted to a rubber content of 15 - 16% and coagulated in coagulation tanks using formic acid or acetic acid. Lumps of coagulum are formed after the acid has reacted for 3-4 hours. After milling and washing, sheets between 2.5 and 3.5 mm thick, 24 cm wide and 90 or 135 cm in length are produced. The final mill is an embossed one, which gives the sheets their ribbed structure. Appropriately grooved rollers imprint on each sheet "ribs", which expand the surface area for drying. After final milling, the sheets are hung on lines and dried in smokehouse at successively higher temperatures ("Ribbed Smoked Sheets"). On

individual smallholdings, sheets are often dried by natural ventilation ("white unsmoked sheets") and sold to a dealer who smokes and grades them. Blemishes are then removed manually and sheets are visually graded. They are finally pressed into bales with talc to prevent adhesion. The process of making sheet rubber is relatively simple and it is still commonly used on smallholdings and smaller estates. RSS grades still depend heavily on visual inspection, there is thus a high probability of inconsistency in grading. Ribbed Smoked Sheets are marketed based on visual assessment of quality. To establish acceptable grades for commercial purposes, the international Rubber Quality and Packing conference, stipulated the grade description whose details are given in the so-called Green Book.[2]

2.1.3 RSS grades description

RSS1

Each bale must be packed free of mould but very slight traces of dry mould on wrappers or bale surfaces adjacent to wrapper found at the time of delivery will not be objected to provided there is no penetration of mould inside the bale. Oxidized spots or streaks, weak, heated, undercured, oversmoked, opaque and burnt sheets are not permissible. The rubber must be dry, clean, strong sound and free from blemishes, rust, blisters, sand, dirty packing and any other foreign matter, except slight specks. Small pinhead bubbles, if scattered, will not be objected to.

RSS2

Slight rust, and slight amount of dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to, provided these conditions either singly or in combination, do not exist to an objectionable extent on and in more than 5% of the number of bales included in the delivery, lot or tender as determined by the number of bales inspected. Small bubbles and slight specks of barks, if scattered, will not be objected to. Oxidized spots or streaks, weak, heated, undercured, oversmoked, opaque and burnt are not permissible. The rubber must be dry, clean, strong sound and free from blemishes, blisters, sand, dirty packing and all other foreign matter other than specified above as permissible.

RSS3

Rust and dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to, provided these conditions, either singly or in combination, do not exist to an objectionable extent on and in more than 10% of the number of bales included in the delivery, lot or tender as determined by the number of bales inspected. Slight blemishes in color, small bubbles and small specks of bark are permissible. Oxidized spots or streaks, weak, heated, undercured, oversmoked, opaque and burnt sheets are not permissible. The rubber must be dry, strong and free of blemishes, blisters, sand dirty packing and all other foreign matter other than specified above as permissible.

RSS4

Rust, dry mould on wrappers, bale surfaces and interior sheets, found at time delivery will not be objected to provided these conditions, either singly or in combination, do not exist to an objectionable extent on or in more than 20% of the number of bales included in the delivery, lot or tender as determined by the number of bales inspected. Medium

size bark particles, bubbles, translucent stains, slightly sticky and slightly over smoked rubber as permissible but should not be evident to a marked degree. Oxidized spots, or streaks, weak, heated, undercured opaque and burnt sheets are not permissible. The rubber must be dry, firm and free of blemishes, blisters, sand, dirty packing and all other foreign matter other than specified above as permissible.

RSS5

Rust, dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to provided these conditions, either singly or in combination, do not exist to an objectionable extent on or in more than 30% of the number of bales included in the delivery, lot or tender as determined by the number of bales inspected.

Packaging

30 kg, 33.33 kg, and 35 kg individually wrapped in polyethylene bags in choices of wooden pallets/loose bale or 60 kg, 90 kg, 111.11 kg powder coated bare bales

2.2. Technically specified natural rubber (TSR) - Standard rubber

The conventional grading system outlined above had many disadvantages, in that it is based on subjective assessments and only recognizes visual distinctions that could not have much technical significance. A major step towards evolving a more sophisticated classification for rubber was the development of a grading system strictly based on technical specifications. The International Standards Organization (ISO) first published the draft Technical Specifications for Natural Rubber in 1964. Based on these specifications, Malaysia introduced their Standard Malaysian Rubber (SMR) scheme in 1965 and since then all the natural-rubber-producing countries have started producing and marketing NR as Technically Specified Rubbers (TSR). This resulted in the introduction of further national standards in addition to SMR : Standard Thai Rubber (STR), Standard Indonesian Rubber (SIR), Standard Sri Lanka Rubber (SSR), Standard Vietnam Rubber (SVR), Indian Standard Natural Rubber (ISNR), etc. The advantages of Technically Specified Rubbers over the conventional sheet and crepe grades of rubbers are as follows:

- 1 Since it is available in a limited number of well-defined grades, correct choice of grades according to requirements by the consumers is rather easy.
- 2 Since it is possible to assess the actual content of foreign and volatile matter, mistakes can be avoided in deciding the actual worth of the material.
- 3 Since it is marketed as compact, polyethylene wrapped bales, degradation of the rubber on storage, handling and transportation can be reduced.
- 4 Since sizes have been standardized and the bales are compact, considerable savings can be made in transport through mechanized handling and containerization.

2.2.1 Technically specified natural rubber (TSR) Processes

2.2.1.1 Latex Process

Quality control starts early since the first step, before acquiring the raw material from local farmers, is latex sample analysis in a laboratory. A filtering phase eliminates particles and impurities from latex. Different chemical composition is added to latex

depending on the type of produced TSR. The latex is then poured on a series of long moulds, so that through chemical reaction, latex changes its status from liquid to solid in about 12 hours. After this step, thick rubber sheets are obtained. Thick sheet rubber is transformed in thin sheet rubber by a creeper machine, then thin sheet rubber are reduced to small pieces of 2-3 millimeters by a shredding machine. After passing through a 110°C oven, the small pieces of rubber are compressed into blocks. The block rubber weight is precisely set to 33.33 kg per block.

2.2.1.2 Cup-lump Process

Cup-lumps are naturally coagulated rubber found in latex collecting cups. They are collected apart from the latex. In processing factories, received cup-lumps are spread out in the reception area for contamination picking and DRC determination. Big Slabs of Cup-lumps must be reduced to smaller sizes for effective removal of the contaminants and determination of the contamination levels. Contaminants removed, cup lumps are stored according to grade and are let to rest in order to obtain leveled characteristics. Upon designated time, cup lumps enter the TSR line, where they are slab-cut, washed and strained to further removal of embedded contaminants. Processed cup lumps are collected in a tank with water overflowing to remove: 1. floating particles such as raffia, woodchips, branches, 2. sinking material such as dirt, sand and gravel. After a series of size reduction, rubber crumbs are milled as crepes in series of decreasing thickness to obtain aggregated rubber crumbs. Crumbs are placed in trolley and oven-dried at 120°C for 7-8 minutes depending on the nature of the input cup lumps. Biscuits are baled and packed in PE pouches. Each bale passes through a metal detector to prevent any possible metal contamination that can cause serious damages to customer machines. Bales are inspected and sampled for white spot contamination and physical characteristics. Baled TSR blocks are packaged according to customer's specifications. Rubber bales are tested for physical properties and are graded as such.

2.2.2 Standard Specification for NR Technical Grades

Table 2.3 Specifications for Technically Graded Natural Rubber [3]

Property	Rubber Grade ^A				
	L	CV ^B	5	10	20
Dirt,retained on 45 µm sieve, %max	0.05	0.05	0.05	0.10	0.20
Ash,%max	0.60	0.60	0.60	0.75	1.00
Volatile matter,%max	0.80	0.80	0.80	0.80	0.80
Nitrogen,%max	0.60	0.60	0.60	0.60	0.60
Initial plasticity, min	30	-	30	30	30
Plasticity retention index, min	60	60	60	50	40
Color index, max	6.0	-	-	-	-
Mooney viscosity	-	60±5	-	-	-

^ASkim rubber is not permitted in any grade, and Grades L, CV, and 5 must be produced from intentionally coagulated latex.

^Bother Mooney ranges of Grade CV are available, CV-50±5 and CV-70±5, CV without suffix is the 60±5 as shown in the table.

2.3 Materials used in this study

A series of NR samples and one commercial synthetic polyisoprene were collected and stored at room temperature under dark cover for the time of the study (around 4 years). No particular precaution was taken to avoid the normal ageing of test materials under the conditions specified above. Since no particular order was observed in submitting the test materials to the various experiments of the study, it follows that any normal ageing effects, if any, are incorporated in the reported results. However, no severe anomaly was observed that could have suggested sizeable ageing effects.

Table 2.4: Materials used in this study

Sample Code	Material description	Origin	Mooney ML(1+4) _{100°C}
STR5E	NR, Standard Thai Rubber, STR5L	Thailand	81
STR56E	NR, Constant viscosity rubber, STR5CV60	Thailand	63
OMNRE	NR, Optimized molecular weight rubber, OMNR	Thailand	65
RSS3E	NR, RSS3	Thailand	100
RSS3	NR, RSS3	(IFOCA)	91
SMR10	NR, Constant viscosity Standard Malaysian rubber, SMR10CV60	Malaysia (IFOCA)	71
IR	IR, commercial grade polyisoprene	(IFOCA)	79

STR5L is a technically specified light-colored rubber grade, obtained by coagulating freshly collected high quality latex. Wet crumbs are then placed in open trays and in a forced air dryer at temperature of 110 – 125°C, before testing at a certified TSR laboratory. Rubber passing the TSR L specification has a maximum 0.04% dirt content, a maximum 0.4% ash content, a maximum 0.6% nitrogen content, initial Plasticity, $P_o = 35$ (min) and a minimum PRI of 60. STR5CV60 is a technically specified ‘constant viscosity’ grade, produced from field latex with its viscosity stabilized to a specified Mooney viscosity (i.e. $ML(1+4)_{100°C} = 60 \pm 5$), through the addition of a suitable chemical. Dirt, ash and N_2 contents are maximum 0.05%, 0.6% and 0.6%, respectively. PRI is a minimum of 60. On storage, this grade of rubber is expected to remain within eight hardness units. Optimized molecular weight NR (OMNR) is new grade currently being developed in Thailand. Selected field latex is coagulated, its viscosity is reduced and stabilized through a chemical treatment (undisclosed). No stabilizer or oil is added. OMNR is relatively similar to STR5CV60 but is expected to show no variation on ageing. Whole field latex is used to produce RSS. Collected latex is first diluted to 15% solids, and then coagulated for around 16 hours with diluted formic acid. Coagulated material is then milled, water removed, and sheeted with a rough surface to facilitate drying. Sheets are dried in a smokehouse for one to seven days. RSS grades consist of deliberately coagulated rubber sheets and are graded according to their color, consistency and observed impurities. RSS3 meets the following specification: 0.20% dirt content (maximum); 1.00% ash content (maximum); 0.60% nitrogen content (maximum); $P_o = 30$ (min) and PRI = 50 (min). SMR10CV60 is a technically specified ‘constant viscosity’ grade, produced from clean and fresh field coagulum or from unsmoked sheets. Its viscosity stabilized to a specified Mooney viscosity (i.e. $ML(1+4)_{100°C} = 60 \pm 5$), through the addition of suitable chemical. Dirt, ash and N_2 contents are maximum 0.10%, 0.75% and 0.60%, respectively. Initial Plasticity, P_o is 30 (min) and PRI is a maximum of 50. On storage, this grade of rubber is expected to remain within eight hardness units.

2.4 Test techniques for macromolecular characteristics

2.4.1 Analytical techniques

2.4.1.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) determinations were performed on a Perkin-Elmer DSC-7 with a heating rate of 10°C/min under nitrogen atmosphere. The sample weight was about 5-10 mg. Calibration was achieved with indium as reference material.

2.4.1.2 Nuclear magnetic resonance (NMR)

¹H NMR liquid state spectra were recorded at room temperature on a Bruker 400 Fourier Transform spectrometer at 400.13 MHz in CDCl₃ solution using tetramethylsilane (TMS) as internal standard. Solid-state NMR experiments were carried out at room temperature on a BRUKER AVANCE 300 MHz wide bore spectrometer at 75.47 MHz using Cross-Polarization (CP) combined with Magic Angle Spinning (MAS). The spectra were recorded at spinning frequencies equal to 5 kHz. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) used as an external reference. For CP-MAS experiments, we chose the ¹H radio frequency field strength such as the $\pi/2$ pulse duration was equal to 4 μ s. The frequency field phase is switched to $\pi/2$ simultaneously to the application of a frequency field to the carbons matching the Hartmann-Hahn during the contact time t_{CP} . A high power proton decoupling is applied during acquisition. The reconstruction of the spectra was performed with the DM2000 software using four adjustable parameters for each NMR line: isotropic chemical shift, line width, line-shape and line intensity. The ¹³C CP magnetization curves versus contact time of each carbon of the epoxy resin were built up from the line intensities.

2.4.1.3 Raman Spectroscopy

Raman spectra of all samples were recorded at room temperature on a T64000 Jobin-Yvon multichannel spectrometer adjusted in a simple spectrograph configuration with a 600 lines/mm grating. In this spectrometer the systematic single spectrograph is attached to an Olympus microscope, which is equipped with a computer, controlled stepping microscope stage. The system utilizes the so call, back scattering configuration in which the scattered light is collected using the same objective as is used to focus the laser onto the sample. The sample was illuminated with a Coherent Argon-Krypton Ion laser using the 647.1 nm red line in order to minimize luminescence and fluorescence bands compared to shorter possible wavelengths. To improve the signal/noise ratio, each spectrum was accumulated 20 times during 30 seconds. The wavenumber range selected was 500-3200cm⁻¹.

2.4.1.4 GPC-MALLS for Molecular Weight measurements

Macromolecular characteristics were assessed in CIRAD (Montpellier, France) using size exclusion chromatography coupled with multi-angle light scattering (SEC-MALS). The

SEC-MALS equipment consists of an online degasser (Elite™, Alltech Associates, Inc., Deerfield, IL), a Waters 515 pump, a refractive index detector (Waters 2410) and a multi-angle light scattering detector (Dawn DSP, Wyatt Technology Co, Santa Barbara, CA). Three PLgel-Mixed-A (Polymer Laboratories, Varian Inc; Palo Alto, CA) mixed bed columns (20 mm, 300 mm x 7.8 mm internal diameter) with a guard column were used. The columns were maintained at 45°C and THF (tetrahydrofuran) was used as mobile phase with a flow rate of 0.65 ml/min; the injected volume was 150 mL. The data from MALS detectors were analyzed with the Astra software, V 5.3.2.22 (Wyatt Technology) using either the Berry or the Zimm method. Test solutions were prepared by dissolving 25 +/- 5 mg of rubber in 40 ml THF (HPLC grade) stabilized with 2,6-di-tert-butyl-4-methylphenol. After one-week storage in darkness at 30°C, solutions were filtered through 1 µm, glass fiber paper (Pall Co, Port Washington, NY), so that with respect to the polymer concentration before and after filtration the gel content was assessed. Kim *et al.* have published details of the technique. [4, 5]

2.4.2 Gel content measurement

2.4.2.1 Gel assessment techniques in literature

Campbell and Fuller [6] studied the separation of rubber into sol and gel components by dissolving with dichloromethane. They cut the rubber into small cubes and poured it in dichloromethane solvent. The rubber-solvent was gently agitated for a few minutes before allowing the dissolution to proceed undisturbed for one or two days. After this interval, the solution was run out of the funnel. The dissolved rubber was recovered by evaporation of solvent under vacuum at 35°C. The solvent was returned to the funnel, and the procedure repeated. After the recovery of four fractions from solution, the process was stopped. They claimed that fraction obtained were sol fraction, sol+microgel fraction and macrogel fraction. Allen and Bristow [7] reported the measurement of gel content by immersing samples of rubber in solvent (carbon tetrachloride, chloroform, toluene, cyclohexane, tetrahydrofuran, 2,2,4-trimethyl pentane, n-butyl acetate, n-propyl acetate) for the stated times in the dark without shaking or stirring for 48 hours. For 3 solvents (n-propyl acetate, cyclohexane, toluene) gel contents were determined at intervals for periods 16 days. Equilibrium is not established in 48 hours, and there is continued slow dissolution of rubber. Pummerer *et al.* [8] used a continuous extractor, in which ether was boiled. The extraction was carried out in a stream of carbon dioxide. A fraction of rubber extracted in 24 hours. The first fraction was removed after 6 hours, since in the beginning a relatively large quantity of rubber was dissolved, and the solution became too viscous. To isolate the rubber, most of the ether was evaporated at 45°C in a carbon dioxide current and the residue dried in a high vacuum at 45°C. Gregg and Macey [9] studied the measurement of gel content by immersing samples of rubber in diethyl ether and allowed to stand for 16 hours. The solution was carefully decanted from the swollen rubber gel and replaced with fresh ether and extraction was repeated until substantially all of the soluble rubber was removed. The soluble rubber was evaporated by distillation, and the insoluble fraction was dried in a stream of nitrogen. Yunyongwattanakorn and Sakdapipanich [10] studied the physical property changes in natural rubber during long-term storage. They reported gel content, as determined in dried toluene to give a

concentration of 0.1 % w/v and kept in the dark without stirring for one week at room temperature. The insoluble fraction was separated from sol fraction by centrifugation. The weight percentage ratio between the gel fraction and the original rubber used was determined as gel content. They found that the gel content at the initial period of NR (STR XL, STR5L and STR5CV60) of the production was found to be almost zero. The gel content of these rubbers was found to increase during storage and then leveled off at about 5% after keeping (under ambient condition) for 14 months. Tanaka and Yunyongwattanakorn [11] studied the effect of an accelerated storage hardening in P₂O₂. They found that the gel content of FNR from fresh latex increases to about 60% after 2 days (initial FNR had gel content almost zero). Tan and Yusof [12] studied the effect of solvents in ENR (epoxidized NR) gel content measurements. They found that toluene and THF (tetrahydrofuran) were good solvents for the determination of the gel content of NR and ENR. They determined the gel contents by immersing samples in solvent for 48 h at room temperature without agitation. The gel fraction of the radiation cross-linked rubbers had been reported by several authors [13,14] by immersing samples in solvent at room temperature (25°C) for 48 hours (equilibrium swelling time was determined from experiments). Gel fraction was calculated from the weight of the samples before and after swelling as follows:

$$\text{Gel fraction} = W_2/W_1 \quad 2.1$$

where W₁ is the initial weight of the polymer and W₂ is the weight of insoluble portion of polymer in the gel.

Table 2.5: Natural Rubber gel contents (%) as reported by various authors

Sample	Solvent	% gel content	Reference
SMR L	dichloromethane	16	[6]
Pale crepe	toluene	18	[7]
	THF	16	
	chloroform	27	
	carbon tetrachloride	29	
RSS	ether	13	[8]
STR5L	toluene	5	[9]
STR XL	toluene	6	
STR5CV	toluene	4	
Fresh natural rubber (FNR ^a)	toluene	0	[10]
NR	toluene	1.1	[11]
	THF	4.1	
ENR60 ^b	toluene	45.1	[11]
	THF	45.9	

^a FNR was prepared by casting freshly tapped NR latex into a thin film on a glass plate and drying at room temperature for 24 h followed by drying in a vacuum.

^b ENR60 is 60% epoxidized NR.

As shown in Table 2.5, gel contents as found in literature are quite varied. The type of solvent might be influential but even if one considers results obtained by using toluene only, it is obvious that no convincing trend can be seen even if, paradoxically, most rubber engineers do believe that gel content is an important parameter in Natural Rubber technology. Apart from temperature that might affect the swelling of the polymer by the solvent, a key aspect rarely addressed in the literature is the necessary time for equilibrium swelling. Most authors do allow several days of swelling before measuring it but without specifically considering the kinetics that would indeed allow documenting the equilibrium. A gel content measuring procedure was consequently designed with respect to extraction kinetic considerations.

2.4.2.2 Measuring Gel content with respect to extraction kinetics

Gel content was determined through immersing in toluene solvent under static condition as follows: 0.1 gram of rubber sample was cut into small pieces and poured into 50 milliliters of toluene. The rubber solvent system was gently agitated for a few minutes before allowing the dissolution to proceed undisturbed for stated times (4 days, 16 days, 24 days,.. so that equilibrium time was determined from experiments). After each immersion interval, 3 x 10 milliliters of the solutions were drawn out. The dissolved rubber was recovered by evaporation of the solvent under vacuum at 50°C for 24 hours. Sol fraction and gel fraction were calculated from the weight of the samples before and after exposure to solvent as follows:

$$\text{Sol fraction}_{\text{at time } i} = \frac{W_i V_1}{W_1 V_2} \quad 2.2$$

$$\text{Gel fraction}_{\text{at time } i} = 1 - \text{Sol fraction}_{\text{at time } i} \quad 2.3$$

where W_1 is the initial weight of rubber, W_i is the weight of rubber in 10 milliliters of solution at time i , V_1 is the volume of all the solution and V_2 is 10 milliliters. The overall process is depicted in Figure 2.2. The gel fraction for any given solvent immersion time is averaged out of results from the 3 dried extracts.

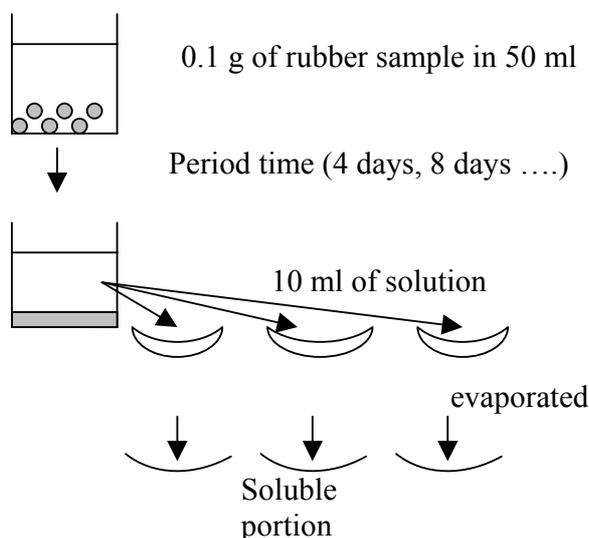


Figure 2.2: Procedure to assess gel and sol contents of natural rubber

2.5 Processing techniques

2.5.1 Mastication with a Banbury mixer

Mastication is expected to severely affect the quality of NR compounds because of the likely associated changes in viscoelastic properties. As it is a common belief (but rarely demonstrated) in the rubber industry that constant viscosity grades are less sensitive to mastication, a series of experiments were made in order to compare the mastication effects on a Ribbed Smoked Sheet and a CV grade. Experiments were designed in order to masticate NR samples at various mastication times, different for RSS3 (240s, 480s, 960s, 1440s, and 1680s) and for SMR10CV60 (60s, 120s, and 240s). Indeed CV grades are known to exhibit around half the molecular weight of RSS grades, so that it was a priori considered that longer mastication times would be needed for RSS3 than for SMR in order to obtain equivalent Mooney viscosity. Mastication was made in a Banbury mixer with full water cooling on. The nominal capacity of the mixer is 2000 cm³. Mastication was performed at 30°C and 40 rpm at fill-factor of 0.7. The raw rubber sample was cut in small pieces to load to the mixer. Mastication was carried out by loading the rubber in the mixer, moving the ram down and running the rotors for stated times. Then the masticated rubber was dumped and quickly cooled down and sheeted-off on a 15x6.5 cm two-roll mill. The masticated NR was passed 10 times through the mill nip (5 mm gap), without banding so that further mixing is avoided before obtaining the sheet. All mastication experiments on SMR10CV and RSS3 are described in Table 2.6.

Table 2.6: Mastication times of SMR10CV and RSS3 in Banbury mixer with fill factor=0.7: Mooney viscosity readings on material at dump are also given

Code	Rubber grade	Mastication time (s)	Rotor speed (rpm)	Mooney viscosity ML(1+4) _{100°C}
SMRM1	SMR10CV	60	40	55
SMRM2	SMR10CV	120	40	52
SMRM3	SMR10CV	240	40	49
RSSM1	RSS3	240	40	78
RSSM2	RSS3	480	40	76
RSSM3	RSS3	960	40	61
RSSM7	RSS3	960	50	58
RSSM8	RSS3	1440	50	51
RSSM9	RSS3	1680	50	48

2.5.2 Compounding with a Haake mixer

Compounding was made in two steps : first a preparation of the masterbatch (i.e. all ingredients but the curing chemicals), second the addition of curing agents. The mixing of rubber and other compounding ingredients was performed in a laboratory mixer, i.e. Haake Rheomix. The nominal capacity of the mixer is 300 cm³, and a dead-weight of 5 kg is used to maintain the ram. The fill factor was adjusted to 0.7. Mixing was achieved at 40 rpm, with an initial temperature of 80°C. A standard ASTM type formulation with a conventional sulfur cure system was considered, as given in Table 2.7. The experiment was designed to prepare compounds with different NR grade samples (STR5L, STR5CV60, OMNR, RSS3E, RSS3, SMR10CV60, and IR). The raw rubber sample was cut in small pieces to load the mixer. Mixing was carried out by charging the rubber into the mixer and pre-masticating for 30s. Then ingredients were added in two steps, first ½ black + ZnO + Stearic Acid, then the remaining ingredients. The overall mixing time was mixed for 5 min (+ 30 s premastication). After that, the compound was taken from the Rheomix to a 15x6.5 cm two-roll mill for sheeting purposes (see below). Table 2.8 shows the mixing sequences for this normal procedure. Table 2.9 described all the prepared rubber compound samples.

Table 2.7 : Compounds formulation in phr (part per 100 rubber)

Ingredient	phr
NR	100
Carbon black N330	50
ZnO	5
Stearic acid	3
Naphtanic oil	5
TMQ	1
IPPD	1
Sulfur	2.5
CBS	0.6

2.5.3 Two rolls mixer

A 15x6.5 cm two-roll mill was used for sheeting purposes and for incorporating curing agents. For sheeting, the sample was passed through the mill, without banding, 10 times. In the case of mixing curing agent, the masterbatch was milled for 1 min for pre-heating, then the cure system was added, then the compound was mixed for 3 min.

Table 2.8 : Mixing steps for a normal procedure

Time (s)	Operation
0	Introduce the rubber, lower the ram
30	Carry up the ram, Add ½ carbon black + ZnO, lower the ram
90	Carry up the ram, Add ½ carbon black + stearic acid + oil + TMQ + IPPD, lower the ram
330	Discharge

2.5.4 Compression molding for test plaques

Compression molding was used to prepare specimens for RPA testing and for curing plaques and small cylinders for mechanical testing. For RPA testing, samples whose shape and dimensions mimic the instrument cavity were prepared; according to an established procedure in the laboratory. RPA samples were compression molded at 140°C for 20 min for gum rubbers, at 100°C for 5 min for compounded rubbers. In the cases of mechanical testing, the specimens were prepared by compression molding at 160°C for 95 % of the overall curing time, as assessed with a vulcametry test.

Table 2.9 : Description of compounded rubber samples

Samples code	treatment
STR5B	Masterbatch filled N330 (50phr) STR5L
STCVB	Masterbatch filled N330 (50phr) STR5CV60
OMNRB	Masterbatch filled N330 (50phr) OMNR
RSSEB	Masterbatch filled N330 (50phr) RSS3E
RSS3B	Masterbatch filled N330 (50phr) RSS3
SMRCV	Masterbatch filled N330 (50phr) SMR10CV60
IRCOB	Masterbatch filled N330 (50phr) IR
NB5L0	Masterbatch unfilled STR5L
NB5CV	Masterbatch unfilled STR5CV60
NBOM0	Masterbatch unfilled OMNR
NB3E0	Masterbatch unfilled RSS3E
NB300	Masterbatch unfilled RSS3
NBSMR	Masterbatch unfilled SMR10CV60
NBIR0	Masterbatch unfilled IR
mRSS1	Masterbatch filled N330 (50phr) pre-masticated RSS3 4 min 40rpm
mRSS2	Masterbatch filled N330 (50phr) pre-masticated RSS3 8 min 40rpm
mRSS3	Masterbatch filled N330 (50phr) pre-masticated RSS3 16 min 40rpm
mRSS7	Masterbatch filled N330 (50phr) pre-masticated RSS3 16 min 50rpm
mRSS8	Masterbatch filled N330 (50phr) pre-masticated RSS3 24 min 50rpm
mRSS9	Masterbatch filled N330 (50phr) pre-masticated RSS3 28 min 50rpm
mSMR1	Masterbatch filled N330 (50phr) pre-masticated SMRCV 1 min 40rpm
mSMR2	Masterbatch filled N330 (50phr) pre-masticated SMRCV 2 min 40rpm
mSMR3	Masterbatch filled N330 (50phr) pre-masticated SMRCV 4 min 40rpm

2.6 Rheometrical test techniques

2.6.1 Mooney viscometer

Mooney viscosity tests were run according to ASTM D1646 [15] using a Gibitre Instruments Mooneycheck.

2.6.1.1 Test specimen preparation

The test specimen consisted of two pieces of the material being tested having a combined volume of $25 \pm 3 \text{ cm}^3$. This volume is approximately 1.67 times for large rotor and will ensure that the cavity is completely filled. For convenience the mass of the test specimen of correct volume may be calculated as follow :

$$m = v \times d \quad 2.4$$

where m is mass of the test specimen, v is volume in cm^3 (25 cm^3), d is density in g/cm^3 (0.92 for gum NR). The test pieces was cut from the sample with dimensions that fit within the die cavity without projecting outside it before the viscometer is closed, by using a 45 mm diameter cutting die. A hole punched in the center of one of the test pieces facilitated the centering of the rotor stem. It is not permissible to slip the test piece around the rotor stem by cutting it edgewise. The test specimen was as free of air and volatile material as it is practical to make it and was free of pockets, which may trap gasses against the rotor or die surfaces.

2.6.1.2 Measuring Mooney viscosity

The large rotor should be used unless the Mooney viscosity would exceed the torque capacity of the instrument. This was not the case in all our experiments, so that the large rotor was always used. The temperature of the two dies is normally within 0.5°C of each other ($100 \pm 0.5^\circ\text{C}$ for NR). After prewarming in the empty and closed cavity, the hot rotor was removed, the stem was quickly inserted through the center of one of the test pieces, the other test piece placed on top of the rotor and the assembly replaced in the viscometer. The cavity was immediately closed which activated the timer. The specimen was let to warm-up in the closed Mooney viscometer test cavity for exactly 1 min and then the motor was started which drives the rotor. It is recommended that viscosity readings be continually recorded for 4 min. Result of a sample test is reported as follows : $50 \text{ ML}_{1+4}(100^\circ\text{C})$ where 50 is the viscosity number, M indicates Mooney, L indicates the use of the larger rotor, 1 is the time in minutes that the specimen was permitted to warm in the machine before starting the motor, 4 is the time in minutes after starting the motor at which the reading is taken, and 100°C is the temperature of test.

2.6.2 Rubber Process Analyzer

The measurement of rubber viscoelastic properties with traditional dynamic mechanical rheological testers (DMRTs) has not been commonly done in the rubber industry [16]. Conventional DMRT rubber testing requires complex sample preparation. Uncured

samples are especially difficult to hold in a traditional DMRT test apparatus. Uncured sample thickness is also hard to keep uniform. Cured samples must be molded separately for most DMRT testing in order to have samples with correct dimensions. Many sample preparation procedures require a high degree of operator skill not always available in a rubber factory. Variation in sample preparation and loading procedures can increase the variation in the data. Different procedures for uncured and cured rubber also mean that uncured and cured samples are tested as two different tests instead of one. This increases total test time significantly. Rubber test samples kept under pressure give more repeatable and reproducible measurements of resistance to deformation. A pressurized sample cavity prevents the formation of porosity in the sample as well as slippage along the die or sample interface which improves repeatability. Good repeatability and reproducibility are necessary to expand the DMRT to statistical process control. Most DMRTs do not confine the test sample under pressure. Viscoelastic properties of rubber vary with changes in applied strain, frequency and temperature. Testing at several different frequencies, strains and temperatures is usually necessary in order to thoroughly characterize the viscoelastic properties of a rubber sample. The optimal test conditions will vary with the sample. Samples are often tested over several frequencies, strains or temperatures in one test called a sweep. Temperature sweeps with traditional DMRTs can result in very long test times due to the time required to reach a new stable temperature setting. The use of computers makes it easier to set up complex DMRT tests and to reduce the time for data reduction. However, many traditional DMRT instruments still require a highly skilled operator to run the test and reduce the data. The problems listed above were the primary consideration in the design of a new DMRT. The Rubber Process Analyzer RPA®2000, was designed to solve many of the present problems associated with getting good viscoelastic test information from uncured and cured rubber samples [17]. This instrument, formerly developed by Monsanto Instruments, now manufactured and sold by Alpha Technologies is a torsional dynamic rheometer, whose test cavity design is similar to that of the Moving Die Rheometer, a well known rotorless vulcameter [18]. As usual with commercial instruments, the brand name is misleading: the instrument can handle other polymer materials than rubber and whilst results obtained are somewhat related to processing behavior, there is for sure no direct link between RPA data and the complex rheological problems arising in polymer processing. For instance tests are performed in dynamic strain conditions, in near isothermal environment, while processing involves shear and extensional strains, which are generally unsteady and in non-isothermal conditions. Equivalence between the shear and the dynamic viscosity functions, i.e. the so-called Cox-Merz rule [19], is generally not found with complex polymer systems such as filled rubber compounds. Therefore there cannot be, with such materials, direct relationships between the properties measured with a standard dynamic rheometer, operated in ideal laboratory conditions, and the set of complex rheological events that take place on the factory floor.

The RPA is a torsional dynamic rheometer with an unique test gap design, an advanced temperature control and fully automated operation modes. Controlled through an external computer, it offers easy handling and operation with highly stiff materials such as filled rubber compounds, and numerous testing capabilities in terms of frequency and strain sweeps. Test results however make sense providing one knows well the limits and

capabilities of the instrument, with respect to the viscoelastic properties of tested materials.

2.6.2.1 Instrument Design and Concept

In the RPA, the test material is held in a sealed biconical cavity, thus under pressurized conditions, and submitted to harmonic torsional strain. The resulting torque is measured and through the appropriate built-in data treatment, split into real and imaginary components in order to yield dynamic viscoelastic data, such as G' and G'' . The instrument is designed for easy loading of highly viscous materials, and for operating in the industrial environment, i.e. it is a compact test device, with an easy access test chamber and all provisions for safe handling. Whilst prototypes were operating and evaluated in selected laboratories by the late eighties, presentations of the instrument with practical demonstrations of its testing capabilities were made in the early 1990's [17,20].

2.6.2.2 Instrument description and operation

Essentially the RPA consists of two main parts: the test instrument itself and an outside (PC) computer for test monitoring, data recording and treatment. The testing part consists in a biconical test chamber with grooved dies to avoid slippage. The cavity is closed through the action of a ram operated with a pressure of 40 bar (4 MPa) and a slight excess of test material is needed for reliable torque reading to be made. Two hard fluoroelastomer seals provide the peripheral closure of the cavity. The excess material flows in a circular spew channel and further contributes to the sealing of the cavity. Tests are thus made in pressurized conditions, and therefore porosity does not develop in the sample when the instrument is operated as a curemeter. The lower die can be oscillated (in torsion) at controlled strain and frequency. The advantage of this test geometry is that the strain rate is constant in the gap (which is not the case with parallel plate devices). The torque measuring system is attached to the upper die and calibrated with a torsion spring mounted between the two dies. The heart of the instrument is a special direct drive motor, which can move the lower die sinusoidally over a wide range of strains and frequencies. The temperature control system has a resolution to the nearest 0.1°C which, combined with the thinness of the sample, allows near isothermal tests to be performed in the $40\text{-}200^{\circ}\text{C}$ range (note : this range depends on the instrument model). Temperature changes are very quick and monitored by the controlling computer. The RPA test cavity is not exactly biconical but consists of a flat central portion of 7.6 mm diameter that determine truncated conical dies of 41.25 mm diameter and angle $3^{\circ}35'$ (or $3.58^{\circ} = 0.0625$ radian) (see Figure 2.3 for dimensions). The periphery of the cavity consists of two hard fluoroelastomer seals with an angle $\beta = 30^{\circ}$ with respect to the mid plan. There are grooves in the upper and lower dies in order to prevent slippage of the tested material.

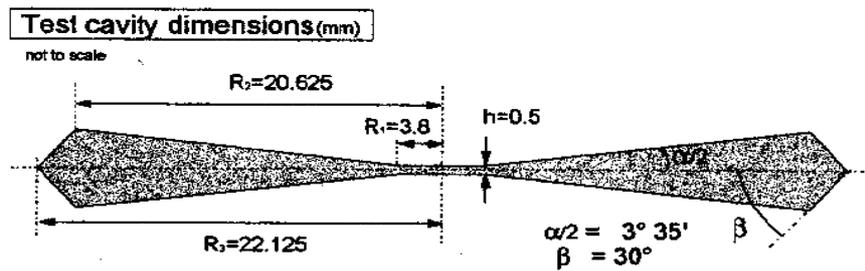
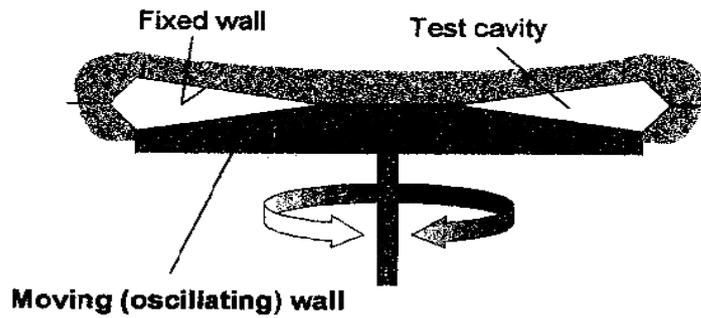


Figure 2.3 : Rubber Process Analyzer; measuring principle and test cavity dimensions

2.6.2.3 Measuring Principle and Operating Range

When the cavity is closed, the sample is molded and maintained under pressure in such a manner that the flat central part of both dies are separated by a gap of around 0.25 mm. The harmonic strain is exerted on the sample by the lower (oscillating) die and transmitted torque is measured on the upper (fixed) wall. The sample periphery is neither free, nor spherical and its shape is imposed by the design of the seals. Dynamic tests in a closed cavity were demonstrated to yield the same results as tests with open gap (i.e. parallel disks or cone-and-plate) rheometers [21].

In the RPA, the phase angle is actually not measured but the assumption is made that the sinusoidal strain produces a sinusoidal torque response (note that this is strictly valid only if the tested material provides a linear viscoelastic response, at the selected test conditions). The complex torque signal $S^*(t, \omega)$ is first treated in such a manner that during one cycle several discrete values are read with respect to equal periods on the time scale. For any complex (sinusoidal) torque, one has:

$$S(t, \omega) = S^* \sin(\omega t + \delta) = S' \sin(\omega t) + S'' \cos(\omega t) \quad 2.5$$

and through discrete Fourier transform the selected values of $S(t)$ with their location are used to calculate S' , S'' and the phase angle δ , by considering the following equalities:

$$S^* = \sqrt{S'^2 + S''^2} \quad \text{and} \quad \delta = \tan^{-1} \frac{S''}{S'} \quad 2.6$$

The dynamic shear moduli are obtained using a shape factor for the considered test gap, i.e.: $B = \frac{2\pi R^3}{3\alpha}$ where R and α are respectively the radius of the cavity (20.625 mm) and the angle between the two conical dies (0.125 radian), and the following relationships:

$$G^* = \frac{S^*}{B\gamma} \quad G' = \frac{S^* \cos \delta}{B\gamma} \quad G'' = \frac{S^* \sin \delta}{B\gamma} \quad 2.7$$

where γ is the strain angle. Test data are automatically recorded and stored in the PC memory.

The operating capabilities of the RPA are as follows :

Frequency range : 0.21 to 209.44 rad/s (~0.33 to 33.3 Hz)

Temperature range : 40 to 200°C

Strain range : 0.5 to 90 deg (depending on frequency)

2.6.3 Fourier Transform rheometry

Fourier transform (FT) rheometry is an improvement of harmonic (so-called dynamic) testing of polymer materials, which allows both the linear and the non-linear viscoelastic domains to be accurately investigated. It consists in considering the frequency spectrum of the torque signal obtained when submitting a material to high strains. Standard dynamic testing requires strict proportionality between strain and stress for valid resolution of the (measured) complex modulus into its elastic and viscous components. No such condition is needed for FT rheometry, which finds its roots in large amplitude oscillatory strain (LAOS) experiments [22,23,24]. Contrary to standard methods, this new technique suits particularly well complex polymer systems such as filled rubber compounds. Indeed one of the main characteristics of those materials is their strong non-linear viscoelastic behavior, as illustrated for instance by the well known Dynamic Strain Softening effect , also called Payne effect [25], i.e. the significant reduction of elastic modulus with increasing strain amplitude of filled (vulcanized) elastomers. Dynamic modulus decrease upon increasing strain amplitude has also been observed in unvulcanized systems [26,27], but the associated loss of stress-strain proportionality (i.e. the basic condition for linear viscoelastic testing) and the corresponding distortion of the harmonic signals were not directly considered, owing to instrument limitations. Any dynamic rheometer can conveniently be modified for FT testing, in order to capture the full strain and torque signals generated when submitting samples to harmonic deformations at fixed frequency and temperature. Filled rubber materials need special instruments for rheometrical testing, for instance the Rubber Process Analyzer RPA® (Alpha Technologies). Such an instrument was modified for capturing strain and torque signals [23].

2.6.3.1 Test protocols for strain sweep experiments

Strain sweep are performed with the RPA, according to protocols given in Table 2.10. Each protocol describes strain sweep experiments through two subsequent runs separated by a resting period of 2 min. At least two samples of the same material are tested, using protocols named “S-sweep_05Hz_A” and “S-sweep_05Hz_B” such that, through inversion of the strain sequences (i.e. run 1 and run 2), sample fatigue effects would be detected, if any. At each strain sweep step, data acquisition is made in order to record 10240 points at the rate of 512 pt/s. At 0.5 Hz test frequency, twenty cycles are consequently recorded at each strain step, with the RPA set to apply a sufficient number of cycles (i.e. 40 cycles; the so-called “stability” condition) for the steady harmonic regime to be reached. An experiment lasts some 23 minutes and two samples are tested in such a manner that the strain sequences of the successive runs are inverted, with the strain range documented by 20 experimental points. Differences are expected between runs 1 and 2 for materials sensitive to strain amplitude. This experimental approach was designed in order to obtain the maximum number of data in the shortest test time (less than one hour), whilst documenting in the meantime the test repeatability and the material homogeneity.

Table 2.10 : RPA strain sweep test protocols

Test protocol Sweep_05Hz_A			Test protocol Sweep_05Hz_B		
RPA test conditions			RPA test conditions		
Temp. (°C) : as selected			Temp. (°C) : as selected		
Freq. (Hz) : 0.5			Freq. (Hz) : 0.5		
Sample conditioning			Sample conditioning		
Preheating : 3 min, at rest			Preheating : 3 min, at rest		
Fixing : 30 sec; 1 Hz; 0.20 deg.			Fixing : 30 sec; 1 Hz; 0.20 deg.		
Preheating : 2 min, at rest			Preheating : 2 min, at rest		
Strain Sweep (run 1)	Dwell time	Strain Sweep (run 2)	Strain Sweep (run 1)	Dwell time	Strain Sweep (run 2)
Strain deg	2 min, at rest	Strain deg	Strain deg	2 min, at rest	Strain deg
0.5		0.6	0.6		0.5
0.9		1.4	1.4		0.9
2.3		4.3	4.3		2.3
7.0		12.0	12.0		7.0
18.0		24.0	24.0		18.0
30.0		34.0	34.0		30.0
39.0		43.0	43.0		39.0
47.0		51.0	51.0		47.0
55.0		60.0	60.0		55.0
64.0		68.0	68.0		64.0

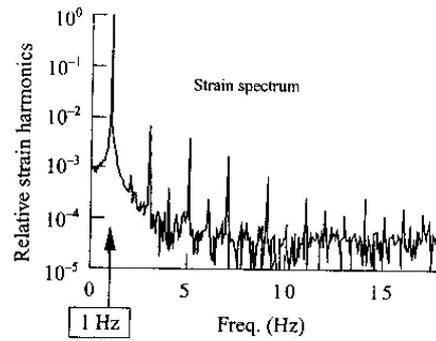
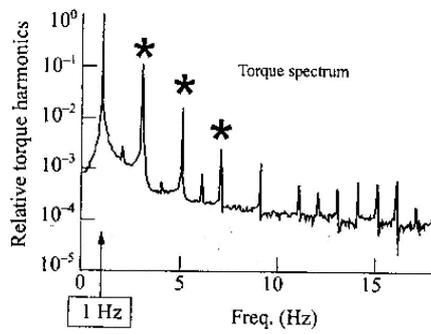
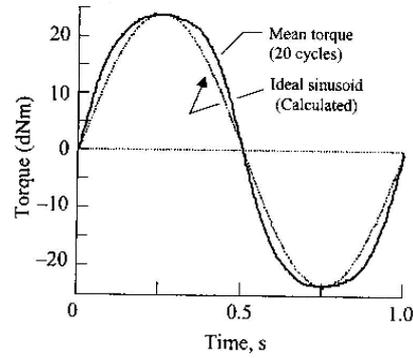
2.6.3.2 Fourier transform analysis

The modified RPA yields both strain and torque signals, as recorded data files of actual harmonic strain and stress readings versus time. Conditions for optimal data capture : first the actual test conditions in terms of temperature, frequency and strain angle are selected, then a sample is positioned on the lower die and the cavity is closed. The test is started and the data acquisition system is activated in order to record, at each strain step, the selected number of data points (pts) with respect to the acquisition parameters used (i.e. 10240 pts at 512 pts/s in this study).

