

NOVEL SILANISED SILICAS FOR A NEW GENERATION OF GREEN PASSENGER TYRE ELASTOMERS

By

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A dissertation submitted to Imperial College London for the degree of
Doctor of Philosophy

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PREFACE

The last few years of my life have been a great experience of self realisation. I have explored and investigated of the effect of silica surface chemistry modification with a variety of silanes on elastomers. My PhD journey at Imperial College London has been a steep learning curve and I have gone through a collaborative effort with help, guidance and support from a large network of people. I am thankful for being afforded the opportunity to take part in such an endeavour, in an environment of support, friendship and guidance.

I particularly like to thank Dr. Jerry Heng Y. Y. and Dr. Daryl R. Williams for their supervision, support and encouragement during which this research was undertaken. Their advice and guidance at all stages of the research in determining the progress of the research has been immensely invaluable. I will also always remember all this advice.

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Most importantly, special thanks also go out to my family and loved ones for their kind support, and encouragement to pursue this PhD. This has not been possible without my family sacrifices and constant belief in my abilities. Mum and dad have always been inspirational, since the conception of my PhD journey.

DECLARATION

The work described in this thesis was carried out in the Department of Chemical Engineering, Imperial College London, United Kingdom, and at the Tun Abdul Razak Research Centre, United Kingdom, between June 2012 and Jun 2016. Except where acknowledged, the material described in this thesis is the original work of the author and includes nothing which is the outcome of work in collaboration. No part of this thesis has been submitted for a degree at any other university.

FOR MY FAMILY AND FRIENDS

ABSTRACT

The thesis presents a study into the surface properties of silica and determining the silica surface thermodynamic. The effect of silica surface energies on the dispersibility of silica in the elastomer phase has been computed for the first time, this is made possible by silanising the silica sample with a series of coupling and non-coupling organosilanes having a range of functional groups. The relationship between the surface chemistry and surface energies, as determined by thermogravimetry combined with an infrared spectroscopy (TGA-IR) and Inverse Gas Chromatography (IGC) respectively is investigated, resulting in a coherent understanding of the modified silica surface thermodynamics of various organosilanes.

IGC analysis enabled the determination of the specific surface energy/ dispersive surface energy profiles of modified silicas at different surface coverage. A property of particular interest is the work of cohesion of silica particles, which is found to be correlating well with silica microdispersion in the elastomer phase, as determined using a TEM-network visualisation method and dynamic mechanical analysis (DMA) where the hysteresis effects were greatly reduced for silanised silica-filled vulcanisates. From this study, it is clear that surface energy measurements could be used as a good indication and explanation of the dispersibility of silica in the elastomer phase.

From all the silica-filled vulcanisates considered in this study, it is observed that significant improvements in tensile strength, reinforcement index, angle tear and DIN abrasion resistance were shown by silicas modified with coupling organosilanes. Both

types of organosilanes improved the less abrasive Akron abrasion resistance compared to untreated silica-filled vulcanisate, but there was no clear difference between the two types. This investigation opens up some possible routes to improving tyre tread compound design.

PUBLICATIONS

This thesis has resulted in the following papers and conference proceedings.

Journal Papers

1. Yen Wan Ngeow, Daryl R. Williams, Andrew V. Chapman and Jerry Y. Y. Heng, Dispersibility of Functionalised Silica in Elastomers Investigated by IGC and TEM Network Visualisation Techniques. ***Anal. Chem.*** 2016. In preparation.
2. Yen Wan Ngeow, Daryl R. Williams, Jerry Y. Y. Heng and Andrew V. Chapman, Investigating the Effect of Silica Surface Modification on Rubber Vulcanisates . ***European. Polymer J.*** 2016. In preparation.
3. Yen Wan Ngeow, Andrew V. Chapman, Jerry Y. Y., Heng, Daryl R. Williams, Susanna Mathys and Colin D. Hull. Characterisation of Silica Modified with Silane Using Thermogravimetric Analysis Combined with Infrared Detection. ***Rubb. Chem. Tech.*** 2016. In preparation.

Selected Refereed International Conferences

1. Yen Wan Ngeow, Daryl R. Williams, Jerry Y. Y. Heng and Andrew V. Chapman, Investigating the effect of silica surface modification on rubber vulcanisates. International Rubber Conference, Kitakyushu, Japan, October 24-28, 2016. Accepted.
2. Yen Wan Ngeow, Andrew V. Chapman, Jerry Y. Y. Heng, Daryl R. Williams, Susanna Mathys and Colin D. Hull. Characterisation of Silica Modified with Silane Using Thermogravimetric Analysis Combined with Infrared Detection. Technical Meeting of the Rubber Division of American Chemical Society, Pittsburgh, US, October 10-13 2016. Accepted.
3. Yen Wan Ngeow, Jerry Y. Y. Heng, Daryl R. Williams and Andrew V. Chapman, The Surface Free Energies of Silanised Silica Particles and Their Influence on Mechanical Properties in Elastomer. Advances on Dynamic Vapour Sorption Methods and Surface Energy Characterisation, Imperial College London, 30 July 2015.
4. Yen Wan Ngeow, Jerry Y. Y. Heng, Daryl R. Williams and Andrew V. Chapman. The Surface Free Energies of Silanised Silica Particles and Their Influence on Mechanical Properties in sSBR/BR Compounds. Joint Conference of 5th UK-China and 13th UK Particle Technology Forum Leeds, 12-15 July 2015.
5. Yen Wan Ngeow, Jerry Y. Y. Heng, Daryl R. Williams and Andrew V. Chapman. Influence of Particle Surface Free Energies on the Mechanical Properties of Tyre Compounds. Chemical Engineering PhD Symposium, Imperial College London, 29 June 2015.
6. Yen Wan Ngeow, Jerry Y. Y. Heng and Daryl R. Williams. Novel Approach For Understanding the Effect of Silica Silanisation through Dynamic Mechanical Analysis for Silica-Filled sSBR/BR Compound. The 20th Join Annual Conference of The Chinese Society of Chemical Science and Technology, UK and The Society of Chemical Industry (CSCST-SCI), Imperial College London, 14th September 2013.

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NOTATIONS AND ABBREVIATIONS

Symbol	Definition
a_m	molecular cross-sectional area
α_{OH}	silanol number
c	polymer chain density (number of polymer chains per volume)
E	Young's modulus of filled rubber
E_b	elongation at break
E_o	Young's modulus of unfilled rubber
E_t	elongation at the point of tangent
f	contact force
F	Force
F_c	gas flow rate (standard cubic centimeters per minute, sccm)
F_m	maximum force
F_t	force at the point of tangent
δ	difference of phase or phase lag
δ_{OH}	concentration of OH groups (mmol OH/g of silica)
G	shear modulus
G'	dynamic stored shear modulus

G''	dynamic loss shear modulus
ΔG_i	free energy of immersion
γ	shear strain
γ_0	amplitude of oscillatory shear strain
$\gamma(t)$	shear strain at time t
γ_L^+	liquid acid component surface energy
γ_L^-	liquid basic component surface energy
γ_S	surface free energy of filler particle
γ_S^d	dispersive component of surface free energy
γ_S^{ab}	specific (acid-base) component of surface energy
γ_S^T	total surface energy
γ_l^d	elastomer dispersive component of surface free energy
γ_l^{sp}	elastomer specific component of surface free energy
j	James-Martin correction factor
k	Boltzmann constant
ρ_r	density of rubber
ρ_s	density of solvent
η	Viscosity

η_o	initial viscosity
ϕ	volume fraction
L_b	length at break
L_0	initial test length
m_i	relative weight of insolubles in the compound
m_f	relative weight of filler in the compound
m_t	total weight of the compound
M_H	maximum torque (highest elastic stiffness)
M_L	minimum torque (lowest elastic stiffness)
M50	modulus of stress at 50% strain
M100	modulus of stress at 100% strain
M300	modulus of stress at 300% strain
N_A	Avogadro's number ($6.02214 \times 10^{23} \text{ mol}^{-1}$)
n	amount of adsorbate adsorbed to the particle
n_m	amount of adsorbate adsorbed in a complete monolayer
P_{in}	inlet pressure
P_{out}	outlet pressure
ρ_R	density of elastomer

ρ_s	density of solvent
R	universal gas constant (8.31447 JK ⁻¹ mol ⁻¹)
σ	shear stress
σ_0	amplitude of oscillatory shear stress
$\sigma(t)$	shear stress at time t
$\tan \delta$	loss tangent
T	absolute temperature
T_g	glass transition temperature
TS	tensile strength
T_s	tear strength
t_{90}	time to achieve 90% cure (90% of the difference between M_L and M_H)
t_0	time taken for the methane gas to pass through the column
t_R	time taken to elute the molecular probes
$ts1$	time to scorch (time for the torque to rise by 1 dNm)
V_r	volume swelling or volume fraction of rubber in a swollen gel
γ_L^+	liquid acid component surface energy
γ_L^-	liquid basic component surface energy
V_N	net retention volume

V_s	volume loss of the standard elastomer
V_t	volume loss of the test elastomer sample
ν	crosslinks per unit volume
W	width
W_{adh}	work of adhesion
W_{coh}	work of cohesion
W_{BR}	bound rubber weight
$W_{dry\ gel}$	weight of dry gel
W_{tol}	solvent weight
$W_{wet\ gel}$	weight of wet gel
W_t	original weight of sample
ω	angular frequency
6PPD	N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine
ARI	Abrasion Resistance Index
BET	Brunauer-Emmett-Teller
BR	cis-1,4 polybutadiene rubber
BRC	bound rubber content
BS	British Standard
CBS	N-cyclohexyl-2-benzothiazole sulfenamide

CTAB	cetyltrimethylammonium bromide
DIN	Deutsches Institut für Normung
DMA	dynamic mechanical analysis
DCDMS	Dichlorodimethylsilane
DPG	N,N'-diphenylguanidine
DTSPM	[3-(di-(tridecyloxypenta(ethyleneoxy)) ethoxysilyl]-propyl mercaptan
EC	European Commission
FTIR	fourier transform infrared
GR	granule
HAM	high amplitude modulus
HD	highly dispersible
HPLC	high pressure liquid chromatography
IGC	inverse gas chromatography
IR	infrared
IRHD	International Rubber Hardness
ISO	International Organization for Standardization
IUPAC	Union of Pure and Applied Chemistry
LAM	low amplitude modulus
LPP	liquid phase process

LiAlH ₄	lithium aluminium hydride
MDR	moving die rheometer
ML	Mooney large
MP	micropearl
MTES	methyltriethoxysilane
MTMS	methyltrimethoxysilane
MU	Mooney units
NaOH	sodium hydroxide
OTES	octyltriethoxysilane
pphr	parts by weight per hundred parts of rubber
RH	relative humidity
RI	reinforcement index
RT	room temperature
SEA	surface energy analyzer
SEM	scanning electron microscopy
SSA	specific surface area
sSBR	solution styrene-butadiene rubber
TGA	Thermogravimetric analysis
TEOS	tetraethoxysilane
TEM	transmission electron microscopy
TESPD	bis[3-(triethoxysilyl)propyl] disulfide

TESPO	3-(triethoxysilyl)propyl thio-octanoate
TESPO/M	Reaction product of TESPO, TESPM and 2-methyl-1,3-propanediol
TESPT	bis-(3-triethoxysilylpropyl) tetrasulfide
TMCS	trimethylchlorosilane
TMQ	1,2-dihydro-2,2,4-trimethylquinoline
VPP	vapour phase process
vOGC	van Oss-Good-Chaudhury
wt%	weight percent
ZnO	zinc oxide

CHAPTER 1 INTRODUCTION

1.1 Background

The advent of tyre labelling legislation has increased the demand for high-performance quality tyres by legislators and consumers. From 1 November 2012, tyres for passenger cars and light trucks sold in Europe have to be labelled for fuel efficiency, wet traction and tyre external rolling noise level as stated in European Regulation (EC) 1222/2009 [1]. A vehicle fitted with a set of 'A' grade tyres for fuel efficiency and wet grip performance is estimated to consume 7.5% less fuel compared to 'G' grade tyres [2]. It is worth noting that the three most important properties of tyre performance are high traction (wet and dry) for tyre handling performance, low rolling resistance for fuel saving, and high wear resistance for durability. These three parameters are described as the 'magic triangle' properties of tyre performance.

Tyre manufacturers are continually improving their product performance by focusing on safety, longevity and fuel economy for the tyre of tomorrow [1]. Michelin estimates that its 'green tyres' have saved more than 14.4 billion litres of fuel, corresponding to 36 million tonnes of CO₂ emissions since they were launched in 1992 using silica filler with the bifunctional silane, TESPT [3]. Roger Williams [2] reported that tyre industry will strive to reduce rolling resistance by half in the coming 25 to 30 years.

The start of elastomer history is the use of natural rubber by the indigenous people of the south of America. In 1525, Padre d'Anghieria reported natural rubber was

used as an elastic ball for game [4]. The natural rubber latex was tapped from one of their local trees near the village. Then the latex was called 'caa-o-chu' [5]. Since the discovery of natural rubber application by scientists, the elastomer was developed and widely used to fabricate water-resistant fabric. However, the natural rubber usage was limited, because it became soft and sticky when warm and stiff and brittle when cold [6].

Between 1839 and 1845, Charles Goodyear, Thomas Hancock and others developed the vulcanisation process to crosslink the unsaturated elastomer chains using sulfur and heat [7], creating a three dimensional elastic network and reducing the temperature sensitivity. The development of vulcanisation process in elastomer technology increased the application of elastomer when Robert William Thomson (1846) and John Boyd Dunlop (1888) successfully introduced the pneumatic tyre [8]. In 1895, French industrialists André and Édouard Michelin first fitted pneumatic vulcanised elastomer tyres to a car for the Paris-Bordeaux-Paris race [3]. The demand for elastomer materials increased rapidly along with the development of automobiles

Another important aspect of the elastomer technology development was the use of carbon black as a reinforcing filler when added to the elastomer. It was introduced by the B. F. Goodrich Company (Benjamin Franklin Goodrich) in 1921 [3]. Carbon black is one of the oldest manufactured products. It can be traced back to the ancient Chinese and Egyptians. In the fifteenth century, one of the many usages of carbon black at that time was as a pigment for printed books [9]. When carbon black is used as a reinforcing filler for elastomers, the modulus of carbon black-filled elastomer is increased and the

fracture properties such as tensile strength, tear and abrasion resistance are improved compared to unfilled elastomer [6].

In 1948, precipitated silica was introduced by the Columbian Chemical Division of Pittsburgh Plate Glass Co.. However, the reinforcing effect of precipitated silica in hydrocarbon elastomers was rather less effective compared to the conventional reinforcing carbon black fillers. In the late 1960s, it was realised that the addition of 3-mercaptopropyltrimethoxysilane in sulfur-cured silica-reinforced elastomer compounds resulted in improved mechanical properties [10]. However, the use of reactive mercapto-silanes was restricted by short scorch times during vulcanisation [11].

In 1972, Degussa AG (currently known as Evonik Industries AG) made a breakthrough in the silica-silane filler system by introducing bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) [12,13]. In 1992, Michelin successfully introduced their 'green tyre' using the TESPT-silica system in the tyre's tread compound, together with the use of a solution styrene-butadiene rubber (sSBR) and a highly dispersible silica in the SBR/BR (styrene-butadiene rubber/ butadiene rubber) blend, with the advantages of reduced rolling resistance, good wet grip and comparable wear resistance [14] of passenger car tyres. Neubauer [15] reported that the 'green tyre' is expected to reduce fuel consumption of a vehicle by 3% to 4% compared to a carbon black tread.

The parameters of the silica that play an important role for elastomer reinforcement are the particle size, structure and surface activity [9,16,17,18]. The

particle size and the specific surface area of the particle can be related to the interfacial area between the silica surface and the elastomer chains. Silica structures can be related to the degree of irregularity of the aggregation development of the primary particles [19,20]. According to Thomas Gross [3], if the filler is not well dispersed, the inelastic filler-filler aggregates or agglomerates are significant. These aggregated filler particles can trap part of the elastomer, which is termed as 'occluded elastomer' [21,22]. This increases the effective filler volume and affects the compound properties, such as the viscosity and modulus of the filled-elastomer. Energy is required to disrupt these interactions when a tyre rolls and deforms on the rough road surface. If the filler particles are dispersed well in the elastomer matrix, the elastic behaviour of the elastomer composite improves, as well as the rolling resistance of the tyre.

Both of the above parameters will not bring significant effects without the involvement of the third parameter, the surface chemistry or the surface activity of the filler particles [13,23]. This parameter is responsible for the relative strength of filler-filler interactions, filler-elastomer interactions, and filler interaction with other ingredients during compounding. Besides that, it is also well known that the particle surface is heterogeneous in nature. The energetic heterogeneity and the geometric heterogeneity of the particle surface, which have close association with each other, influence the reinforcement of the elastomer [24]. Heng et al. revealed the importance of surface energy and surface roughness to provide mechanical locking and adhesion between fibres used as a filler and the elastomer matrix [25].

It is important to understand the surface chemistry heterogeneity of silica, which has an effect on silica and elastomer interactions. Conventionally, solid surface wetting phenomena and thermodynamics were determined through contact angles such as sessile drop measurements. However, these techniques have several uncertainties due to the intrinsic limitations imposed by various empirical models and material dependence [26]. More recently, inverse gas chromatography (IGC) and atomic force microscopy (AFM) are used and the former is used to determine the surface energy heterogeneity of solid particles using vapour probes [27]. The adsorption of vapour on the solid can reveal useful information on the physico-chemical properties of the solid material.

The strategy developed here in this thesis aims to evaluate the surface energy heterogeneity of silica and the silica dispersion effect in the elastomer phase. Various measurements with vapour probes at finite dilution for surface energy determination are undertaken on untreated and silica surfaces modified with coupling and non-coupling silanes. The effects on silica dispersibility in the elastomer phase and the mechanical properties of silica-filled elastomer vulcanisates are reported in detail in this thesis.

1.2 AIMS OF THE RESEARCH

The aim of the research is determine the role of silica surface energy on the dispersion of silica in the elastomer phase and the mechanical properties of filled elastomer. The thermodynamics of the silica-elastomer interface, such as wettability of silica by

elastomer, adhesion of silica with elastomer phase and the agglomeration/ aggregation of silica in the elastomer phase are believed to be greatly influenced by the surface energetics properties of the silica and the elastomers. The research will allow us to distinguish the dominant factors which influence the elastomer reinforcement especially as regards to abrasion resistance.

The research will primarily focus on the specific elastomer compounds used in the passenger tyre tread applications, which are sSBR/BR blends reinforced with precipitated silica. Therefore the specific strategy of this research is delineated as follow:

- To establish the validity and suitability of experimental methods for determination of surface properties of the silica,
- To measure and review current models for determining the surface energy of silica, including silica silanised with coupling and non-coupling organosilanes,
- To determine the effects of silanised silica, such as on silica dispersion in the elastomer phase and on the mechanical properties of silica-filled vulcanisates,

1.3 Thesis Outline

The structure of this thesis is as follows. Chapter 1 describes the background of the current research work and the aims of this research. Theoretical principles of intermolecular and surface energies as well as the properties of silica as a reinforcing filler for elastomer and the development empirical models for predicting the modulus of filled elastomers are described in Chapter 2. Chapter 3 is dedicated to the general

methodology of silanising silica and incorporation of silica into the elastomer through a dry mixing process. The silanised silica prepared includes the use of both bifunctional coupling and non-coupling organosilanes. The subsequent characterisation techniques and their sample preparation for analysis are detailed in the relevant chapters. Chapter 4 describes the surface chemistry of silica as determined by thermogravimetric analysis combined with an infrared spectroscopy (TG-IR). In Chapter 5, the surface energies of untreated and silanised silica as measured by inverse gas chromatography are presented. This is followed by the evaluation of the silica dispersion in the elastomer matrix as determined by using reflected light microscopy for silica macrodispersion analysis, which is discussed in Chapter 6. This chapter also discussed the silica microdispersion using a transmission electron microscopy (TEM) - network visualisation technique. Chapter 7 describes the rheology characterisation of silica-filled elastomer. Further discussion on the effect of modified silicas on the mechanical properties of silica-filled vulcanisates is discussed in Chapter 8. Chapter 9 contains the conclusions and suggestions for further work.

This thesis will not only highlight the surface thermodynamics and chemistry of untreated and silanised silicas, but also emphasise its significance in the mechanical properties of silica-filled elastomers for tyre tread applications.

CHAPTER 2 OVERVIEW OF REINFORCING FILLERS FOR ELASTOMERS AND SILICA TECHNOLOGY

2.1 Introduction

The present chapter provides an overview and discussion of reinforced elastomers using silica as reinforcing filler. The application of a pure elastomer is limited and fillers such as silica are used to improve the mechanical properties of the elastomer. These fillers are characterised by their reinforcing properties, depending on their surface area, structure and surface activity.

The differences in surface chemistry between carbon black and silica require different mixing procedures to obtain effective rubber reinforcement. The presence of silanol functional groups and the attraction of weakly bound water produce a hydrophilic reactivity on the silica surface [28]. This hydrophilicity hinders strong bonding with the organic surface of a synthetic rubber such as solution styrene-butadiene rubber (sSBR). Therefore, a bifunctional silane coupling agent grafted on the silica surface is used thus to reduce the polarity differences between the silica and the olefinic hydrocarbon elastomer. This results in coupling between the silica and elastomer during the vulcanisation process [29,30]. However, the application of the silane chemistry and silica reinforcement need further understanding and development to optimise properties such as the abrasion resistance properties of a silica compound compared to a carbon black compound.

A description of the production of synthetic silicas and its particulate properties is given in Chapter 2.2. The surface activities of silica are usually characterised and investigated using adsorption methods. Such methods are analysed and discussed in this section. In Chapter 2.3, the elastomer and its elasticity characteristics are reviewed, while in Chapter 2.4 several theoretical models are reviewed to understand how fillers influence the underlying physical phenomenon of elastomeric composites.

2.2 Fillers

The use of carbon black as a filler for rubber compounds was started approximately one decade earlier than use of silica. However, in comparison to carbon black, silica was used mainly for coloured compounds, such as soles for athletic footwear. It was not widely used for tyre tread applications due to the reduction in abrasion resistance and the resultant reduction in the mileage performance of the tyre.

The work of silica started as early as 1864 by Graham and the production of silica through solution and gelation (sol-gel) technology was first patented in the 1900s [31]. Since then, numerous studies on silica surface properties and their application have been made, in particular by Iller [32] and Zhuravkev [33] and Kiselev and his co-workers [34]. The use of silica filler for reinforcing elastomers is attracting increasing attention, especially for use in tyre compounds. The recent popularity of using silica in car tyre tread applications began in 1992, when Michelin introduced its 'Green Energy Saving' tyre [15,35]. The company claimed that using a high dispersible silica, in an sSBR/BR (butadiene rubber) blend enables tyres to be more fuel efficient, saving up to

7% in fuel consumption. In comparison with carbon black, silica reduces the rolling resistance of tyres, thus providing lower fuel consumption [15,36] at equivalent wear resistance and wet traction [37,29]. However, the strong interactions between silica particles cause difficulty when mixing silica with nonpolar olefinic hydrocarbon elastomers.

Thus organosilanes are used to achieve the optimal reinforcing effect of silica, by modifying the silica surface and enabling coupling with the elastomer. Fillers are selected based on their potential to reinforce the elastomer matrix based on aggregate particle size and structure for effective reinforcement and surface chemistry for compatibility with rubber. The typical fillers used for tyre compound applications are carbon black and silica. For the interest of this study, the later will be reviewed and discussed.

2.2.1 Production of Synthetic Silica

Silica or silicon dioxide is the most abundant natural mineral on earth. This material can be sourced from detrital rocks as silicate minerals or stems from the accumulation of testa from biological organisms (protozoa and spongiae). It is also available through precipitation of silica in solution (flint, millstones and grindstones). As for the manmade or synthetic silicas, the widely used methodologies to produce these silicas are the vapour phase process (VPP) and the liquid phase process (LPP), as illustrated in Figure 2.1 [38]. In 1931, Kistler produced the first highly porous synthetic silica, which he called 'aerogel', by supercritically drying the silica gel obtained by hydrolytic polycondensation

of silicic acid [39]. These synthetic silicas tend to be amorphous and often have more than a few m^2/g surface area.

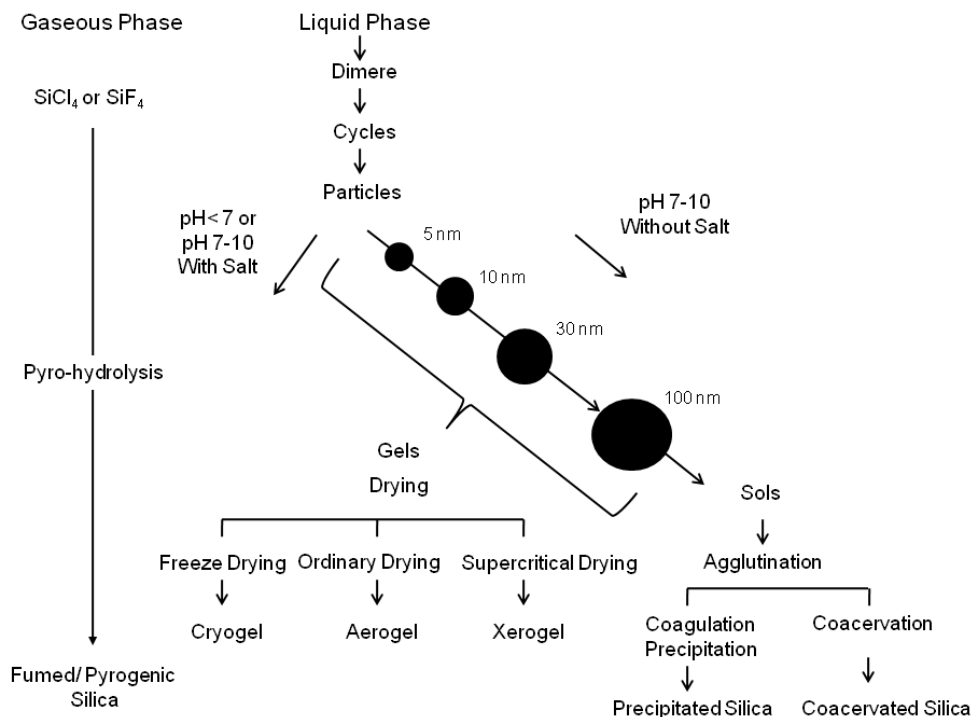


Figure 2.1: Preparation of synthetic silicas [38,40].

At elevated temperature, fumed or pyrogenic silica is obtained by decomposition of a precursor in the vapour phase. The flame pyrolysis process is generally conducted at temperatures ranging from $1200\text{ }^{\circ}\text{C}$ to $1400\text{ }^{\circ}\text{C}$ and followed by rapid thermal quenching [41,42]. Pratsinis [42] reported that silicon tetrachloride (SiCl_4) is continually vaporised, mixed with dry air and hydrogen and fed to the burner, where silica aerosol is formed. This is followed by separating the silica from HCl-containing gasses by cyclone separators or filters. The net reaction can be described as follows.

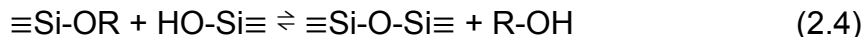
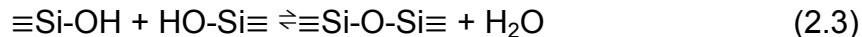


The specific area and true density of fumed silica, which is composed of aggregated amorphous silica is approximately 50 to 380 m²/g [42,43] and 2.2 g/cm³ [43], respectively.

The liquid phase process of obtaining silica is also known as a solution-gelation (sol-gel), or inorganic polymerisation process. The oldest way of producing silica gel is by often referred to as silica gel, but gel silica may also be used, by acidulation of aqueous sodium silicate solution with an acidification agent such as sulfuric acid, whilst sol silica is produced under alkaline conditions. The process was discovered by van Helmont [31] in 1640, when he dissolved silicate materials in alkali and then acidified to obtain precipitated silica.

The details of the sol process are reviewed by Iler [44,45,32], using a range of concentrated solutions of SiO₂ and NaOH in water solutions and experimental conditions (pH, temperature and time). The reactions involved in synthesising silica by the sol-gel process are generally as shown in the following equations [31]. The process is carry out in an organic covalent through the simultaneous or sequential reactions of hydrolysis (Equation 2.2) and polycondensation, releasing water (Equation 2.3) and/ or alcohol (Equation 2.4).





In general, the production of silica through the solution process, with particle diameters between 50 nm and 2000 nm, depends on the type of silicate ester, alcohol, volume ratios employed, as well as the polycondensation of silicic acid in different acidic or basic mediums [31]. Today, the Stöber process [46] is widely used by the industry to manufacture monodispersed silica sols, where the silica is obtained in ammonia-catalysed hydrolysis of tetraethoxysilane (TEOS) in the presence of a low molar-mass alcohol, such as ethanol.

Synthetic silicas with primary particle diameters below 40nm are generally used as rubber reinforcement for abrasion resistance, tensile and tear strength improvements. The processing problems and high production cost of fumed silica have limited use of this type of silica in the elastomer industry [28]. Mora-Barrantes et al. reported that, due to the high surface area, the fluffy powder nature and their low apparent density, it is difficult to incorporate fumed silicas into the elastomer phase [47]. Therefore, sol silicas, specifically precipitated silicas, are generally used for tyre tread compounds.

Figure 2.2 illustrates the classification of filler by particle size for reinforcement. Fillers are typically classified into non-reinforcing, semi-reinforcing and reinforcing fillers. Fumed and precipitated silicas are classified as reinforcing fillers.

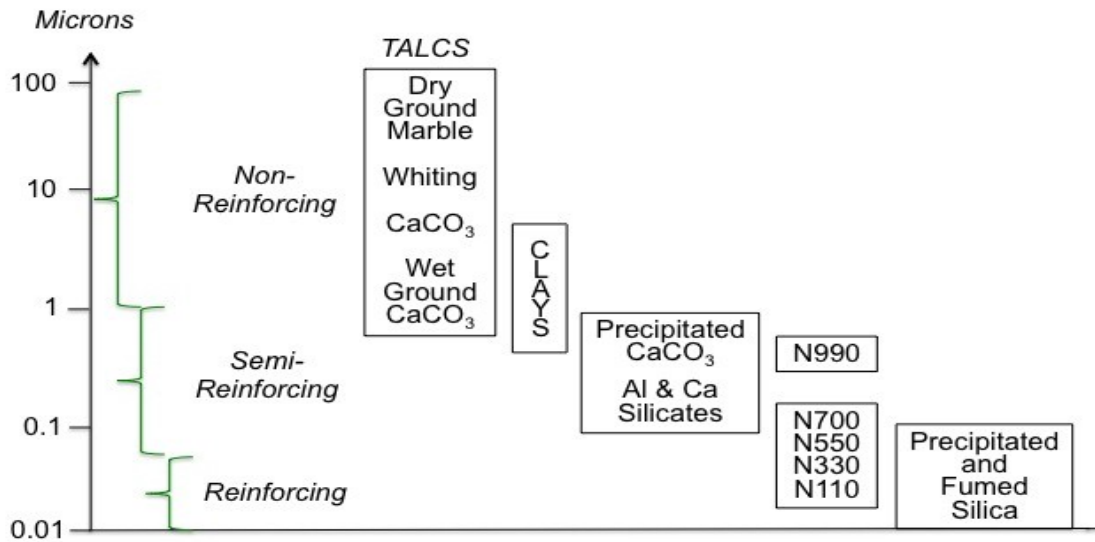


Figure 2.2: Classification of fillers by particle size [48].

From Figure 2.2, the nomenclature system for elastomer grade carbon black (eg. N110 to N990) is indicated by the letter 'N'. The letter indicates a normal curing rate typical for furnace blacks that received no special modification on carbon black filled elastomer compound [49]. The second character in the system is a digit designated to the average surface area of the carbon black. The third and fourth characters in the system are arbitrarily assigned digits [49].

The typical commercial description of precipitated silica is presented in Tables 2.1 and 2.2.

Table 2.1: Typical commercial precipitated silica specification [28].

Property	Range
BET (N ₂), surface area (m ² /g)	
Reinforcing	125 – 250
Semi-reinforcing	35 – 100
Free water at 105 °C (%) - loss	6 ± 3.0
Bound water, silanols (%)	3 ± 0.5
pH	
Reinforcing	5 – 7
Semi-reinforcing	6 – 9
Salt content (%)	0.5 – 2.5
Specific gravity in rubber	2.0 ± 0.05

Table 2.2: Type of commercial silica [50].

Silica Surface Area* (m ² /g)	Conventional	Semi-HD [#]	HD [#]
100 ± 20	Ultrasil 360 (GR), AS 7, 880 Hubersil 1613,1633,1635 Hi-Sil 315 Zeosil 125 GR Zeolex 23, 80	Ultra VN2 (GR) Zeosil 115 Gr, 1135 MP	Zeosil 1115 MP Zeopol 8715
160 ± 20	Ultrasil VN3 Hubersil 1714, 1715, 1743, 1745 Hi-Sil 170, 210, 233,255, 243 LD Zeosil 145 GR, 174 G Zeolex 25	Ultrasil 3370 GR Hi-Sil 243 MG, EZ Huberpol 135 Zeosil 145 MP, 165 GR	Ultrasil 7000 GR Zeosil 1165 MP Zeopol 8745, 8755
200 ± 20	Hi-Sil 170, 185, 195 Zeosil 195 GR	Hi-Sil 190G Zeosil 195 MP, 215 GR	Ultrasil 7005 Zeosil 1205 MP Hi-Sil 2000

* CTAB surface area measurement.

[#] Highly dispersible.

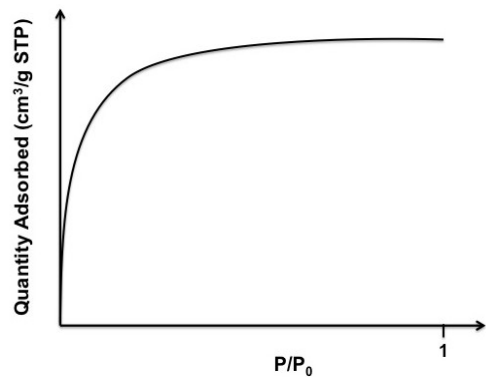
2.2.2 Specific Surface Area of Silica

The commonly probe molecules used for silica specific surface area measurement are nitrogen (N_2), as in the Brunauer-Emmett-Teller (BET) adsorption method, N_2 normally used, but the BET theory also applies for other gasses, such as argon, CO_2 etc., and N-cetyl-N-N,N'-trimethylammonium-bromide (CTAB).

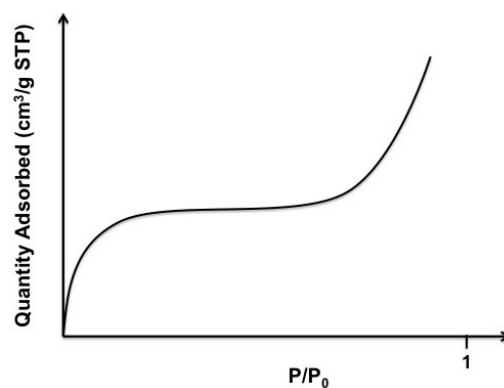
The customary cross-sectional area for nitrogen is $16.2 \text{ \AA}^2$ at 77.4K [48], which is equivalent to approximately 2.27 Å in radius. BET measurement using N_2 includes the micropores in the silica, known as the pore-filling phenomenon. CTAB molecules are larger than N_2 and hence the CTAB adsorption method does not include the measurement of silica micropores.

The adsorption isotherms or gas adsorption analyses generally follow one of the six forms, which are assigned numbers according to Brunauer, as shown in Figure 2.3 [51].

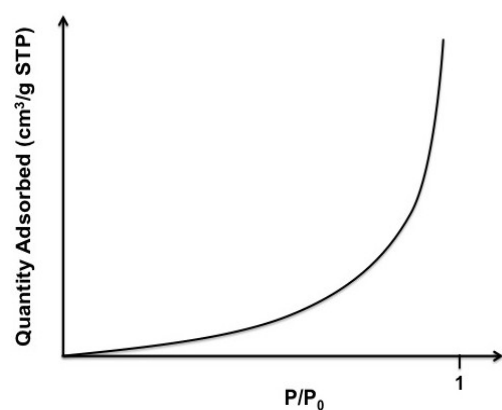
a. Type I isotherm



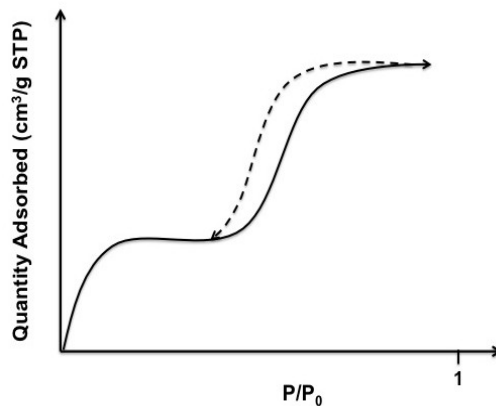
b. Type II isotherm



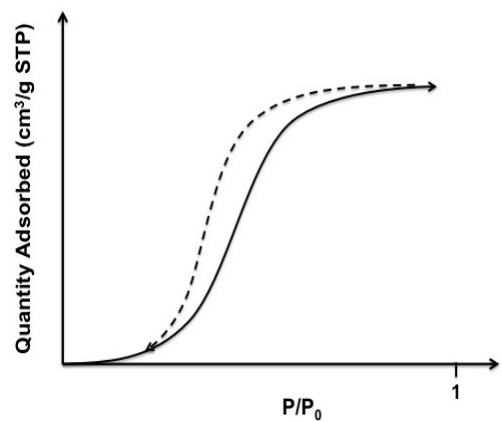
c. Type III isotherm



d. Type IV isotherm



e. Type V isotherm



f. Type VI isotherm

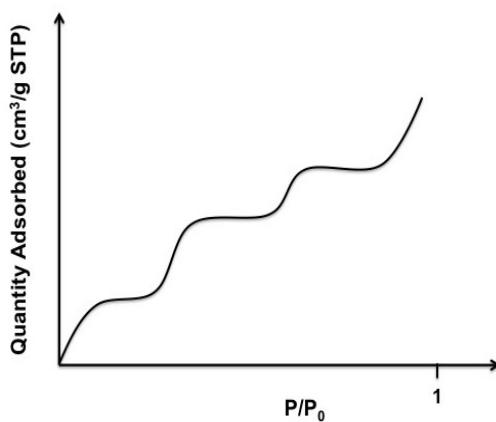


Figure 2.3: Isotherm classification from a) to f) according to quantity adsorbed/desorbed versus relative pressure (equilibrium pressure/ saturation pressure, P/P_0) [51].

The isotherms shown in Figure 2.11 each reflect some unique conditions. Each of the isotherms is discussed as follows [51]:

a) Type I isotherm

The Type I isotherm could be chemisorption with the formation of a few molecular layers on the adsorbent surface. It could be physical adsorption for a solid sample with a microporous surface. At low relative pressures, the adsorbates fill the micropores or cover the micropore walls increasing the quantity of adsorption. As the relative pressure increases, a plateau is reached due to no additional adsorption after the micropores have been filled with adsorbates.

b) Type II Isotherm

This type of isotherm occurs when adsorption occurs on particles with pore diameters larger than or $\geq 2\text{nm}$ or on nonporous particle surfaces. Inflection occurs upon the completion of the first adsorbed monolayer.

c) Type III isotherm

The occurrence of a type III isotherm is due to the adsorbate molecules having greater affinity between themselves than to the adsorbent surface. As the relative pressure increases, the interactions with the adsorbed layer continue to be greater than with the adsorbent surface.

d) Type IV isotherm

This isotherm occurs on porous adsorbents with a pore radius range of approximately 15-1000 Å. The slope increases at higher relative pressures as the pores are being filled.

d) Type V isotherm

The Type V isotherm has similar adsorbate-adsorbent interactions as the type III isotherms. However, the adsorbent for the type V isotherm has a similar pore size range as those exhibiting type IV isotherms.

f) Type VI isotherm

The Type VI isotherm indicates a nonporous adsorbent surface with an almost uniform surface.

2.2.3 Surface Chemistry of Silica

The filler size and the specific surface area of the filler can be related to the interfacial area between the particle surface and the elastomer chains. Filler structures can be related to the degree of irregularity of the aggregation development of the primary particles [52,53]. These aggregated primary particles can trap part of the elastomer, which is termed as 'occluded elastomer' [21,22]. It increases the effective filler volume and affects the compound properties, such as the viscosity and modulus of the filled elastomer.

Both of the above parameters (filler size, surface area and filler structure) will not bring significant effects without the involvement of the third parameter, the surface chemistry or the surface activity of the filler particles [54,55]. This parameter is responsible for the relative strength of filler-filler interactions, filler-elastomer interactions, and filler interactions with other ingredients during compounding.

Besides that, it is also well known that the particle surface is heterogeneous in nature. The energetic heterogeneity and the geometric heterogeneity of the particle surface, which have a close association with each other, influence the reinforcement of the elastomer [56]. Heng *et al.* revealed the importance of surface energy and surface roughness to provide mechanical locking and adhesion between fibre as a filler and the elastomer matrix [57].

The degree of heterogeneity depends on the preparation of the silica material, chemical impurities or unavoidable dislocations. The aim in the present study is to establish the silica surface energy heterogeneity and the dispersion of modified silicas in rubber compounds. A broad spectrum of adsorption sites on the particle surface will eventually have an effect on the bonding configurations [58]. Apart from particle surface morphology, there are many sources for heterogeneity due to the emergence of acidic and basic centres. The heterogeneity sites on the particles can be reduced by pre-treatment with heat or surface chemistry modification [59].

The presence of functional groups such as silanol groups or adsorbed species on the silica surface can be detected through spectroscopic techniques. These techniques include vibrational spectroscopy and solid-state nuclear magnetic resonance (NMR)

spectroscopy. The former technique [60,61,62] has been widely used since the 1960s and had a profound effect on understanding the surface chemistry of silica. It includes Fourier transform infrared (FTIR), Raman and diffuse reflectance FTIR, and provides detailed information regarding hydrogen bonding, physical adsorption, and chemisorptions. However, vibrational spectroscopy cannot readily quantify the species on the surface without carrying out time-consuming calibration [63].

Solid-state NMR on the other hand can be used to determine the relative motional freedoms of the adsorbed species and provides quantitative data relative to the absolute numbers of the adsorbed species [64]. Both of the spectroscopic techniques complement each other and provide useful information the structure of the adsorbed species on the filler surface. FTIR spectroscopy remains popular today as an inexpensive analytical technique, where the IR spectrum can be recorded in about one second. NMR requires expensive equipment and often requires a longer time for data acquisition.

Recently, the combination of thermogravimetric analysis (TGA) allows the qualitative analysis of adsorbed species when the evolved in the TGA is investigated by IR [65]. Law et al. [66] used TGA to investigate the grafting of alkoxysilanes on the silica surface.

As for the surface thermodynamics of filler, this can be characterised by using contact angle or Inverse Gas Chromatography (IGC). The free energy of interaction between two phases involves work of adhesion, W_{adh} , where W_{adh} is measured in energy per unit surface area of a material. There are several kinds of intermolecular

interaction present between the two phases. Fowkes [67], proposed that the total surface free energy, γ_S^T is given by the sum of the following interactions:

$$\gamma_S^T = \gamma_{adh}^d + \gamma_{adh}^p + \gamma_{adh}^i + \gamma_{adh}^h + \gamma_{adh}^{da} + \gamma_{adh}^{\pi} + \gamma_{adh}^e \quad (2.6)$$

where the superscripts are referring to London dispersion forces, dipole-dipole interactions (Keesom force), dipole-induced dipole interactions (Debye force), hydrogen bonds, donor-acceptor bonds, π -bonds and electrostatic interactions, respectively.

The γ_S^T is a combination of the dispersive component (γ_S^d) and specific (acid-base) surface energy (γ_S^{ab}). The dispersive component includes the London, Keesom and Debye forces also known as Lifshitz – van der Waals interactions [68]. The donor-acceptor bonds and π -bonds are considered as specific interactions [69]. For the current research, the electrostatic interactions were not investigated.

Silicas are characterised by higher specific components γ_S^{sp} , of surface free energy and lower dispersive components γ_S^d , compared to carbon black. The high specific components γ_S^{sp} , of silica would leads to strong agglomeration [29] of the silica particles and rapid re-agglomeration even after mixing with elastomer [30]. According to Mihara et al. [30], although the silica network is broken during reactive mixing with the silane bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT), the silica tends to re-agglomerate afterwards. The high γ_S^d of carbon black would facilitate strong bonding interactions between filler and non-polar olefinic hydrocarbon elastomers [29].

The studies have shown the significant role played by the filler particles' surface energy on the mechanical properties of filled rubbers [70,71]. By understanding and modifying the surface energy of silica quantitatively, silica dispersion efficiency could be improved and the level of interaction with different elastomers enhanced.

2.2.4 Silica Surface Silanol Groups

In the 1930s, the studies of obtaining silica through condensation processes with silicic acids showed the presence of hydroxyl groups and they are chemically bonded to the silica surface [33]. These hydroxyl groups are formed from the water evolved during the calcinations process of silica gel [72]. The hydroxyl groups play an important role in silica surface adsorption characteristics and substantially change the silica surface area [73]. Besides that, at a sufficient concentration of hydroxyl groups, the silica surface exhibits hydrophilic characteristics. However, when the silica is dehydroxylised, the surface will become hydrophobic. These silanol groups can be subdivided as follows:

- a. Geminal (Two hydroxyl groups on the same silicon atom, = $Si(OH)_2$)
- b. Isolated (A single hydroxyl group on a silicon atom, $\equiv SiOH$)
- c. Vicinal (Two hydroxyl groups on neighbouring silicon atoms)

According to Hewitt [28] the isolated silanol groups are the most reactive and can interact with soluble zinc, amine derivatives, glycols and other additives that influence the vulcanisate properties of silica filled-rubber compounds. Figure 2.4 illustrates the types of silanol groups found on a silica surface [28].

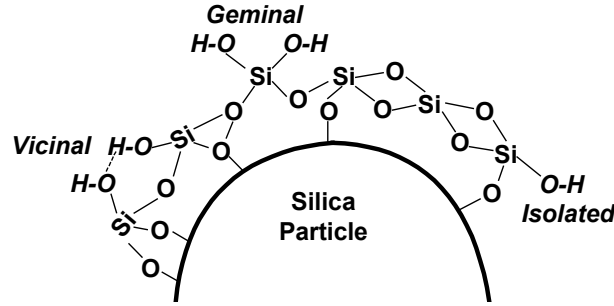


Figure 2.4: Types of silanol groups on the silica surface [28].

The presence of silanol groups on silica surfaces attracts a transient layer of free adsorbed water which can be removed when the silica is treated under vacuum between room temperature and 200 °C. This weakly bound water is adsorbed onto the silanol groups on silica surface in multiple layers. The first layer is adsorbed through multiple hydrogen bonding and this is followed by more weakly bound layers outward from the silica surface. On the silica surface, there is also the presence of siloxane groups bridging two silicon atoms through an oxygen atom ($\equiv Si - O - Si \equiv$).

The surface concentration of the hydroxyl groups (per nm²) or the silanol number, α_{OH} , is determined as:

$$\alpha_{OH} = \delta_{OH} N_A \times 10^{-21} SSA_{Silica}^{-1} \quad (2.5)$$

Where, δ_{OH} is the concentration of OH groups on the silica surface per unit mass of the silica sample (mmol of OH/g of silica), SSA_{Silica} is the specific surface area (nm²/g) with respect to BET with nitrogen or krypton adsorption and N_A is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$). There are a number of experimental methodologies that are used to determine the α_{OH} . Techniques such as deuterium-exchange [34,72,73,74],

thermogravimetric analysis (TGA) [75], IR spectroscopy [62,74], reaction with LiAlH_4 [76], esterification with methanol [75] and treatment with NaOH (Sears method) [75] are commonly used to determine α_{OH} or other components on the silica surface.

It is important to note that the concentration of the functional groups depends on the preparation of the silica sample and on the conditions of thermal treatment of the silica sample (or type of pre-treatment) before the measurement is carried out. Zhuravlev [72] reported that it is necessary to take into account the possible changes which occur simultaneously with loss of the weakly physisorbed water molecules or of different surface functional groups, and which occur in the energetics of the dehydration (removal of physically adsorbed water), dehydroxylation (removal of silanol groups) and rehydroxylation (the restoration of the hydroxylated surface) processes.

Zhuravlev's experimental results using deuterium-exchange technique with mass spectrometric analysis showed that the α_{OH} values at a given temperature of silica pre-treatment are similar for all the 100 different amorphous silica samples considered in his study, with specific surface area varying between 11 and 905 $\text{m}^2 \text{g}^{-1}$ [72]. Table 2.3 showed the probable surface concentration of the different types of OH groups for a completely hydroxylated amorphous silica [73].

Table 2.3: Probable surface concentration of the different types of OH groups for a completely hydroxylated silica [72,73].

Temperature of vacuum pretreatment, T (°C)	Total OH groups, $\alpha_{OH,T}$ (OH/nm ²)	Isolated OH groups, $\alpha_{OH,I}$ (OH/nm ²)	Geminal OH groups, $\alpha_{OH,G}$ (OH/nm ²)	Vicinal OH groups, $\alpha_{OH,V}$ (OH/nm ²)
180-200	4.60	1.20	0.60	2.80
300	3.55	1.65	0.50	1.40
400	2.35	2.05	0.30	0
500	1.80	1.55	0.25	0
600	1.50	1.30	0.20	0
700	1.15	0.90	0.25	0
800	0.70	0.60	0.10	0
900	0.40	0.40	0	0
1000	0.25	0.25	0	0
1100	0.15	0.15	0	0
1200	0	0	0	0

Table 2.3 showed that the average silanol number, α_{OH} , for completely hydroxylated amorphous silica surface is 4.6 OH/nm² for a pre-treatment of 180 °C - 200 °C. As for pre-treatment temperatures at 400 °C and above, α_{OH} was found to be 2.35 OH/ nm² and less in Table 2.3. The values are higher than 4.6 OH/nm² to those reported by other groups [34,74,77]. The average area for a single Si atom on the surface holding one OH group is 0.217 nm².

2.3 Elastomers

The term 'elastomer' is applied to a set of polymeric materials consisting of linked polymer chains, which provide the elastomer with elastic properties when stress or strain is removed. The polymeric material has the ability to undergo reversible elastic deformations, a perfectly elastic material will return exactly to its original shape [78,79]. However, to meet the conditions of instantaneous and reversible deformation, the glass transition temperature of the elastomer must be significantly lower than the test temperature.

The crosslinking occurring during the vulcanisation process converts the elastomer into a three dimensional elastic network of interlinked polymer chains through the formation of covalent bonds as shown in Figure 2.5. The appearance of crosslinks in the network enhances the elastic properties of the unvulcanised elastomer, which without crosslinks relies on entanglements to provide an elastic network.

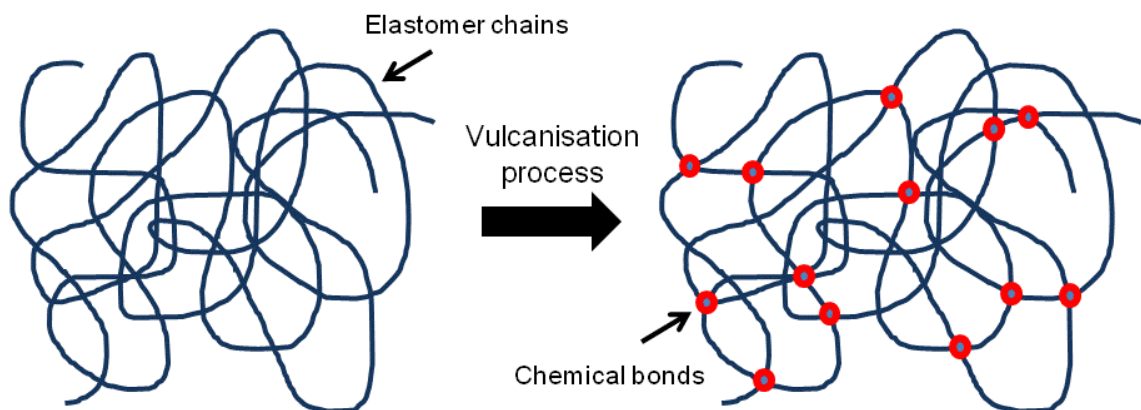


Figure 2.5: Schematic drawing of vulcanisation process.

The distribution of crosslinks has a decisive effect on the elastic properties [80,81]. There are several types of crosslinking processes notably the sulfur-based and the peroxide-based systems. Peroxide vulcanisation provides carbon-carbon bonds between macromolecular chains. The most commonly used cross-linking process is the use of sulfur, which is also applied in this study. The sulfur reacts with the unsaturated elastomer chains, creating covalent crosslinks connecting the allylic carbons of the elastomer chains. Figure 2.6 shows the types of sulfur chemical structures obtained through sulfur crosslinking of an unsaturated elastomer. Usually, the crosslinking networks are a mixture of mono-, di-, and poly-sulfidic linkages [82,83,84]. The crosslink density and the proportions of the different types of crosslinking process determine the properties of the vulcanised elastomer [83]. For example, higher concentrations of monosulfidic crosslinks improve the thermal stability of the vulcanisate, while polysulfidic crosslinks improve strength and fatigue properties [83].

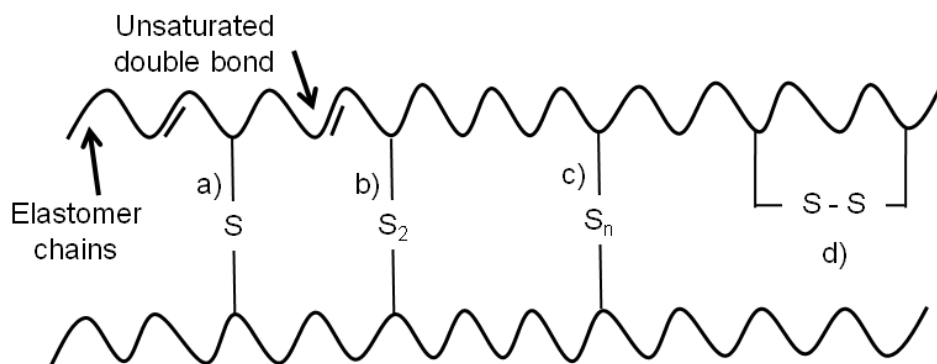


Figure 2.6: Types of sulfur crosslinks after the vulcanisation process. a) Monosulfidic cross-link b) Disulfidic cross-link c) Polysulfidic cross-link d) Intrachain cyclic sulfide [83].

Boonkerd et al. [85] stated that the concentrations of the different types of sulfur linkages formed depends significantly upon the sulfur to accelerator ratio used in the vulcanisation process, the curing temperature and the curing time. All the elastomer vulcanisates prepared for the current study were cured using the same silica structure, the same amount of sulfur, and the same curing time and temperature.

The elasticity in elastomers can be presented in a typical tensile force curve as shown in Figure 2.7. The curve displays three different regions [83]:

- i. At low deformation (Region I) also known as Hookean, the relation between tensile and strain is linear. The deformation is approximately 1%.
- ii. At higher deformation up to 600% (Region II), the curve is non-linear and this is related to the conformational entropy produced during the deformation process.
- iii. At Region III, the sharp increase in tensile strength is due to the extensibility limit of the elastomer chain network and to a strain-induced crystallisation process for natural rubber (if the elastomer undergoes strain crystallisation).

The deformation process shown in Figure 2.7 is connected with the changes in the thermodynamic quantities internal energy and entropy.

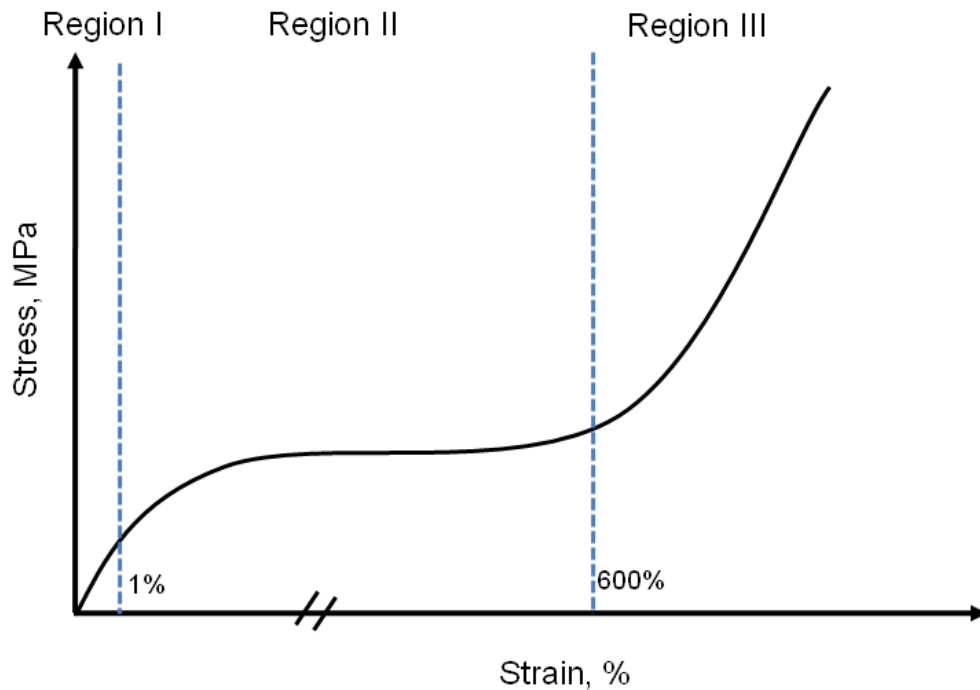


Figure 2.7: The curve of stress versus strain of a typical cross-linked natural rubber.

2.4 Elastomer Reinforcement

Generally, filler particles are used to reinforce rubber to improve its mechanical properties and to meet the required product specifications. The most commonly used fillers for tyre elastomers are carbon black and silica. These fillers are classified by their primary particle size or surface area and qualitatively by their surface activity eg. By reference to their hydrophobic nature or to specific surface functionalities.

The particle size of filler in this case can be referred to as surface area per weight, which has an influence on the level of reinforcement. The characteristic of filler

surface activity denotes the presence of functional groups on filler surface that enables effective coupling between filler and rubber [86].

2.4.1 Dynamic Mechanical Properties of Filler Reinforced Elastomer

The three most important properties of tyre performance are high traction (wet and dry) for tyre handling performance, low rolling resistance for fuel saving, and high wear resistance for durability. These three parameters are described as the ‘magic triangle’ properties of tyre performance as shown in Figure 2.8:

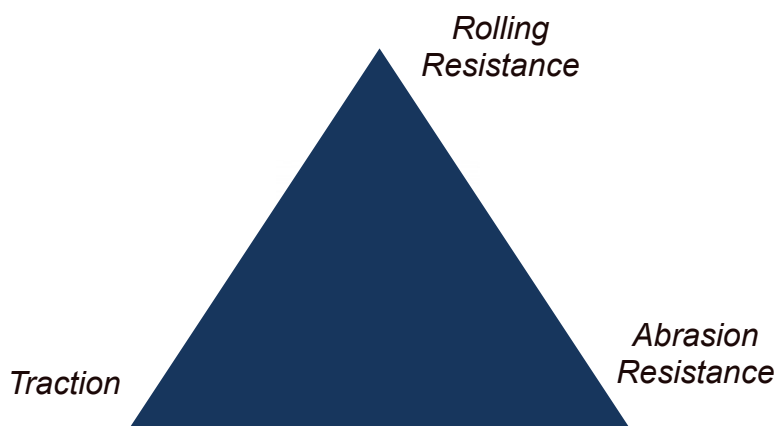


Figure 2.8: The ‘magic triangle’ properties of tyre performance.

The tyre performance was constrained by these three properties using conventional tyre compound formulations. Improvement in any one of the properties conventionally led to a trade off in the other two properties.

However, the development of highly dispersible silica has enabled on overall the improvement in two of these three properties [87]. Therefore, the tyre tread compound formulation plays a major role to expand the design limitations of this 'magic triangle'.

Dynamic mechanical analysis (DMA) is often used to indicate the performance of tyre tread compounds as measured on small test pieces in the laboratory and can correlate with actual tyre performance data.

Based on the above indications, understanding hysteresis loss of rubber compounds is of great importance. When a tyre is rolling, the rubber compound is undergoing dynamic deformation. The kinetic energy of the rubber compound is elastically stored and dissipated over a period of time as reflected in the loss modulus as well as the loss tangent.

During a DMA test, a viscoelastic solid is undergoing sinusoidal shear deformation, with shear strain $\gamma(t)$ and angular frequency ω as illustrated in Figure 2.9.

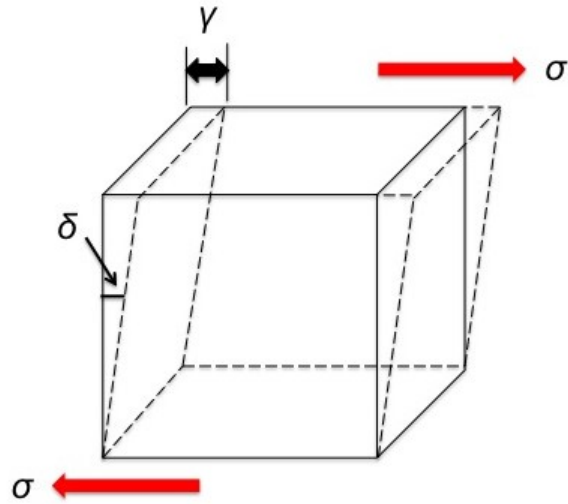


Figure 2.9: Schematic diagram of vibrating shear deformation of a rubber sample.

The equation for sinusoidal shear strain, $\gamma(t)$, is expressed as:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad (2.6)$$

where γ_0 is maximum strain.

The sinusoidal shear stress, $\sigma(t)$, having phase lag, δ , with strain is:

$$\begin{aligned} \sigma(t) &= \sigma_0 \sin(\omega t + \delta) \\ &= (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t \end{aligned} \quad (2.7)$$

Comparing Equations 2.7 and 2.6, leads to the following expressions:

Storage modulus, G' ,

$$G'(\omega) = \frac{\sigma_0}{\gamma_0} \cos \delta \quad (2.8)$$

And for Loss Modulus, G'' ,

$$G''(\omega) = \frac{\sigma_0}{\gamma_0} \sin \delta \quad (2.9)$$

The loss tangent, or $\tan \delta$, is defined as

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)} \quad (2.10)$$

where storage modulus, $G'(\omega)$, is a measure of the stored energy representing the elastic characteristic of the material and loss modulus, $G''(\omega)$ is a measure of the energy dissipated as heat, representing the viscous characteristic of the material. Figure 2.10 shows a stress and strain sketch of a viscoelastic material with phase angle δ [83].

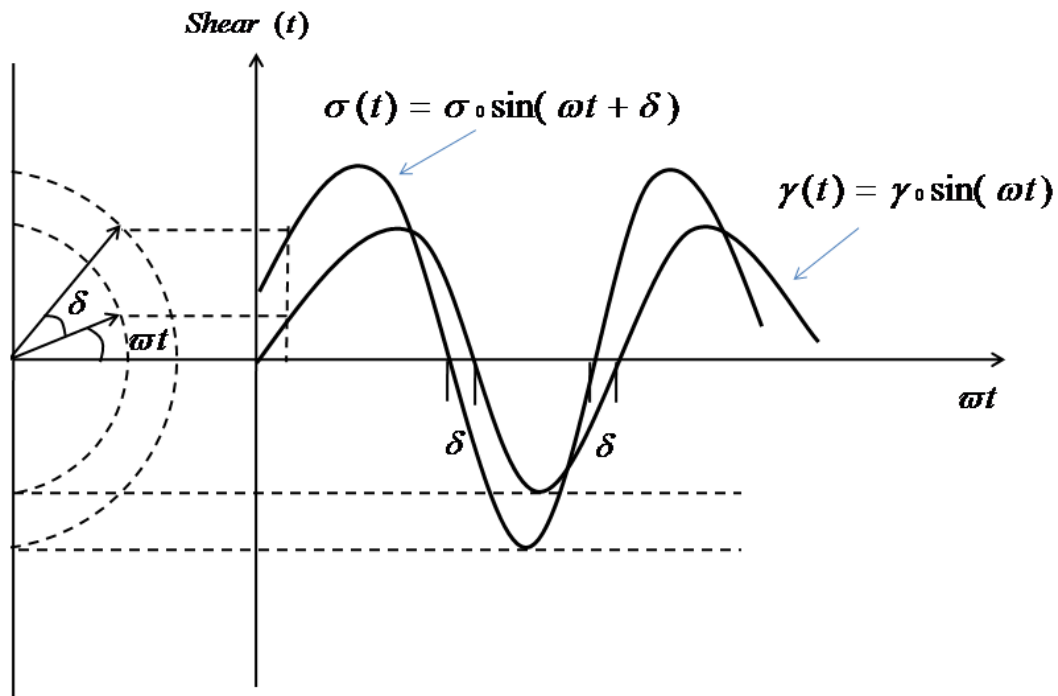


Figure 2.10: Sketch of a typical stress leading strain sinusoidal deformation by phase angle δ for a viscoelastic material [83].

A typical $\tan \delta$ versus temperature curve that relates to wet grip and rolling resistance of a rubber compound is illustrated in Figure 2.11.

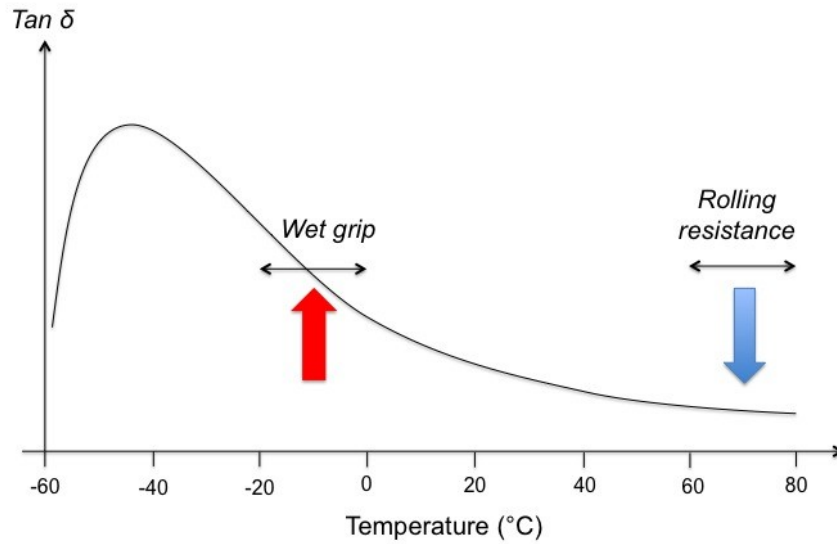


Figure 2.11: Dependence of $\tan \delta$ on temperature for a viscoelastic material.

When a elastomer compound is near its glass transition temperature, the compound is in a leathery state and the $\tan \delta$ is at the maximum value. At a temperature near 0 °C, the $\tan \delta$ is indicative of wet traction performance of the rubber compound. Higher $\tan \delta$ correlates with better wet traction performance. It is generally accepted that when the temperature reaches the tyre running temperatures (the region of 60 °C to 70 °C), the lower $\tan \delta$ value indicates lower hysteresis [88]. This in turn leads to lower drag force and improves rolling resistance performance. Lower $\tan \delta$ is preferred for low rolling resistance performance [70,89].

The presence of a filler in the rubber matrix greatly influences the dynamic properties of the rubber. During dynamic strain, the filler network undergoes breakdown

and reformation, the polymer chain undergoes disentanglement and rubber detaches from filler particles [90,91]. Studies by Wang [92] have showed that the dynamic properties are affected by the filler loading, filler surface chemistry, filler particle size, and filler structure.

2.4.2 Filled Elastomers

Most unfilled elastomers are weak materials and generally rely upon filler reinforcement to achieve the desired mechanical properties. Depending on the grade, carbon black fillers are produced with primary particle and aggregate size ranging from 5 to 100 nm and 70 to 500 nm, respectively [93]. Carbon black fillers exhibit zig-zag chain structure and form either physical or chemical bonds with the organic surface of the rubber [86], probably mainly physical [94]. Compared to carbon black fillers, precipitated silica exhibits a smaller range of primary particle sizes, ranging from 2 to 40 nm, and forms aggregates from 100 to 500 nm in size [93]. Silica particles form strong filler-filler particle networks and require the presence of a surface functional group to provide substantial coupling with an unsaturated hydrocarbon rubber. These filler-filler interactions that affect the extent of rubber reinforcement have been described by Payne et al. [95], who have shown the hysteresis of filled rubber that relates to breakdown and reformation of the filler-filler network as illustrated in Figure 2.12.

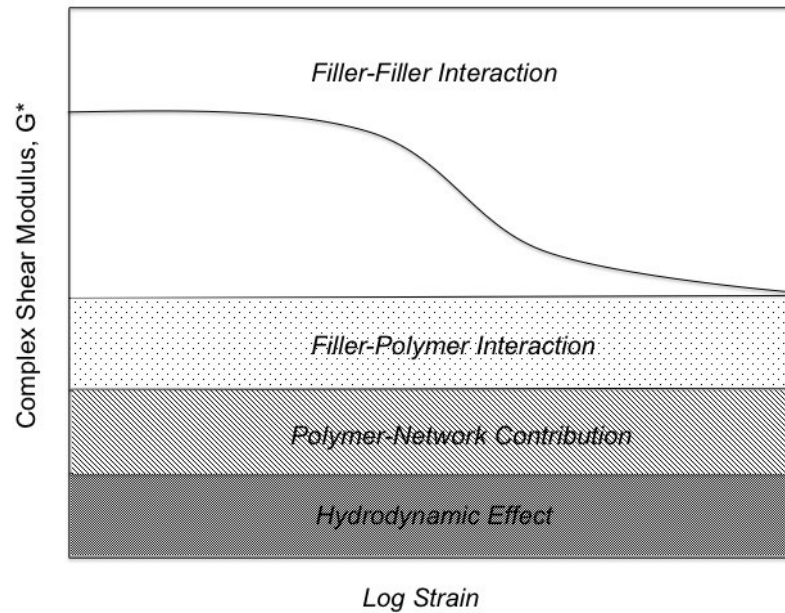


Figure 2.12: Dynamic shear modulus of elastomer vulcanisate.

The hydrodynamic effect is based on low loading of spherical rigid particles with the assumption that there are no interactions between particles and these particles are fully wetted and suspended in a fluid [96]. Further development of the hydrodynamic effect is described by Guth [97], who described the viscosity taking into account filler interparticular interactions at higher concentrations.

The bound rubber relates to filler-rubber interaction, or partial insolubilisation of rubber due to adsorption of macromolecules on the reinforcing filler. The phenomenon has been extensively studied and several models, such as bound rubber and chain entanglement models, have been developed to understand the interaction between filler and elastomer [98,99,100,101,102]. According to the bound rubber theory proposed by

Meissner [103,104], the coupling between filler and elastomer is assumed to be as follows:

- i. Each reactive site on the filler particle surface can form one bond with one structural unit of the polymer.
- ii. Bonds are formed randomly between filler surface and structural units of the polymer.
- iii. The bonds are sufficiently permanent to resist the swelling action of a solvent.

Other studies on filler-rubber interaction include that by Medalia [105,106], who investigated the concept of occluded rubber where the rubber is partly trapped in the filler aggregates and shielded from deformation. The occluded rubber increases the effective volume of filler, acts as filler rather than contributing to the elastic behaviour of the rubber matrix at low strain. This phenomenon increases the effective filler volume and enhances the strain modulus of the filled rubber. Ouyang [107] proposed immobilised glassy-state bound rubber covering filler aggregates. He suggests that the main source of the energy dissipation of rubber compound at low strains is due to rubber molecular chain friction rather than filler-rubber interfacial slippage.

The attachment of elastomer chains on the filler particle surface, through a wetting process forms a glassy elastomeric layer that exhibits elastic dynamic behaviour between loosely bound rubber and the totally immobilised glassy elastomer and shifts the loss tangent of the rubber material near the vicinity of the filler particles [108]. The bound rubber shell of the filled-elastomer can be categorised into three relaxation regimes; the loosely bound rubber (rubber like), the totally immobilised glassy rubber (in brittle manner) on the filler surface, and a third component of rubber with intermediate mobility.

As for filler-filler interactions, it is usually related to the breakdown and reformation of filler aggregates in the rubber matrix during relatively low strain hysteresis, usually described as the Payne effect. Payne et al. [95,109] observed a sigmoidal decrease of the storage modulus versus increasing strain amplitude (on a logarithmic scale) in filled rubber and also the loss modulus exhibiting a maximum value at the strain where the storage modulus was decreasing most rapidly. This phenomenon of strain dependent modulus can be separated into three regions [109]:

- a. The low amplitude modulus (LAM) region
- b. The transition region
- c. The high amplitude modulus (HAM) region

In the LAM region, typically below 0.1% in strain, the storage modulus is nearly constant. However, the loss modulus increases slowly due to a small breakdown and

reformation of the filler-filler network under the periodic sinusoidal strain. The fillers are interacting with each other through van der Waals forces and hydrogen bonds.

In the transition region, the storage modulus decreases significantly and a maximum loss modulus occurs. These changes depend on the filler loading and the effectiveness of filler dispersion and filler-filler interactions.

In the HAM region, at 5 to 10% in strain, the reduction of modulus continues at a much slower rate due to the inability of filler reformation at high amplitude. This phenomenon of strain dependent modulus is reversible once the strain is released. It is independent of type of rubber but is dependent on the type of filler [110]. Figures 2.13 and 2.14 illustrate typical strain dependent storage modulus and loss modulus, respectively, for a carbon black filled-elastomer [91].

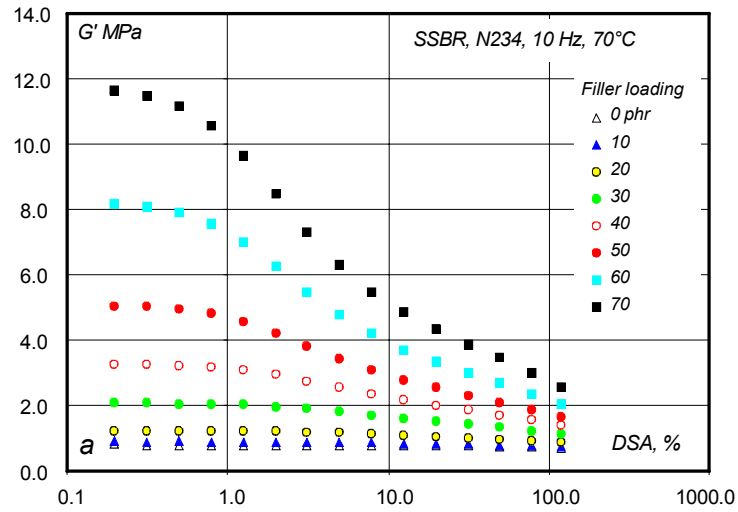


Figure 2.13: Typical strain dependence of storage modulus for filled rubber under various filler loadings [91].

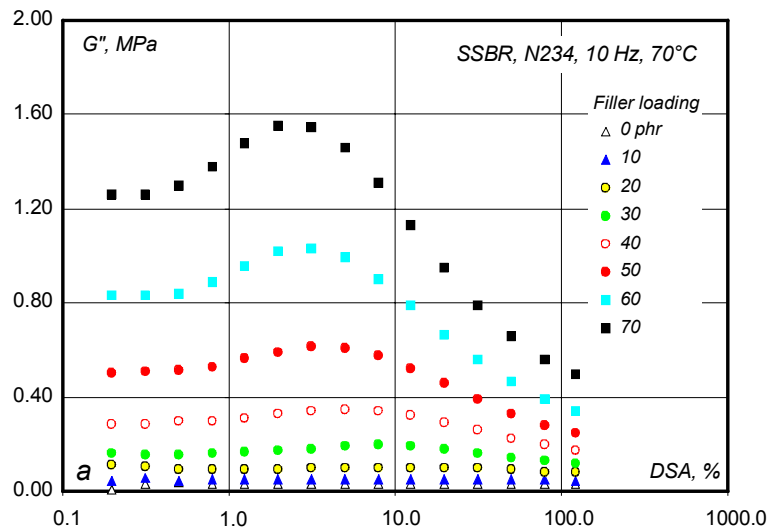


Figure 2.14: Typical strain dependence of loss modulus for filled-rubber under various filler loadings [91].

According to Fröhlich et al. [111] the primary filler factors influencing rubber reinforcement are:

- i. The primary particle size of the filler, which relates to the effective contact area between the filler and the rubber matrix.
- ii. The structure of the filler particle, which affects the mobility and slippage of rubber chains under strain.
- iii. The surface activity of filler, which plays a major role in filler–filler and filler–rubber interactions.

A recent study [112] has shown that the loss modulus peak is not significantly affected by the surface area of the filler in carbon black-filled sSBR or by silane coupling of the silica surface to the SBR matrix. However, a notable difference in loss tangent (the ratio of loss modulus to storage modulus) was observed with these fillers. Higher reinforcement was observed through increases in storage and loss modulus in the rubber state above the T_g temperature.

Studies by Stöckelhuber et al. [113,114] have shown that the high polar component of silica surface energy resulted in a strong filler network, which led to a high tendency for filler flocculation. Thus, the stiffness of silica-filled sSBR increased. Their studies also showed that filler surface energy has a significant influence on the work of adhesion between the filler surface and the rubber matrix. Their hypothesis of a 'layer fiber model' showed [114] that when elastomer chains slipped off the surface of filler

particles and became trapped in intra-aggregate gaps, high-strength resulted between the elastomers and the fibres in a uniaxial direction.

2.5 Silica Surface Modification by Silane

The increasing use of silica/silane technology in the tyre industry implies that silica surface modification is needed to achieve the desired application. Silanisation of silica improves dispersion of silica aggregates dispersion in the elastomer matrix and reduces hysteresis during dynamic strain. The silane has the ability to form a covalent bond between organic and inorganic materials. The general formula for a silane is as follows:



R is organofunctional group and X is a hydrolysable group typically alkoxy, acyloxy, halogen or amine. In the elastomer industry, the organofunctional groups are chosen for their reactivity and compatibility with the chosen polymer.

An example of this silane is TESPT, which has been widely used for the tyre tread compound. The use of TESPT has allowed for improvement of the mechanical properties of elastomer vulcanisates. This coupling agent facilitates the interaction of the silica, which is hydrophilic with the hydrophobic organic chains of the elastomer matrix. The strength of bond of this interaction between silica and elastomer is responsible for the macroscopic properties of silica-filled sSBR/ BR vulcanisates used in tyre treads.

Many studies have been devoted to TESPT technologies, and the mechanisms of reaction of this silane and silica are still under debate. The interaction between silica and silane varies from physisorption to covalent bonding depending on the temperature [30,37], reaction conditions and whether the silica is dehydrated or hydrated [65].

In the case of dehydrated silica, at low temperatures, the adsorption involves the formation of H-bonding between the silanol groups and on the silica surface and the ethoxy groups from the silane. At temperatures between 100 °C and 200 °C range, it is postulated that direct condensation of silane with the silica silanol groups is involved with the release of ethanol, as shown in Figure 2.15.

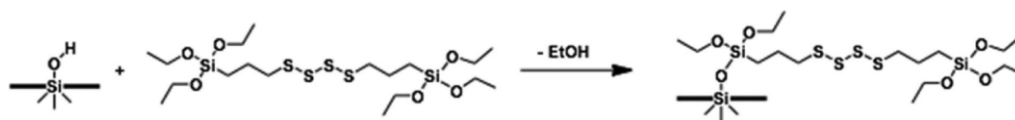


Figure 2.15: Direct condensation process between TESPT and the silanol groups from the silica surface [65].

In the case of hydrated silica, Hunsche et al. [115] and Vilmin et al. [65] reported that the reaction mechanism involves the presence of water molecules and the hydrolysis of TESPT ethoxy groups, which lead to the formation of reactive silanol groups (Figure 2.16a). According to Hunsche et al. [115], grafting of TESPT on to the silica then occurs through a condensation process with the silanol groups on the silica surface (Figure 2.16b). The hydrolysed silane can also undergo oligomerisation with vicinal silane species through nucleophilic substitution to form polycondensed silane species by releasing ethanol (Figure 2.16c) or water (Figure 2.16d) and forming

siloxane bridges. Vilmin et al. [65] believe that, even when water is present, the silanols on the silica react directly with the ethoxy silane, releasing ethanol.

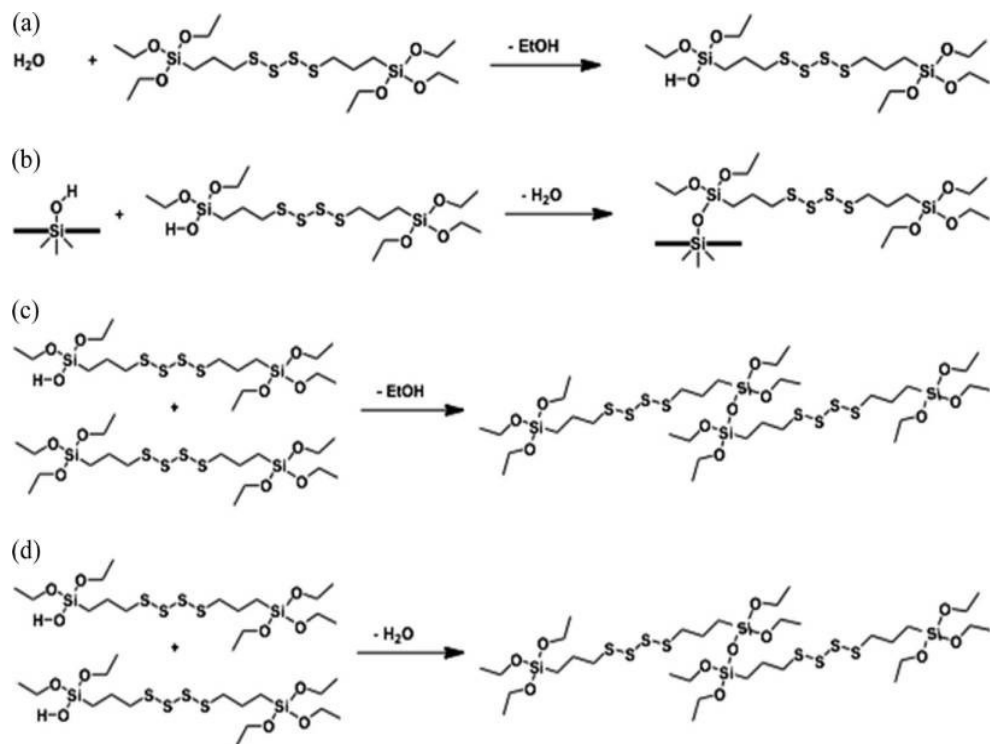


Figure 2.16: Suggested reaction mechanisms of TESPT with silica: a) One ethoxy group of TESPT is hydrolysed, b) Grafting of silica silanol group with hydrolysed silane through condensation process, c) Oligomerisation reaction between a nonhydrolysed and a hydrolysed vicinal species, or d) Reaction between two hydrolysed vicinal species [65].

CHAPTER 3 EXPERIMENTAL METHODOLOGY FOR THE PREPARATION OF SILANISED SILICA AND SILICA-FILLED ELASTOMER

3.1 Introduction

Silica surface grafting to make the surface less hydrophilic is regarded as an effective approach to reduce the interaction between silica particles and with the possibility of enhancing the coupling between silica and elastomer. The grafting of silica surface can be induced via reaction with silane. The general approach employed here for silica surface modification is described in this Chapter. Silica surface grafting with different silanes provides a basis for understanding the effect of silica surface energy on the dispersibility of silicas in the elastomer phase and its effect on the properties of silica-filled elastomers. These properties are determined by inverse gas chromatography as reported in Chapter 4, by 'Transmission Electron Microscopy (TEM) - network visualisation' analysis as reported in Chapter 6, by Rheological analysis of silica-filled elastomer compound as reported in Chapter 7, and by silica-filled elastomer vulcanisate mechanical analysis as reported in Chapter 8.

3.2 Materials

3.2.1 Silanes

The silanes used for silica surface modification are bifunctional coupling and monofunctional non-coupling silanes. The molecular structures of these silanes are shown in Figures 3.1 and 3.2, for coupling and non-coupling silanes respectively. The coupling silanes, which are also known as sulfur-functional organosilanes, were:

- a) TESPT (Si 69[®]) : bis[3-(triethoxysilyl)propyl] tetrasulfide
- b) TESPM (VP Si 263[®]) : 3-(triethoxysilyl)propyl mercaptan
- c) TESPd (VP Si 266[®]) : bis[3-(triethoxysilyl)propyl] disulfide
- d) DTSPM (VP Si 363[®]) : [3-(di-(tridecyloxypenta(ethyleneoxy))ethoxysilyl)-
propyl mercaptan
- e) TESPO (NXT[®]) : 3-(triethoxysilyl)propyl thio-octanoate
- f) TESPO/M : Reaction product of TESPO, TESPM and 2-methyl-
(NXT[®] Z45) 1,3-propanediol

Silanes a) to d) were kindly supplied by Evonik Industries AG, Germany. Silanes e) and f) silanes were kindly provided by Momentive Performance Materials Inc., US. TESPO/M is a co-oligomer combining the mercapto-silane, TESPM, with the blocked mercapto-silane, TESPO, in the ratio 55:45 [116]. In Figure 3.1f, R² is a –CH₂CHMeCH₂– group and R¹ is –CH₂CHMeCH₂– or residual –Et. [116,117].

As for non-coupling silanes:

- a) OTES (Dynasylan[®] OCTEO) : octyltriethoxysilane
- b) MTMS : methyltrimethoxysilane
- c) MTES : methyltriethoxysilane
- d) TMCS : trimethylchlorosilane
- e) DCDMS : dichlorodimethylsilane

Dynasylan® OCTEO silane was supplied by Evonik Industries AG, Germany and the rest of the non-coupling silanes were purchased from Sigma-Aldrich Co. Ltd., UK.

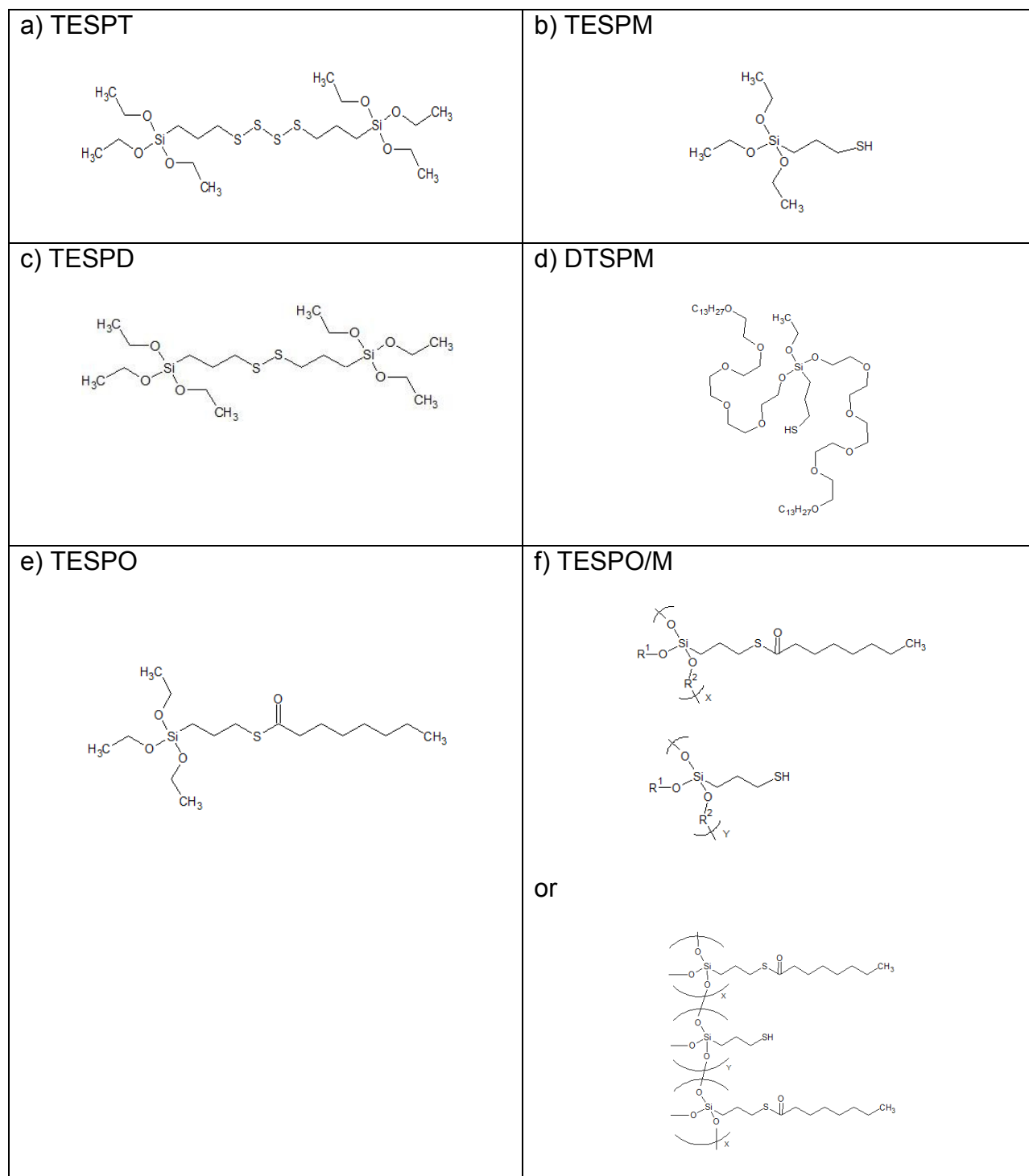


Figure 3.1: Molecular structure of bifunctional coupling silanes: a) TESPT, b) TESPM, c) TESP, d) DTSPM, e) TESPO and f) TESPO/M.

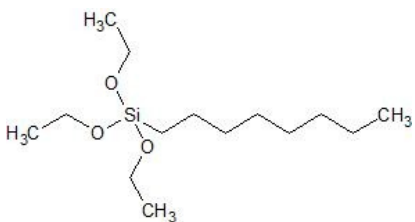
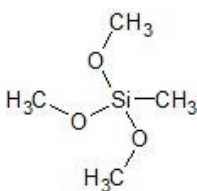
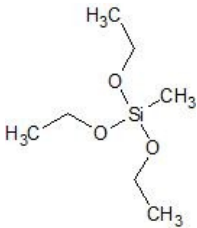
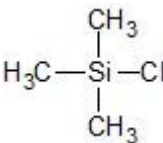
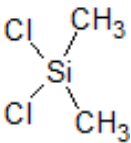
a) OTES 	b) MTMS 
c) MTES 	d) TMCS 
e) DCDMS 	

Figure 3.2: Molecular structure of non-coupling silanes: a) OTES, b) MTMS c) MTES, d) TMCS and e) DCDMS.

3.2.2 Silica

The fillers used for this study were the precipitated silicas Zeosil[®] 1115 MP, Zeosil[®] 1165 MP and Zeosil[®] Premium 200 MP (Solvay SA, France) and Ultrasil[®] VN3 GR (Evonik Industries AG, Germany). These silicas were grafted with silanes as discussed in section 3.2.1. The reported surface chemistry of these silicas is presented in Table 3.1.

Table 3.1: Silica surface properties [118,77,28,75]

Filler	Zeosil 1115 MP ^d	Zeosil 1165 MP	Zeosil Premium 200 MP	Ultrasil GR ^e VN3
^a BET, m ² /g	111	158	219	165
^b CTAB, m ² /g	107	155	197	-
^c Loosely bound water, %	6.0	7.0	6.5	-
Diameter of primary particles, nm	25	20	10	-
Mean diameter of aggregates, nm	90	53	65	-
pH, 5 g/ 95 g water suspension	6.5	6.3	6.5	6.5
Specific gravity in rubber	2.0±0.05	2.0±0.05	2.0±0.05	2.0±0.05

^aBET (Brunauer, Emmet, Teller) specific surface area

^bCTAB (Cetyltrimethylammonium bromide) specific surface area

^cWeight loss after 2 hrs at 105 °C

^dMP (Mircop pearl) form

^dGR (Granule) form

3.2.2 Elastomers

The elastomers that were used for this study include oil-extended solution styrene-butadiene rubber (sSBR, VSL 5025-2 HM with 25% styrene and 50% vinyl content, containing 37.5 pphr (parts by weight per hundred parts of elastomer) oil, LANXESS Deutschland GmbH, Germany) and cis-1,4 polybutadiene rubber with about 98% cis content (BR, Europrene Neo cis-BR-40, Polimeri Europa, Italy).

3.3 Silanising Silica

The grafting of silica particles was performed under a Dean-Stark apparatus experimental set-up (Figure 3.3). The glass reactor was placed in an oil bath and filled with 120 g of silica particles suspended in 600 ml of toluene. The oil bath was heated to 120 °C for 45 minutes and the solution stirred (with a magnetic stirrer) to reflux the toluene, and eliminate and separate the physisorbed water adsorbed on the silica surface. The silane solution (~15 V/V% toluene) was then added to the reactor and the mixture refluxed for 1 hr. However, the temperature of the oil bath was lowered to 55 °C for silica silanised with MTMS, MTES, TMCS and DCDMS as these silanes have lower boiling points than the toluene. Two loadings of the silane TESPT were used, 8% w/w silica (including the physisorbed water), corresponding to the standard amount used in rubber compounding for tyre applications, and 12% w/w. The loadings of the other silanes were normalised to the 8% w/w TESPT loading to have the same number of silane groups available for silanisation, by taking account of both the molecular weight and the number of silane groups in each molecule. The experiments were carried out three times to study the reproducibility of the silanisation.

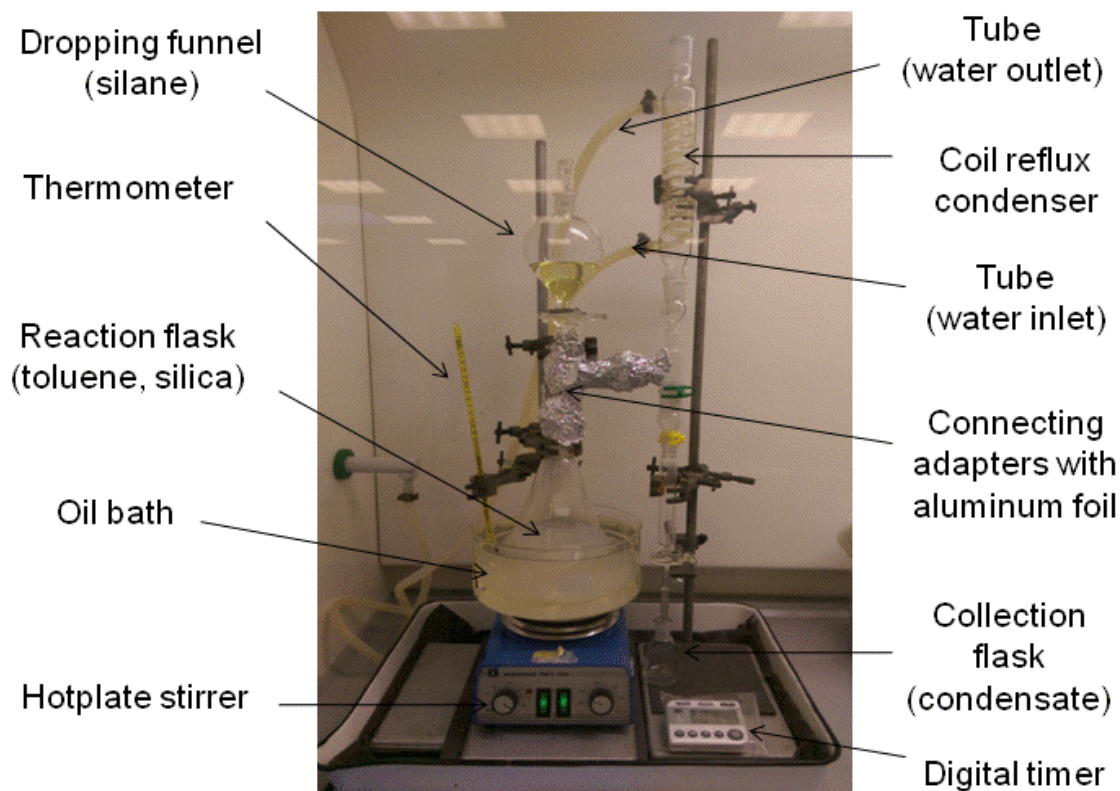


Figure 3.3: A Dean-Stark apparatus experimental set-up for silica silanisation.

3.4. Silica-Filled Elastomer Preparation

The sSBR/BR elastomers were reinforced with untreated or silanised silica at 55 parts per hundred parts of rubber (pphr) using a passenger tyre tread type of formulation as shown in Table 3.2. Zeosil® 1165 MP silica, a widely used silica for passenger tyre tread compound was used in this study to evaluate the silica dispersion in the elastomer phase and the silica-filled elastomer properties.

Table 3.2: Compound formulations [119].

Compound	pphr
sSBR ^a	96
BR ^b	30
Zeosil 1165 MP	55
Nytex 4700	10
Zinc oxide	3
Stearic acid	2
6PPD ^c	1
TMQ ^d	1
Silane ^e	4.4 (or varied) [#]
Sulfur	1.5 (or varied)*
CBS ^f	1.06
DPG 75 ^g	2.67

^asSBR : Oil-extended solution Styrene-Butadiene Rubber (VSL5025-2 HM), containing 37.5 pphr oil

^bBR : Polybutadiene Rubber (BR40)

^c6PPD : N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine

^dTMQ : 1,2-dihydro-2,2,4-trimethylquinoline

^eSilane : Non-coupling and coupling type silanes

^fCBS : N-cyclohexyl-2-benzothiazole sulfenamide

^gDPG 75 : 75% active N,N'-diphenylguanidine

[#] Assuming 100% grafting, the standard amount of TESPT used during silanisation was equivalent to 4.4 pphr, corresponding to 8% w/w on silica (including physisorbed water). This is the proportion routinely used in elastomer compounding, 50% more TESPT was also used, corresponding to 6.6 pphr or 12% w/w on silica. The loadings of the other silanes were normalised to the standard 8 w/w% TESPT loading, to have the same number of silane groups available by taking account of both the molecular weight and the number of silane groups in each silane molecule.

Some of the silanes contain different sulfur contents. However, only TESPT donates free sulfur into the vulcanisation system [120]. Therefore the sulfur added during mixing was adjusted to normalise the crosslink density of each vulcanisate. The summary of silane and sulfur contents was presented in Table 3.3.

Table 3.3: Summary of silanes and sulfur contents for compounds C1 to 12 and CA.

No.	Sample Name	Silane Loading (pphr)	Sulfur loading (pphr)	Remarks for the elastomer filled with modified silica
1.	C1	-	1.5	Untreated silica
2.	C2	4.4	1.0	Silica grafted with TESPT (8 % w/w)
3.	C3	6.6	0.8	Silica grafted with TESPT (12 % w/w)
4.	C4	4.7	1.5	Silica grafted with TESPM
5.	C5	4.5	1.5	Silica grafted with TESP
6.	C6	16.0	1.5	Silica grafted with DTSPM
7.	C7	6.0	1.5	Silica grafted with TESPO
8.	C8	5.2	1.5	Silica grafted with TESPO/M
9.	C9	4.7	1.5	Silica grafted with OTES
10.	C10	2.3	1.5	Silica grafted with MTMS
11.	C11	3.0	1.5	Silica grafted with MTES
12.	C12	1.8	1.5	Silica grafted with TMCS
13.	CA	4.4	1.0	Reactive mixing of untreated silica with TESPT (8 % w/w)

The mixing was carried out following a three-stage procedure typically used to optimise the coupling between silica and elastomer in reactively mixed silane-coupled silica-filled sSBR/BR compounds, using a Brabender-PolyLab (ex Plasticorder

PL2000E) internal mixer fitted with a 350S mixing head (tangential rotors), as shown in Figure 3.4. The mixing stages were carried out on sequential days.

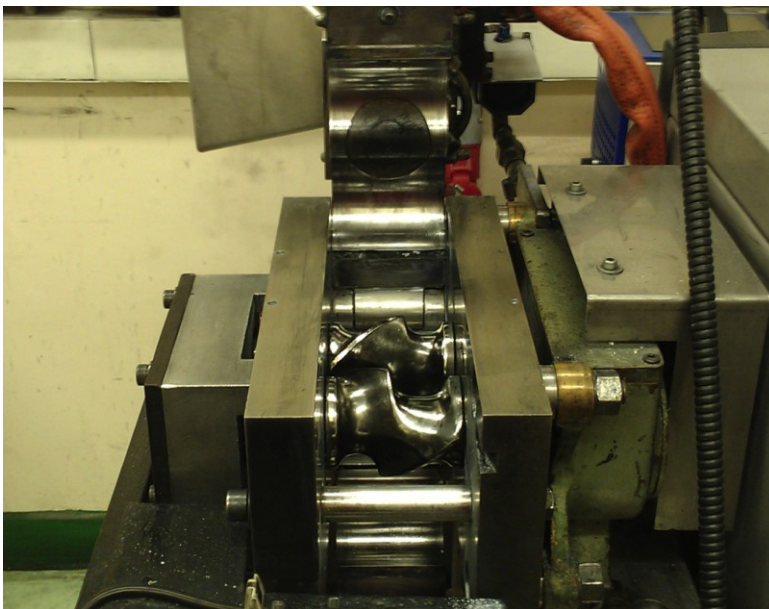


Figure 3.4: A Brabender-PolyLab internal mixer fitted with 350S tangential rotors.

In the first stage (the masterbatch stage), all ingredients apart from zinc oxide, antioxidants (6PPD and TMQ), sulfur and CBS were added. This mixing technique was applied to optimise interaction between silica and elastomer via silane. The process oil (Nytex 4700) was blended with the second batch of filler prior to mixing. The mixer was used throughout with the circulating oil temperature was set at 50°C, the rotor speed was at 80 revolutions per minute (rpm) and a 0.7 fill factor. The following is the mix cycle for the first stage:

Stage 1 (Masterbatch Stage)

0 s	:	Elastomer + $\frac{3}{4}$ silica + silane
2 min	:	$\frac{1}{4}$ silica + process oil + stearic acid
3 min	:	Sweep
7 min	:	Dump

In the second stage (remill stage), the compounds were mixed with zinc oxide and antioxidants, with the temperature was set at 50°C, rotor speed was at 80 rpm and a 0.7 fill factor. The following is the mix cycle for second stage:

Stage 2 (Re-mill Stage)

0 s	:	Compound (from stage 1) + zinc oxide + antioxidants
4 min	:	Dump

In the finalising stage, the compounds were mixed with the curatives (CBS and sulfur), with the temperature set at 30 °C, the rotor speed at 50 rpm and a 0.7 fill factor, dumping before the compounds reached 110 °C. The following is the mix cycle for the finalising stage:

Stage 3 (Finalising Stage)

0 s	:	Compound (from stage 2) + curatives
1 min	:	Sweep
2 min	:	Dump

All the compounds were sheeted on a 12" x 6" open two-roll mill at room temperature by passing them through three times after each stage of mixing in the internal mixer. Table 3.4 shows the summary dump temperatures after first stage mix cycle (masterbatch stage) for compounds C1 to C12 and CA.