A specific calculation program, written using the FT algorithm available in MathCad 8.0[®] (MathSoft Inc.), is used to obtain the amplitude of the main stress and strain components (corresponding the test frequency) and the relative magnitudes (in %) of the odd-harmonic components, i.e. $I(n \times \omega_1)/I(\omega_1)$ (note that $I(n \times \omega_1)/I(\omega_1)$ or the abridged form $I(n/1)$, is used to describe the n^{th} relative harmonic component of any harmonic signal; $S(n \times \omega_1)/S(\omega_1)$ or $S(n/1)$ specifically means that a strain signal is considered; $T(n \times \omega_1)/T(\omega_1)$ or $T(n/1)$ is used for the torque signal). The number of data points used, the frequency resolution (Hz), the acquisition time (s) and the sampling rate (point/s) are also provided. Figure 2.4 shows the averaged torque signals recorded when submitting a gum SMR10CV to 12 degree strain at 100°C and 1 Hz frequency. FT is a mathematical treatment of harmonic signals that resolves the information gathered in the time domain into a representation of the measured material property in the frequency domain, as a spectrum of harmonic components. If the response of the material is strictly linear, then the proportionality between (applied) strain and (measured) torque is kept, the torque signal is simple sinusoid and consequently the torque spectrum consists of a single peak at the applied frequency, for instance 1 Hz, in the case of the experiment displayed in Figure 2.4. A non-linear response is characterized by a number of additional peaks at odd multiples of the applied strain frequency, as clearly shown in the middle left part of figure 2.4 (torque spectrum). At 168% strain, gum SMR10CV60 clearly exhibits a non-linear response, as shown by the distortion of the torque signal, which reflects a lack of proportionality between the applied strain (perfectly sinusoidal) and the measured torque. FT can also be applied on the strain signal in order to quantify its quality. As shown in the middle right inset, there are some peaks at odd multiples of the frequency, which are slightly higher than the noise. As a logarithmic scale is used, their importance is however exaggerated as demonstrated by their actual relative values displayed in the lower insert table (built with the appropriate signal analysis software). For instance, the 3rd relative torque harmonic is 10.26%, quite significant indeed, whilst the 3rd relative strain harmonic is only 0.61%. Through simultaneous FT treatment of both the torque and strain signals, it has been demonstrated that, at large strain amplitudes, the RPA submits materials to a nearly pure strain sinusoidal signal [23]. However, strain signal quality degenerates as the strain angle decreases and a correction method had to be developed. As demonstrated by Wilhelm *et al.* [28,29] only odd torque harmonics are significant in terms of material's response. Indeed, if a shear strain of maximum strain amplitude, γ_0 (rad) is applied at a frequency ω (rad/s) to a viscoelastic material, the strain varies with time, t (s) according to $\gamma(t) = \gamma_0 \sin(\omega t)$ and the shear stress response can be expected to be given by a series of odd harmonics, i.e.:

$$\sigma(t) = \sum_{j=1,3,5}^{\infty} \sigma_j \sin(j\omega t + \delta_j) \quad 2.8$$

providing one assumes that, over the whole viscoelastic domain (i.e. linear and non-linear), the viscosity function, $\eta = f(\dot{\gamma})$ can be approximated by a polynomial series with respect to the shear rate. If the tested material exhibits a pure linear viscoelastic response, Equation 2.8 reduces to the first term of the series, as considered in most standard dynamic test methods. With a simple homogeneous polymer material, non-linearity occurs with the application of high strain. The distortion is generally more severe with compounded rubbers and, in addition, has been observed to affect more the right part of the half-signal, when active fillers are used in the formulation. There is thus a substantial difference between the non-linear viscoelastic behavior of a pure, unfilled polymer and of a filled material. The former essentially exhibits non-linearity through the application of a sufficiently large strain and this behavior was called extrinsic non-linear viscoelasticity (occurring through external causes, i.e. the applied strain), whilst the latter shows intrinsic non-linear viscoelasticity (owing to the internal morphology of the material). It is quite obvious that standard strain sweep experiments, whilst possibly detecting the occurrence of the non-linear viscoelastic response, have absolutely no capability to distinguish extrinsic and intrinsic characters.



Nr pts	Freq.resol	Main freq.	3 rd harm.	5 th harm.	7 th harm.	9 th harm.	11 th harm.	13 th harm.	15 th harm.
t _{acq}	Sampling pt/s	Main torque a.u.	T(3/1) %	T(5/1) %	T(7/1) %	T(9/1) %	T(11/1) %	T(13/1) %	T(15/1) %
		Main strain a.u.	S(3/1) %	S(5/1) %	S(7/1) %	S(9/1) %	S(11/1) %	S(13/1) %	S(15/1) %
8192	0.063	1	3	5	7	9	11	13	15
16.0	512	1180.0	10.261	1.493	0.245	0.129	0.048	0.041	0.054
		546.8	0.610	0.344	0.156	0.066	0.026	0.012	0.011

Figure 2.4 : Recorded torque signal when submitting a SMR CV60 gum sample to 12° strain (167.6%) at 1 Hz; Fourier Transform resolution of torque and strain signals into harmonic components; odd harmonic components analysis [30].

2.6.3.3 Modeling the effect of strain amplitude on FT rheometry results

According to the strain sweep test protocol described above, RPA-FT experiments and data treatment yield essentially two types of information, which reflect on how the main torque component, i.e. $T(1\omega)$, and the relative torque harmonic vary with strain amplitude. Such variation can be conveniently modeled with simple mathematical relationships. Let us consider the main torque component ; the ratio $T(1\omega)/\gamma$ has obviously the meaning of a complex modulus, i.e. $G^* = 12.335 \times \frac{T(1\omega)}{\gamma}$ [with G^* in kPa, $T(1\omega)$ in arbitrary units and γ in %] and, for a material exhibiting linear viscoelasticity within the experimental window, a plot of G^* vs. γ shows the most familiar picture of a plateau region at low strain, then a typical strain dependence. Such a behavior is well modeled with the following equation:

$$G^*(\gamma) = G^*_f + \left[\frac{G^*_0 - G^*_f}{1 + (A\gamma)^B} \right] \quad 2.9$$

where G^*_0 is the modulus in the linear region, G^*_f the final modulus, A the reverse of a critical strain for a mid-modulus value to be reached, and B a parameter describing the strain sensitivity of the material.

Odd torque harmonics become significant as strain increases and are therefore considered as the non-linear viscoelastic ‘signature’ of tested materials, only available through FT rheometry. With respect to strain amplitude, relative torque harmonic components generally vary according to S-shape curves. Leblanc [30,31] initially proposed that such behavior is modeled with an equation that considers a maximum plateau value at a high (infinite) strain:

$$TH(\gamma) = TH_{\max} \times [1 - \exp(-C\gamma)]^D \quad 2.10$$

where γ is the deformation (%), TH_{\max} a maximum plateau value at a high (infinite) strain, C and D fit parameters. TH stands for either the total harmonic content [i.e. $TTHC = \sum T(n\omega/1\omega)$] or any relative torque harmonic, for instance $T(3/1)$, $T(5/1)$, etc. In some materials, the (extrapolated) maximum value was found to be larger than the maximum measured data and was therefore considered with care. Experimentally, it was also frequently observed that if the likeliness of a near plateau value at a large strain was supported by test data, one could also consider TH_{\max} as a pure mathematical artifact, since it is explicit in the fitting equation. Overall, harmonic content curves $TTHC(\gamma)$ are by nature ‘envelop’ curves of all detected harmonics, and are actually obtained up to the 15th one with the up-dated RPA. It is quite obvious that, for a given set of experimental data, the actual value of $TTHC_{\max}$ is dependant on the number of data points used in running the FT algorithm. Leblanc [32] demonstrated that using 8192 (i.e. 2^{13}) points is sufficient to give an acceptable signal/noise ratio and confidence up to the 15th harmonic. However, if the number of data points used is infinite, the total harmonic content (extrapolated) at infinite strain would also be infinite because the number of harmonics is

infinite, though they get smaller as their position on the frequency axis increases. It follows that a far more realistic model to consider odd harmonic variation with strain amplitude is provided for by the following equation [30,31]:

$$TH(\gamma) = (TH_0 + \alpha \gamma) \times [1 - \exp(-C \gamma)]^D \quad 2.11$$

where the member $TH_0 + \alpha \gamma$ expresses a linear variation of harmonics in the high strain region, while the member $[1 - \exp(-C \gamma)]^D$ describes the onset of non-linear viscoelastic response as illustrated in Figure 2.5. The physical meaning of parameters TH_0 and α is obvious and as shown in the lower part of the figure, parameter D somewhat reflects the extent of the linear viscoelastic region (i.e. no harmonics), while parameter C indicates the strain sensitivity of the non-linear character. It is worth noting that in using Equations 2.10 or 2.11, one may express the deformation (or strain) γ either in degree angle or in %.

Obviously all parameters remain the same except α and C , whose values depend on the units for γ . Conversion factor is : $\frac{100 \times \pi}{180 \times 0.125}$.

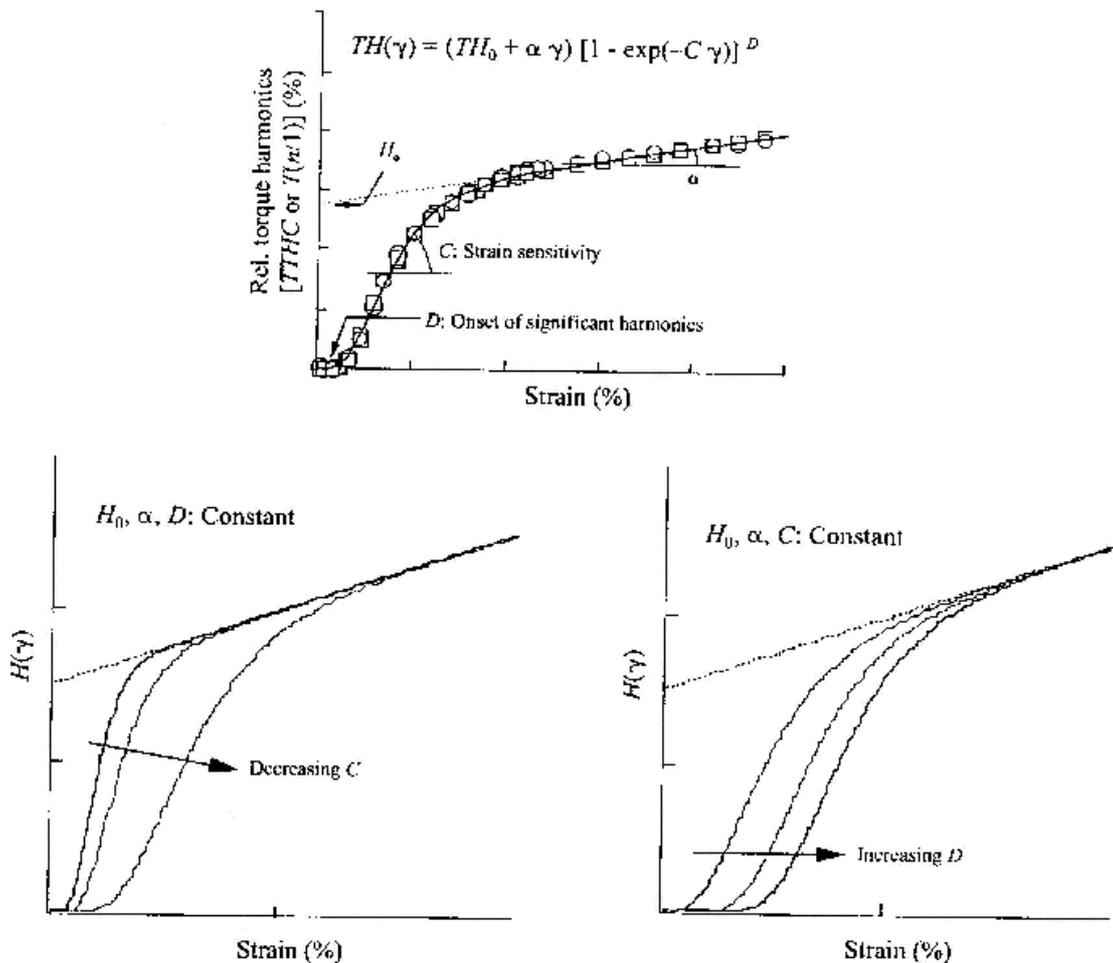


Figure 2.5 Modeling torque harmonic variation with strain amplitude [30]

2.7 Mechanical testing

2.7.1 Tensile testing

Cured rubber sheets, as obtained by compression molding of rubber compounds, were cut into dumbbell shape using a die-punching machine. Static physical properties tests were performed test according to ASTM D412-98a [33] using a Gibitre Instruments Tensorcheck tensile testing machine with the crosshead speed of 500 mm/min. Fives specimens were measured in order to get the average value for each sample. Tensile stress at any specified elongation was calculated as follows :

$$T(x) = F(x)/A \quad 2.12$$

where $T(x)$ is tensile stress at (x) % elongation (MPa), $F(x)$ is force at specified elongation (MN), A the cross sectional area of the unstrained specimen (m^2). The elongation was calculated as follows :

$$E = 100[L-L_0]/L_0 \quad 2.13$$

where E is the elongation in percent, L the observed distance between benchmarks on the extended specimen, L_0 the initial distance between benchmarks.

2.7.2 Hardness

Hardness was tested according to ASTM D2240-02b [34] using Zwick & Co.KG. The specimen was prepared by compression molding of rubber compounds. Threes specimens were tested in order to get the means of testing.

2.8 References Section 2

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3 Experimental results

3.1 Gum samples analysis results

3.1.1 DSC analysis

Table 3.1.1 shows the glass transition temperature T_g as measured through DSC on several grades of Natural Rubber. All T_g readings were made on the second heating thermogram so that any thermal history effect is avoided. As can be seen, there is no significant difference in the T_g values that are about -63°C in cases. Since, whatever the grade, all NR samples do correspond to high *cis*-1,4 polyisoprene, such results are as expected.

Table 3.1.1 : DSC results on different NR grades

Sample	T_g ($^\circ\text{C}$)
OMNR	-64
STR5L	-63
STR5CV60	-63
RSS1	-64
RSS3	-63

3.1.2 NMR analysis

Figure 3.1.1 shows the ^1H -NMR solid spectra of different NR grades. The ^1H -NMR spectra exhibit three main characteristic signals of proton adjacent to the $\text{C}=\text{C}$ (c), methylene (b) and methyl protons (a) at 5.25, 2.18, and 1.80 ppm, respectively. There is no significant difference in the shifting chemical, in full agreement with the results of ^1H -NMR analysis in solution, as shown in Figure 3.1.2.

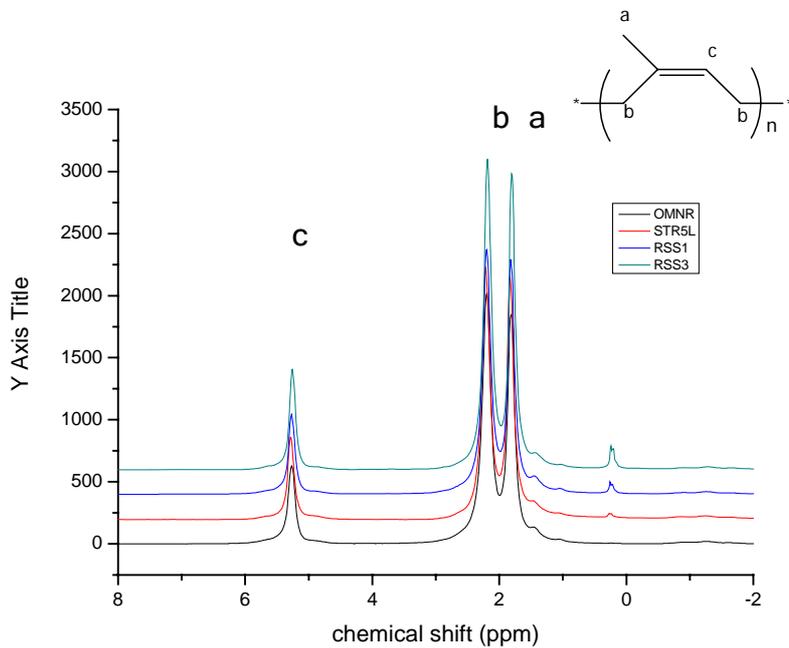


Figure 3.1.1 : ^1H -NMR solid MAS 10 kHz of different NR grades

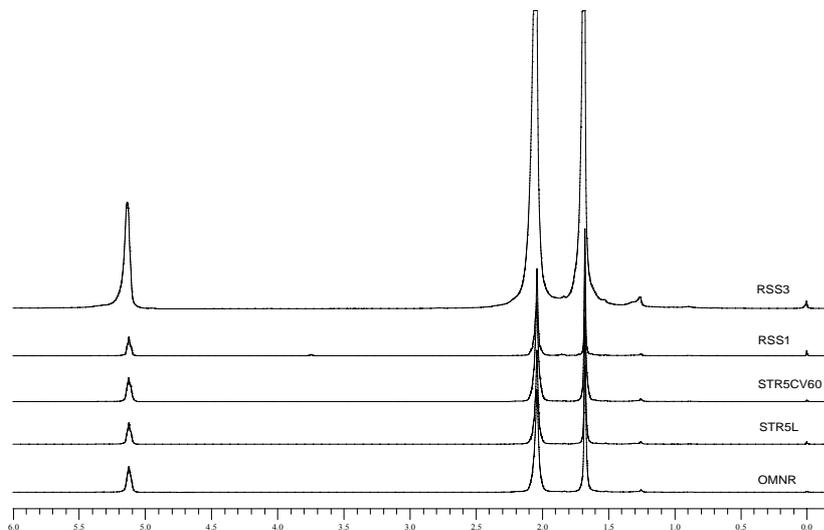


Figure 3.1.2 : ^1H -NMR liquid-state of different NR grades

In the case of ^{13}C -NMR solid MAS (Figure 3.1.3), spectra provide evidence for mobile components of the chains. It can be observed the 5 characteristic peaks of 5 carbons of the polyisoprene : ^{13}C -NMR peaks at 134.8, 125.3, 32.5, 26.7 and 23.6 ppm indicate carbon signals of $=\text{C}$ - (2), $=\text{CH}$ - (3), $-\text{CH}_2-$ (1,4), and $-\text{CH}_3$ (5), respectively. The ^{13}C -NMR solid MAS spectra do not show any differences between the various grades tested.

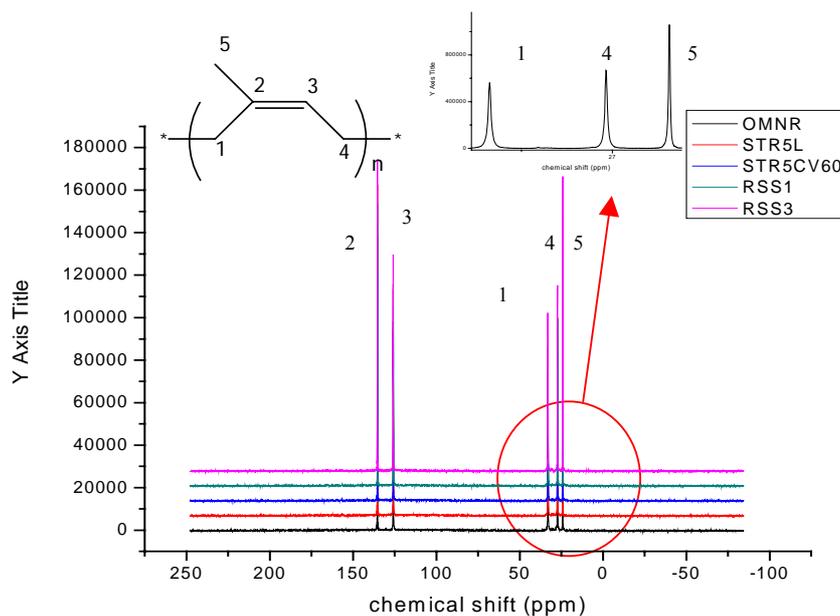


Figure 3.1.3 : ^{13}C -NMR solid MAS 10 kHz of different NR grades

Figure 3.1.4 compares the experimental spectra of NR by using ^{13}C cross-polarization, magic angle spinning (CP-MAS) technique which can detect the signal of immobile component. As suggested by Larsen *et al.*[10] The cross polarization (CP) can be used to distinguish mobile components from immobile components. Figure 3.1.5 specifically shows the ^{13}C -NMR solid CP-MAS spectrum of STR5L sample, where carbon signals of =C- (2), =CH- (3), -CH₂- (1,4), and -CH₃ (5) at 134.8, 125.3, 32.5, 26.7 and 23.6 ppm respectively are indicated. A comparison stack plots between ^{13}C -NMR solid CP-MAS (Figure 3.1.6) of the different NR grades focusses on the C-4 signal which is likely the best to distinguish small differences on the chains. The line widths of CP-MAS spectra of natural rubber correspond to immobile and mobile components of the polyisoprene chains. Small differences are seen between the various NR grades but too small to be really informative about structural differences, if any.

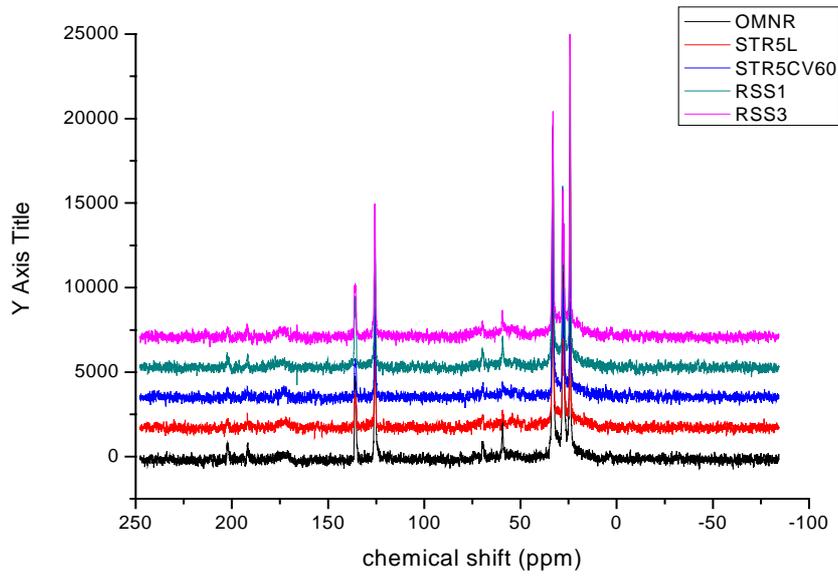


Figure 3.1.4 : ^{13}C -NMR solid CP-MAS 5 kHz of different NR grades

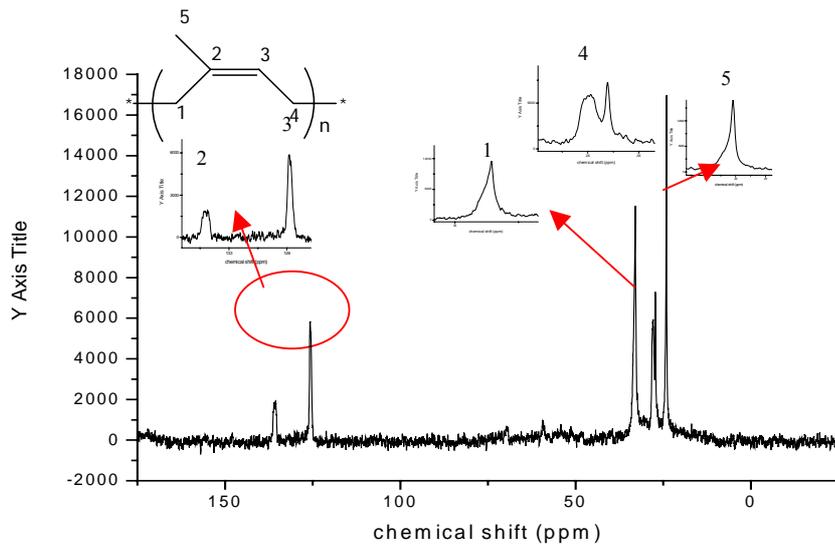


Figure 3.1.5 : ^{13}C -NMR solid CP-MAS 5 kHz of the STR5L sample

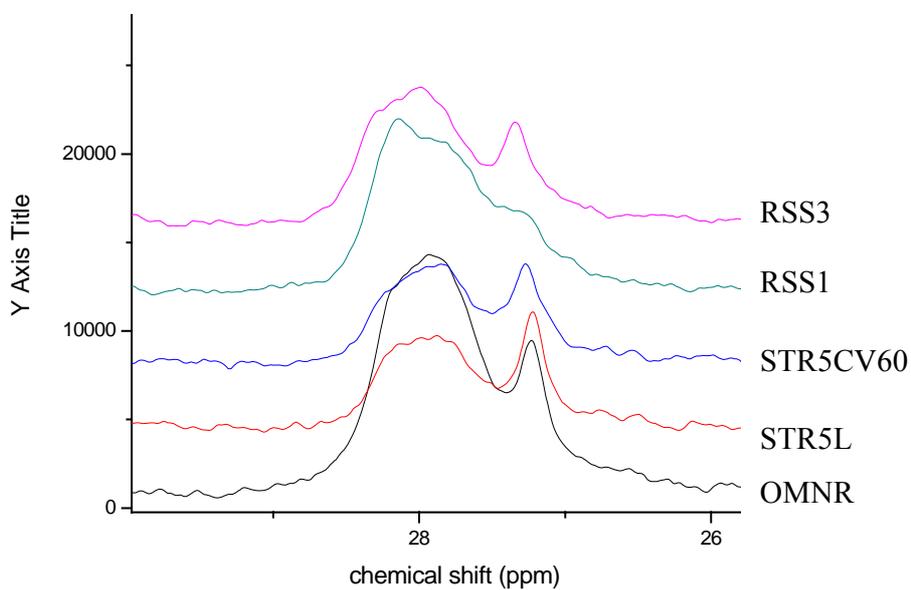


Figure 3.1.6 : ^{13}C -NMR solid CP-MAS 5 kHz of C-4 signal of different NR grades

Table 3.1.2 : The proportion of mobile and rigid carbons of the chains

Sample	C-1		C-2		C-3		C-4		C-5	
	mobile	immobile								
OMNR	30	70	5	95	30	70	12	88	34	66
STR5L	24	76	8	92	45	55	28	72	43	57
STR5CV60	79	21	5	95	16	84	27	73	74	26
RSS1	39	61	5	95	24	76	18	82	22	78
RSS3	11	89	10	90	9	91	8	92	32	68

Table 3.1.3 : Ratio “immobile/mobile” contribution to the level of the signals of the C-4

Sample	Mobile component (%)	Immobile component (%)	Ratio immobile/mobile
OMNR	12	88	7.9
STR5L	28	72	2.6
STR5CV60	27	73	2.7
RSS1	18	82	4.6
RSS3	8	92	12.3

From the NMR spectra of natural rubber , the curve fitting (DMFit2006) was used to simulate the line width and the integrated area of each carbon signal. The result of the % mobile components , % immobile components and ratio “immobile/mobile” are shown in Tables 3.1.2 and 3.1.3. For the C-4 signal, likely offering the more discriminant information, STR5L and STR5CV60 exhibit a higher mobile component than the other samples, and RSS3 shows the most immobile component. Such data are somewhat in agreement with molecular weight measurements (see hereafter) : RSS samples have expectedly the highest molecular weight (M_n above 1000 kg/mol) whilst STR5L and STR5CV60 have the lower molecular weight ($M_n \cong 500$ kg/mol). OMNR appear different : it has a low molecular weight in the $\cong 500$ kg/mol range but exhibits a high immobile/mobile ratio. This is likely due to the chemical treatment, unfortunately undisclosed.

3.1.3 Raman analysis

The Raman spectrum of STR5L is shown in Figure 3.1.7. Other samples exhibit qualitatively similar features. The assignments of the peaks are summarized in Table 3.1.4

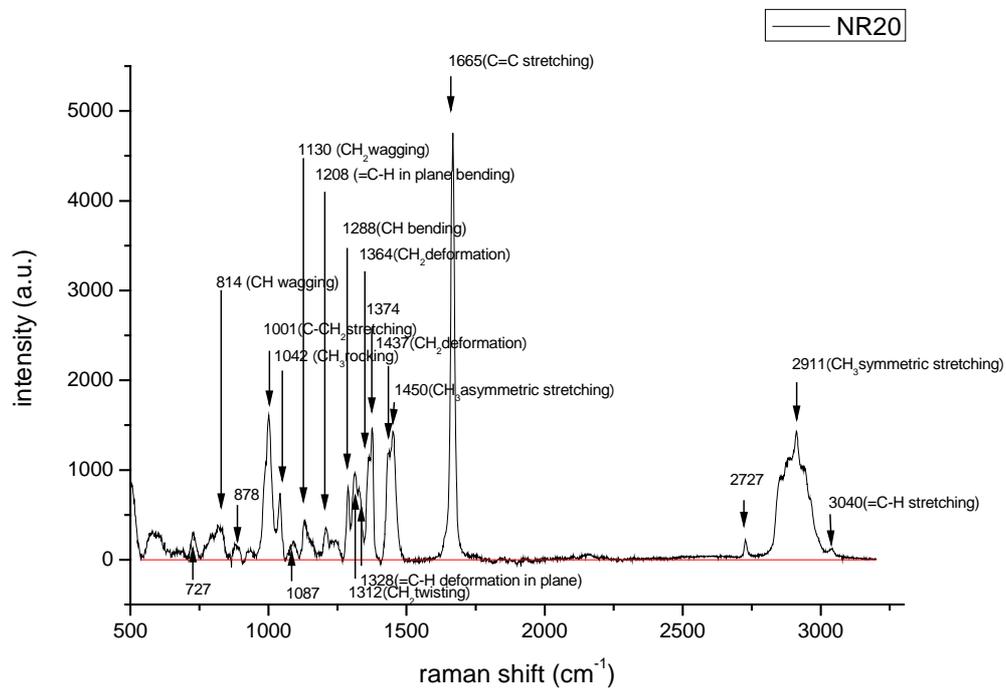


Figure 3.1.7 : Raman spectrum of STR5L, with peak assignments

Table 3.1.4 : Wavenumber (cm⁻¹) and assignment of bands observed in Raman spectra of NR samples

Wavenumber (cm⁻¹)	Description of assignments
3040	=C-H stretching
2964	CH ₃ asymmetric stretching
2938	CH ₂ asymmetric stretching
2911	CH ₃ symmetric stretching
2852	CH ₂ symmetric stretching
1665	C=C stretching
1452	CH ₃ asymmetric stretching
1433	CH ₂ deformation
1364	CH ₂ deformation
1328	=C-H deformation in plane
1312	CH ₂ twisting
1288	CH bending
1243	CH ₂ twisting
1130	CH ₂ wagging
1042	CH ₃ rocking
1000	C-H ₂ stretching
835	=CH out of plane bending
814	CH wagging
790	CH ₂ rocking

3.1.4 Sol and gel contents

Gel content results as obtained through the swelling kinetic method are given in Table 3.1.5 and illustrated by Figure 3.1.8.

Table 3.1.5 : Sol and gel contents of Natural Rubber samples as determined through toluene swelling at various times.

Sample	Time (day)	Sol content (%)	Gel content (%)
OMNR	4	93	7
	16	95	5
	24	95	5
STR5L	4	91	9
	16	94	6
	24	94	6
STR5CV60	4	95	5
	16	97	3
	24	97	3
RSS3E	4	80	20
	16	90	10
	24	90	10
RSS3	4	66	34
	16	91	9
	24	92	8
SMR10CV	4	91	9
	16	96	4
	24	96	4

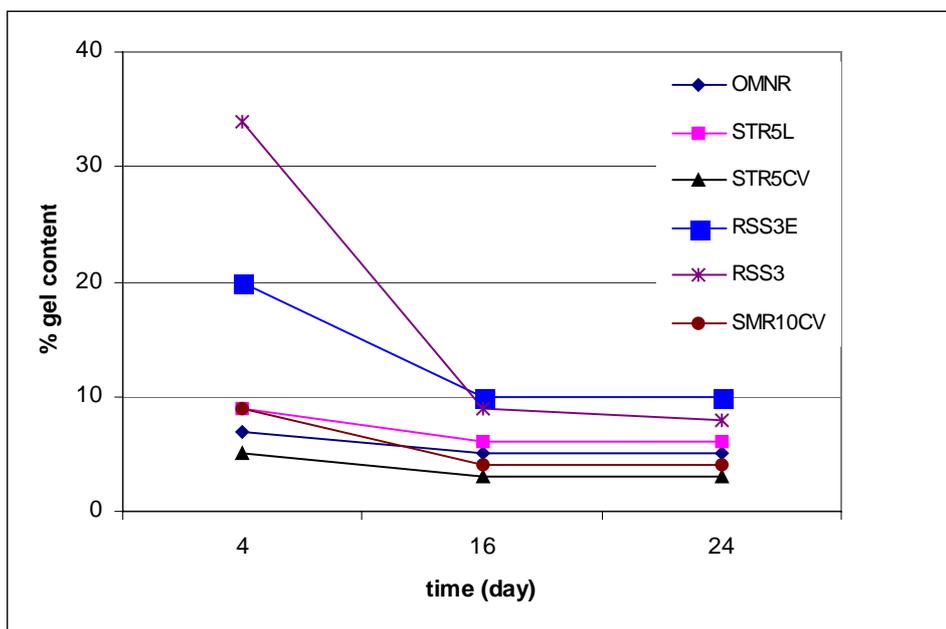


Figure 3.1.8 : Gel content (%) of Natural Rubber grades after various immersion times in toluene at room temperature

Figure 3.1.8 shows how the percent gel content of Natural Rubber samples changes with solubilization time. As can be seen quite an extended immersion time is needed for stable measurements to be obtained. Sixteen days (at room temperature) can be considered as a safe period for near equilibrium results to be obtained, considerably longer than most immersion periods mentioned in literature. Table 3.1.6 compares all the samples through the gel content values after 16 days immersion in toluene. Mooney viscosity readings and molecular weight (as measured in CIRAD, Montpellier) are also tabulated.

Table 3.1.6 : Gel contents of Natural Rubber samples as determined through immersion in toluene for 16 days, versus Mooney viscosity and number averaged molecular weight results.

Sample	ML(1+4) _{100°C}	Mn (kg/mol)	Gel content (%)
OMNR	65	464	5
STR5L	81	679	6
STR5CV60	63	491	3
RSS3E	100	1143	10
RSS3	91	1051	8
SMR10CV	71	454	4

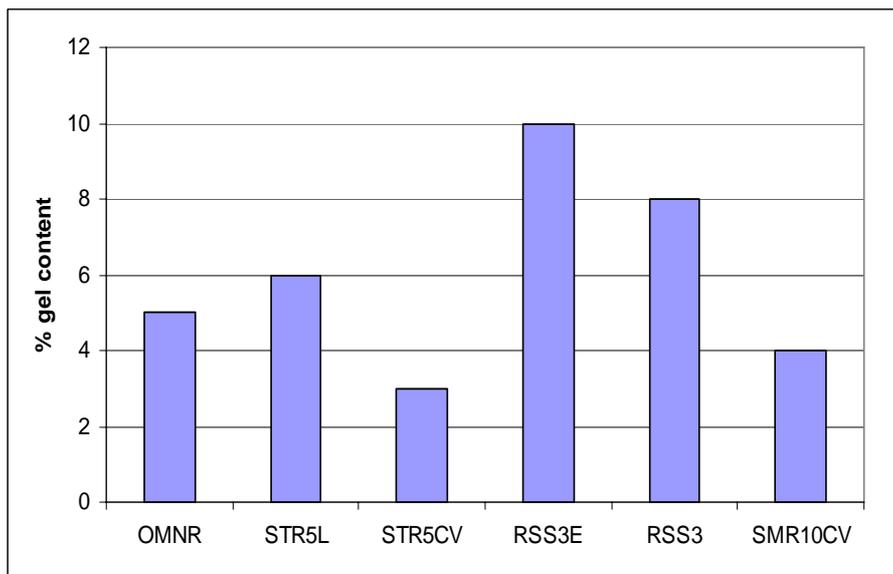


Figure 3.1.9 : Gel contents of Natural Rubber samples as determined through immersion in toluene for 16 days

As can be seen in Figure 3.1.9, the Ribbed Smoked Sheet grades exhibit the highest gel content, the two CV grades the lowest, while OMNR and STR5L show results in-between.

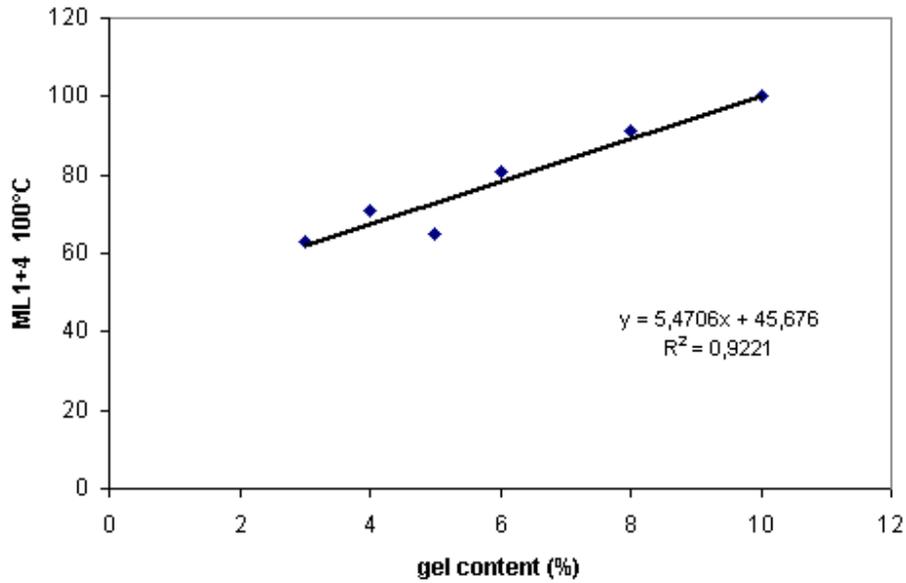


Figure 3.1.10 : Mooney viscosity versus gel content of different NR grades

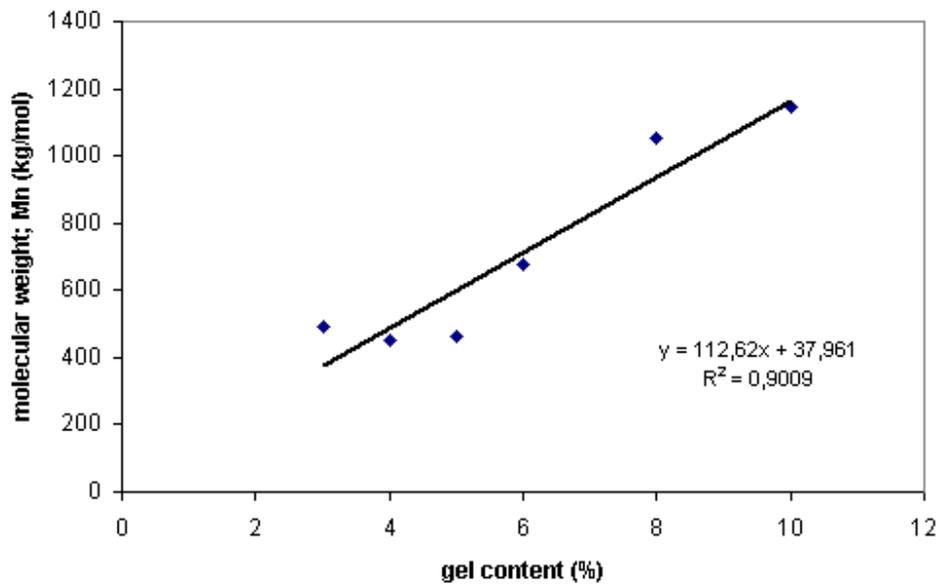


Figure 3.1.11 : Molecular weight versus gel content of different NR grades

Figures 3.1.10 and 3.1.11 show that there are approximate linear relationships between the Mooney viscosity or the number average molecular weight and the gel content. The percent gel contents of OMNR, STR5L, STR5CV and SMR10CV are found to be about 5%; in the case of RSS3 and RSS3E they are found to be about 8% and 10%, respectively. OMNR, STR5L, and STR5CV are produced from field latex. These results are in agreement with works reported by Subramaniam [1] and Saktapianich and Yunyongwattanakorn. [2], that showed that NR latex, either freshly coagulated or in its initial period of production, contains only small amounts of gel. SMR10CV is produced

from field coagulum or from unsmoked sheets but its viscosity is stabilized; therefore the low gel content result suggests that the hydroxylamine salt is an effective gel formation prohibiting agent. RSS grades are produced from field latex but sheets are smoked and such grades are known to exhibit the highest molecular weights. The measured higher gel contents suggests that such characteristics enhance gel formation. The Mooney viscosity versus gel content of different grades of NR are plotted in Figure 3.1.10. As can be seen, the Mooney viscosity increased with increasing gel content in agreement with similar observations reported by Sakdapipanich *et al.* [3]. These authors found that the Mooney viscosity increases with increasing gel content but the correlation is quite poor. Figure 3.1.11 show molecular weight versus gel content of different NR grades NR; as can be seen, the same trend as with the Mooney viscosity is noted.

3.1.5 RPA results on gum NR samples

3.1.5.1 Complex modulus versus strain

Complex modulus G^* versus strain curves of gum NRs are shown in Figure 3.1.12. In all cases, the two tested samples (a and b) gave identical results thus demonstrating the excellent homogeneity of tested materials as well as the reproducibility of the testing method. For STR5L, STR5CV60, OMNR, and SMR10CV samples, very small differences were seen between run1 and run2 data, which indicates that either there are no significant strain history effects or that strain effects are immediately recovered during the 2 minutes resting period between runs. But in the cases of RSS3 and RSS3E some differences can be seen between run1 and run2 data, which indicate that either there are permanent strain history effects or that the 2 min dwell time is not enough for the rubber to completely recover the severe strain of run 1. All figures clearly show that all tested samples do exhibit a linear region. Note that complex modulus (G^*) remains constant with increasing strain up to the critical strain. After this critical strain is exceeded, the complex modulus starts to decrease. This critical strain corresponds to the beginning of the non-linear region. All gum NR samples exhibit no strain effects up to around 60 % strain. Such a behavior is well modeled with the following equation:

$$G^*(\gamma) = G^*_f + \left[\frac{G^*_0 - G^*_f}{1 + (A\gamma)^B} \right] \quad 3.1$$

Where G^*_0 is the modulus in the linear region, G^*_f the final modulus, A the reverse of a critical strain for a mid-modulus value to be reached, and B a parameter describing the strain sensitivity of the material. Fit parameters of Equation 3.1 are given in Table 3.1.7, from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. Modeling G^* versus strain experiments with Equation 3.1 yields three parameters, whose physical meaning is immediate, and which allow a direct comparison between test materials. For gum (unmasticated) NR samples (Figure 3.1.12 or Table 3.1.7), RSS3 and RSS3E have the highest complex modulus, and STR5L is stiffer than STR5CV60, OMNR, and SMR10CV, respectively. The mid-modulus critical strain ($1/A$) is somewhat related with the extent of the linear viscoelastic region. In the cases of gum un-masticated NR samples (Figure 3.1.13), SMR10CV has the highest

critical strain and while no significant difference is seen with the other samples, it can be considered that SMR10CV has the largest linear zone of all the tested samples. The parameter B is an indication of the strain sensitivity of the material but reveals however small, if any, differences between the gum (unmasticated) NR samples tested (Figure 3.1.13). Figure 3.1.14 shows the variation of fit parameter (linear complex modulus G^*_0 , mid-modulus strain $1/A$, strain sensitivity B) versus molecular weight (M_n) of difference grades NR (OMNR, STR5L, STR5CV60, RSS3E, RSS3, and SMR10CV60). Fit parameters and correlation coefficient are given in Table 3.1.8. The results show good correlations between the molecular weight of the different NR grades and the linear complex modulus, the mid-modulus strain, and the strain sensitivity. The linear complex modulus increases with increasing molecular weight with run2 higher than run1 for very high molecular weight grades, as expected with respect to the strain induced crystallization likely occurring during run1 and clearly reflected in strain history effect. The mid-modulus strain $1/A$ slightly decreases with increasing M_n with run1 higher than run2. It could be said that when the NR sample has the higher molecular weight, it tends to show a smaller linear zone. In what strain sensitivity B is concerned, there are no significant effect that could be assigned to molecular weight differences. Figure 3.1.15 shows the variation of the linear complex modulus versus Mooney viscosity. As expected, the linear complex modulus G^*_0 increases with increasing molecular weight, and so does the Mooney viscosity. However an increase in stress resistance can be attributed to the crystallization of rubber chains on straining [4]. Thus, the higher linear complex modulus (G^*_0) in RSS3 (higher molecular weight) samples when compared with the other samples can be attributed to a higher crystallizability. It is reasonable to assume that crystallization on stretching is related to the number of branch points per chain and chain entanglement. This assumption suggests that the branch points and/or chain entanglements of the RSS3 samples are higher than those of other samples. The RSS3 samples have the highest gel content. Thus, the higher complex modulus compared with the other samples could be attributed to the higher gel content. Kawahara *et al.* [5] studied the relationship between the green strength and the gel content of rubber from NR latex. They found that the green strength increases with increasing the gel content. However, they reported also that the gel content has no direct relationship with the green strength but instead it is the long-chain branching in NR that plays an important role in the high green strength.