Table 3.4: Summary of compounds filled with untreated or silanised silicas.

No.	Sample Name	Dump Temperatures after First Stage Mix Cycle (°C)
1.	C1 (Untreated Silica)	174
2.	C2 (TESPT 8%)	164
3.	C3 (TESPT 12%)	158
4.	C4 (TESPM)	153
5.	C5 (TESPD)	152
6.	C6 (DTSPM)	163
7.	C7 (TESPO)	162
8.	C8 (TESPO/M)	160
9.	C9 (OTES)	165
10.	C10 (MTMS)	159
11.	C11 (MTES)	151
12.	C12 (TMCS)	142
13.	CA (TESPT 8%, reactively mixed)	160

3.5 Cured Button Preparation

The cure properties of the compounds were analysed using a rotorless Moving Die Rheometer (MDR) 2000 (Alpha Technologies Ltd., UK) and the compounds were cured in an electric press at 172 °C for 12 minutes to produce the test pieces. These include 9 x 9 x 2 mm sheets and buttons in various sizes for hardness, DIN and Akron abrasion and dynamic mechanical thermal tests according to BS ISO standards.

3.6. Characterisation

3.6.1 Quantitative Analysis of Silica Surface Functional Groups by TGA-IR (Thermogravimetric Analysis Coupled to a Fourier Transform Infrared Spectrometer)

The amount of physisorbed water and silanol groups on the untreated silica, as well as the adsorbed silane on the modified silica surface, was measured with a Thermogravimetric Analyser Pyris 1 TGA with a Spectrum 100 FT-IR Spectrometer through a Balanced Flow FT-IR EGA System TL 8000 (Perkin Elmer Inc., US). The silanised silica samples were heated from room temperature (RT, 16 - 22 °C) to 800 °C at a heating rate of 30 °C/ min in an inert gas (nitrogen, flow rate 300 mL/ min) environment and then in oxygen when the sample temperature reached 800 °C for 15 mins.

The amount of physisorbed water and silanol groups was first calculated. Then the measured weight losses were determined relative to dry silanised silica. The TGA weight loss curves were normalised at 200 °C for convenience in comparing the TGA curve shapes. The evolved gasses from the volatiles and decomposition products were

examined by infrared spectroscopy from RT to 800 °C using Perkin Elmer Spectrum 10™ software.

3.6.2 Silica Surface Energy Characterisation

The silica surface energy determination was carried out using an Inverse Gas Chromatography-Surface Energy Analyzer (IGC-SEA, Surface Measurement Systems Ltd., London UK). Approximately 60 mg of untreated or silanised silica was packed into a standard pre-silanised column (300 x 2 mm ID). The untreated and silanised silica was conditioned *in-situ* in the SEA with a helium gas purge at a standard 10 cm³ per minute (sccm) and 0% relative humidity (RH) for 12 hrs at 110 °C. A series of purely dispersive n-alkane vapor probes, hexane, heptane, octane, nonane, and decane, and polar probes toluene, ethyl acetate and dichloromethane (HPLC grades, Sigma-Aldrich Co. Ltd., UK.) were injected at 90 °C. The properties of these probes are listed in Table 3.5.

Table 3.5: Properties of probe molecules used in IGC-SEA.

Probes	$a_m(\gamma_{LV}^d)^{1/2}$ [1]
	$\text{m}^2(\text{J/m}^2)^{1/2}$
n-Hexane	6.99×10^{-20}
n-Heptane	8.16×10^{-20}
n-Octane	9.19×10^{-20}
n-Nonane	1.04×10^{-19}
n-Decane	1.15×10^{-19}
Toluene	7.77×10^{-20}
Ethyl Acetate	4.62×10^{-20}
Dichloromethane	3.83×10^{-20}

^[1] Values obtained from SMS-Cirrus SEA Control Software (version 1.3.0.5).

These probes were injected to cover 0.01% to 1.0% of the silica particle surface. The details for determination of surface heterogeneity of solid particles is reviewed in Chapter 2 and elsewhere [121,122,123,124]. The dead time, t_0 , and the solute retention time, t_R (the time taken between injection and the peak maximum), of each alkane injection were measured and the net retention volume, V_N , determined by the SEA instrument using SMS-Cirrus SEA Control Software (version 1.3.0.5, Surface Measurement Systems, London, U. K.).

3.6.3 Silica Macrodispersion Analysis

The silica macrodispersion in filled elastomer vulcanisates was evaluated by using a Dispergrader 1000 NT (Alpha Technologies, Ohio, US). The light source was set at an angle of 30° with respect to the sample surfaces and 100x magnification was used [125]. The hardness button vulcanisates were sliced using a razor at room temperature to produce a fresh clean surface for this study. The light dots that appeared on the captured grey image (Figure 3.5) were associated with the silica agglomerates (size from 1 to 40 μm) and the dark background was associated with the elastomer phase. The images were then transformed into black and white images by numerical treatment. Five images were analysed for each sample to determine the average silica agglomerate macrodispersion in the elastomer matrix.

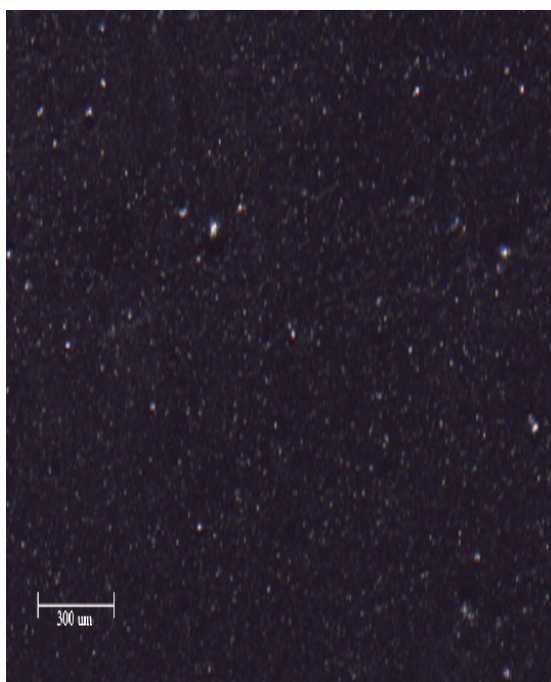


Figure 3.5: A typical Dispergrader image of a filled elastomer vulcanisate [126].

3.6.4 Network Visualisation and Silica Microdispersion Analysis

The silica microdispersion in filled elastomer vulcanisates was evaluated by TEM network visualisation analysis [127]. The silica-filled vulcanised sheets were extracted by refluxing with acetone overnight using a Soxlet apparatus and then dried in a vacuum oven to remove the solvent. The samples were swollen in a styrene solution that contained 2% w/w di-n-butyl phthalate and 1% w/w benzoyl peroxide for approximately 3 days. The swollen samples were then trimmed to approximately 2 x 2 x 10mm in size and sealed in a gelatin capsule filled a fresh sample of the same styrene solution. The capsules were then heated at 68 °C in a metal block to achieve polymerisation of the styrene for 3 or 5 days, by which time the samples were totally hardened.

The hardened samples from the capsule were then sliced to an estimated thickness of between 80 and 150 nm by using a PowerTome PC ultra-microtome with a CR-X-unit and a 45° glass knife set a 6°. Each cut section was collected on a TEM nickel grid with the aid of distilled water and relaxed briefly with xylene vapor. The microtomed samples were then examined with a Phillips CM12 transmission electron microscope operating at 80 kV.

The TEM micrographs of the silica-filled elastomer vulcanisates at a magnification setting of 22,000x were analysed to determine the area of each silica aggregate in the images using Image Pro Plus 6.1 software. Five or ten micrographs were analysed for each sample to obtain an average aggregate size distribution. A

background correction and a bandpass filter were used to increase the image contrast between the silica aggregates and their background. A Variance edge detecting filter was used on the image to identify the edge of the silica particles. This was saved as Image A. A binary image was then produced followed by an Open operation to expand the areas containing the silica aggregates. This was saved as Image B. Image B and Image A were merged to produce an image in which the silica aggregates were easier to separate from the background using a segmentation operation. The resulting Image C was used for counting and sizing the silica aggregates. For this study, aggregates larger than about 100 nm² in area were included in the count and objects touching the borders were excluded.

3.6.5 Rheometry and Mooney Viscosity of Uncured Compounds

The rheometry was carried out on the uncured compounds, one day after mixing on a Monsanto MDR 2000E rheometer at 172 °C and 0.5 ° arc. The Mooney viscosities of the compounds were measured on a Mooney viscometer at 100 °C to determine the ML (1+4) values. The '1+4' is referring to 1 minute was taken to heat the compounds before beginning the Mooney viscosity measurement for 4 minutes, while L refers to the use of the large 38.1 mm diameter rotor.

3.6.6 Bound Rubber Content (BRC g/g)

Bound rubber measurements were performed 7 days after the finalising stage. Approximately 250 mg to 500 mg of uncured compound was swollen in 25 ml toluene in a closed glass bottle at room temperature stored in the dark for 7 days. During this period the bottle was gently swirled without disrupting the swollen gel. The swollen gel was then weighed on a pre-weighed lens tissue after removal of excess solvent and then dried at 40 °C to constant weight. Bound rubber content (BRC) was calculated from Equations 3.1. and 3.2.

$$BRC = \frac{[W_{dry\ gel} - W_t(m_i/m_t)]}{W_t[m_f/m_t]} \quad (3.1)$$

where the $W_{dry\ gel}$ is the weight of dry gel, $W_{wet\ gel}$ is the weight of wet gel, W_t is the original weight of the sample, m_i is the relative weight of insolubles in the compound, the m_f is the relative weight of filler in the compound and m_t is the total weight of the compound.

$$V_r = \frac{W_{BR}/\rho_R}{W_{BR}/\rho_R + W_{tol}/\rho_{tol}} \quad (3.2)$$

where the W_{BR} is the bound rubber weight $[W_{dry\ gel} - W_t(m_i/m_t)]$, ρ_R is the density of the elastomer, W_{tol} is the solvent weight $(W_{wet\ gel} - W_{dry\ gel})$ and ρ_{tol} is the solvent density.

3.6.7 Mechanical Properties of Cured Compounds

3.6.7.1 International Rubber Hardness (IRHD)

The IRHD of the vulcanisates were measured in three different places on the vulcanisate surface according to the BS ISO 48:2010 [128], type S2 test. The thickness of the moulded samples was approximately 10 mm. The mean value was given as representative of the particular compound. The relation between penetration and Young's modulus for an elastic material is

$$D = 61.5R^{-0.48}[(F/E)^{0.74} - (f/E)^{0.74}] \quad (3.3)$$

where D is the depth of penetration, R is the radius of the ball (mm), F is the total indenting force (N), E is the Young's modulus (MPa), and f is the contact force (N). The diameter of the indenter ball is 2.5 ± 0.01 mm and the total force on the indenter ball is 5.7 ± 0.03 N for the type S2 test.

3.6.7.2 Tensile Test

The tensile properties of the vulcanisates were tested using an Instron tensile-testing machine (Series 5567, Illinois Tool Works Inc., Chicago, US) at a constant rate (500 mm/min) of traverse of the driven grip according to BS ISO 37:2011 [129]. Dumb-bell test pieces (as shown in Figure 3.6) with thickness 2 ± 0.2 mm were prepared using dies and cutter in accordance with ISO 23529.

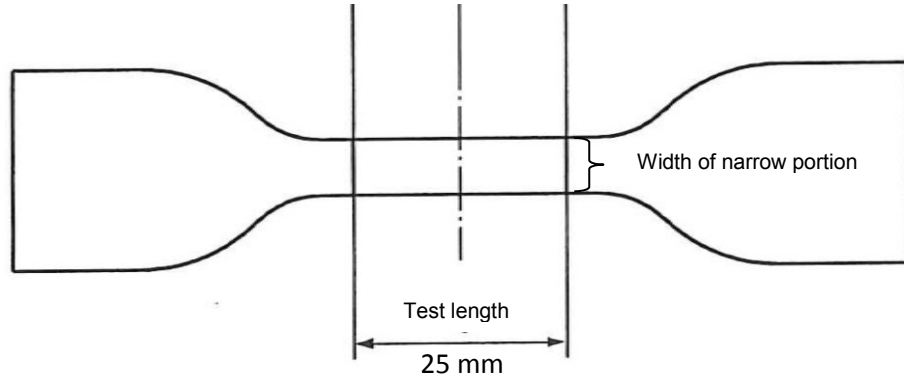


Figure 3.6: Dumb-bell test piece [129].

Five test pieces were prepared from each vulcanisate. The measurements were taken during the uninterrupted stretching of the test piece and when it breaks at ambient temperature. The tensile strength, TS , is expressed as

$$TS = \frac{F_m}{Wt} \quad (3.4)$$

where the F_m is the maximum force recorded, W is the width of narrow portion of the test piece (4.0 ± 0.1 mm) and t is the thickness of the test piece over the test length. The elongation at break, E_b , is expressed using the equation

$$E_b = \frac{100(L_b - L_0)}{L_0} \quad (3.5)$$

where the L_b is test length at break and the L_0 is the initial test length. The stresses at 50% strain (M50), 100% strain (M100) and 300% strain (M300), referred to as moduli,

are obtained by drawing tangents on the linear stress-strain curves at the respective strains. The true modulus is expressed as

$$\text{Modulus} = \frac{F_t/Wt}{E_t} \quad (3.6)$$

where F_t is force at the point of the tangent and E_t is the elongation at the point of the tangent.

3.6.7.3 Tear Strength

The tear strength of the vulcanisates was tested using the same Instron tensile-testing machine (Series 5567, Illinois Tool Works Inc., Chicago, US) according to BS ISO 34:2010 [130], at a constant rate of 500 mm/min. For this study, angle test pieces with 2 ± 0.2 mm were prepared using dies and cutter in accordance with ISO 23529. Figure 3.7 illustrates the diagram of an angle test piece.

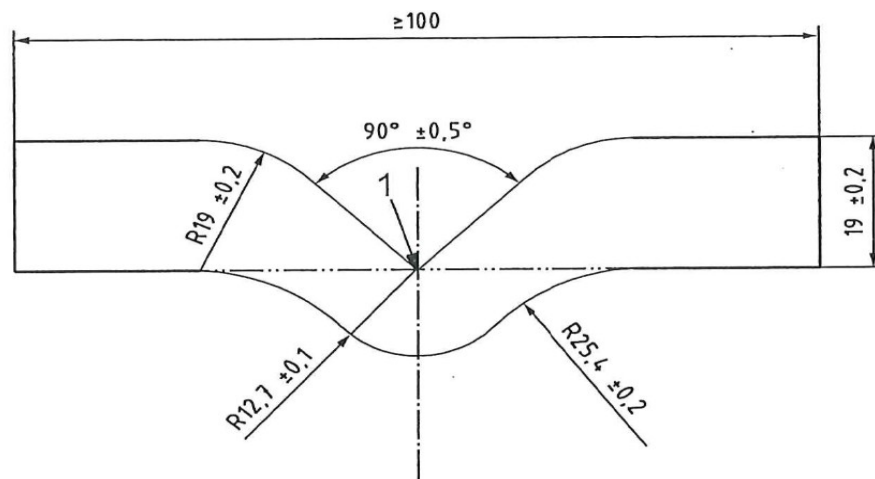


Figure 3.7: Angle test piece [130].

Three test pieces were prepared from each vulcanisate. The tear strength, T_s , is expressed as

$$T_s = \frac{F_m}{t} \quad (3.7)$$

3.6.7.4 Abrasion Resistance

The expression of abrasion resistance is the ratio of the volume loss of a standard elastomer to the volume loss of the elastomer under test due to the abrasive action of rubbing over an abrasive surface. For this study DIN (Method A, non-rotating test piece) and Akron abrasion (Method B, rotating test piece) were carried out according to BS ISO 4649:2002 [131] and BS 903: Part A9:1988 [132] respectively. The schematic diagrams for Method A and Method B are illustrated in Figures 3.8 and 3.9, respectively. For Method A, the test piece is moulded to a cylindrical shape with 16 ± 0.2 mm diameter and a minimum thickness of 6mm. The abrasive cylinder (Figure 3.8) is rotated at 40 ± 1 revolution/ min. As for method B, the test piece is moulded to a disk shape with 12.5 mm thickness and 63.5 mm diameter. The test piece is rotated at 250 ± 5 revolution/ min. The slip angle is set at $15^\circ \pm 0.5^\circ$ with slip velocity of 210 mm/s.

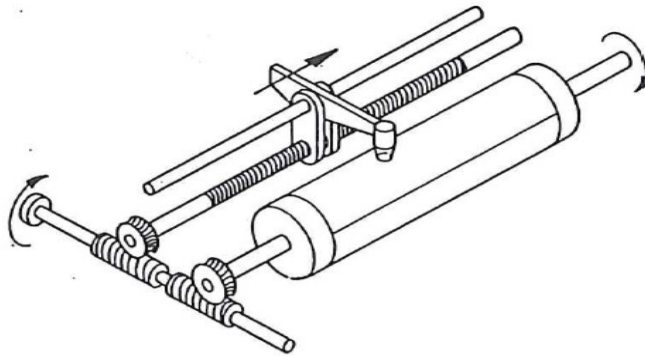


Figure 3.8: Abrasion machine for method A (DIN) [132].

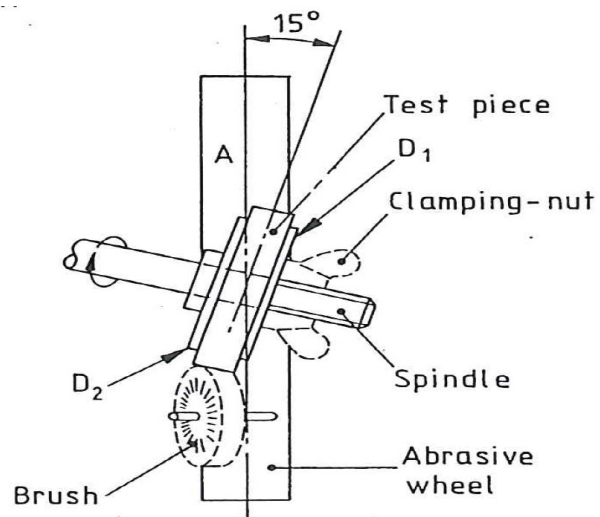


Figure 3.9: Abrasion machine for method B (Akron) [132].

The abrasion resistance index, ARI is expressed as

$$ARI = \frac{V_s}{V_t} \times 100 \quad (3.8)$$

where the V_s is volume loss of the standard elastomer and V_t is the volume loss of the test elastomer determined under the same test conditions.

3.6.7.5 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analysis (DMA) was performed using a Metravib DMA+1000 test system (01-dB Metravib, Limonest France). The instrument was configured with planar shear fixtures and moulded double shear test pieces were prepared, containing 2 test pieces of 10 mm nominal diameter and 2 mm thickness of the silica-filled vulcanised elastomers. Dynamic strain amplitude sweeps from 0.01% to 100% maximum strain and back to 0.01% at a frequency of 1 Hz were applied at 23 °C. The samples were conditioned for 16 hrs under standard laboratory temperature and humidity conditions. The Metravib's Dynatest interface software was used to record the material stiffness and phase shift experimental data, and to calculate parameters of interest, such as storage modulus, loss modulus and loss tangent. The repeatability of the measurements of storage modulus and loss modulus were within the range of 5%. Details of DMA theories are reviewed in Chapter 2.

3.7 Conclusions

The experimental methodology described here for the preparation of silanised silica with coupling or non-coupling silanes and of silica-filled elastomers was found to be reproducible. These silanised silicas enabled the measurements of surface energy using IGC and hence provided a direct description of the effect of silica surface

thermodynamics on the work of cohesion between silica particles (Chapter 5). The results for silica-filled elastomers are presented in Chapters 6 to 8.

CHAPTER 4 THERMOGRAVIMETRIC ANALYSIS OF SILANISED SILICA

4.1 Introduction

The surface activity of a filler particle is one of the parameters responsible for the relative strength of filler-filler interactions, filler-elastomer interactions, and filler interaction with other ingredients during compounding. The decisive role of the silica surface chemistry such as silanol groups [133,32] and grafted silanes is well known for various silica-reinforced elastomer properties [91,134]. It is thus necessary to obtain both qualitative information on the silica surface chemical properties and quantitative data on the silica surface functional groups.

In this chapter, thermogravimetric analysis with fourier transform infrared characterisation (TGA-IR) of the evolved gas is used to investigate the untreated and silanised silicas. Two types of silanes have been studied: one is coupling silanes and the other is sulfur free non-coupling silanes. The aim is to understand the changes of silica surface chemistry when the silica surface is grafted with organosilanes.

The total weight of weakly bound water and silanol groups on the silica surface was determined. The results were then used to measure the amounts of the silanes grafted on the modified silica surface. The derivative TGA curves of the silanised silica show distinct peaks, which correspond to the type of organosilanes bound to the silica surface and their breakdown during TGA. The evolved gas from the TGA analysis was

analysed by IR to identify the functional groups displaced from the silanes grafted onto the silica surface.

All the silanised silicas (S2 to S12) investigated in this study were prepared in the laboratory except for Coupsil 8113, which is a commercial silica grafted with TESPT, 13% w/w [135,136]. The study shows that approximately 29% to 78% of the silanes were grafted on to the silica during the 1 hr silanisation process. In the TGA between room temperature (RT, 17-21 °C) and 200 °C, water molecules were mainly detected through the IR analysis and at moderate temperatures (200-495 °C) mainly alcohol (ethanol). At higher temperatures other groups from the silanes were detected. The work demonstrates the suitability of the TGA-IR technique to investigate the effectiveness of the silica silanisation process.

4.2 Thermogravimetric Analysis with Fourier Transform Infrared Spectroscopy (TGA-IR)

The presence of weakly bound physisorbed water is well known for strongly influencing the silane reactivity with the silica surface [137]. In the elastomer industry, modification of the silica surface chemistry has been shown to improve the mechanical performance of silica-filled elastomer vulcanisates [138,134]. The interface between the silica and the elastomer is one of the important parameters responsible for the properties of silica-filled elastomers. For example, the type of filler used in elastomer reinforcement produces different rupture behaviour [139].

Hence, understanding the effectiveness of the silane grafting process, which in industry usually occurs during reactive mixing, as well as the resulting effects of the modified silica-elastomer interface, is of primary importance for the design of silica-filled elastomer compounds with improved mechanical properties for tyre applications. Zeosil® 1165 MP silica from Solvay SA, France were silanised with a wide range of silanes in a Dean-Stark apparatus experimental set-up and analysed using the TGA-IR technique.

As discussed in Chapter 2, the silane reaction mechanisms for dehydrated and hydrated silicas undergo different processes depending on the reaction conditions [137]. Silanising dehydrated silicas at temperature below 100 °C, the ethoxy groups of the widely used silanes react with the silanol groups of the silica surface through hydrogen bonds [140]. At higher temperatures between 100 °C and 200 °C, the ethoxy groups of the silane react with the silanol groups of the dehydrated silica through a condensation process and release ethanol molecules [140,141,142].

As for hydrated silica (its normal state when used industrially), a widely accepted mechanism [143] for TESPT silane is that the water acts as a promoter by hydrolysing the ethoxy groups of the silane and releasing ethanol. Then the hydroxy-silane undergoes a condensation process with the silanol groups of silica, leading to the grafted silica surface. The hydrolysed silane could also undergo oligomerisation with vicinal silane species to form (poly)condensed silane species through nucleophilic substitution by releasing ethanol or water molecules, and formation of siloxane bridges.

Others [140] believe that, even when water is present, the silanols on the silica react directly with the ethoxysilane, displacing ethanol.

It is also suggested that from the above mechanism for hydrated silica silanisation with TESPT, a horizontally grafted and polymerised monolayer of TESPT at the silica surface would be formed. The ethoxy group of one part of the TESPT is considered reacted with the silica silanol groups through one siloxane bond with the other ethoxy groups being involved in oligomerisation reactions [140,143] with other silane molecules, and through them to the silica. It is also worth noting that Law et al. [144] reported that the ethoxy groups from a similar di-silane, TESPd, could bond at either one end or both ends to silanol sites on the silica surface, where two distinct peaks were observed in their TGA derivative curves. The current study has taken this work a step further by using IR analysis to investigate the amount of TESPT or TESPd that has reacted on the silica surface and whether these silanes are singly-bound or doubly-bound at both ends to the silica.

In this chapter, thermogravimetric analysis with fourier transform infrared characterisation (TGA-IR) of the evolved vapour allows accurate measurement of the silanised silicas and comparison with untreated silica. In this study, the weight changes observed in the TGA-IR studies can be associated with the dissociation of silane species from the silica surface and the evolved vapours can be analysed through the recorded IR spectra. The silica itself is thermally stable at temperatures above 1000 °C. During the temperature ramp from RT to 200 °C, the weakly bound physisorbed water is released from the silica surface. In the case of the untreated silica, this is followed by

condensation of surface silanol groups at temperatures between 200 °C and 800 °C, forming siloxane bridges and releasing water. The physisorbed water and surface silanol groups are taken into consideration in quantifying the amount of silane grafted on the silanised silica surface. It was anticipated that in the TGA of TESPT and TESP, dissociation of the di- and poly-sulfide groups will lead to TGA weight losses at lower temperatures where the silane is singly bound, rather than doubly bound. The weight % derivative peak maxima were used to distinguish the two binding pathways and the results applied to the rest of the silanes as well.

4.3 Results and Discussion

The investigation into the silica surface functional groups or the water system is important for elucidating the surface reactivity of silica for practical applications [145]. In this connection, investigation of the surface chemistry of amorphous silicas used for elastomer reinforcement and the effect of the silica surface energy and chemistry in silica-filled sSBR/BR systems are of interest. For this study, the term moisture describes the weakly bound physisorbed water on the silica surface. The moisture on the silica surface evolves between RT and 200 °C during the TGA temperature ramp. As for the term silanol groups, it describes the OH groups bound to Si atoms on the silica surface. The silanol groups are formed in the course of silica synthesis during the condensation polymerisation of $\text{Si}(\text{OH})_4$, and the silanol groups can be formed as a result of rehydroxylation of dehydroxylated silica [133]. The type of silanol groups present on silica surface (germinal, vicinal, isolated) is discussed in Chapter 2. Kiselev [146]

investigated the silica surface dehydroxylation at high temperature where physically adsorbed water is formed from OH group.

The process of the removal of physisorbed water and the hydroxyl groups from the surface of the silica samples has been investigated using the TGA-IR method. The results for the as received silicas (Zeosil[®] 1115 MP, Zeosil[®] 1165 MP, Zeosil[®] 200 MP and Ultrasil[®] VN3 GR) were investigated and are shown in Figure 4.1. The weight% lost is presented as a function of temperature. For this analysis (Figure 4.1), the weight changes were measured upon heating (10 °C/ min) in an inert gas environment and the weight % curves were normalised at 200 °C, so that the % weight losses were with respect to dry silica. The changes in weight % from RT to 200 °C were due to the removal of physically adsorbed water on the silica surface [73]. The physically adsorbed water and silanol groups per silica surface area, α_{OH} (OH/ nm²), were determined and presented in Table 4.1. The α_{OH} of these silicas is determined using Equation 2.5 (Chapter 2).

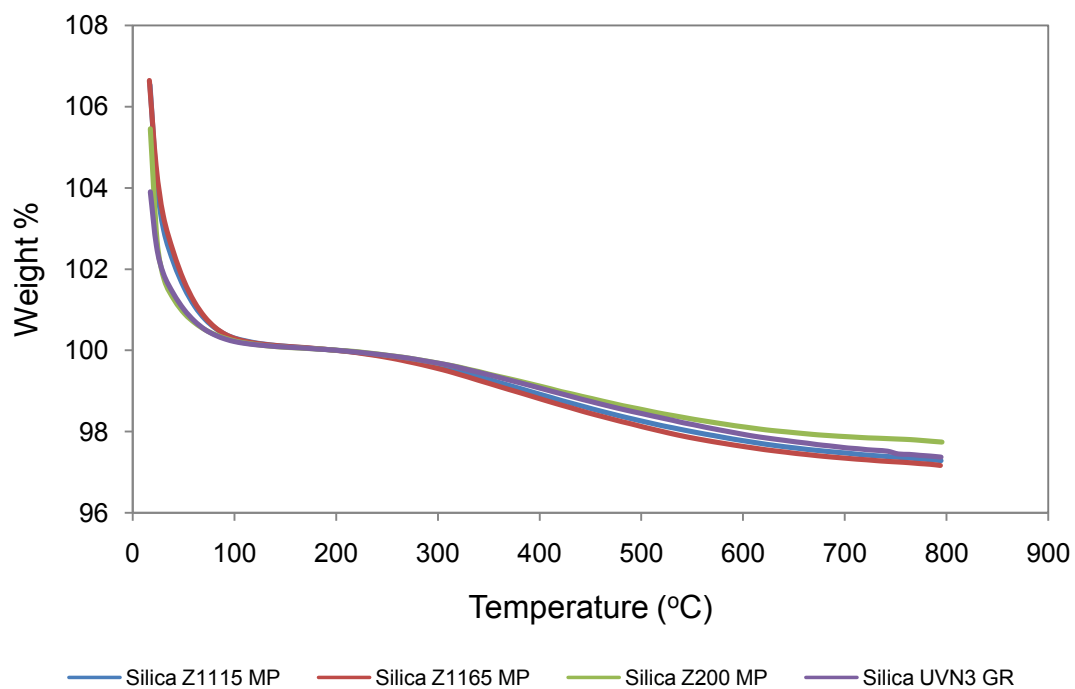


Figure 4.1: Silica surface physisorbed and silanol groups comparison.

Table 4.1: Silica surface physisorbed water and silanol groups.

Filler	Zeosil [®] 1115 MP	Zeosil [®] 1165 MP	Zeosil [®] Premium 200 MP	Ultrasil [®] VN3 GR
Physisorbed water, % (<200 °C)	6.1	7.2*	5.2	3.9
- Guy et al. [75]	-	7.0	6.5	-
- Majeste and Vincent [147]	7.6	6.5	-	-
- Blume et al. [148]	-	-	-	5.5
Physisorbed water (H ₂ O/nm ²)	12.1	15.3*	10.2	7.7
Silanol number, α _{OH} (OH/ nm ²) (200-800°C)	15.4	12.9*	6.6	10.4
- Guy et al. [75,149]	-	14.6	8.7	-
- Castellano et al. [150]	-	12.5	-	-
- Vilmin et al. [137]	-	12.2	-	-
- Majeste and Vincent [147]	8-10	6-8	-	-
- Blume et al. [148]	-	-	-	12.3

* Average of three TGA determinations

The concentration of physically adsorbed water is in a good agreement with the values reported in literature [75,147,148]. It is worth noting that the physically adsorbed water depends on the processes of silica preparation and treatment [73], as well as the ambient conditions when the silica is tested. The silanol concentrations are also in good agreement with literature values [137,75,149,150] based TGA or IR analysis. Lower values (eg. 3.7 OH/ nm² and 7.5 OH/ nm² for Zeosil[®] 1165 MP) are reported by other analytical methods, such as hydroxide treatment (Sears method) and esterification with methanol [75]. It is believed that these methods are only measuring silanols on the surface, while TGA measures all silanols, including those within pores. Zhuravlev [73]

studied a range of fully hydroxylated amorphous silica and reported that the α_{OH} is 11.8 OH/ nm² for based on measurements between 200 °C and 1100 °C. The data that Zhuravlev obtained was through a deuterio-exchange method, the silica surface pores are accessible to krypton molecules (macropores $d > 2000\text{-}4000$ Å; mesopores, $30\text{-}32$ Å $< d < 2000\text{-}4000$ Å; supermicropores, $12\text{-}14$ Å $< d < 30\text{-}32$ Å; d is the diameter of the silica pores. For this study, the silica samples under study have a mesoporous structure. Blume [148] estimated the α_{OH} of silica (UVN3 GR) by integrating the peak areas in IR spectra.

In the case of silanised silica investigation, Zeosil® 1165 MP was used and grafted with different silanes. These silanes include coupling and non-coupling silanes. The used of in situ time-resolved characterisation techniques, can help to analyse the grafted silane on the silica surface. In this respect, the IR spectroscopy module, which was attached to the TG is a well suited technique for probing the evolved gas where the TG heating rate was set at 30 °C/ min. The samples were analysed at temperatures between RT and 800 °C. The silica is thermally stable even at temperature above 1000 °C and the release of physically adsorbed water and dehydration of the silanol groups on the silica is considered in the analysis of the TGA data for the grafted silica samples.

Comparing the silanisations carried out with 8% TESPT over different reaction times (10 mins to 24 hrs) as shown in Figure 4.2, the TGA plots were very similar, indicating that the silanisation was largely completed during these periods. The effect of silica silanised over different reaction times is further evaluated using IGC technique in

Chapter 5. The TGA weight losses were split into three ranges, based on the peaks in the TGA derivative plots (the rate of weight loss). The first of these (RT-200 °C) corresponds to loss of physisorbed water. The second (200-495 °C), based on IR is mainly ethanol displacement, but also includes weight losses from dissociation of the S-S bonds in mono-substituted grafted silicas. The remaining groups are lost between 495 °C and 800 °C. There is no evidence of the third weight loss (495 °C to 800 °C) increasing with time, which could have indicated conversion of mono- to di-substituted silane, or additional silanisation, but there is evidence of a small drop in the second weight loss (200-495°C) over the first hour, indicating a small increase in loss of ethoxy groups between 10 mins and 1 hr reaction time. Previous studies [142,143,151] have all indicated that about two of the ethoxy groups in triethoxysilyl groups react during silanisation. Thus, in analysing the TG data, it was assumed that four of the ethoxys were displaced after the standard 1 hr reaction time, and the % disubstituted was thus calculated as 53%. It was assumed that 53% disubstitution remained constant with varying reaction time, and the % alkoxy loss was calculated for the other reaction times. This appears to increase a little from 59% to 67%, with reaction time increasing from 10 mins to 1 hr, but thereafter remains roughly constant.

The weight % lost at the beginning is mainly due to physisorbed moisture on the silanised silica surface. Figure 4.3 shows the repeatability test of silica silanised with TESPT 8% w/w for 1 hr with a 0.04 weight % standard deviation between 200 °C and 800 °C.

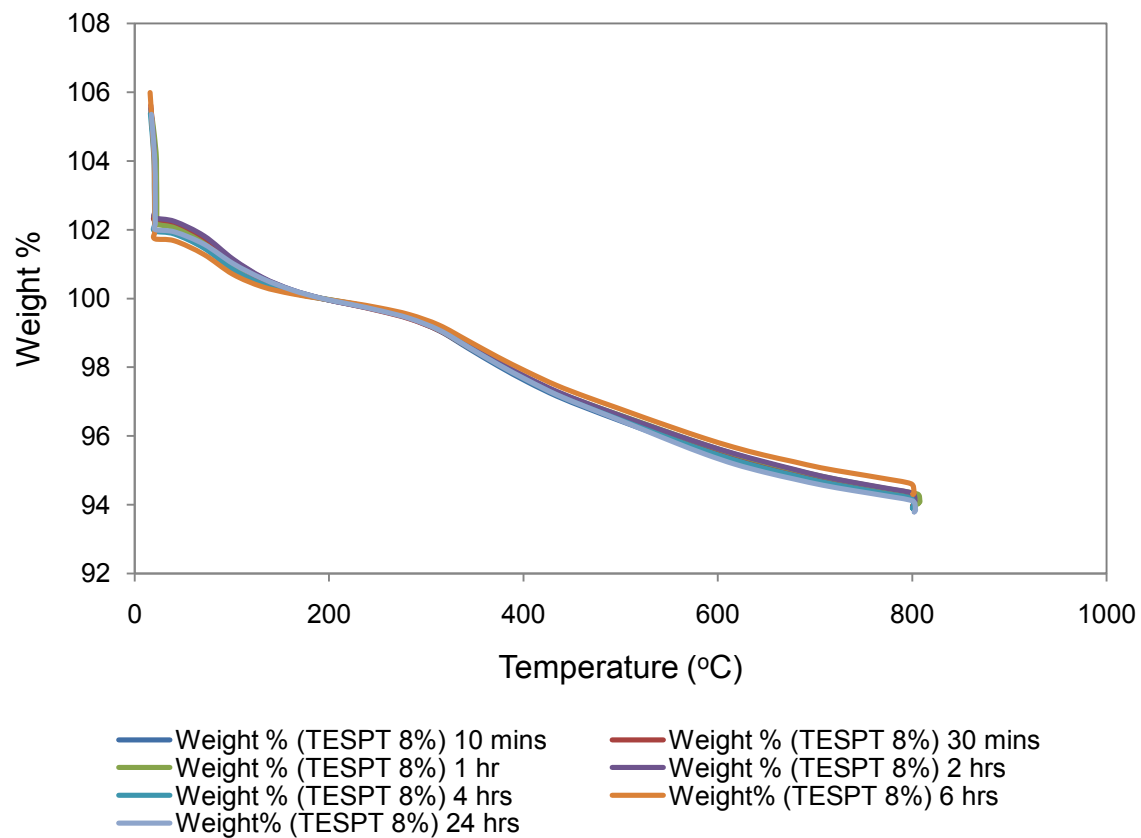


Figure 4.2: Silica (Z1165 MP) silanised with TESPT 8% w/w for different times.

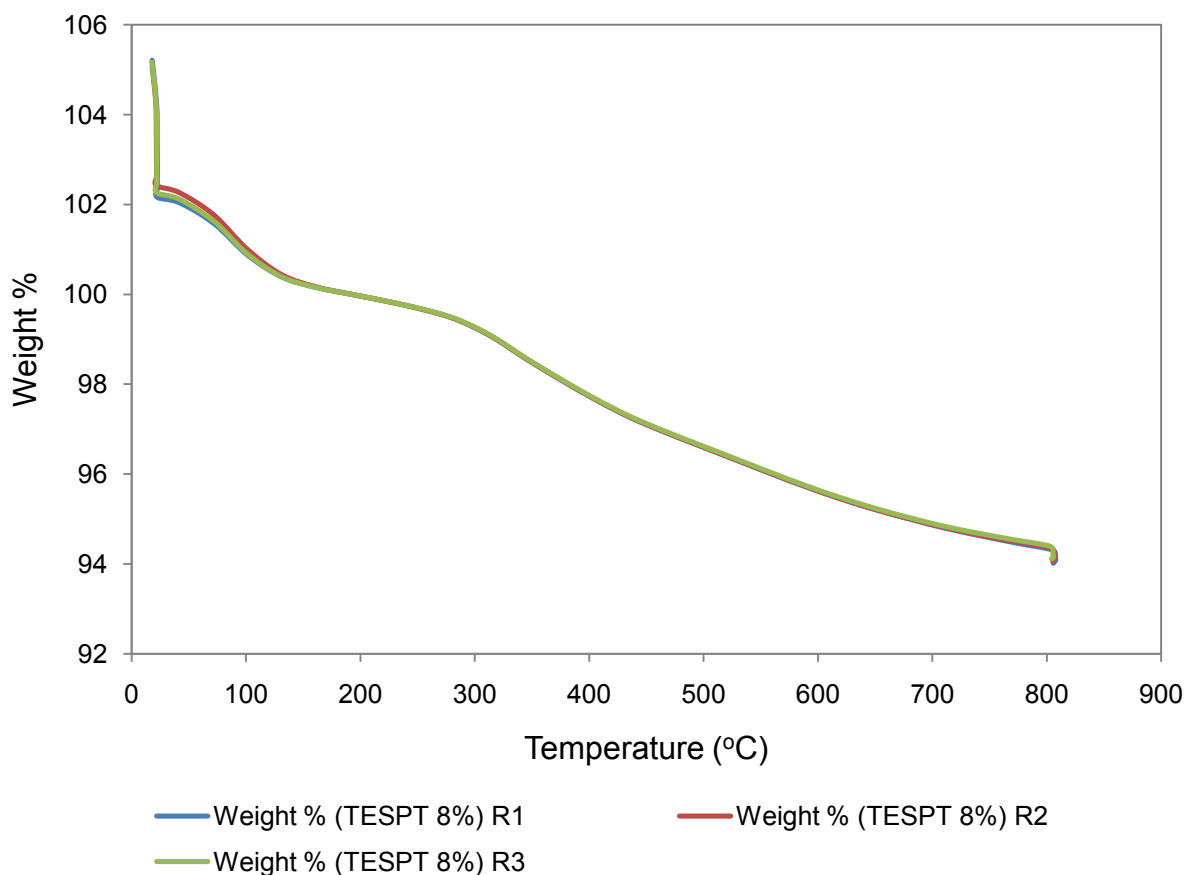
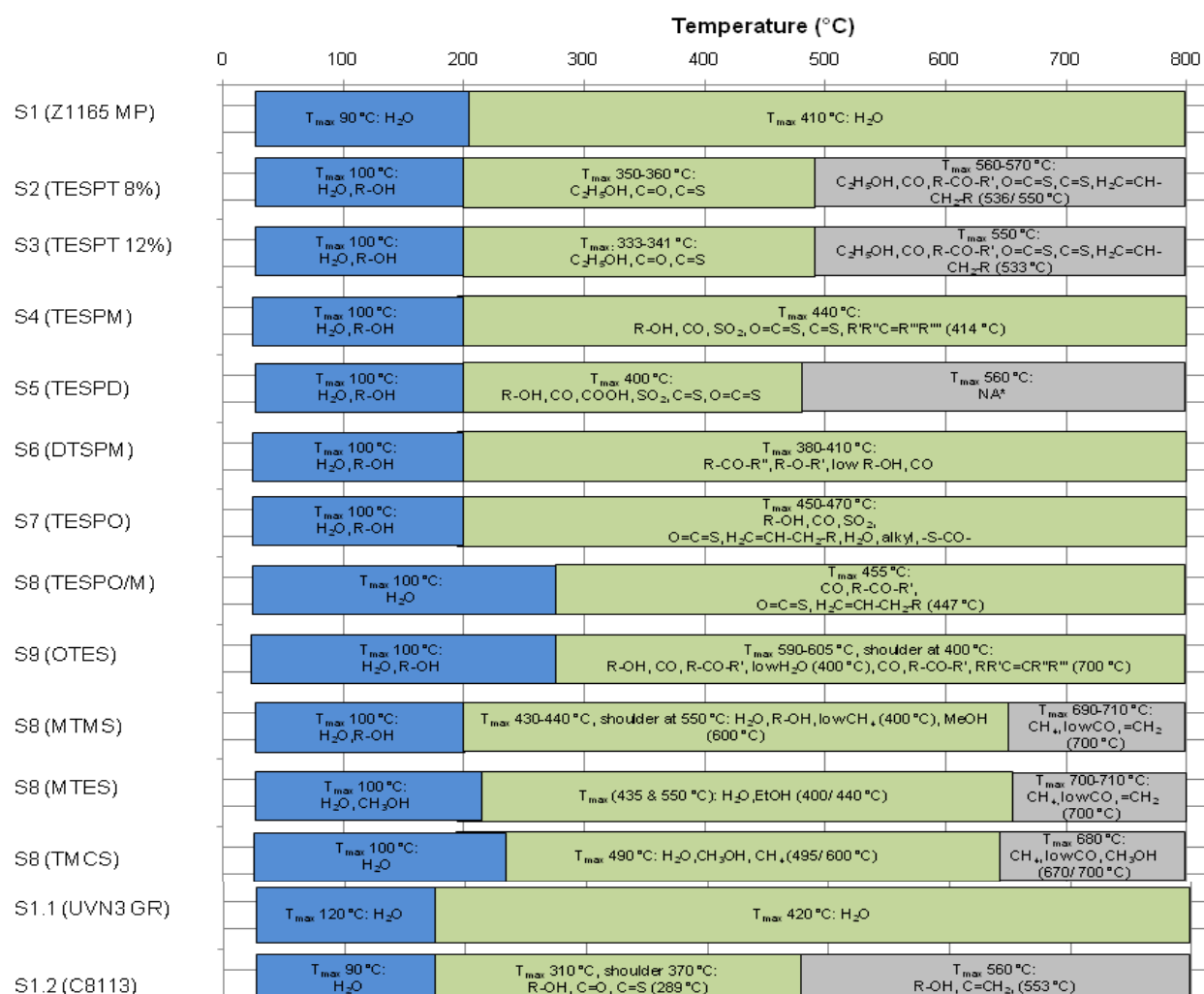


Figure 4.3: Repeated analysis of silica (Z1165 MP) silanised with TESPT 8% w/w for 1 hr.

This part of the section in Chapter 4 is devoted to the investigation and validation of chemisorption of silane on the silica surface. The weight loss of the untreated and silanised silicas species as the TGA temperature increased from RT to 800 °C are presented in Figure 4.4. Various silanes were studied independently for silica silanised for 1 hr. In this range, desorption of different groups from the grafted silane species as evolved gas was characterised using IR spectroscopy.



* Unable to detect the decomposition species of S5 (TESPD) at 560 °C.

Figure 4.4: Dissociation molecular structure detected through IR spectroscopy analysis during TGA test.

The thermal energy from the TGA during temperature ramp induces bond cleavages both within the grafted silane molecule and between the grafted silane and the silica. The weight % changes for the silanised silica occurs as the dissociation species are removed by the inert carrier gas. The structures of the decomposition species generated at different temperatures can be determined from the dissociation energies required for the different homolytic bond cleavages, and also other processes

that might occur, such as condensation of the silanol groups of hydrolysis of alkoxy groups. Table 4.2 shows the IR bands of evolved vapours and gases.

Table 4.2: IR bands of evolved vapours and gases [**152,153**].

Group	Broad band (cm ⁻¹)
Alkene (RCH=CHR')	~ 1600 - 1500
Allylic group (H ₂ C=CH-CH ₂ -R)	~ 910 - 900
Carbon monoxide (C=O)	~ 2170 - 2120
Carbon dioxide (CO ₂)	~ 2360
Carbonyl group - aldehyde, ketones (R-CO-R')	~ 1730 - 1720
Carboxylic acid (COOH)	~ 1780 - 1760
Carbonyl sulfide (O=C=S)	~ 2071
Ethanol (C ₂ H ₅ OH)	~ 1064 - 1054
Ether group (R-O-R')	~ 1102
Methane (CH ₄)	~ 3013, ~ 1302
Methanol (CH ₃ OH)	~ 1052 - 1010
Physisorbed water (H ₂ O)	~ 3741
Sulfur dioxide (SO ₂)	~ 1375 - 1340
=CH ₂ group	~ 920-900
C=S group	~ 1540 - 1520
-CH ₃ group	~2977, ~2897, ~1444, ~ 1394

As examples, the IR spectra of S1 (Untreated Silica) at 76 °C is presented in Figure 4.5, and Figures 4.6, 4.7 and 4.8 show the IR spectra of S2 (TESPT 8%) at 91°C, 350 °C and 536 °C respectively. The decomposition products identified by IR and molecular bond dissociation energies (Table 4.3) were used to assess the temperature

ranges over which different weight losses were occurring in the TGA. These are brought together in Table 4.4 and form the basis for the interpretation of the TGA data.

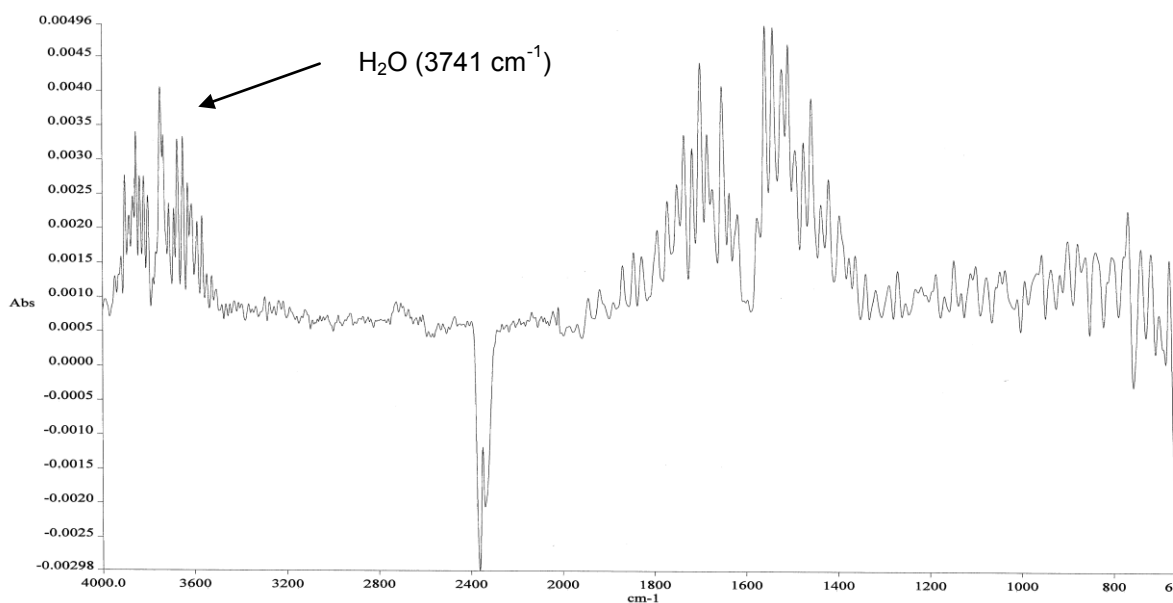


Figure 4.5: IR spectra of evolved vapours of S1 (Untreated silica-Z1165 MP) at 76 °C.

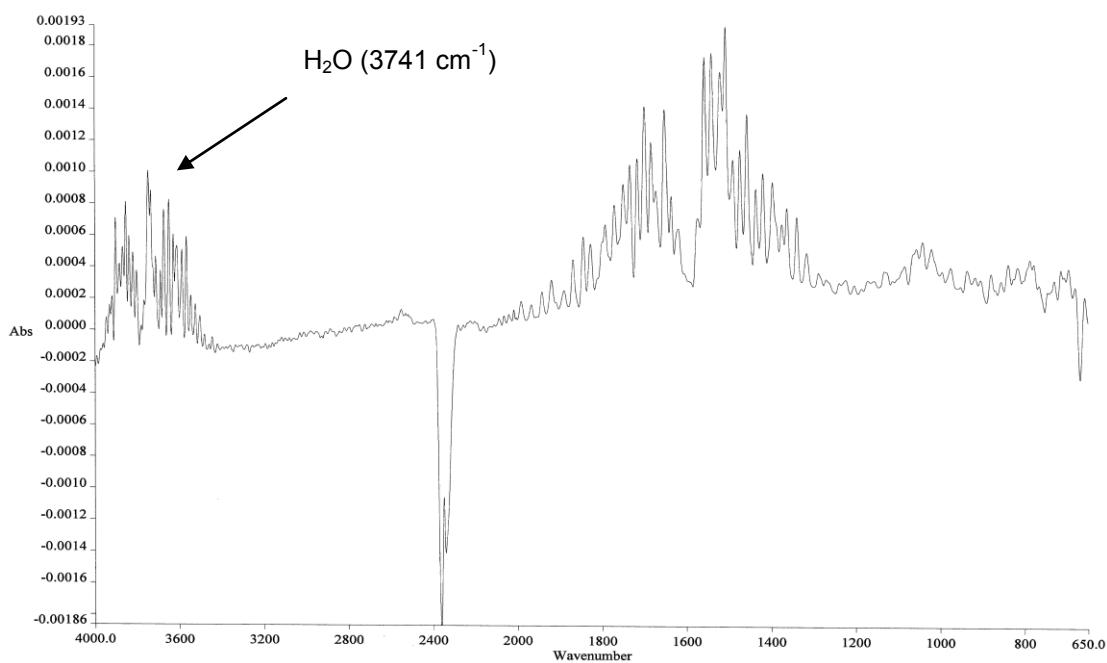


Figure 4.6: IR spectra of evolved vapours of S2 (TESPT 8%) at 91 °C.

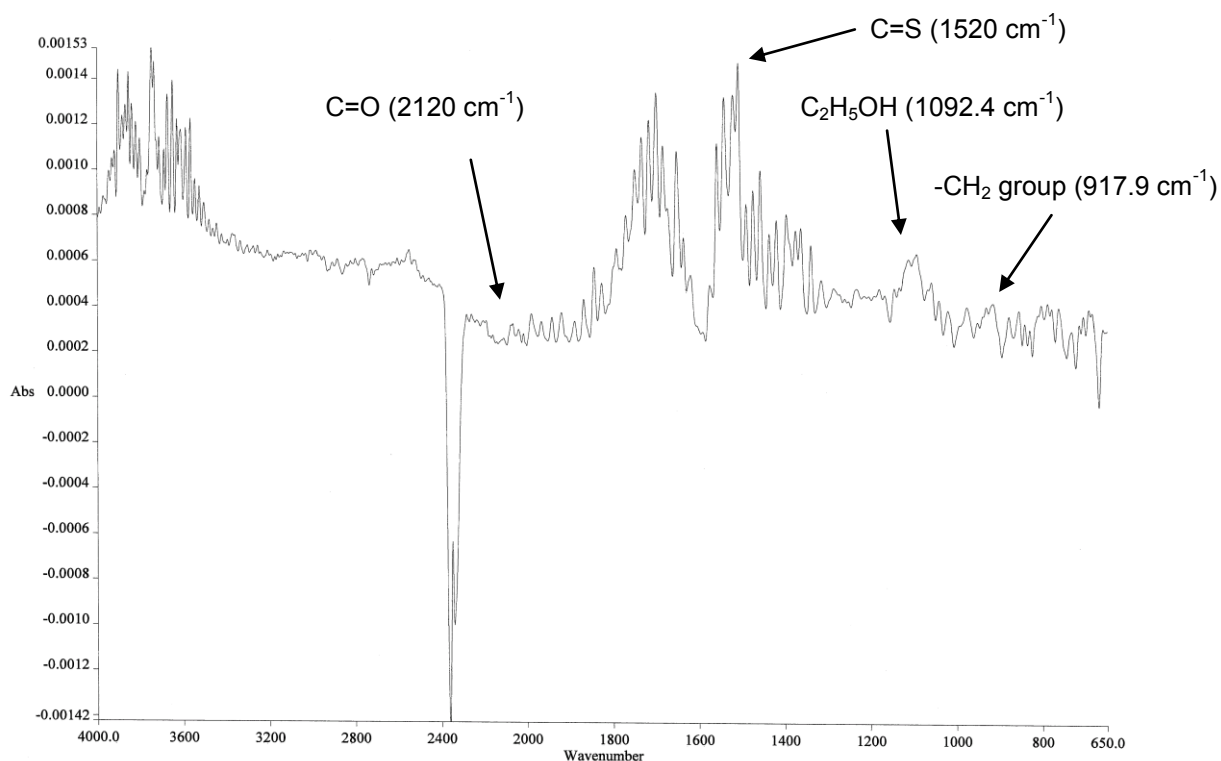


Figure 4.7: IR spectra of evolved vapours of S2 (TESPT 8%) at 350 °C.

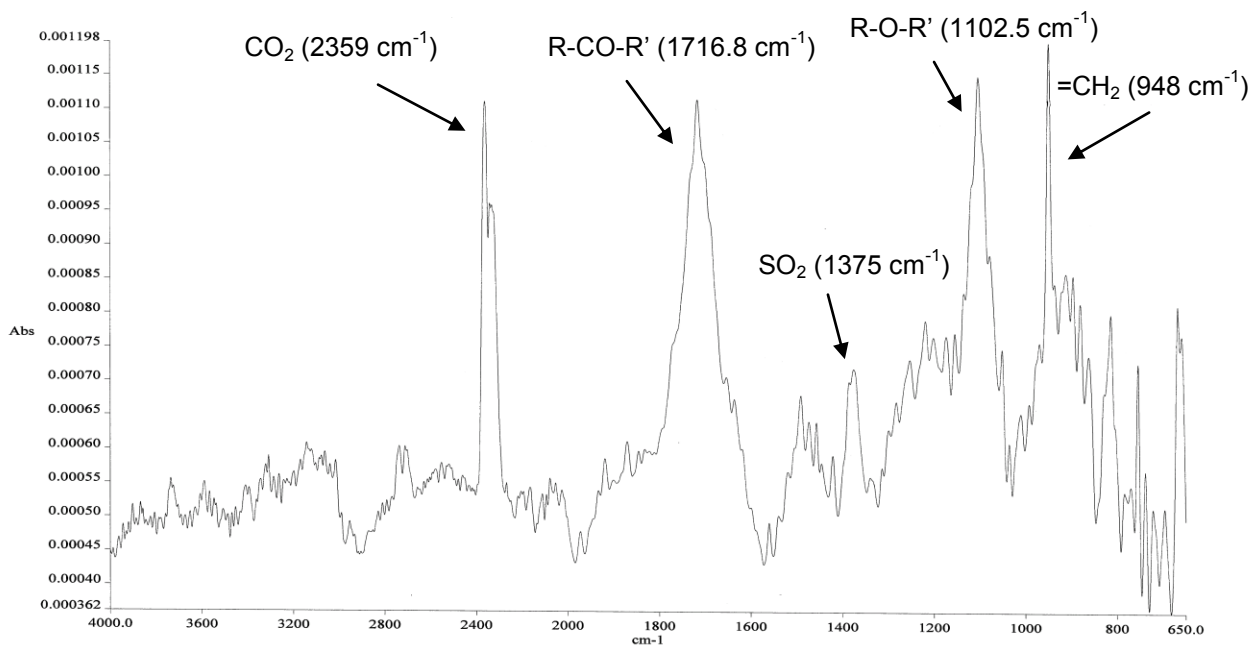


Figure 4.8: IR spectra of evolved vapours of S2 (TESPT 8%) at 536 °C.

Table 4.3: Bond dissociation energies.

Bond		Dissociation Energies (kJ/ mole)	Reference
CS-SC	MeS-SMe	261	[154]
	MeS-SMe	280	[154]
	EtS-SEt	289	[154]
	EtS-SEt	293	[155]
	nPrS-SnPr	285	[154]
	BuS-SBu	268	[155]
	RS-SR'	285	[156]
	RS-SR'	310	[157]
C-SSC	CH ₃ -SSEt	235	[158]
	Et-SSR	241	[156]
	Et-SSR	226	[157]
CSS-SSC	EtSS-SSEt	133	[158]
	MeSS-SSMe	151	[159]
	RSS-SSR'	142	[156]
	RSS-SSR'	141	[157]
CS-SSC		222	[157]
	HSS-SR	226	[157]
RCH ₂ -SH	nPr-SH	302	[160]
	Pr-SH	303	[156]
	nPr-SH	286	[161]
RCO-SR'	MeCO-SPr	310	[156]
Si-C		451	[162]
		435	[163]
		318	[164]
		360	[165]
	SiH ₃ -Me	375	[166]
O-CH ₂ R	Me-OMe	335	[163]
	C-O	358	[164,165]
	Et-OMe	355	[166]
	Et-OH	391	[166]
	Me-OH	376	[167]
	Me-OH	370	[167]
C-C		346	[164]

Table 4.4: Order of weight losses in TGA at elevated temperature.

Temperature	Group lost or bond broken	Comments
22 – 200 °C	H ₂ O	Decreases as silica surface is coated/ silanised, but also affected by ambient humidity
Mainly 200 - 495 °C, peaking at ~310 °C in Coupsil 8113, but also at lower & higher temperatures.	EtOH, MeOH	From displacement of alkoxy groups by H ₂ O or SiOH, leading to silica-silane or silane-silane siloxane groups, probably mainly the latter, equating to a net ROR weight loss, or R + ½O per alkoxy lost
200 – 800 °C	H ₂ O from 2SiOH → SiOSi	Decreases a little as SiOH is silanised
~ 390 °C	Hydrolysis of larger alkoxy groups in DTSPM & TESPO/M	
~ 400 °C	CSS-SSC, loss of half of monosubstituted TESPT group	Homolysis, 133-142 kJ/ mol
≥ 400 °C	CS-SSC, loss of half of monosubstituted TESPT group	Homolysis, 222-226 kJ/ mol
≥ 400 °C	C-SSC, loss of half of monosubstituted TESP and S atom	Homolysis, 226-241 kJ/ mol
~ 470 °C	S-COR hydrolysis, TESPO, TESPO/M	Hydrolysis probably before homolysis (310 kJ/ mol)
~ 500 °C	C-SH, loss of S from DTSPM, TESPO/M	Homolysis, 286-303 kJ/ mol
> 495 °C	C-C	Homolysis, 346 kJ/ mol
> 495 °C	Si-C	Homolysis, 318-451 kJ/ mol

Except in the case of TMCS-treated silica, it is assumed that at the end of the TGA process (at 800°C), of the original silane, only the silicon atoms bonded to the silica via oxygen and any other siloxane linkages to these silicons remain. In the case of TMSC, the trimethylsilyl groups can be more easily lost as trimethylsilyl alcohol [168], it is assumed that these are also displaced during the TGA.

Based on the IR evidence, it is assumed that ethanol and methanol displacement leading to siloxanes, occurs mostly in the range between 200 °C and 495 °C. Although there is IR evidence of some alcohol lost below 200 °C in most silanised silica samples [S2 (TESPT 8% w/w), S3 (TESPT 12% w/w), S4 (TESPM), S5 (TESPD), S6 (DTSPM), S7 (TESPO), S9 (OTES), S10 (MTMS)]. It is also observed that alcohol is lost above 495 °C for S2 (TESPT 8% w/w), S10 (MTMS) and S12 (TMCS) samples.

In the case of S2 (TESPT 8% w/w), S3 (TESPT 12% w/w) and S5 (TESPD), the weak bonds as regards to homolysis are the SS-SS, S-SS and C-SS bonds in TESPT-silica and TESPD-silica. It is assumed that this homolysis process mainly occurs below 495 °C, leading to weight losses when TESPT and TESPD are bound to silica at one end only (mono-substituted or singly bound), but not when these silanes (TESPT and TESPD) are bound at both ends (di-substituted or doubly bound). There is IR evidence for these losses with the observation of C=O and C=S groups from TESPT-silica in isothermal measurement that 333 °C and 344 °C. From Figures 4.10, 4.11 and 4.13, three derivative weight % peaks are observed. However, the possibility that these homolytic weight losses are still occurring above 495 °C cannot be ruled out.

It is assumed that the alcohol, displacement, and CSS-SSC, CS-SSC and C-SSC homolysis occur during the second period of weight % loss (200 °C to 495 °C), all the ethoxy groups, which remained after the silanisation process are lost, and that –SSR is lost from silica-R'-SSR (singly bound, where R' is bound to silica, but R is not). The remaining groups are lost from 495 °C to 800 °C. Figures 4.9 to 4.23 show the

weight % lost and derivative weight % for the different silica samples (S1 to S13 and S2.1 to S.2.2).

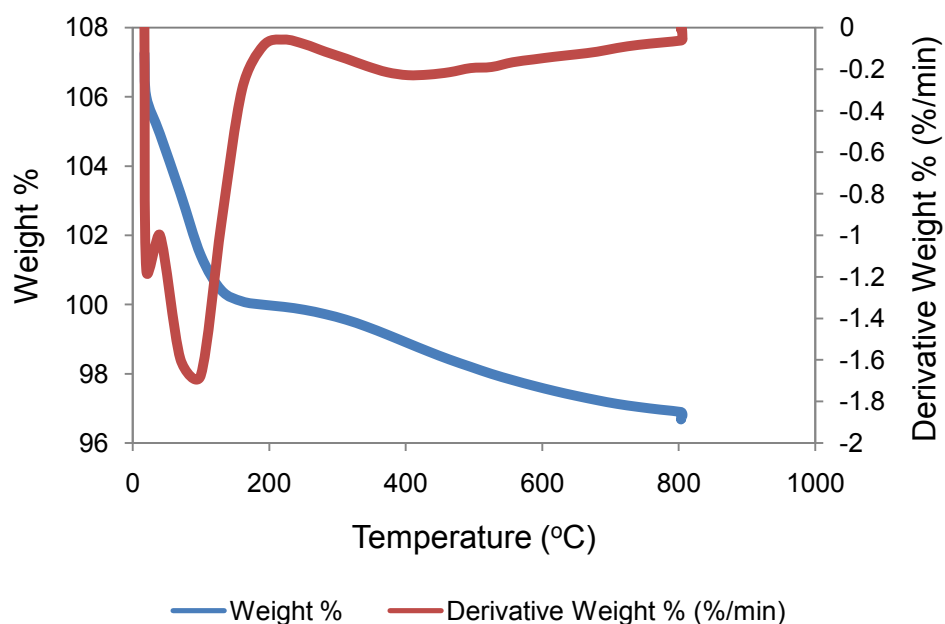


Figure 4.9: Weight % and derivative weight % of S1 (Untreated silica-Z1165 MP).

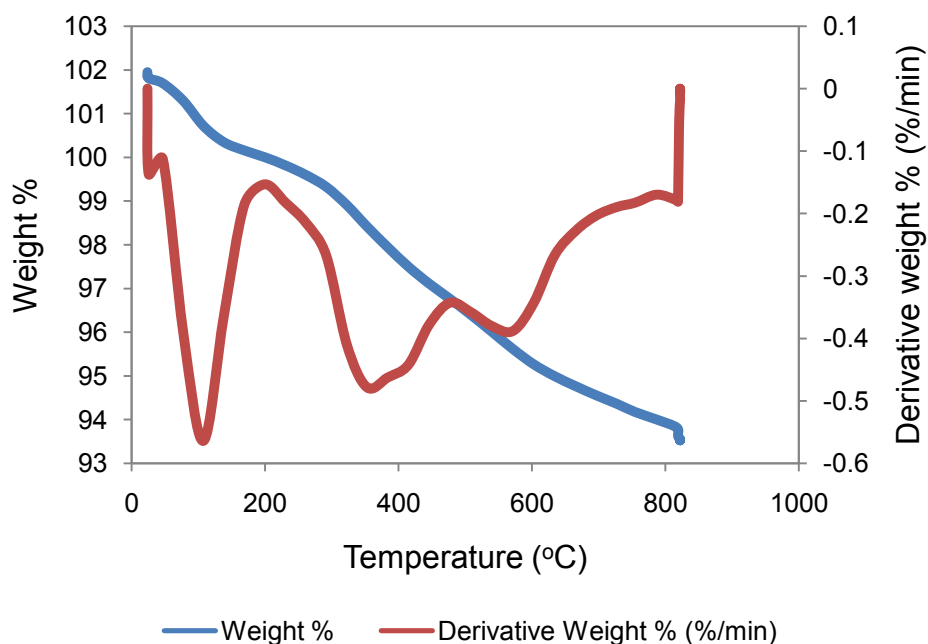


Figure 4.10: Weight % and derivative weight % of S2 (TESPT 8% w/w).

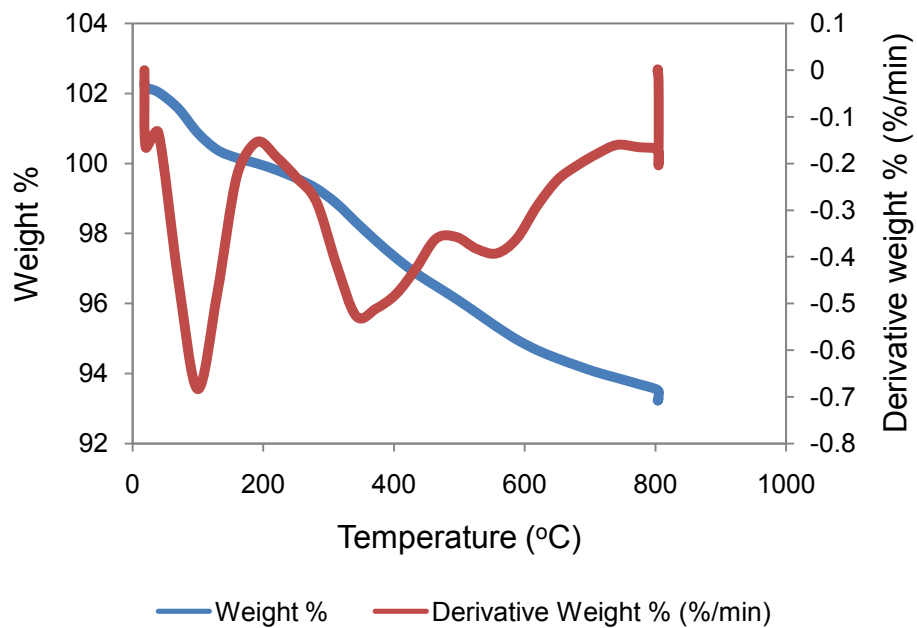


Figure 4.11: Weight % and derivative weight % of S3 (TESPT 12% w/w).

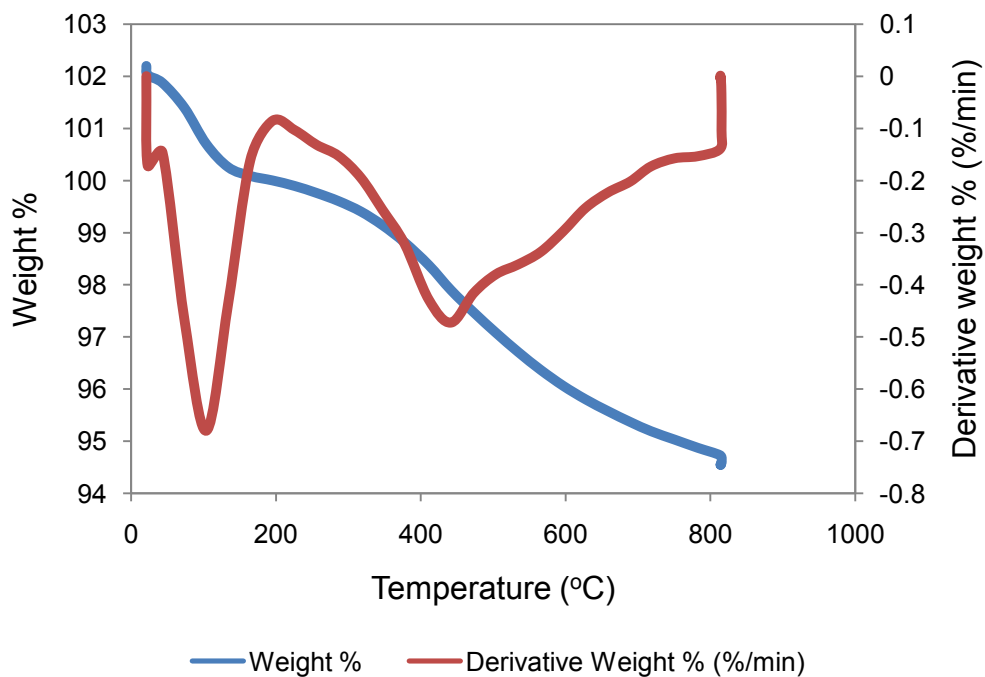


Figure 4.12: Weight % and derivative weight % of S4 (TESPM).

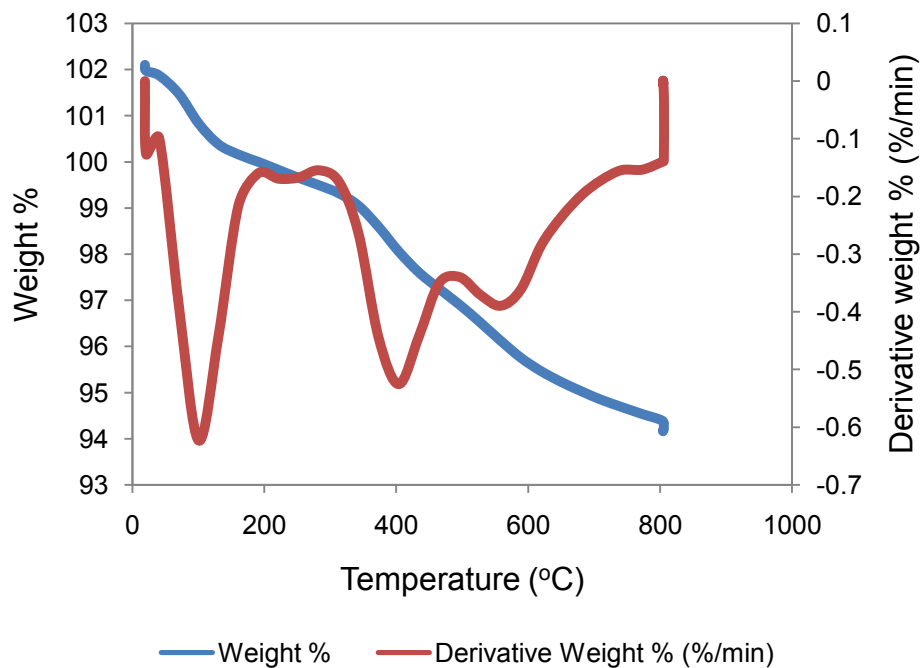


Figure 4.13: Weight % and derivative weight % of S5 (TESPD).

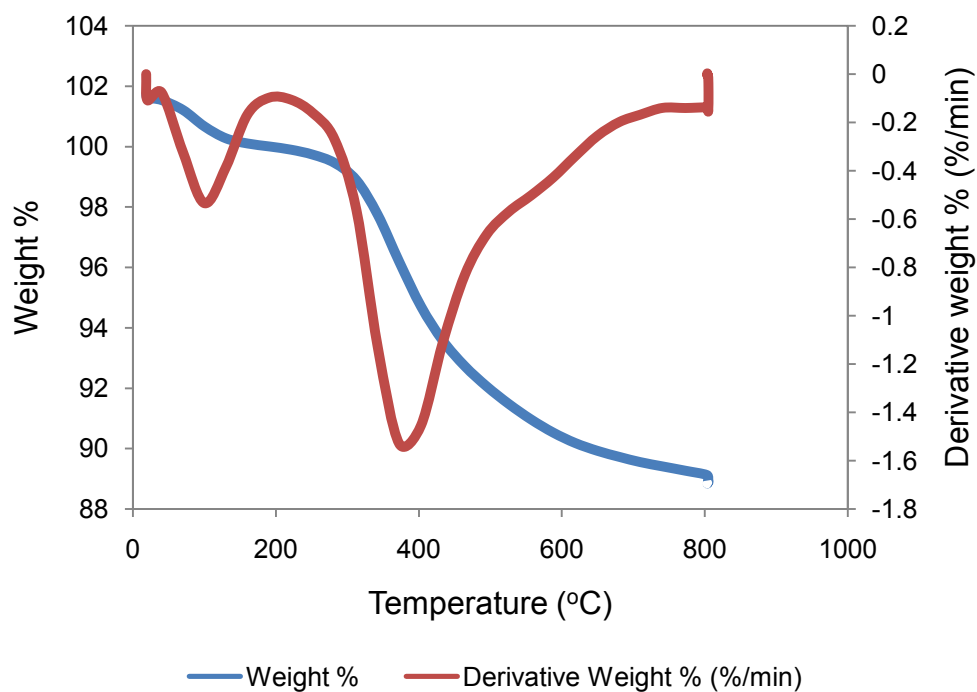


Figure 4.14: Weight % and derivative weight % of S6 (DTSPM).

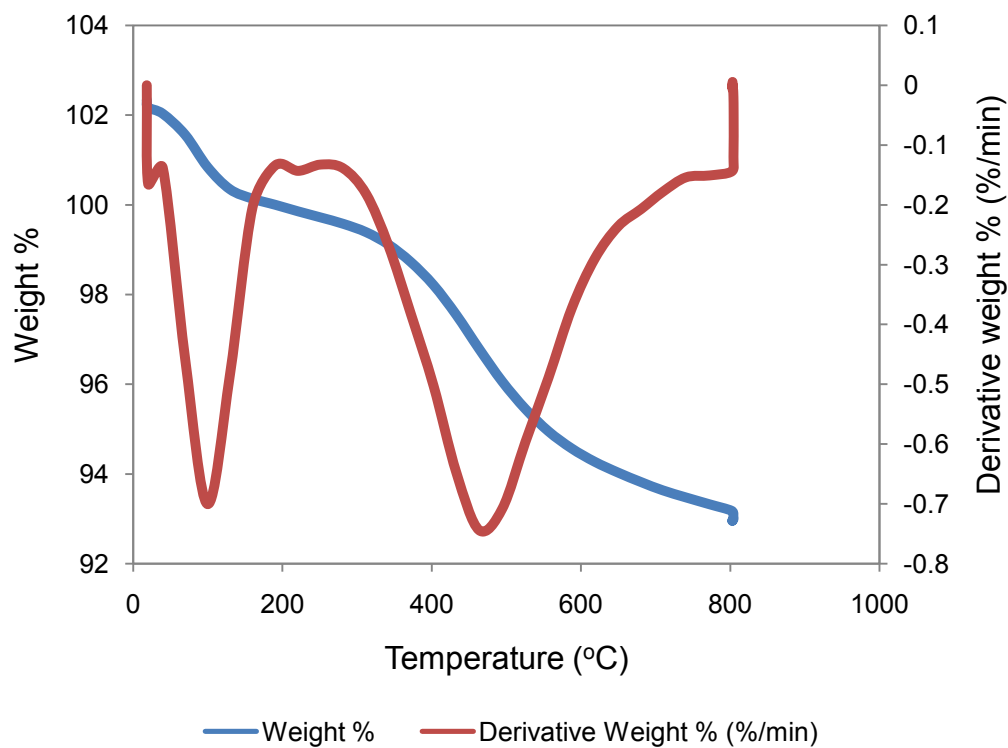


Figure 4.15: Weight % and derivative weight % of S7 (TESPO).

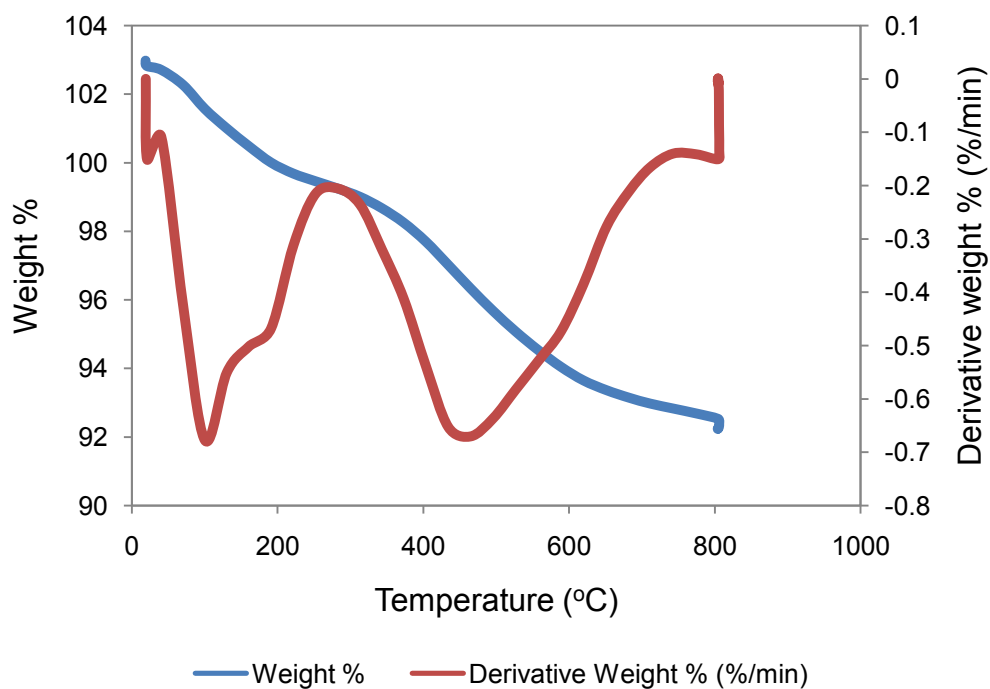


Figure 4.16: Weight % and derivative weight % of S8 (TESPO/M).

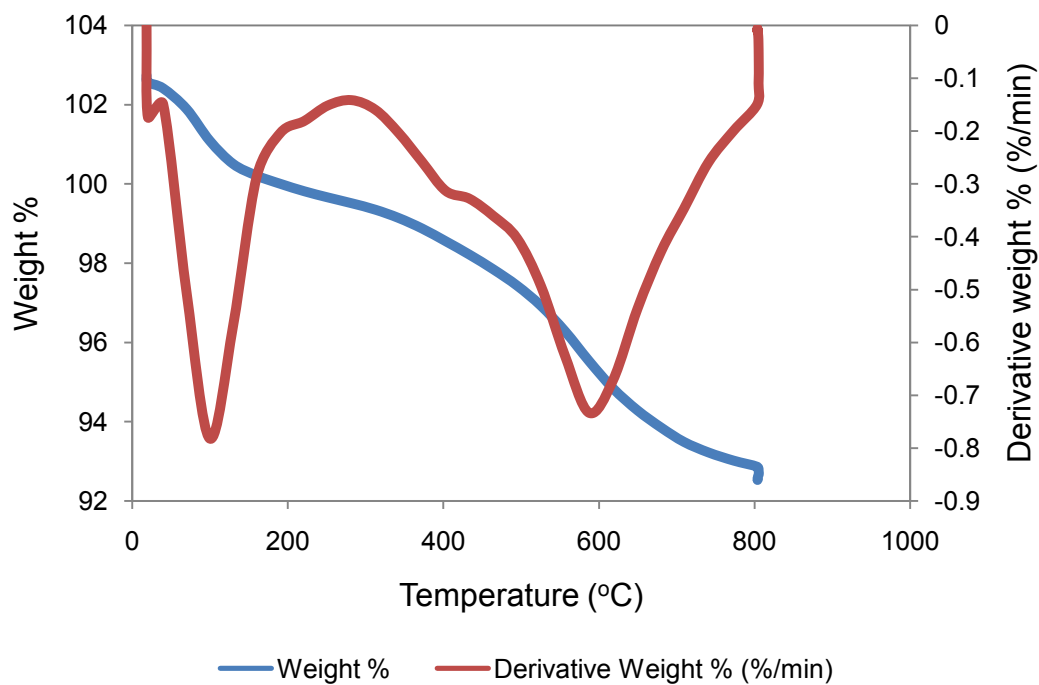


Figure 4.17: Weight % and derivative weight % of S9 (OTES).

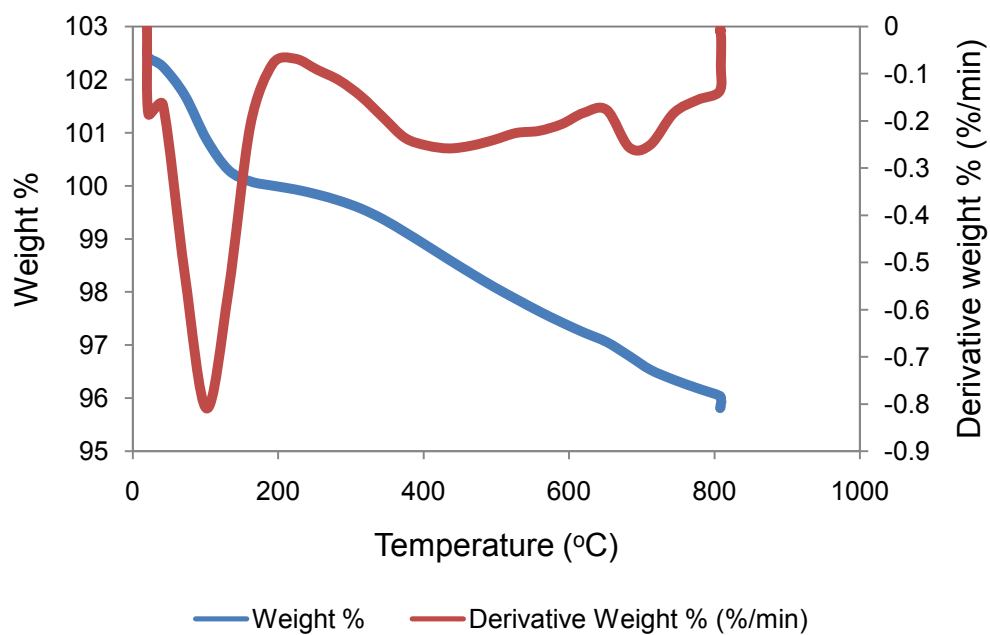


Figure 4.18: Weight % and derivative weight % of S10 (MTMS).

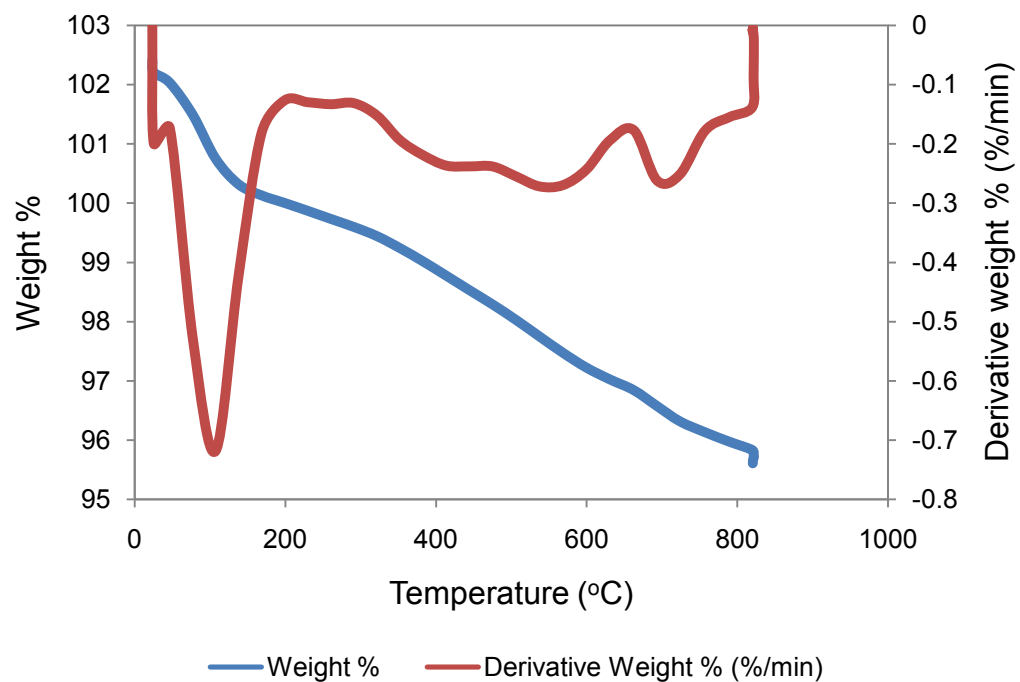


Figure 4.19: Weight % and derivative weight % of S11 (MTES).

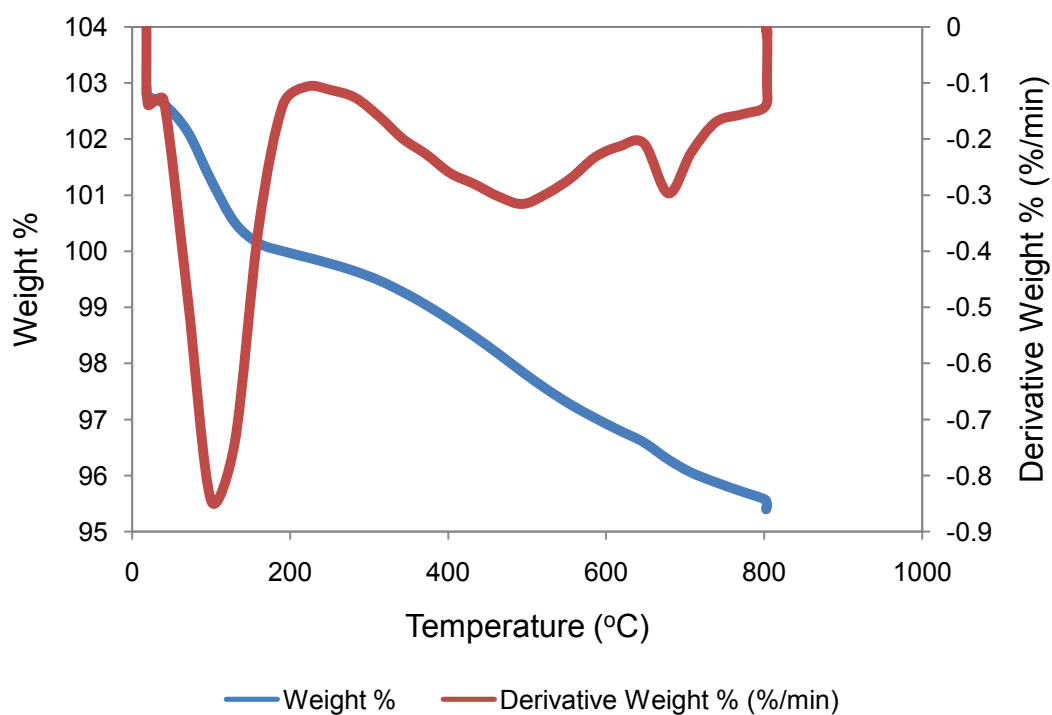


Figure 4.20: Weight % and derivative weight % of S12 (TMCS).

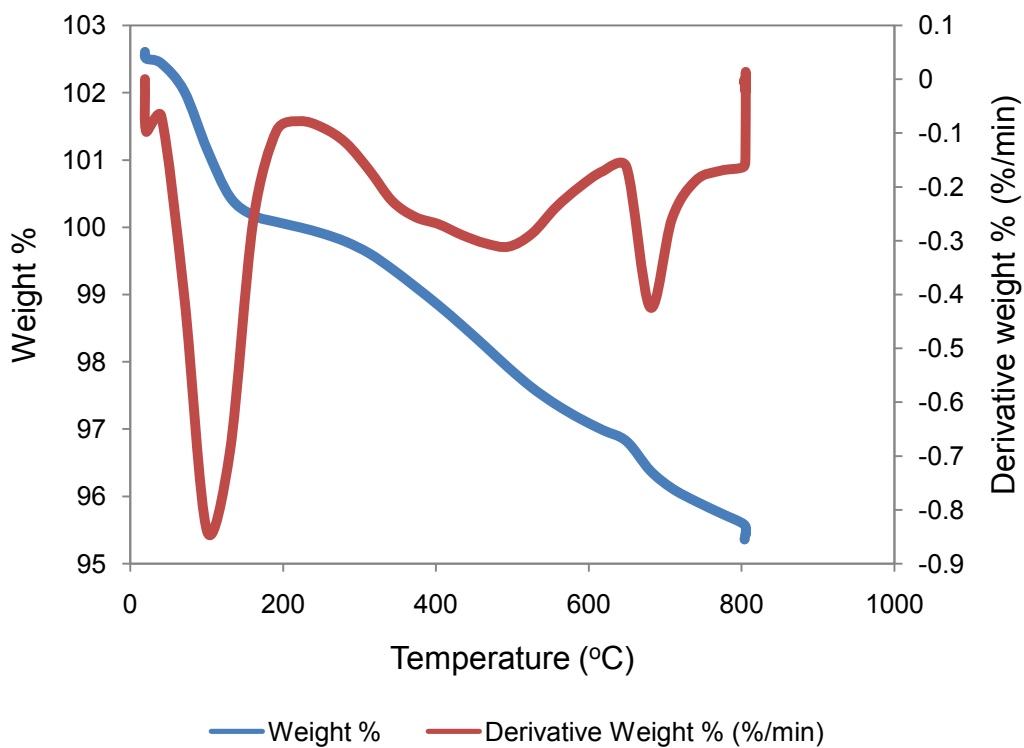


Figure 4.21: Weight % and derivative weight % of S13 (DCDMS).

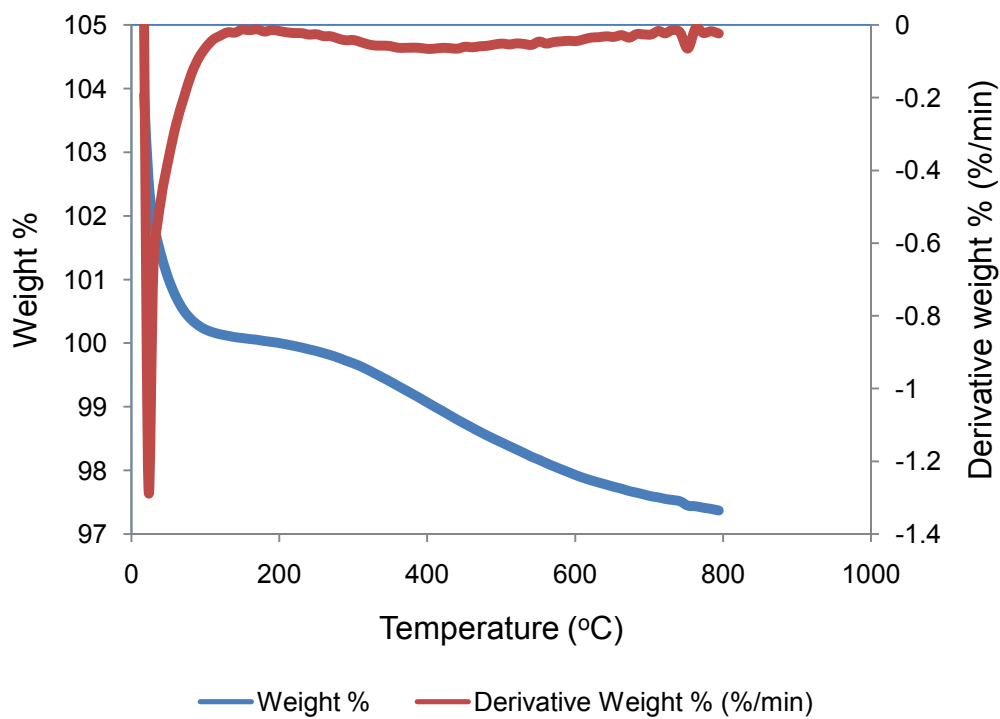


Figure 4.22: Weight % and derivative weight % of S2.1 (Untreated silica-UVN3 GR).

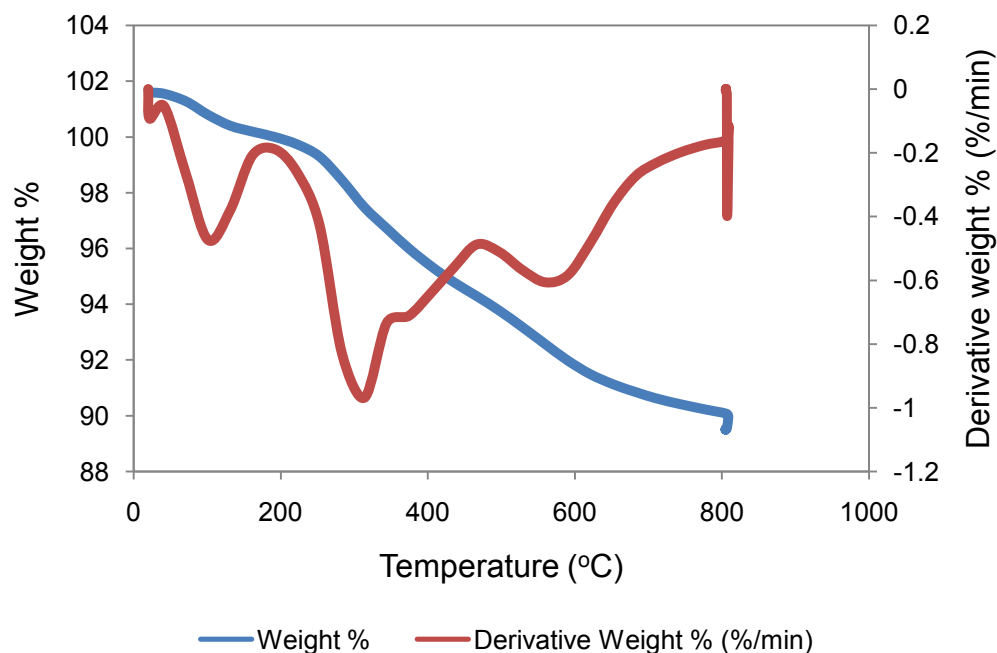


Figure 4.23: Weight % and derivative weight % of S2.2 (C8113).

Although, in the case of OTES-treated silica (S9), the IR spectroscopy indicates that the ethoxy groups are lost at lower temperatures, as with TESPT and TESPD silicas, in the derivative weight % TGA plot (Figure 4.17), there is only shoulder on the main peak at about 600 °C. Thus, the losses of the alkoxy and alkyl groups cannot be clearly differentiated. For all other silanes treatments, there was either only one major weight loss from the silane group (one main peak in the derivative plot), or the different weight losses could not be clearly separated.

All the weight losses were corrected to provide weight loss relative to the sample weight at 200 °C. At this temperature it is assumed that all moisture has been lost, so that the weight % losses are with respect to dry silanised silica. This avoids concerns

that the original moisture content in the sample may vary depending on the ambient humidity in the laboratory, which is not controlled.

The weight losses from 200 °C to 495 °C or 800 °C, and from 495 °C to 800 °C were corrected for the expected loss due to dehydration of silanols, based on the observed weight losses in the TGAs of the corresponding untreated silica over the same temperature ranges. Allowances were also made for the silanols lost through silanisation, although these accounted for only 3% to 13% of the calculated original silanol concentrations.

As discussed above, previous studies [142,143,153] have all indicated that about one or two ethoxy groups in triethoxysilyl groups react during silanisation. In analysing the TGA results, it is assumed that in the case of the triethoxy and trimethoxysilanes, one or one and the half or two ethoxy groups in each trialkoxysilyl group were lost during the silanisation. With these assumptions, the proportion of disubstitution of the disilanes TESPT and TESPd could be calculated, using the corrected weight loss from 200 °C to 495 °C, relative to the total weight loss from 200 °C to 800 °C. The results are collected together in Tables 4.5, 4.6 and 4.7, with the values in bold considered the more likely. Averages from bold values are summarised in Figure 4.24. Generally, the assumption from the prior studies that two out of three alkoxy groups are converted to siloxane (in the case of the triethoxy and trimethoxy silanes) seems correct, and this was followed. However, the MTMS and MTES silanisations were carried out at a much lower

temperature (55 °C), and so it seems reasonable to assume that 1.5 to 2 alkoxy groups were lost.

Table 4.5: Di-silanes - grafting efficiency and % disubstitution.

Ethoxy groups displaced:		Grafting efficiency, range, %			% Disubstituted, range		
		2	3	4	2	3	4
Silane	No [#]						
Coupsil 8113*	1	74	86	97	60	52	46
TESPT, 8%	11	41-52	49-59	55-66, mean 60	69-76	60-66	52-58, mean 53
TESPT, 12%	2	34-37	40-43	45-48	60-66	51-57	45-50
TESPD	2	54-55	61-63	71-73	92-97	79-84	67-71

[#] Number of batches prepared and analysed by TGA-IR (Coupsil 8113 was a commercial sample)

* The silanisation conditions for this commercial silanised silica are not known, but the TGA plot is very different indicating a significantly greater proportion of ethoxy groups remaining. Thus it is likely that only 1-1.5 ethoxy groups have been displaced.

Table 4.6: Mono-ethoxysilanes-grafting efficiency.

Ethoxy groups displaced:		Grafting efficiency, range, %		
		1	1.5	2
Silane	No [#]			
TESPM	2	47	54	64
DTSPM	2	27-32		
TESPO	3	43-50	46-53	50-57
TESPO/M	1	64		
OTES	2	37-70	41-78	47-87
MTMS*	2	50-51	64-65	91-92
MTES*	2	39-40	51-51	72-74

[#] Number of batches prepared and analysed by TGA-IR.

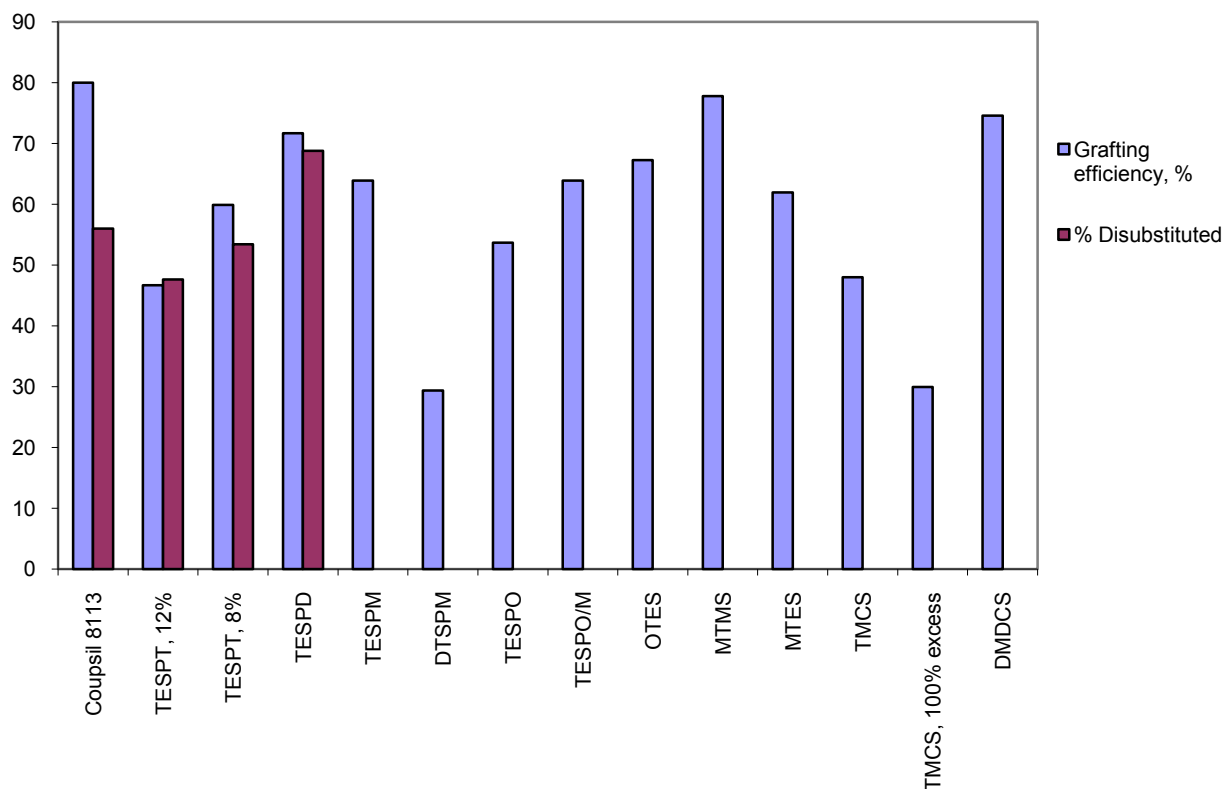
* These silanisations were carried out at a lower temperature, where there may be fewer than two alkoxy groups displaced.

Table 4.7: Chlorosilanes - grafting efficiency.

Chloro groups displaced		Grafting efficiency, range, %	
		1	1.5
Silane	No [#]		
TMCS	2	45-51	
TMCS, 100% excess	1	30	
DMDCS	1	75	97

[#] Number of batches prepared and analysed by TGA-IR.

Figure 4.24: Grafting efficiency of silanes.



The TGA data analysis shows that the efficiency of the silica silanisation process carried out in this study for 1 hr varied between 29% and 78% and mainly at the upper end of this range, with a median efficiency of 63%.

The study also estimated that approximately 50% to 69% of silica silanised with TESPT and TESPd is disubstituted or doubly bound to silica. These values of % disubstituted calculated initially appear somewhat higher than anticipated, and are higher than reported by Law et al. [144]. However, Law et al. made no allowance for additional ethoxy groups lost during silanisation, and assumed that the silane group weight losses at lower temperatures were due entirely to dissociation of singly bound silane, with ethoxy groups displaced at higher temperatures. The IR studies in the current work have revealed that the ethoxy groups are in fact displaced at lower temperatures, as would be expected. If reaction at either end is statistically random, then 64% grafted would correspond to 25% disubstitution. However, three factors may increase the observed % disubstitution. Firstly it seems likely that the silica would react more readily at the other end of an already bound silane than with a new silane molecule that is dispersed within the solvent.