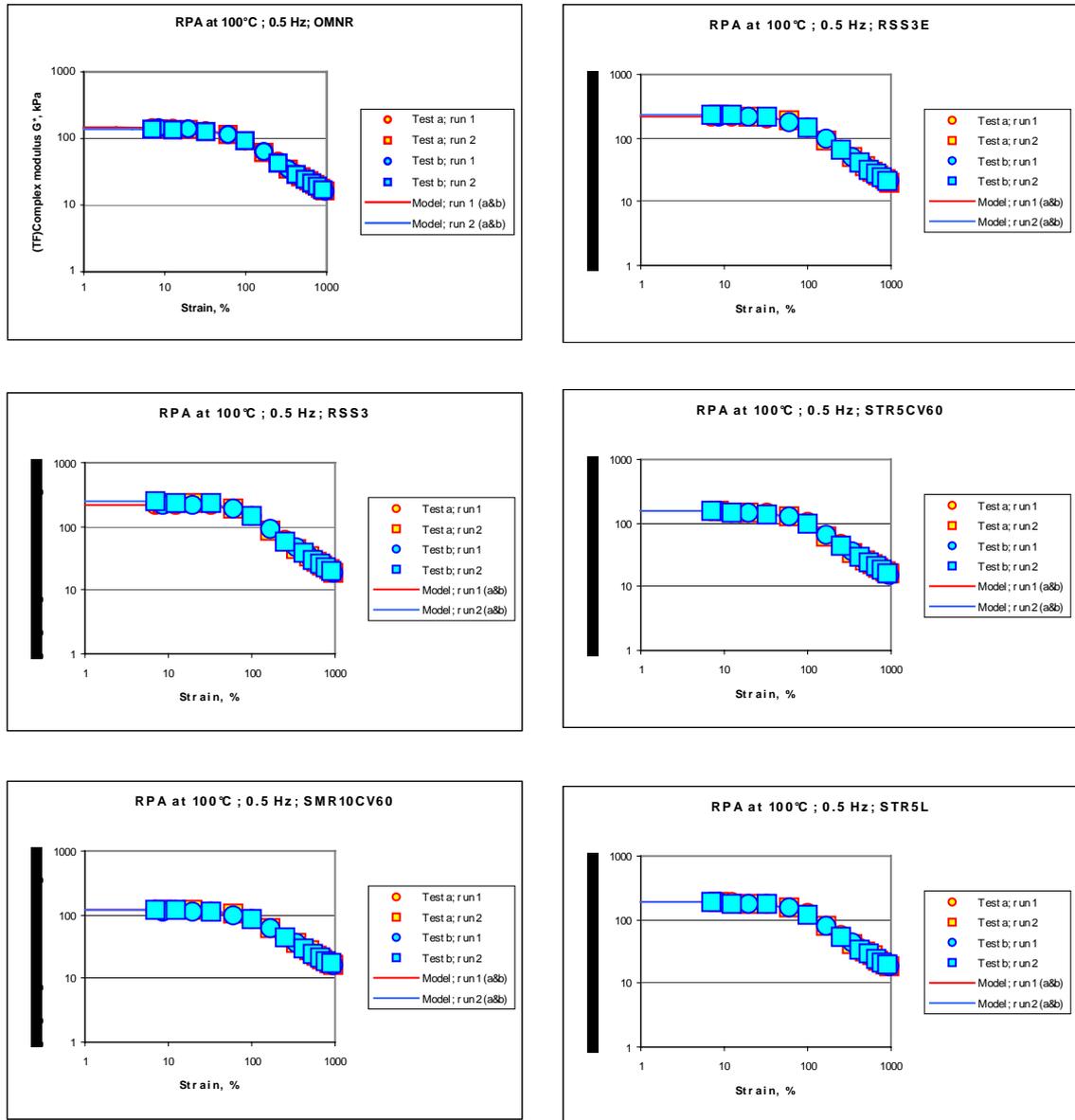


Figure 3.1.12 : RPA-FT at 100 °C on Natural Rubber gum samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

Table 3.1.7 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz on gum (unmasticated) NR samples; fit parameters of Equation 3.1

Sample	Run (a & b)	G* ₀ kPa	G* _f kPa	1/A%	B	r ²
OMNR	1	146.4	11.36	126.0	1.560	1.0000
	2	139.0	14.00	130.6	1.755	0.9997
STR5L	1	188.6	13.77	135.4	1.737	0.9998
	2	187.3	16.59	127.2	1.860	0.9997
STR5CV60	1	152.3	11.92	132.5	1.714	0.9999
	2	151.7	14.79	125.4	1.892	0.9998
RSS3	1	223.4	17.41	130.3	1.996	0.9997
	2	242.3	17.86	111.6	1.913	0.9997
RSS3E	1	221.5	15.32	134.9	1.734	0.9999
	2	233.1	16.66	122.9	1.769	0.9998
SMR10CV60	1	117.4	11.49	154.6	1.622	0.9999
	2	122.4	12.26	153.6	1.676	0.9999

Table 3.1.8 : Mooney viscosity 1+4 at 100°C and molecular weight of different NR grades

Sample	ML1+4 100°C	Mz (kg/mol)	Mw (kg/mol)	Mn (kg/mol)
OMNR	65	2407	1130	464
STR5L	81	2375	1278	679
STR5CV60	63	2779	1323	491
RSS3	91	2934	1755	1051
RSS3E	100	2596	1685	1143
SMR10CV60	71	1537	798	454

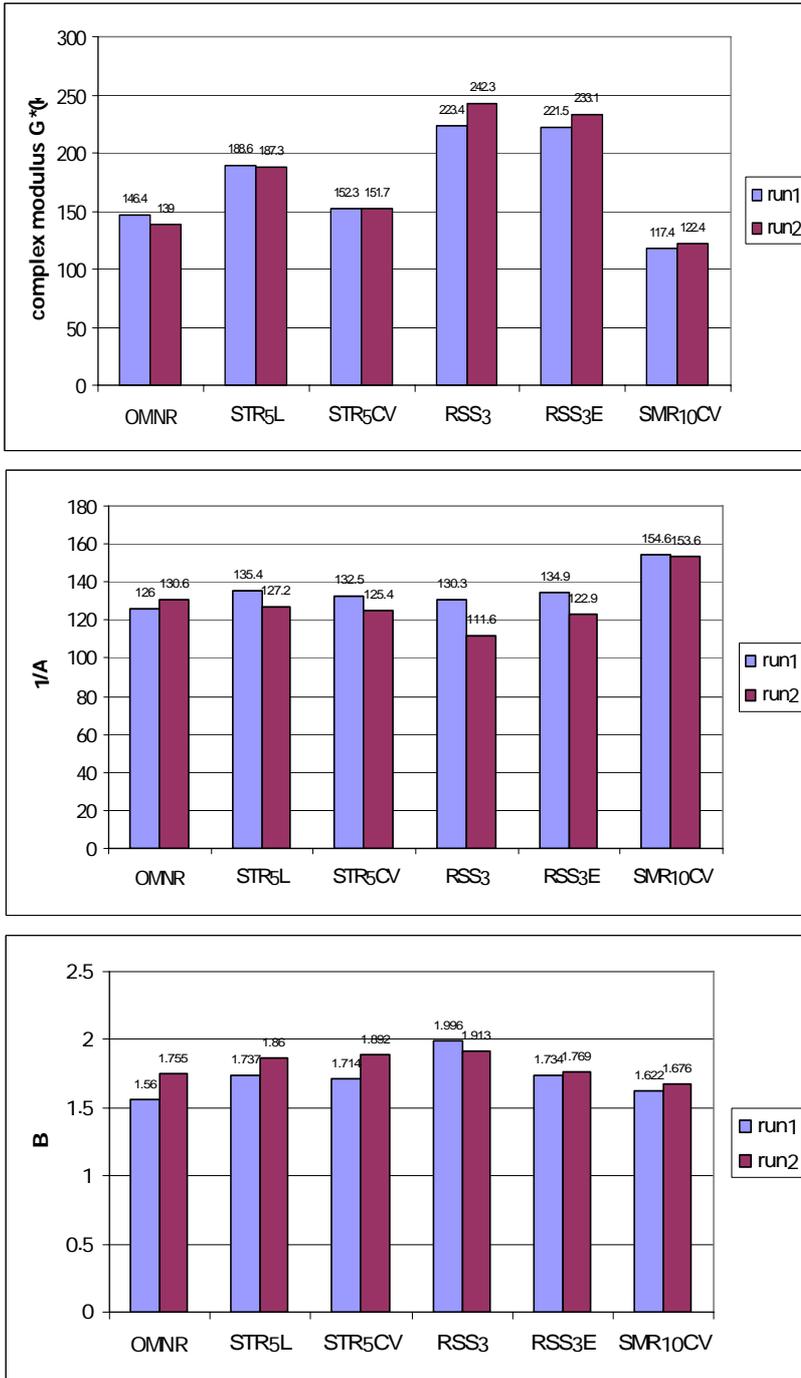


Figure 3.1.13 : Comparing test materials through parameters of Equation 3.1

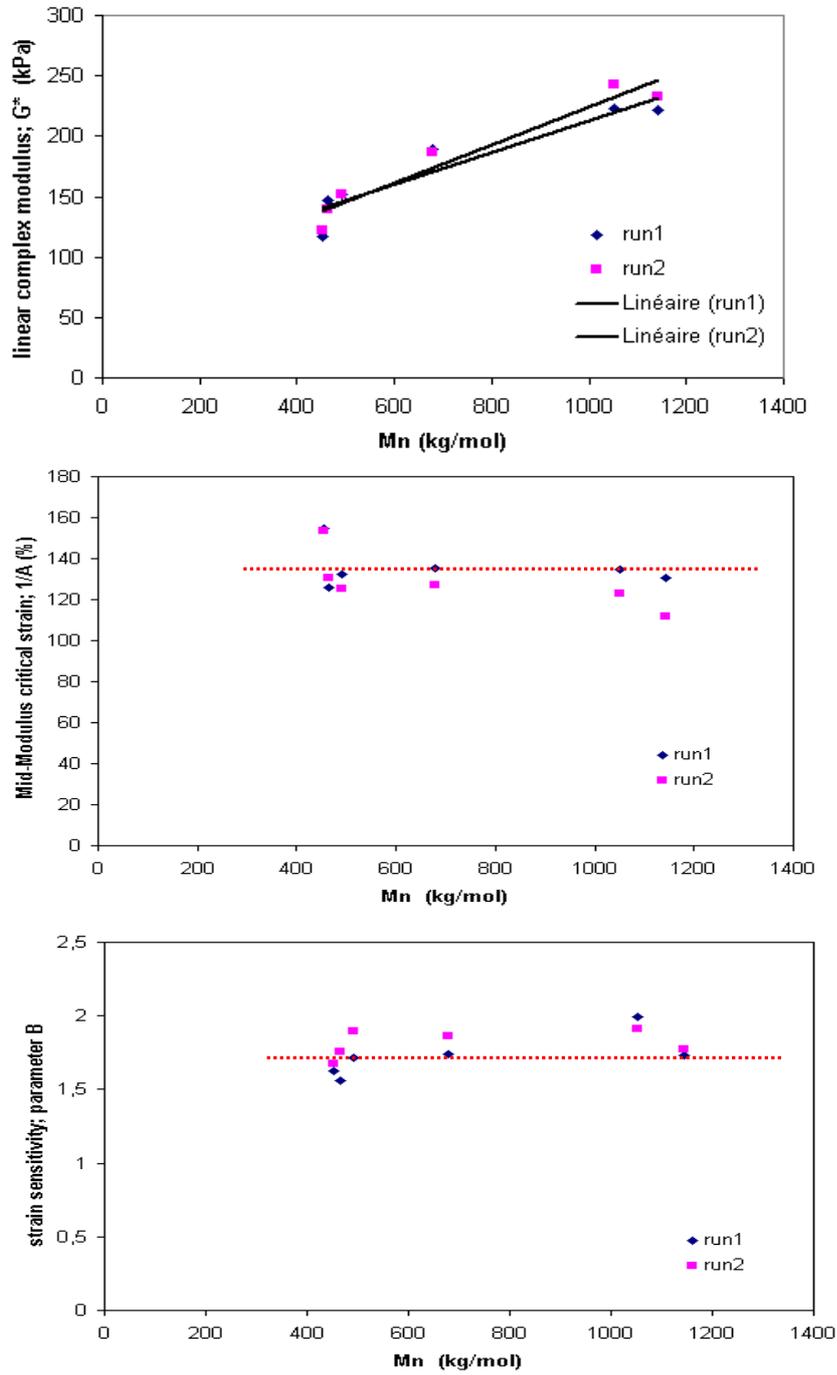


Figure 3.1.14 : Fit parameter from equation 3.1 versus molecular weight of different NR grades

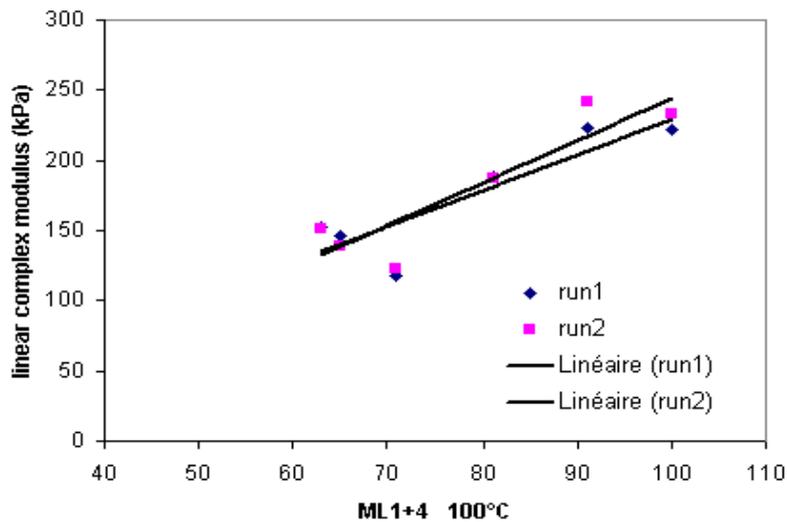


Figure 3.1.15 : Linear complex modulus versus Mooney viscosity of different NR grades

3.1.5.2 Quarter torque signal integration

FT analysis of strain signal allows clear qualification of the non-linear response of viscoelastic materials submitted to high strain, but experiments with complex polymer systems have revealed that, at high strain, the torque signal can be distorted either ‘on the left’ or ‘on the right’, with respect to a vertical axis drawn at the first quarter of the cycle. Such differences do not reflect in the FT spectrum. Therefore, in order to supplement FT analysis, quarter cycle integration was developed as an easy data treatment technique to distinguish both types of distortion. The ratio of the first to second quarter torque signal integration, i.e. Q1/Q2, offers a clear distinction of the non-linear response of certain materials. With most pure polymers, Q1/Q2 ratio is always higher than one and tends to increase with strain amplitude. In such a case, the torque signal is always distorted ‘on the left’ (i.e. $Q1 > Q2$). With certain complex systems, Q1/Q2 is generally higher than one at (very) low strain, and then quickly passes below one as strain increases. It is believed that Q1/Q2 lower than one reflects some structural character of the material, which enhances their non-linearity. Figure 3.1.16 shows Q1/Q2 ratio versus strain amplitude for all gum (unmasticated) NR samples. In all cases, run2 has Q1/Q2 ratio higher than run1, thus demonstrating that the sample is sensitive to strain history, especially normal grades (RSS3, RSS3E, and STR5L). However viscosity stabilized grades (OMNR, STR5CV60, and SMR10CV) exhibit a smaller difference between runs 1 and 2 data. If one considers that gel regions in NR bring a kind of structural character in the material, then one would expect that some of the gel content is destroyed during run 1, so that Q1/Q2 ratio is higher during run 2, as indeed observed with the certain NR grades. Such results obviously call for a study of the mastication effect on NR samples (see hereafter). It is quite interesting to observe that partially RSS3 and RSS3E (Figure 3.1.16) tend to show intrinsic non-linearity (as revealed by Q1/Q2 ratios), which would result from a heterogeneous character, possibly due to semi-permanent aggregates of many molecules, i.e. gel.

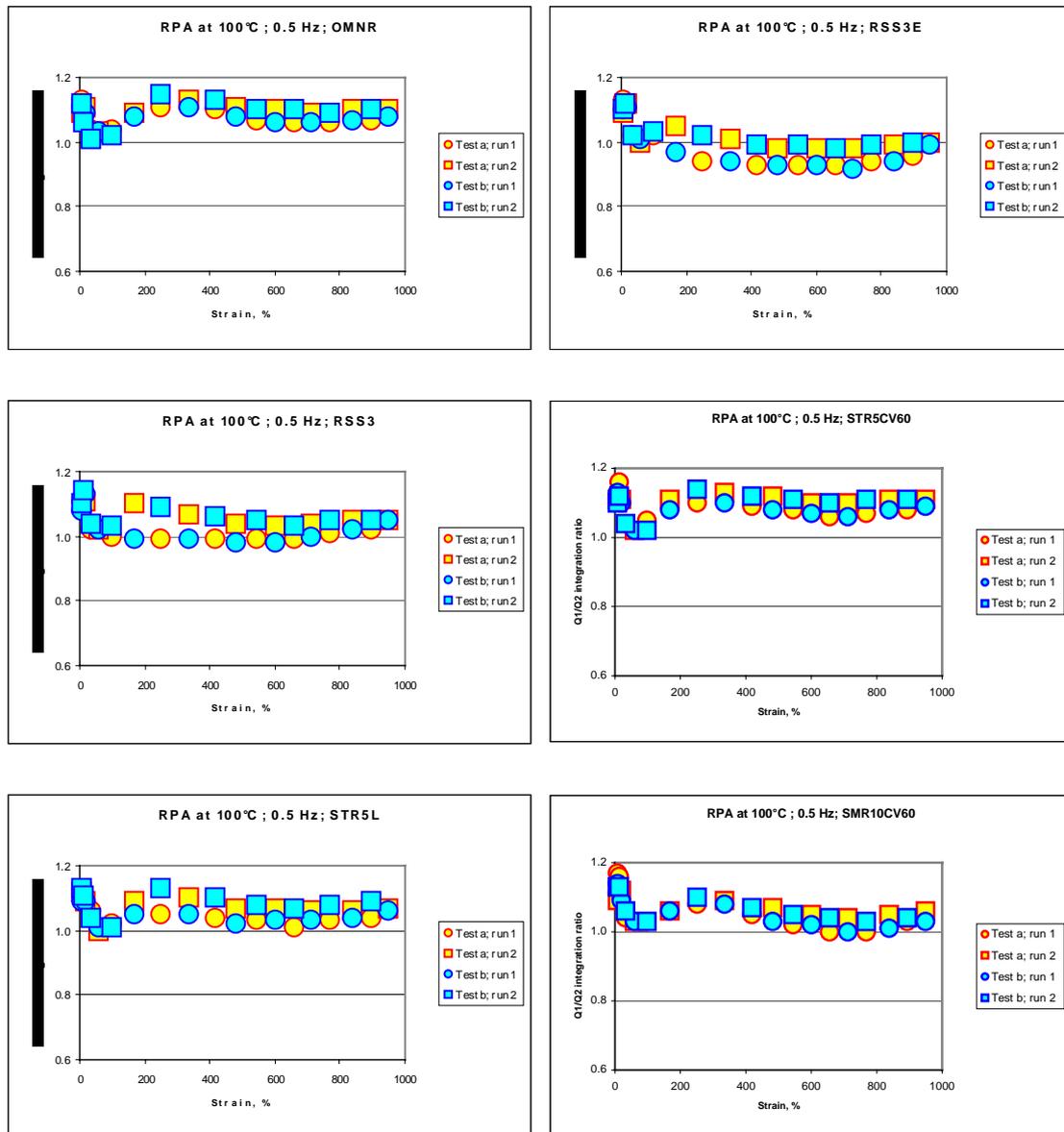


Figure 3.1.16 : Assessing the extrinsic/intrinsic non-linear viscoelastic character through quarter cycle torque integration of Natural Rubber gum samples; RPA-FT strain sweep tests at 0.5 Hz

3.1.5.3 Torque harmonics vs. strain

Figure 3.1.17 shows torque harmonics versus strain, i.e. the 3rd relative torque harmonic T(3/1), the 5th relative torque harmonic T(5/1); and the total torque harmonic content TTHC (i.e. the sum of the odd harmonics up to the 15th). Data are well reproducible with no difference between tests a and b, and no difference between runs 1 and 2. Torque signal harmonic appear sensitive to strain history, especially RSS samples (RSS3 and RSS3E; Figure 3.1.17), since torque harmonics of run 2 are higher than run1. As expected with respect to its highest molecular weight, strain induced crystallization occurring during run 1 is likely modifying the non-linear response as clearly reflected by torque harmonics. For STR5L, STR5CV60, and SMR10CV samples respectively, smaller differences are seen between runs 1 and 2 data. For STR5L (normal grade) and STR5CV60 (viscosity stabilized grade), the normal grade show a higher difference between runs 1 and 2 than the viscosity stabilized grade. In the case of OMNR, whose viscosity is reduced and stabilized, no difference is seen between runs 1 and 2. Whilst grades are similar, the two Ribbed smoked Sheets samples (RSS3 and RSS3E) exhibit significant differences that are likely related to their very origin (Thailand in the case of RSS3E; unknown in the case of RSS3). All NR samples exhibit S-shape curves which, at large strain, appear indeed to be converging towards a linear variation with strain. Such a behavior is modeled with the following equation:

$$TH(\gamma)=(TH_0+\alpha\gamma)\times[1-\exp(-C\gamma)]^D \quad 3.2$$

where the member $(TH_0+\alpha\gamma)$ expresses the linear variation of harmonics in the high strain region, while the member $[1-\exp(-C\gamma)]^D$ describes the onset of the non-linear viscoelastic response. Parameter D somewhat reflects the extent of the linear viscoelastic region (no harmonics), while parameter C indicates the strain sensitivity of the non-linear character. Fit parameters of Equation 3.2 are given in Tables 3.9 from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. For gum unmastered NR (Figure 3.1.18), no significant difference was seen between the different grade NR, except SMR10CV grade which tends to show slightly lower values for parameter α and parameter C than the other samples. It is interesting to observe that, for RSS3 and RSS3E, parameters TH_0 is higher for run 2 than for run 1, while viscosity stabilized grades (OMNR, STR5CV, SMR10CV) show run 1 higher than run 2. The contrary result is observed for parameter α , RSS3 and RSS3E show run 1 higher than run 2 but the viscosity stabilized and STR5L grades show run 2 higher than run 1. For parameter C, all samples show run 2 higher than run 1. Parameter D, for all samples except RSS3, shows run 2 higher than run 1.

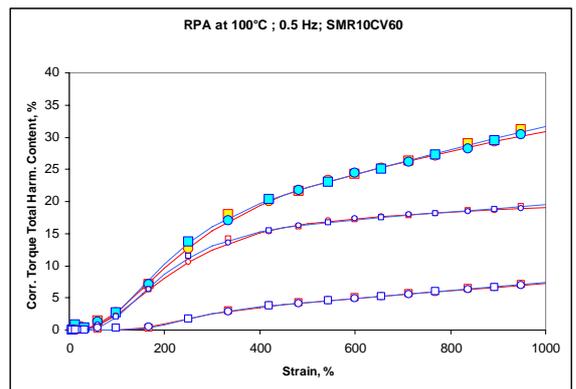
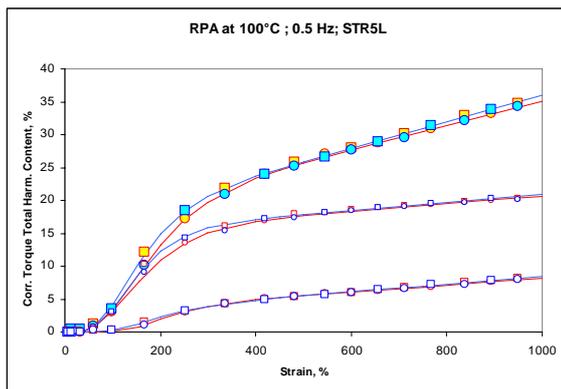
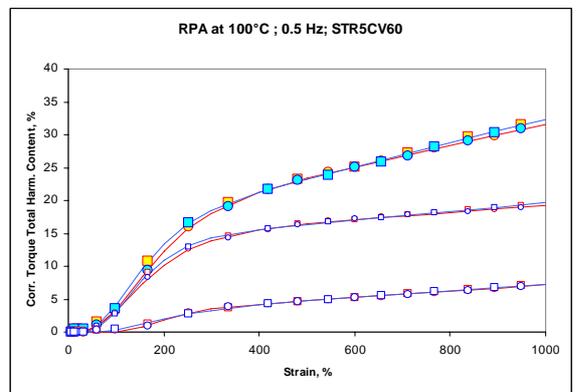
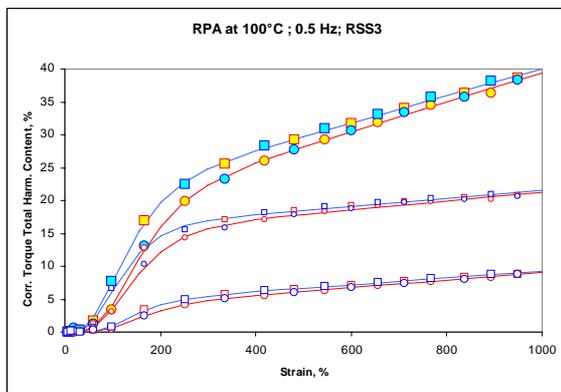
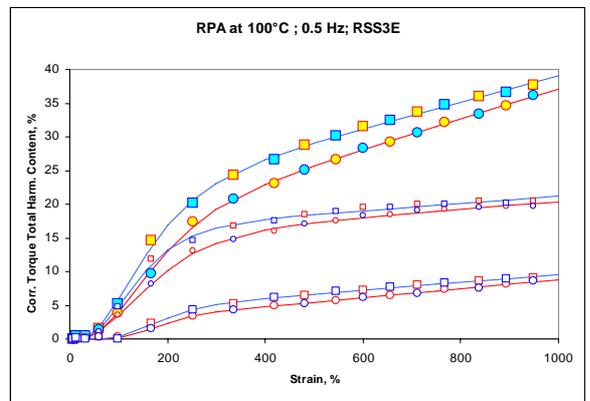
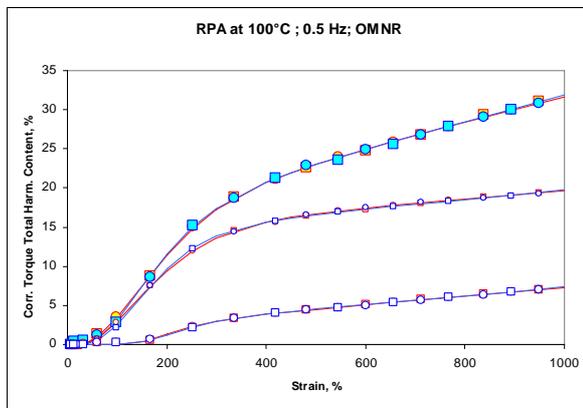


Figure 3.1.17 : RPA-FT; total harmonic content vs. strain for Natural Rubber gum samples

Table 3.1.9 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz of gum (unmasticated) NR samples; fit parameters of Equation 3.2

Sample		TTHC		T(3/1)		T(5/1)	
		Run1	Run2	Run1	Run2	Run1	Run2
OMNR	TH ₀	15.51	14.53	14.5	13.73	1.754	1.755
	α	0.0161	0.0174	0.0051	0.006	0.0055	0.0056
	C	0.0103	0.0119	0.0106	0.0128	0.0173	0.0169
	D	3.594	4.548	3.855	5.352	24.23	24.66
	r ²	0.999	0.998	0.999	1	0.9995	0.9997
STR5L	TH ₀	16.9	16.05	14.97	14.84	2.939	2.646
	α	0.0182	0.0199	0.0057	0.0061	0.0052	0.0058
	C	0.0124	0.0151	0.0129	0.0161	0.0157	0.0141
	D	5.03	5.857	4.906	6.622	16.3	8.382
	r ²	0.9999	0.9999	0.9998	0.9998	0.9995	0.9997
STR5CV	TH ₀	15.5	14.45	13.86	13.12	2.366	2.203
	α	0.0161	0.0179	0.0054	0.0065	0.0048	0.0051
	C	0.0122	0.0143	0.0124	0.0159	0.019	0.0131
	D	4.58	5.042	4.359	6.464	27.51	6.555
	r ²	0.9999	0.9998	0.9999	0.9999	0.9995	0.9996
RSS3	TH ₀	16.96	19.37	14.53	15.38	3.319	4.118
	α	0.0225	0.0207	0.0067	0.0062	0.0057	0.0051
	C	0.0156	0.0168	0.0162	0.019	0.0161	0.0189
	D	6.463	4.959	6.643	5.705	8.006	9.844
	r ²	0.9998	0.9998	0.9997	0.9995	0.9996	0.9996
RSS3E	TH ₀	14.72	19.37	14.88	15.78	2.115	3.865
	α	0.0224	0.0197	0.0055	0.0054	0.0067	0.0057
	C	0.012	0.0126	0.0104	0.015	0.0201	0.0162
	D	4.05	3.841	3.356	4.731	20.48	11.64
	r ²	0.9998	0.9997	0.9996	0.9992	0.9997	0.9993
SMR10CV	TH ₀	15.85	13.42	15.83	13.81	1.479	1.284
	α	0.0151	0.0183	0.0032	0.0057	0.0057	0.0061
	C	0.0081	0.0109	0.0081	0.0113	0.0129	0.0173
	D	3.063	4.247	3.214	4.972	12.34	34.69
	r ²	0.9998	0.9996	1	0.9999	0.9994	0.9995

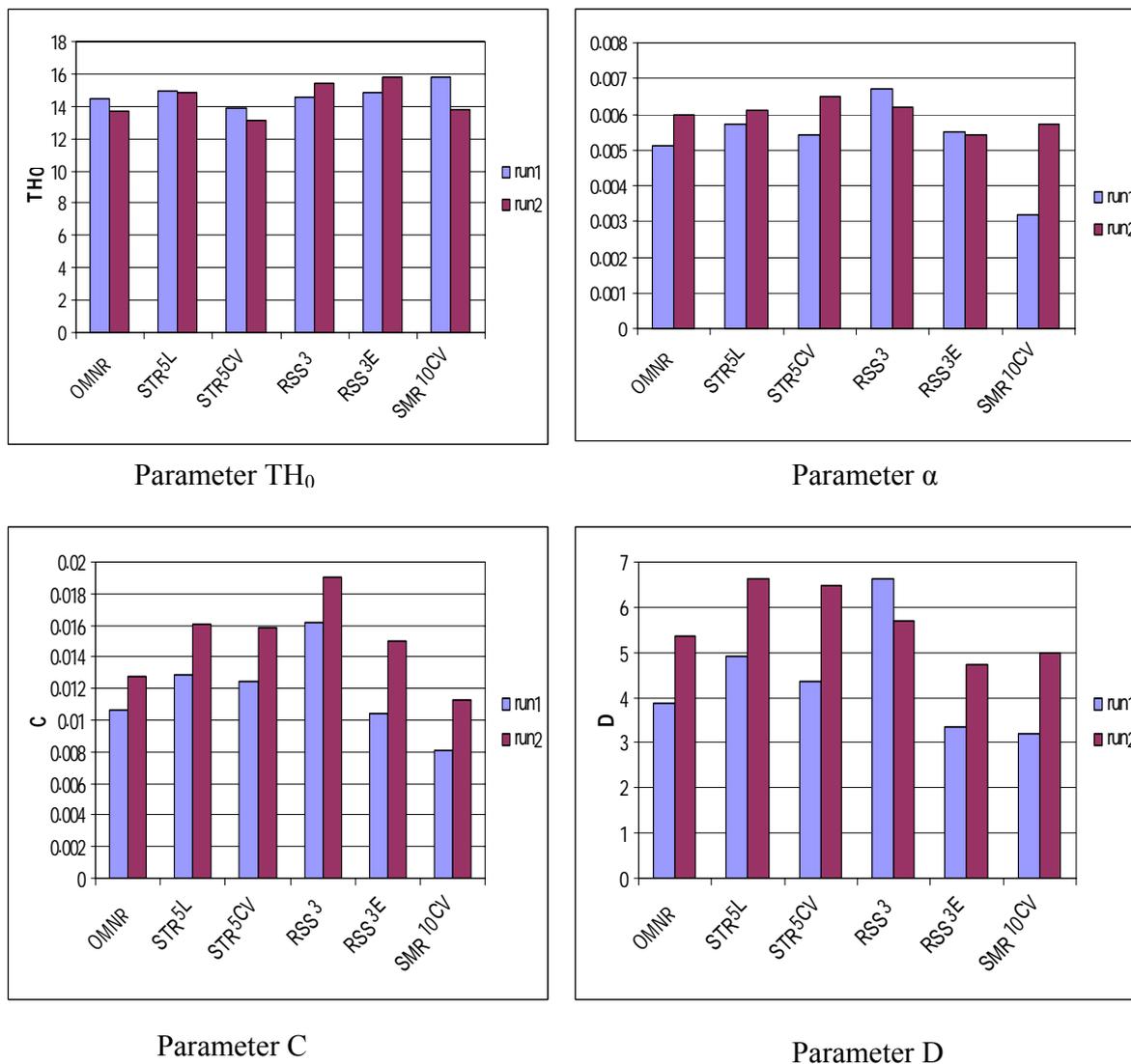


Figure 3.1.18 : RPA-FT on NR samples; 3rd relative torque harmonics T(3/1) with strain amplitude; comparing parameters given in Table 3.1.9

3.1.6 Conclusions Section 3.1

The ¹³C cross-polarization, magic angle spinning (CP-MAS) technique can distinguish the mobile from the immobile components so that significant differences can be observed between the NR grades tested. The gel content of OMNR, STR5L, STR5CV60 and SMR10CV is found to be around 5%, and in the case of RSS3 and RSS3E to be around 10%. All gum NR samples clearly show a linear viscoelastic region up to around 60% strain. RSS3 and RSS3E have the highest complex modulus and STR5L is stiffer than STR5CV60 OMNR and SMR10CV, respectively. For the mid-modulus critical strain (1/A), SMR10CV has the highest critical strain and while no significant difference is seen with the other samples, it can be considered that SMR10CV has the largest linear zone of

all the tested samples. Parameter B shows little difference between the various gum NR samples. Results show a good correlation between the molecular weight (Mn) of the different NR grades and the linear complex modulus. RSS samples (RSS3, RSS3E) exhibit an intrinsic non-linearity character but viscosity stabilized grades (OMNR, STR5CV60, SMR10CV) essentially show extrinsic non-linearity. Torque signal harmonics appear sensitive to strain history, torque harmonic of run 2 being generally higher than run 1. RSS grades exhibit the strongest strain history effects, according with their highest molecular weight. For STR5L (normal grade) and STR5CV60 (viscosity stabilized grade), the normal grade shows a higher strain history effect.

3.2 Studying mastication effects on selected NR grades

3.2.1 Effect of mastication on gel content and molecular weight

Tables 3.2.1 to 3.2.4 give all the results of the study on the mastication effects on SMR10CV and RSS3 samples. With respect to the planned experimental programme, some data are missing because unexpected problems and failure were met with the equipment. Available results allow however quite of clear idea of mastication effects to be obtained and are therefore reported as such. Molecular weight measurements in CIRAD, Montpellier were performed only on a limited series of masticated RSS3 samples, sufficient however to demonstrate several important aspects of the study.

Table 3.2.1 : Gel contents of masticated SMR10CV and RSS3 as determined by immersion in toluene at equilibrium time (16 days)

sample	Gel content (%) (measured in 1 month after mastication)	Gel content (%) (measured 1 year after mastication)
SMR10CV (unmasticated)	4	6
SMRM1 (60s)	1	5
SMRM2 (120s)	0	4
SMRM3 (240s)	0	1
RSS3 (unmasticated)	8	10
RSSM1 (240 s; 40 rpm)	2	6
RSSM2 (480 s; 40 rpm)	2	7
RSSM3 (960 s; 40 rpm)	0	2
RSSM7 (960 s; 50 rpm)	0	2
RSSM8 (1440 s; 50 rpm)	0	2
RSSM9 (1680 s; 50 rpm)	0	1

Table 3.2.2 Mixing energy and Mooney viscosity of masticated RSS3

Sample	Bale 1		Bale 2			
	Banbury mixer		Banbury mixer		Haake Rheomix	
	ME (MJ/m ³)	ML(1+4) 100°C	ME (MJ/m ³)	ML(1+4) 100°C	ME (MJ/m ³)	ML(1+4) 100°C
RSS3 (unmasticated)	-	91	-	90	-	90
RSSM1(240s;40rpm)	756	78	830	77	n.a	71
RSSM2(480s;40rpm)	1328	76	1191	76	n.a	62
RSSM3(960s;40rpm)	2414	61	2611	52	n.a	52
RSSM7(960s;50rpm)	n.a	58	-	-	-	-
RSSM8(1440s;50rpm)	n.a	51	-	-	-	-
n.a. : not available because of problems/failure of the equipment						

Table 3.2.3 : Mixing energy and Mooney viscosity of masticated SMR10CV in Banbury mixer

Sample	ML(1+4) _{100°C}	ME (MJ/m ³)
SMR10CV	71	-
SMRM1(60s)	55	176
SMRM2(120s)	52	330
SMRM3(240s)	49	610

Table 3.2.4 : Molecular weight of masticated RSS3 (in Banbury mixer)

Sample	Mz (kg/mol)	Mw (kg/mol)	Mn (kg/mol)
RSS3 (unmasticated)	2934	1755	1051
RSSM1 (240s)	2050	1303	834
RSSM2 (480s)	1723	1132	735
RSSM3 (960s)	1189	792	511

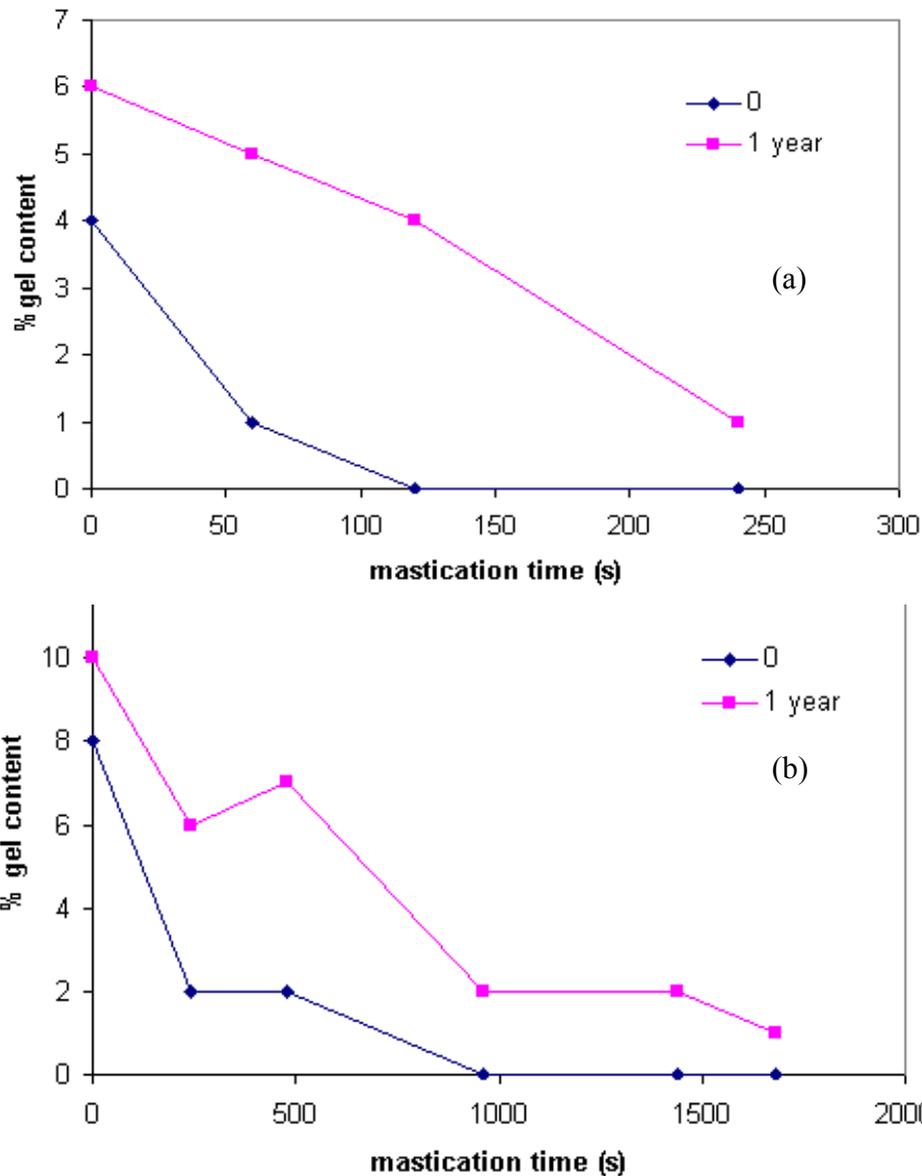


Figure 3.2.1 : Gel content (%) of masticated SMR10CV(top) and RSS3 (bottom) as measured by immersion in toluene for 16 days (equilibrium time); measurements were performed 1 month and 1 year after mastication; note the different mastication time scales for the two NR grades.

The gel content of masticated SMR10CV is illustrated in Figure 3.2.1 (a), the gel contents of masticated RSS3 is shown in Figure 3.2.1 (b). Gel content measurements were performed either directly after the mastication experiments or after one year storage (room temperature, in darkness) of masticated samples. As can be seen, one year storage brings around 2 % higher gel content on unmasticated samples but the relative mastication effects remain essentially unaffected by the storage. An unexpected

observation is that the constant viscosity grade exhibits the same gel content increase upon storage as the Ribbed Smoked Sheet grade. For both NR grades, the percentage gel content decreases with increasing mastication time, but in a faster manner in the case of the constant viscosity grade. For masticated SMR10CV, the gel content was found to be almost zero when the mastication time reached 120 s (SMRM2). In the case of masticated RSS3, the gel content was found to be almost zero when the mastication time reached 960 s (RSSM3). There is thus a marked difference between the two grades in what the mastication sensitivity is concerned. From molecular weight measurements (see gum samples analysis result; Table 3.1.8), the Ribbed Smoked Sheet (RSS3) has molecular weights about twice higher than the CV grade (SMR10CV60), so that the significantly larger mastication times required to vanish the gel content of RSS3 is at first sight an expected result if one considers that the gel content is commensurable with the molecular weight. As noted above, the gel content of NR samples after ageing for 1 year under ambient condition tends to show a slight increase of about 2-4 % in both cases (SMR10CV60 and RSS3). This result is in agreement with the work of Yunyongwattanakorn *et al.* [6], which showed that the gel content of NR increases during storage and then levels off at about 5% after keeping the material for 14 months under ambient condition. Figure 3.2.2 shows that, whatever the NR grade is, there is a simple correlation between the mixing energy (in Banbury mixer) and the mastication time. The correlation coefficient is about 0.99 in all cases (not only with respect to the different grades; CV grade (SMR10CV) and normal grade RSS3; but also with respect to the same grade (RSS3) but with samples from different bales). It is interesting to see that for the same mastication time (240s), RSS3 samples need slightly higher mixing energy than SMR10CV, an effect likely related to their higher molecular weights. The relationships between Mooney viscosity or molecular weight and mixing energy for masticated RSS3 samples are illustrated in Figure 3.2.3. In both cases, near perfect linear correlations are observed (correlation coefficient of about 0.97). That, upon mastication, both the Mooney viscosity and the molecular weight (as measured through GPC or related techniques) of a given NR grade decrease with increasing mixing work input is a frequently reported observation. But it would be dubious to conclude that the simple Mooney test is a safe indication of the molecular weight of an elastomer since synthetic rubbers do not show any significant decrease in M_n upon mastication while their Mooney viscosity does [7, 8].

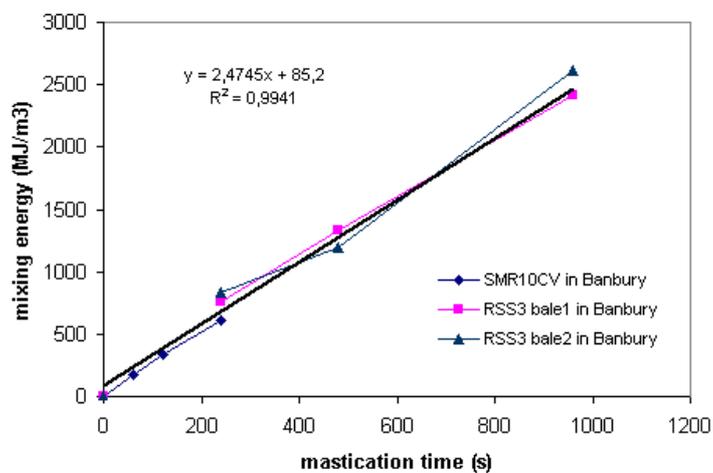


Figure 3.2.2 : Mixing energy versus mastication time in Banbury mixer for RSS3 and SMR10CV samples

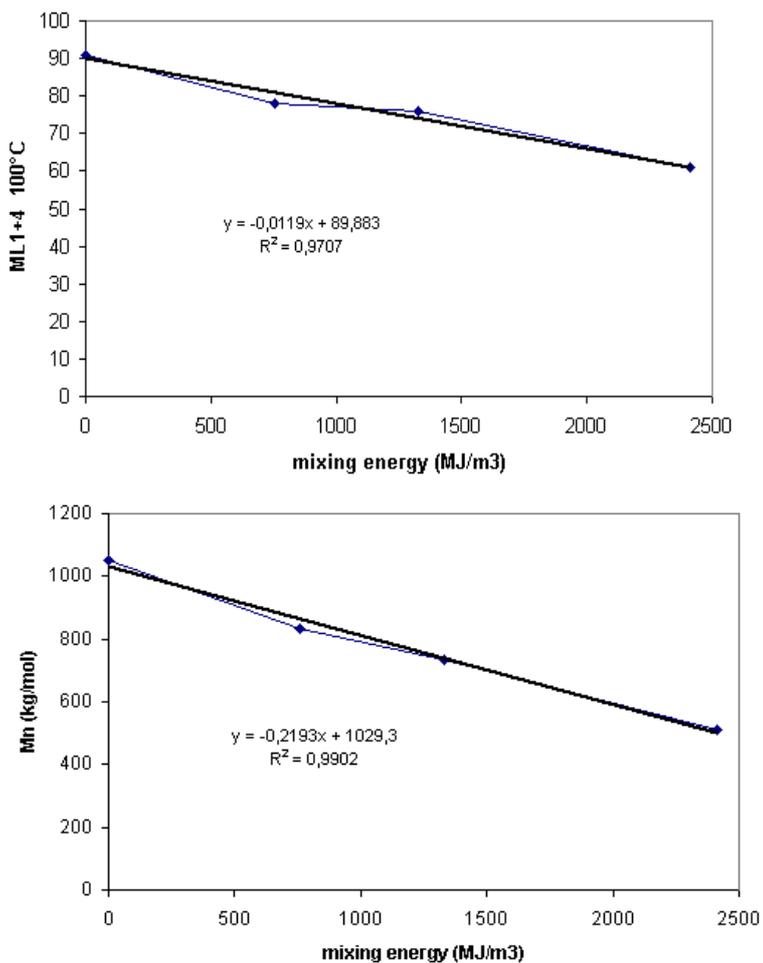


Figure 3.2.3 : Molecular weight (Mn) and Mooney viscosity versus mixing energy of masticated RSS3 in Banbury mixer

3.2.2 RPA results on masticated NR samples

3.2.2.1 Complex modulus versus strain

Complex modulus G^* versus strain curves of masticated NRs are shown in Figures 3.2.4 and 3.2.5. In all cases, the two tested samples (a and b) gave identical results thus demonstrating the excellent homogeneity of tested materials as well as the reproducibility of the testing method. It is seen that the general trend is a slight decrease of the complex modulus as mastication time increases. Dynamic strain softening (DSS) effects of masticated samples can be easily analyzed by using a model corresponding to equation 3.1 described above. Fit parameters of Equation 3.1 are given in Tables 3.2.5 and 3.2.6, from RPA-FT results at 0.5 Hz.

RSS3 and SMR10CV samples were masticated for different times in Banbury and Haake mixers. Figure 3.2.6 shows the modulus in the linear region (G^*_0) versus mastication time for SMR10CV (a) and RSS3 (b). It is seen that the complex modulus (G^*_0) decreases with increasing mastication time. According to Hamed [9], who studied the role of the molecular weight of NR on the green strength, the latter property decreases when the molecular weight decreases. Our results show a similar trend if one considers that the green strength and the complex dynamic modulus in the linear region, i.e. G^*_0 , are the same type of information. As can be seen in Figure 3.2.6, this effect is quite large in the case of RSS3 but more modest with SMR10CV in agreement with the expected benefits of hydroxylamine stabilization. For gum unmasticated RSS3 samples (the lower left plot in Figure 3.2.6 (b)), run1 yields a higher complex modulus (G^*_0) than run2; an effect that could be assigned to some strain-induced crystallization. However, the difference between runs 1 and 2 decreases with increasing mastication time. Such a result is not observed with SMR10CV (Figure 3.2.6 (a)), a small difference is seen between run1 and run2 data but the difference does not change when increasing the mastication time.

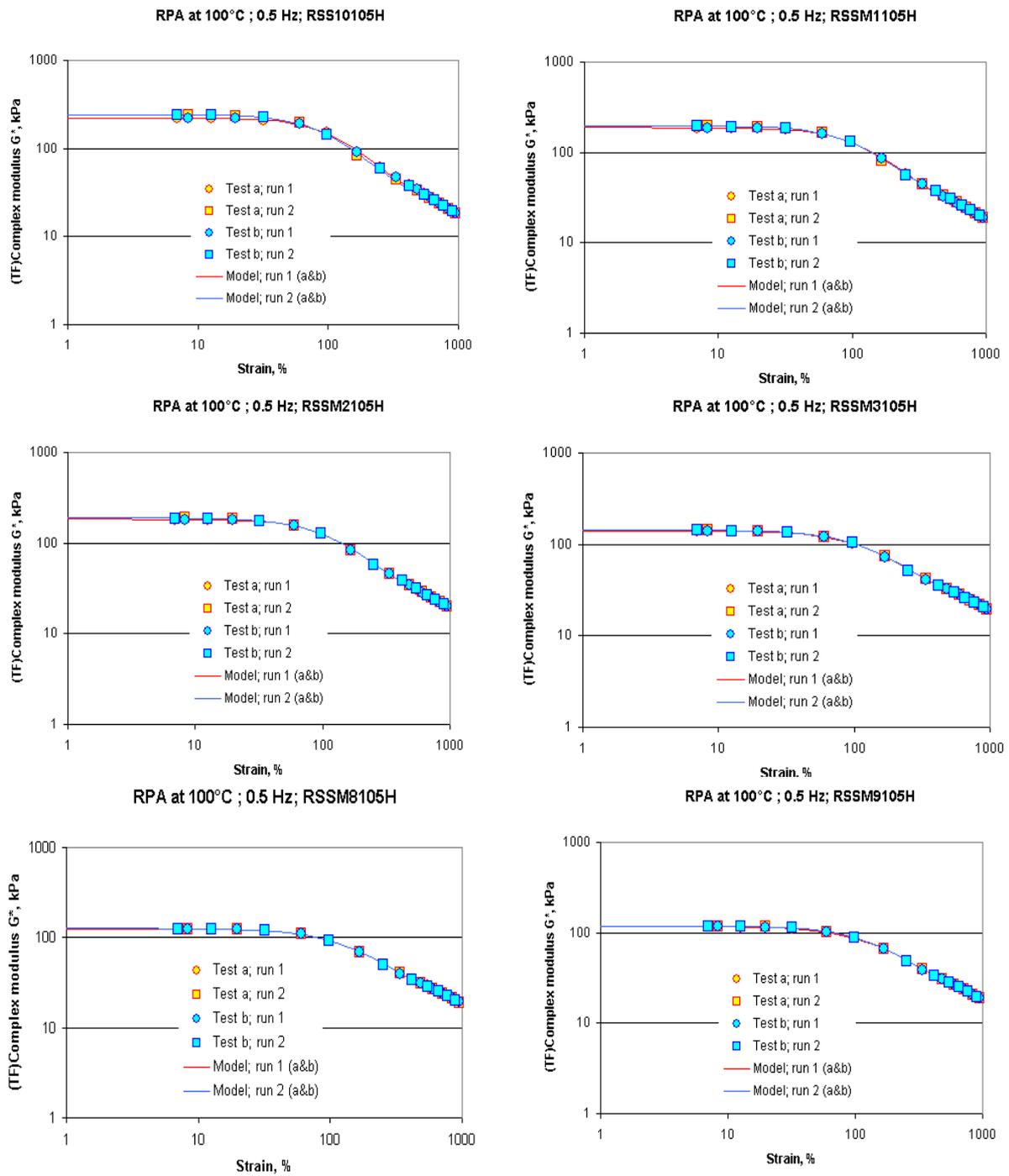


Figure 3.2.4 : RPA-FT at 100 °C on masticated RSS3 gum samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

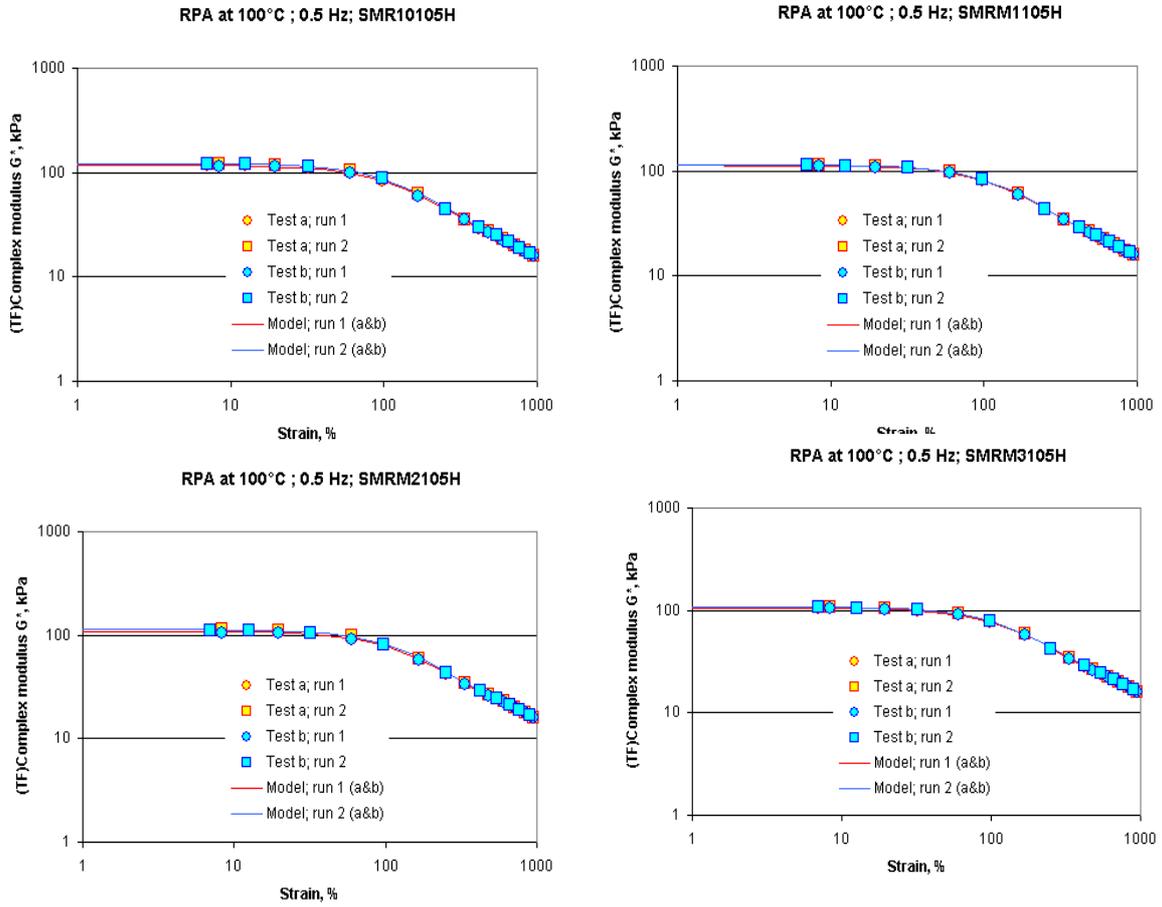


Figure 3.2.5 : RPA-FT at 100 °C on masticated SMR10 gum samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

Table 3.2.5 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz on masticated RSS3; fit parameters of Equation 3.1

sample	RSS3(bale1) In Banbury		RSS3(bale2) In Banbury		RSS3(bale2) In Haake		
	Run1	Run2	Run1	Run2	Run1	Run2	
RSS3(unmasticated)	G^*_0 (kPa)	223.4	242.3	228.4	233.1	228.4	233.1
	1/A%	130.3	111.6	126.1	112.3	126.1	112.3
	B	1.996	1.913	1.847	1.872	1.847	1.872
	r^2	0.9997	0.9997	0.9996	0.9997	0.9996	0.9997
RSS3(240s; 40 rpm)	G^*_0 (kPa)	188.4	196.5	183.6	188.7	161.9	165.6
	1/A%	138.7	129.1	137.8	127.8	143.4	134.1
	B	1.877	1.883	1.88	1.853	1.848	1.888
	r^2	0.9999	0.9997	0.9998	0.9997	0.9998	0.9998
RSS3(480s; 40 rpm)	G^*_0 (kPa)	183.1	189	180.7	188.9	151.6	153.6
	1/A%	141	134.7	138.5	127.3	145.9	141
	B	1.831	1.82	1.873	1.85	1.811	1.848
	r^2	0.9998	0.9998	0.9998	0.9997	0.9999	0.9998
RSS3(960s; 40 rpm)	G^*_0 (kPa)	141.5	143.5	134.1	142	128.5	128.9
	1/A%	152.8	152.5	152.5	144	151.5	152.2
	B	1.758	1.703	1.763	1.684	1.763	1.749
	r^2	0.9999	0.9999	0.9998	0.9998	0.9995	0.9999
RSS3(960s; 50 rpm)	G^*_0 (kPa)	133.2	135	-	-	-	-
	1/A%	157.7	157.4	-	-	-	-
	B	1.751	1.705	-	-	-	-
	r^2	0.9999	0.9998	-	-	-	-
RSS3(1440s; 50 rpm)	G^*_0 (kPa)	125.1	126.2	-	-	-	-
	1/A%	163	163	-	-	-	-
	B	1.709	1.659	-	-	-	-
	r^2	0.9999	0.9998	-	-	-	-
RSS3(1440s; 50 rpm)	G^*_0 (kPa)	117.1	119	-	-	-	-
	1/A%	168.9	168.2	-	-	-	-
	B	1.67	1.639	-	-	-	-
	r^2	0.9999	0.9999	-	-	-	-

Table 3.2.6 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz on masticated SMR10CV; fit parameters of Equation 3.1

sample	SMR10CV In Banbury		
	Run1	Run2	
RSS3(unmasticated)	G^*_0 (kPa)	117.4	122.4
	1/A%	154.6	153.6
	B	1.622	1.676
	r^2	0.9999	0.9999
RSS3(60s; 40 rpm)	G^*_0 (kPa)	112.7	114
	1/A%	157.4	157.8
	B	1.675	1.703
	r^2	0.9999	0.9998
RSS3(120s; 40 rpm)	G^*_0 (kPa)	109.2	113.2
	1/A%	158.4	157.8
	B	1.676	1.688
	r^2	0.9994	0.9997
RSS3(240s; 40 rpm)	G^*_0 (kPa)	105.6	108.2
	1/A%	161.2	161
	B	1.64	1.659
	r^2	0.9999	0.9998

Table 3.2.7 : Tan δ at 10% strain of masticated RSS3 and SMR10CV

sample	Test a		Test b	
	Run1	Run2	Run1	Run2
RSS3 ^a (unmasticated)	0.194	0.200	0.193	0.195
RSSM1 ^a (240s;40rpm)	0.265	0.271	0.262	0.272
RSSM2 ^a (480s;40rpm)	0.292	0.294	0.291	0.296
RSSM3 ^a (960s;40rpm)	0.407	0.413	0.406	0.416
RSSM7 ^a (960s;50rpm)	0.433	0.424	0.433	0.432
RSSM8 ^a (1440s;50rpm)	0.455	0.469	0.464	0.473
RSSM9 ^a (1680s;50rpm)	0.502	0.502	0.496	0.503
RSS300 ^b (unmasticated)	0.190	0.205	0.193	0.202
RSS304 ^b (240s;40rpm)	0.267	0.282	0.263	0.283
RSS308 ^b (480s;40rpm)	0.275	0.293	0.273	0.290
RSS316 ^b (960s;40rpm)	0.424	0.437	0.418	0.439
RSS00 ^c (unmasticated)	0.207	0.219	0.206	0.218
RSS04 ^c (240s;40rpm)	0.283	0.299	0.285	0.300
RSS08 ^c (480s;40rpm)	0.321	0.335	0.318	0.334
RSS16 ^c (960s;40rpm)	0.406	0.414	0.399	0.411
SMR10CV (unmasticated)	0.405	0.394	0.411	0.391
SMRM1 ^d (60s;40rpm)	0.411	0.416	0.429	0.422
SMRM2 ^d (120s;40rpm)	0.435	0.427	0.460	0.435
SMRM3 ^d (240s;40rpm)	0.460	0.445	0.471	0.454
^a RSS3 sample bale1 masticated in Banbury mixer ^b RSS3 sample bale 2 masticated in Banbury mixer ^c RSS3 sample bale 2 masticated in Haake Rheomix ^d SMR10CV sample masticated in Banbury				

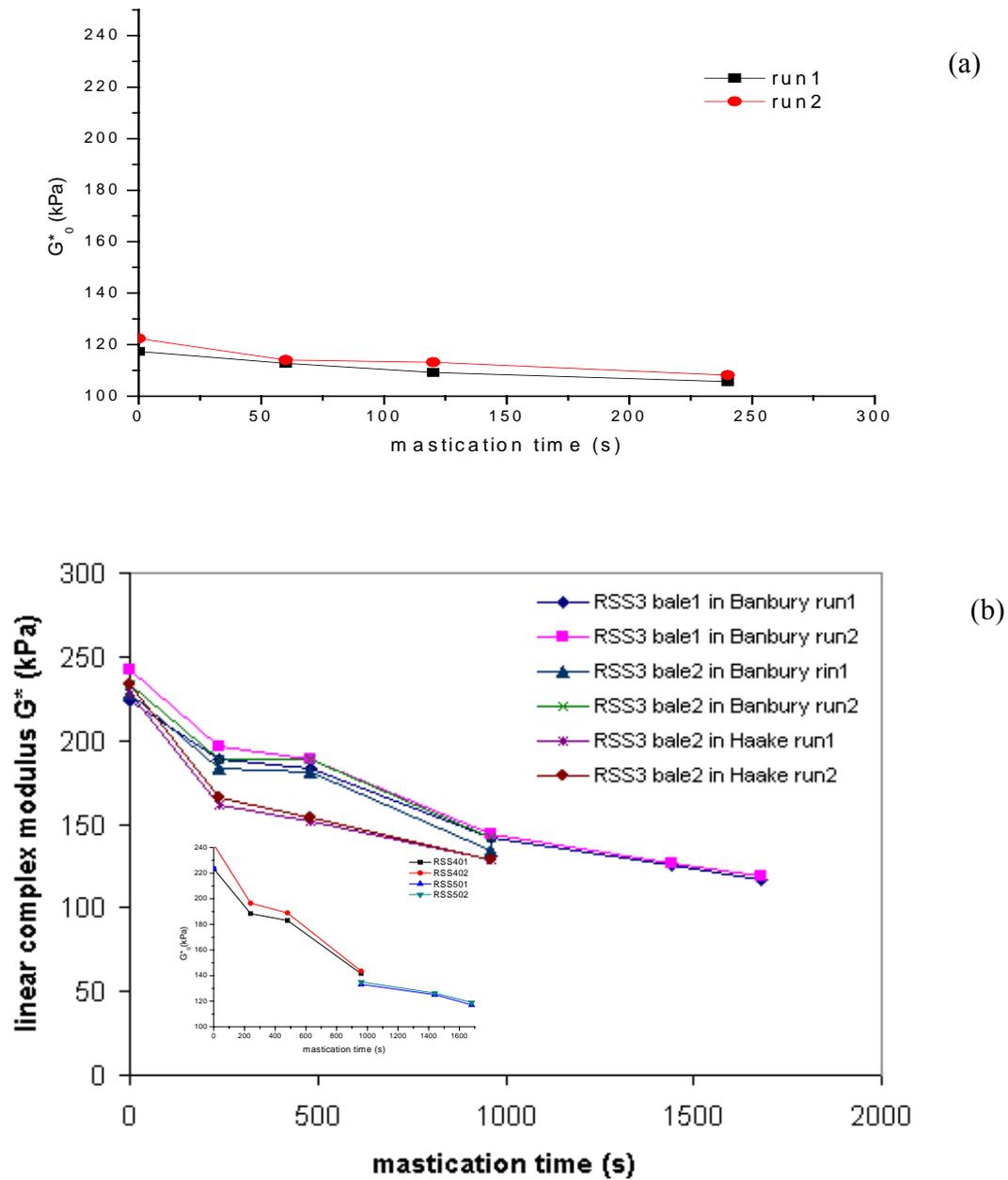


Figure 3.2.6 : RPA-FT at 100 °C on masticated NR samples; G^*_0 vs. mastication time; (a) SMR10CV; (b) RSS3

The mid-modulus critical strain ($1/A$) is somewhat related with the extent of the linear viscoelastic region. For masticated NR samples, the critical strain value changes with longer mastication time (Figure 3.2.7) : a net increase is clearly observed in the case of RSS3 while SMR10CV exhibits a more modest one. In the case of masticated SMR, very

small, if any, differences are seen between run1 and run2. Masticated RSS3 shows a completely different behavior : the difference between run1 and run2 decreases when increasing the mastication time until no significant difference is seen when the mastication time equals 960 s (RSSM3) as shown in the lower left plot of Figure 3.2.7 (b). In the case of SMRM3 and RSSM9, both samples have the same Mooney viscosity [$ML(1+4)_{100^{\circ}C} = 49$ and 48 respectively], but RSSM9 has a significantly higher complex modulus (G^*_0) and critical strain ($1/A$) than SMRM3. This implies that NR samples can indeed have very similar Mooney viscosities, but will process very differently. The parameter B is an indication of the strain sensitivity of the material. In the case of masticated NR samples (Figure 3.2.8), parameter B obviously decreases with longer mastication time for RSS3 but SMR10CV shows only a slight increase in the first period of mastication time (60s), followed by a slight decrease. Figure 3.2.9 shows the variation of $\tan\delta$ versus mastication time of masticated RSS3 (a) and masticated SMR10CV (b). As can be seen, $\tan\delta$ increases with increasing mastication time, a net increase in the case of RSS3 and only a slight one in the case of SMR10CV. This would suggest that the (dynamic) viscous character of NR is somewhat increased through mastication, with respect to dynamic elasticity. This is in agreement with the correlation between $\tan\delta$ and molecular weight of masticated RSS3 samples as shown in Figure 3.2.10. In all cases (Figure 3.2.6 to Figure 3.2.10), there are no significant difference when samples are taken from two bales of the same grade (RSS3 bale 1 and bale2) and the mixing equipment (Haake Rheomix or Banbury mixer) imparts no significant effect.

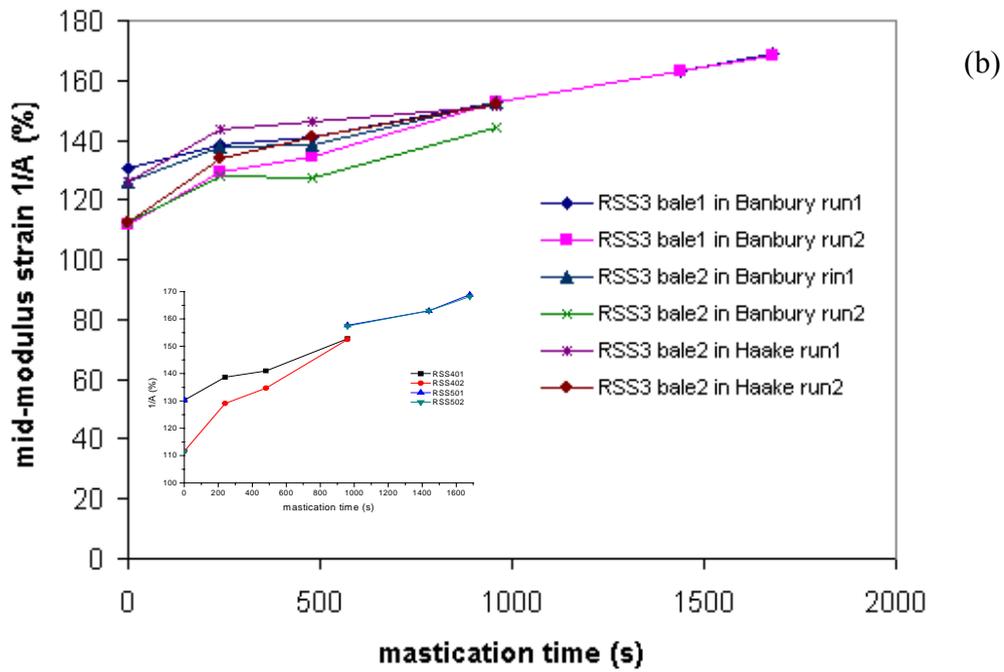
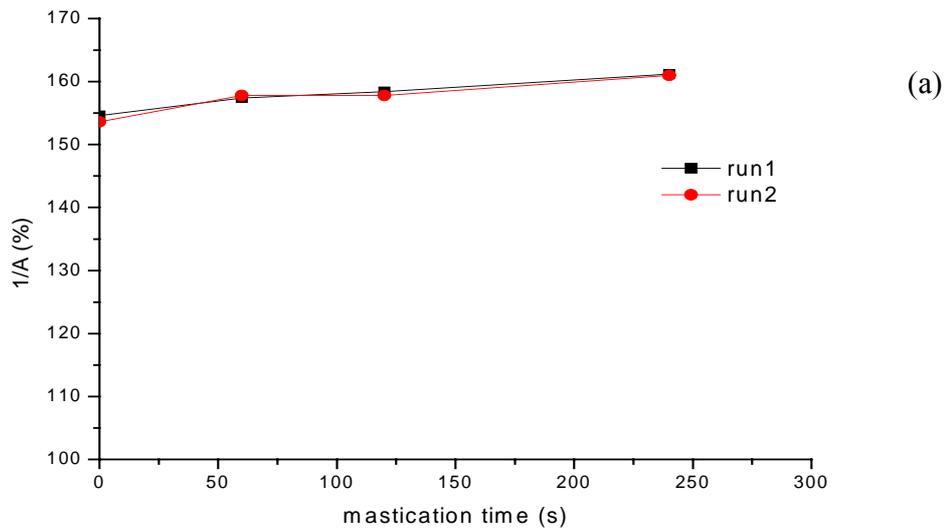
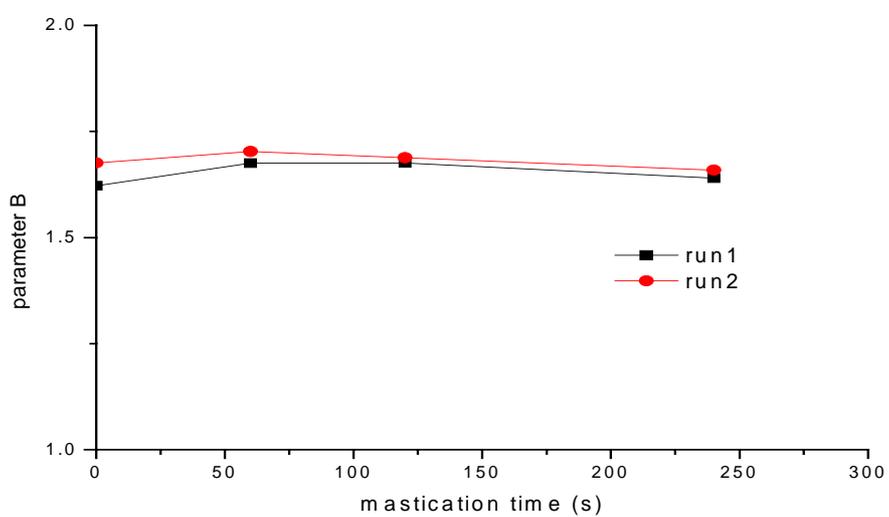
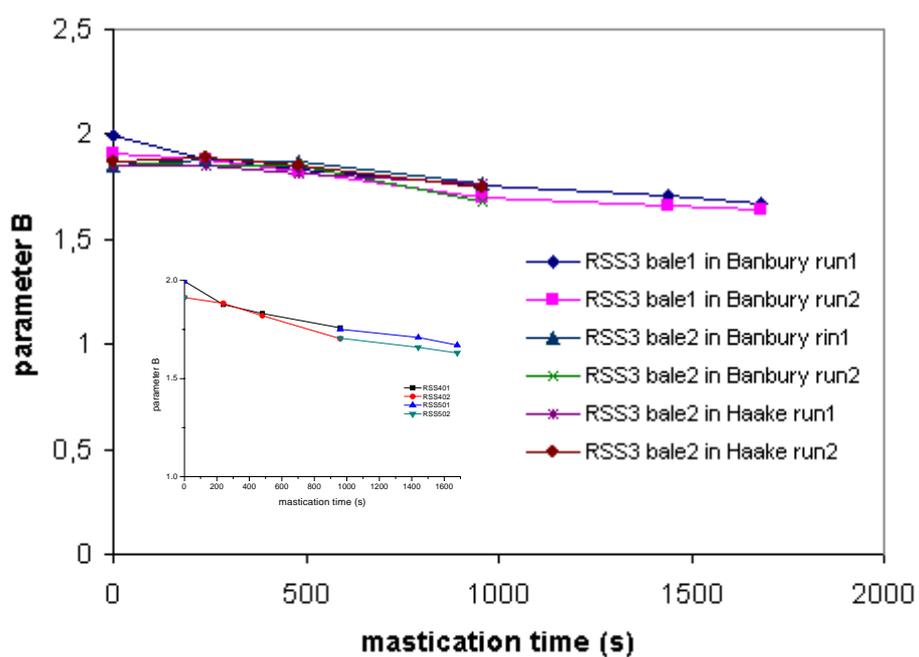


Figure 3.2.7 : RPA-FT at 100 °C on masticated NR samples; parameter 1/A of Equation 3.1 vs. mastication time; (a) SMR 40rpm; (b) RSS 40 rpm; RSS 50 rpm



(a)



(b)

Figure 3.2.8 : RPA-FT at 100 °C on masticated NR samples; parameter B of Equation 3.1 vs. mastication time; (a) SMR10CV; (b) RSS3

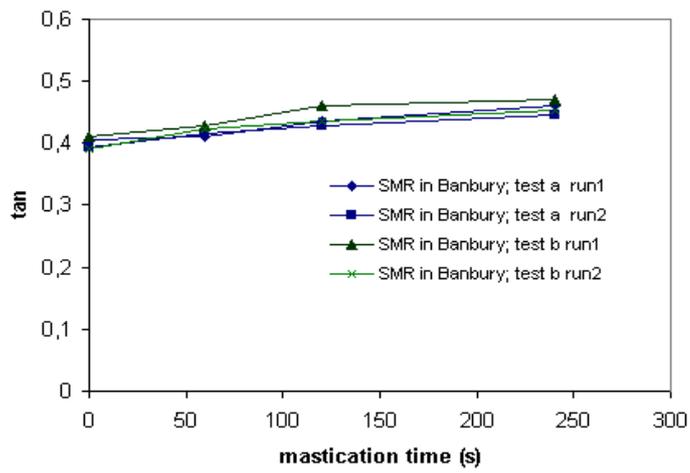
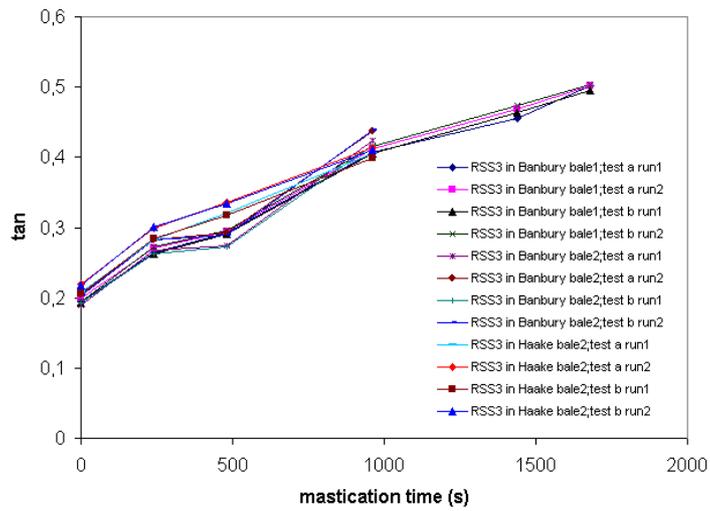


Figure 3.2.9 : Tan δ at 10% strain of masticated RSS3 and SMR10CV

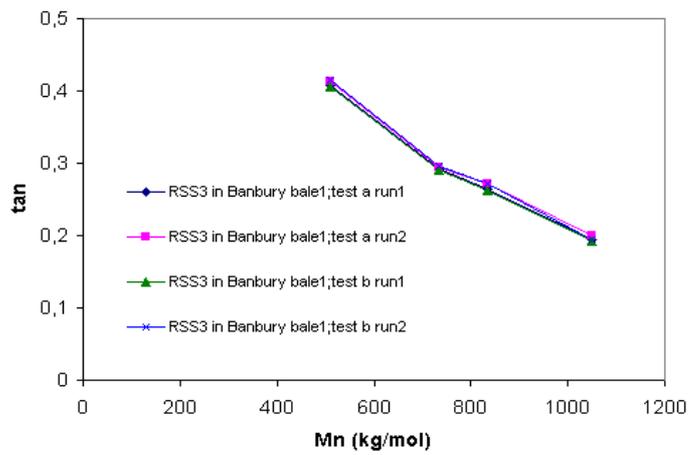


Figure 3.2.10 : Tan δ at 10% strain versus molecular weight of masticated

3.2.2.2 Quarter torque signal integration

Figure 3.2.11 and Figure 3.2.12 show Q1/Q2 ratio versus strain amplitude for all gum masticated NR samples. In all cases, run2 has Q1/Q2 ratio higher than run1, thus demonstrating that the sample is sensitive to strain history. If one considers that gel regions in NR brings a kind of structural character in the material, then one would expect that some of this gel is destroyed during run1, so that Q1/Q2 ratio is higher during run 2, as indeed observed with the certain NR grades. A corresponding evolution is thus expected with masticated NR samples (Figure 3.2.11 and Figure 3.2.12). For instance, the gel content of RSS3 sample when the mastication time is longer than 960 s (RSSM3 in Figure 3.2.11) is found to be almost zero, and therefore Q1/Q2 ratios exhibit very small, if any, difference between runs 1 and 2. Accordingly, with SMR10CV samples, when the mastication time is more than 120 s (SMRM2 in Figure 3.2.12), the gel content of the samples is found to be almost zero, and Q1/Q2 ratios show no significant difference between runs 1 and 2. This implies that the gel content in NR is sensitive to strain history effects. It is quite interesting to observe that RSS3 (Figure 3.2.11) tend to partially show intrinsic non-linearity (as revealed by Q1/Q2 ratios), which would result from a heterogeneous character, possibly due to semi-permanent aggregates of many molecules, i.e. gel, and that this character disappears upon mastication (Figure 3.2.11). The masticated RSS3 samples remain nevertheless extrinsically non-linear because they exhibit non-linearity through the application of a sufficiently large strain as well as gum unmasticated OMNR and STR5CV samples. In the case of masticated NR samples (Figure 3.2.11 to Figure 3.2.12), Q1/Q2 ratio is higher than one at very low strain, then quickly decreases to about one and re-increases up to maximum value at a given strain, i.e. X (%) as indicated in the figures. This strain value (X) increases with longer mastication time then remains constant when the mastication time is longer than 120 s for SMR10CV and longer than 960 s for RSS3 sample. This must be correlated with the gel content of masticated samples which is found to be almost zero.

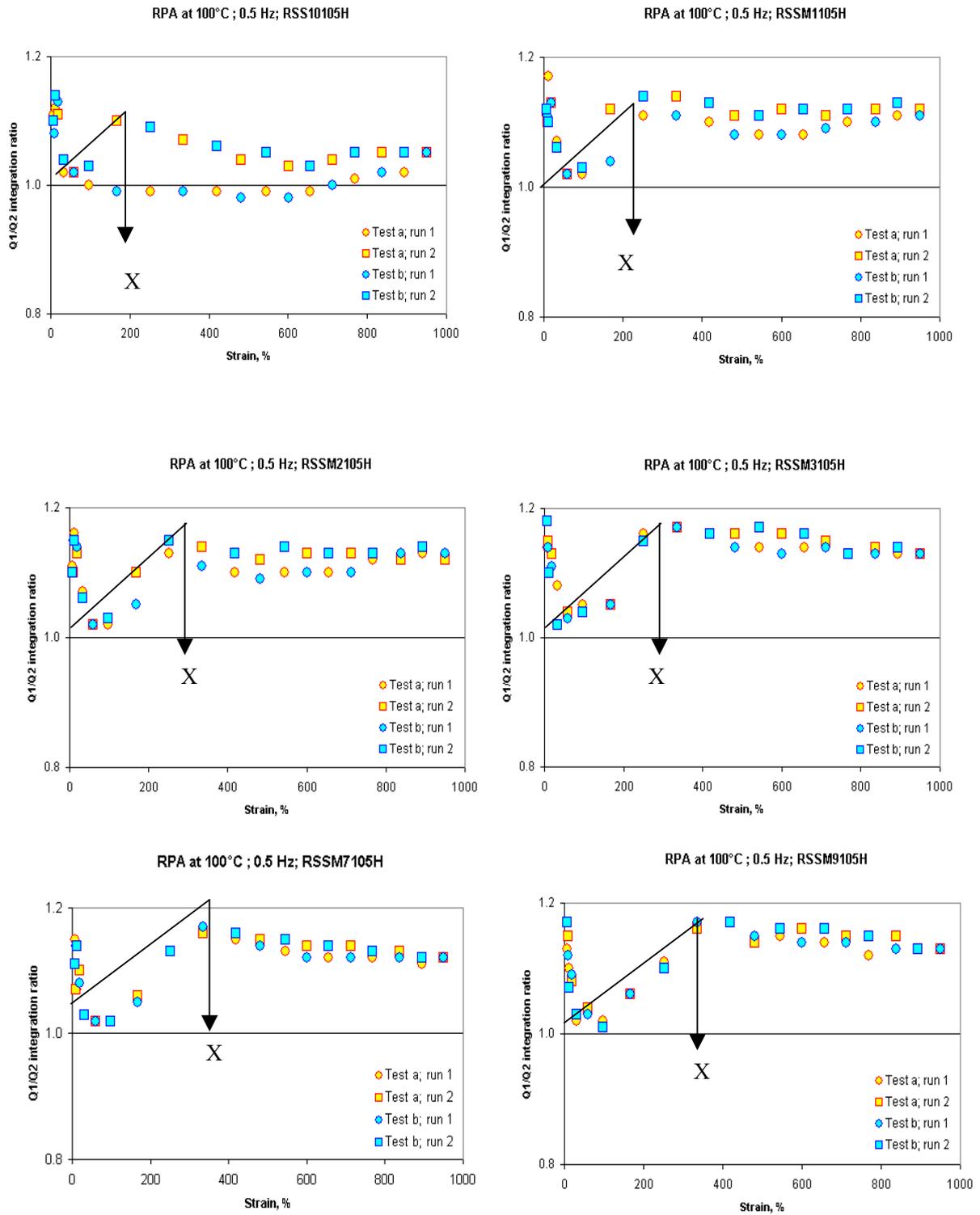


Figure 3.2.11 : Assessing the extrinsic/intrinsic non-linear viscoelastic character through quarter cycle torque integration of masticated RSS3 gum samples; strain sweep tests at 0.5 Hz

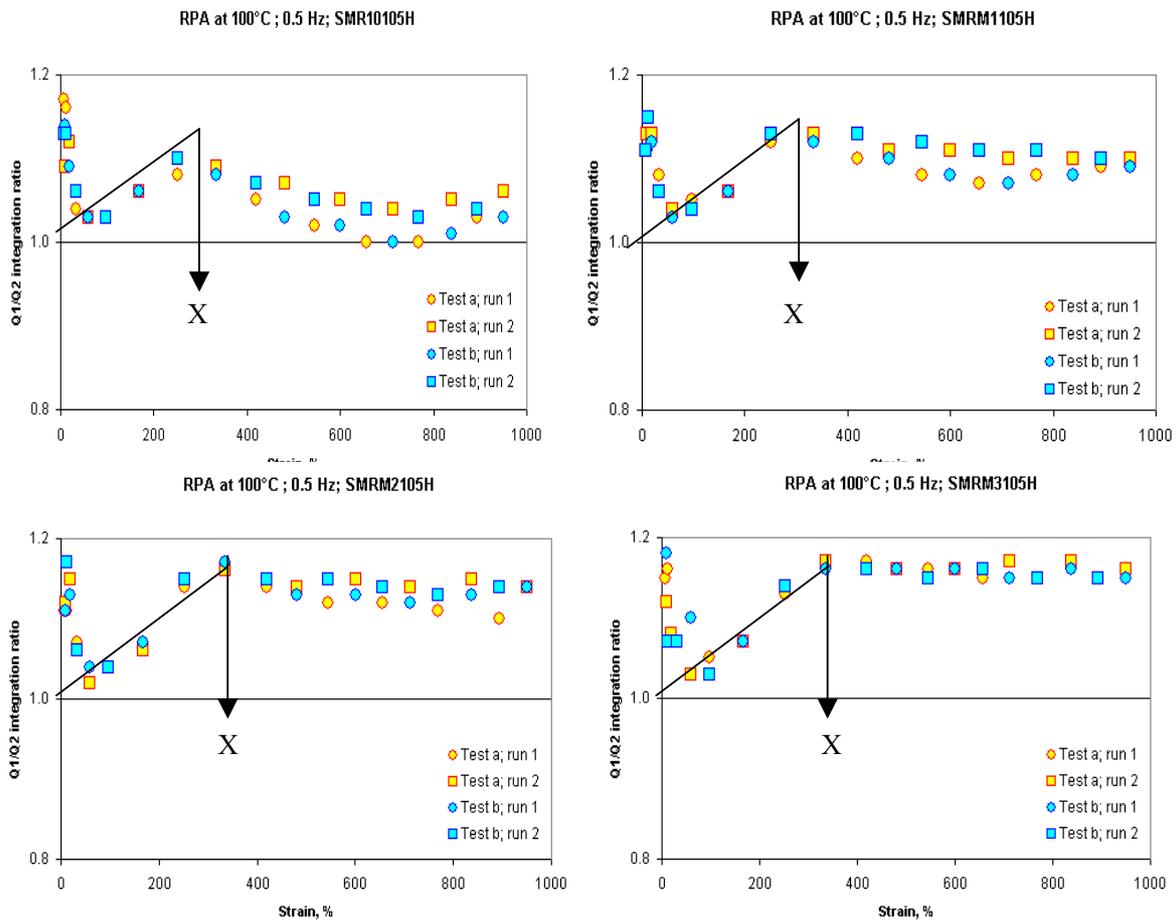


Figure 3.2.12 : Assessing the extrinsic/intrinsic non-linear viscoelastic character through quarter cycle torque integration of masticated SMR10CV gum samples; strain sweep tests at 0.5 Hz

3.2.2.3 Torque harmonics vs. strain

Figures 3.2.13 and 3.2.14 show torque harmonics versus strain, i.e. the 5th relative torque harmonic T(5/1); the 3rd relative torque harmonic T(3/1); and the total torque harmonic content TTHC (i.e. the sum of the odd harmonics up to the 15th). Data are well reproducible with no difference between tests a and b, and no difference between runs 1 and 2. Torque signal harmonic appear sensitive to strain history, especially RSS3 sample : torque harmonics curves of run 2 are higher than run1. As expected with respect to its highest molecular weight, strain induced crystallization occurring during run 1 is likely modifying the non-linear response as clearly reflected by torque harmonics. As can be seen, the difference disappears when RSS3 samples is masticated for 960 s (Figure 3.2.13; RSSM3). The same result can be seen for masticated SMR10CV but the difference disappears when SMR10CV is masticated for 60 s only (Figure 3.2.14; SMRM1). Accordingly the gel content of masticated samples was found to be almost

zero. This implies that mastication can eliminate strain history effects of NR materials and that the constant viscosity grade (SMR10CV) is more sensitive than the RSS grade. All NR samples exhibit S-shape curves which, at large strain, appear indeed to be converging towards a linear variation with strain. Such a behavior is modeled with equation 3.2 as introduced above. It is worth reminding here that the first member of this equation, i.e. $TH_0 + A\gamma$ expresses a linear variation of harmonics in the high strain region, while the second member $[1 - \exp(-C\gamma)]^D$ describes the onset of non-linear viscoelastic response. Parameter D somewhat reflects the extent of the linear viscoelastic region (no harmonics), while parameter C indicates the strain sensitivity of the non-linear character. Fit parameters of Equation 3.2 are given in Table 3.2.8, from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. For masticated NRs, parameter TH_0 of SMR10CV decreases with larger mastication time and test results shown run 1 higher than run 2 but the differences tend to decrease with increasing mastication time. For RSS3, the parameter TH_0 slightly decreases when increasing the mastication time then increases when the mastication time is larger than 1440 s. In what the parameter C is concerned (Figure 3.2.16), an increase with mastication time is initially observed with SMR10CV, followed by a decrease when the mastication time is longer than 120s; moreover results show run 2 higher than run 1, but the differences decrease with increasing mastication time. In the case of RSS3, the parameter C slightly increases at first then decreases with longer mastication times. It is quite interesting to observe that at first run 2 results are higher than run 1 ones, then the differences tend to decrease when the mastication time is longer than 960 s, with also an inversion, run 1 results higher than run 2. Figure 3.2.17 shows parameter α of masticated NR samples. For SMR10CV, parameter α increases with increasing mastication time then remains constant when the mastication time is longer than 240 s. In the case of RSS3, parameter α increases with mastication time, with the highest value occurring at 480 s then decreases with longer mastication time. The same results can be observed for parameter D (Figure 3.2.18). Parameter D of SMR10CV increases first then decreases with increasing mastication time; the highest value is at 60 s with run 2 higher than run 1. Similar results are observed for RSS3 with the highest value at 480 s. In all cases (Figure 3.2.15 to Figure 3.2.18), there are no significant difference by the difference bale for the same grade (RSS3 bale 1 and bale2) and no significant difference due to the mixing equipment (Haake Rheomox or Banbury mixer) as already reported in 3.2.2.1 by using fit model parameters for dynamic strain softening of the complex modulus.