Secondly, conversion of alkoxy groups at the other end of mono-grafted silanes to siloxanes during the TGA process will in effect convert at least some of them to disubstituted. As this conversion occurs mainly below the temperature at which the monosubstituted silanes fragment, the apparent proportion disubstituted would be greatly increased.

Thirdly, the fragmentation of the mono-grafted silane (CSS-SSC, CS-SSC, C-SSC dissociation) may not be completed at 495°C, especially in the case of the stronger bonds in TESP. This could explain the higher observed % disubstitution with TESP.

In the case of TESPT, conversion of alkoxy to siloxane during TGA appears likely to be the main factor, while in the case of TESP the stronger C-SSC bond may also be significant.

The bulkier silanes, DTSPM (S6) and TESPO (S7), show lower grafting efficiencies, especially the very bulky DTSPM. This presumably reflects the limited silica surface available for grafting, and indeed the level for DTSPM recommended by the manufacturer is much lower than would be needed to have the same number of silane groups as 8 % w/w TESPT. The ether groups in DTSPM will be coating the silica surface through hydrogen bonding with unreacted silanols, and thus preventing them from reacting with another DTSPM molecule. The grafting efficiency with 12% w/w TESPT is also lower than that with 8% w/w. Again this appears to reflect the limited silica surface available for grafting, and is consistent with the view that there are diminishing returns when using more than the standard 8% w/w. A similar result was found with TMCS when double the amount was used in the silanisation.

Although varying the amount of TESPT used was only briefly investigated, the limited evidence suggests that using more reduces the proportion disubstituted, as might be anticipated. It is assumed that TGA weight losses up to 200°C are primarily

due to weakly bound water. The amount will be dependent on the ambient humidity, which was not controlled in the laboratory where the TGA measurements were carried out. However, from the figure it is clear that silanisation reduces bound moisture by reducing the surface area available to the water and the number of silanol groups on the surface available for hydrogen-bonding with the water molecules. By far the most bulky silane (DTSPM), which also will bond to more than just one silanol, shows the smallest moisture content, even though the grafting efficiency is significantly lower. This demonstrates that this silane can be successfully used at a lower molar level, as recommended by the manufacturer. It appears that smaller silanes lead less surface coverage and hence to more absorbed moisture, even though their grafting efficiencies were relatively high. Comparing the silanisations carried out with 8% TESPT over different reaction times (10 mins – 24 hrs), the moisture contents are very similar consistent with very similar levels of silanisation and surface coverage, discussed above. It is possible that there is a slight increase in moisture content between 10 mins and 1 hr reaction time, which would be consistent with the small loss of ethoxy groups, discussed above, reducing slightly the size of the bound silane groups and hence the surface coverage.

4.4 Conclusions

The functional groups on the silicas were studied using TGA-IR methods from RT to 800 °C in an inert carrier gas environment. The TGA methods allow the process of dehydration (removal of physically adsorbed water) and dehydroxylation (the condensation of silanol groups on the silica surface) of amorphous silica. The removal of these functional groups shown through the loss of physisorbed water between RT and 200 °C, and loss of water from the silanol groups between 200 °C and 800 °C. The variations in the physisorbed water weight lost are mainly due to the ambient conditions when the silica sample was tested. The results were used for estimating the actual silane grafted on silica surface.

The TGA-IR methods allow the measurement of the efficiency of silica silanisation using the different silanes. In the case of S2 (TESPT 8% w/w), S3 (TESPT 12% w/w) and S5 (TESPD), three derivative weight % peaks were observed. In the second period of weight loss, it is assumed that ethanol is displaced to form siloxanes, and that the weaker SS-SS, S-SS and C-SS bonds undergo homolysis, leading to weight losses from singly bound TESPT or TESPD.

The study generally assumes two out of three alkoxy groups are converted to siloxane. The bulkier silanes, DTSPM (S6) and TESPO (S7), show lower grafting efficiencies. This presumably reflects the limited silica surface available for grafting. The grafting efficiency with 12% w/w TESPT (S3) is also lower than that with 8% w/w (S2)

as is the case when double the amount of TMS was used. Again this appears to reflect the limited silica surface available for grafting.

The TGA data showed that the efficiency of the silica silanisation process for 1 hr ranges from 29% and 78% and mainly at the upper end of this range with a median efficiency of 63%.

The commercial silanised silica, Coupsil 8113, has a high grafting efficiency (about 86%), and appears to have much less loss of ethoxy groups during the silanisation process. However, it is not known how the silica was silanised. The study also estimated that approximately 53% and 69% of silica silanised with TESPT (8% w/w) and TESP, respectively is disubstituted.

CHAPTER 5 EXPERIMENTAL DETERMINATION OF SURFACE ENERGY OF UNSILANISED AND SILANISED SILICA

5.1 Introduction

The silica particle size and structures will not bring significant effect without the involvement of the third parameter, the surface chemistry or the surface activity of the filler particles [169,55]. This parameter is responsible for the relative strength of filler-filler interactions, filler-elastomer interactions, and filler interaction with other ingredients during compounding. Besides that, it is also well known that the particle surface is heterogeneous in nature. The energetic heterogeneity and the geometric heterogeneity of the particle surface, which have close association with each other, influence the reinforcement of the elastomer [56].

In this chapter, the aim is to establish the silica surface energy heterogeneity and the dispersion of modified silicas in elastomer compounds. An investigation is carried out to understand the changes of silica surface energy when the silica surface chemistry is modified. The surface energy of the silica as a function of surface coverage were determined using Inverse Gas Chromatography. Its effect on silica dispersion in the elastomer matrix was evaluated using a “TEM network visualisation” method, discussed in Chapter 6.

A broad spectrum of adsorption sites on the particle surface will eventually have an effect on the bonding configurations [58]. Apart from particle surface morphology, there are many sources for heterogeneity due to the emergence of acidic and basic

centers. The heterogeneity sites on the particles can be reduced by pretreatment with heat or surface chemistry modification [59].

In the present study, the surface free energy profiles of silica (Zeosil® 1165 MP) were characterised by using an Inverse Gas Chromatography-Surface Energy Analyzer (IGC-SEA). This silica was silanised with bifunctional coupling and monofunctional non-coupling types of silanes. The work includes understanding the dispersive surface energy profiles for a series of n-alkane probe molecules.

5.2 Inverse Gas Chromatography (IGC)

In IGC, a series of known molecular probes are injected in a column containing the sample (i.e. powder or fiber) of interest. Well-defined adsorbates (molecular probes) are injected and their interactions with the sample inside the column are analysed. The adsorption and desorption isotherm of the adsorbates provide the surface characteristics of the column filling itself.

During the IGC experiment, the probability of the injected molecular probes interacting initially with highest-energy sites is higher followed by lower-energy sites on the surface of the sample. This approach allowed the determination of the surface heterogeneity and the surface energy profiles of our samples.

As discussed in Chapter 2, there are several kinds of intermolecular interaction present between the two phases. The total surface free energy, γ_S^T , is a combination of the dispersive component (γ_S^d) and the specific (acid-base) surface energy (γ_S^{ab}). The

total surface free energy, γ_s^T is given by the sum of the dispersive component, which includes the London, Keesom and Debye forces also known as Lifshitz – van der Waals interactions [170], and the specific interactions including donor-acceptor bonds and π -bonds are considered as specific interactions [69]. For this study, the electrostatic interactions were not investigated.

For these IGC experiments, helium gas is used as the carrier gas, and methane, as a non-interacting or non-adsorbed gas, is used to measure the dead time, t_0 , the time taken by the methane to pass through the column. The characterisation of the silica surface is achieved by measuring the net retention time ($t_R - t_0$) taken to elute the sample. Therefore, the net retention volume, V_N , is calculated via

$$V_N = j \cdot F_c \cdot (t_R - t_0) \quad (5.1)$$

where F_c is the helium gas flow rate in the inverse gas chromatography column, j is the mass James-Martin correction factor, which is used to correct the net retention time for the pressure drop and packing density of silica within the column. t_R is the time taken to elute the molecular probes and t_0 is the time taken for the methane gas to pass through the column. The James-Martin correction factor, j , is defined as

$$j = \frac{3}{2} \left[\frac{(P_{in}/P_{out})^2 - 1}{(P_{in}/P_{out})^3 - 1} \right] \quad (5.2)$$

where P_{in} and P_{out} are the inlet and outlet pressures, respectively.

The isothermal adsorption and desorption of the adsorbates and the calculated V_N of the molecular probes injected into the column can be related to the standard Gibbs free energy change of adsorption, ΔG_{ad}^0 , and to the work adhesion, W_{adh} :

$$-\Delta G_{ad}^0 = RT \ln V_N + C_1 = N_A \cdot a_m \cdot W_{adh} \quad (5.3)$$

where N_A is the Avogadro number, a_m is the molecular cross-sectional area of the adsorbed molecular probe, and C_1 is a constant that depends on the chosen reference state.

For the dispersive component by applying Fowkes' principle for Lifshitz-van der Waals interactions, equation (5.3) leads to:

$$RT \ln V_N = N_A \cdot a_m \cdot 2 \sqrt{\gamma_{SV}^d \gamma_{LV}^d} + constant \quad (5.4)$$

The γ_{LV}^d is the dispersive surface energy of the liquid probe. The γ_{SV}^d of solid and molecular vapor interaction is calculated from the slope of a linear regression of $RT \ln V_n$ versus $N_A a_m \sqrt{\gamma_{LV}^d}$, the n-alkane line, using the approach of Schultz et al. [171]. Alternatively, γ_{SV}^d can be determined by using the contribution of the methylene group (CH_2) in the n-alkane series according to the Dorris and Gray method [172,173]. For this

study, the Schultz et al. approach was used to determine the dispersive surface energy of the untreated and silanised silica samples.

When polar molecular probes are used, the Lewis acid-base surface interactions can provide a better understanding of the surface chemical-physical properties of the filler and the elastomer. The Gibbs free energy change of adsorption, G_{ad}^0 , for dispersive and specific (acid-base) components is expressed as the sum of the two components:

$$\Delta G_{ad}^0 = \Delta G_d^0 + \Delta G_{ab}^0 \quad (5.5)$$

Therefore the difference between the alkane regression line and that from the polar molecular probes equates to G_{ab}^0 . Using the G_{ab}^0 value and applying the van-Oss-Good-Chaudhury (vOGC) or Gutmann approach [174], the parameters for acid-base polar interactions can be determined. In this work, the vOGC approach and the Della Volpe theory [175,176] of acid-base components are used to determine γ_s^{ab} and obtain the Lewis acid (electron acceptor, γ_s^+) and Lewis base (electron donor, γ_s^-) surface energies of the untreated and silanised silicas.

By knowing the surface energies of the individual components, the work of adhesion (W_{adh}) silica to elastomer and of cohesion (W_{coh}) within the silica can be obtained using the following equations:

$$W_{adh} = 2 \left[\gamma_{SV}^d + (\gamma_{SV}^+ \gamma_{LV}^-)^{\frac{1}{2}} + (\gamma_{SV}^- \gamma_{LV}^+)^{\frac{1}{2}} \right] \quad (5.6)$$

$$W_{coh} = 2 \left[\gamma_{SV}^d + (\gamma_{SV}^+ \gamma_{SV}^-)^{\frac{1}{2}} + (\gamma_{SV}^- \gamma_{SV}^+)^{\frac{1}{2}} \right] \quad (5.7)$$

As indicated by Equations 5.6 and 5.7, there is a direct correlation between the work of cohesion and the surface energy of a solid particle. For the present study, it is the work of cohesion between solid particles that is of interest. As the surface energy increases, the work of cohesion increases. Therefore, particle aggregation is higher. This study investigated the surface energy of the untreated and modified silicas and compared this to the aggregate dispersion in the silica-filled elastomer vulcanisates.

5.3 Experimental Methods

The materials preparation for current study is discussed in details in Chapter 3. The silica used for this study is Zeosil[®] 1165 MP. As for the silica particle surface modification, bifunctional coupling (TESPT, TESPM, TESP, DTSPM, TESPO and TESPO/M) and monofunctional non-coupling silanes (OTES, MTMS, MTES and TMCS) were used for this study. A summary of the prepared samples is given in Table 5.1.

Table 5.1: Summary of untreated and silanised silicas.

No.	Sample Name	The type of silanes specie grafted on silica
1.	S1	Untreated silica
2.	S2	TESPT (8 % w/w) - bis[3-(triethoxysilyl)propyl] tetrasulfide
3.	S3	TESPT (12 % w/w) - bis[3-(triethoxysilyl)propyl] tetrasulfide
4.	S4	TESPM - 3-(triethoxysilyl)propyl mercaptan
5.	S5	TESPD - bis[3-(triethoxysilyl)propyl] disulfide
6.	S6	DTSPM - [3-(di-(tridecyloxypenta(ethyleneoxy))ethoxysilyl)propyl mercaptan
7.	S7	TESPO - 3-(triethoxysilyl)propyl thio-octanoate
8.	S8	TESPO/M - a co-oligomer combining the mercapto-silane, TESPM, with the blocked mercapto-silane TESPO
9.	S9	OTES - octyltriethoxysilane
10.	S10	MTMS - methyltrimethoxysilane
11.	S11	MTES - methyltriethoxysilane
12.	S12	TMCS - trimethylchlorosilane

The molecular structures of these silanes are shown in Chapter 3, in Figures 3.1 and 3.2, for coupling and non-coupling silanes respectively. The loadings of the silanes were normalised to the 8% w/w TESPT loading to have the same number of silane groups available for silanisation, except for the S3 sample, which was silanised with 12% w/w TESPT. The consideration for calculating the silane loadings includes both the molecular weight and the number silane groups in each molecule.

The filler surface energy determination was carried out using an Inverse Gas Chromatography-Surface Energy Analyzer. A series of purely dispersive n-alkane vapor probes, hexane, heptane, octane, nonane, decane, toluene, ethyl acetate and dichloromethane were injected at 90 °C. These probes were injected to cover 0.01% to 1.0% of the silica particle surface. The details for determination of surface heterogeneity of solid particles is reviewed in Chapter 2 and elsewhere [121,122,123,124].

5.4 Results and Discussion

5.4.1 Dispersive Surface Energy Profiles

The values for the dispersive surface energy component of the untreated and silanised silicas are presented as a function of surface coverage, n/n_m , where n is the amount of adsorbate adsorbed and n_m is the monolayer capacity of the silica particles. S1 is untreated silica and S2 to S7 are silica silanised with coupling silanes. These were silanised with TESPT, TESPM, TESP, DTSPM, TESPO and TESPO/M respectively. As for the silica silanised with non-coupling silanes, the samples are represented by S8 to S10. The corresponding silanes were OTES, MTMS, MTES and TMCS, respectively.

The adsorption isotherms for the n-alkanes (hexane, heptane, octane and nonane) were calculated from 10 to 15 chromatographic peaks and for decane from less than 10 chromatographic peaks. The retention volumes for the series of chromatograms are expressed as the amount of adsorbate versus relative pressure (P/P_o) for untreated silica (S1) in Figure 3. It is observed that the adsorption isotherm can be considered as a Type II isotherm according to the Brunauer, Emmet and Teller [177] classification or the International Union of Pure and Applied Chemistry (IUPAC). This indicates a good interaction between the adsorbates and the silica samples during the IGC analysis. Similar isotherms were observed for the rest of the silanised silicas (S2 to S12).

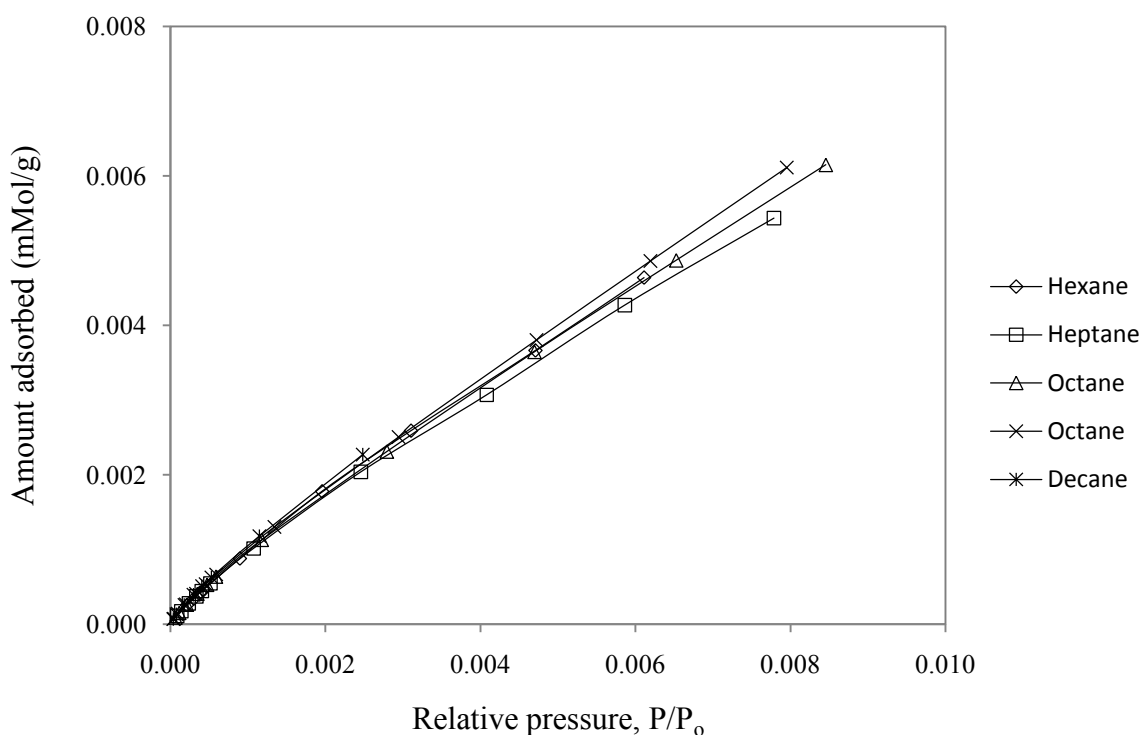


Figure 5.1: Adsorption isotherms of the n-alkanes on untreated silica.

The rear profiles of the chromatographic peaks for the injected n-alkane molecules obtained from this study were sharp with little tailing exhibiting asymmetric Gaussian peaks [172]. The average ratio calculated for centre of mass over peak maximum is approximately 1.1 [178,179], with a standard deviation of 0.08. The inlet pressure showed a standard deviation of 0.5%. The total error in the isotherms is presumed to be low with standard deviations between 0.3% and 0.5% for the surface coverage analysed in this study. The isotherm profiles for different silicas are expressed as energy per unit surface area of the adsorbent, as displayed in Figure 5.2

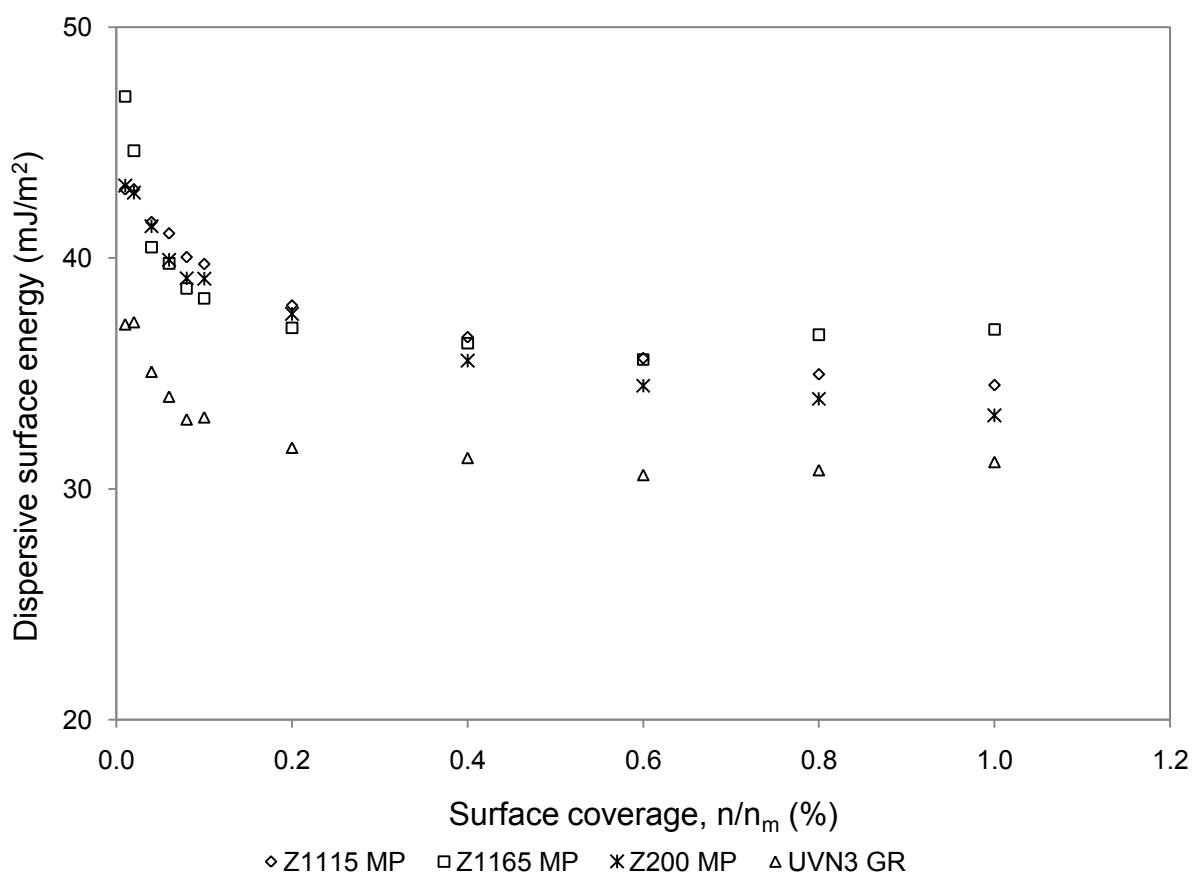


Figure 5.2: Dispersive surface energy (γ_s^d) profiles as a function of surface coverage of different silicas.

The γ_S^d profiles of Figure 5.2 show that the surface energy values change as a function of surface coverage. The γ_S^d of Z1165 MP at low surface coverages appears to be relatively a little higher than γ_S^d of Z1115 MP and Z200 MP. The lowest γ_S^d at low surface coverages is that of UVN3 GR. The TGA results have shown that the silanol concentration of these silicas varied (Chapter 4, Table 4.1), where UVN3 GR has the lowest silanol concentrations. It was suggested by Wolff et al. [180] that the concentration of silanol groups on the silica surface may be related to the concentration of high energy sites for γ_S^d . However, the number of silanol groups did not play a dominant factor for γ_S^d as investigated by them when they compared fumed and precipitated silica particles with known numbers of silanol groups per unit surface area [180,181].

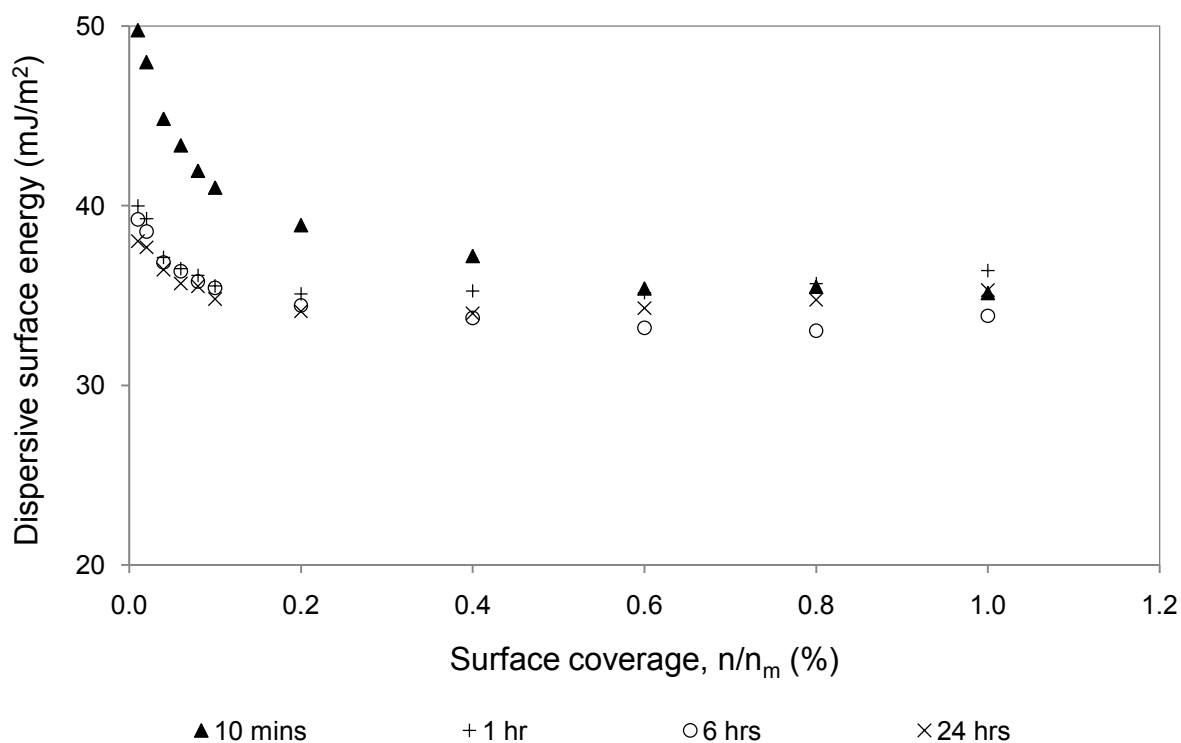


Figure 5.3: Dispersive surface energy of silica (Z1165 MP) silanised with TESPT 8% w/w for different times.

In the case of Z1165 MP silanised with TESPT 8% w/w for different times between 10 mins and 24 hrs, the IGC results indicate that the silanisation was largely completed after 1 hr (Figure 5.3). This is largely in agreement with the TGA results, which indicated no change after 1 hr, and some conversion of ethoxy groups to siloxanes between 10 mins and 1 hr, but little or no change in the % TESPT grafted. Conversion of ethoxy to siloxane would involve loss of silanol on the silica and/ or increased coverage of the surface, possibly explaining the drop in γ_s^d at low surface coverage between 10 mins and 1 hr. The sensitivity of the molecular probes used in the IGC analysis has exhibited the suitability of this technique to analyse the effect of surface thermodynamic of silanised silica.

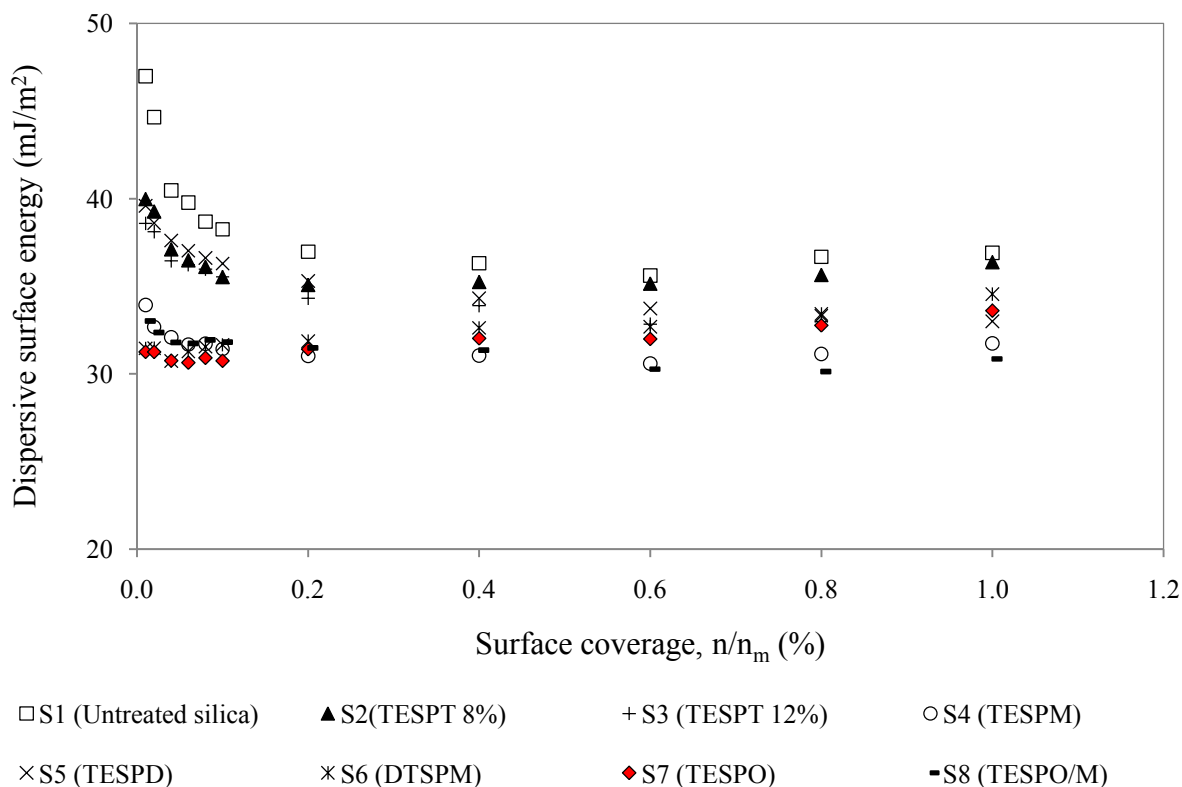


Figure 5.4: Dispersive surface energy (γ_s^d) profiles as a function of surface coverage of untreated and silanised silica with coupling silanes.

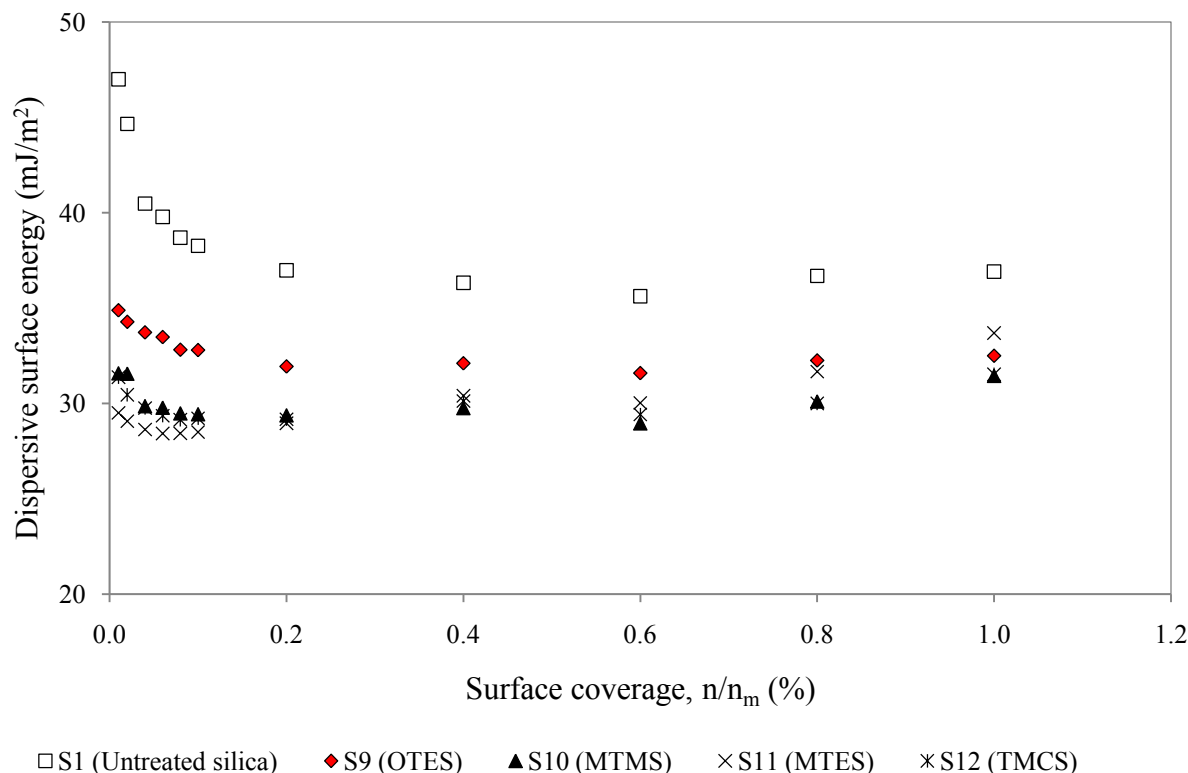


Figure 5.5: Dispersive surface energy (γ_S^d) profiles as a function of surface coverage of untreated and silanised silica with non-coupling silanes.

The γ_S^d profiles of Figures 5.4 and 5.5 show that the surface energy values change as a function of surface coverage. This indicates that the untreated silica (S1) is energetically fairly heterogeneous before the silanisation process. Samples S6 (DTSPM), S7 (TESPO) and S8 (TESPO/M) show a relatively homogeneous energetic surface. The γ_S^d of these samples decreases a little followed by a relatively small increase with the surface coverage of the fillers. The probe molecules were first adsorbed onto the high-energy sites at low surface coverages; this was followed by adsorption at the less energetic sites as the surface coverage increased.

The interaction between the injected probe molecules and the less energetic sites would be weaker [121] and might lead to lateral interaction between the probe molecules as the surface coverage increases [182]. This phenomenon can be observed as the relatively small increase in the γ_S^d as the surface coverage increases. The highest energetic sites occupy approximately 0.2% to 0.4% of the filler surface.

It is also observed that the untreated silica (S1) shows higher γ_S^d than the silanised silicas regardless of whether coupling or non-coupling. The γ_S^d of S1 at low surface coverage (Henry's law region) is similar to the values measured by Castellano et al. [183,184] and Guy et al. [185] for the same silica. The higher γ_S^d for S1 points towards the availability of a large number of higher energetic sites compared to the silanised silicas. The significant differences in γ_S^d between untreated and silanised silica particles are related to their surface chemistry. The density of these silanol groups would be higher for untreated silica as it is these groups that react with the silanes.

The other reason for lower γ_S^d of silanised silica S6, S7 and S8 may be due to the presence of the long alkyl functional groups from the DTSPM, TESPO and TESPO/M silanes. These silanes would cover a large fraction of the surface of the silica and thus reduce the exposure of the higher energetic sites to the adsorption of the $-CH_2-$ groups from the n-alkane molecules. This observation was reported by Wang and Wolff when they silanised their silica particles with octadecyltrimethoxysilane [186]. Figure 5.6 illustrates how the DTSPM may be attached to the silica surface. The polyether side-

chains from DTSPM can interact with the silanol groups or water molecules on the silica surface through hydrogen bonds.

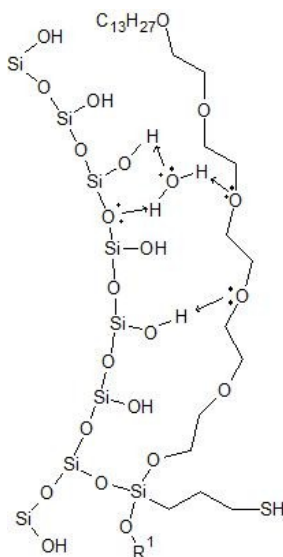


Figure 5.6: Chemical structure of DTSPM attached to silica surface.

The silicas silanised with TESPT (S2 and S3) exhibit similar γ_S^d profiles, even though the TESPT loadings differ by 4% w/w silica. Silanised silica S5 (TESPD), with a similar chemical structure to TESPT except having a shorter sulfur bridge, exhibits a similar γ_S^d profile to S2 and S3. As a comparison, the γ_S^d values are close to those observed by Wang and Wolff in their investigation of silica silanised with TESPT [186].

Based on TGA-IR and IGC studies, all the modified silicas were silanised for the same time, 1 hr it was believed that this would be sufficient time for the silanisation to be largely completed, apart from perhaps in the case of OTES with the bulky alkyl

group, which has been shown to react much slower [187]. Investigation of the effect of TESPT reaction time discussed in Chapter 4 and earlier in this chapter, in which it was found that there was little change after 1 hr. The silicas silanised with DTSPM, TESPO and TESPO/M, containing long alkyl functional groups, exhibited the lowest and most homogenised γ_S^d profiles, presumably due to their greater surface coverage.

As for the silicas silanised with non-coupling silanes, similar γ_S^d profiles are observed apart from S9 (OTES), which exhibits a higher profile, possibly arising from incomplete silanisation [187]. Silica silanised with TMCS (S12) showed the lowest γ_S^d across most surface coverages measured possibly due to greater surface coverage. Both S10 (MTMS) and S11 (MTES) silanised silicas showed similar γ_S^d profiles. For this study, S9 (OTES) showed a moderate reduction of γ_S^d compared with the S1, when measured at low surface coverage, comparable to the γ_S^d value measured by Wang and Wolff using trimethoxyoctadecylsilane at 90 °C [186].

Values for γ_S^d at infinite dilution have been reported previously for silica silanised with TESPT [188,189], TESPO [190], TESPd [191] and OTES [191]. Taking into account the different IGC conditions used, and that a different silica was used with TESPd and OTES, the values reported are in good accord with the surface energies observed in Figures 5.4 and 5.5 when zero surface coverage is approached.

5.4.2 Specific Surface Energy Profiles

The surface properties of the silica also include the specific interactions resulting from the presence of polar functional groups on the surface, such as hydroxyl groups. Applying the vOGC approach [174], the specific (acid-base) surface energy profiles are obtained by using a monopolar acidic probe (dichloromethane) and a monopolar basic probe (toluene). For the present study, the acid γ_L^+ and base γ_L^- parameters of the polar probes proposed by Della Volpe and Siboni were used [192]. They proposed that the acid-base parameters (γ_L^+ and γ_L^-) be determined utilising water as a reference and that water is acidic rather than amphoteric as suggested by van Oss et al. [175,176]. It is noted that the scale of acidity to basicity of the polar probes is still being debated [172]. For the investigation in the present study, these acid-base parameters were applied to determine the specific surface energy profile of the untreated silica and the silanised silica.

The γ_S^+ and γ_S^- of the untreated and modified silicas were determined by first measuring the ΔG_{ab} of the polar probes (toluene and dichloromethane) at a range of surface coverages. Similar to the γ_S^d profiles, the values of γ_S^{ab} , determined from the specific interaction free energy of toluene and dichloromethane, are higher for the untreated silica than for the silanised silica, as displayed in Figures 5.7 and 5.8. It is calculated that the γ_S^{ab} were reduced between 37% and 91% and between 36% and 52%, for coupling and non-coupling silanes respectively. This is due to the presence of a high concentration of silanol groups on the untreated silica surface, which have the ability to polarise the toluene molecule; their number is reduced when the silica is

silanised. In the case of dichloromethane, it is considered that hydrogen bonds are formed between the hydrogen atoms of dichloromethane and the hydroxyl groups on the untreated silica surface. From the present study, it is calculated that the total surface energies were reduced between 7% and 50% when the silicas were silanised.

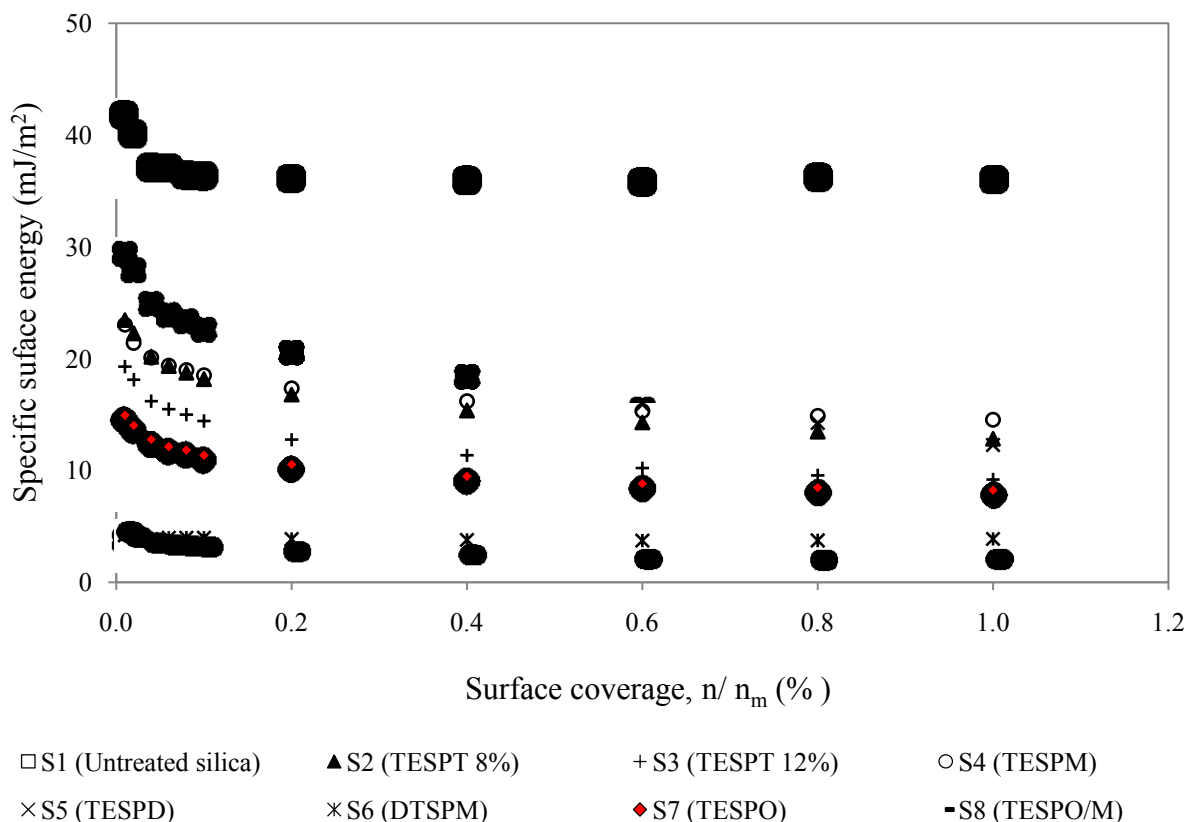


Figure 5.7: Specific surface energy (γ_s^{ab}) profiles as a function of surface coverage for untreated and silanised silica with coupling silanes.

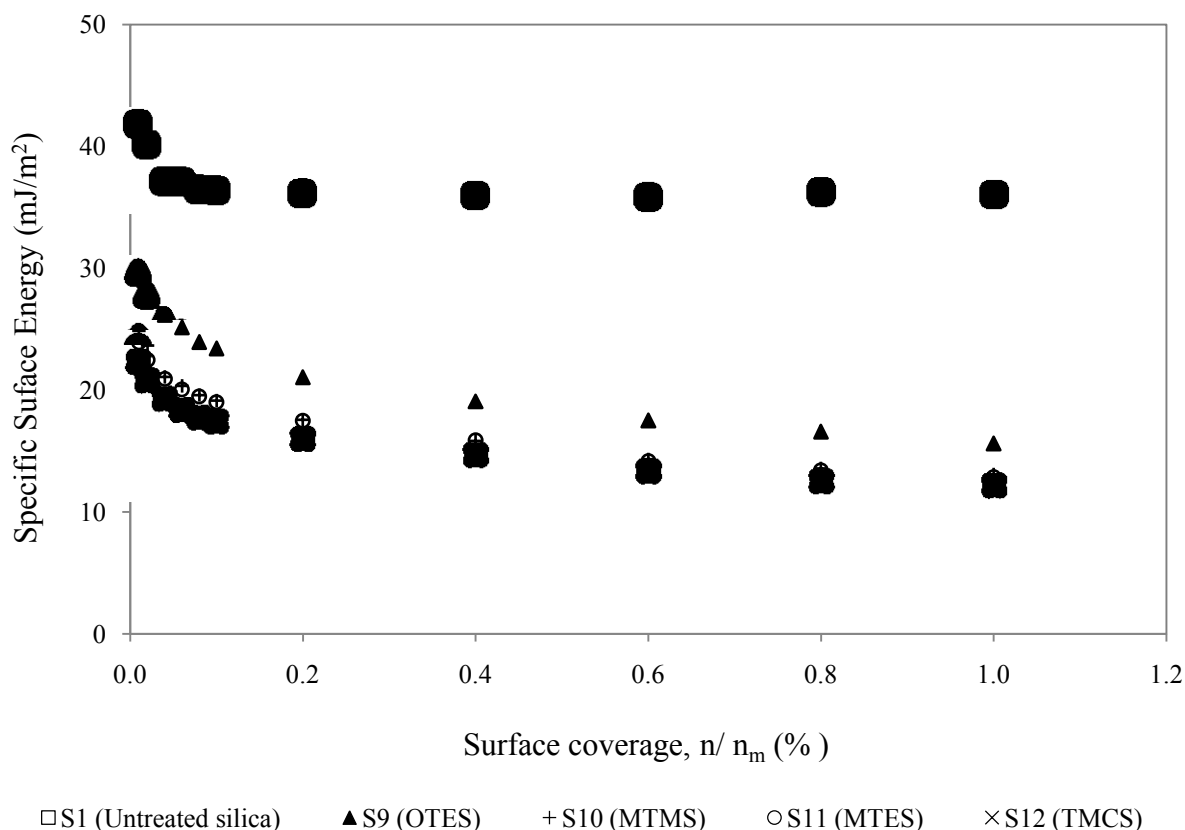


Figure 5.8: Specific surface energy (γ_S^{ab}) profiles as a function of surface coverage for untreated silica and silanised silica with non-coupling silanes.

The γ_S^{ab} profiles resulting from interactions with the polar probes at different surface coverages show a reduction of specific surface energy when the silicas are silanised. The results indicate that silica surface modification has reduced the number of polar functional groups or has covered the polar energetic sites, and thus could reduce the silica aggregation in the elastomer matrix. It is also observed that S6 (DTSPM) and S8 (TESPO/M) exhibit the lowest γ_S^{ab} and a relatively homogeneous γ_S^{ab} surface profile. For S6, this could be due to the coverage of the silica surface by polyether side-chains from the DTSPM, which interact with the silanol groups on the silica surface through

hydrogen bonding. It is likely that the DTSPM silane could have provided a better surface coverage compared to the TESPO silane, which consists of long alkyl functional groups.

TESPO/M is a silane with co-oligomer combining the mercapto-silane, TESPM, with the blocked mercapto-silane TESPO. Thus, S8 (TESPO/M) contains both mercaptosilane (-SH) and long alkyl chain ($-C_7H_{15}$) structures [193]. This structure provides higher surface coverage and a higher degree of reactivity compared to S4 (TESPM) and S7 (TESPO).

5.4.3 Total Work of Cohesion Profiles

The values of the dispersive and specific surface energies of the untreated and modified silica were used to calculate the thermodynamic total work of adhesion (W_{adh}) and cohesion (W_{coh}) using Equations 5.6 and 5.7. The influence of particle surface energy could be directly related to their role in the reduction of cohesive forces between particles [194]. As shown in Figures 5.9 and 5.10, the W_{coh} of S2 to S12 were significantly reduced compared to the untreated silica (S1). Thus the results show that silanising silica with appropriate silanes can act as an aggregate modifier through increasing the particle detachment.

The W_{coh} between untreated silica particle was determined as 150 mJ/ m² at 0.1% surface coverage. For similar surface coverage, it was calculated that the W_{coh} were reduced between 29% and 53% and between 25% to 37%, for silica silanised with

coupling and non-coupling silanes respectively. It is observed again that S6 (DTSPM) and S8 (TESPO/M) show the largest reduction in W_{coh} .

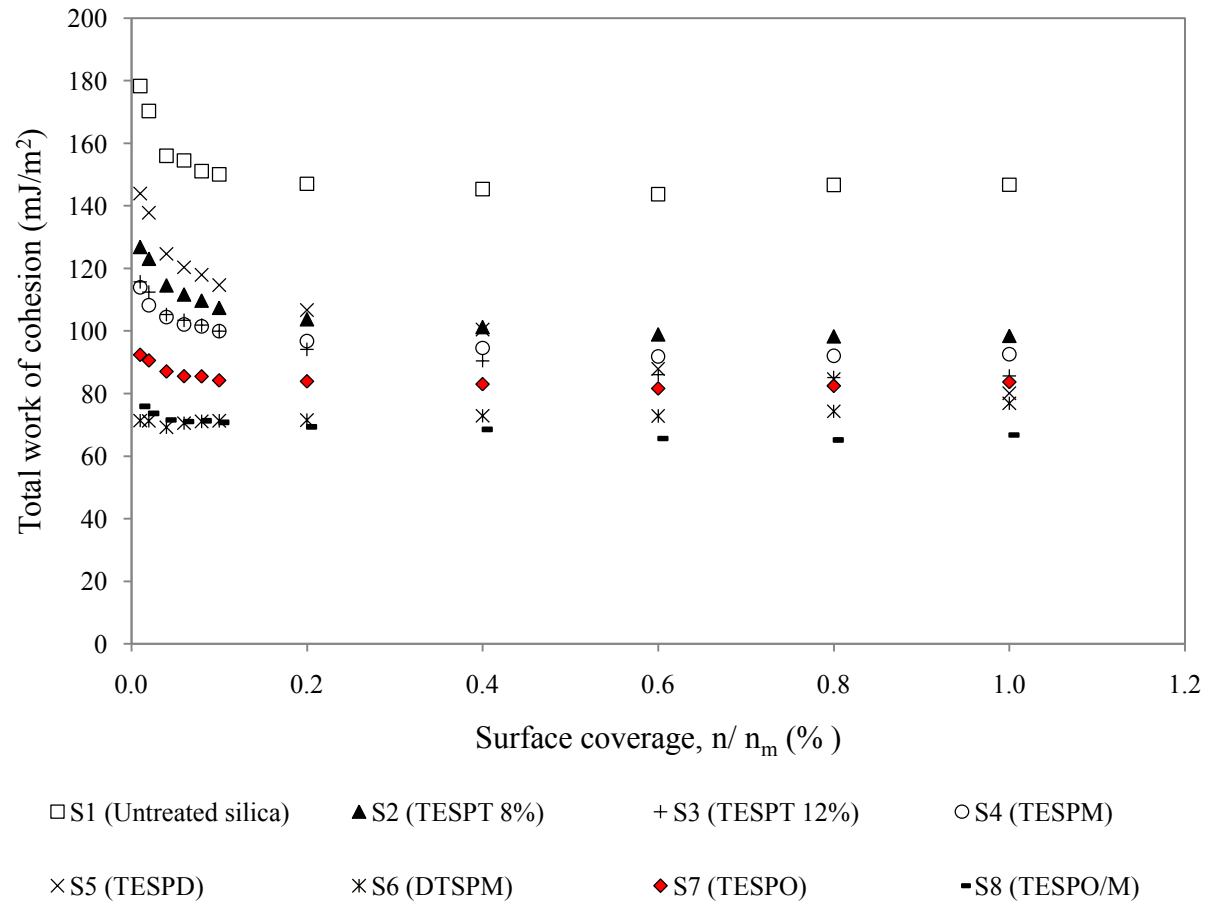


Figure 5.9: Total work of cohesion (W_{coh}) profiles as a function of surface coverage of untreated and silanised silica with coupling silanes.