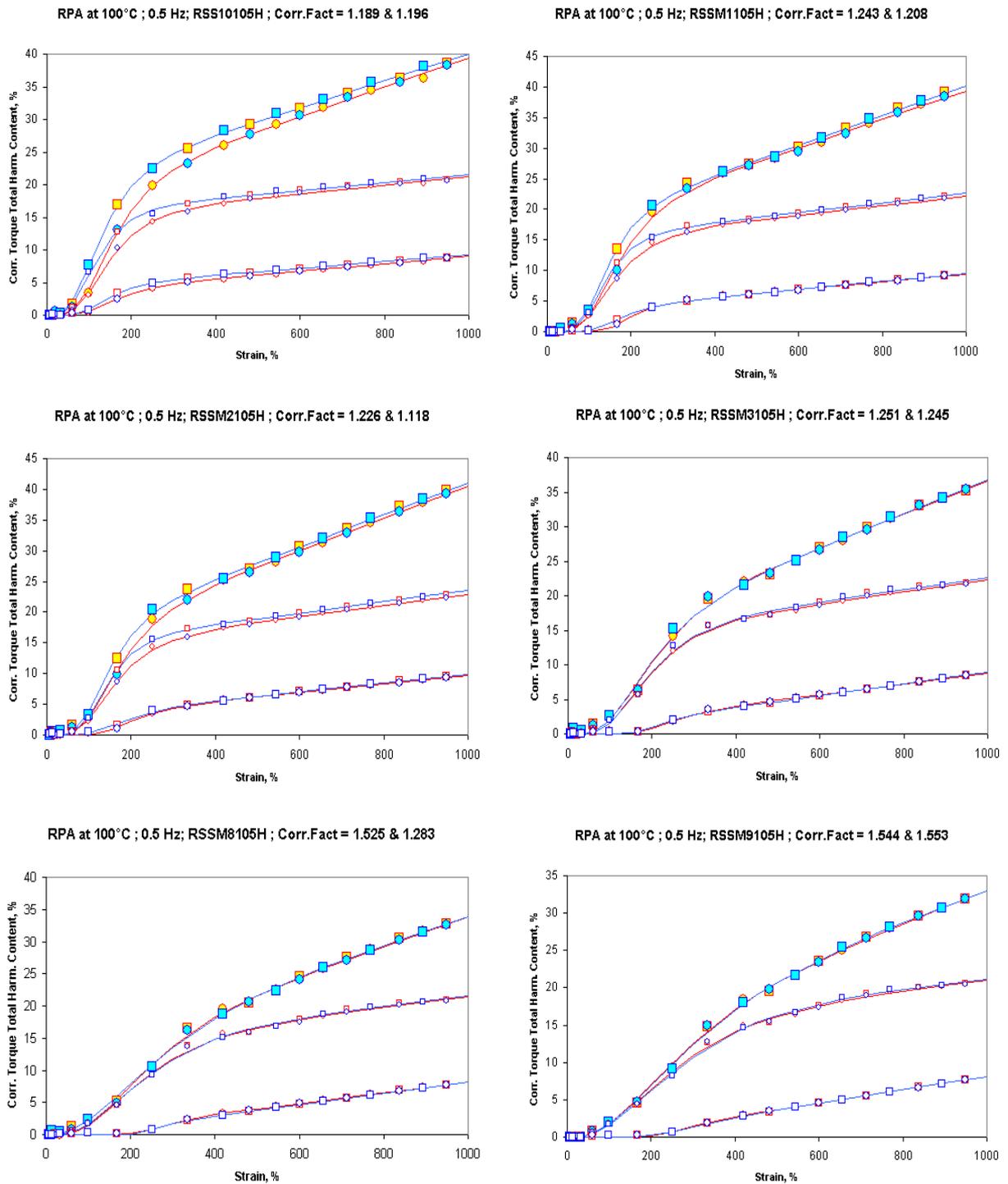


Figure 3.2.13 : RPA-FT; total harmonic content, 3rd and (th harmonics vs. strain for masticated RSS3 gum samples

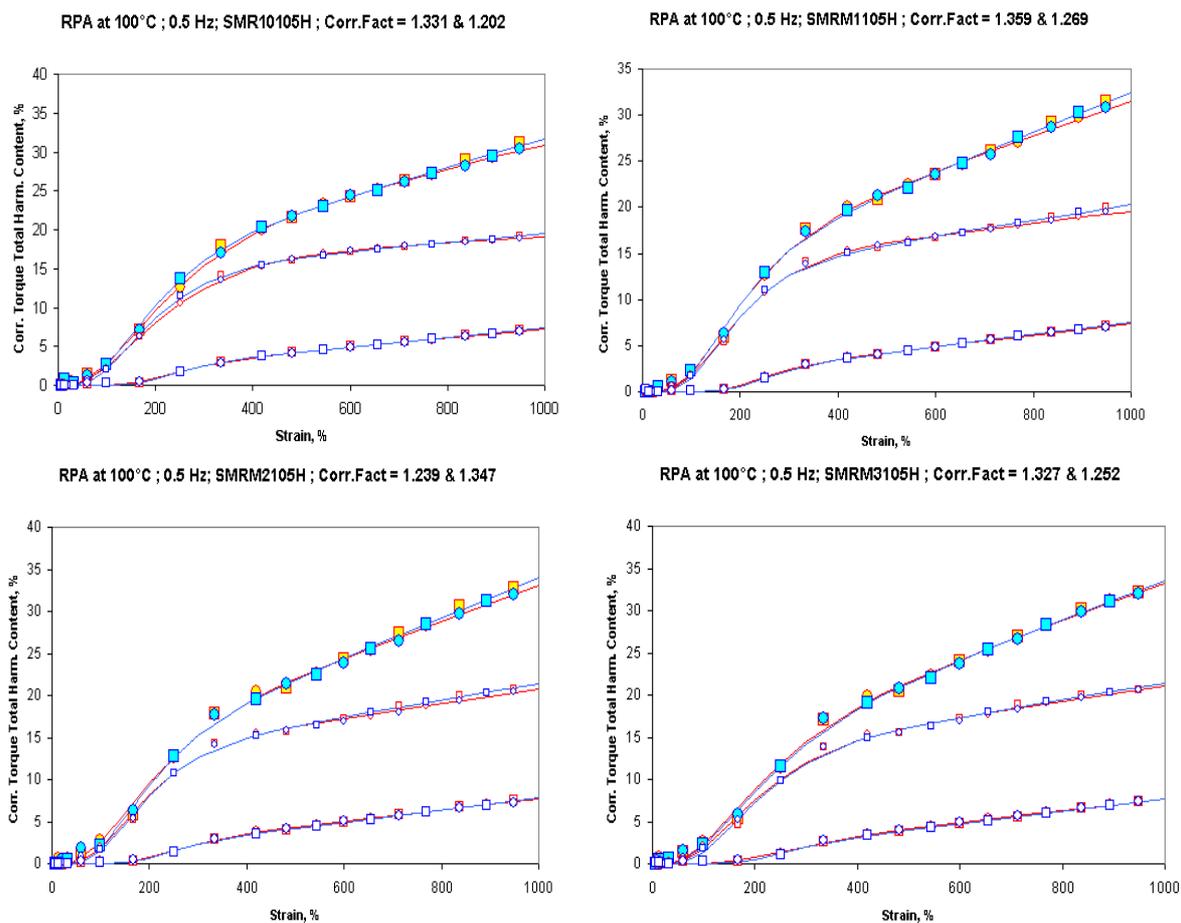


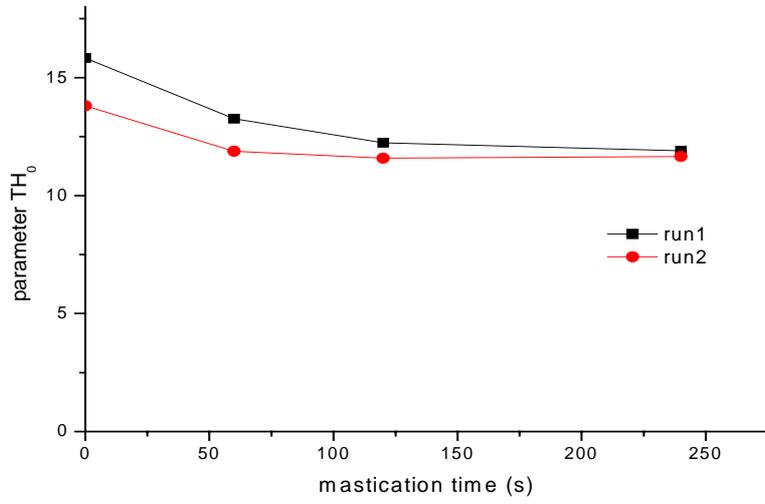
Figure 3.2.14 : RPA-FT; total harmonic content, 3rd and 5th harmonics vs. strain for masticated SMR10 gum samples

Table 3.2.8 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz on masticated RSS3; fit parameter T(3/1) of Equation 3.2

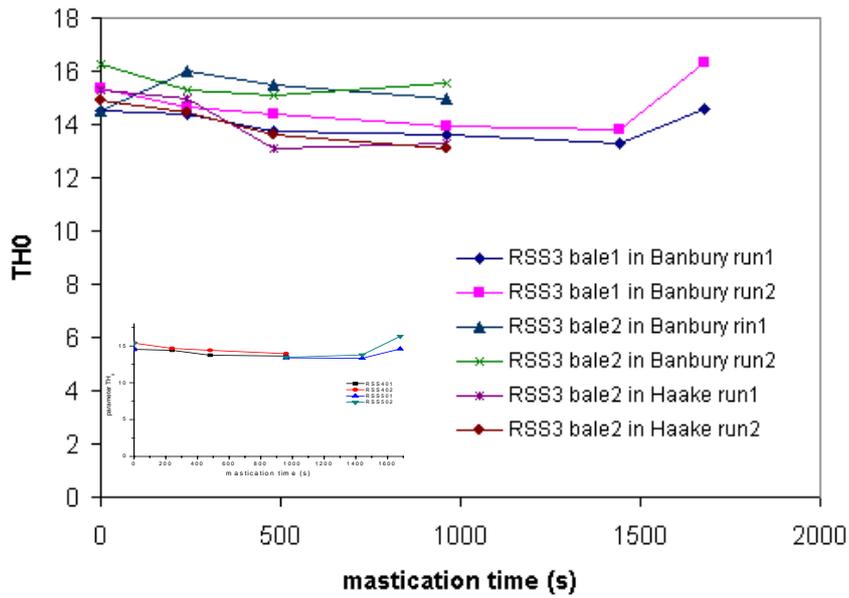
sample	RSS3(bale1) In Banbury		RSS3(bale2) In Banbury		RSS3(bale2) In Haake		
	Run1	Run2	Run1	Run2	Run1	Run2	
RSS3 (unmasticated)	TH ₀	14.53	15.38	14.52	16.26	14.52	16.26
	α	0.0067	0.0062	0.0059	0.0048	0.0059	0.0048
	C	0.0162	0.019	0.0129	0.0137	0.0129	0.0137
	D	6.643	5.705	4.111	3.967	4.111	3.967
	r ²	0.9997	0.9995	0.9997	0.9993	0.9997	0.9993
RSS3 (240s; 40rpm)	TH ₀	14.41	14.66	15.98	15.27	14.96	14.45
	α	0.0077	0.008	0.0046	0.0059	0.0052	0.006
	C	0.0157	0.0202	0.0132	0.0148	0.0133	0.0143
	D	7.456	10.44	5.574	5.757	5.792	5.794
	r ²	0.9998	0.9999	0.9998	0.9998	0.9998	0.9999
RSS3 (480s; 40rpm)	TH ₀	13.73	14.41	15.47	15.07	13.1	13.6
	α	0.0092	0.0091	0.0055	0.0064	0.0087	0.0086
	C	0.0159	0.0194	0.014	0.0161	0.0157	0.0152
	D	7.657	10.37	5.86	6.749	7.572	7.115
	r ²	0.9999	0.9999	0.9998	0.9999	0.9999	0.9998
RSS3 (960s; 40rpm)	TH ₀	13.62	13.96	14.95	15.53	13.32	13.12
	α	0.0087	0.0086	0.0075	0.007	0.0086	0.0088
	C	0.0127	0.0127	0.0109	0.0106	0.0116	0.0118
	D	6.742	6.777	5.528	5.041	5.456	6.001
	r ²	0.9995	0.9991	0.9993	0.9991	0.9995	0.9993
RSS3 (960s; 50rpm)	TH ₀	13.39	13.46	-	-	-	-
	α	0.0086	0.0089	-	-	-	-
	C	0.0117	0.0117	-	-	-	-
	D	6.287	5.984	-	-	-	-
	r ²	0.9993	0.9993	-	-	-	-
RSS3 (1440s; 50rpm)	TH ₀	13.31	13.79	-	-	-	-
	α	0.0081	0.0078	-	-	-	-
	C	0.0093	0.0085	-	-	-	-
	D	4.591	3.955	-	-	-	-
	r ²	0.9994	0.9993	-	-	-	-
RSS3 (1680s; 50rpm)	TH ₀	14.6	16.3	-	-	-	-
	α	0.0065	0.0049	-	-	-	-
	C	0.0071	0.0062	-	-	-	-
	D	3.322	3.022	-	-	-	-
	r ²	0.9994	0.9995	-	-	-	-

Table 3.2.9 : RPA-FT strain sweep experiments at 100 °C and 0.5 Hz on masticated SMR10CV; fit parameter T(3/1) of Equation 3.2

sample		SMR10CV In Banbury	
		Run1	Run2
SMR10CV (unmasticated)	TH ₀	15.83	13.81
	α	0.0032	0.0057
	C	0.0081	0.0113
	D	3.214	4.972
	r ²	1	0.9999
SMR10CV (60s; 40rpm)	TH ₀	13.26	11.88
	α	0.0063	0.0084
	C	0.0113	0.0133
	D	5.309	7.128
	r ²	0.9998	0.9995
SMR10CV (120s; 40rpm)	TH ₀	12.24	11.59
	α	0.0085	0.0098
	C	0.0117	0.0129
	D	5.353	6.661
	r ²	0.9993	0.9994
SMR10CV (240s; 40rpm)	TH ₀	11.9	11.66
	α	0.0092	0.0097
	C	0.0105	0.0111
	D	4.568	5.539
	r ²	0.9992	0.9992

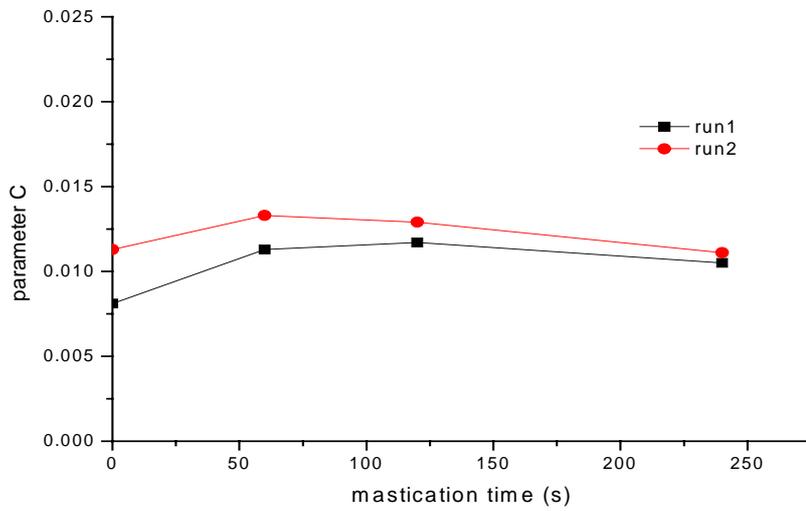


(a)

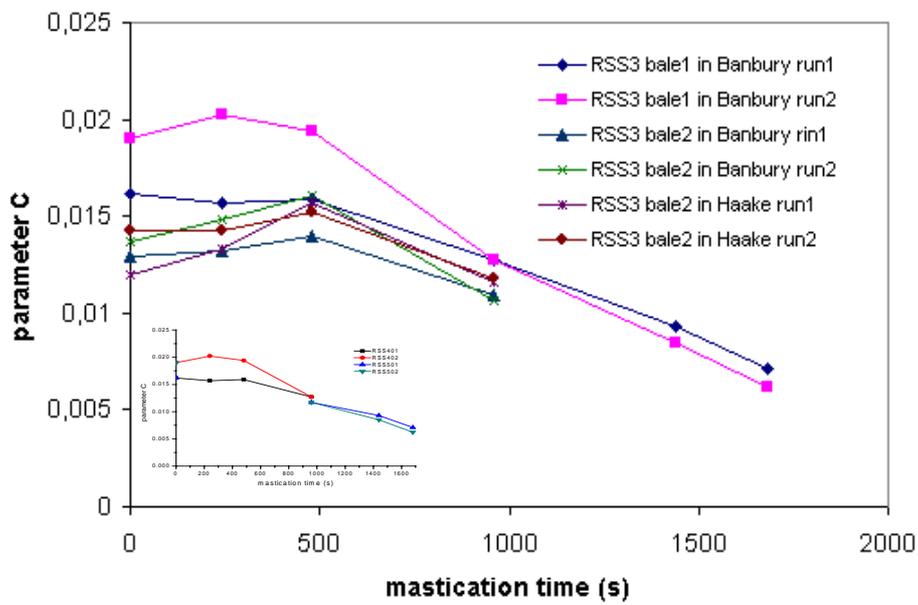


(b)

Figure 3.2.15 : RPA-FT (TH₀ of T(3/1)) on masticated NR samples; variation of torque harmonics with strain amplitude; (a) SMR10CV; (b) RSS3



(a)



(b)

Figure 3.2.16 : RPA-FT (parameter C of T(3/1)) on masticated NR samples; variation of torque harmonics with strain amplitude; (a) SMR10CV; (b) RSS3

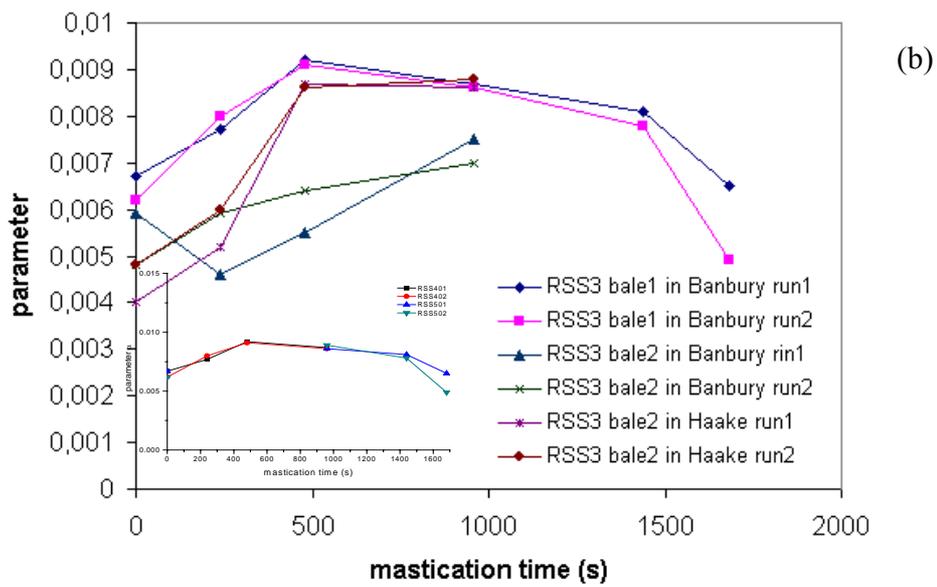
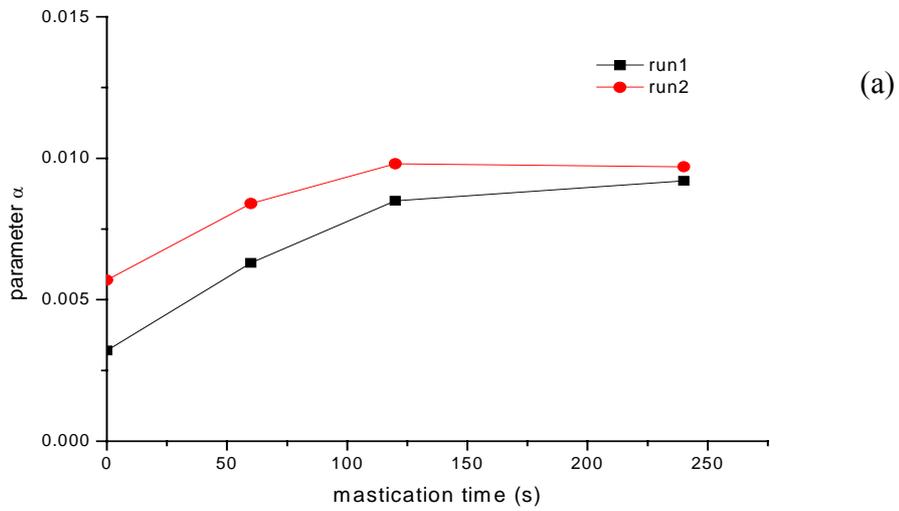
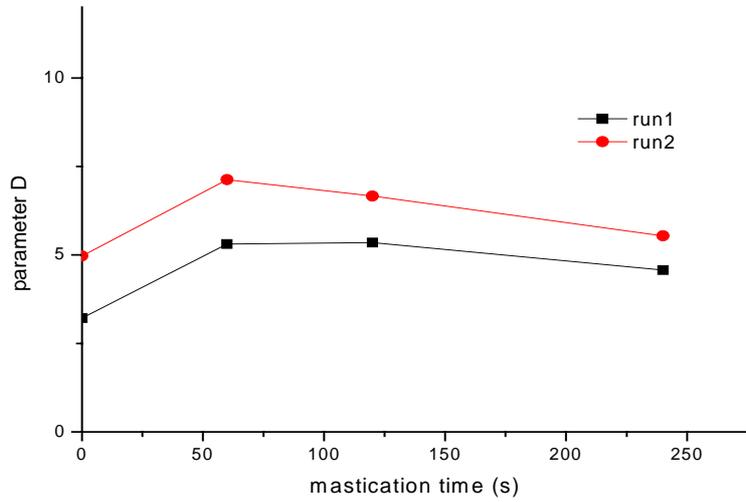
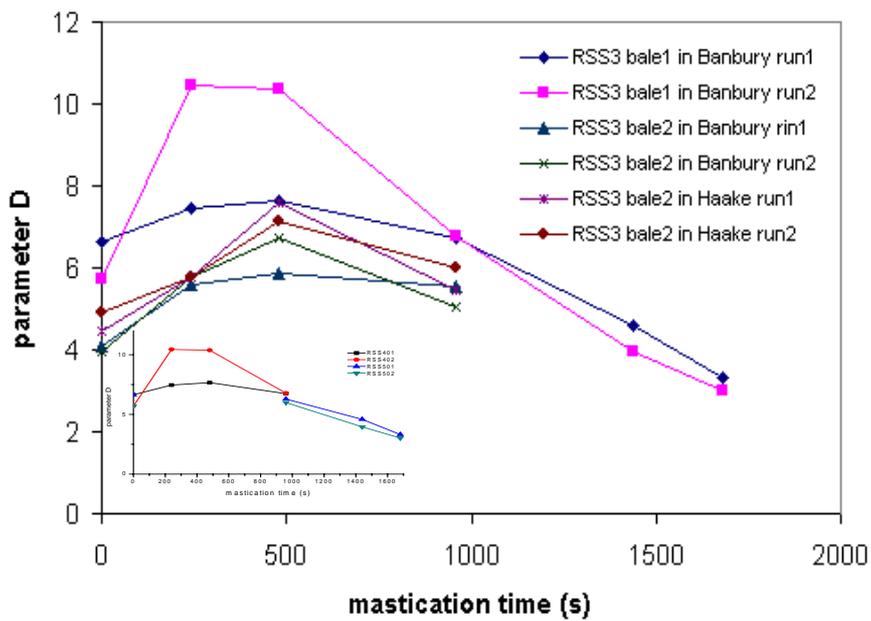


Figure 3.2.17 : RPA-FT (parameter α) on masticated NR samples; variation of torque harmonics with strain amplitude; (a) SMR10CV; (b) RSS3



(a)



(b)

Figure 3.2.18 : RPA-FT (parameter D of T(3/1)) on masticated NR samples; variation of torque harmonics with strain amplitude; (a) SMR10CV; (b) RSS3

3.2.3 Conclusions Section 3.2

The gel content of masticated SMR10CV and RSS3 decreases with increasing mastication; to eventually vanish for excessive mastication times. It indicates that the gel can be destroyed by mastication. In the case of masticated NR, it was found that the complex modulus decreases with longer mastication time. A correlation between the gel's mastication sensitivity and complex modulus can therefore be considered. The critical strain ($1/A$) of NR samples increases with increasing mastication time, thus indicating that the strain region for linear behavior of NR is somewhat extended by mastication. In the case of similar Mooney viscosity (SMRM3, RSSM9; $ML(1+4)_{100^\circ C} = 49, 48$) samples, RSSM9 has a significantly higher complex modulus (G^*_0) and critical strain ($1/A$) than SMRM3, this implies that NR samples can have very similar Mooney viscosities, but will likely process very differently. RSS3 sample exhibit intrinsic non-linearity. Mastication is found to change the intrinsic non-linearity of RSS3 to extrinsic non-linearity; a result suggesting that some structures, initially present in gum RSS3, impart an intrinsic non-linear character to the material, but as they are destroyed by mastication, the non-linear viscoelastic reverts to an extrinsic one, i.e. only due to large strain amplitude. Such results are provided by the quarter signal integrations of RPA tests on masticated NR samples, and are well in line with the observation that the gel content decreases with increasing mastication time. This underlines the strong relationships between gel content and rheological properties of Natural Rubber. Torque signal harmonics appear sensitive to strain history, torque harmonic of run 2 being generally higher than run 1. RSS3 grade exhibits the strongest strain history effects, but the difference between runs 1 and 2 disappears when samples are masticated, up to 960 s for RSS3 (RSSM3) and up to 60s for SMR10CV (SMRM1). This implies that mastication can somewhat eliminate the sensitivity to strain history effects of NR, with the constant viscosity grade (SMR10CV) being more affected than the RSS grade.

3.3 Compounding - NR samples

3.3.1 RPA tests on compounded rubber

3.3.1.1 Complex modulus versus strain

Complex modulus G^* versus strain curves of carbon black (N330) filled compounds are shown in Figures 3.3.1 to 3.3.4. In all cases, the two tested samples (a and b) gave identical results thus demonstrating the excellent homogeneity of tested materials as well as the reproducibility of the testing method. For all filled (N330) unmasticated rubber compound samples (Figure 3.3.1), differences can be seen between data gathered through run 1 and run 2 (run 1 is higher than run 2), which indicate that either such materials exhibit somewhat permanent strain history effects or that the resting period (2 minutes) between the two runs is not long enough to totally erase memory of strain during run 1. Because all samples exhibit differences between run 1 and run 2, irrespective of the relaxation properties of the grade and because relaxation properties of Ribbed smoked Sheet grades and CV grades are known to be significantly different, one would however favor the conclusion that carbon black (N330) filled Natural Rubber compounds are indeed sensitive to permanent strain history effects. The difference between run 1 and run 2 for filled compounds of viscosity stabilized rubber grades (OMNR, STR5CV60, SMR10CV60) is higher than for filled compounds of field latex grades (STR5L, RSS3, RSS3E), which indicates that the strain history effect of filled compounds of CV grades is higher than filled compounds of field grades. But this behavior is not observed with unfilled rubber compounds (Figure 3.3.4), which show no significant difference between run 1 and run 2. For filled compounds, it can be observed that all tested samples do not exhibit a linear region within the experimental window of the RPA (Figures 3.3.1 to 3.3.3), i.e. that no constant complex modulus (G^*) region is observed but dynamic strain softening (DSS) upon increasing strain amplitude. For filled compounds with viscosity stabilized grades (STR5CV60, SMR10CV60, OMNR), the non-linear behavior occurs at a higher critical strain (after this critical strain is exceeded, the complex modulus starts to decrease) than for filled compounds of field latex grades (STR5L, RSS3, RSS3E). But in the cases of unfilled rubber compounds no strain effects (i.e. essentially a linear behavior is seen) are observed before 150 % strain (i.e. $1/A$). Such a behavior is well modeled with equation 3.1, previously introduced.

Fit parameters of Equation 3.1 are given in Tables 5 to 7, from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. Figure 3.3.5 shows the modulus in the linear region (G_0^*) for the filled compounds of the different NR grades. For filled compounds of field latex grades (STR5L, RSS3 and RSS3E), no significant difference are seen in G_0^* . In the case of viscosity stabilized (OMNR, STR5CV60, and SMR10CV60) grades as well as for the synthetic polyisoprene (IR), the complex moduli as given by equation 3.1 are higher than for field latex grades, but it must be noted that both G_0^* and G_f^* are extrapolated values, and therefore of limited meaning, if any, when their numerical value is too far from measured data. For instance, the higher complex modulus (G_0^*) of filled (N330) compounds of viscosity stabilized

grades is not expected with respect to common compounding experience, so that such results are likely modelling artefacts because the tested range is too far from the linear region. Thus, it is better to consider recalculated values within the experimental range. Figure 3.3.6 shows the complex modulus at 10% strain for the filled (a) and the unfilled (b) compounds of the different grades NR. It is expectedly observed that filled compounds (Figure 3.3.6 (a)) of field latex grades (STR5L, RSS3 and RSS3E) exhibit higher complex modulus values than viscosity stabilized grades (OMNR, STR5CV60 and SMR10CV) with run 1 higher than run 2 in all cases, in full agreement with corresponding result from unfilled compounds (Figure 3.3.6 (b)) with different NR grades. Indeed, unfilled compounds of field latex grades (STR5L, RSS3 and RSS3E) show higher values than viscosity stabilized grades (OMNR, STR5CV60 and SMR10CV60) and the synthetic IR sample, in close comparison with similar results on gum rubber samples (see part 3.1 gum samples analysis; Figure 3.1.11). But filled compounds have higher complex modulus than unfilled compounds by about 40% for all NR grades. This effect is well known and due to the reinforcing character of the carbon black. In the case of G_f^* (Tables 3.3.1 to 3.3.2), negative values have no physical meaning and must therefore be discarded but even positive values have no real meaning as they correspond to infinite strain amplitude, by mathematical virtues of Equation 3.1. In the case of filled compounds of pre-masticated NR samples (Figure 3.3.7), the complex modulus in the linear region (G_0^*) increases with increasing pre-mastication time but again such an observation has likely no physical meaning because the calculated values are too far from the measured range and recalculated $G^*(10\%)$ must be considered. Figure 3.3.8 shows the complex modulus at 10% strain versus pre-mastication time for RSS3 (a) and SMR10CV (b) compounds. It is seen that the complex modulus $G^*(10\%)$ decreases with increasing pre-mastication time of NR samples, as one would expect from practical experience in the factory. A net decrease is clearly observed in the case of RSS3 while SMR10CV exhibits only a slight decrease, with run 1 higher than run 2. The difference between runs 1 and 2 is constant when increasing the pre-mastication time. In agreement with results from gum masticated NR (see part 3.2 mastication effects; Figure 3.2.6), the complex modulus in the linear region (G_0^*) decreases with increasing mastication time but in the case of gum masticated NR, the difference between runs 1 and 2 decreases when increasing the mastication time. The mid-modulus critical strain ($1/A$) of filled and unfilled compounds is shown in Figure 3.3.9. As can be seen, filled compounds of field latex grades (STR5L, RSS3 and RSS3E) exhibit a linear region at very low strain of about 40% strain ($1/A$). Conversely, for filled compounds of viscosity stabilized (OMNR, STR5CV60 and SMR10CV60) and IR grades, the general trend is a non-linear behavior ($1/A$ is found to be almost zero). It seems that in the case of filled compounds with pre-masticated rubber (Figure 3.3.10), the critical strain decreases with increasing pre-mastication time of gum rubber. Contrary to results obtained with gum masticated NR, this value increases with increasing mastication time (see part 3.2; Figure 3.2.7). For unfilled compounds of different grades NR, a linear behavior is observed up to a high critical strain values ($1/A$ is about 150%) with run 2 higher than run 1 and no significant differences between all samples, as previously reported in the case of gum rubber samples. Parameter B of filled and unfilled compounds is shown in Figure 3.3.11. Filled compounds of field latex grades (STR5L, RSS3 and RSS3E) show higher values

than viscosity stabilized (OMNR, STR5CV60 and SMR10CV60) and IR grades. For unfilled compounds, there is no significant difference between all unfilled compounds. But it can be seen that the unfilled IR compound is very different, with a B value lower than the other samples. In the case of filled compounds of pre-masticated NR (Figure 3.3.12), parameter B decreases with increasing pre-mastication time of the gum. The decrease of B is larger when pre-masticating RSS3 than when pre-masticating SMR10CV60.

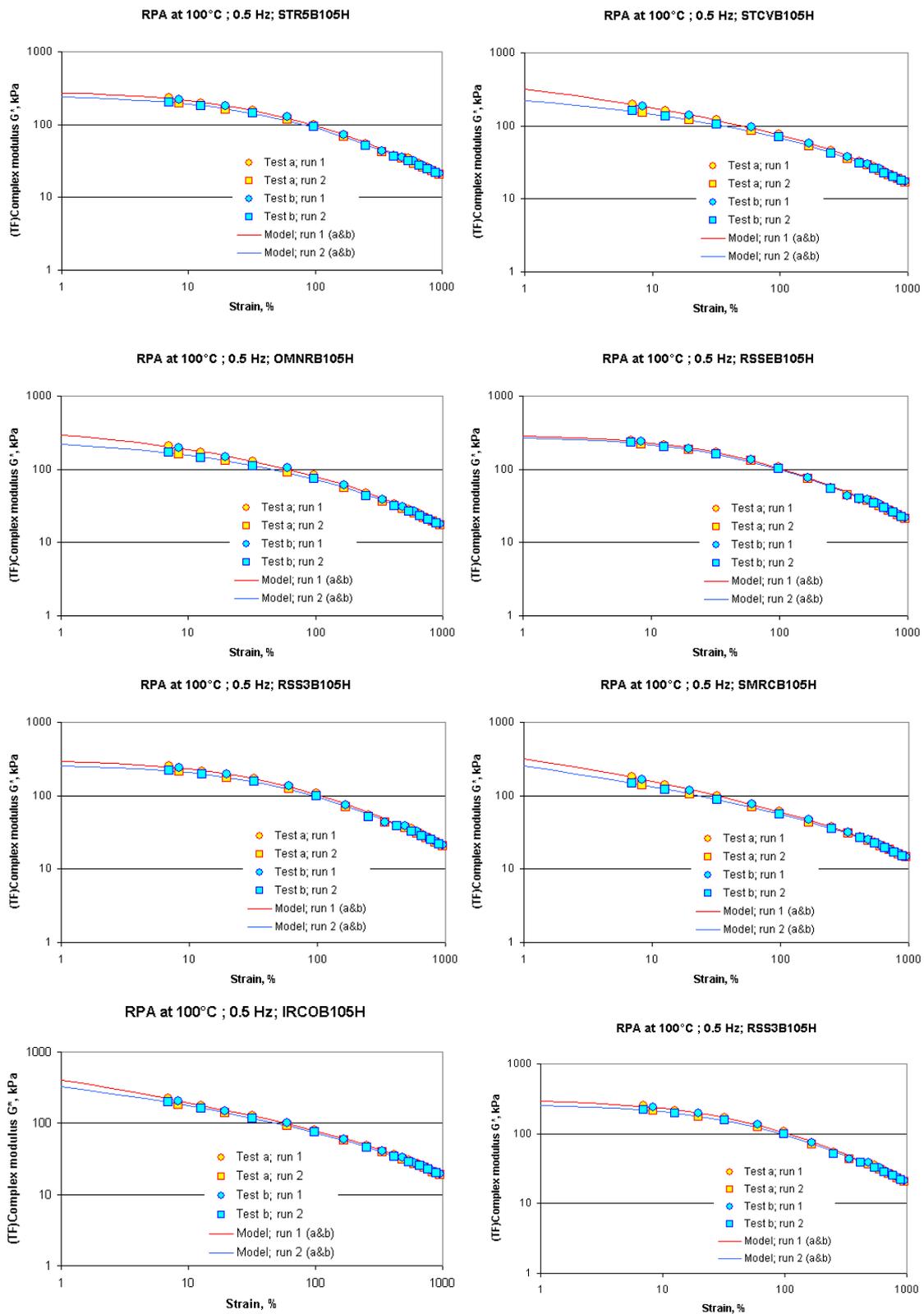


Figure 3.3.1 : RPA-FT at 100 °C on filled (N330) rubber compound samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

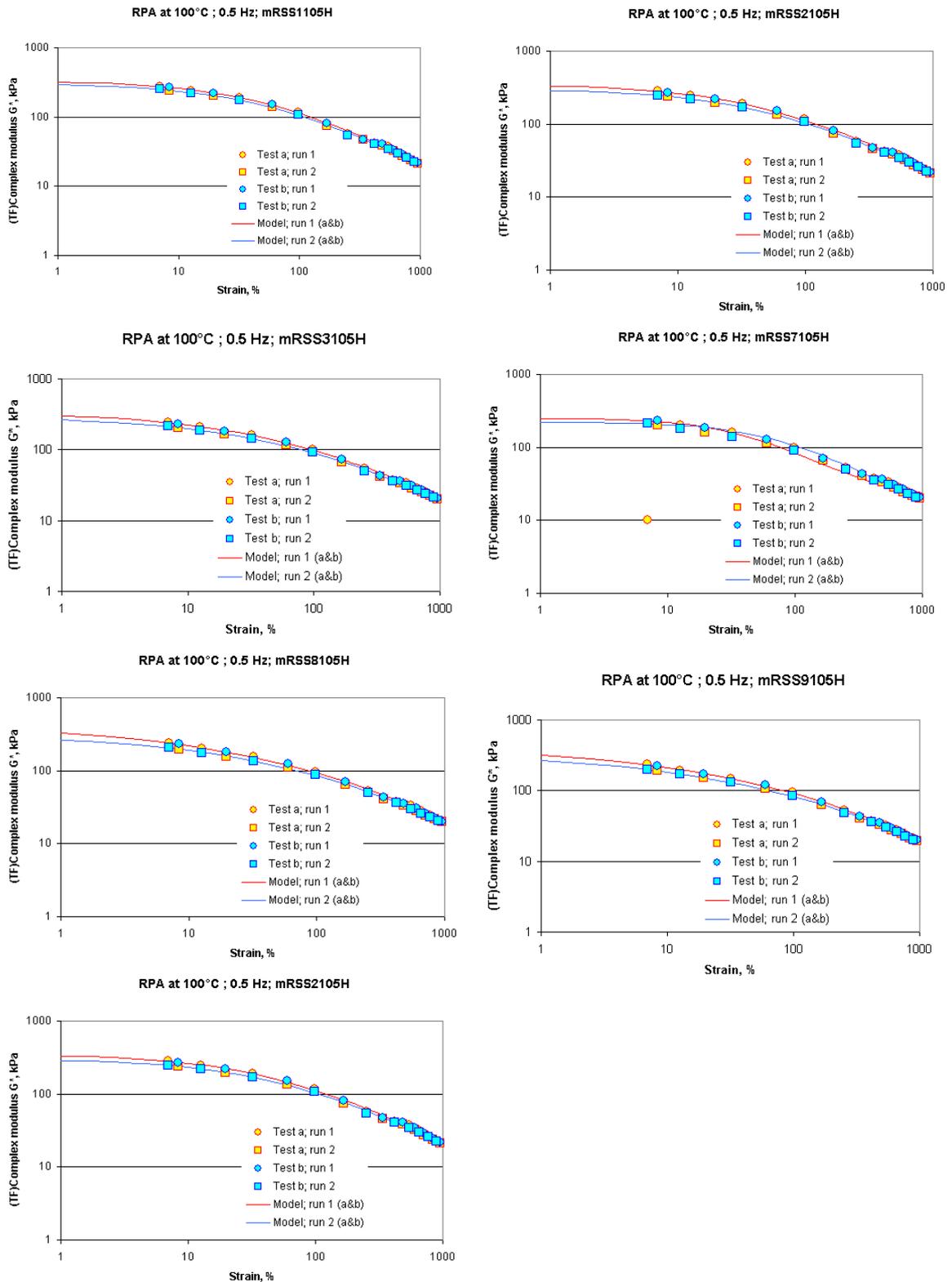


Figure 3.3.2 : RPA-FT at 100°C on filled (N330) pre-masticated RSS3 compound samples; complex modulus vs. strain; strain sweep tests at 0.5 Hz

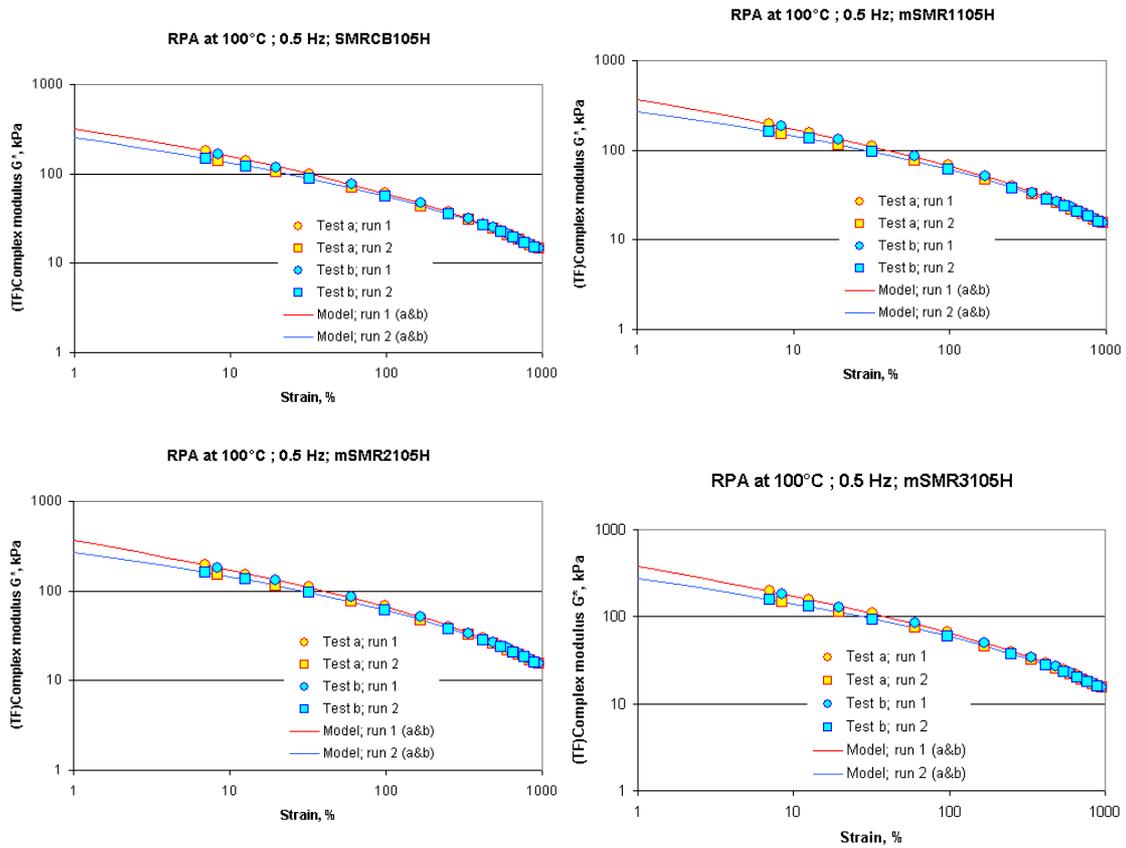


Figure 3.3.3 : RPA-FT at 100°C on filled (N330) pre-masticated SMR10CV60 compound samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

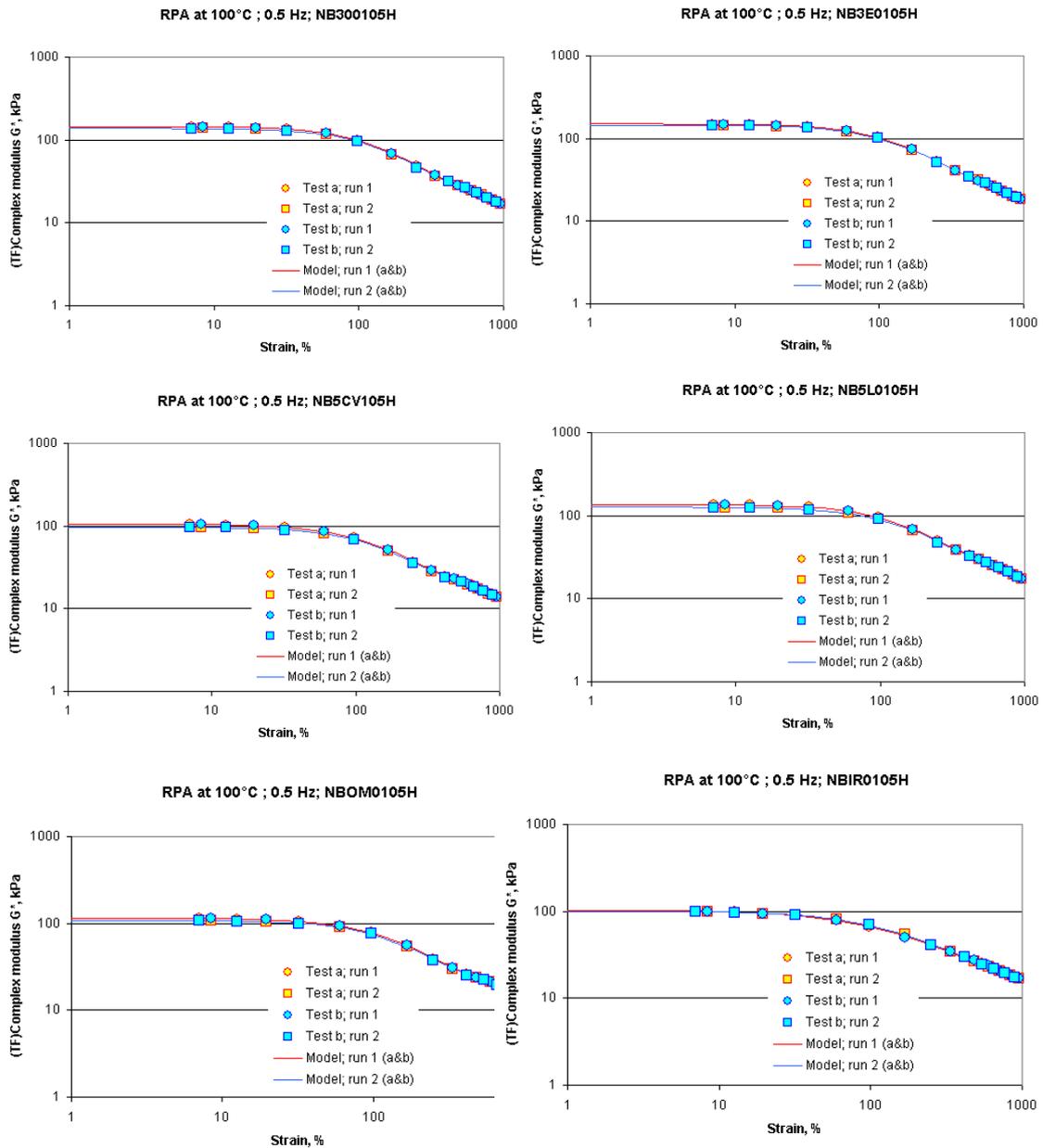


Figure 3.3.4 : RPA-FT at 100°C on unfilled rubber compound samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz

Table 3.3.1 : RPA-FT strain sweep experiments at 100°C and 0.5 Hz of filled (N330) unmastered rubber compounds fit parameters of Equation 3.1

sample	Run (a & b)	G_0^* (kPa)	G_f^* (kPa)	G^* at 10% (kPa)	1/A (%)	B	r^2
STR5L	1	291.2	-7.62	212.78	41.8	0.7220	0.9994
	2	252.6	-6.12	190.90	48.5	0.7349	0.9997
STR5CV	1	788.7	-43.11	176.17	0.5	0.3373	0.9996
	2	317.2	-30.2	145.21	10.5	0.4143	0.9999
OMNR	1	397.7	-24.6	187.38	10.2	0.4869	0.9996
	2	262.0	-18.48	155.35	25.0	0.5331	0.9998
RSS3E	1	300.0	-4.06	229.19	45.8	0.7835	0.9993
	2	281.3	-4.11	216.67	48.3	0.7798	0.9996
RSS3	1	306.7	-5.54	231.48	44.1	0.7738	0.9993
	2	264.3	-3.82	205.66	50.6	0.7850	0.9997
SMR10CV	1	698.3	-14.05	156.82	0.7	0.4373	0.9997
	2	805.2	-27.18	131.67	0.1	0.3299	1.0000
IR	1	3580	-41.81	193.76	0.0	0.3085	0.9998
	2	762.6	-31.96	175.18	0.6	0.3623	0.9999

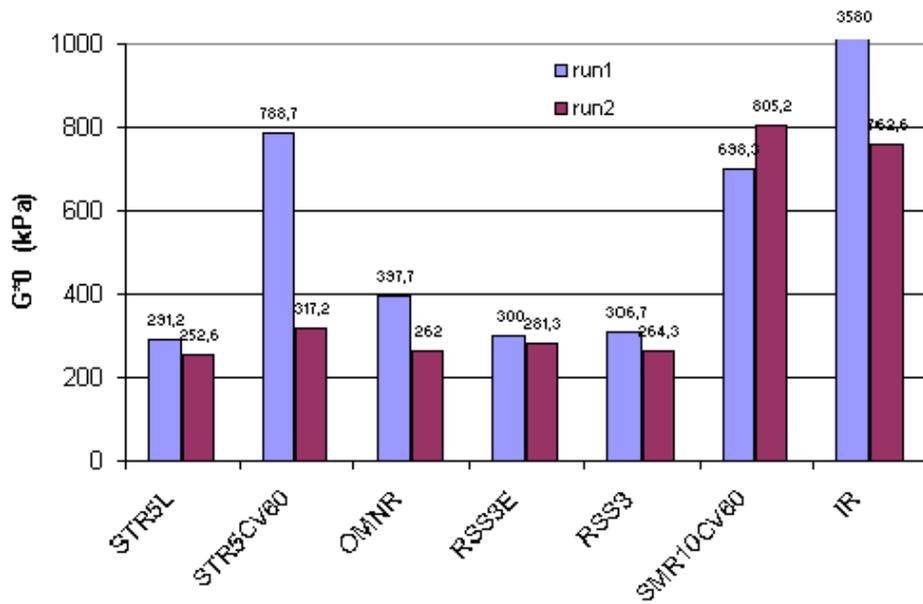
Table 3.3.2 : RPA-FT strain sweep experiments at 100°C and 0.5 Hz of filled (N330) of pre-masticated RSS3 and SMR10CV fit parameters of Equation 3.1

sample	Run (a & b)	G_0^* (kPa)	G_f^* (kPa)	G^* at 10% (kPa)	1/A (%)	B	r^2
mRSS1	1	317.2	-10.88	220.38	35.2	0.692	0.9987
240s;40rpm	2	262.8	-6.79	194.67	44.2	0.730	0.9997
mRSS2	1	320.2	-9.35	222.70	34.3	1.831	0.9998
480s;40rpm	2	265.3	-6.57	196.57	43.9	0.703	0.9993
mRSS3	1	346.5	-18.73	205.37	22.2	0.581	0.9995
960s;40rpm	2	273.4	-14.23	178.72	32.1	0.611	0.9998
mRSS7	1	370.7	-23.37	199.40	16.4	0.531	0.9996
960s;50rpm	2	274.3	-16.55	169.93	27.6	0.571	0.9998
mRSS8	1	422.9	-27.86	199.22	10.3	0.484	0.9996
1440s;50rpm	2	290.7	-18.94	169.52	22.7	0.538	0.9999
mRSS9	1	509.2	-32.96	195.37	4.8	0.430	0.9997
1680s;50rpm	2	303.1	-21.88	163.72	17.8	0.497	0.9999
mSMR1	1	750.4	-9.92	149.73	0.50	0.449	0.9996
60s;40rpm	2	1390	-25.19	123.68	0.0	0.310	1.0000
mSMR2	1	2578	-15.03	147.55	0.0	0.382	0.9996
120s;40rpm	2	1115	-22.58	122.10	0.0	0.322	0.9999
mSMR3	1	2922	-13.80	150.52	0.0	0.392	0.9996
240s;40rpm	2	1154	-22.67	123.02	0.0	0.323	1.0000

Table 3.3.3 : RPA-FT strain sweep experiments at 100°C and 0.5 Hz of unfilled rubber compounds fit parameters of Equation 3.1

sample	Run (a & b)	G_0^* (kPa)	G_f^* (kPa)	G^* at 10% (kPa)	1/A (%)	B	r^2
STR5L	1	136.3	12.38	134.67	150.7	1.592	0.9999
	2	126.6	13.06	125.31	156.2	1.626	0.9999
STR5CV	1	105.2	10.34	103.81	142.2	1.586	0.9999
	2	96.6	10.95	95.59	149.1	1.656	0.9998
OMNR	1	114.6	11.81	113.34	139.0	1.668	0.9998
	2	107.4	12.26	106.40	143.6	1.705	0.9998
RSS3E	1	150.1	12.89	148.33	146.5	1.616	0.9999
	2	145	13.38	143.41	149.2	1.630	0.9999
RSS3	1	145.6	12.83	144.08	141.5	1.682	0.9999
	2	137.9	14.39	136.77	143.0	1.761	0.9998
SMR10CV	1	76.6	7.80	75.56	172.2	1.467	0.9995
	2	74.4	8.72	73.74	176.3	1.592	0.9998
IR	1	102.8	8.38	99.2	147.4	1.200	0.9998
	2	100.5	8.06	97.99	165.0	1.277	0.9999

(a) filled



(b) unfilled

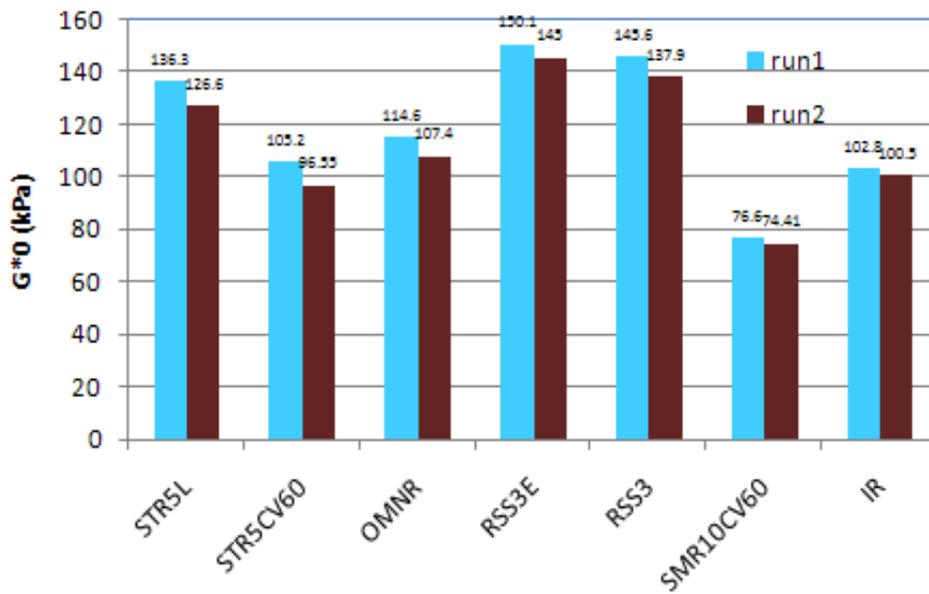


Figure 3.3.5 : RPA-FT at 100°C on (a) filled and (b) unfilled rubber compounds ; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1

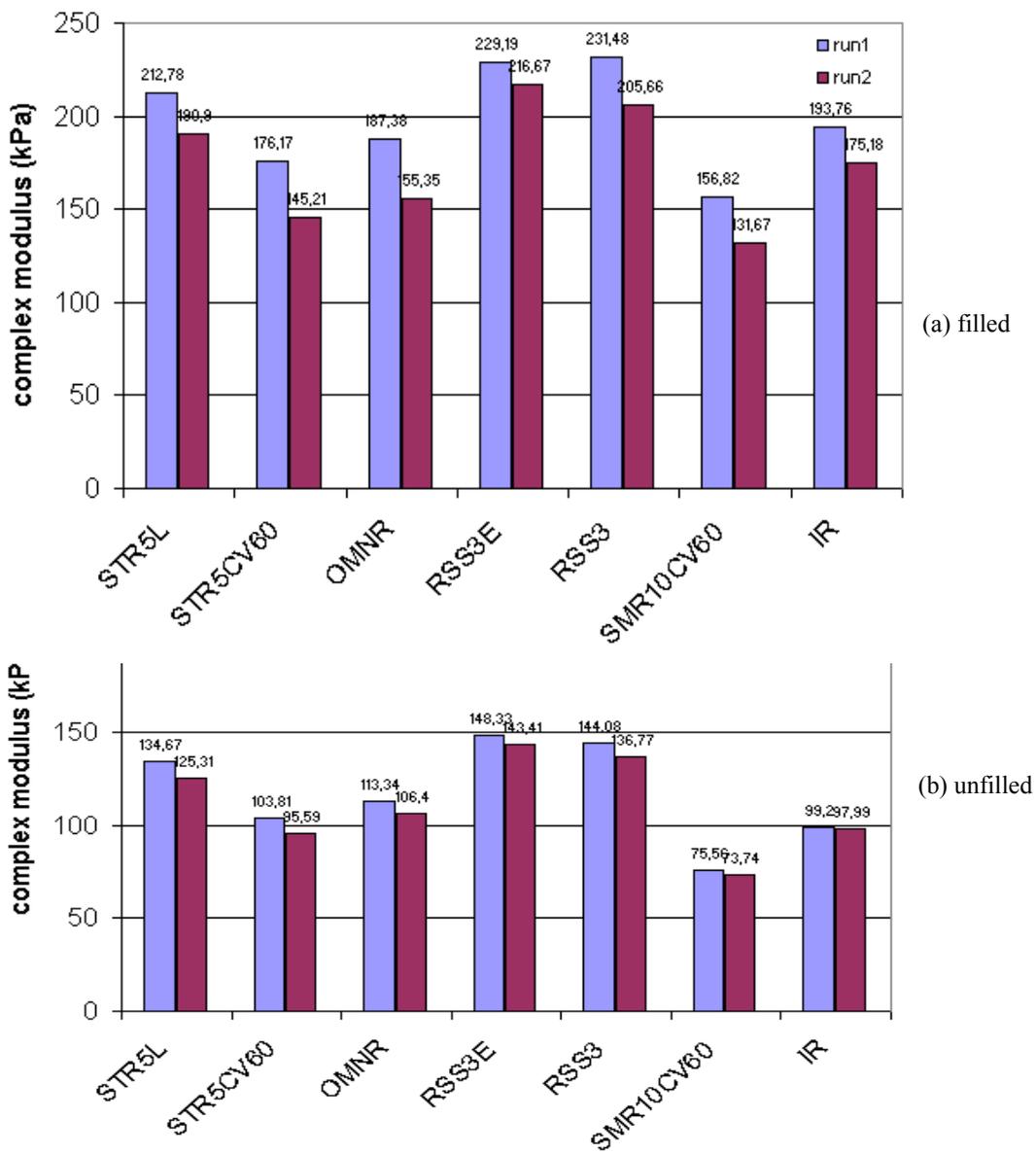
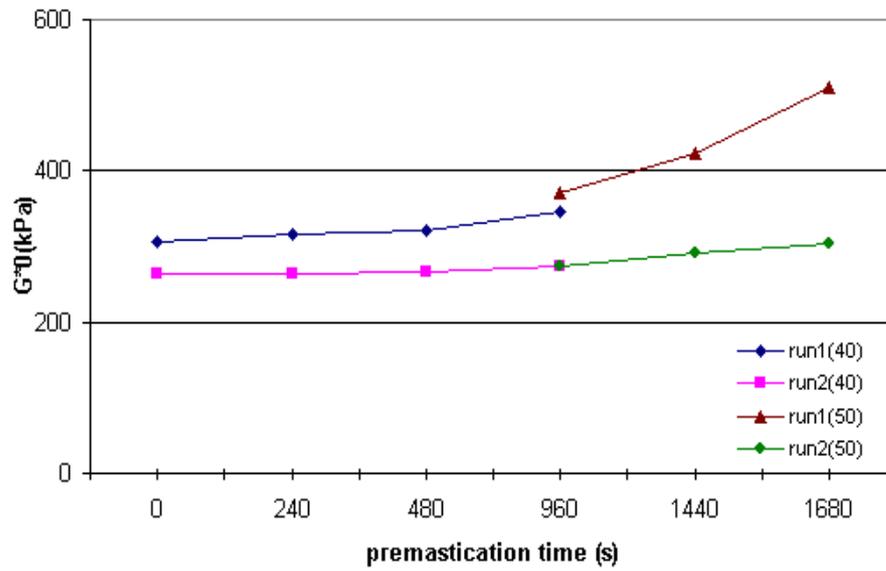
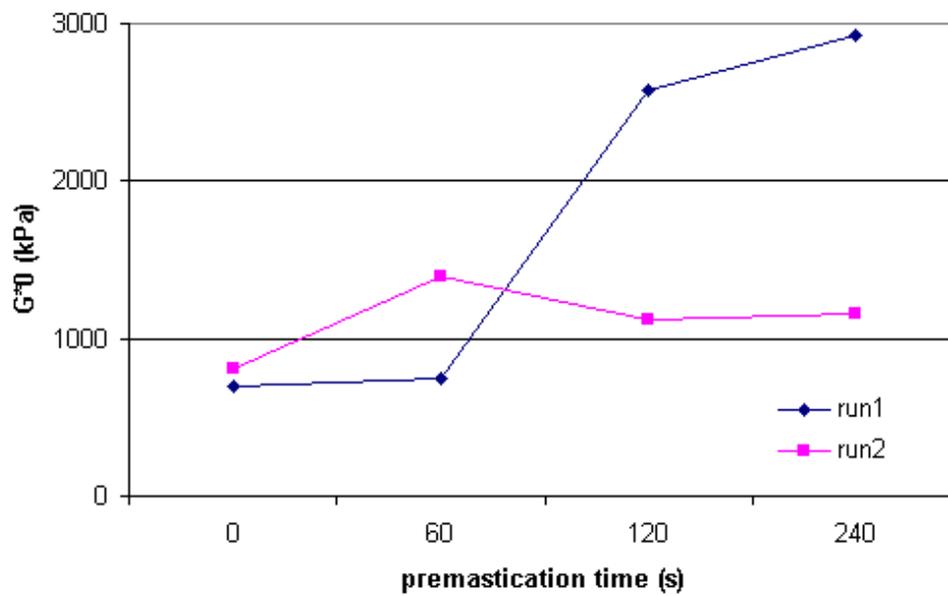


Figure 3.3.6 : RPA-FT at 100°C on (a) filled and (b) unfilled rubber compounds ; complex modulus at 10% strain vs. rubber grades ; strain sweep tests at 0.5 Hz

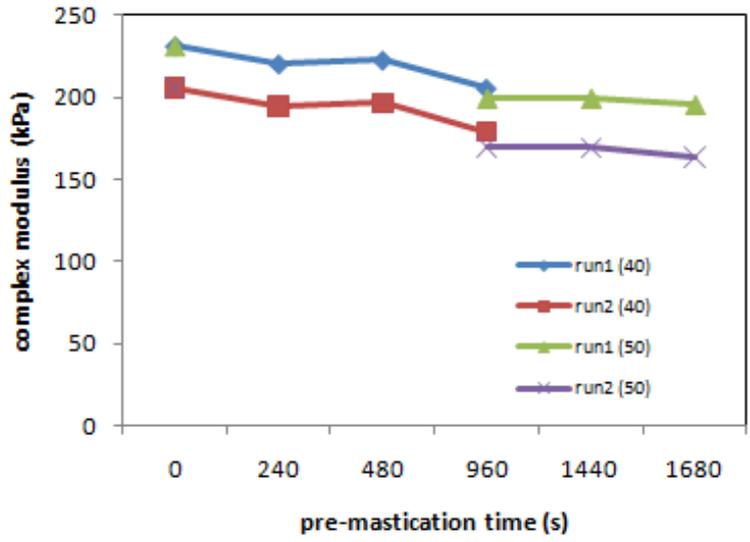


(a) RSS3

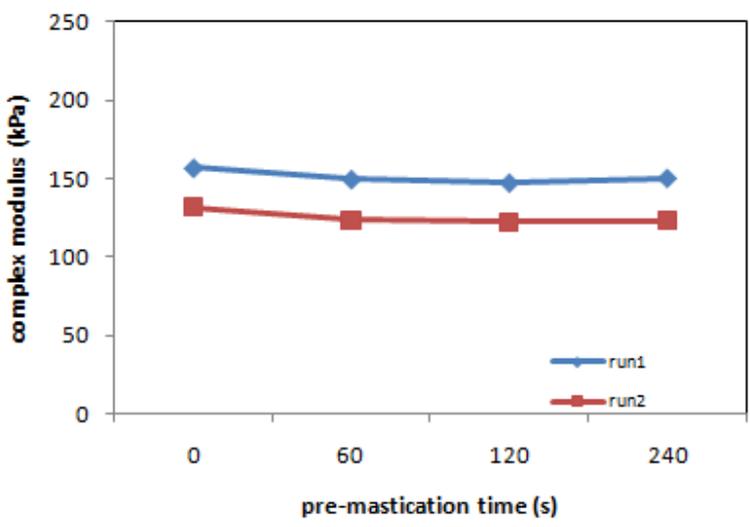


(b) SMR10CV

Figure 3.3.7 : RPA-FT at 100°C on filled pre-masticated (a) RSS3 and (b) SMR10CV60 compounds ; complex modulus G^*_0 vs. pre-mastication time ; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1

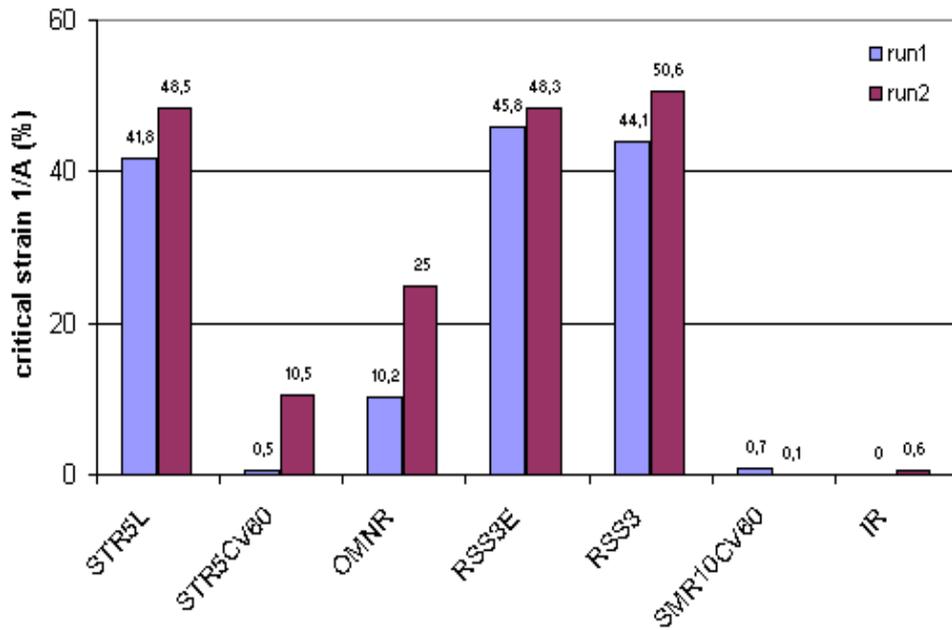


(a) RSS3

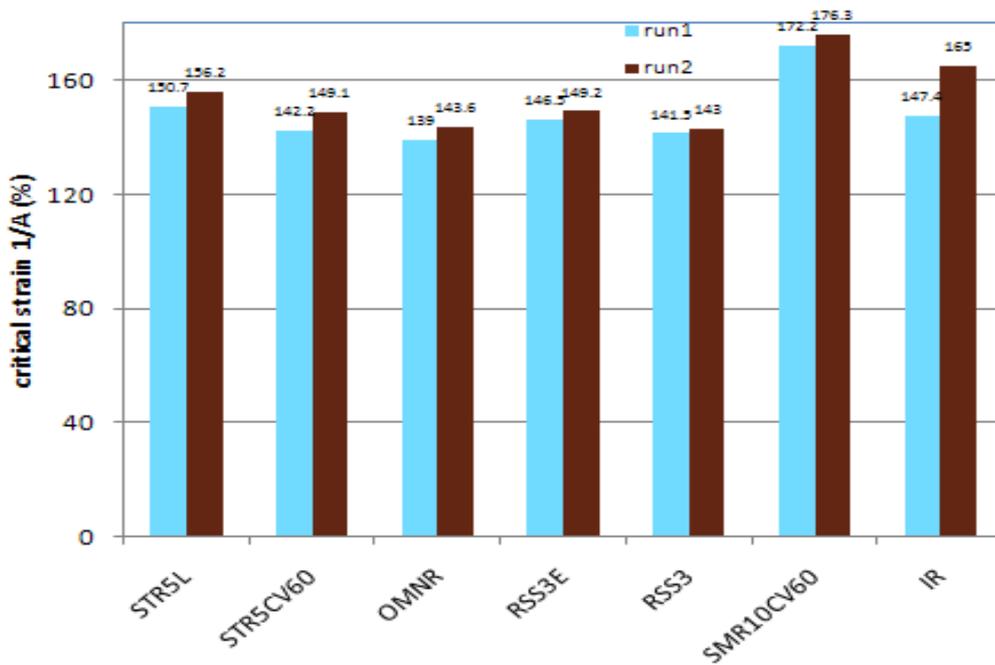


(b) SMR10CV

Figure 3.3.8 : RPA-FT at 100°C on filled pre-masticated (a) RSS3 and (b) SMR10CV60 compounds ;complex modulus at 10% strain vs. pre-mastication time; strain sweep tests at 0.5 Hz



(a) filled



(b) unfilled

Figure 3.3.9 : RPA-FT at 100°C on (a) filled and (b) unfilled rubber compounds ; mid-modulus critical strain (1/A) vs. strain ; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1

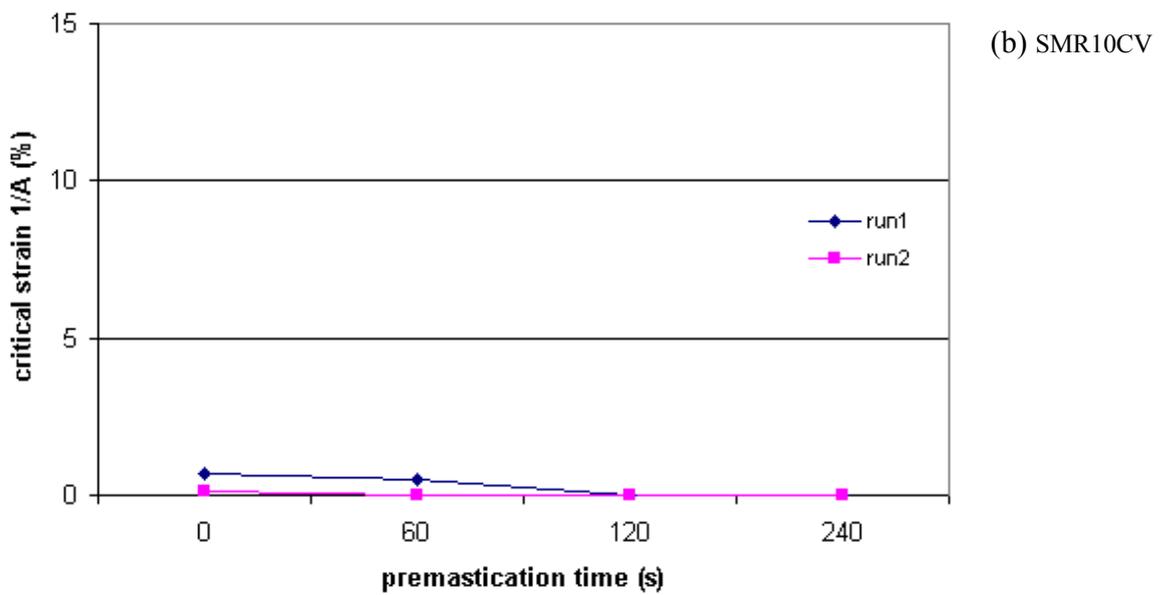
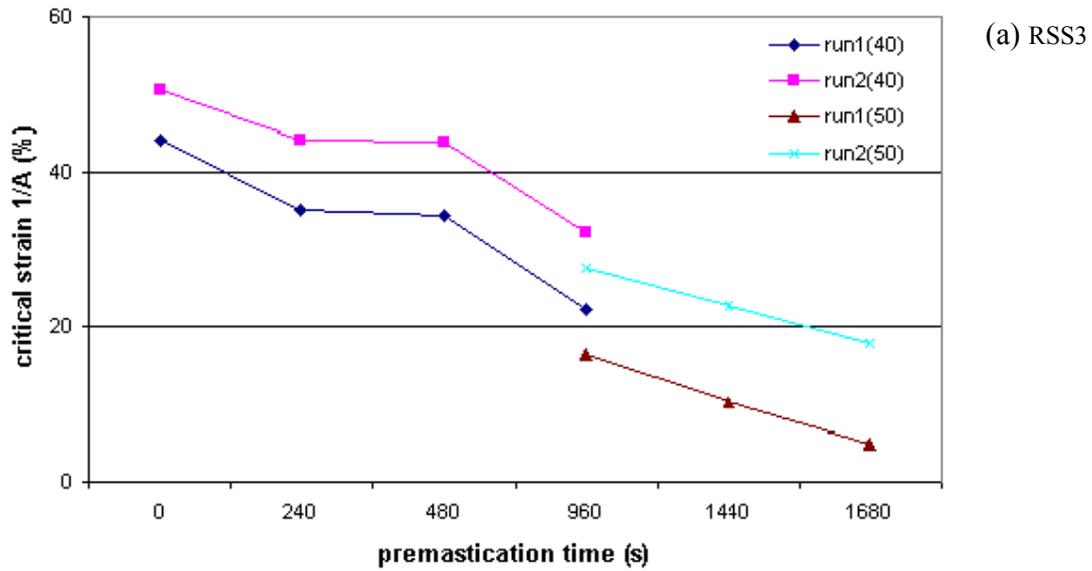
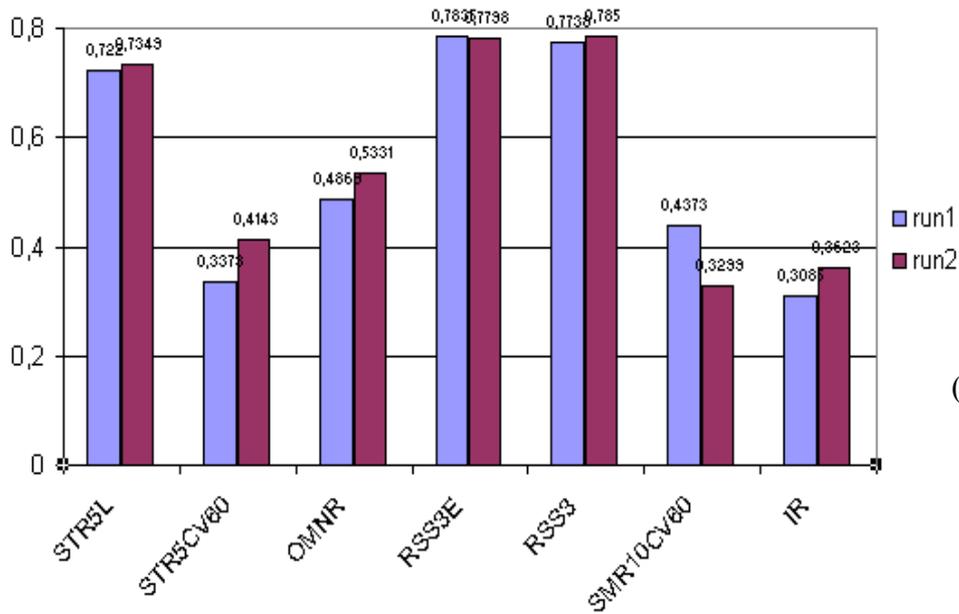
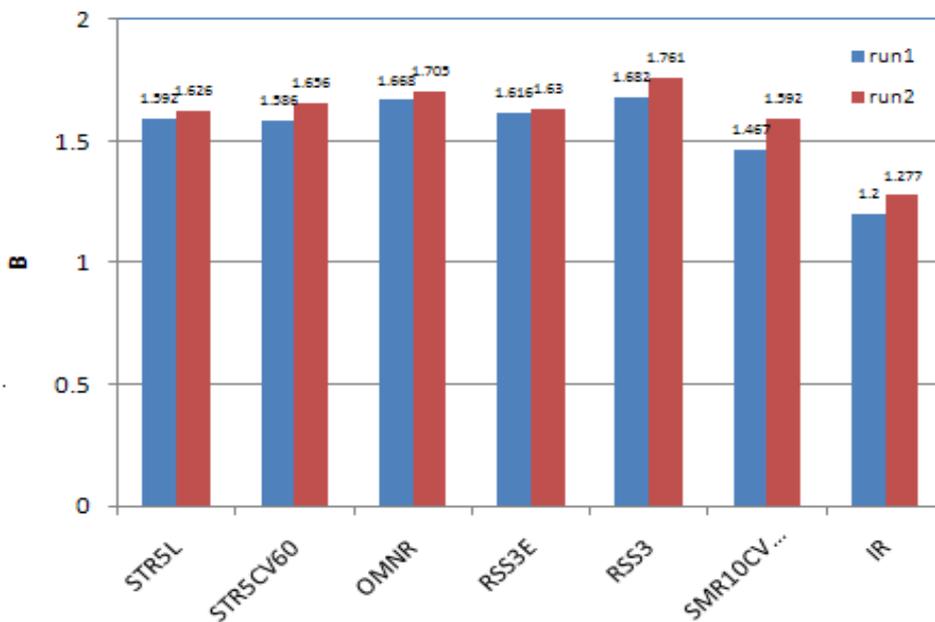


Figure 3.3.10 : RPA-FT at 100°C on filled pre-masticated (a) RSS3 and (b) SMR10CV60 compounds ; mid-modulus critical strain (1/A) vs. strain ; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1

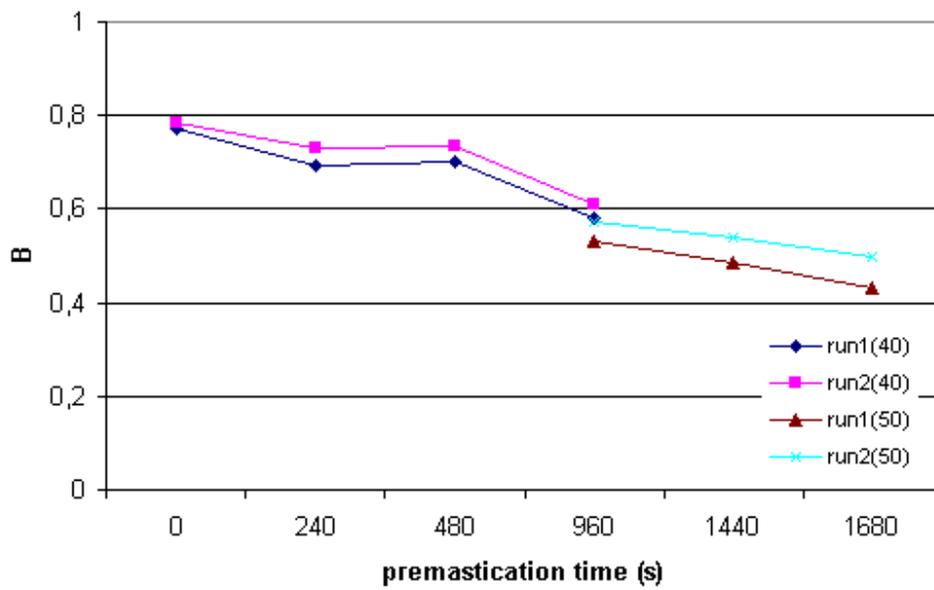


(a) filled

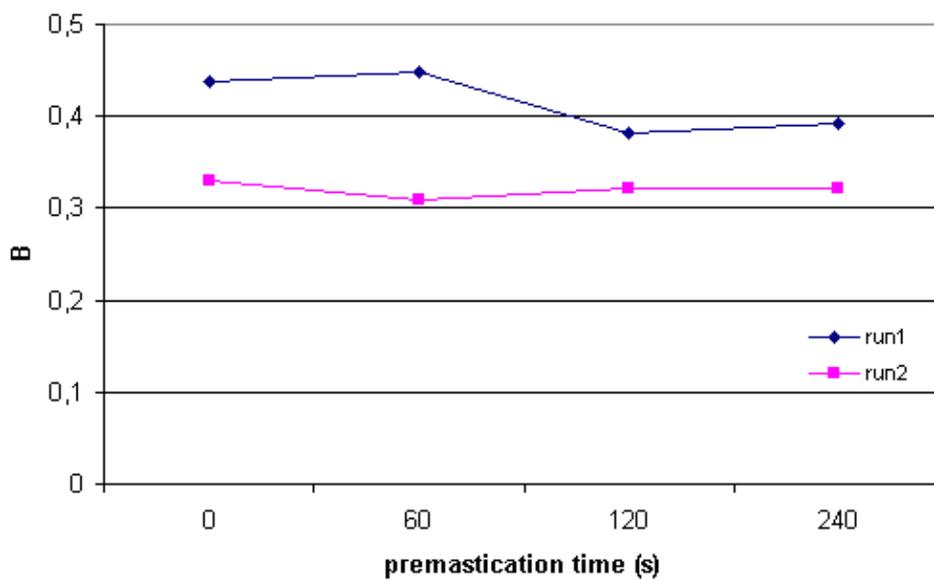


(b) unfilled

Figure 3.3.11 : RPA-FT at 100°C on (a) filled and (b) unfilled rubber compounds ; parameter B vs. strain ; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1



(a) RSS3



(b) SMR10CV

Figure 3.3.12 : RPA-FT at 100°C on filled pre-masticated (a) RSS3 and (b) SMR10CV60 compounds ;parameter B vs. strain ; strain sweep tests at 0.5 Hz; fit parameters of Equation 3.1

3.3.1.2 Quarter torque signal integration

Figure 3.3.13 shows the Q1/Q2 ratio versus strain amplitude for filled (N330) rubber compounds. With the filled (N330) compound, Q1/Q2 ratio is first lower than one at low strain, and then passes above one as strain increases. A Q1/Q2 ratio equal to 1 means perfect symmetry of the torque signal, expected only for a perfect linear material submitted to a perfectly sinusoidal strain. Q1/Q2 higher than 1 means that the (half) torque signal is distorted “on the left”, an observation generally made with pure polymers when submitted to large strain amplitude, and labeled “extrinsic non-linearity”. When the half torque appears distorted “on the right”, it is generally because there is an internal structure of the material that brings an additional non-linearity; in such a case, one uses the term “intrinsic non-linearity”. With respect to Figure 3.3.13, it can therefore be said that intrinsically non-linearity (occurring through the internal morphology of the material) changes to extrinsically non-linear (occurring through external causes, i.e. the applied strain) as strain increases. In all cases, run 2 shows a higher Q1/Q2 ratio than run 1, thus demonstrating that samples are indeed sensitive to strain history, as reported above from G^* vs. strain data. There are slight differences in the difference between run 1 and run 2 for the different rubber grades. It tends to show that the non-linear character changes from intrinsic to extrinsic when the sample is submitted to a previous strain. Figures 3.3.14 and 3.3.15 show the Q1/Q2 ratio versus strain for filled (N330) compounds with pre-masticated NR (RSS3 and SMR10CV60). In the case of filled compound with pre-masticated RSS3 (Figure 3.3.14), run 2 shows a higher Q1/Q2 ratio than run 1 but the difference between both runs decreases with increasing pre-mastication time, in agreement with previously reported results on quarter torque signal integration on gum masticated samples. The same result can be observed from filled (N330) compound with pre-masticated SMR10CV60 (Figure 3.3.15). It indicates that this behavior is essentially reflecting pre-mastication. In the case of unfilled rubber compounds (Figure 3.3.16), Q1/Q2 ratio is higher than one at very low strain then quickly decreases to about one then increases again as strain increases. It is interesting to observe that there is a difference between the two runs (run 2 higher than run 1) for unfilled compounds of field latex grades (STR5L, RSS3 and RSS3E) but that this behavior is not observed with viscosity stabilized (OMNR, STR5CV60, SMR10CV60) and IR grades. They are all extrinsically non-linear, and essentially exhibit the behavior of gum masticated rubber samples. Figure 3.3.17 shows Q1/Q2 ratio at 97.7 % strain (7 deg) of gum NR samples and filled N330 compounds of masticated RSS3 and SMR10CV samples. For filled N330 compounds, Q1/Q2 ratio is lower than one.

This is contrary to results obtained with gum NR samples, for which Q1/Q2 ratio is higher than one. This effect is attributed to the presence of carbon particles but hardly corresponds to differences in FT torque spectra. In other terms, there is a substantial difference between the non-linear viscoelastic behavior of a gum and of a filled NR samples. For gum NR non-linearity is obtained through the application of a sufficiently large strain and this behavior corresponds to extrinsic non-linear viscoelasticity (because occurring through external causes, i.e. the applied strain), whilst the filled NR shows intrinsic non-linear viscoelasticity (because owing to the internal morphology of the material).

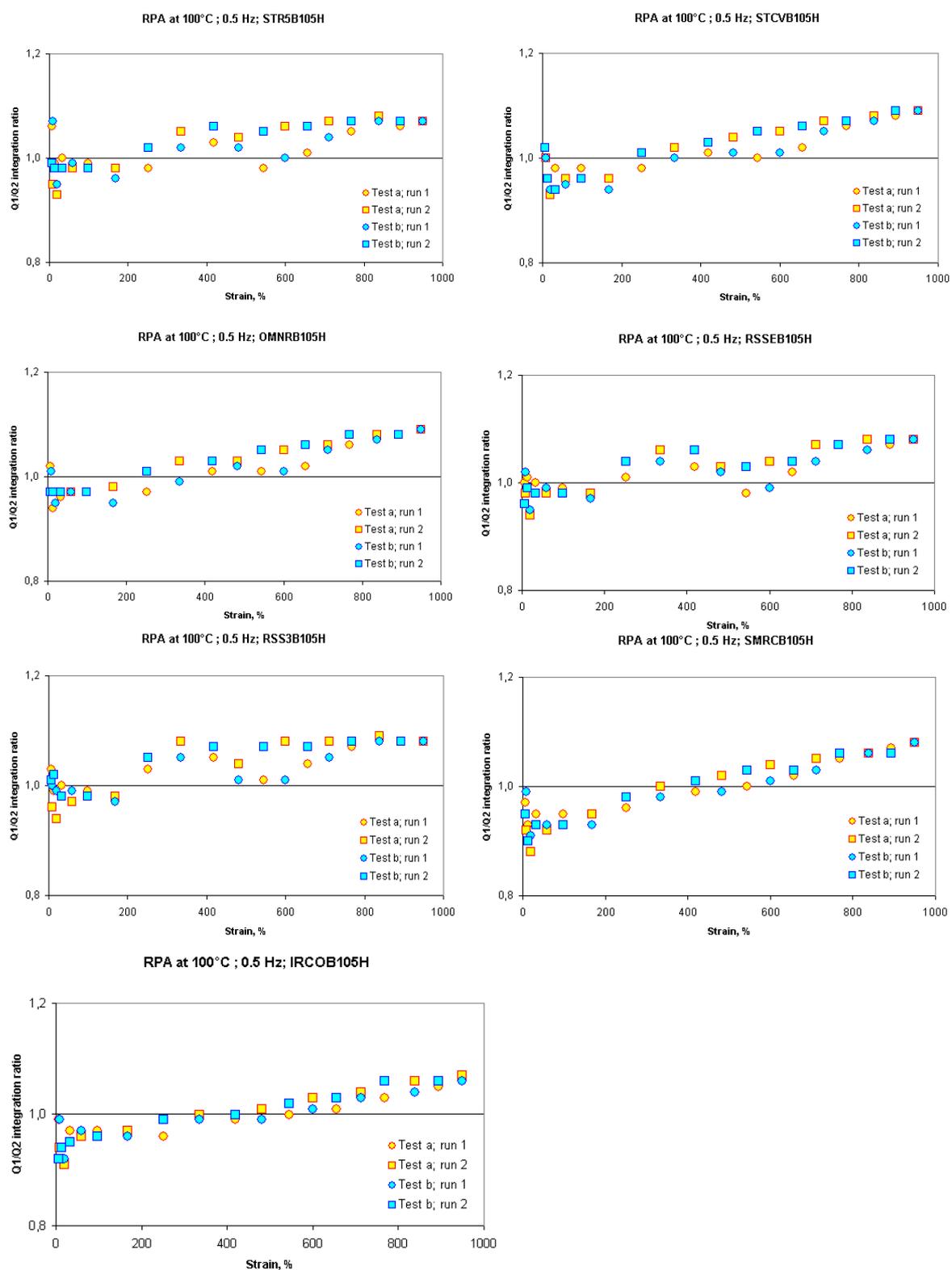


Figure 3.3.13 Assessing extrinsic/intrinsic non-linear viscoelastic characters through quarter cycle torque integration of filled (N330) compounds; strain sweep tests at 0.5 Hz

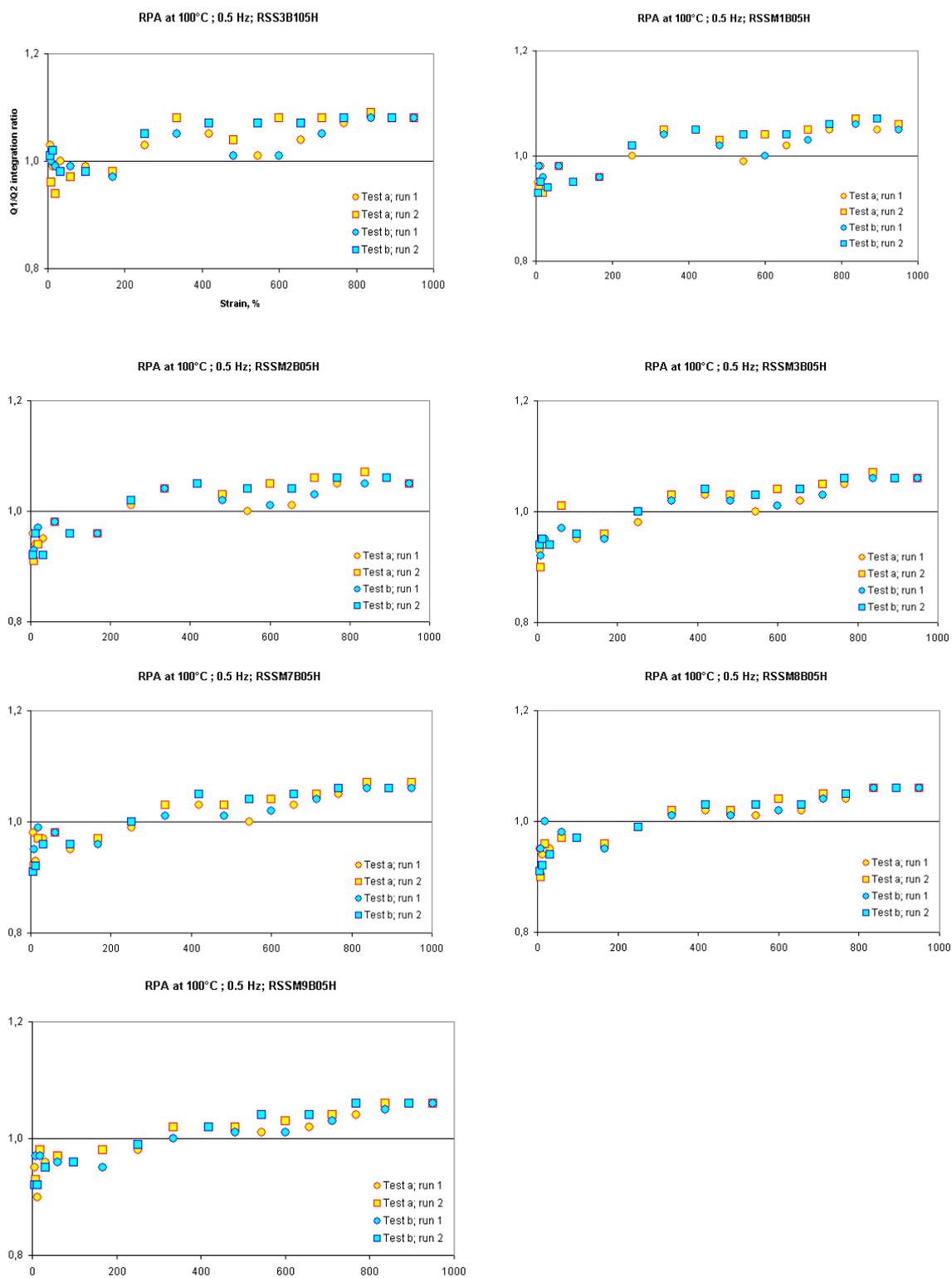


Figure 3.3.14 Assessing extrinsic/intrinsic non-linear viscoelastic characters through quarter cycle torque integration of filled (N330) pre-masticated RSS3 compounds; strain sweep tests at 0.5 Hz

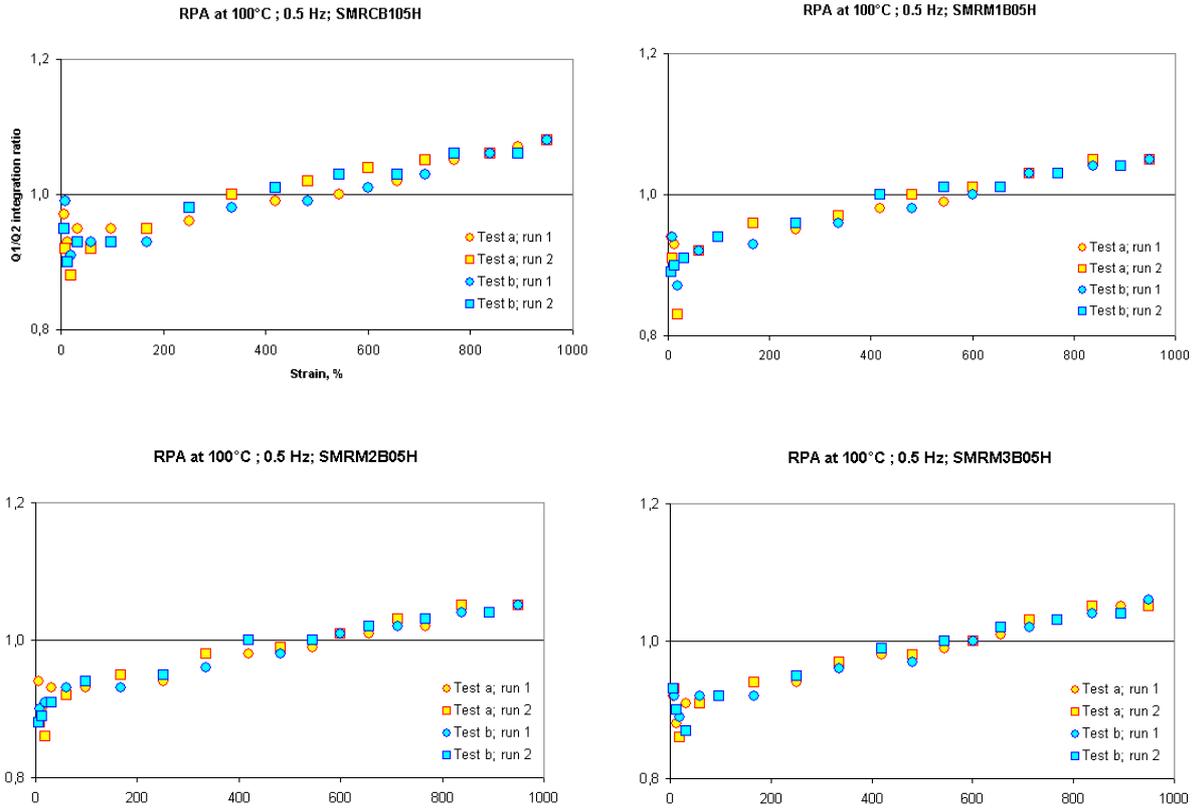


Figure 3.3.15 Assessing extrinsic/intrinsic non-linear viscoelastic character through quarter cycle torque integration of filled (N330) pre-masticated SMR10CV60 compounds; strain sweep tests at 0.5 Hz

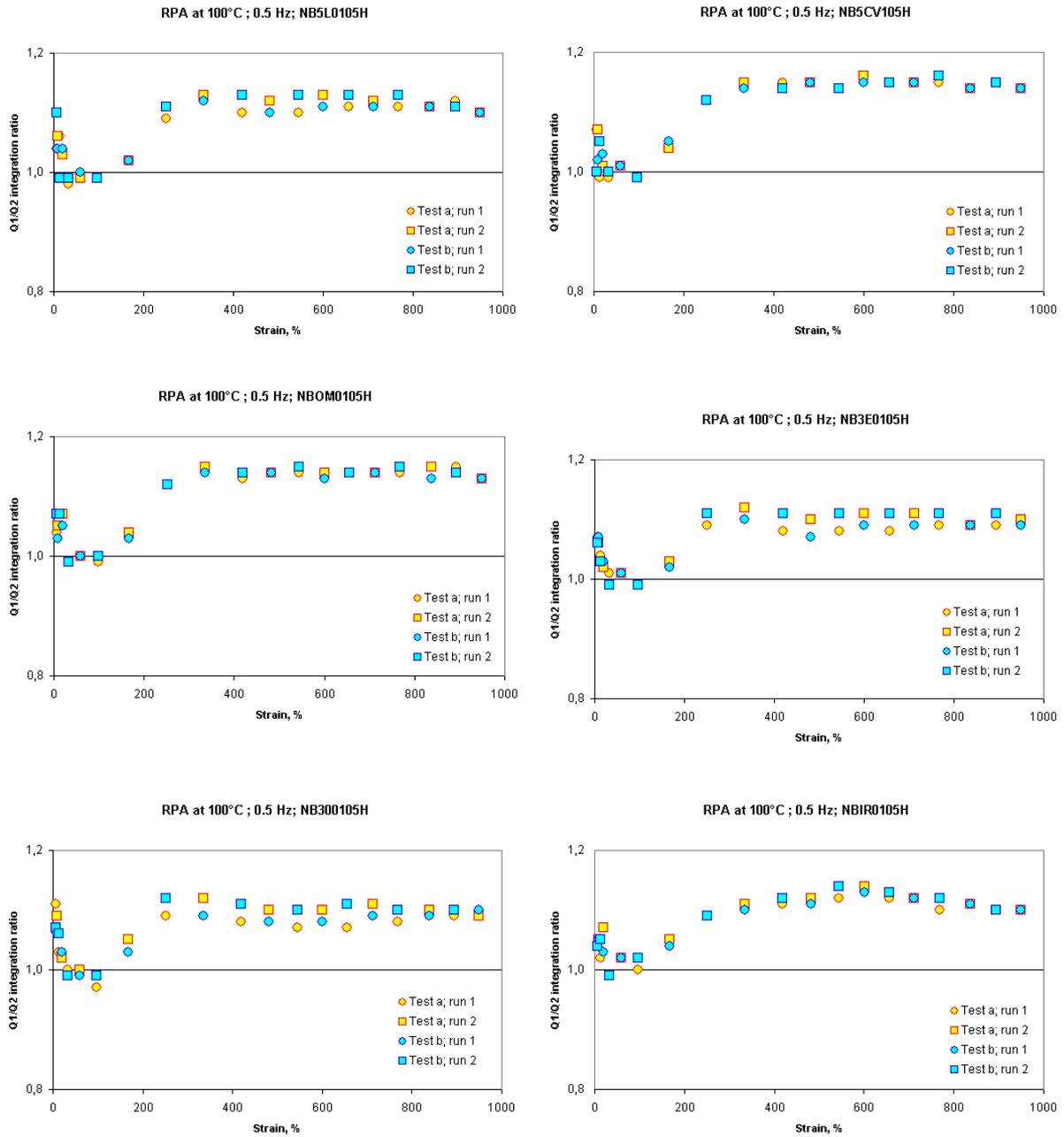


Figure 3.3.16 : Assessing extrinsic/intrinsic non-linear viscoelastic characters through quarter cycle torque integration of unfilled compounds; strain sweep tests at 0.5 Hz

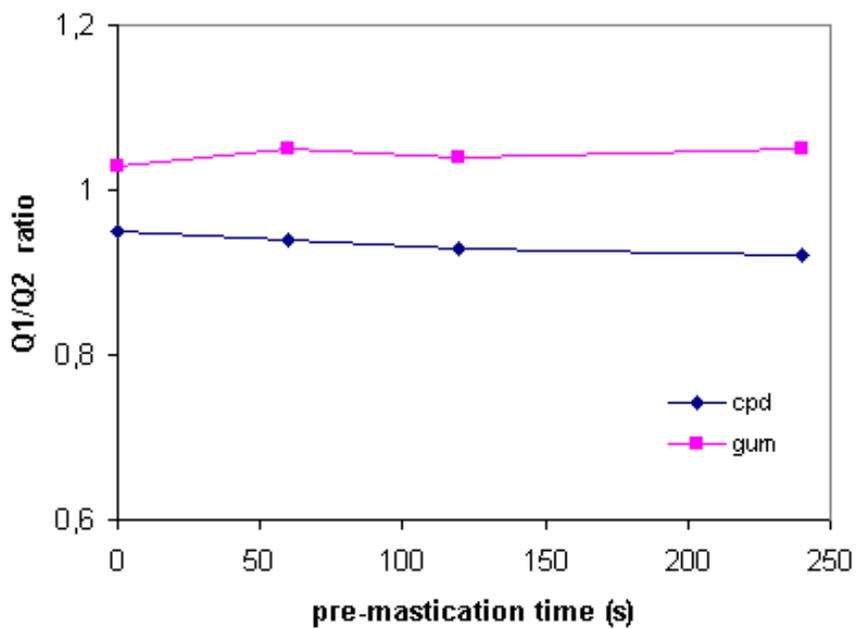
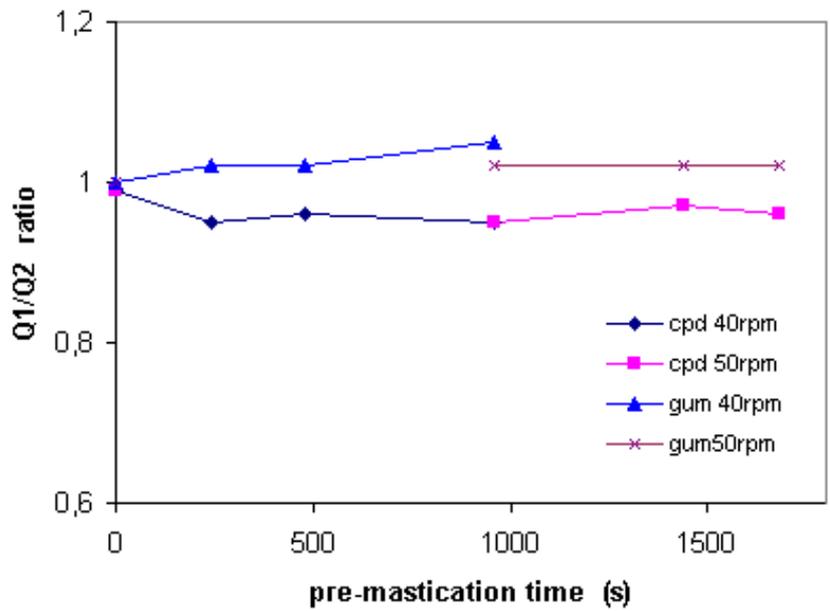


Figure 3.3.17 Q1/Q2 ratio at 7 deg (97.7 % strain) of RSS3 (a) and SMR10CV (b) samples ;effect of mastication time and N330 carbon black loading

3.3.1.3 Torque harmonics vs. strain

Figures 3.3.18 to 3.3.21 show the 3rd relative torque harmonic versus strain. Data are well reproducible with no difference between tests a and b. Figure 3.3.18 compares the results obtained on filled compounds, prepared either with the various NR grades (STR5L, STR5CV60, OMNR, RSS3E, RSS3, SMR10CV60) or synthetic polyisoprene (IR). As can be seen, the 3rd relative torque harmonic increases with increasing strain. For RSS3, RSS3E and STR5L, it is quite interesting to observe that the curves exhibit a peak whose maximum value is reached when the strain is around 400%. But this behavior is not observed with viscosity-stabilized grades (OMNR, STR5CV60, SMR10CV60) and is also not appearing with IR. In such cases, the 3rd relative torque harmonic increases with the strain amplitude according to a smooth curve. Torque signal harmonics appear somewhat sensitive to strain history, especially the RSS3 compound. For STR5L, STR5CV60, SMR10CV60 and OMNR samples, smaller differences were seen between runs 1 and 2 data. For filled (N330) compounds, essentially a non-linear behavior is observed in the whole experimental strain window, except RSS3 grades (RSS3 and RSS3E), which tend to exhibit a linear behavior at very low strain, in agreement with complex modulus versus strain results. In the case of filled (N330) pre-masticated RSS3 compounds (Figure 3.3.19), the size of the peak at around 400% strain decreases as pre-mastication time increases and the peak disappears when the mastication time exceeds 960 s (RSSM7). As can be seen, in agreement with results on gum-masticated samples, the difference between runs 1 and 2 disappears when RSS3 is masticated for more than 960s (see part 3.2; Figure 3.2.13). For filled (N330) compound of pre-masticated RSS3 grade, a trend similar to what is observed with viscosity stabilized grades is seen if the pre-mastication time of the rubber sample is sufficient (in this case more than 960s). But this result is not observed with the SMR10CV60 sample (Figure 3.3.20); there is indeed no significant difference when increasing the pre-mastication time of SMR10CV60 sample. In the case of unfilled compounds (Figure 3.3.21), the 3rd relative torque harmonic increases with increasing strain with a small peak at 400% strain. Contrary to filled (N330) compound, unfilled compounds show a linear behavior at low strain for all NR samples, with no significant difference between the different grades.