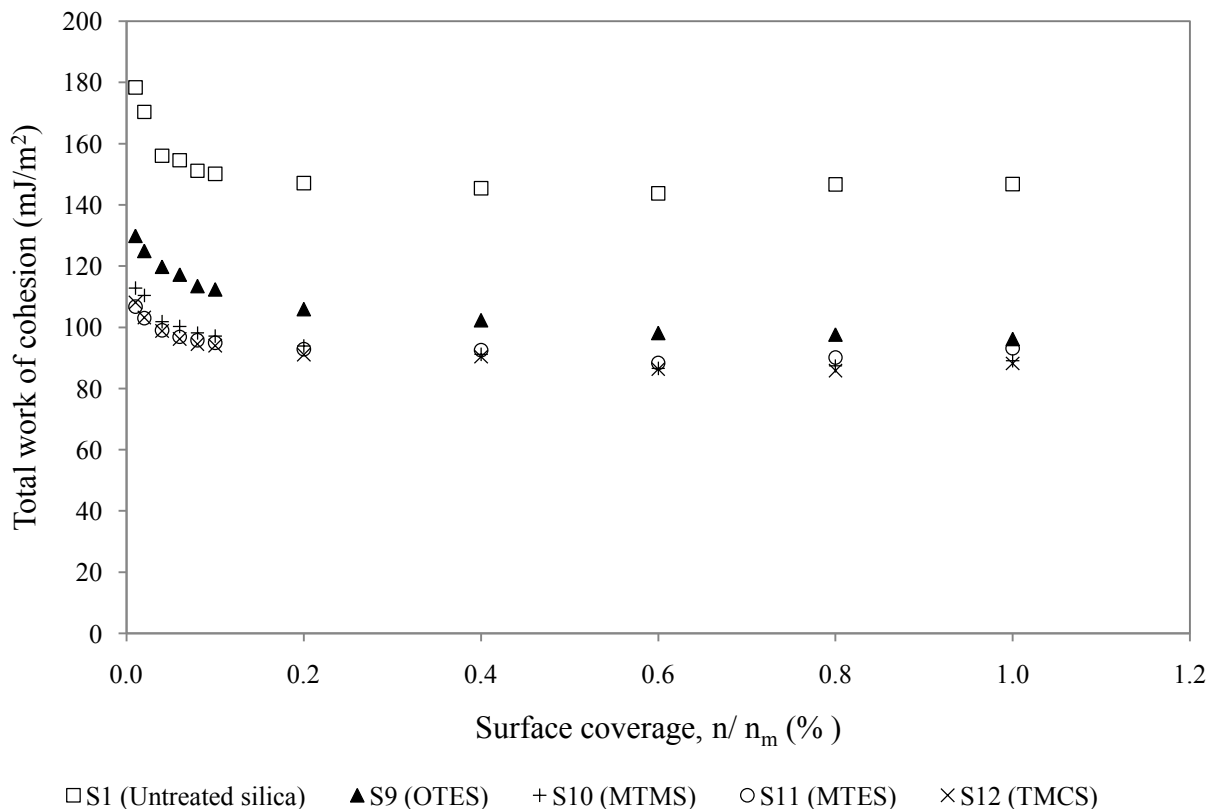


Figure 5.10. Total work of cohesion (W_{coh}) profiles as a function of surface coverage of untreated and silanised silica with non-coupling silanes.

As discussed above, the untreated silica exhibits higher dispersive and specific surface energies compared to silanised silica. The values show the higher adsorption energies of untreated silica by a series of *n*-alkane molecules. This could indicate a stronger interaction between the non-polar elastomer and the untreated silica. However, these values are considered low compared to other types of rubber fillers such as reinforcing grade carbon blacks [195].

On the other hand, the lower adsorption energy of the polar probes, such as toluene and dichloromethane, which associated with a low specific surface energy, and

the calculated total work of cohesion of the silanised silica, indicates that the pronounced aggregation of untreated silica [53] will be reduced when the silica is silanised with coupling and non-coupling silanes.

5.5 Conclusions

In this chapter, the changes in dispersive and specific silica surface energy when the silica surface is silanised were investigated. Surface energy profiles were determined by IGC as a function of surface coverage by the molecular probes at finite dilution.

The γ_S^d profiles of untreated silica (S1) show the heterogeneous nature of the silica surface. Silanisation changes the surface energetic profile. Silanised silicas S6 (DPSPM) and S7 (TESPO) exhibit a relatively homogeneous dispersive surface energy with surface coverage. The silanised silicas with silanes that have similar chemical structure (TESPT and TESP) exhibit similar dispersive surface free energy profiles. The presence of long alkyl chains on the silanised silica significantly reduces the surface energy.

The γ_S^{ab} profiles, determined by applying the vOGC approach and the Della Volpe and Siboni acid-base scale, exhibited similar effects to those observed with the γ_S^d components. However, only silica silanised with DTSPM showed a relatively homogeneous γ_S^{ab} surface profile due to the presence of the polyether side-chains. For this study, running the IGC at finite dilution has enabled surface energy mapping of the silica, while at infinite dilution only the highest energetic sites on the silica surface will be

measured. The W_{coh} of silica was reduced when the silica was silanised. The study has shown that the W_{coh} of silica could be used as an indicator to evaluate the degree of dispersion of silica aggregates, which is discussed in Chapter 6.

CHAPTER 6 SILICA DISPERSION IN ELASTOMER

6.1 Introduction

The mixing of filler into an elastomer system changes the properties of the filled elastomer considerably. Depending on the material parameters and the mixing procedures of incorporating the filler into the elastomer compounds, the filler undergoes different dispersion states, from small aggregates to large agglomerate filler networks.

In this chapter, the macrodispersion and microdispersion of silica in the compounds are investigated to evaluate the effect of the silica surface modified by silanes in the elastomer compounds. As presented in Chapters 4 (TGA-IR) and 5 (IGC), the type of silane has been varied. The IGC (Chapter 5) has shown that the silanes influence the silica surface energy and the silica-silica interactions, such as the work of cohesion. Hence, the dispersion of the silanised silica in the elastomer compounds would be affected.

A reflected light microscope was used to analyse the macrodispersion (for typical agglomerate sizes 1-20 μm) of silica in the filled elastomer vulcanisates. As for the silica microdispersion (for typical aggregate sizes 5-150 nm) in filled elastomer vulcanisates, the samples were evaluated using a TEM-network visualisation analysis. The effects of the work of cohesion of the silica samples were correlated with the microdispersion of the untreated silica and silanised silica aggregates in the elastomer matrix.

6.2 Silica Dispersion in Elastomers

In order to obtain optimal vulcanisate properties, studies have suggested that the filler must be sufficiently dispersed in the elastomer compounds [196,197,198]. Le et al. [199,200] suggested that poor filler macrodispersion is determined by the filler agglomerates (with a size larger than 6 μm) in the elastomer compounds, and is responsible for the decrease in ultimate tensile strength and tearing energy. Microdispersion leading to smaller aggregates of filler lowers the hysteresis and increases resistance to tearing and abrasion of the filled vulcanisates [199].

During mixing of filled elastomer, the silica agglomerates are broken down into smaller agglomerates aggregates, and eventually into small aggregates of a few particles. The dispersion measurement is a direct way of determining the filler dispersion in the elastomer compounds. It is generally analysed to the size of agglomerates and aggregates. These sizes, are often referred to as filler macrodispersion and microdispersion. Traditionally the Philips scale is used in order to classify the degree of macrodispersion of filler in elastomers [201,125]. Macrodispersion measures the filler agglomerates greater than 1 μm in size. As for the silica microdispersion, the typical aggregate sizes are between 5 and 300 nm.

Optical microscopy has long been the preferred method for filler dispersion analysis because of its relative simplicity [202]. Reflected light microscopy has become a popular tool for evaluating the filler agglomerate dispersion [125] and this method is often referred to as providing filler macrodispersion. However, the drawbacks for optical

microscopes are the limit in resolution power due to the wavelength of visible light [202]. As for nanoscale analysis, more complicated and costly methods such as atomic force microscopy (AFM) [203,204] and transmission electron microscopy (TEM) [198] are used. Scanning electron microscopy (SEM) is generally used as a sub-micron microscopy. These sophisticated tools use complex equipment and require long sample preparation and testing times.

For this study, the macrodispersion and microdispersion of the silica were evaluated using an optical analysis system (Dispergrader 1000NT) and a TEM-network visualisation technique respectively. In order to determine the degree of silica dispersion, the silica distribution in the compounds was assumed to be homogeneous.

The sSBR/BR elastomers were reinforced with untreated or silanised silica at 55 parts per hundred parts of rubber (pphr) using a tyre tread formulation as shown in Chapter 3, Table 3.2. The sulfur loading for each vulcanisate was adjusted to normalise the crosslink density of each silica-filled elastomer vulcanisate. This is done due to different sulfur contents of some of the silanes. The mixing was carried out following a three-stage procedure typically used for silica-filled sSBR/BR compounds. For this study, a reactive mixing temperature of 140 °C and above was achieved, and the mixing was continued for at least 4 minutes. This would allow sufficient time for complete silanisation of the untreated silica [205], when silanising by reactive mixing.

Compound CA was prepared through reactive mixing of untreated silica with TESPT at 8% w/w. For comparison purposes, all the compounds (C1 to C12) were prepared following the same mixing procedures.

6.3 Results and Discussion

6.3.1 Silica Macrodispersion Analysis

Figures 6.1 and 6.2 show the SEM micrographs of untreated silica (S1) and a silanised silica (TESPT 8% w/w, S2) at 500x magnification. It is observed that the untreated silica (Zeosil[®] 1165 MP) in micropearl form is broken down during the silanisation process. The SEM micrographs suggest that the silica in micropearl form were broken down by the magnetic stirrer during the silanisation process.

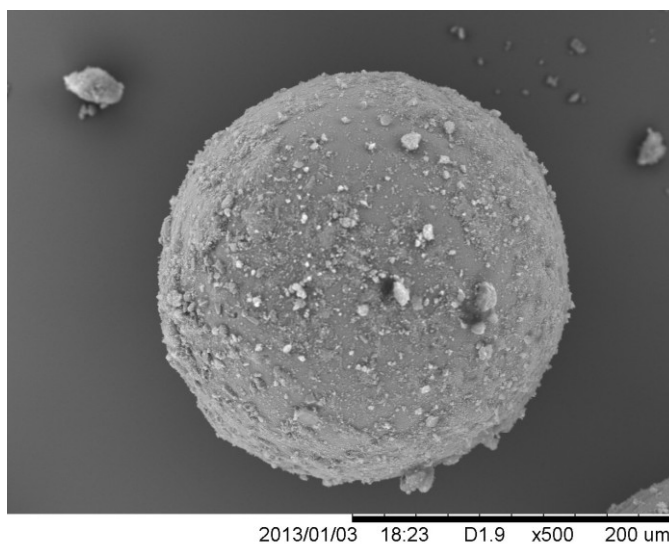


Figure 6.1: SEM micrograph of untreated silica in micropearl form (S1).

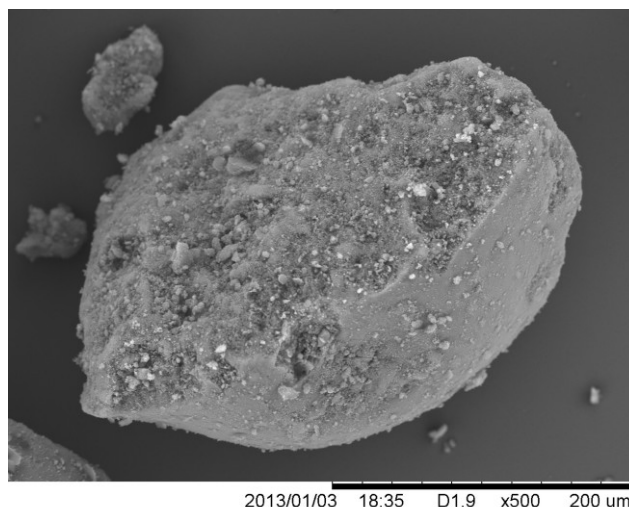


Figure 6.2: SEM micrograph of silica silanised with TESPT 8% w/w (S2).

The silica macrodispersion in filled elastomer vulcanisates was evaluated using an optical analysis system – the Dispergrader 1000NT. Figures 6.3 displays the measured macrodispersion of silica in filled vulcanisates of compounds C1 to C12 and reactively mixed compound CA. The experiments did not reveal significant differences between the untreated silica compound (C1) and the rest of the silanised compounds (C2-C11), except possibly for compound C12. This probably not surprising, as the extended mixing used in reactive mixing would be expected to break down almost all of the silica agglomerates into aggregates too small to be detected by this technique.

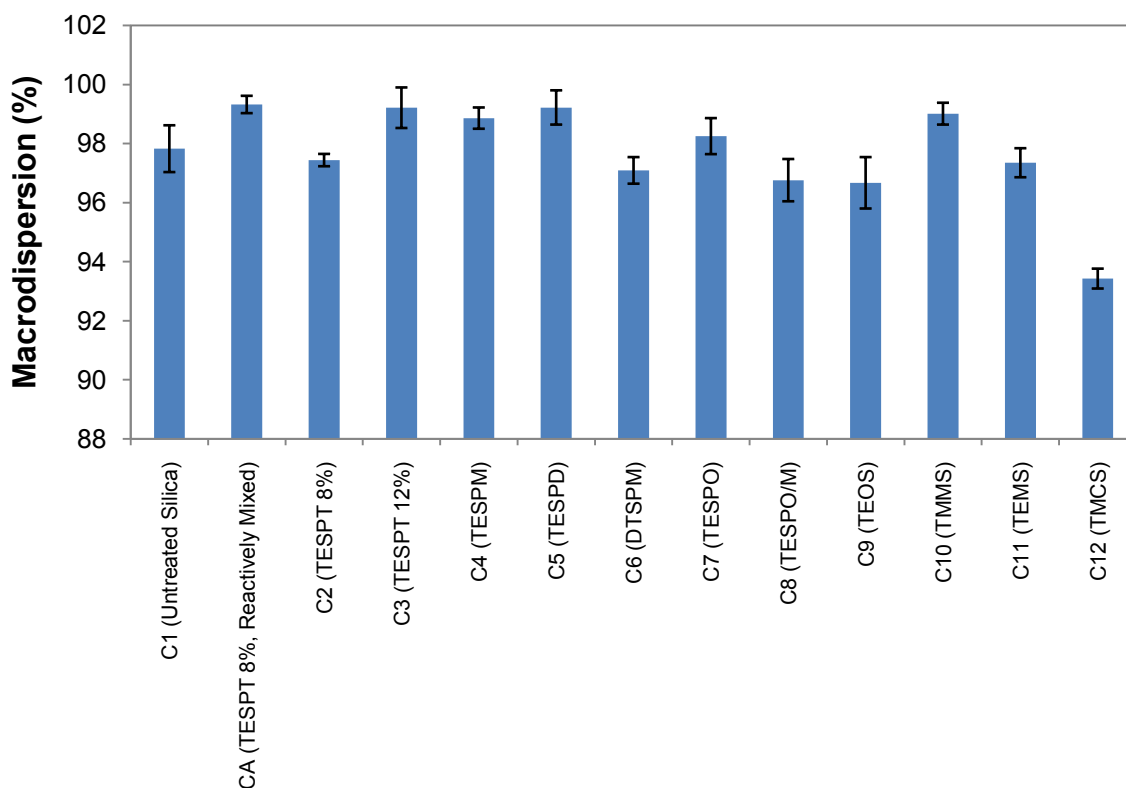


Figure 6.3: Macrodispersion of silica-filled elastomer vulcanisates containing untreated or silanised silica.

6.3.2 Silica Microdispersion Analysis

Figure 6.4 shows the TEM micrographs of untreated silica (S1). The silica microdispersion in the filled elastomer vulcanisates was evaluated by TEM network visualisation analysis [206]. The TEM micrographs of the silica-filled elastomer vulcanisates at a magnification setting of 22,000x were analysed to determine the surface area of each silica aggregate in the images using Image Pro Plus 6.1 software. For this study, aggregates larger than about 100 nm² in area were included in the count and objects touching the borders were excluded. Two sets of five micrographs were analysed initially for each sample to obtain an average aggregate size distribution.

Fresh compounds were then prepared in every case apart from C8 and C10-C12 and a further five micrographs analysed using these. The results were then combined to give average aggregate size distributions from fifteen micrographs in most cases, or from ten micrographs in the case of compounds C8 and C10 to C12.

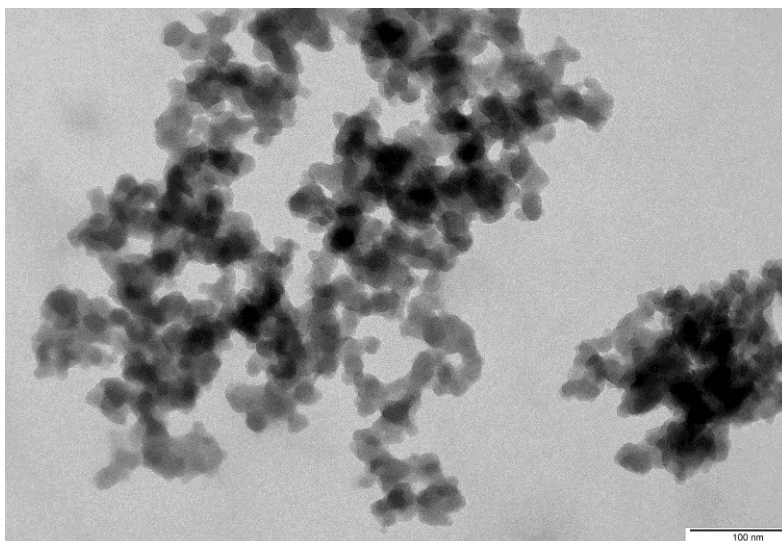
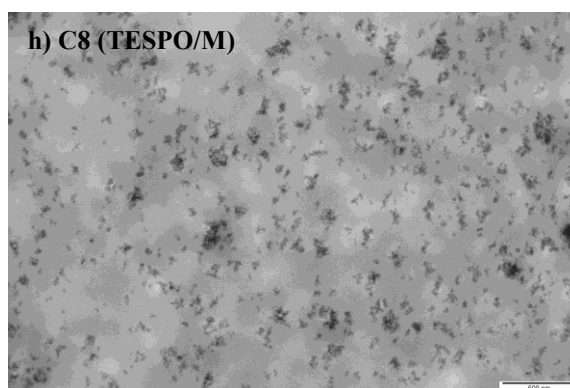
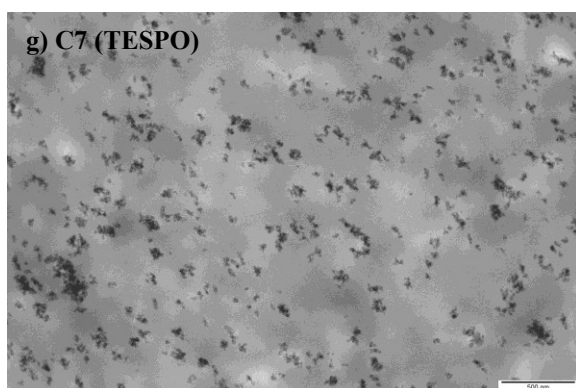
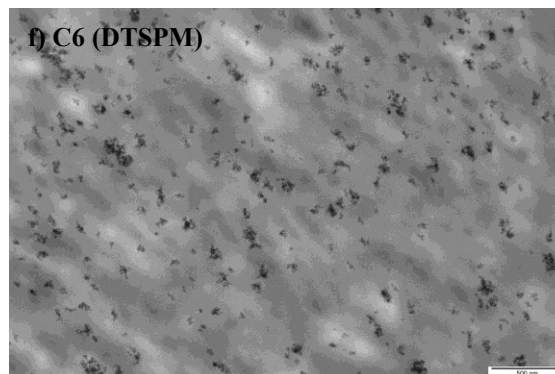
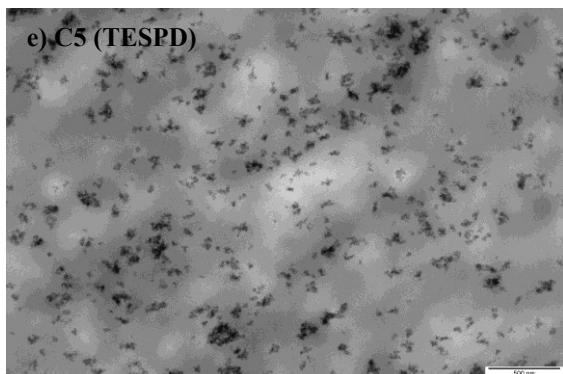
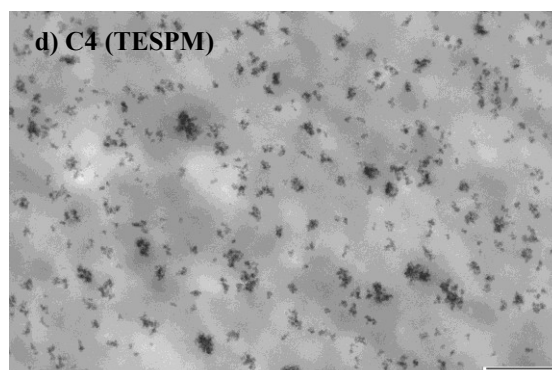
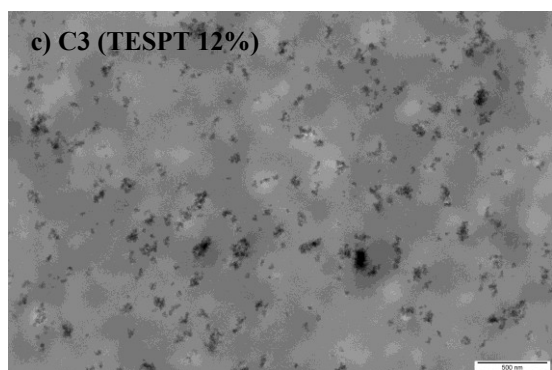
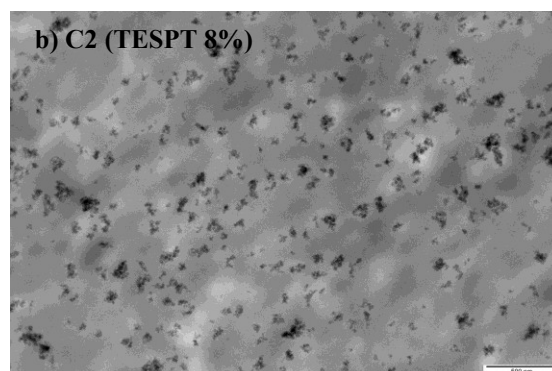
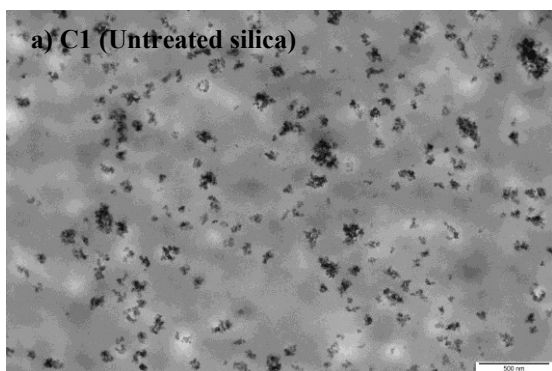


Figure 6.4: TEM micrograph of untreated silica (S1).

A method has been developed to determine filler aggregate distribution in the elastomer matrix, which is based on a 'TEM-network visualisation' technique and is described above in the experimental section (Chapter 3) [206]. In the procedure, the styrene swelling and polymerisation has spread the silica aggregates, enabling the individual aggregates to be readily distinguished in the micrographs. Thus, the technique provides a method for evaluating the distribution of silica aggregate sizes, unlike in normal TEM, where overlap of the aggregates makes analysis of their size distribution very difficult, even at silica levels much lower than those normally used in tyre compounds. Figure 6.5 shows typical TEM micrographs of the silica-filled elastomer vulcanisates for compounds C1 to C12, containing silicas S1 to S12, respectively as well as compound CA where the untreated silica was silanised with TESPT 8% w/w through reactive mixing in the internal mixer.



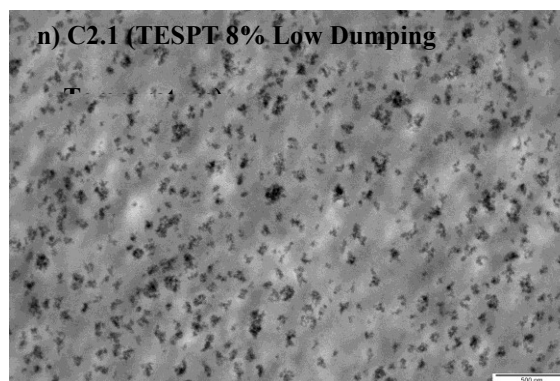
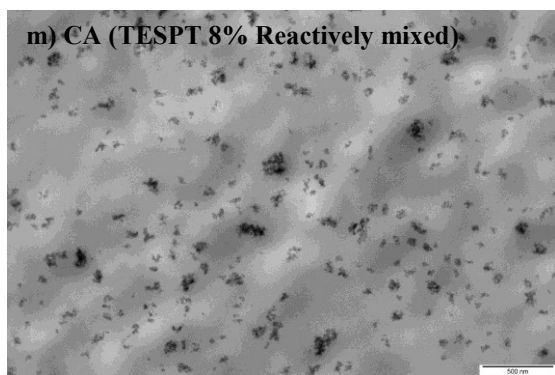
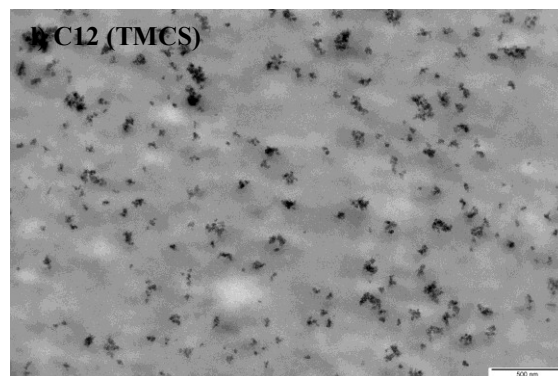
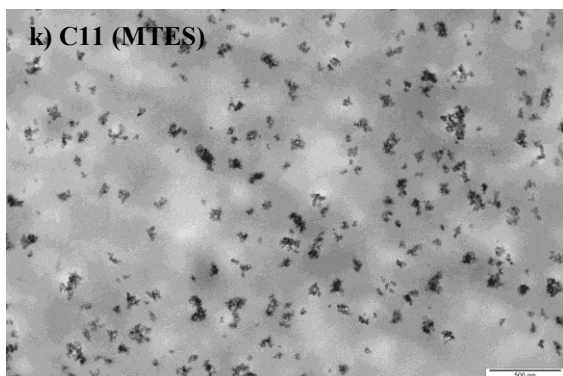
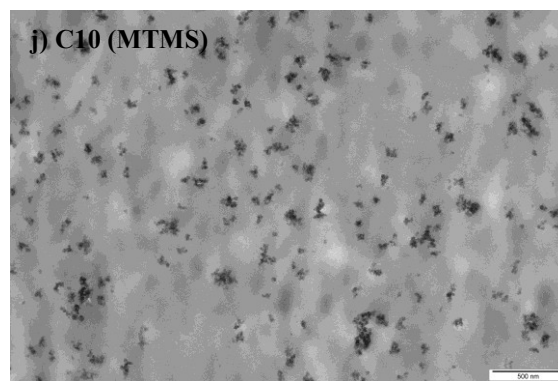
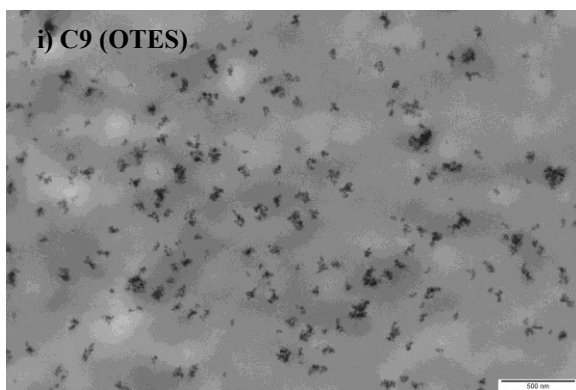
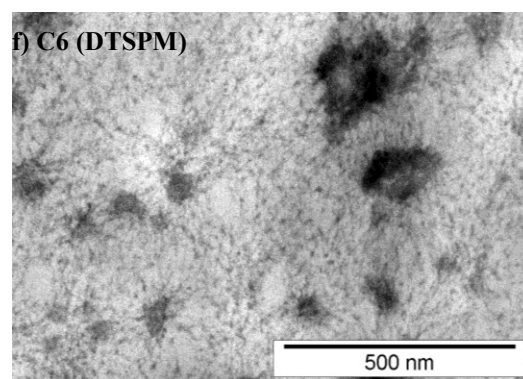
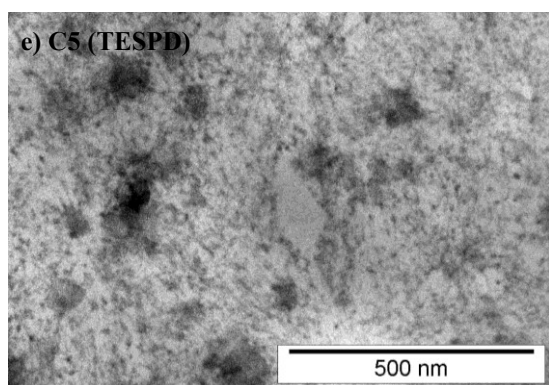
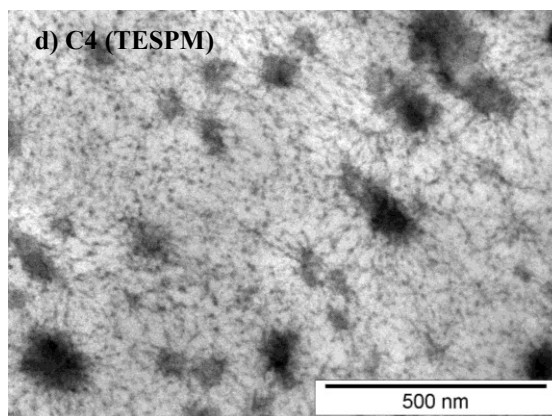
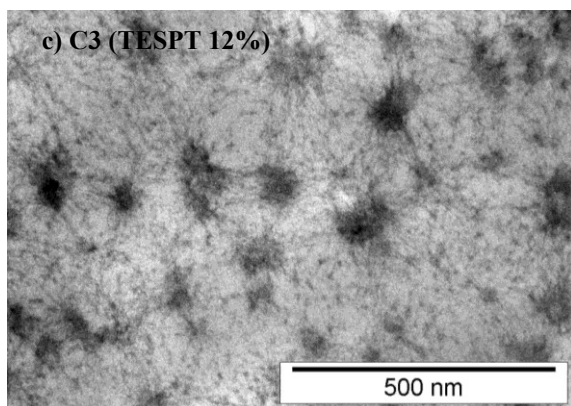
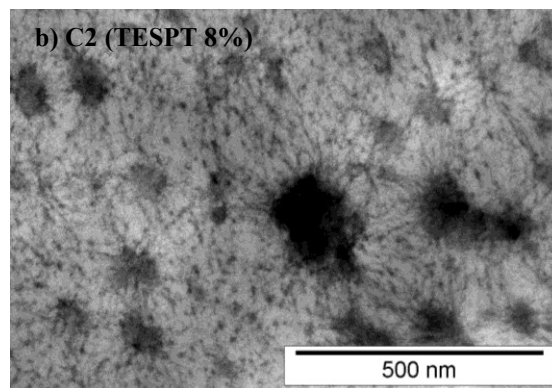
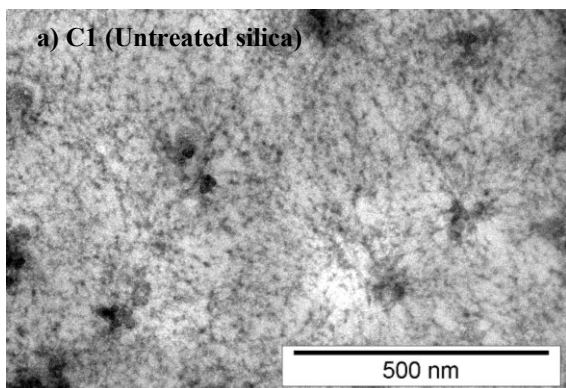
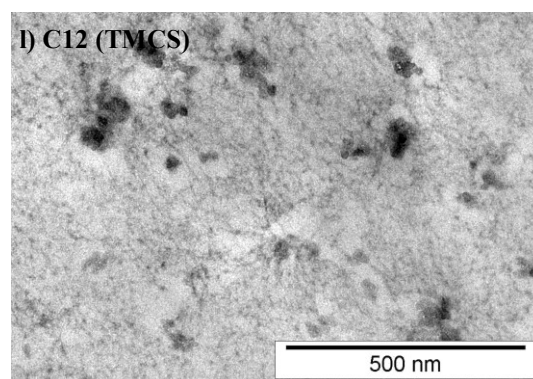
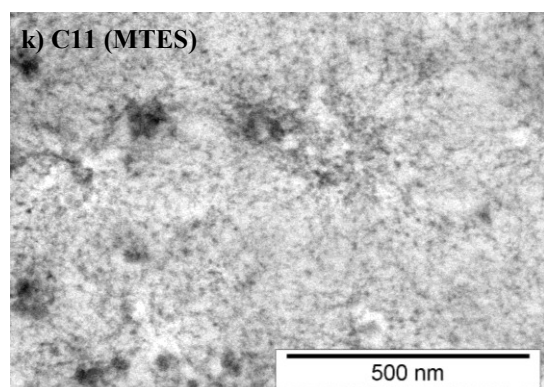
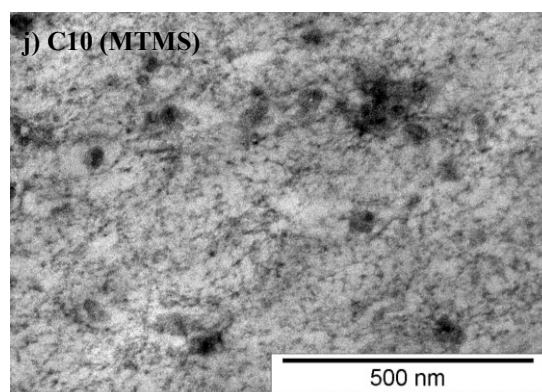
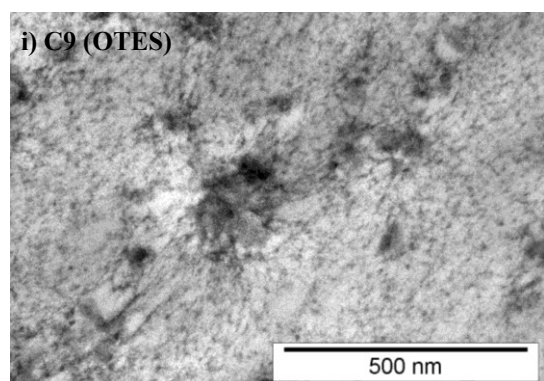
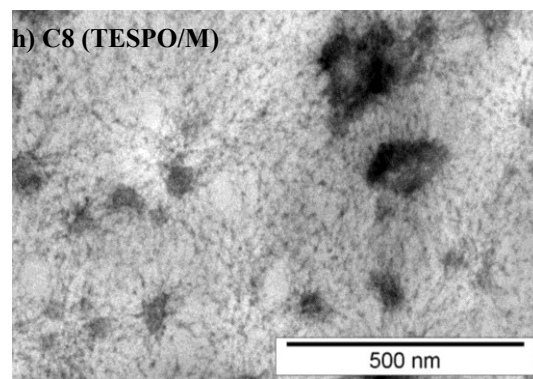
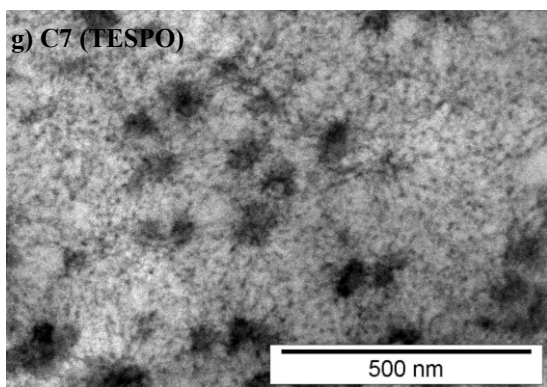


Figure 6.5: TEM micrographs of silica-filled elastomer vulcanisates containing untreated or silanised silica.

From the TEM micrographs shown in Figure 6.5, the microdispersions of the silica in the elastomer appear to be similar. However, a relatively greater proportion of larger silica aggregates are apparent in C1, the untreated silica-filled elastomer vulcanisate. As anticipated, without silane treatment, the higher degree of silica interaction resulted in poor microdispersion for C1. Similar conclusions were drawn by Castellano et al. [207] when they compared untreated silica and silica silanised with TESPT. In their study, the TEM micrographs were prepared without going through styrene swelling and polymerisation process for their compounds, which were filled with only 35 pphr of untreated or modified silica, and it is much more difficult to distinguish the silica aggregates.

Through 'TEM-network visualisation' technique, evidences of coupling between silica silanised with coupling silanes and elastomer were observed in Figure 6.6 (C2 to C8 and CA), when the silica-filled elastomer vulcanisates were stained with osmium tetroxide vapour for 1 hr. The staining effect revealed the elastomer network distribution in the vulcanisates surrounding the silica aggregates silanised with coupling silanes were significantly different from that in C1 (untreated silica), C9 to C12 (silica silanised with non-coupling silanes) and C2.1 (silica silanised with TESPT 8% w/w but dumped at 145 °C). For example, tight elastomer networks were observed coupled to silica aggregates in Figure 6.6 (b), in contrast with vacuoles (or voids) were observed surrounding the silica aggregates where there is no coupling silanes, which are most evident in Figure 6.6 (I).





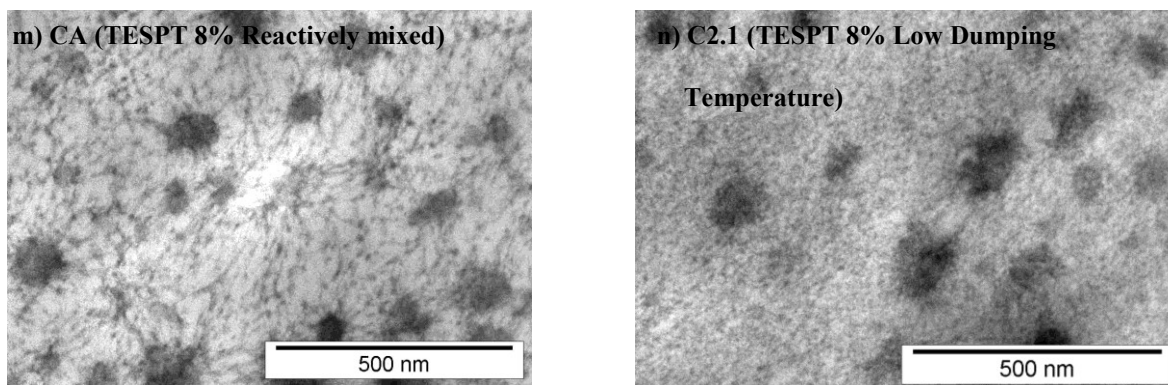


Figure 6.6: TEM micrographs of stained silica-filled elastomer vulcanisates containing untreated or silanised silica.

The cumulative silica aggregate size distributions, calculated from image analysis of the micrographs are plotted in Figures 6.7 to 6.9. An additional compound (CA) was prepared in this study where the silica was silanised with TESPT (8% w/w) through reactive mixing during elastomer compounding. Commercially, the elastomer industry normally follows this procedure, rather than using silica that has been silanised prior to mixing with the elastomer. The mixing conditions were similar to those used for the rest of the silica-filled compounds prepared for this study, to ensure that all the compounds underwent a similar thermal and mechanical history.

It is apparent that the silica microdispersions in C2 and CA are very similar, as shown in Figure 6.7. This indicates that the silica has been efficiently silanised during the reactive mixing. It also appears that, as might be anticipated, the silanes have improved the microdispersions, for silica silanised with both coupling and non-coupling silanes. This correlates with the findings from the surface energy analysis where the total work of cohesion of the silanised silicas was reduced compared to untreated silica

(S1), discussed above. It is also observed that the silica microdispersions in C2.1 (Figure 6.7), which was reactively mixed with TESPT 8% w/w but the compound was dumped at 145 °C, showed lower microdispersion compared to C2 and CA. Figures 6.5 and 6.6 also show a relatively greater proportion of larger silica aggregates are apparent in C2.1 and less formation of elastomer networks surrounding the silica particle in C2.1 respectively. This indicates that a limited amount of silica-elastomer coupling has occurred during the mixing for C2 and CA and prevented the reaggregations of silica.

The network visualisation TEM micrographs showed that the microdispersions of silanised silicas are fairly similar. For silica silanised with coupling silanes (see Figure 6.7), the microdispersions appear to be almost identical. From Figure 6.8, it is observed that the microdispersion of silica silanised with non-coupling silanes appears better in the C12 vulcanisates; C9, C10 and C11 are very similar. In C12 the silica was silanised with TMCS of the non-coupling silanes, silanisation with TMCS led to the lowest work of cohesion (Chapter 5). The TGA data analysis shows the silanisation efficiencies and the TMCS is actually relatively low.

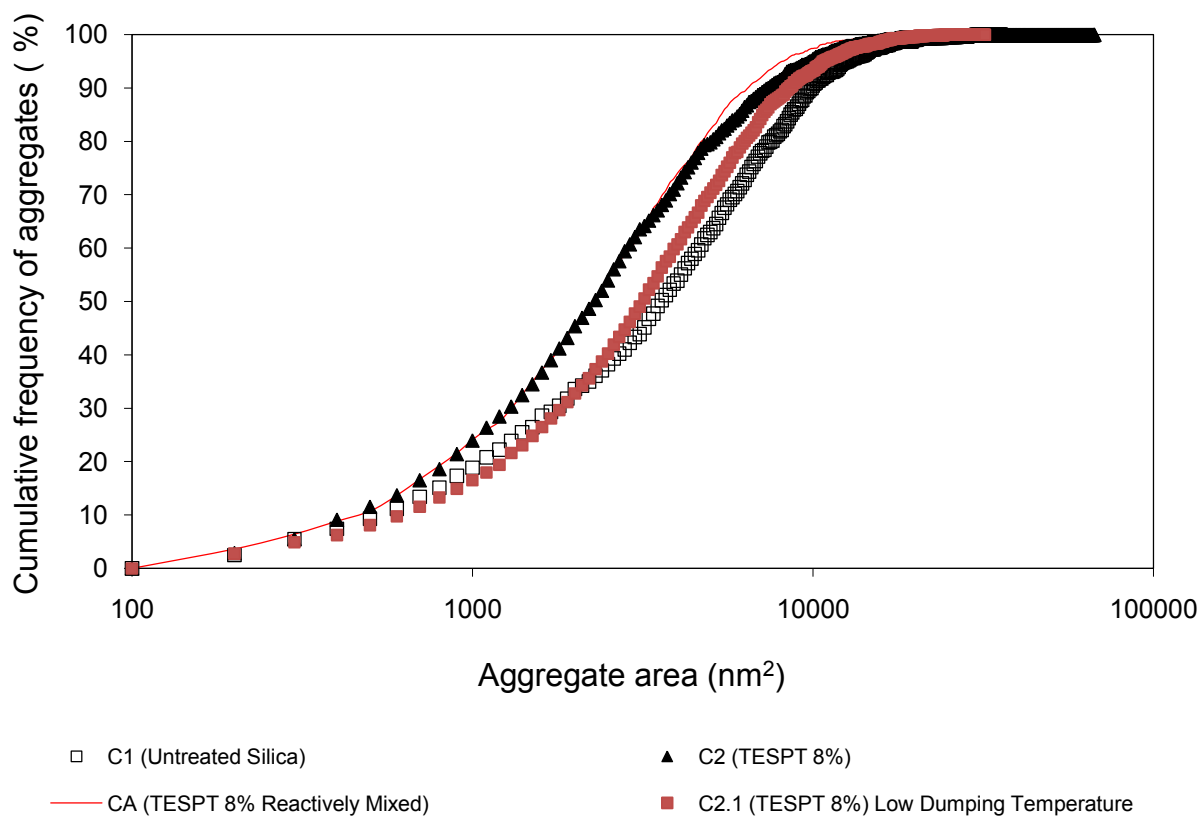


Figure 6.7: Cumulative aggregate size distributions in elastomer vulcanizates containing untreated silica and silica silanised with TESPT.

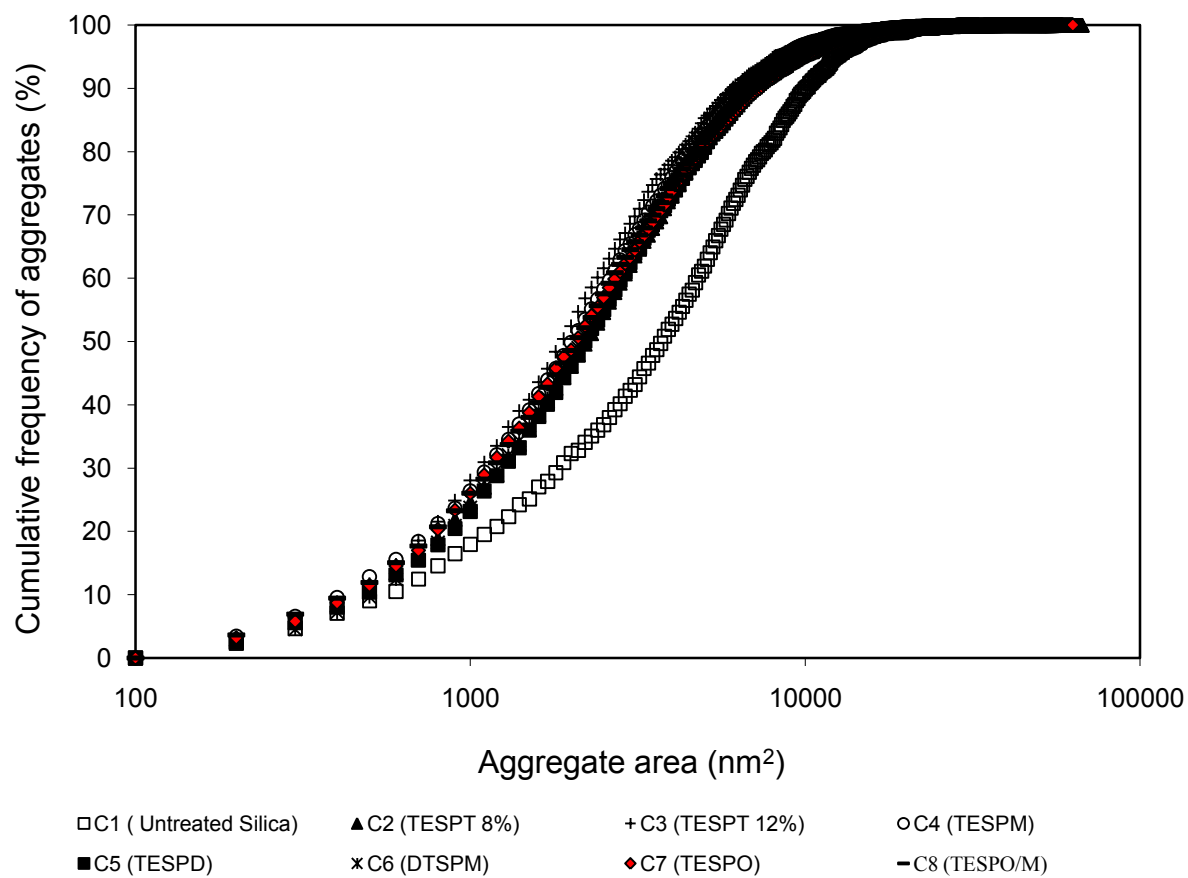


Figure 6.8: Cumulative aggregate size distributions in elastomer vulcanisates containing untreated silica and silanised silica with coupling silanes.

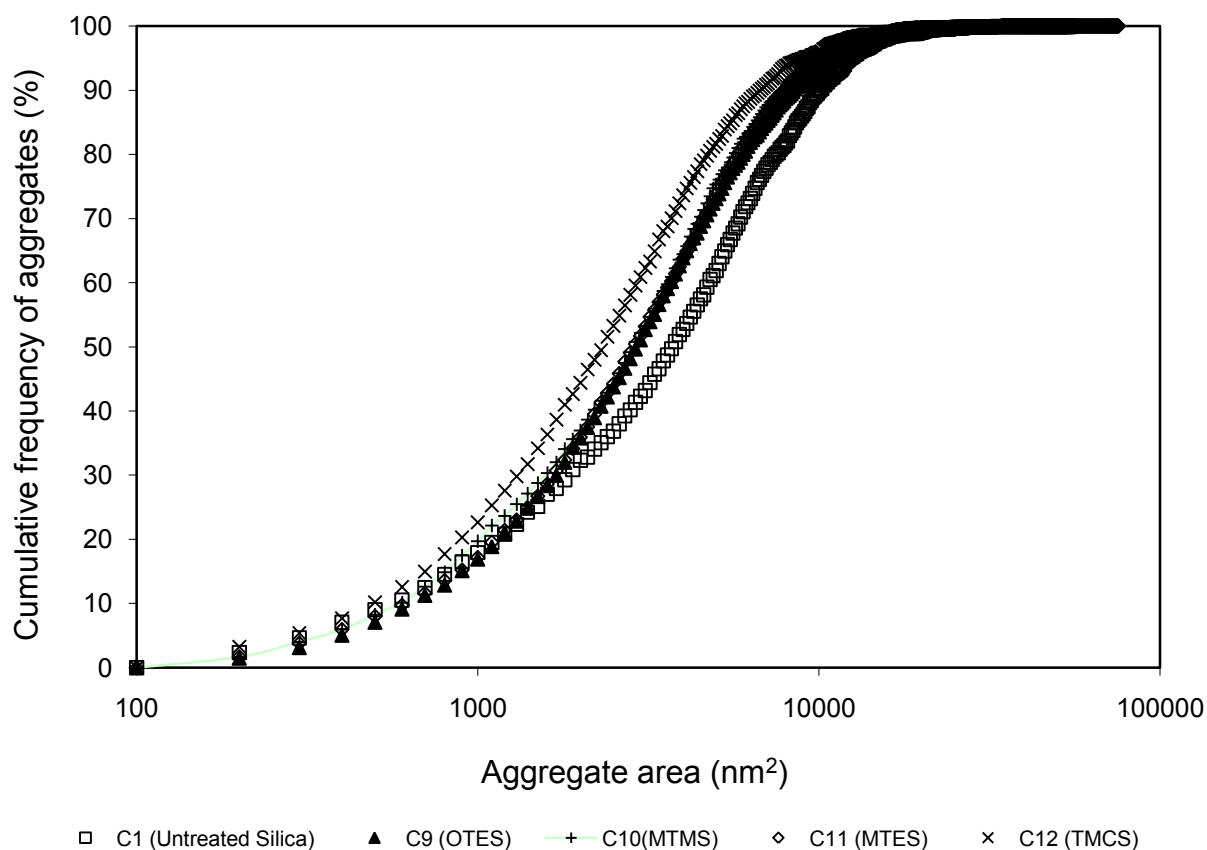


Figure 6.9: Cumulative aggregate size distributions in elastomer vulcanisates containing untreated silica and silica silanised with non-coupling silanes.

Figure 6.10 displays the correlation between silica surface area at 50% cumulative frequency in the elastomer vulcanisates and the total work of cohesion at 0.1% surface coverage (determined through IGC measurements, Chapter 5) for untreated silica and silanised silica. The results show that the dispersibility of silica in the sSBR/BR elastomer matrix was improved with decreasing total work of silica cohesion. The binding of coupling or non-coupling silane on the silica surface, has led to improvement in silica aggregate microdispersion in the sSBR/BR elastomer matrix. The coupling silanes are intended to couple with the sSBR and BR polymer chains through their sulfur-containing groups during the sulfur vulcanisation, rather than during mixing

of silica with elastomer. However, in the case of the more reactive coupling silanes containing -S-S- or -SH groups i.e. all apart from the protected TESPO, it is likely that a limited amount of premature coupling to the polymer would occur during the mixing [208].

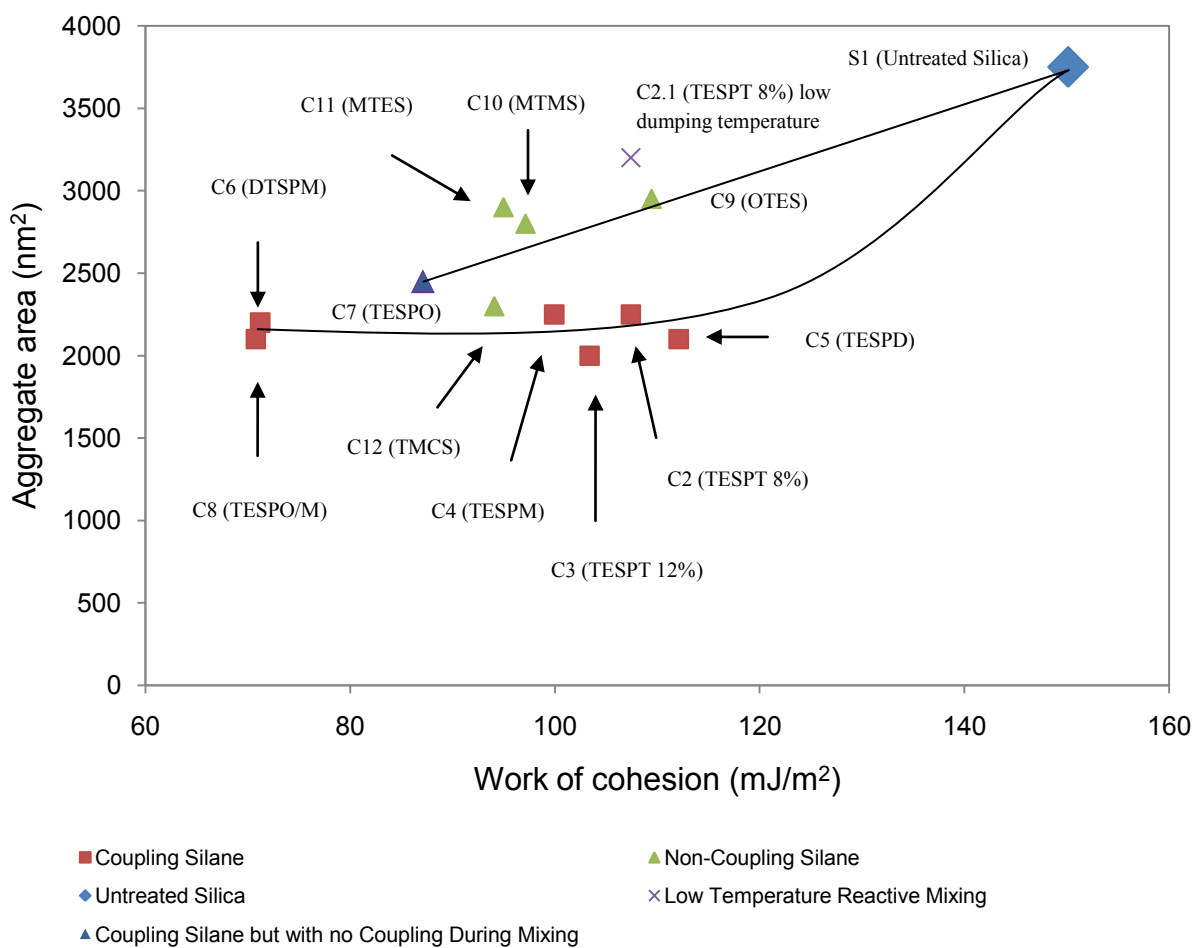


Figure 6.10: Correlation between silica surface area at 50% cumulative frequency in the elastomer vulcanisates and the total work of cohesion at 0.1% surface coverage for untreated and silanised silica.

However, as shown in Figure 6.10, the results appear to split into two groups. In the case of the non-coupling silanes, and one of the coupling silanes, TESPO, there is a steady decrease in aggregate size with decreasing work of silica cohesion, as the silica surface is modified. In the case of the coupling silanes apart from TESPO, all the modified silicas have similar microdispersions, and the aggregate sizes are significantly lower than observed with the first group of mainly non-coupling silanes, and than expected simply from the decreasing work of cohesion. This indicates that there may be a second factor improving the microdispersion.

Any coupling of silica to polymer occurring during mixing should show up as a significant increase in bound rubber in the mixed uncured compound. The bound rubber contents are compared in Figure 6.11. They show a clear distinction between the untreated silica, or silica treated with TESPO or the non-coupling silanes, and silica treated with the other coupling silanes. This is very good evidence that a limited amount of silica-elastomer coupling has occurred during the mixing, even though the dump temperatures, measured within the dumped compound, were all kept below 165 °C, and were generally between 150 °C and 160 °C. The amount of coupling occurring during mixing appears to follow the expected order of reactivity, i.e. $\text{--SH} > \text{tetrasulfide} > \text{disulfide}$. Any premature coupling occurring during mixing, however limited, would be expected to increase the viscosity of the compound and thus the shear forces breaking up the silica agglomerates. In addition the coupling may also lock in the dispersion, preventing reagglomeration, or flocculation, of the filler, which has been reported to occur on storage after mixing [209,210,211,212]. The results suggest that

microdispersion is dependent on both the surface properties of the silica and whether any silica-elastomer coupling occurs during the mixing process; its extent will be decided by end of the mixing process.

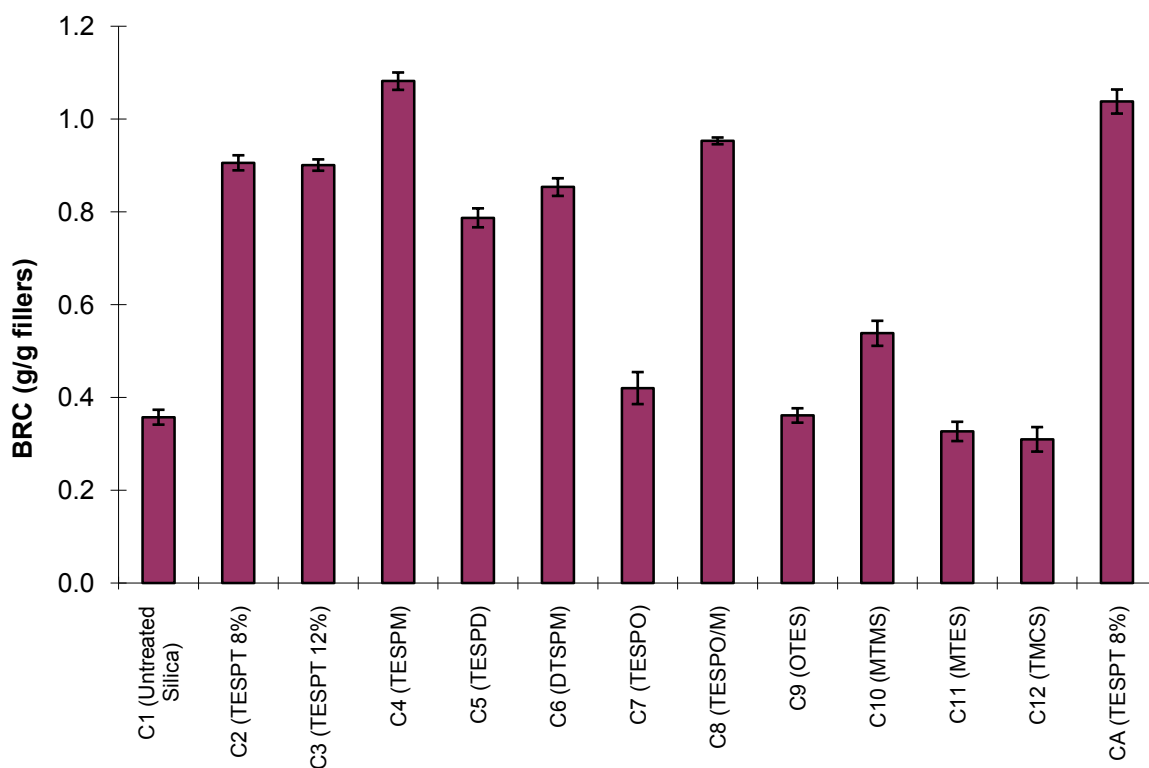


Figure 6.11: Bound rubber content (BRC) of compounds C1 to C12 and CA.

Reducing the mixing temperature will reduce or avoid any premature coupling. This was indicated when reactively mixing with silica and TESPT, (compound C2.1). In this case the extent of TESPT grafting is also likely to be decreased. It is clear that reducing both premature coupling and silanisation has led to a much smaller improvement in microdispersion.

6.4 Conclusions

In this chapter, the effects on macrodispersion and microdispersion of the silanised silicas in an sSBR/BR elastomer matrix were investigated. The SEM micrographs show evidence of untreated silica having been broken down during the silanisation process. The macrodispersion analysis showed possibly slightly fewer silica agglomerates when the silicas were silanised with coupling silanes. However, any differences in macrodispersion may not be significant. This is probably not surprising considering the extended mixing procedures used.

TEM micrographs, obtained by a network visualisation procedure, have provided a good estimation of silica microdispersion in the elastomer matrix. The results showed that silanising silica, using coupling or non-coupling silanes, improves the microdispersion in the elastomer matrix. As shown in Figure 6.10, silica modification with the non-coupling silanes and the protected coupling silane, TESPO, leads to a steady improvement in microdispersion with decreasing work of cohesion. In the case of the more reactive coupling silanes, TESPM, TESPO/M, DTSPM, TESPT and TESPD, there is a further improvement in microdispersion. This is believed to be due to a small

amount of coupling between silica and elastomer has occurred during mixing, which has been demonstrated by bound rubber measurements.

It is interesting to note that a small amount of premature coupling during mixing seems to be beneficial, as normally great care is taken to limit premature coupling by controlling the mixing temperature, and indeed silane coupling agents have been developed or proposed to avoid concerns about premature coupling and elastomer crosslinking. Of course, there is need to avoid more than a small amount of premature coupling or crosslinking, as this will make the compound too stiff to handle or even 'scorch' the compound.

Effective silica microdispersion in the elastomer is believed to lead to improvements in key physical and mechanical properties in filled-elastomer vulcanisates, which will be discussed in the following chapters. It is worth noting that the work of adhesion of silica to elastomer and the interfacial coupling between the silica and the elastomer chains would also have an effect on the filled-elastomer vulcanisate mechanical properties.

This chapter has demonstrated that an understanding of particle surface chemistry is important for determining the effectiveness of particle microdispersion.

CHAPTER 7 RHEOLOGICAL CHARACTERISATION.

7.1 Introduction

The reinforcing silica filler, which can be more than 40% of tyre tread compounds, plays a key role to achieve the desired mechanical properties in elastomer vulcanisates. The rigid particles, with active functional groups present, have a strong impact on the static and dynamic behavior of the elastomer. The IGC analysis showed that the specific surface energy, γ_s^{ab} profiles of the silanised silicas were reduced, compared with the untreated silica, indicating that the hydrophilic or the polar behaviours functional groups on the silica surface or their numbers has been reduced. The effects of silica surface modification were shown by the TEM-network visualisation study, where the aggregate microdispersion of the modified silicas in the elastomer phase was greatly improved.

In this chapter, various experimental techniques are used to evaluate the effect of different silane modifications in elastomer compounds in particular on the Mooney viscosities and cure characteristics. The attached silane species on the silica surface determine the silica surface energy, work of cohesion between silica, and hence its dispersion efficiency and interaction with elastomer chains. All of the silanes influence silica-silica interactions, and hence the degree of the silica network, whereas silica grafted with coupling silanes contributes to the crosslinking between the silica and the elastomer. The degree of the silica network affects the filler volume fraction and the reinforcement behavior.

The study in this chapter provides a better insight into the effect of silica modified with different silanes on the rheological properties of the silica-filled compounds.

7.2 Rheological Investigation

Knowledge of elastomers processability or the rheological properties is essential when these materials are subjected before crosslinking to steady shearing deformation, such as calendaring and extrusion during the production of elastomer components. Elastomeric materials exhibit non-classical properties, such as non-Newtonian viscosity, viscoelasticity and thixotropy.

Quantitative analysis of uncured elastomers started in the 1920s. Marzetti of Pirelli proposed the use of a capillary rheometer, also known as an extrusion rheometer, and Williams developed a parallel plate compression plastometer [213]. Since then Mooney proposed a shearing disc viscometer.

However, it was found that the disk shaped rotor does not induce a viscometric flow field due to edge effects, resulting in higher yield shear stresses than expected [214]. Besides that, the presence of elastic memory, stress relaxation and recoil of elastomers during disk shearing may contribute to sample slippage in the chamber [213]. The geometry of the rotor and cavity were redesigned, grooves and a pressurised chamber were developed to overcome these issues.

After World War Two, and the development of the Mooney shearing disk viscometer, Mooney rheometers have been most widely used to investigate the rheological properties of elastomers and elastomer compounds.

7.2.1 Mooney Viscometer/ Crosslinking Process Analysis

The primary application of rheological measurements on compounded elastomer is to investigate the processing properties after the compounding steps. The viscosities of elastomers are temperature dependent. The material is less viscous at higher temperatures. The viscosity of the elastomer or elastomer compound can be measured by the following methods:

- a) Rotational viscometers
- b) Capillary rheometers
- c) Oscillating rheometers
- d) Compression plastimeters

The most commonly used method to investigate the viscosity of an elastomer is using a rotational viscometer. Melvin Mooney developed the Mooney viscometer and this has been used since the 1930s [215]. The Mooney viscometer consists of a chamber in which a disk-shaped rotor turns within the heated elastomer, while the torque and rotor speed measurements are continuously recorded and converted viscosities units (Figure 7.1). In the current study viscosity measurements were carried out one day after the final stage of mixing using a WAV3 Mooney viscometer (Wallace Instruments Ltd., UK). The silica-filled elastomer compounds (approximately 25 g of

compound) were preheated at 100 °C for one minute before the rotor (38.1 mm diameter) started and then the Mooney viscosity (ML_{1+4}) was recorded for 4 minutes at 2 rpm [216]. The compounds were tested using a large rotor.

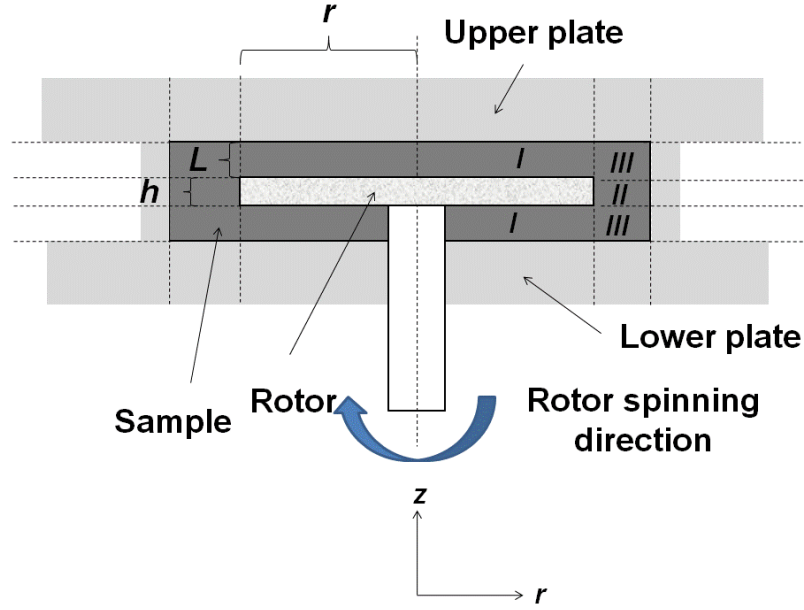


Figure 7.1: Typical schematic diagram of Mooney viscometer [217,218].

In the absence of slippage, the shear rate, γ_r , at the periphery of the rotor between the parallel plates is expressed as follow:

$$\gamma_r = \frac{rv}{L} \quad (7.1)$$

where the γ_r is the shear rate, r is the radius of the rotor, v is the angular velocity (rotor speed), L is the distance of the separation of the plates and h is the height of the rotor plate. The total torque, T that is exerted from the rotor consists of sections I and II (Figure 7.1),

$$T = T_I + T_{II} \quad (7.2)$$

where the T is proportional to the reading of the dial on the rheometer, and T_I and T_{II} are the torque exerted from sections I and II respectively. It is assumed that the influence of section III is negligible [218]. The torque developed between the two parallel plates is

$$T_I = 2 \int_0^r \sigma_z r (2\pi r dr) \quad (7.3)$$

where σ_z is the shear stress which corresponds to γ_r . The torque exerted in the concentric cylinders is

$$T_{II} = \sigma_r 2\pi r^2 h \quad (7.4)$$

where σ_r is the shear stress in section II.

As for the crosslinking reaction characteristics of the silica-filled elastomers, a rotorless Moving Die Rheometer (MDR) 2000 (Alpha Technologies Ltd., UK) was used. Figure 7.2 is a schematic diagram of a sealed bi-conical die rheometer. Each sample weighed approximately 5 g and these samples were tested under isothermal conditions (172 °C) with constant strain (0.5 ° arc) and frequency (1.667 Hz).

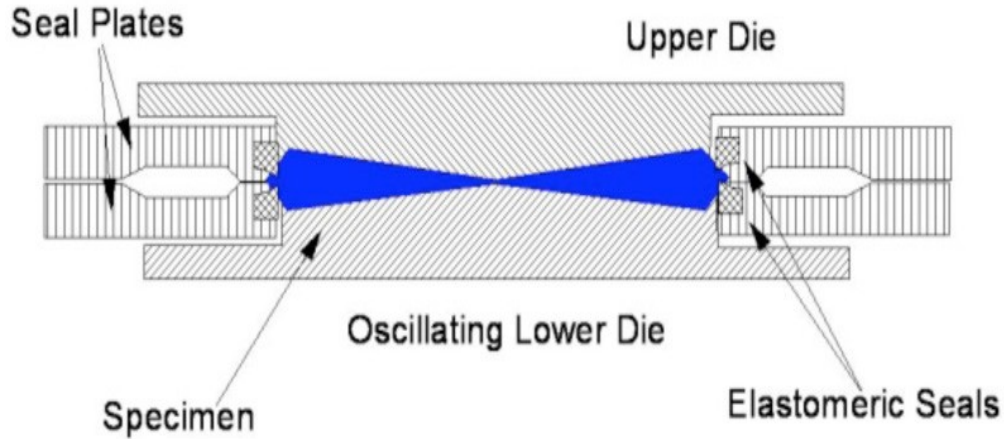


Figure 7.2: Schematic diagram of a sealed bi-conical dies of MDR 2000 rheometer [219].

In the absence of slippage, the shear rate in the bi-conical rotor, would be roughly constant and uniform and is expressed as

$$\gamma_r = \frac{v}{\beta} \quad (7.5)$$

where the β is the angle between the upper platen and rotor, and v is the rotor rotation rate.

7.3 Results and Discussion

7.3.1 Rheological Analysis

The Mooney viscosities of the uncured untreated and silanised silica-filled elastomer compounds are presented as a function of time when the compounds were continuously heated from 1 to 4 minutes at 100 °C after a 1 minute preheated conditioning. C1 is the untreated silica-filled sSBR/BR compound and C2 to C8 are the compounds containing silica silanised with coupling silanes. These compounds were silanised with TESPT

(8%), TESPT (12%), TESPM, TESP, DTSPM, TESPO and TESPO/M silanes, respectively. Compound CA was prepared where the untreated silica was silanised with TESPT (8% w/w) through reactive mixing in the internal mixer. As for the silica silanised with non-coupling silanes, the uncured compounds are denoted by C9 to C12. These silanes were OTES, MTMS, MTES and TMCS, respectively. Figure 7.3 shows the Mooney viscosity of silica-filled elastomer compounds silanised with TESPT.

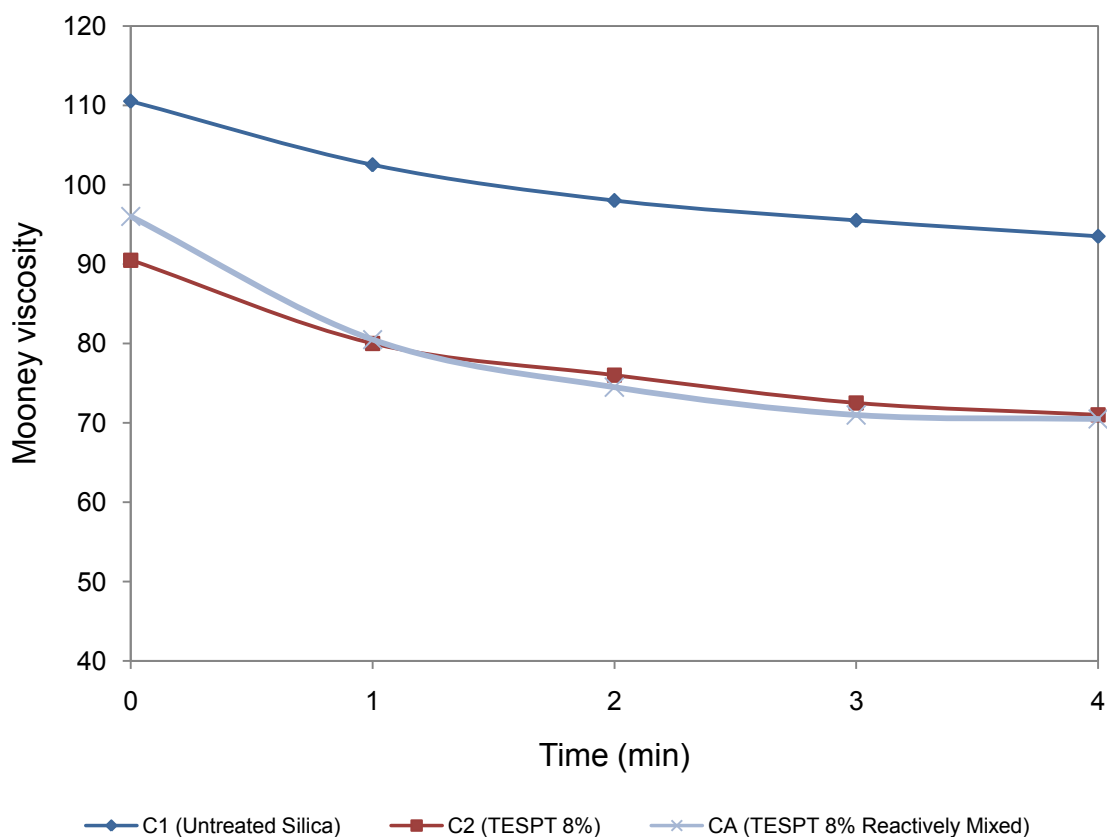


Figure 7.3: Mooney viscosity comparison of silica-filled elastomer compounds silanised with TESPT.

As shown in the figure, the Mooney viscosities of the C2 and CA uncured compounds are very similar and significantly lower than that of the untreated silica compounds, as would be expected if the silanisation has promoted the breakdown of the silica network and the dispersion of the silica aggregates. Similar results were also found in microdispersion analysis (Chapter 6) indicating that the silica has been efficiently silanised during the reactive mixing. Figure 7.4 and Table 7.1 show the Mooney viscosities of the silica-filled elastomer compounds from C1 to C12.

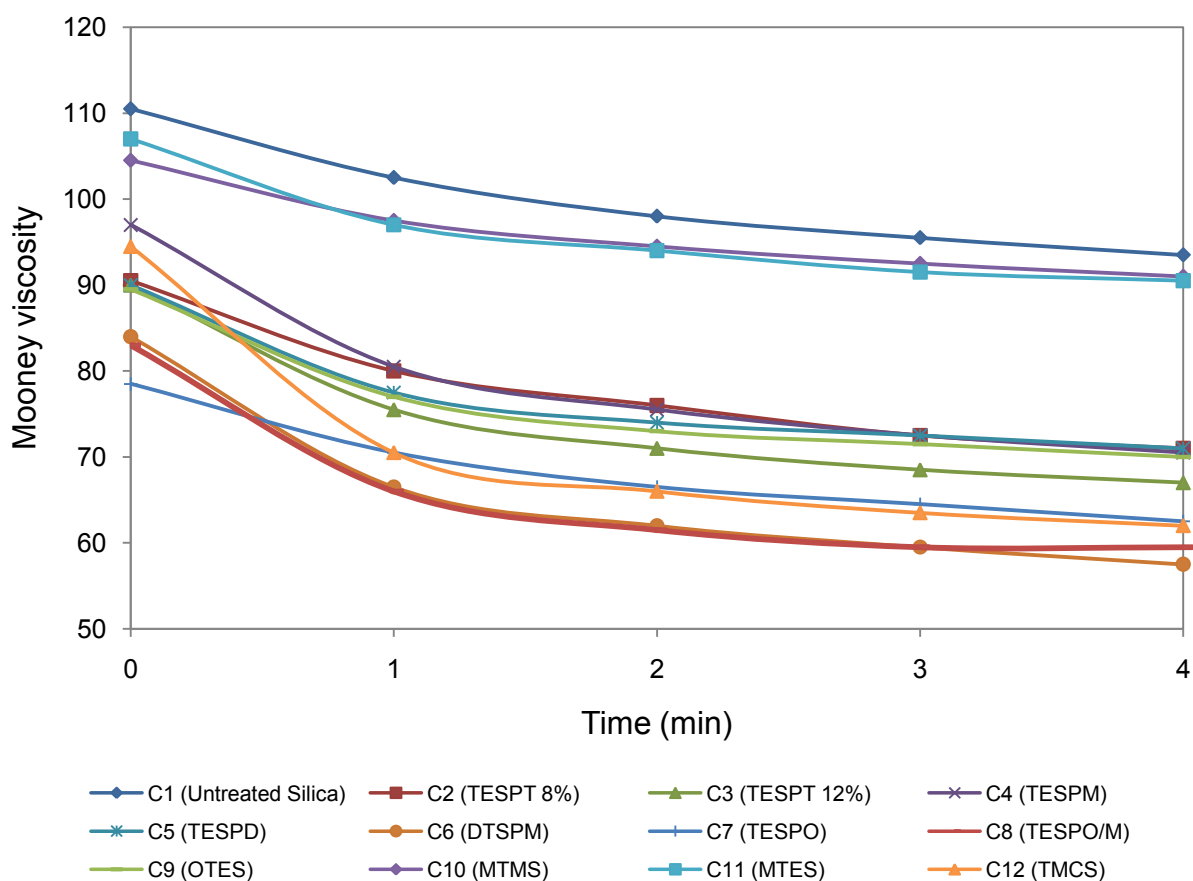


Figure 7.4: Mooney viscosity of silica-filled elastomer compounds.

It is observed that the untreated silica compound (C1) shows the higher Mooney viscosity than the silanised silica compounds regardless of whether coupling or non-coupling silanes were used. The higher Mooney viscosity for C1 indicates a higher density of silica networks in the elastomer matrix, where the silica particles are bonded through hydrogen bonds.

Among all the silanised silica-filled elastomer compounds, compounds C10 (MTMS) and C11 (MTES) showed the highest Mooney viscosities and compounds C6 (DTSPM) and C8 (TESPO/M) the lowest. The presence of long alkyl chains from DTSPM and TESPO/M covering the hydrophilic surface of these silicas prevents the hydrogen bonding or the formation of siloxane bonds with adjacent silica particles. These observations were in good agreement with the low and homogenised surface energy characteristics measured through IGC and also the better microdispersion. The smaller molecular size of MTMS and MTES provides less effective hydrophobation of the surface and contributes to re-agglomeration of silica aggregates; these compounds exhibit approximately 64% higher Mooney viscosities compared to compound C6 (DTSPM). Overall, it appears that bulkier silanes provided more surface coverage and consequently lowered the viscosity.

Comparing the Mooney viscosity traces in Figure 7.4, those of compounds C12 (TMCS), C6 (DTSPM) and C8 (TESPO/M) stand out with significantly larger viscosity decreases during the testing. The three silanes used differ from the others in that they do not have trimethoxy- or triethoxysilyl groups. Lin et al. [209] have observed that

increases in Mooney viscosity can occur after ambient ageing of silica-filled compounds containing silanes. They attributed the viscosity increases to hydrolysis of the additional ethoxy groups leading to siloxane bonding and silica-silane-silica bridges and also in the case of the more reactive silanes, TESPM and TESPT, to silica-elastomer coupling through the silane, especially when mixed at higher temperatures. The former seems a more likely explanation for the smaller decreases in Mooney viscosity observed with triethoxy- and trimethoxy silanes in the current study, as the compounds with TESPM and TESPT do not display smaller decreases in viscosity than those with the other trialkoxysilanes. Silica-rubber coupling would be expected to be extremely slow at 100 °C – the temperature used for the Mooney viscosity testing, while the TGA-IR study (Chapter 4) has shown that alcohols are displaced at this temperature.

It is worth mentioning that in silica-filled elastomer compounds, the silica grafted with coupling silanes must also be considered as a source of reactive sulfur functional groups. The sulfur in the mercaptan or di- or polysulfide is intended to react with the unsaturated hydrocarbon elastomer chains during curing process (172 °C), rather than during mixing, to give a silica silane-functionalised elastomer. However, it was shown in the bound rubber analysis that some sulfur covalent bonds were formed between these modified silicas (silica modified with coupling silane other than TESPO) and the with elastomer during mixing. However, this very limited silica-elastomer coupling during mixing does not seem to have had a significant effect on the Mooney viscosity.

Table 7.1: Mooney viscosity of silica-filled elastomer compounds.

Silane Used for Silica Modification	Mooney viscosity (MU) ML(1+4) at 100 °C*
C1 (Untreated Silica)	90.5
C2 (TESPT 8% w/w)	71.0
C3 (TESPT 12% w/w)	67.0
C4 (TESPM)	70.5
C5 (TESPD)	71.0
C6 (DTSPM)	57.5
C7 (TESPO)	62.5
C8 (TESPO/M)	59.5
C9 (OTES)	70.0
C10 (MTMS)	91.0
C11 (MTES)	93.5
C12 (TMCS)	62.0
C13 (TESPT 8% w/w, Reactively Mixed)	70.5

* In Mooney units with large rotor setting at 100 °C. 1 min pre heat time and 4 mins when the motor was turning and the reading were taken.

7.3.2 Crosslinking Analysis

The crosslinking of the silica filled-elastomer compounds was analysed using a Moving Die Rheometer at 172 °C for 30 minutes. A comparison is made between the untreated and silanised silica-filled elastomer compounds. Figure 7.5 shows the rheographs of untreated and TESPT silanised silica-filled elastomer compounds. At the beginning, the torque or the stiffness of the compounds decreased due to softening effects. Then a sharp increase is observed indicating that the vulcanisation reaction had started.

The curves for the TESPT-silanes compounds C2, C3 and CA became plateaus after 10 minutes, while that of the untreated silica-filled compound C1 exhibits a marching curve (continuous torque rise), higher torque difference ($M_H - M_L$), short scorch time (t_{s1}) and longer optimum cure time (t_{90}). M_H is the highest elastic stiffness of the vulcanised compounds and M_L is the minimum elastic stiffness of the unvulcanised compounds. The scorch time, t_{s1} , is the time for the onset of the crosslinking process, indicated by an increase 1 dNm in torque from M_L , and the optimum cure time, t_{90} , is the time taken to achieve 90% of the torque difference, $M_H - M_L$.

These observations suggest that the effect of silica networks in the unsilanised compound C1 causes an increase in the compound stiffness. The short scorch time exhibited by compound C1 can be linked to the flocculation of the untreated silica as shown in Figure 7.5, with a flocculation shoulder, similar to that in Figure 2 of Mihara et al. study [220] and Figure 2 of Pamela et al. [221]. It has been documented that the silica tends to flocculate due to poor compatibility with hydrocarbon elastomers [222]

and strong self association through hydrogen bonding [223]. The filler flocculation process can occur during compound storage or during annealing the uncured compound at elevated temperatures prior to the onset of crosslinking process before the shear force is apply [209,223,224].

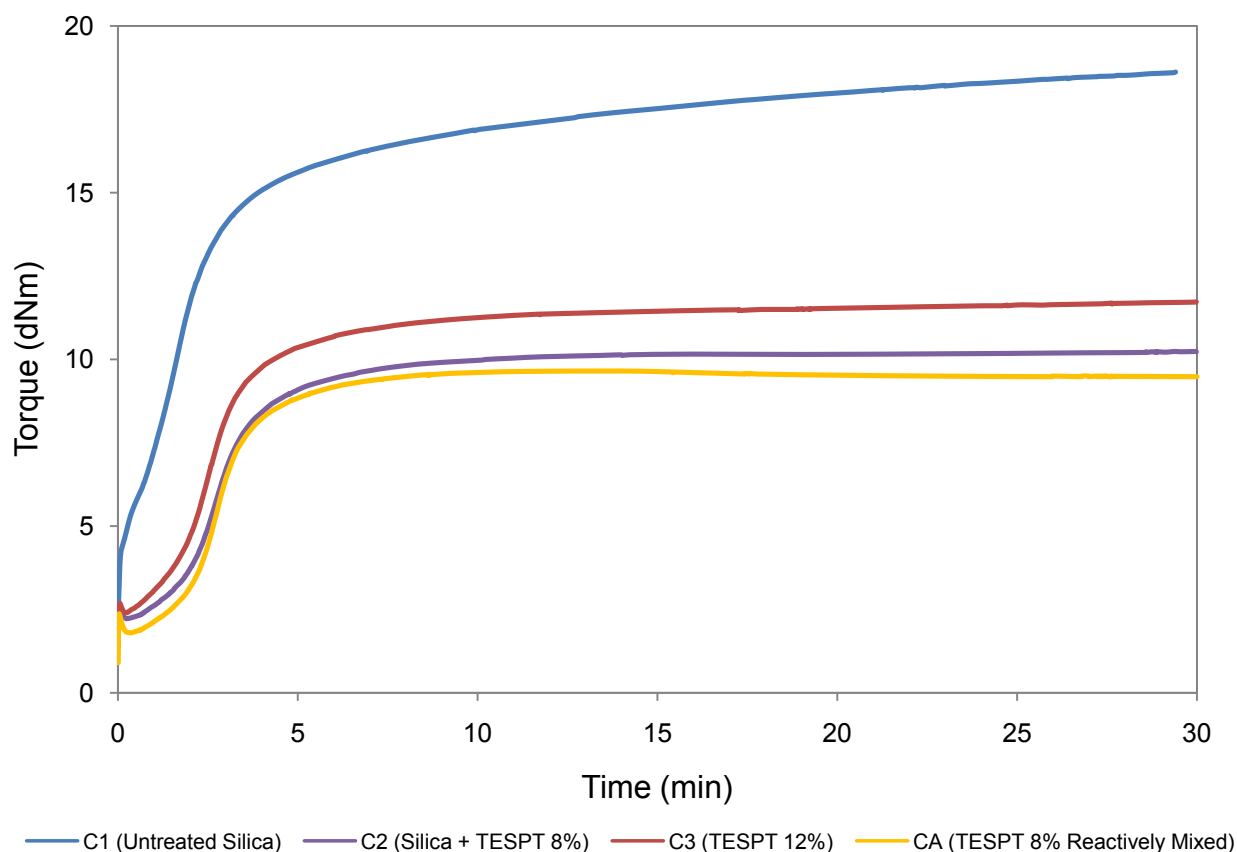


Figure 7.5: Cure characteristics of untreated and TESPT silanised silica-filled elastomer compounds.

It is also observed that the CA compound which was silanised during mixing with 8% w/w of TESPT exhibited very similar crosslinking characteristics as the C2 compound with 8% pre-silanised silica. Even though the total sulfur content formulated for compound C3 (with 12% w/w TESPT) is normalised to compound C2, it has

exhibited approximately 17% higher torque difference, possibly reflecting the increased covalent bond between the silanised silica and the elastomer.

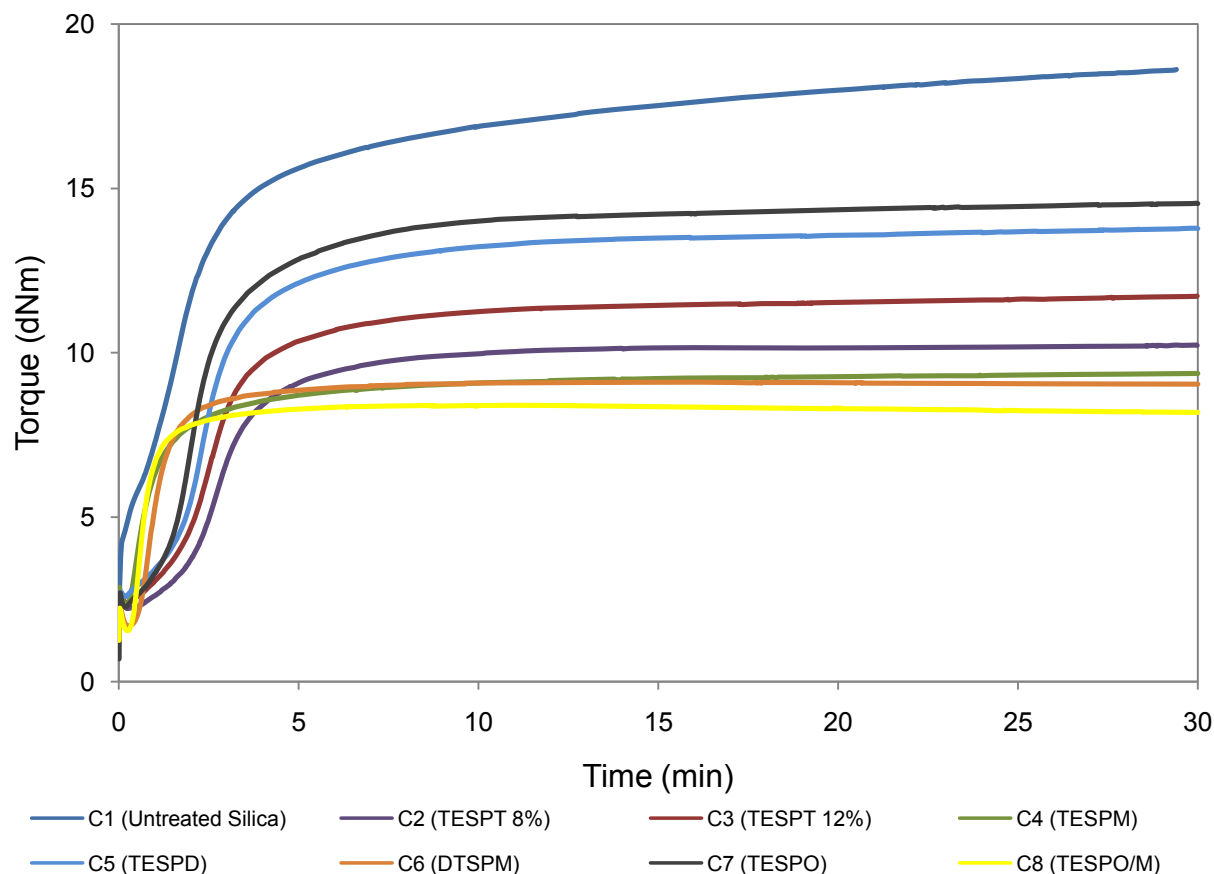


Figure 7.6: Cure characteristics of the silica-filled elastomer compounds for coupling silanes.

The comparison of the compounds filled with silica silanised with different coupling silanes is presented in Figure 7.6. Figure 7.6 shows that the other silanised silica-filled elastomer compounds showed similar effects with lower M_H compared to the unsilanised compound C1 and achieving plateau curves. The results show that the scorch time, t_{s1} , and optimum cure time, t_{90} , of the compounds filled with silanised silica improved by suppressing the hydrophilic nature of silica surface and preventing silica

networking. Compound filled with TESPO silanised silicas shows the highest M_H follows by C5 (TESPD), for silica silanised with coupling silanes. Even though TESPd had shorter sulfur bridges, it exhibited higher torque maximum compared to compounds C2 (TESPT 8%) and C3 (TESPT 12%). The M_H values of compounds C2 (TESPT 8%) and C4 (TESPM) are close to the values observed by Ten Brinke et al. using the same silanes, similar formulation and reactive mixing procedures but higher silica loading at 80 pphr measured at 160 °C [225].

The compounds filled with silicas silanised with DTSPM and TESPO/M, containing long alkyl functional groups, exhibit the lowest M_L and as shown with its homogenised γ_S^d profiles through the IGC analysis presumably due to their greater surface coverage. However, compound C7 containing TESPO with blocked mercapto silane with its long alkyl chains might have affected the interaction between the silica and the elastomer chains and hence did not effectively reduce the silica flocculation process.

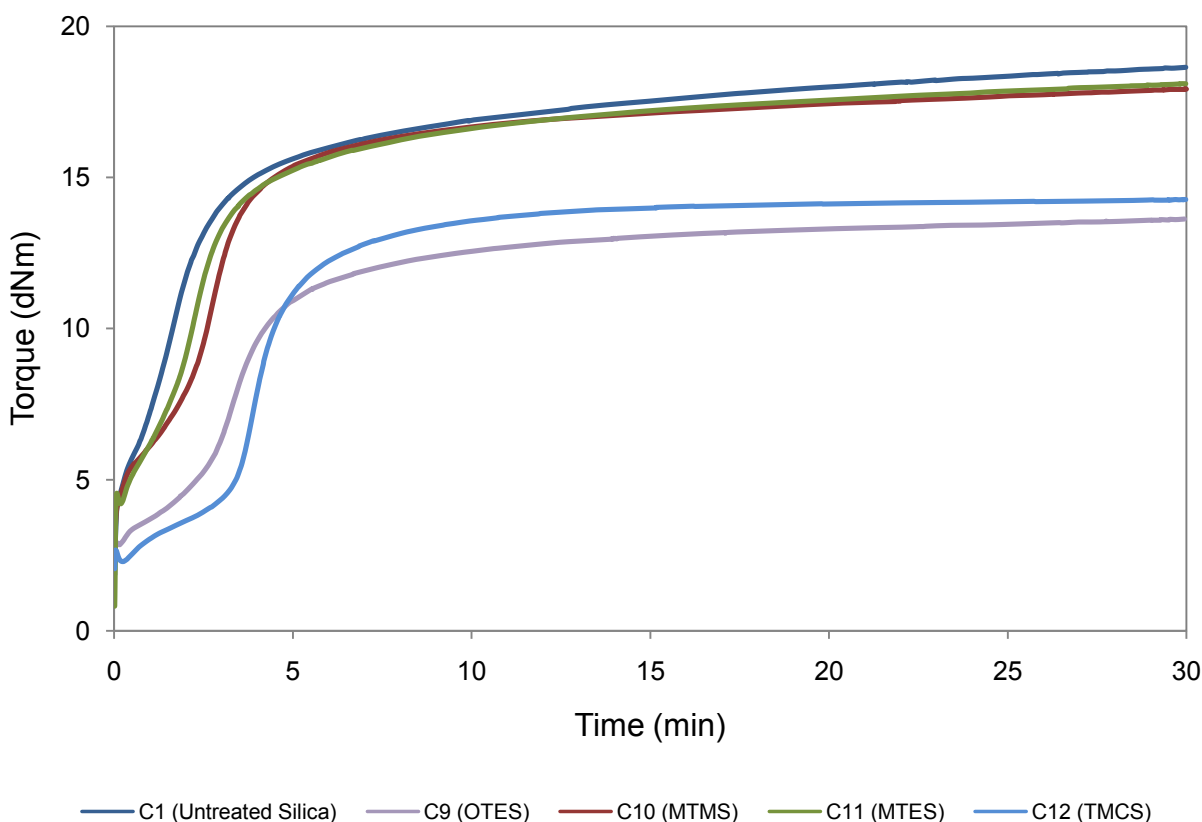


Figure 7.7: Cure characteristics of silica-filled elastomer compounds for non-coupling silanes.

As presented by Figure 7.7, compounds filled with silicas silanised with non-coupling silanes, all exhibit higher torque rises and flocculation shoulders, and also marching curves apart from compound C12 (TMCS). There appears to be an inverse correlation between the torque rise and the expected reactivity of the sulfur-containing group within the silane towards the elastomer. Thus, TESPO with a protected mercaptan leads to the highest torque rise, followed by the disulfide, TESP, the tetrasulfide, TESPT and finally the most reactive, the mercaptans, TESP, DTSPM and TESPO/M. The summary of cure characteristics for silica-filled elastomer compounds for coupling and non-coupling silanes are presented in Tables 7.2 and 7.3 respectively.

The bound rubber contents, measured in the unvulcanised compounds, follow this trend in reactivity, as shown in Figure 7.9. It would appear that the coupling of silica to elastomer, occurring during mixing, although limited in extent, is a key factor in shielding the silica surface, limiting silica networking during the rheometer cure and this controlling and limiting the observed torque rise. The three compounds based on the more reactive mercapto silanes (TESPM, DTSPM, and TESPO/M) show much shorter scorch times, as might be expected.

The non-coupling silanes thus appear to be much less effective in preventing silica networking during the rheometer curve, indicating again that silica-elastomer coupling is an important factor. Of the non-coupling silanes MTMS and MTES may be distinguished from OTES and TMCS. The cure curves with MTMS and MTES are quite similar to the unsilanised cure curve, while the bulkier OTES and TMCS appear to have had some effect on limiting the silica networking and thus increases the scorch time. A summary of observed torque maxima, M_H for the compounds C1 to C12 and CA is presented in Figure 7.8.

Table 7.2: Cure characteristics of silica-filled elastomer compounds for coupling silanes.

Compound	C1 (Untreated Silica)	CA* (TESPT 8%)	C2 (TESPT 8%)	C3 (TESPT 12%)	C4 (TESPM)	C5 (TESPD)	C6 (DTSPM)	C7 (TESPO)	C8 (TESPO/ M)
Rheometry at 172 °C									
Minimum torque (M_L), dNm	6.16	1.80	2.22	2.40	2.31	2.59	1.69	2.27	1.56
Maximum torque (M_H), dNm	18.6	9.65	10.2	11.7	9.37	13.8	9.11	14.6	8.4
Torque different ($M_H - M_L$), dNm	12.5	7.85	8.02	9.33	7.06	11.2	7.42	12.3	6.84
Time corresponding to 90% rise to torque maximum (T_{90}), min	14.0	5.07	6.03	6.43	4.77	6.57	2.43	6.22	1.83
Scorch time (T_{s1}), min**	0.98	1.77	1.67	1.28	0.43	1.15	0.67	0.98	0.47

* Reactively mixed.

** Time required for the increase of 1 unit from minimum torque. This number is an indication of the time required for the beginning of the crosslinking process.

Table 7.3: Cure characteristics of silica-filled elastomer compounds for non-coupling silanes.

Compound	C9 (OTES)	C10 (MTMS)	C11 (MTES)	C12 (TMCS)
Rheometry at 172 °C				
Minimum torque (M_L), dNm	2.84	5.96	4.20	2.29
Maximum torque (M_H), dNm	13.6	17.9	18.1	14.3
Torque different ($M_H - M_L$), dNm	10.8	17.6	18.4	15.6
Time corresponding to 90% rise to torque maximum (T_{90}), min	10.0	10.5	10.6	7.80
Scorch time (T_{s1}), min**	1.37	0.52	1.53	1.22

** Time required for the increase of 1 unit from minimum torque. This number is an indication of the time required for the beginning of the crosslinking process.

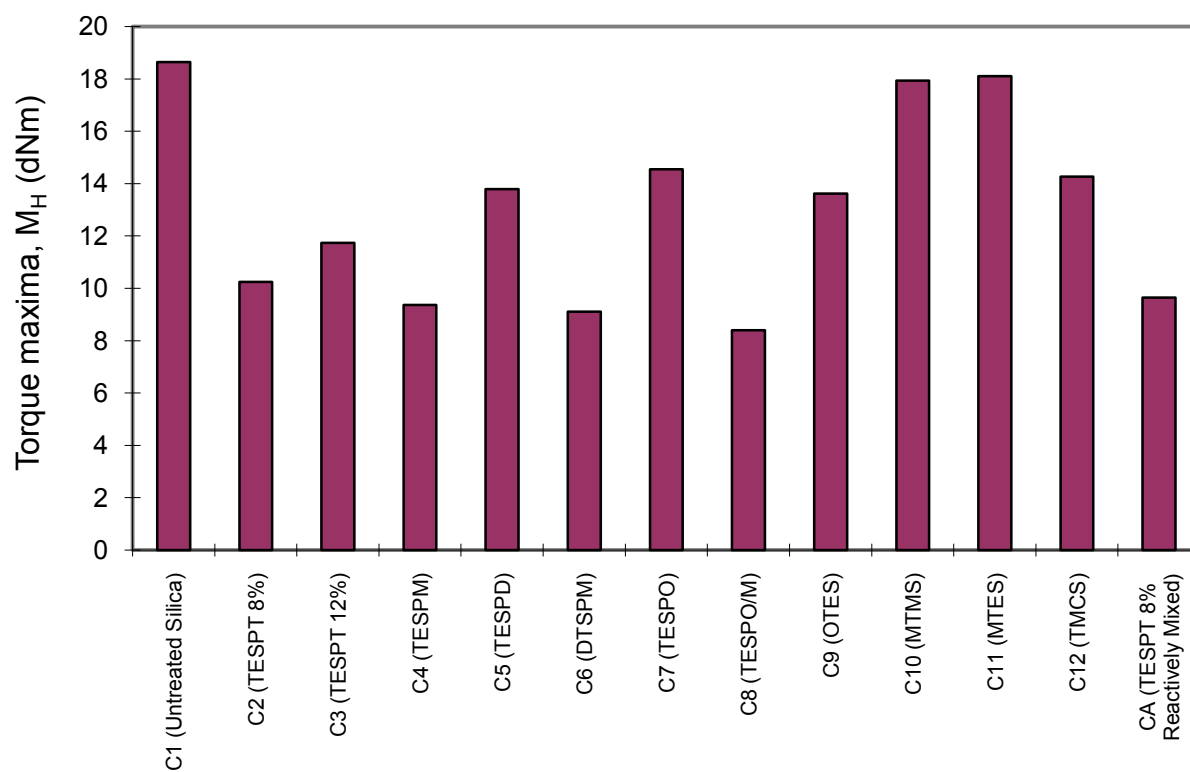


Figure 7.8: Torque maxima (M_H) of silica-filled elastomer compounds.

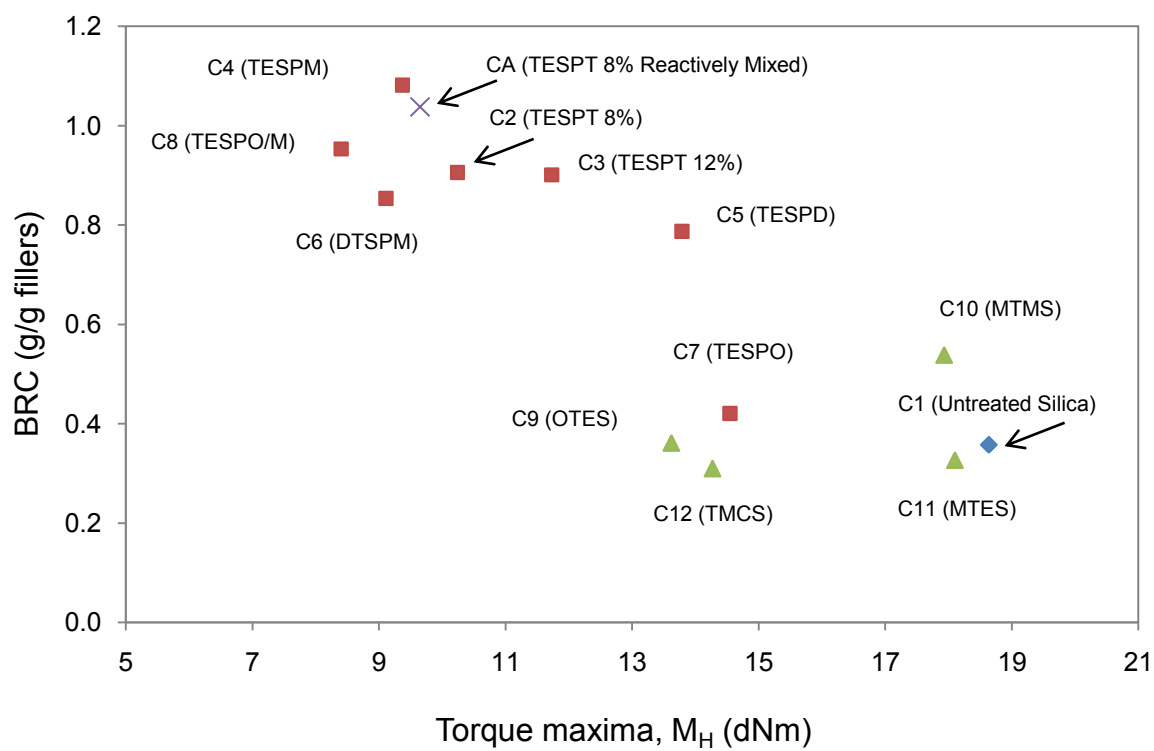


Figure 7.9: Bound rubber content (BRC) versus torque maxima (M_H) of silica-filled elastomer compounds.