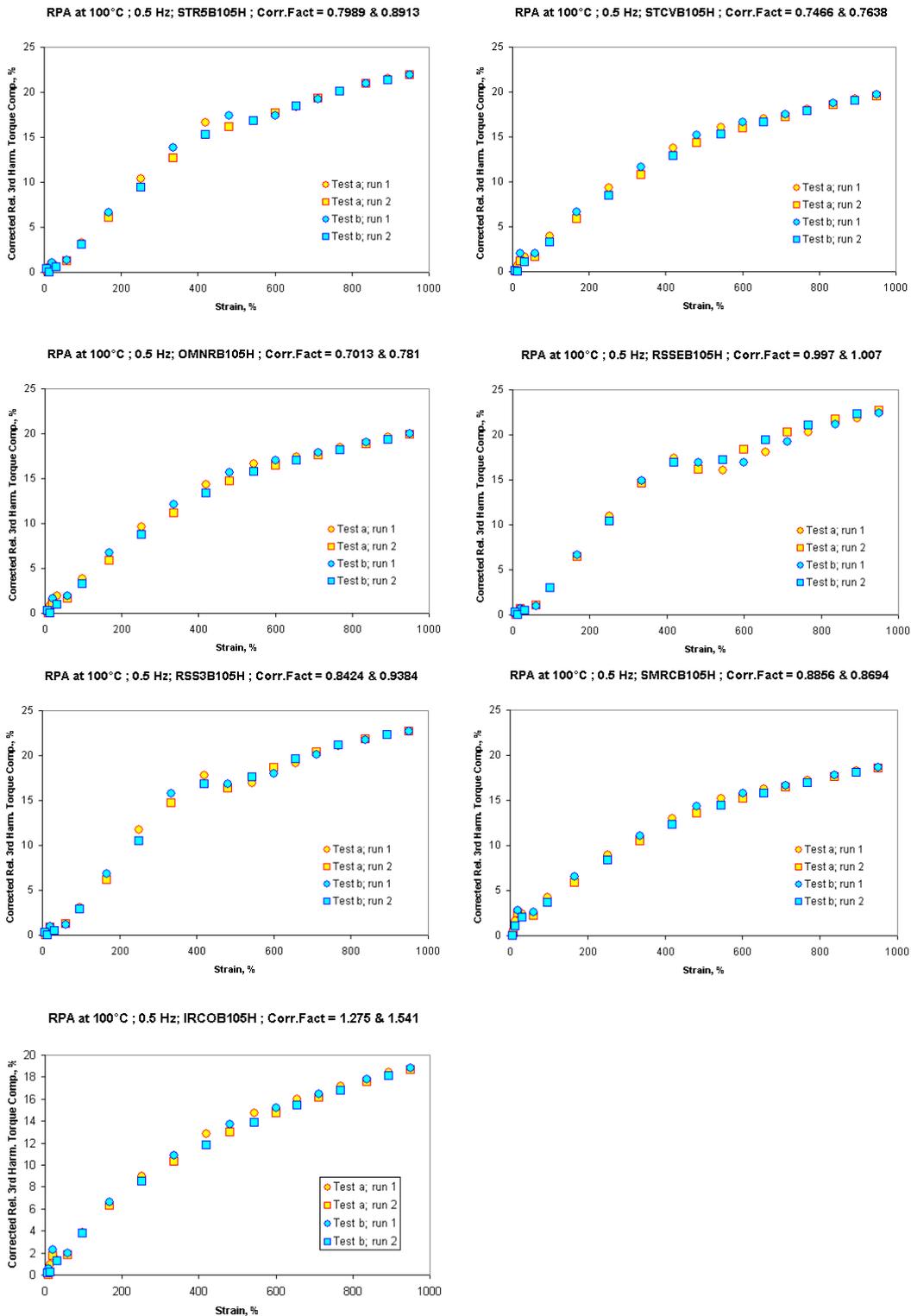


Figure 3.3.18 RPA-FT; total harmonic content vs. strain of filled (N330) compound samples; strain sweep tests at 0.5 Hz

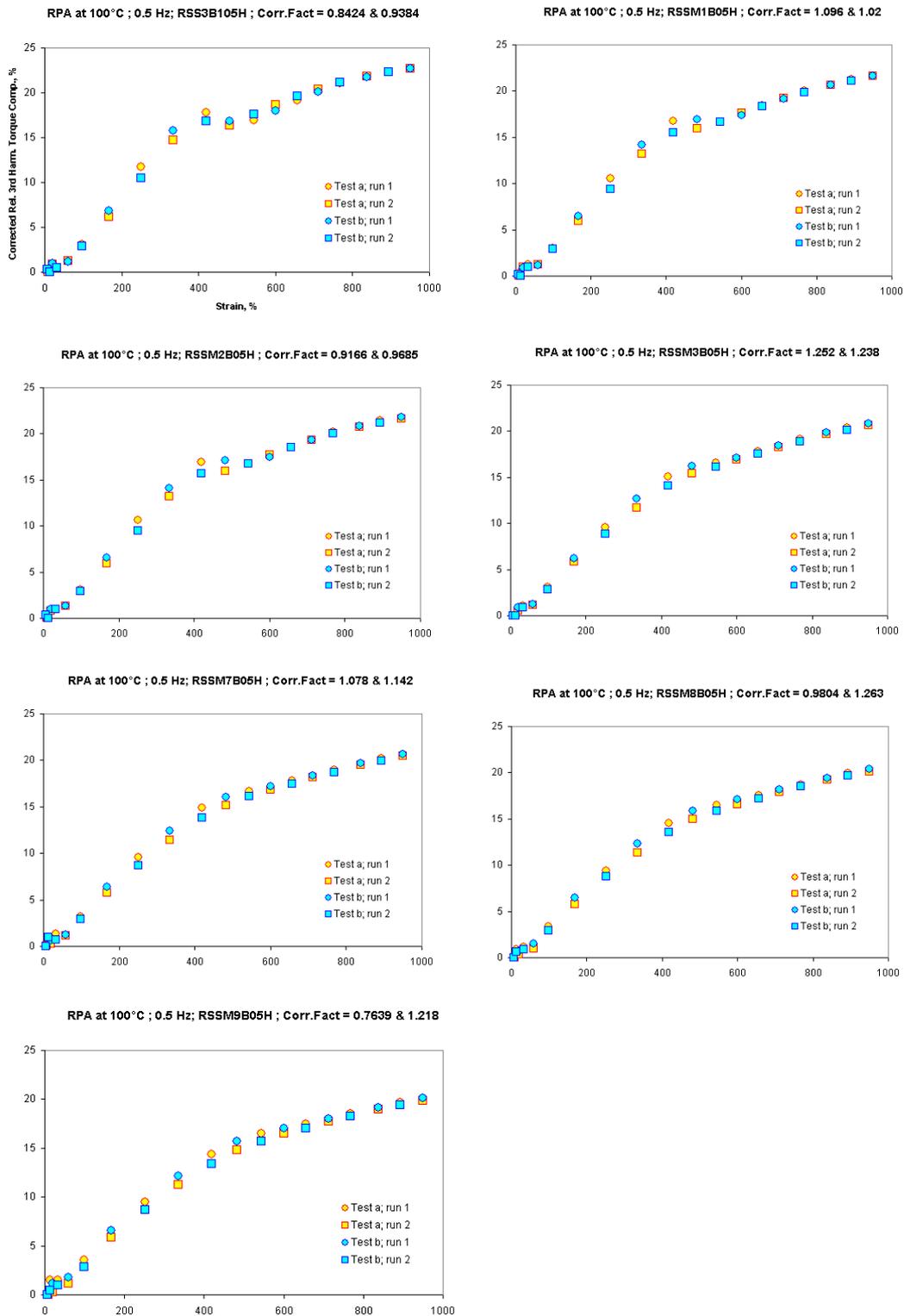


Figure 3.3.19 RPA-FT; total harmonic content vs. strain of filled (N330) pre-masticated RSS3 compounds; strain sweep tests at 0.5 Hz

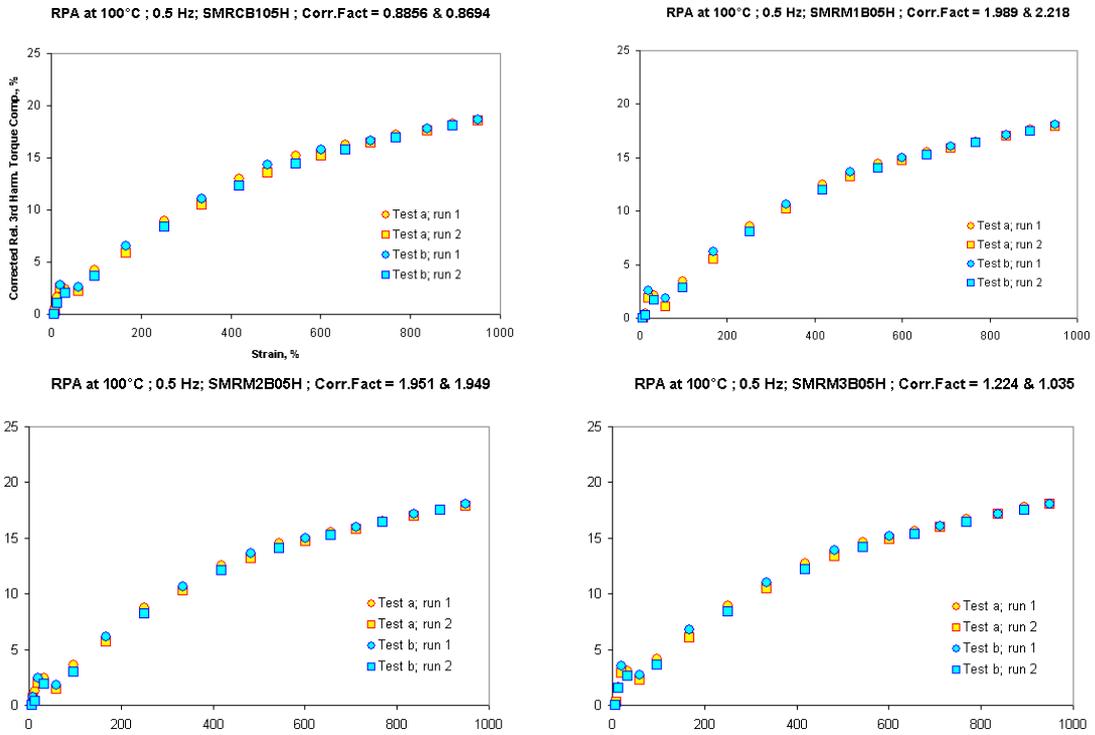


Figure 3.3.20 RPA-FT; total harmonic content vs. strain of filled (N330) pre-masticated SMR10CV60 compounds; strain sweep tests at 0.5 Hz

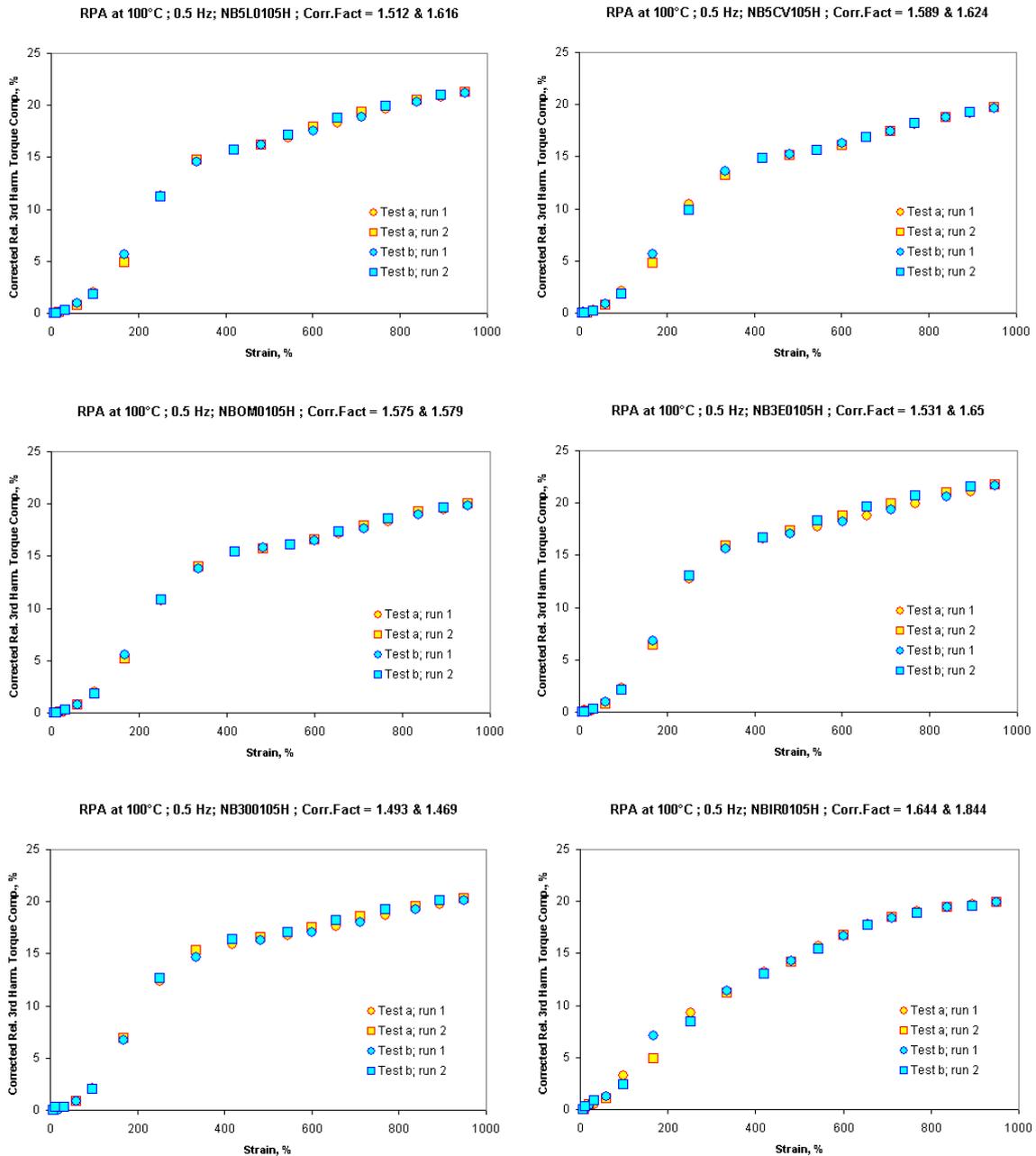


Figure 3.3.21 : RPA-FT; total harmonic content vs. strain of unfilled rubber compounds; strain sweep tests at 0.5 Hz

Table 3.3.4 : Physical properties of filled (N330) cured of different grades rubber

Sample	Hardness (shore A)	T.S. (MPa)	300%Modulus (MPa)	E.B. (%)
OMNR	62	24.0	11.8	513
STR5CV60	63	24.7	12.2	513
STR5L	62	24.2	12.4	500
RSS3E	61	25.6	12.8	510
RSS3	58	24.2	11.8	507
SMR10CV60	60	23.7	10.9	539
IR	61	25.1	11.2	544

Table 3.3.5 : Physical properties of filled (N330) cured of pre-masticated RSS3 and SMR10CV60

Sample	Hardness (shore A)	T.S. (MPa)	300%Modulus (MPa)	E.B. (%)
RSS3	58	24.2	11.8	507
RSSM1	59	25.6	11.7	525
RSSM2	58	26.3	11.8	539
RSSM3	57	26.4	11.7	543
RSSM7	57	25.6	11.8	533
RSSM8	58	26.2	11.9	531
RSSM9	61	25.0	11.4	536
SMR10CV60	60	23.7	10.9	539
SMRM1	60	23.1	9.8	554
SMRM2	58	23.0	10.3	539
SMRM3	61	23.1	10.2	544

Table 3.3.6 Physical properties of unfilled cured of different grades rubber

Sample	Hardness (shore A)	T.S. (MPa)	300%Modulus (MPa)	E.B. (%)
OMNR	40	23.5	1.9	752
STR5CV60	38	25.2	1.8	776
STR5L	39	24.4	1.7	776
RSS3E	41	24.4	1.9	756
RSS3	41	25.4	2.0	755
SMR10CV60	38	20.0	1.7	736
IR	38	23.2	1.7	766

3.3.2 Physical properties of cured rubber

Tables 3.3.4 to 3.3.6 report the physical properties of cured rubber samples. No significant difference in hardness is observed in all cases with the same formulation, i.e. about 60 shore A for filled N330 50 phr and around 40 shore A for unfilled formula. This means that the filler is playing the major role with nearly no effect of the NR grade used. Concerning the 300% modulus, no significant difference is also seen in all cases with the same formulation, about 12 MPa for filled N330 50 phr and about 2 MPa for unfilled formula, except cured SMR10CV60, which tends to show a slightly lower value than the other samples. (about 10 MPa). The same results can be observed for tensile strength (T.S.); no significant difference in all cases, about 24-25 MPa for both filled N330 50 phr and unfilled compound, with the exception of SMR10CV60, which tends show a slightly lower value than the other samples about 23 MPa for filled N330 50 phr and about 20 MPa for unfilled formula. In the case of elongation at break (E.B.) no significant differences are observed in all cases with the same formulation, about 520% for filled N330 50 phr and about 750% for unfilled formula. As expected the % E.B. decreases when compounding with carbon black.

3.4 Conclusions Section 3.3

In the uncured state, filled rubber compounds exhibit a viscoelastic behavior that is substantially different from what can be observed with gum rubbers. It is especially the critical strain ($1/A$) that underlines this difference in the case of gum-masticated rubber. The critical strain increases with increasing mastication time, contrary to results obtained with filled compounds, for which it decreases with increasing pre-mastication time. In other words, filled compounds are more non-linear when using gum rubbers with a larger linear domain. Viscosity stabilized grades (OMNR, STR5CV60, and SMR10CV60) exhibit stronger history effects than field grades (STR5L, RSS3, and RSS3E), in contrast with results on gum rubber samples. According to results in terms of 3rd relative torque

harmonic, compounds with field grades (STR5L, RSS3, and RSS3E) exhibit a peak with a maximum value at around 400% strain, but viscosity stabilized grades compounds (OMNR, STR5CV60, and SMR10CV60), show essentially smooth curves as strain increases. Physical properties of cured rubber for the same formula (but different rubber grades) show no significant difference. This implies that compounds of different NR grades (similar or different in Mooney viscosity and molecular weight) with the same formula can have very different processing properties, but after curing, (static) physical properties are nearly identical and essentially reflect the reinforcing role of the filler (i.e. carbon black).

3.4 References Section 3

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4. Overall conclusions

This research thoroughly studied Natural Rubber, from gum up to compounded and vulcanized samples, using different grades and various techniques, spectroscopic, physico-chemical or rheological. Results from spectroscopic techniques were not found able to reveal significant differences between the various NR grades considered, despite the fact that from field latex to constant viscosity grades, the sampling was covering the main possibilities of *Hevea Braesiliensis* technology. A few interesting observation were made however, using advanced capabilities of spectroscopy. For instance, by using ^{13}C cross-polarization magic angle spinning (CP-MAS) technique, it was possible to distinguish the mobile from the immobile components so that significant differences between the various NR grades were observed. RSS grades were found to exhibit the highest gel content amongst all the tested rubber samples, in general agreement with molecular weight, Mooney viscosity and complex modulus.

An advanced rheometrical technique like Fourier Transform rheometry was found to offer interesting possibilities to distinguish between the various NR grades, sometimes in a very subtle manner. By performing strain sweep experiments in dynamic conditions, at fixed frequency and temperature, FT rheometry was found a method of choice, giving access to quite a large number of viscoelastic information, both in the linear as well as in the nonlinear domains. For instance complex modulus (G^*) behavior was modeled with a relatively simple equation that gave an excellent fitting in all cases and yielded three parameters whose physical meaning is immediate. Such parameters allow a direct comparison between test materials. All gum NR samples were tested in identical conditions and results clearly show that all tested samples exhibit a linear region up to around 60% strain. A good correlation between the molecular weight of the difference NR grades and their linear complex modulus was observed. RSS samples exhibit intrinsic non-linearity but viscosity stabilized grades show extrinsic non-linearity. Torque harmonics behavior was modeled with a four parameters equation. For gum rubber samples, the fitting was excellent in all cases. RSS grades exhibit the strongest strain history effects, according to their highest molecular weight; this result is in agreement with well-known processing difficulties of such grades when manufacturing rubber products.

The study of mastication effect focused on two grades, RSS3 and SMR10CV that more or less represent extreme situations. In order to achieve a comparable reduction in rheological properties, RSS3 samples were found to require higher mixing energy than SMR10CV, in likely relation with the higher molecular weight of the former. A correlation between Mooney viscosity/molecular weight and mixing energy of the NR samples was established, i.e., Mooney viscosity/molecular weight decrease with increasing work input. A fine analysis of our results allows concluding that through mastication effects during the process the gel content of NR is destroyed with consequently a decrease in complex modulus. The extent of the linear region (through the typical strain $1/A$) is increased and the strain history effect is eliminated. As a consequence the nonlinear viscoelastic character changes from intrinsic to extrinsic. This implies that the mastication may have eliminated the sensitivity to strain history effects of NR, with the constant viscosity grade (SMR10CV) being more affected than the RSS one. The relationship between $\tan \delta$ and mastication time shows that $\tan \delta$ increases with increasing mastication time, in agreement with known relationships between $\tan \delta$ and molecular weight of masticated rubbers. This indicates that the viscous character of NR is somewhat increased by mastication, or alternatively that the elastic character is reduced.

Complex modulus (G^*) of filled compounds is well modeled by the same equation as for gum materials, with an excellent fitting in all cases. However the linear region is not observable

in the experimental strain window of the equipment (and likely no other instrument would permit to observed it) so that the extrapolated modulus in the linear region (G^*_0) must be considered with care. Fit equation parameters allow however to recalculate the complex modulus in the observable strain region, thus offering an exact comparison between the different compounds, and hence grades. It was found that filled compounds with field latex grades (i.e. STR5L, RSS3 and RSS3E) exhibit higher complex modulus values than viscosity-stabilized grades (i.e. OMNR, STR5CV60 and SMR10CV), in complete agreement with results on unfilled compounds. But filled compounds have also higher complex modulus than unfilled compounds, by around 40% for all grades NR. This effect obviously reflects the reinforcement by carbon black particles. Filled rubber compounds exhibit a different behavior from gum-masticated rubbers especially in what the critical strain ($1/A$) is concerned. Filled compounds are found to be more non-linear when using gum rubbers with a larger linear domain. Moreover filled compounds with viscosity stabilized grades exhibit stronger history effects than filled compounds with field latex grades, in contrast with results on gum rubber samples. According to results in terms of 3rd relative torque harmonic, compounds with field grades exhibit a peak with a maximum value at around 400% strain, but viscosity stabilized grades compounds show essentially smooth curve as strain increases. Subsequently physical properties of cured rubber for the same formula, but different rubber samples, show no significant difference. This clearly implies that compounds with different grade of Natural Rubber, similar or different in Mooney viscosity and molecular weight, with the same compounding formula can have unique and different processing properties, but after cure, (static) physical properties are nearly identical and essentially affected the reinforcing role of the filler, i.e. carbon black.

Characterizing Gum Natural Rubber Samples Through Advanced Techniques

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ABSTRACT: Owing to its origin, Natural Rubber exhibits more variation than synthetic polymers. If, over the years, NR specifications have evolved from mere visual inspections towards the more complex Technically Specified Rubber (TSR) schema, industrial practice shows that, even for typical TSR grades, significant variations still exist within each shipment, especially in regard to processability. It follows that mastication is quite systematically needed in industrial operations, without or with processing aids or so-called peptizers. Typical NR compounding operations consume therefore time and mixer capacity, a situation, which obviously calls both better characterization methods of (gum) natural rubber and eventually improved grades. There are nowadays promising new techniques to analyze and characterize polymer materials, some of which are a priori attractive for a better specification of NR grades. One such technique is the so-called

Fourier Transform rheometry, a dynamic testing method to investigate both the linear and the non-linear viscoelastic domains of polymer materials. Other are spectroscopic methods like solid Nuclear Magnetic Resonance (NMR), either liquid or solid, whose results might be complemented by Size Exclusion Chromatography with special detection techniques, e.g. SEC-MALS, and Differential Scanning Calorimetry (DSC). The purpose of the work reported here was to investigate a series of gum NR grades using such techniques, with the objectives not only to demonstrate their interest but also to cross-validate their results. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3058–3071, 2011

Key words: rheology; rubber; NMR; viscoelastic properties; microstructure

INTRODUCTION

Despite its industrial success, production specifications of Natural Rubber (NR) remain relatively poor, when compared to synthetics, as only the so-called technically specified (i.e., TSR) grades are characterized with respect to basic rubber test techniques, such as the Mooney viscosity, the (Wallace) Plasticity (P_0), and the Plasticity Retention Index (PRI).¹ Other popular grades, such as ribbed smoked sheets (RSS) for instance are still classified with respect to visual inspection criteria only.²

NR exhibits larger variation than synthetic elastomers, because around 50 different clones of *Hevea Brasiliensis* are nowadays in use, therefore introducing inevitable production differences, further enhanced by climate, soil and other local effects, plus obviously seasonal influences on tapping. The composition of (dry) NR is rather complex, with up to 3% proteins, 2% acetone-soluble resins, minor quantities

of sugar and inorganic salts, and even traces of minerals such as copper and manganese. Over the years, NR specifications have evolved from the mere visual inspection still in usage for RSS grades to the more complex TSR-schemes which include certain values on P_0 , PRI, N_2 content, etc., expectedly to guarantee a certain quality and consistency. However, practice shows that, even for typical TSR grades, a lot of variation still exists especially with respect to processability, for which specifications based on Mooney viscosity³ and on basic elasticity related measurements [e.g., plasticity number and recovery value^{4*}] do not warrant an easy processing and hence constant rheological properties of final compounds. On the factory floor, rubber engineers know well that qualitatively the best NR grades have also the highest initial viscosity and, consequently, are the most difficult to process, requiring for instance premastication, without or with processing aids or so-called peptizers, a practice which obviously consumes both time and mixer

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*Note that ISO 2007 : 1991, Rubber, unvulcanized - Determination of plasticity - Rapid-plastimeter method, uses a principle similar to this test method but the apparatus, test conditions, and procedure are somewhat different.

capacity. There is thus a need for both better characterization methods of (gum) natural rubber grades.

Most rubber processing operations occur at high rate of strain, and therefore it is essentially the nonlinear viscoelastic response of rubber materials that is of interest, whilst all current test methods in use for NR grades characterization are essentially (near) linear viscoelastic methods, e.g., Mooney viscosity, P_0 , and PRI. Not many instruments or test techniques allow the nonlinear viscoelastic domain to be investigated in confidence, and in what harmonic testing methods are concerned, only closed test cavity torsional dynamic rheometers proved to give reproducible and meaningful results. To extend its capabilities, a commercial dynamic rheometer was purposely modified to develop what has been called "Fourier Transform" (FT) rheometry.^{5,6} The capabilities of this technique in delivering data likely related with macromolecular characteristics have so far been approached with a number of polymer materials⁷⁻⁹ and the aims of this article are to offer a further demonstration by comparing advanced molecular characterization results with FT rheometry data, using a series of typical Natural Rubber samples.

MACROMOLECULAR CHARACTERIZATION TECHNIQUES

Differential scanning calorimetry

Differential scanning calorimetry (DSC) determination was performed on a Perkin-Elmer DSC-7 with a heating rate of 10°C/min under nitrogen atmosphere. The sample weight was about 5–10 mg. Calibration was achieved with indium as reference material.

Nuclear magnetic resonance

¹H NMR liquid state spectra were recorded at room temperature on a Bruker 400 Fourier Transform spectrometer at 400.13 MHz in CDCl₃ solution using tetramethylsilane (TMS) as internal standard. Solid-state NMR experiments were carried out at room temperature on a Bruker Avance 300 MHz wide bore spectrometer at 75.47 MHz using Cross-Polarization (CP) combined with Magic Angle Spinning (MAS). The spectra were recorded at spinning frequencies equal to 5 kHz. Chemical shifts are expressed in ppm downfield from TMS used as an external reference. For CP-MAS experiments, we chose the ¹H radio frequency field strength such as the $\pi/2$ -pulse duration was equal to 4 μ s. The frequency field phase is switched to $\pi/2$ simultaneously to the application of a frequency field to the carbons matching the so-called Hartmann-Hahn condition during the contact time t_{CP} . A high power proton decoupling is applied during acquisition. The reconstruction of the spectra was performed with the

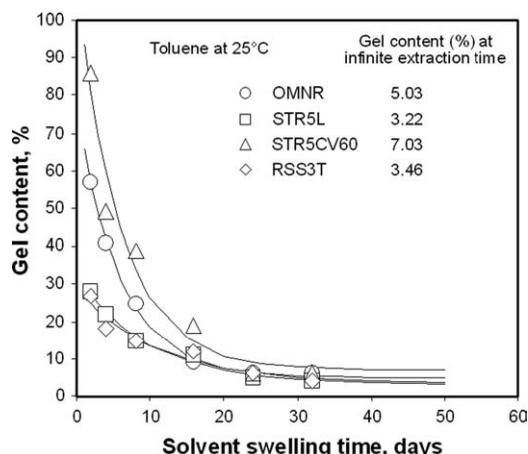


Figure 1 Assessing the gel content through a solvent swelling kinetic method.

DMFit2006 software using four adjustable parameters for each NMR line: isotropic chemical shift, line width, line-shape, and line intensity¹⁰ The ¹³C CP magnetization curves versus contact time of each carbon of the epoxy resin were built-up from line intensities.

Gel content through solvent swelling

It is widely accepted that dry natural rubber samples can have a gel component, defined as the proportion that does not dissolve in a good solvent of the gum rubber. Many methods have been reported¹¹⁻¹⁴ for assessing the gel content but none is so far well established because results remain sensitive to the choice of solvent, the time allowed for solubilizing, and of course the temperature. The following simple procedure was therefore used that focuses on swelling kinetics. A sample of around 1 gm is cut in small pieces and poured in 50 mL of toluene at room temperature. The rubber solvent system is gently agitated for a few minutes before allowing the dissolution to proceed undisturbed for selected periods (e.g., 2 days, 4 days, 8 days, etc. until equilibrium time is likely reached). The swollen rubber pieces sediment at the bottom of the flask so that, after each period, 10 mL of supernatant solution are carefully drawn out using a fine-tipped pipette. The dissolved rubber in the supernatant sample is recovered by evaporating the solvent under vacuum at 50°C for 24 h. The sol and gel fractions, i.e., Φ_{sol} and Φ_{gel} are calculated using:

$$\Phi_{sol} = \frac{W_i V_1}{W_1 V_2} \quad \text{and} \quad \Phi_{gel} = 1 - \Phi_{sol}$$

Where W_1 is the initial weight of rubber, W_i is the weight of rubber in the 10 mL supernatant solution at time i , V_1 the overall volume (i.e., 50 mL) and $V_2 = 10$ mL. This procedure yields gel fractions after various

period so that the fraction for an infinite solubilizing time is easily obtained by extrapolation, using a single three parameters exponential decay equation, as illustrated in Figure 1. As can be seen, relatively minor differences are seen between the NR samples, providing an "infinite" extraction time is considered. Large gel contents are observed only for less than 10 days dwell time in the solvent but the results are transient. Such results suggest that an alternative method consists in assessing the supernatant rubber content after some 50 days swelling time.

Gel permeation chromatography with MALS detection (SEC-MALS)

Macromolecular characteristics were assessed in CIRAD (Montpellier, France) using size exclusion chromatography coupled with multiangle light scattering (SEC-MALS). The SEC-MALS equipment consists of an online degasser (EliteTM, Alltech Associates, Deerfield, IL), a Waters 515 pump, a refractive index detector (Waters 2410) and a multiangle light scattering detector (Dawn DSP, Wyatt Technology, Santa Barbara, CA). Three PLgel-Mixed-A (Polymer Laboratories, Varian, Palo Alto, CA) mixed bed columns (20 mm, 300 mm \times 7.8 mm internal diameter) with a guard column were used. The columns were maintained at 45°C and THF (tetrahydrofuran) was used as mobile phase with a flow rate of 0.65 mL/min; the injected volume was 150 mL. The data from MALS detectors were analyzed with the Astra software, V 5.3.2.22 (Wyatt Technology) using either the Berry or the Zimm method. Test solutions were prepared by dissolving 25 ± 5 mg of rubber in 40 mL THF (HPLC grade) stabilized with 2,6-di-*tert*-butyl-4-methylphenol. After 1-week storage in darkness at 30°C, solutions were filtered through 1 μ m, glass fiber paper (Pall Co, Port Washington, NY), so that with respect to the polymer concentration before and after filtration the gel content was assessed. Kim et al. have published details of the technique.^{15,16}

RHEOLOGICAL CHARACTERIZATION TECHNIQUES

Mooney viscometer

Mooney torque ML(1+4) was assessed using a standard instrument, according to ASTM D 1646-03a test method.^{17,18} A large rotor (diameter: 19.05 mm; thickness: 5.54 mm) was used.

Fourier transform rheometry

Principle of the technique

Fourier Transform (FT) rheometry is a technique that documents the nonlinear viscoelastic behavior of polymer materials through performing large am-

plitude oscillatory strain (LAOS) experiments. No commercial instruments are yet available but the technique is easily implemented on appropriate instruments. Essentially, Fourier transform rheometry consists in capturing strain and torque signals during dynamic testing and in using the appropriate calculation algorithm to resolve it into their harmonic components.

FT is simply a mathematical treatment of harmonic signals that resolves the information gathered in the time domain into a representation of the measured material property in the frequency domain, as a spectrum of harmonic components. If the response of the material is strictly linear, then proportionality between (applied) strain and (measured) torque is kept, the torque signal is a simple sinusoid and consequently the torque spectrum consists of a single peak at the applied frequency. A nonlinear response is thus characterized by a number of additional peaks at odd multiples of the applied strain frequency. At high strain, a nonlinear response is observed so that the torque signal becomes distorted, which reflects a lack of proportionality between the applied strain (perfectly sinusoidal) and the measured torque. FT can also be applied on the strain signal to quantify its quality.

Wilhelm et al.^{5,19} demonstrated that only odd torque harmonics are significant in terms of material's response. Indeed, if a shear strain of maximum strain amplitude γ_0 (rad) is applied at a frequency ω (rad/s) to a viscoelastic material, the strain varies with time t (s) according to $\gamma(t) = \gamma_0 \sin(\omega t)$ and the shear stress response can be expected to be given by a series of odd harmonics, i.e.:

$$\sigma(t) = \sum_{j=1,3,5,\dots}^{\infty} \sigma_j \sin(j\omega t + \delta_j) \quad (1)$$

providing one assumes that, over the whole viscoelastic domain (i.e., linear and nonlinear), the viscosity function $\eta = f(\dot{\gamma})$ can be approximated by a polynomial series with respect to the shear rate. If the tested material exhibits a pure linear viscoelastic response, eq. (1) reduces to the first term of the series, as considered in most standard dynamic test methods.

Up-dating a torsional dynamic tester for Fourier transform rheometry

Any commercial torsional dynamic tester can be conveniently updated for Fourier transform rheometry, but conventional open gap rheometers, for instance parallel disks and cone-and-plate instruments have been shown to be limited to relatively low strain amplitude experiments²⁰ on materials exhibiting a relatively modest elasticity. Indeed laboratory practice shows that open gap rheometers give poorly reproducible results with very stiff and/or highly elastic

materials, essentially because it is nearly impossible to reproducibly position such materials in the testing gap. Because they were designed for easy handling of very stiff materials, such as filled rubber compounds, closed cavity torsional testers are particularly suitable for Fourier transform rheometry and, therefore, the appropriate modifications were brought to a Rubber Process Analyzer, RPA 2000® (Alpha Technologies, now a division of Dynisco LLC, Franklin, MA) to capture strain and torque signals. Details on the modification and the measuring technique were previously reported.²¹ Essentially, strain and torque signals, as provided by the instrument, are collected by means of an electronic analogic – digital conversion card. Test results consist thus in data files of actual harmonic strain and stress readings versus time. Proprietary data handling programs are then used to perform Fourier transform calculations and other data treatments. Through simultaneous FT treatment of both the torque and strain signals, it has been demonstrated that, at large strain amplitude, the RPA submits materials to a nearly pure strain sinusoidal signal.⁹ However, strain signal quality degenerates as strain angle decreases and a correction method had to be developed, as explained below.

Fourier Transform analysis yields essentially two types of information: (1) the main signal component, i.e., the peak in the FT spectrum that corresponds to the applied frequency [hereafter noted either $T(1\omega)$ or $S(1\omega)$ with respect to the torque or strain signals respectively], (2) the harmonics, with the third (i.e., the peak at 3 times the applied frequency) the most intense one. A specific calculation program, written using the FT algorithm available in MathCad 8.0® (MathSoft Inc.), is used to obtain the amplitude of the main stress and strain components (corresponding the test frequency) and the relative magnitudes (in %) of the odd-harmonic components, i.e., $I(n \times \omega_1)/I(\omega_1)$. Note that we used $I(n\omega_1)/I(\omega_1)$ or the abridged form $I(n/1)$, to describe the n th relative harmonic component of any harmonic signal; $S(n\omega_1)/S(\omega_1)$ or $S(n/1)$ specifically means that a strain signal is considered; $T(n\omega_1)/T(\omega_1)$ or $T(n/1)$ is used for the Torque signal.

Strain sweep test protocols for nonlinear viscoelasticity investigations

When submitting pure polymers to harmonic strain, nonlinear viscoelastic behavior occurs at high strain amplitude and, therefore, strain sweep test is the method of choice to investigate nonlinearity. The appropriate test protocols were developed, which essentially consist in performing strain sweep experiments through two subsequent runs separated by a resting period of 2 min. At least two samples of the same material are tested (more if results reveal test material heterogeneity), in such a manner that, through inversion of the strain sequences (i.e., Run 1 and Run

2), sample fatigue effects are detected, if any. Differences are expected between Runs 1 and 2 for materials exhibiting strain memory effects. With the RPA, the maximum applicable strain angle depends on the frequency, for instance around 68° ($\approx 950\%$) at 0.5 Hz, considerably larger than with open cavity cone-plan or parallel disks torsional rheometers. Whatever the frequency, the lower strain angle limit is 0.5° (6.98%) below which the harmonic content of the strain signal becomes so high that measured torque is excessively scattered and likely meaningless. Test protocols at 0.5 Hz were designed to probe the material's viscoelastic response within the 0.5° to 68° range, with up to 20 strain angles investigated.

FT analysis of the strain (i.e., applied) signal allows its quality to be precisely documented and, if needed, the appropriate correction to be brought on torque harmonics, according to²²:

$$T(n\omega/1\omega)_{\text{corr}} = T(n\omega/1\omega)_{\text{TF}} - \text{CF} \times S(n\omega/1\omega)_{\text{TF}} \quad (2)$$

where $T(n\omega/1\omega)_{\text{TF}}$ and $S(n\omega/1\omega)_{\text{TF}}$ are the n th relative harmonic components of the torque and strain signals, respectively. CF is the correction factor, as derived from a plot of $T(n\omega/1\omega)$ vs. $S(n\omega/1\omega)$. The correction applies also when considering the so-called "total torque harmonic content" (TTHC), i.e., the sum $\sum T(n\omega/1\omega)$ of all the odd harmonics up to the 15th.

Modeling the effect of strain amplitude on FT rheometry results

According to strain sweep test protocols described above, RPA-FT experiments and data treatment yield essentially two types of information, which reflects how the main torque component, i.e., $T(1\omega)$, and the relative torque harmonics vary with strain amplitude. Such variations can conveniently be modeled with simple mathematical relationships.

The ratio of the main torque component over the strain, i.e., $T(1\omega)/\gamma$ has obviously the meaning of a complex modulus, i.e., $G^* = 12.335 \times \frac{T(1\omega)}{\gamma}$ [with G^* in kPa, $T(1\omega)$ in arbitrary unit and γ in %] and, for a material exhibiting linear viscoelasticity within the experimental window, a plot of G^* vs. γ shows the most familiar picture of a plateau region at low strain, then a typical strain dependence. Such a behavior is well captured with the following equation:

$$G^*(\gamma) = G_f^* + \left[\frac{G_0^* - G_f^*}{1 + (A\gamma)^B} \right] \quad (3)$$

where G_0^* is the modulus in the linear region, G_f^* the final modulus, A the reverse of a critical strain for a mid modulus value to be reached, and B a parameter describing the strain sensitivity of the material.

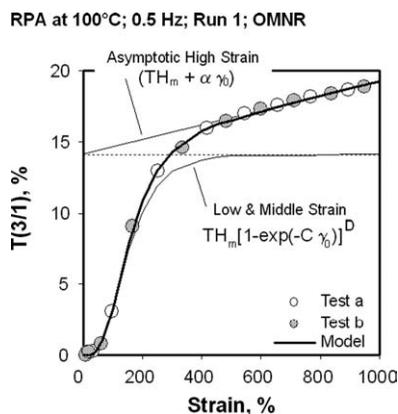


Figure 2 Modeling the variation of relative torque harmonics with strain amplitude; note that for the sake of clarity, the low and middle strain component of the model has been multiplied by TH_m ; otherwise this component plateaus out at 1.

Odd torque harmonics become significant as strain increases and are therefore considered as the nonlinear viscoelastic “signature” of tested materials, only available through Fourier Transform rheometry. Numerous experiments on various pure, unfilled polymers have shown that relative torque harmonics vary with strain amplitude in such a manner that an initial S-shape curve appears bounded by a simple linear variation at high strain. Accordingly, the following model was successfully developed to fit results obtained on simple polymer systems:

$$TH(\gamma) = (TH_m + \alpha\gamma_0) \times [1 - \exp(-C\gamma_0)]^D \quad (4)$$

where γ_0 is the strain magnitude, TH_m , α , C , and D parameters of the model. The member $(TH_m + \alpha\gamma_0)$ expresses an asymptotic linear variation of harmonics in the high strain region, while the member $[1 - \exp(-C\gamma_0)]^D$ describes the onset and the development of the nonlinear viscoelastic response, obviously occurring in the low and middle strain regions, as illustrated in Figure 2.

The physical meaning of parameters TH_m and α is obvious; parameter D somewhat reflects the extent of the linear viscoelastic region (i.e., where no harmonics are detected), while parameter C indicates the strain sensitivity of the nonlinear character. As the strain γ is

smaller and smaller, in other words in the linear viscoelastic region, eq. (4) corresponds to asymptotically zero harmonics, in complete agreement with theory. It is worth noting that in using eq. (4), one may express the deformation (or strain) γ either in degree angle or in %. Obviously all parameters remain the same except C , whose value depends on the unit for γ . The following equality applies for the conversion: $C(\gamma, \text{deg}) = \frac{180\alpha}{100\pi} \times C(\gamma, \%)$, where $\alpha = 0.125$ rad.

EXPERIMENTAL RESULTS AND DISCUSSION

Test materials

With the objective to cover a representative range with a limited number of samples, a series of Natural Rubber grades were collected, thanks to the courtesy of the Rubber Research Program of Thailand. Except wrapping in dark plastic sheets, no particular precaution were observed in sampling and transporting the sample, so that any atmosphere, temperature and other effects, if any, are considered to have affected the test materials in the same manner. A NR grade commercially available in France was included in the study and a commercial high cis-1,4 polybutadiene as typical high elasticity synthetic material. Table I gives a description of the samples and a few characterization results (suppliers’ data).

STR 5L is a technically specified light color rubber grade, obtained by coagulating freshly collected high quality latex. Wet crumbs are then placed in open trays and dried in a forced air dryer at a temperature of 110–125°C, before testing at a certified TSR laboratory. Rubber passing the TSR L specifications has a maximum 0.04% dirt content, maximum 0.4% ash content, a maximum 0.6 nitrogen content, an initial plasticity $P_0 = 35$ (minimum) and a minimum plasticity retention index of 60.

Whole field latex is used to produce RSS. Collected latex is first diluted to 15% solids, and then coagulated for around 16 h with dilute formic acid. Coagulated material is then milled, water removed, and sheeted with a rough surface to facilitate drying. Sheets are dried in a smokehouse for one to seven days. RSS grades consist of deliberately coagulated rubber sheets and graded according to their color, consistency and observed impurities. RSS3F and

TABLE I
Test Samples

Sample code	Material description	Origin	Mooney ML(1+4) _{100°C}
STR 5L	Natural rubber, Standard Thai rubber, 5L grade	Thailand	70
STR 5CV60	Natural rubber, constant viscosity grade	Thailand (Jana)	63
RSS3F	Natural rubber, rib smoked sheet #3	Safic-Alcan, France	75
RSS3T	Natural rubber, rib smoked sheet #3	Thailand	67
OMNR	Natural rubber, optimized molecular weight	Thailand	60.
BR40	98% cis-1,4 Polybutadiene, NeoCis BR40	Polimeri, Italy	43

TABLE II
Mooney Results, Gel Content, and Macromolecular Characteristics

NR sample	Mooney ML(1+4) 100°C	SEC—MALS results				
		Gel content (%)	M_n (Kg/mol)	M_w (Kg/mol)	M_z (Kg/mol)	MWD
STR 5L	70	23.96 ± 1.44	679 ± 31	1278 ± 11	2375 ± 21	1.88
STR 5CV60	63	16.87 ± 1.91	491 ± 2	1323 ± 3	2779 ± 140	2.69
RSS3F	75	34.47 ± 1.39	1051 ± 43	1755 ± 34	2934 ± 60	1.67
RSS3T	67	45.28 ± 0.95	1143 ± 27	1685 ± 29	2597 ± 84	1.47
OMNR	60	15.72 ± 4.29	464 ± 18	1130 ± 73	2407 ± 284	2.43
BR40 ^a	43	0	142	493	N/A	3.2

^a Source : Univ. P. & M. Curie—Polymer Rheology & Processing; molecular weights by GPC.

RSS3T meet the following specifications: 0.20 dirt content maximum, 1.00% ash content (maximum), 0.60% maximum nitrogen content, $P_0 = 30$ (minimum) and PRI = 50 (minimum).

STR 5CV60 is a technically specified “constant viscosity” grade, produced from field latex, whose Mooney viscosity is stabilized to a specified value [i.e., ML(1+4)100°C = 60 ± 5], through the addition of a suitable chemical. Dirt, ash, and N₂ contents (%) are maximum 0.05, 0.6, and 0.6 respectively. PRI is minimum 60. On storage this grade is expected to remain within eight hardness units.

Optimized Molecular Weight Natural Rubber (OMNR) is a new grade currently developed in Thailand, through coagulation of selected field latex products; the viscosity is reduced and stabilized through the addition of a (undisclosed) chemical. No stabilizer or oil is added. OMNR is relatively similar to TSR CV60 but is expected to show no variation on ageing.

Used for comparison purposes, Europrene NeoCis BR40 is a 98% cis-1,4 polybutadiene from a Ziegler-Natta process with a neodymium salt as catalyst, commercially available from Polimeri Europa (Italy).

Mooney, gel content and SEC-MALS data

Table II gives the Mooney results, the gel content and the SEC-MALS data, as kindly provided by CIRAD-Montpellier; data on 98% cis-1,4 polybutadiene are also included.

TABLE III
Differential Scanning Calorimetry Results of Various Sample NR Gums

Sample code	Gum sample T_g (°C)	CH ₂ Cl ₂ extraction		THF extraction	
		Unsolved %	Extracted sample T_g (°C)	Unsolved %	Extracted sample T_g (°C)
STR 5L	-63	10	-63	17	-63
STR 5CV60	-63	21	-62	24	-63
RSS3F	-64	18	-62	26	-62
RSS3T	-63	11	-62	8	-63
OMNR	-64	6	-63	4	-62

As can be seen the gel content data obtained through the solvent swelling kinetic method on NR samples (Fig. 1) do not correspond at all with the data obtained by the CIRAD but it must be noted that the latter were obtained only after 1 week solubilizing and using a filtration technique. Figure 1 above showed that after 1 week the solubilizing process is still far from equilibrium and furthermore, using a 1 μm mesh filter is likely retaining grossly swollen but not (naturally) networked macromolecules. One would conclude that gel content data associated with SEC-MALS measurements are not reliable information. One notes however a nearly perfect linear relationship between the gel content and the number average molecular weight as determined by SEC-MALS. It is also worth underlining that there is no correlation between Mooney results and macromolecular dimensions, either M_n or M_w .

An interesting observation is the larger molecular weight distribution of the two constant viscosity grades (i.e., STR 5CV60 and OMNR) when compared with the RSS and the field latex grades. A careful analysis of the data given in Table II reveals in fact that the chemicals used to stabilize the viscosity do reduce more the number average than the weight average molecular weight, hence the larger (nearly double) MWD. Owing to the limited number of samples studied here, such an observation might be fortuitous and calls for further investigations.

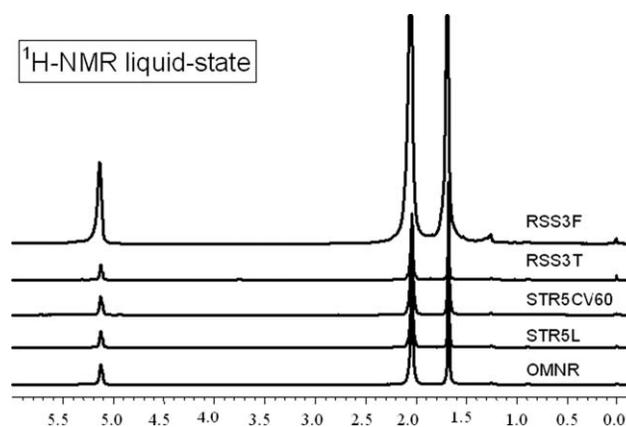


Figure 3 ¹H-NMR liquid-state of natural rubber samples.

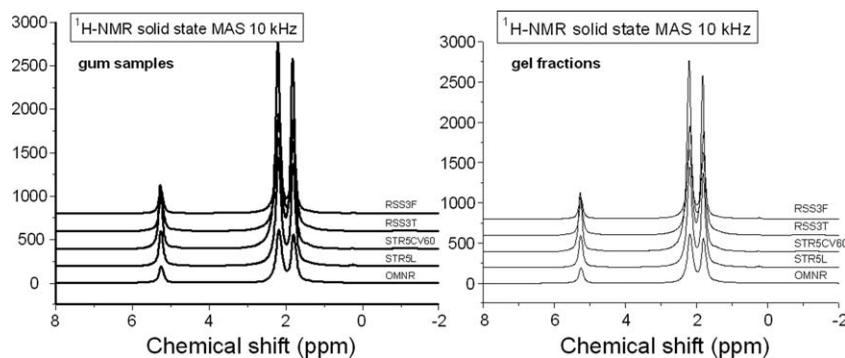


Figure 4 $^1\text{H-NMR}$ solid MAS 10 kHz on gum natural rubber samples (left) compared to gel fractions (right).

Differential scanning calorimetry results

Glass transition temperature T_g was assessed by DSC on dry gum samples as received and on samples after 72 h Soxhlet extraction with either CH_2Cl_2 or THF. T_g was measured on the second heating thermogram to avoid thermal history effects, if any. Table III tends to show that, though OMNR is known to present by far the lowest level of nonrubber components, no significant difference is observed as seen in T_g values for all the samples, either with or without nonrubber ingredients. Note that the polybutadiene sample was found totally soluble either in CH_2Cl_2 or THF and has a T_g of -108°C .

NMR analysis

^1H NMR analysis was firstly performed in liquid state after Soxhlet extraction. As shown in Figure 3, $^1\text{H-NMR}$ spectra exhibit three main characteristic signals: the first one centered at 5.25 ppm corresponds to the alkene proton, the next two signals centered respectively at 2.18 and 1.80 ppm can be related to the methylene and the methyl protons. Similar results are obtained when performing the experiments in solid state. Moreover, no difference

was noticed when analyzing either the soluble or the gel fraction of the various grades of NR gums (Fig. 4). Indeed, for all NR grades investigated, no significant chemical shift was observed whatever the percentage of insoluble fraction in the gum rubber (from OMNR to STR 5CV60 see Table III).

Complementary ^{13}C solid NMR experiments performed on samples either of the soluble or the gel fraction gave expected spectra (Fig. 5). Indeed specific signals centered at 134.8, 125.3, 32.5, 26.7, and 23.6 ppm corresponding respectively to carbon signals $=\text{C}-$ (2), $=\text{CH}-$ (3), $-\text{CH}_2-$ (1), and $-\text{CH}_3$ (5), were observed. No significant chemical shift difference was noticed between the various NR grades. In addition, similar spectra were obtained from the analysis of both the soluble and the gel fractions of each sample.

To further document the analysis, a cross polarization magic angle spinning (CP-MAS) technique was performed as it has been well documented that it gives precious information especially about the amount of mobile regions versus rigid ones in NR gums.²³ A comparison stack plot of $^{13}\text{C-NMR}$ solid CP-MAS of all NR grades investigated in the C-4 region (25–30 ppm width) is given in Figure 6 as it gives the best separation performance.²⁴ The line widths of CP-MAS spectra in this range correspond indeed to immobile and mobile components of the polyisoprene chains. A curve fitting (DMFit2006 software) was used to simulate the

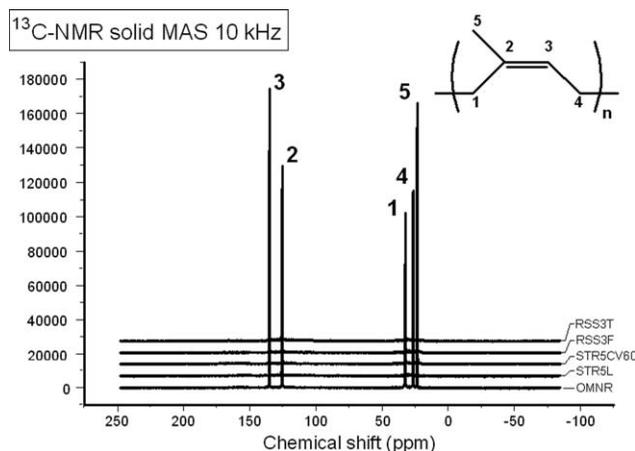


Figure 5 $^{13}\text{C-NMR}$ solid MAS 10 kHz of natural rubber samples.

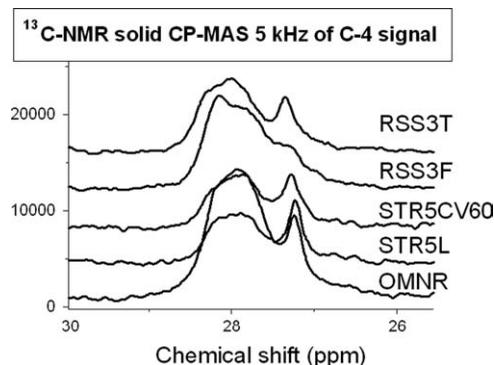


Figure 6 $^{13}\text{C-NMR}$ solid CP-MAS 5 kHz of C-4 signal of natural rubbers.

TABLE IV
 ^{13}C -NMR Solid CP-MAS 5 kHz; Ratio “Immobile/
 Mobile” Contributions to the Signal Intensity in the C-4
 Region

Sample	Mobile component (%)	Immobile component (%)	Ratio immobile/mobile
STR5L	28	72	2.6
STR5CV60	27	73	2.7
RSS3T	18	82	4.6
RSS3F	8	92	12.3
OMNR	22	78	2.9
BR40	100	0	–

line width and the integrated area of each carbon signal. The different percentages of the mobile and immobile fraction and the ratio “immobile/mobile” are thus obtained. It must be noted however that CP-MAS experiments do not really give absolutely quantitative data because rigid regions are overestimated, whilst perfectly evidenced. However, as all reported experiments were performed in exactly the same conditions, results given in Table IV can be considered as valuable (relative) information.

It can be seen that, in comparison with a synthetic elastomer such as high cis-1,4 polybutadiene (Neo-Cis BR40), all NR samples exhibit a high percentage of rigid fraction. This is somewhat unexpected with respect to the structural differences between high cis-1,4 polyisoprene and high cis-1,4 polybutadiene and this observation tends to evidence a strong heterogeneity of the macromolecular structure of Natu-

ral Rubber. In addition two groups of NR can be distinguished: on one hand OMNR, STR5L, and STRCV60 with very little difference, if any, between them, and on the other hand, the smoked sheet grades, RSS3T, and RSS3F, with the latter showing a higher ratio immobile/mobile than the former. If one compares the data in Table IV with the macromolecular characterization by SEC-MALS (Table II), a (weak) relationship is seen between the mobile component content (or the immobile/mobile ratio) and either the gel content or the number average molecular weight, essentially because the two smoked sheet grades are very different from the other ones. A larger sampling of NR grades would however be needed to reinforce this observation.

Experiments with the RPA

With respect to its testing principle, the RPA must be loaded with a volume excess of test material. Numerous experiments on various systems have shown that a tight control of sample volume and shape is essential for accurate and reproducible results. Therefore, before testing, samples were compression molded at 100°C in a 3 cm³ mould mimicking the RPA test cavity geometry (i.e., 0.125 radian reciprocal cone; 20.625 mm radius), in such a manner that the instrument was loaded with test samples having a 5% excess volume. At least two samples of the same material were tested (more if results reveal anomalies). As described above, strain sweep test protocols at 0.5 Hz were used.

RPA at 100°C ; 0.5 Hz

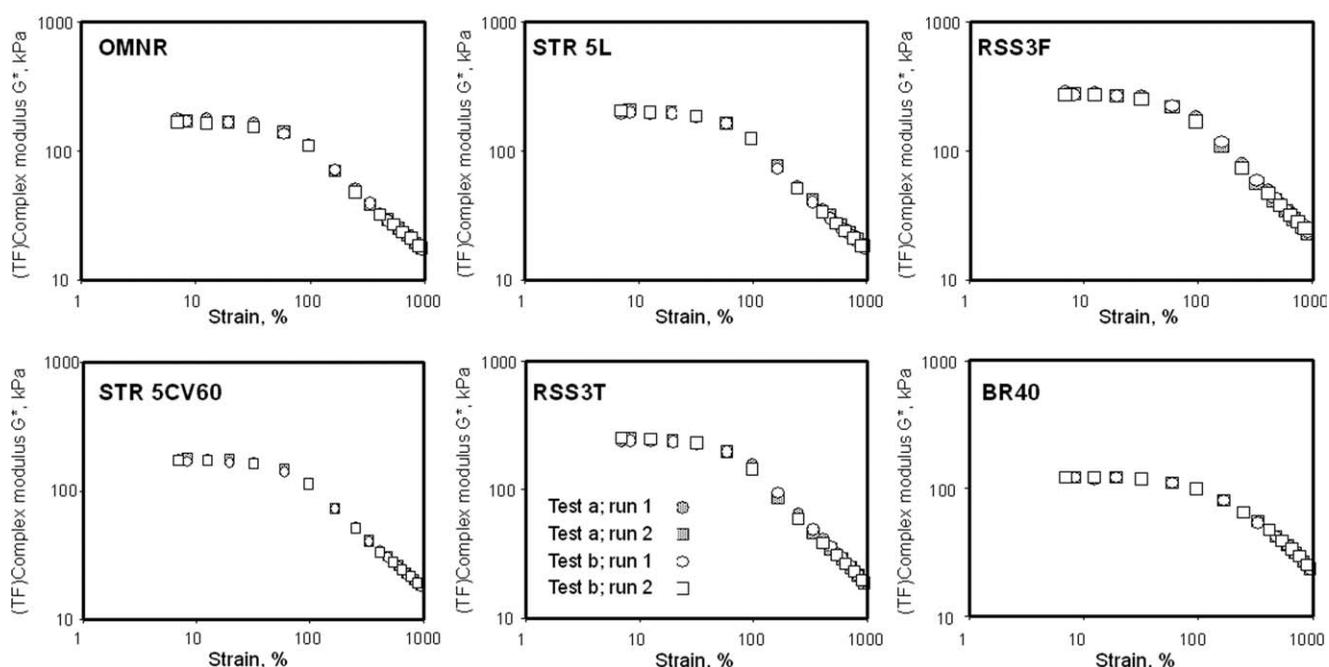


Figure 7 RPA-FT at 100°C on gum Natural Rubber samples; complex modulus G^* vs. strain; strain sweep tests at 0.5 Hz.

TABLE V
RPA-FT Strain Sweep Experiments at 100°C and 0.5 Hz;
Fit Parameters of eq. (3)

Frequency (Hz): 0.5						
Sample	Run (a&b)	G_0^* (kPa)	G_f^* (kPa)	1/A %	B	r^2
STR 5L	1	200.2	14.6	131.1	1.776	0.9993
	2	205.2	17.3	116.7	1.877	0.9992
STR 5CV60	1	181.0	13.1	118.2	1.792	0.9999
	2	180.1	16.1	110.1	1.989	0.9997
RSS3T	1	225.4	15.2	122.5	1.766	0.9998
	2	234.1	18.3	109.2	1.883	0.9997
RSS3F	1	275.3	16.5	127.5	1.721	0.9989
	2	266.3	18.1	121.2	1.758	0.9999
OMNR	1	171.2	12.0	119.2	1.668	0.9999
	2	165.2	15.5	117.0	1.893	0.9998
BR40	1	122.8	12.4	248.8	1.511	0.9998
	2	124.2	11.1	250.4	1.468	0.9998

(RPA-FT) Complex modulus vs. strain

Complex modulus G^* versus strain curves are shown in Figure 7. In all cases, the two tested samples (a & b) give identical results thus demonstrating the excellent homogeneity of tested materials and the reproducibility of the testing method. For all materials no differences are seen between Run 1 and Run 2 data, which

indicates that either there are no significant strain history effects or that strain effects are immediately recovered during the 2 min resting period between runs. It is worth underlining here that G^* data are derived from the main component of the torque signal, as obtained through FT analysis. Qualitatively similar graphs are obtained when using G^* values from the standard RPA (built in capabilities) but with an error by excess, particularly in the nonlinear region.

Figure 7 clearly shows that all tested materials do exhibit a linear region, whose limit depends on the material. NR samples remain linear up to around 20% strain, whilst BR exhibits no strain effect up to around 50% strain.

Fit parameters of eq. (3) are given in Table V from RPA-FT results at 0.5 Hz. As can be seen, the r^2 values reveal that the fitting is excellent in all cases. Modeling G^* vs. strain experiments with eq. (3) yields three parameters, whose physical meaning is immediate, and which allow a direct comparison between test materials (Fig. 8).

G_0^* is the (extrapolated) "linear" modulus. The two stabilized grades, i.e., OMNR and STR 5CV60 exhibit similar values, significantly higher than for polybutadiene BR40. RSS3F has the highest complex modulus, followed by RSS3T, then STR 5L, which is slightly

RPA-FT at 100°C; 0.5 Hz; modelling G^* vs. strain

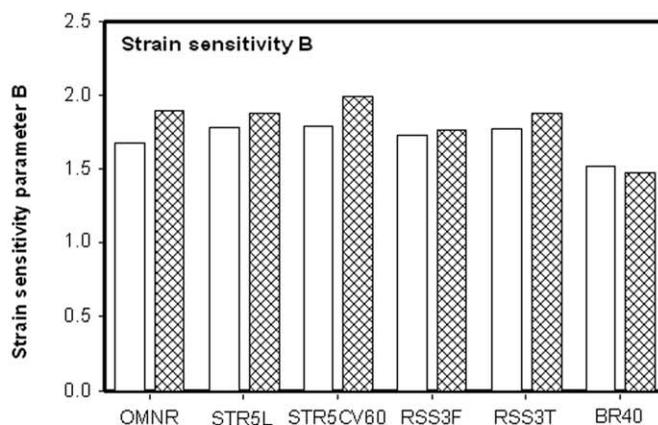
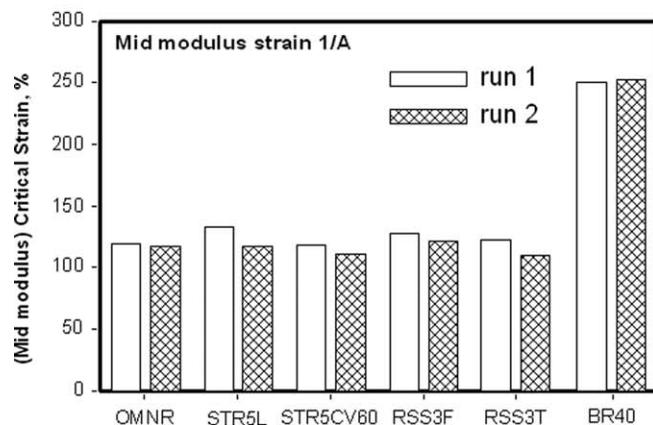
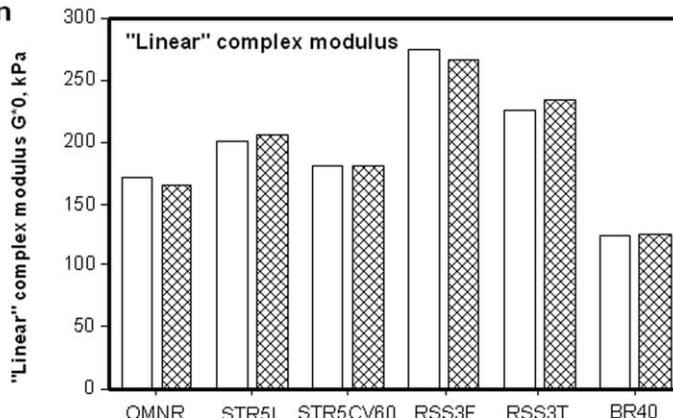
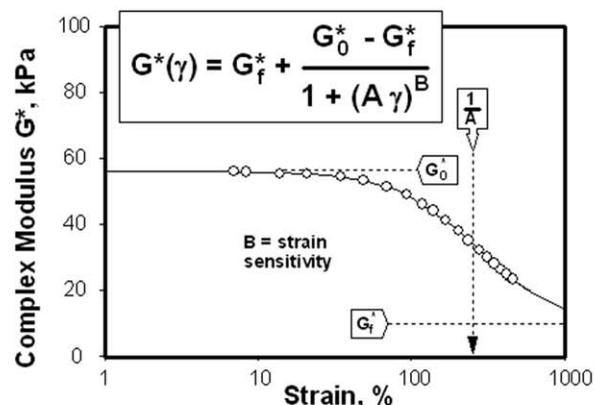


Figure 8 Comparing test materials through parameters of eq. (3).

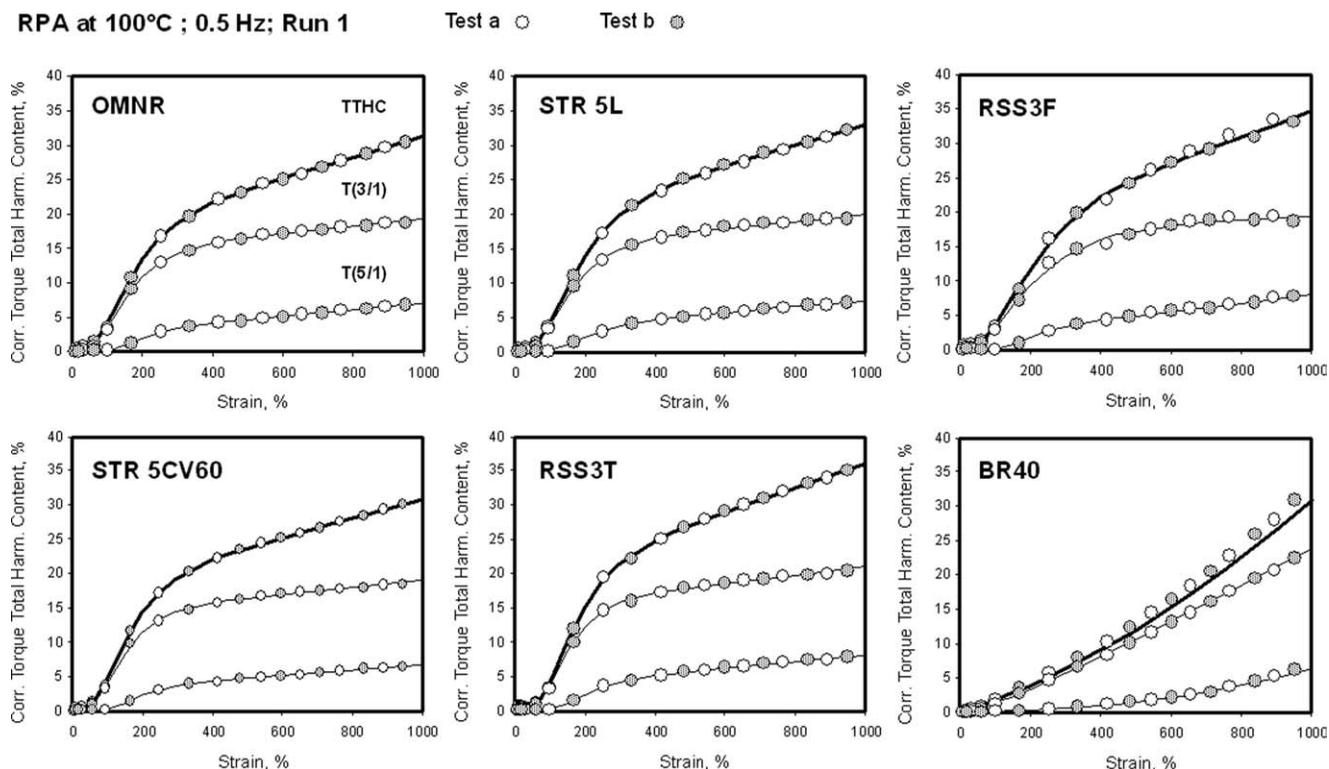


Figure 9 RPA-FT; torque harmonics vs. strain; 5th relative torque harmonic T(5/1); 3rd relative torque harmonic T(3/1); total torque harmonic content TTHC.

stiffer than OMNR and STR 5CV60. The (number averaged) molecular weight is expected to be the prime macromolecular character affecting the complex modulus of polymer on the rubbery and in the terminal flow regions and indeed G^*_0 is directly commensurable with the available characterizing information (Table II). The midmodulus critical strain ($1/A$) is somewhat related with the extent of the linear viscoelastic region and, as shown in the lower left graph of Figure 8, all NR samples are similar, but very different from polybutadiene. The strain sensitivity parameter B is original information, revealing little, if any, differences between the NR grades tested, but larger strain sensitivity that polybutadiene. Differences between run 1 and run 2 data are not large enough to be really significant; one notes however that all NR samples exhibit slightly larger strain sensitivity during Run 2, contrary to polybutadiene.

(RPA-FT) Torque harmonics vs. strain

Figure 9 shows how the torque harmonics varies with increasing strain amplitude for all the samples tested, at 0.5 Hz frequency. Data are well reproducible with no difference between tests a and b. Run 1 data are given but there is hardly any difference with Run 2 data, which indicates that torque harmonics of the series of gum rubber are insensitive to strain history. Drawn curves correspond to fit obtained with eq. (4) and, as expected, the overall

torque harmonic content (TTHC) curve envelopes the single harmonic ones, here T(3/1) and T(5/1). There is a marked difference between NR samples and synthetic polybutadiene, as the latter exhibits harmonics, which varies differently with strain amplitude. NR samples clearly exhibit the S-shape of the model which, at large strain, appears to be converging toward a linear variation with strain. Polybutadiene data might exhibit the same pattern but neither the end of the transition region nor the asymptotic high strain behavior is observed within the experimental strain window of the instrument. In term of chain structure, high cis-1,4 polybutadiene differs from NR only by the absence of pending methyl group and only this difference is sufficient to completely change the “nonlinear viscoelastic signature”. Such a marked difference between the two types of rubber is therefore worth noting.

Fit parameters for TTHC, T(3/1), and T(5/1) vs. strain are given in Table VI.

Torque harmonics quantify the nonlinear viscoelastic behavior and how they vary with increasing strain amplitude is likely reflecting how macromolecular characteristics of polymers monitor the strain response. The third relative torque harmonics T(3/1) is the largest and indeed does capture the essential of the nonlinear behavior, as shown in Figure 9 above. The model [eq. (4)] parameters are consequently reflecting subtle macromolecular differences

TABLE VI
RPA-FT at 100°C; 0.5 Hz on NR Samples; Modeling Relative Harmonics vs. Strain with eq. (4)

Sample		TTHC		T (3/1)		T (5/1)	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
STR 5L	TH _m	18.29	16.34	15.11	14.57	3.06	2.43
	α	0.0147	0.0178	0.0047	0.0058	0.0043	0.0054
	C	0.0115	0.0151	0.0127	0.015	0.0138	0.0222
	D	4.12	5.02	4.41	4.65	10.80	29.09
	r ²	0.9999	0.9998	0.9998	0.9998	0.9995	0.9991
STR 5CV60	TH _m	16.85	15.64	13.86	13.59	2.77	2.33
	α	0.0139	0.0158	0.005	0.0055	0.0039	0.0046
	C	0.0134	0.0151	0.0147	0.0153	0.0163	0.0199
	D	4.75	4.65	5.22	4.54	12.78	18.73
	r ²	0.9998	0.9999	0.9997	0.9998	0.9996	0.9994
RSS3T	TH _m	18.13	19.47	14.89	15.59	3.19	3.44
	α	0.0178	0.0168	0.0059	0.0057	0.0048	0.0047
	C	0.0135	0.0129	0.0157	0.0156	0.0163	0.0183
	D	5.46	3.62	6.52	4.42	16.12	15.18
	r ²	0.9998	0.9997	0.9998	0.9995	0.9998	0.9988
RSS3F	TH _m	16.72	20.93	16.4	17.1	1.80	4.18
	α	0.0176	0.0176	0.0030	0.0036	0.0062	0.0053
	C	0.0093	0.0109	0.0083	0.0123	0.0172	0.0146
	D	3.25	3.05	2.91	3.30	17.53	10.36
	r ²	0.9993	0.9986	0.9989	0.9987	0.9989	0.9980
OMNR	TH _m	16.14	15.28	14.06	13.62	2.37	2.19
	α	0.0152	0.0168	0.0052	0.006	0.0046	0.0051
	C	0.0128	0.0143	0.0135	0.0153	0.0172	0.0173
	D	4.50	4.71	4.84	5.37	17.49	14.82
	r ²	0.9998	0.9997	0.9998	0.9999	0.9994	0.9995
BR40	TH _m ^a	102.90	51.22	23.59	26.03	107.50	63.19
	α ^a	0.0860	0.0754	0.0149	0.0143	0.2061	0.1383
	C	0.0002	0.0003	0.0012	0.0011	0.0001	0.0001
	D	1.06	0.90	1.34	1.32	1.65	1.59
	r ²	0.9999	0.9998	0.9999	0.9998	0.9980	0.9973

^a Since the high strain asymptotic behavior is not observed in the experimental windows, fit parameters for the polybutadiene sample must be considered with care.

between the NR samples considered (see Table VI). As shown in Figure 10, RSS3F and RSS3T are clearly different, as would be expected with respect to their highest molecular weight, and likely their higher gel content. OMNR and STR5CV60 are close but not identical. Such results call obviously for further investigations.

Quarter torque signal integration

As shown above, FT analysis of strain signal allows clearly quantifying the nonlinear response of viscoelastic materials submitted to high strain, but experiments with various polymer systems have revealed that, at high strain, the torque signal can be distorted either "on the left" or "on the right", with respect to a vertical axis drawn at the first quarter of the cycle. Such differences do not reflect in the FT spectrum. Therefore, to supplement FT analysis, quarter cycle integration was developed as an easy data treatment technique to distinguish both types of distortion. The ratio of the first to second quarters torque signal integration, i.e., Q1/Q2 allows clearly distinguishing the nonlinear response of certain materials, between

the strain amplitude effect on a pure and a complex polymer materials. With most pure polymer, Q1/Q2 ratio is always higher than one and increases with strain amplitude; in such a case the torque signal is always distorted "on the left" (i.e., Q1 > Q2). With certain (complex) systems, Q1/Q2 is generally higher than one at (very) low strain, and then quickly passes below one as γ increases. It is believed that Q1/Q2 lower than one is reflecting either some structural character or heterogeneities in materials, which enhances their nonlinearity.

When polymer materials have a sufficient, sizeable level of heterogeneity, they are complex systems which exhibit morphology-induced effects, which superimpose to both time and strain induced effects. We call this behavior intra (or morphology-induced) nonlinear viscoelasticity (because owing to the internal morphology of the material).

Figure 11 shows Q1/Q2 ratio vs. strain amplitude for all samples. The polybutadiene, the stabilized NR grades, i.e., OMNR and STR5CV60, do conform to the expected behavior for pure polymers, i.e., Q1/Q2 always higher than one, thus reflecting essentially a distortion "on the left" of the measured

RPA at 100°C ; 0.5 Hz ; T(3/1) vs Strain

$$TH(\gamma) = (TH_m + \alpha \gamma) [1 - \exp(-C \gamma)]^D$$

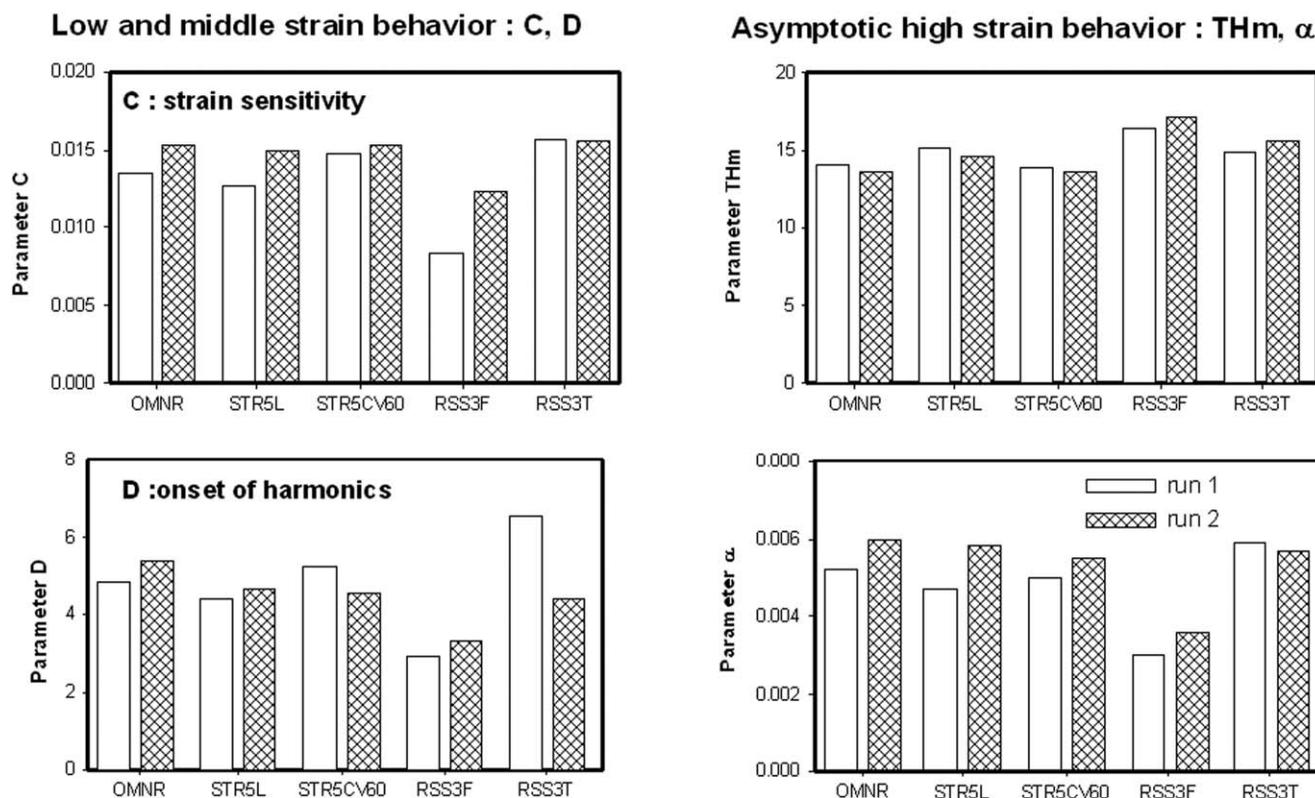


Figure 10 Nonlinear viscoelastic signatures of NR samples; comparing materials through parameters of eq. (4).

torque signal. For such materials, the nonlinearity occurs through the application of a sufficiently large strain, and their behavior is therefore said extra nonlinear viscoelasticity (or “strain-induced”). When polymer materials have a sufficient, sizeable level of heterogeneity, they exhibit morphology-induced effects, which superimpose to both time and strain induced effects. We call this behavior intra (or “morphology-induced”) nonlinear viscoelasticity. It is quite interesting to observe that RSS3F, and partially RSS3T and STR5L, show “intra nonlinearity”, which would reflect an heterogeneous structure, possibly due to semipermanent aggregates of many molecules that would reflect in so-called gel content. Half a century ago, M. Melvin expressed similar views,²⁵ in a theory for the viscosity of raw rubbers. Briefly, he postulated that microscopic rheological units, like small, tacky and elastic solid particles do affect the macroscopic flow of the rubber, through their relative movement and slippage. The number of temporary attachment points per unit area and the mean life of these attachments were key parameters of the theory. As a matter of facts, contemporary views about the likely structure of Natural Rubber^{26–30} supports the existence of such rheological units in grades with a significant amount of gel. Indeed, chain terminal groups of various chemistry appears

to play a key role in the so-called “green strength” of the material, and in other bulk viscosity dependent properties. Through such terminal groups, rubber chains would assemble and form pseudo-crosslinked structures. Dispersed in a gel-free matrix, such units would somewhat give the bulk rubber some of the characteristics of heterogeneous polymer systems, namely the capability to exhibit morphology-induced effects, i.e., $Q1/Q2 < 1$ in dynamic strain sweep experiments, as indeed observed with RSS3F, RSS3T, and STR5L. Conversely OMNR and STR5CV60 (and of course synthetic polybutadiene BRN40), which are reported “gel free,” show essentially extra nonlinearity. One notes incidentally that $Q1/Q2$ tends to be higher in run 2 experiments, except with BR40.

CONCLUSIONS

A set of interesting characterization data has been obtained on a representative but limited series of Natural Rubber samples. Differential scanning calorimetry and spectroscopic investigations yielded relatively expected results, essentially in line with the cis-1.4 polyisoprene macromolecular structure but with little differences, if any, between the various NR grades considered. Macromolecular size

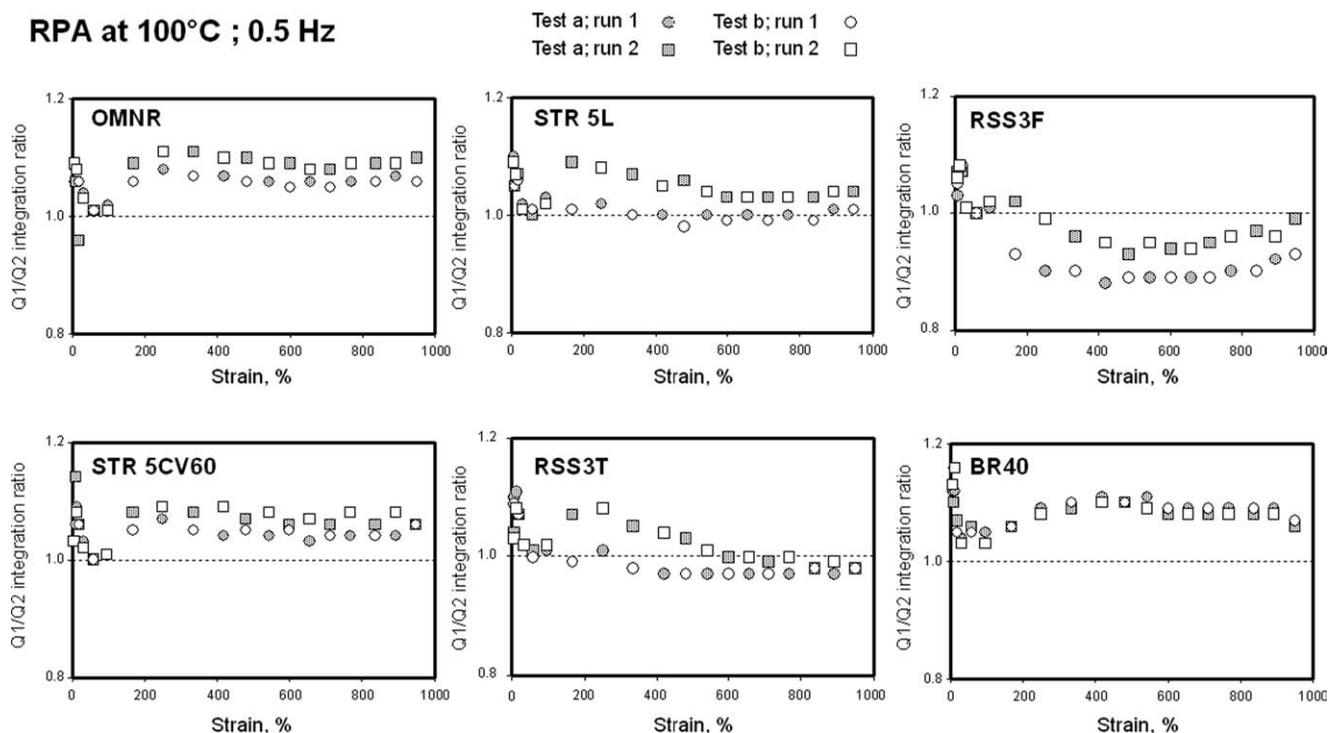


Figure 11 Assessing extrinsic/intrinsic nonlinear viscoelastic character through quarter cycle torque integration.

measurement by SEC-MALS ranked the various grades in the expected order and revealed that CV grades have a broader molecular weight distribution than grades directly coagulated from fresh latex. Because the easier processing associated with (relatively) broad MWD is well-known for synthetic elastomers, this side effect of the viscosity stabilizing chemicals might be the real benefit in using CV grades.

Fourier Transform rheometry is a fast and comprehensive characterization technique, allowing the selected NR grades to be sorted out without ambiguity. Both the linear and the nonlinear domains are conveniently investigated and, through the appropriate data handling and modeling techniques, quite a large set of complementary information is obtained. The linear complex modulus is expectedly related with the macromolecular size but the extent of the linear domain is practically the same for all NR grades, up to around 120% strain at 100°C. It is however the nonlinear viscoelastic behavior, as documented through torque harmonics, that reveals subtle macromolecular differences between the various NR samples. Whilst in principle equivalent, the two RSS grades studied are clearly different, somewhat in line with their high molecular weight, and likely their higher gel content. Conversely, the two CV grades are close but not identical. Quarter cycle integration, as a complementary LAOS data treatment, shows that the RSS and the field latex grades exhibit “intra nonlinearity,” which likely reflects an

heterogeneous structure, possibly due to semipermanent aggregates of many molecules. It is remarkable that an advanced solid NMR technique, such as the cross polarization magic angle spinning (CP-MAS) analysis leads to a similar conclusion, in term of ratio of “immobile/mobile” components of the polyisoprene chain. All NR samples exhibit a high percentage of rigid fraction, an unexpected result with respect to structural differences between high cis-1,4 polyisoprene and polybutadiene. Natural Rubber has thus a strong heterogeneity of its macromolecular structure and two groups can be clearly distinguished: the CV grades on one hand and the smoked sheet grades on the other hand. Such results obviously call for further investigations with a broader sampling.

With respect to the most recent views about the structure of natural rubber, a coherent picture emerges from both the spectroscopic characterization and the nonlinear rheological analysis in the present report. Indeed, FT rheometry demonstrates “intra nonlinearity” with RSS and the field latex grades that is assigned to a heterogeneous structure of the elastomer, possibly due to semipermanent aggregates (or “rheological units”) of many molecules. Contemporary views about the likely structure of natural rubber supports the existence of such rheological units in grades that are not chemically treated for viscosity stabilization. Indeed, chain terminal groups of various chemistry appears to play a key role in the so-called “green strength” of the material, and in other bulk

viscosity dependent properties. Through such terminal groups, rubber chains assemble and form pseudo-crosslinked structures. Dispersed in a gel-free matrix, such units somewhat give the bulk rubber some of the characteristics of heterogeneous polymer systems, namely the capability to exhibit morphology-induced effects.

Whilst not really an objective of the reported work, all the above results can eventually be discussed with respect to present NR grade selection criteria. Notwithstanding the precise information about macromolecular size and features provided by SEC-MALS, DSC, and NMR techniques, it is obvious that such approaches are laboratory methods whose implementation on NR producing sites would likely meet tremendous difficulties, not to mention the necessary investment. In comparison, experiments with torsional dynamic rheometers are no more difficult to perform than Mooney viscometer or Parallel plate tests, require less or equivalent time, and the same sample preparation. Dynamic tests however have the capability to yield a number of significant parameters, some of which directly commensurable with macromolecular weight (e.g., complex modulus) and others likely giving a deep insight in macromolecular features (e.g., harmonics from Fourier Transform experiments) and their role in the processing behavior. The TSR schema is more than 30 years old and essentially reflects available technical capabilities in the late 1980's. With respect to the small and arbitrary series of tested NR samples, the above reported results are obviously limited in scope, but they surely advocate for a reconsideration of the manner technical specified rubber grades are sorting out, with the advantage that RSS grades could also be included in the technical specifications.

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