7.4 Conclusions

In this chapter, the changes in Mooney viscosities and cure characteristics of uncured compounds for untreated or silanised silica in elastomer phase were investigated. The Mooney viscosities and cure characteristics were determined by Mooney viscometer and rheometer respectively.

The Mooney viscosities of untreated silica (C1) show the hydrophilic nature of the silica surface and the development of a strong silica network. Silanisation suppresses the silica aggregates work of cohesion and reduces re-agglomeration after mixing. The bulkier silanes such as DTSPM (C6) and TESPO/M (C8), provide more surface coverage and consequently exhibit the lowest Mooney viscosities. These observations are in good agreement with the low and homogenised surface energy characteristics measured through IGC. Compounds with the smaller silanes, such as C10 (MTMS) and C11 (MTES) are less effective in providing hydrophobic surface coatings, contributing to re-agglomeration of silica particles and hence higher Mooney viscosities. The compounds with silanes containing trimethoxy- or triethoxy-silyl groups display smaller viscosity decreases during the testing at 100 °C. This is attributed to hydrolysis of the additional alkoxy groups leading to silane bonding and silica-silane-silane bridges.

The cure kinetics analysis showed that silanised silica-filled elastomer compounds exhibit lower M_H compared to compound C1 (untreated silica) and achieve plateau curves. The results also show that the scorch time, t_{s1} , and optimum cure time,

t_{90} , of the compounds filled with silanised silica were improved. In the case of the coupling silanes, there appears to be an inverse correlation between the torque rise and the expected reactivity of the sulfur containing group within the silane towards the elastomer. It would appear that the limited coupling of silica to elastomer, occurring during mixing is a key factor in shielding the silica surface and limiting silica networking during the cure. Consequently, the non-coupling silanes are much less effective in preventing silica networking during the rheometer cure.

CHAPTER 8 MECHANICAL AND DYNAMIC CHARACTERISATION OF CURED COMPOUNDS.

8.1 Introduction

When rigid particles such as silica are added into an elastomer system, the dynamic modulus as well as the static behaviour of the filled elastomer is considerably changed [226]. The IGC (Chapter 5) and rheological analysis (Chapter 7) have shown that the silanes influence the silica surface energy and hence the silica-silica interactions. As discussed in previous chapters, the grafted silane species on the silica surface determine the silica dispersion efficiency and its interaction with elastomer chains, as well as the cured characteristics of the silica-filled elastomers. Besides that, silica grafted with coupling silanes contributed the crosslinking between the silica and the elastomer. Thus, the formation of covalent bonds between silica and elastomer affects the mechanical performance of silica-filled elastomers.

The rigid fillers used for this study are commercial grade fillers for tyre tread applications. The main silica used for this study is Zeosil[®] 1165 MP with approximately $158 \pm 4 \text{ m}^2/\text{g}$ specific surface area through nitrogen adsorption. The Zeosil[®] silica fillers were sourced from Solvay SA, France. The elastomers used for this study were solution styrene-butadiene rubber (sSBR, VSL 5025-2 HM with 25% styrene and 50% vinyl content) and cis-1,4-polybutadiene rubber. The silica-filled compounds were formulated using a tyre tread formulation [119].

In this chapter, the mechanical performance of the cured filled compounds is investigated to evaluate the effect of the silane modifications in elastomer compounds. For this purpose, the type of silane has been varied. Abrasion resistance, angle tear, tensile, reinforcement index and dynamic mechanical analysis testing was carried out.

The aim of this chapter is to provide a better insight into the effect of silica - silane filler systems by analysing the mechanical performance of silica-filled compounds and the strain dependency characteristics of their shear moduli. The main focus of this chapter lies on the influence of coupling and non-coupling silanes on silica reinforcement.

8.2 Mechanical Performance

The addition of filler to elastomer has strong impact on the static and dynamic behaviour of the elastomer. In elastomer tearing processes, the strain energy is elastically stored in the elastomer, under the strained state, and is partly utilised to break the molecular bonds to create a new surfaces and also partly dissipated as heat. The tearing behaviour of an elastomer can be characterised by the relationship between the strain rate or the tearing rate and the critical tearing energy. Barquins and Ciccotti [227] observed that a stick-slip motion appeared with unstable peeling when an adhesive tape was pulled and the tape reaches a critical point and started to emit noise. A similar stick-slip phenomenon was observed by Aubrey and Sherriff [228]. In the process of tearing a filled elastomer vulcanisate, a similar effect is likely to occur. The sticking occurs in general when the kinetic force is lower than the static frictional force, while slipping occurs when the kinetic forces becomes higher than the frictional force.

Fukahori and Yamazaki [229] suggested another abrasion phenomenon where microvibrations are generated during frictional sliding due to the natural frequency of the elastomer induced in the slip phase. In their study, they used a 30N normal force and a mean sliding velocity of 20 mm/s. Boonstra and Dannenberg [230] suggested that the abrasion resistance of rubberlike materials depends on two factors: 1) the development of a frictional force at the material surface; 2) the counteraction of the rubbing force by the cohesive force in the elastomer adjacent to the elastomer surface layer.

In elastomer materials, when the smooth moulded elastomer surface is abraded with a harder material, a periodic parallel ridged-wave pattern perpendicular to the sliding direction can be formed on the elastomer abraded surface. This typical pattern can be observed in many processes of rubber abrasion, such as on the surface of an abraded tyre. Fukahori and Yamazaki reported that the abrasion pattern moves slowly along the perpendicular sliding direction, where the crack at the root of the wear pattern is deepened and the protruding flap is torn off [229]. The renowned Schallamach report [231,232] discussed the detachment of the wave pattern when a blunt rigid spherical slider was moved over an elastomer surface.

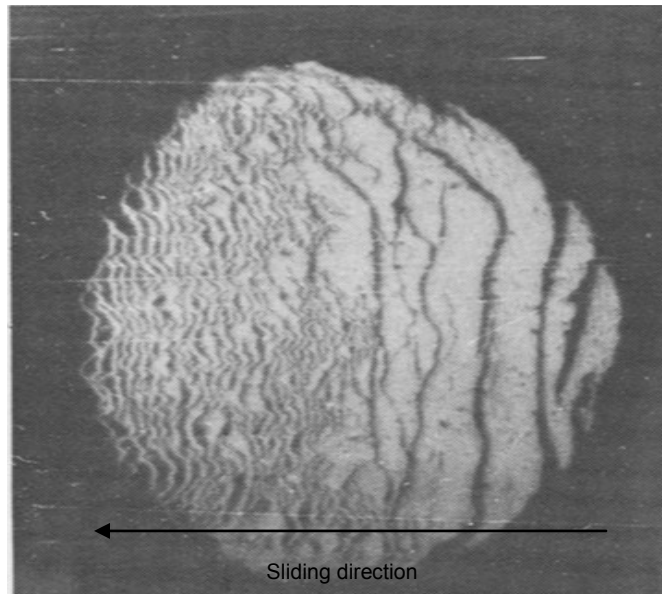


Figure 8.1: Formation of Schallamach wave pattern on abraded elastomer surface [232].

One of the consequences of incorporation of high loading of filler, such as 55 pphr, into an elastomer can be considerable changes in the dynamic properties of the filled elastomer. Wang [233] reported that filler networking is among the parameters that influence the dynamic properties of a filled elastomer. At high silica loading, the silica aggregates can be associated to silica agglomerates. These agglomerates, which in a cluster formation is generally termed as silica secondary structure or silica filler network. The impact of the silica network on the viscoelastic behaviour of an elastomer has been reviewed by Payne [234] and correlates with the Guth and Gold [235] study (Chapter 2, equation 2.12). The equation takes into consideration the effect of the suspended spherical rigid particles on the viscosity of a solvent, in this case the elastomer.

8.3 Dynamic Mechanical Analysis

The addition of filler to elastomer has a strong impact on the dynamic behaviour of the elastomer as well. Besides the strain-independent contribution of the hydrodynamic effect as discussed in Chapter 2, the interaction between filler and elastomer as well as the degree of crosslinking contribute to the modulus. The breakdown of the filler networks, known as the Payne effect, plays a significant role in the understanding of the reinforcement mechanism of filled elastomers. The different contributions to the complex modulus, G^* , of filled elastomer are shown in Figure 2.12.

8.4 Results and Discussion

The grafting of silica and compounding of silica-filled elastomer procedures are discussed in Chapter 3. The compounds were prepared using a passenger tyre tread formulation (See Tables 3.2 and 3.3) but with 55 phr silica loading, and cured at 172 °C for 12 minutes.

Table 8.1: Silanised Silica-Filled Vulcanisate.

Silane Used for Silica Modification	Compound
Untreated Silica	C1
TESPT 8% w/w	C2
TESPT 12% w/w	C3
TESPM	C4
TESPD	C5
DTSPM	C6
TESPO	C7
TESPO/M	C8
OTES	C9
MTMS	C10
MTES	C11
TMCS	C12
TESPT 8% w/w (Reactively Mixed)	CA

8.4.1 Effect on Mechanical Properties

The physical properties and standard variance of the test results for vulcanisates of compounds C1 to C12 are given in Table 8.1. It is observed that the reactivity and types of silane have an impact on the mechanical properties of these compounds. In general, the reactively mixed TESPT compound CA exhibited similar mechanical characteristics compared to compound C2 filled with grafted TESPT (8% w/w) through laboratory silica silanisation. There is also evidence indicating that the silica silanised with coupling silane improved the vulcanisate properties compared to untreated silica-filled compound and led to better mechanical properties compared to non-coupling silanes.

For this study, the hardness test was based on the measurement of the penetration of a rigid metal ball (with a ball diameter of 2.38 ± 0.01 mm and an approximately total force of 5.53 ± 0.03 N) into the elastomer samples and the measurements were converted into the IRHD scale. A hardness of 0 corresponds to the sample having an elastic Young modulus of zero and value of 100 indicates that the sample exhibits infinite elastic Young's modulus [128]. It is worth mentioning that when the load is reduced to zero, attractive surface forces are operating between the metal ball and elastomer sample [236]. This surface attraction may be interpreted in terms of the surface energy of the compounds. However, it is of little significance at higher loads [237]. The goal of this test is to investigate the elastic modulus and the hardness of the compounds due to incorporation of rigid silica aggregates with different surface energy and different degrees of silica aggregate networking.

The hardness of the modified silica-filled compounds (C2 to C12) are generally reduced compared to untreated silica-filled compounds (C1) (Table 8.2). The reactively mixed compound (CA) and C2 compound with 8% w/w TESPT showed similar hardness when indented on the surface by the metal ball. The investigation showed that the silica aggregate networks have been reduced and the compound exhibited a higher degree of elastic characteristics. The coupling silanes have coupled with the elastomer during both mixing at moderate dumping temperatures and during the subsequent cure and showed improved the silica dispersion as shown in the TEM network visualisation study (Chapter 6). The blocked mercaptan-TESPO-silica (C7), which only bonded to the elastomer during the cure, showed a somewhat higher hardness.

Table 8.2: Physical properties of vulcanisates of compounds C1-C9 filled with untreated silica and silica modified by different coupling silanes.

Compound	C1 (Untreated Silica)	CA* (TESPT 8%)	C2 (TESPT 8%)	C3 (TESPT 12%)	C4 (TESPM)	C5 (TESPD)	C6 (DTSPM)	C7 (TESPO)	C8 (TESPO/ M)
Hardness (IRHD)	65±2	47±0	49±0	47±0	47±0	51±0	45±0	57±0	46±0
Akron Abrasion Resistance Index, (ARI) %	101±14	145±11	133±22	128±14	153±29	133±14	140±11	141±17	133±18
DIN Abrasion Resistance Index, %	53.1±1	89.6±2	78.1±2	74.1±1	81.1±3	81.7±1	80.9±2	95.6±1	94.5±5
Angle Tear (kN/m)	30.3±0.6	35.8±1.6	34.4±0.9	34.8±1.8	35.3±1.0	38.8±1.1	35.5±1.1	37.2±0.7	33.1±1.7
Tensile Strength, MPa	15.8±0.5	16.6±1.0	16.2±0.8	16.7±2.4	18.6±0	15.5±1.4	17.7±1.6	16.1±2.9	19.8±0.5
Elongation at Break, %	930±10	621±21	715±14	773±54	681±20	697±60	668±39	654±71	649±20
Modulus 50, MPa	0.74 ±0.01	0.69 ±0.02	0.7 3±0.01	0.69 ±0	0.71 ±0.01	0.78 ±0.01	0.66 ±0.02	0.84 ±0.01	0.72 ±0.02
Modulus 100, MPa	0.9 ±0.01	1.01 ±0.02	0.98 ±0.01	0.92 ±0.02	1.02 ±0.01	1.08 ±0.02	1.0 ±0.03	1.2 ±0.03	1.07 ±0.03
Modulus 300, MPa	1.99 ±0.01	4.33 ±0.09	3.33 ±0.02	2.95 ±0.07	4.01 ±0.2	3.65 ±0.3	4.10 ±0.2	4.31 ±0.3	4.74 ±0.2
Reinforcement Index (M300/M100), RI	2.21	4.29	3.4	3.2	3.93	3.38	4.1	3.6	4.43

* Reactively mixed

Table 8.3: Physical properties of compounds C9-C12 vulcanisate filled with silica modified by different non-coupling silanes.

Compound	C9 (OTES)	C10 (MTMS)	C11 (MTES)	C12 (TMCS)
Hardness (IRHD)	48±0	58±1	61±1	49±1
Akron Abrasion Resistance Index (ARI), %	136±22	122±28	136±27	140±21
DIN Abrasion Resistance Index (ARI), %	44.6±1	54.0±2	53.8±1	45.7±1
Angle Tear (kN/m)	25.3 ±1.1	30.4 ±1.1	32.3 ±1.4	26.5 ±0.7
Tensile Strength, MPa	14.5 ±1.4	16.4 ±1.9	15.5 ±0.6	15.3 ±1.5
Elongation at Break, %	960±31	938±18	905±33	939±19
Modulus 50, MPa	0.6 ±0.01	0.72 ±0.01	0.74 ±0	0.63 ±0.02
Modulus 100, MPa	0.74 ±0.01	0.88 ±0.01	0.9 ±0.01	0.77 ±0.02
Modulus 300, MPa	1.48 ±0.02	1.89 ±0.03	1.95 ±0.07	1.54 ±0.03
Reinforcement Index (M300/M100), RI	2.0	2.15	2.17	2.0

* Reactively mixed

As discussed in Chapter 3, the expression of abrasion resistance is the ratio of the volume loss of a standard elastomer to the volume loss of the elastomer sample under test due to the abrasive action of rubbing over an abrasive surface. The wear process and friction are system-based properties [238]. Besides that, other factors in service, such as temperature build-up at the surface of the tyre, have an effect on the wear rate. As reported by Schallamach [232], a series of abrasion patterns is observed. The abrasion patterns or the formation of ridges are perpendicular to the sliding direction and move in the sliding direction of the abraded surface [239]. The formation of cracks will propagate at the bottom of the front section of the ridges. The propagation of the cracks determines the wear rate of an elastomer. Figure 8.2 shows the typical formation of ridge patterns on the surface of an unfilled and a silica-filled elastomer vulcanisate.

For this study DIN and Akron abrasion resistance tests were carried out. The heat build-up at the end of each test cycle on the surface of all the test pieces was measured as approximately 35 °C to 40 °C. However, the effect of vibration is not taken into account as it is unlikely to quantitatively assess this parameter. The difference between these tests is that the DIN abrasion test is more severe (non-rotating test piece) compared to the Akron abrasion test (rotating test piece). Dusting powers are introduced during the Akron abrasion test to prevent smearing of the abraded rubber particles. Figures 8.3 and 8.4 show the abrasion resistance index DIN and Akron abrasion test results, respectively, expressed as abrasion resistance indices (the higher the index, the greater the abrasion resistance).

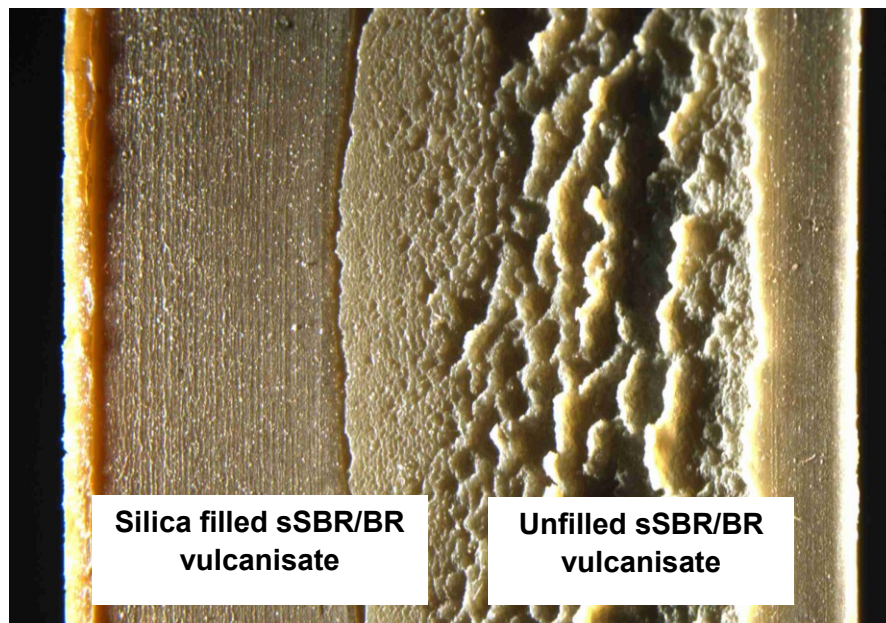


Figure 8.2: Comparison of the formation of ridges on the surface of silica reinforced and unfilled sSBR/BR vulcanisate.

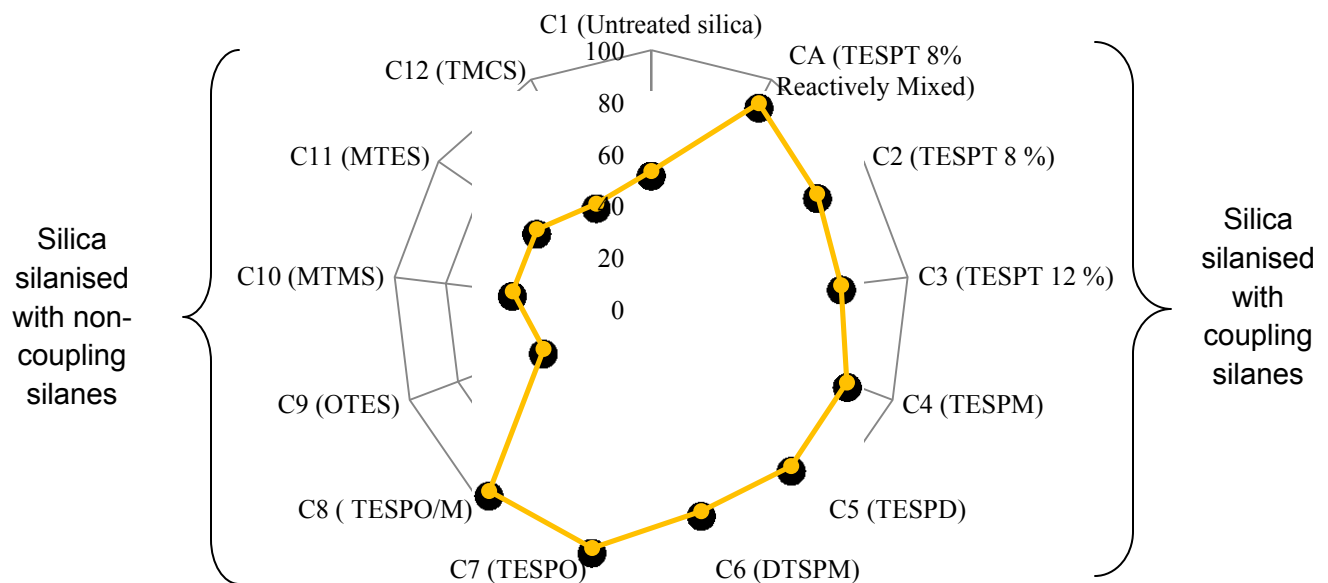


Figure 8.3: DIN abrasion resistance index of vulcanisates of compounds C1-C12.

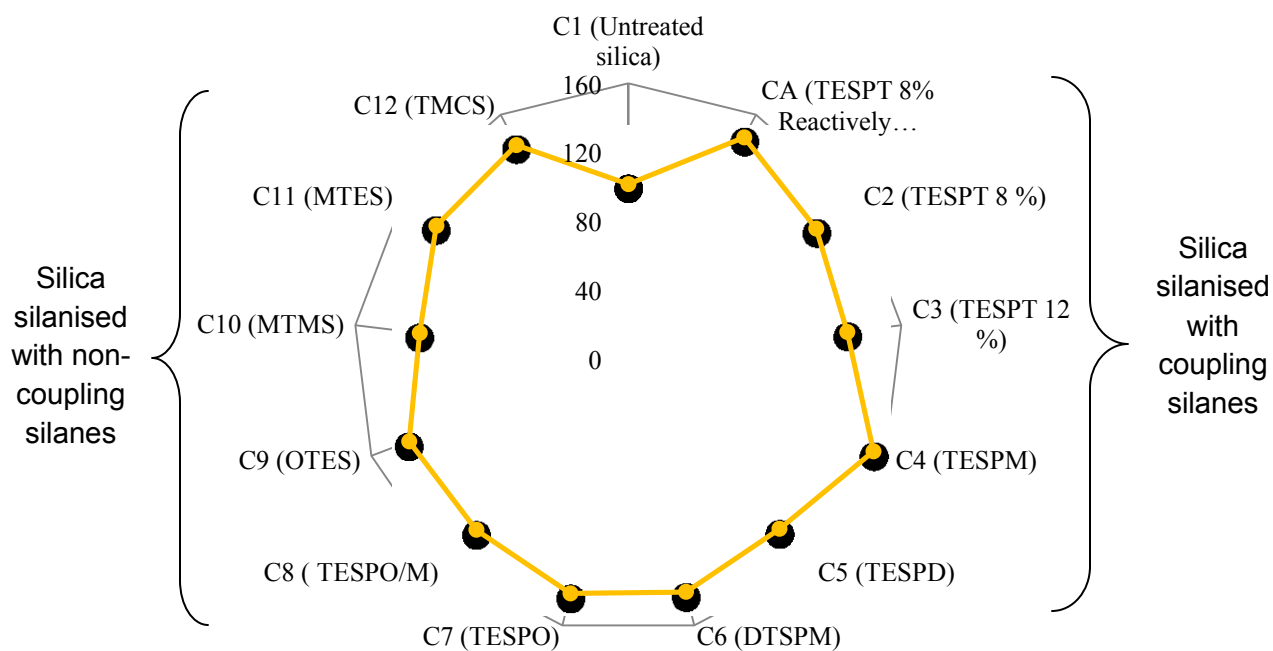


Figure 8.4: Akron abrasion resistance index of vulcanisates of compounds C1-C12.

Figure 8.3 shows that compounds C2 to C8, which used coupling silanes exhibit a significant improvement in DIN abrasion resistance compared to the untreated silica compounds (C1) and the silica compounds (C9 to C12) modified with non-coupling silanes. The results suggest the couplings between the silica particle and the elastomer chains and hence the improvement of the resistance of elastomer to wear. This observation is supported by the stronger tear strengths measured for compounds C2 to C8 as shown in Figure 8.5. The strong tear strength exhibited by these compounds (C2 to C8), prevents the propagation of cracks on the worn surfaces of the elastomer. The stronger tear strengths are presumably due to the coupling of silica to elastomer, which significantly increases the energy needed to break down the elastomer-filler network. In the case of the compounds where the silica is not bonded to the elastomer, cracks are able to propagate along the elastomer-silica interfaces.

Other studies [240] have indicated that strong filler-elastomer interactions are a crucial factor in achieving high abrasion resistance, and consequently, the need for silane coupling agents in silica-reinforced tyre tread compounds. A recent study [241] has indicated that breakdown of the filler-elastomer coupling may play an important part in the mechanism of tyre wear.

The Akron abrasion test is carried out under much less severe conditions. Thus it may be argued that it is closer to the wear processes occurring on the road. However, in the current investigation, the results from the Akron abrasion tests are rather different from those of the DIN abrasion tests. Compared with untreated silica (C1), all of the silanes lead to significantly higher Akron abrasion resistance index. However, there is no clear difference between the coupling and non-coupling silanes; The coupling silanes may on average have marginally higher abrasion resistance variation of the tests. This indicates that elastomer-silica coupling is not a crucial factor in determining the Akron abrasion resistance. Instead, it would appear that dispersion of the silica is the important parameter in Akron abrasion, as both the coupling and non-coupling have been shown to improve this dispersion. Recent work [241] has reported a reverse in ranking when comparing Akron abrasion and on-the-road wear testing, indicating that mechanism is not the same.

It would be interesting to carry out on-the-road wear testing of tyre treads containing coupling and non-coupling silanes, but unfortunately this was beyond the scope of the current project.

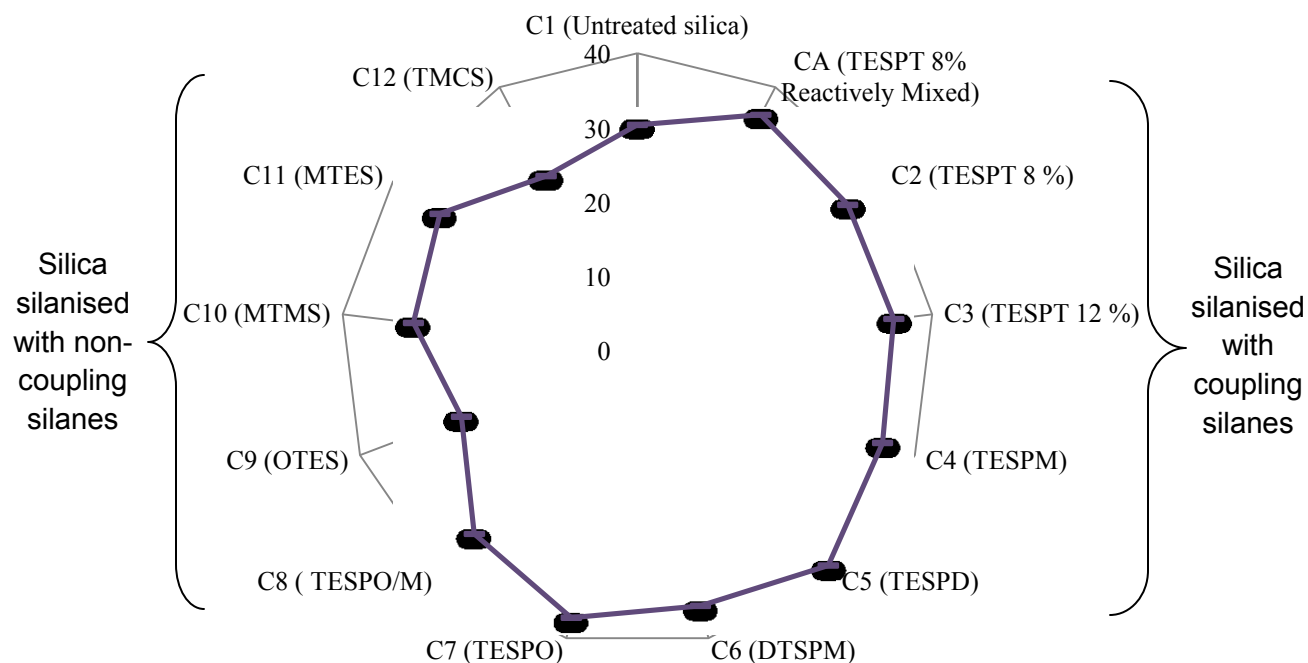


Figure 8.5: Tear strength of vulcanisates of compounds C1-C12.

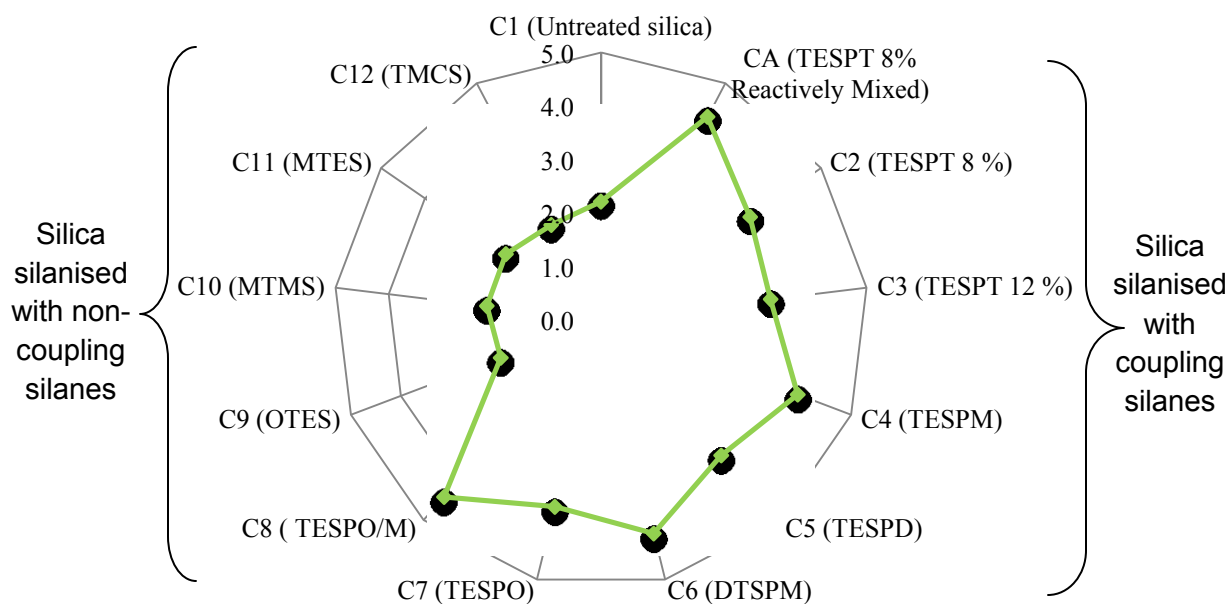


Figure 8.6: Reinforcement index of vulcanisates of compounds C1-C12.

The Reinforcement Index, RI where the value is calculated by dividing the tensile modulus at 300% strained by the tensile modulus at 100% strained of the vulcanisate samples. The results correlate well with the DIN abrasion resistance and tear strength results, confirming the importance of strong elastomer-filler coupling. The strong elastomer-silica coupling in compounds C2 to C8 has increased the modulus at 300% strained and thus these exhibit higher RI. The modulus of the compounds can be investigated through tensile stress-strain analysis (as shown in Figure 8.7). Elastomer vulcanisates (C2 to C8) with the coupling silanes show higher stress at high strains, due to the coupling between elastomer and silica, which limiting the extensibility of the network. In the case of the untreated silica and the non-coupling silanes, the elastomer-

silica interactions are broken at low extensions, allowing the elastomer molecules to slide over the silica surface and the extensibility to be greater.

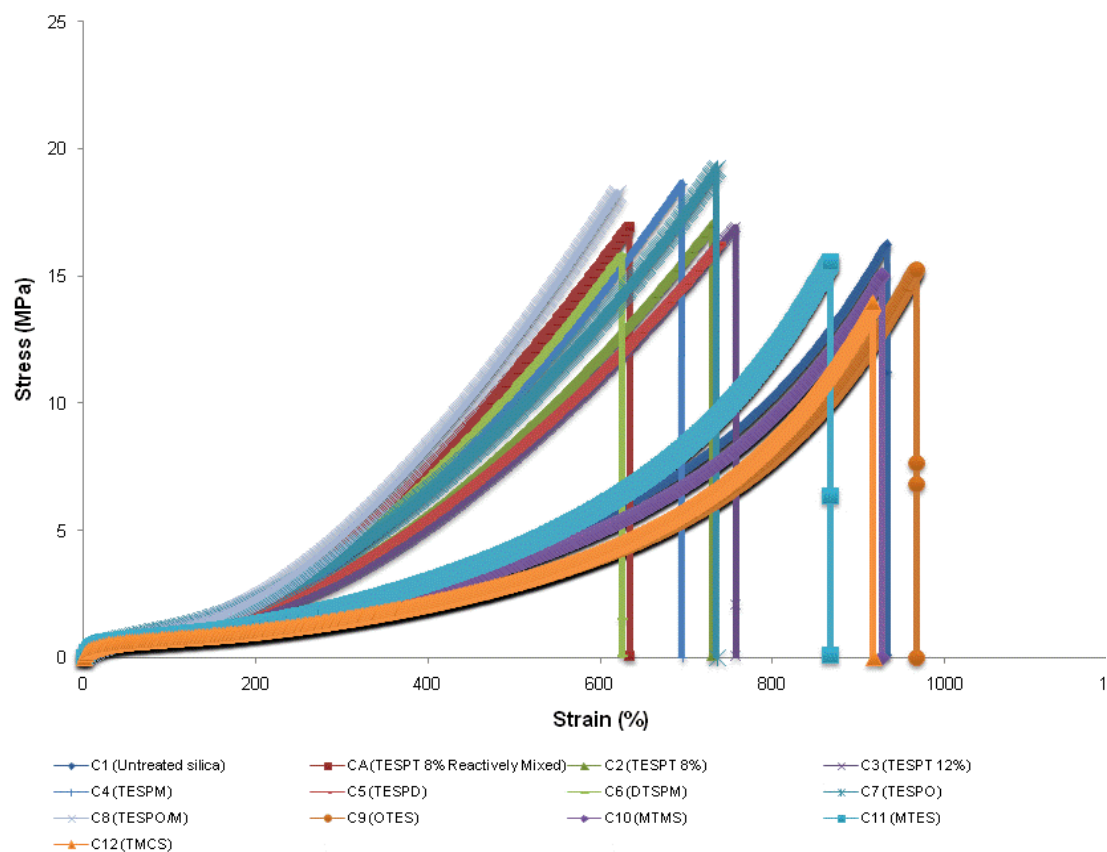


Figure 8.7: Tensile stress-strain behaviour of vulcanisates of compounds C1-C12.

8.4.2 Effect on Dynamic Mechanical Properties

At moderately low strains, the complex modulus from dynamic measurements decreases with increasing strain; this is known as the Payne [242,234] effect. It can be related to the rolling resistance performance of a tyre. For this study, the dynamic mechanical analysis (DMA) was performed using a Metravib DMA+1000 test system with planar shear fixtures and moulded double shear test pieces. The dynamic strain amplitudes were swept from 0.01% to 100% and reversed to 0.01% at a frequency of 1 Hz.

The evolution of dynamic modulus over a range of strain amplitudes is of major importance for the applications of reinforced elastomers. According to Ladouce-Stelandre et al. [243], the decrease in storage modulus, G' , and loss modulus, G'' , of filled elastomer vulcanisates can be attributed to several local mechanisms, namely i) the deformation and reformation of a percolating network of fillers [244,90], which can also involve elastomeric chains that are bound to the filler surfaces [245,90], ii) the adsorption-desorption of elastomeric chains at the interface between the filler and the elastomer molecules [246], and iii) the disentanglement of bulk elastomer from the elastomer bound to the filler surface [247].

The correlation between the amplitude of the non-linearity in the Payne effect and the type of fillers has been attributed to these different local mechanisms. It is the purpose of the present study to investigate the effect of filler surface chemistry on the Payne effect of the silica-filled elastomer vulcanisates. The silanised silicas led to

different uncured compound viscosities and cure characteristics. Under these conditions, it is observed that the amplitude of Payne effect is significantly less in the silanised silica vulcanisates when compared with the untreated silica vulcanisate as shown in Figures 8.8 and 8.9. The results indicate that the filler surface chemistry is affecting the degree of hysteresis in the filled elastomers.

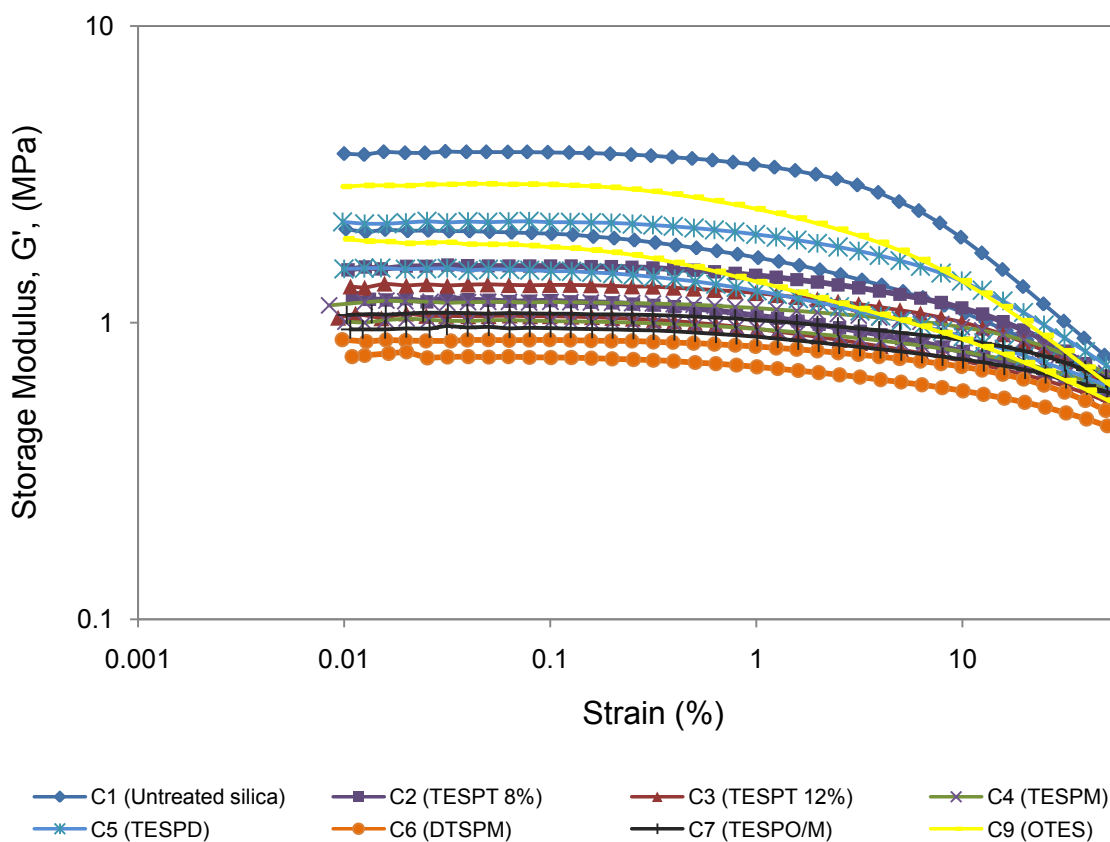


Figure 8.8: Storage modulus of silica-filled elastomer compounds.

The storage modulus, G' , is a measure of the stored energy representing the elastic portion of the compounds. The initial storage modulus of each compound, is

represented by the top curve with the same marker, as shown in Figure 8.8. When the strain amplitude increased from 0.01%, the storage modulus gradually decreases, due to the mechanisms mentioned above. A significant drop in loss modulus is observed at approximately 3% strain amplitude and the storage moduli of these compounds became similar at higher strain amplitudes. This could be attributed to filler-filler and/ or filler-elastomer broken linkages during straining. As the strain amplitude is decreased, the storage modulus of the compounds increased, represented by the bottom curves with the same marker. The silica networks in the elastomer were unable to reform to their original form and exhibited lower storage moduli.

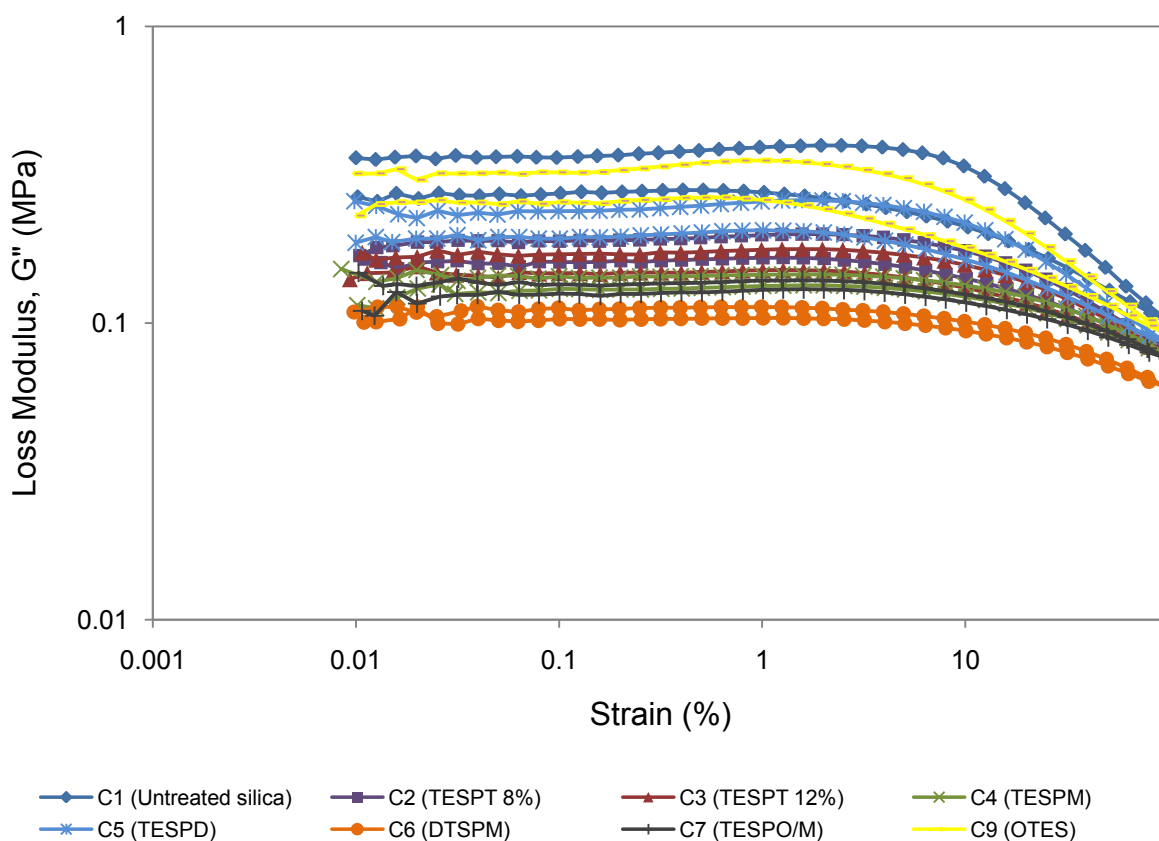


Figure 8.9: Loss modulus of silica-filled elastomer compounds.

Compared to the rest of the test pieces, compound C1 which was filled with untreated silica exhibits the highest storage modulus at low strain. This suggests that the silica network in compound C1 (Untreated Silica) is more developed or stronger and the compound exhibits large Payne effect as the strain amplitude is increased. The highly developed untreated silica network is attributed to its surface characteristics. It is shown that these untreated silicas possess high work of cohesion, while the rest of the silanised silicas are low in work of cohesion. The observations demonstrate that for a silica filled-hydrocarbon elastomer, the interaction between silica aggregates without hydrophobic surface coating is higher.

According to Wang [233], the above observation of decreasing storage modulus may also be explained by the mechanism of trapped rubber in the silica network being released as the strain amplitude is increased. This elastomer is considered partially immobilised and this immobilised elastomer loses its identity as an elastic material and exhibits rigid behaviour resulting high storage modulus at low strains. The effective filler volume fraction decreases as the strain amplitude increased, the breakdown of the silica networks released the trapped elastomer and led to the decrease in storage modulus.

The loss modulus, G'' , is a measure of the energy dissipated as heat, representing the viscous portion of the material. As shown in Figure 8.9, the small initial increase in loss modulus may be primarily attributed to the addition of the unstrained

silica networks with increasing strain amplitude. The loss modulus reaches a maximum value at moderate strain and decreases rapidly as the strain amplitude is further increased. These phenomena are caused by the rapid breakdown and reformation of silica networks.

After the peak value at moderate strain amplitude, the reformation of the silicas in the elastomer matrix decreases more rapidly than its disruption. At a certain extent of high strain amplitude, the silica network is destroyed and the reformation is not possible in the time scale of the dynamic strain frequency. Hence, the effect of the filler network on the loss modulus disappears, as is evident in Figure 8.9.

Compound C1, which is filled with untreated silica shows the highest loss modulus value and decreases more rapidly compared to the rest of the compounds. The high work of cohesion and the more developed silica network are primarily responsible for this observation. Comparing the Payne effects observed with the different silanised silicas in Figures 8.8 and 8.9, the silica silanised with bulkier silanes (C6 and C7) exhibited the lowest storage and loss moduli. C6 and C7 compounds have the smallest Payne effect.

It is also observed that the non-coupling silane (C9) exhibited only small reductions in moduli when compared with the untreated silica compound (C1). Like the coupling silanes, surface modification with the non-coupling silanes will reduce silica networking and thus increase the dispersion of the silica, as observed in Chapter 6.

However, the non-coupling silanes have smaller effect as regards reducing silica networking and increasing silica dispersion, because there is no silica-rubber coupling blocking the surface of the silica and preventing networking between silica aggregates. The reduction in the Payne effect, observed with the non-coupling silane, together with the larger reductions observed with the coupling silanes, provides evidence that the size of the Payne effect is related to the dispersion of the filler and thus to the potential breakdown of filler-filler interactions, i.e. mechanism i) in the discussion by Ladouce-Stelandre et al. [243], although mechanism ii) adsorption-desorption of elastomeric chains on the filler surface cannot be ruled out.

Of all the silanes, DTSPM (C6) appears to have the smallest Payne effect. This silane had the lowest grafting efficiency (Chapter 4), but it is much bulkier than the other silanes and the polyether oxygens are thought to hydrogen-bond with the silanols on the silica surface. Thus the surface coverage should be high and, indeed the work of cohesion was one of the lowest and the microdispersion was the highest. Consequently, the Payne effect was reduced. Commercially, this silane is claimed to provide lower tyre rolling resistance, which would correlate with a smaller Payne effect.

The loss tangent is the ratio of loss modulus to storage modulus, which is representative of the ratio of heat loss to that recovered for a given energy input during dynamic strain. The increase in loss tangent at low strain reflects the small increase in loss modulus and the decrease in storage modulus. When the strain amplitude is further increased, the rate of filler network disruption increased. As discussed above, the loss

modulus passed its maximum value and rapidly decreases due to higher filler disruption relative to reformation. In the case of C1 and C9, with untreated and OTES-treated silica, respectively, the decrease of loss modulus is slightly less rapid than that of storage modulus. Hence, a small increase in the loss tangent curve with increase strain is observed as displayed by Figure 8.10. In the case of the other compounds with coupling silanes, the loss tangent changes little with increasing strain.

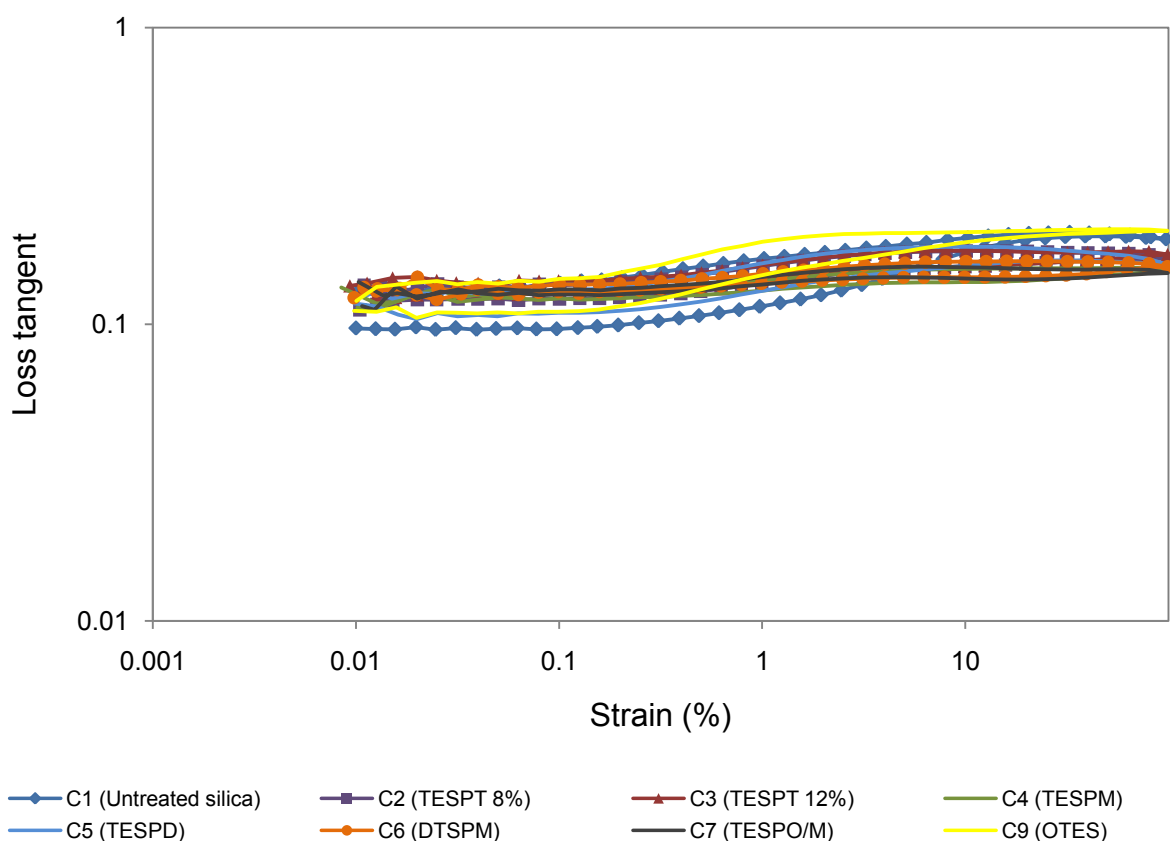


Figure 8.10: Loss tangent of silica-filled elastomer compounds.

As discussed above, untreated silicas form stronger filler networks compared to silanised silica compounds. The results show that generally the untreated silica-filled

elastomer vulcanisate of compound C1 exhibits higher hysteresis due to silica network disruption. When the strain amplitude is increased, more silica networks were broken down and reformed, resulting in higher hysteresis.

8.5 Conclusions

In conclusion, it is shown that strong couplings between silica particles and elastomer chains are crucial in elastomer vulcanisates for improvement in the abrasive wear. The mechanism of abrasion of elastomer composites, appears to involve the breakdown of the interactions between filler and elastomer. With coupling silanes, the resulting couplings between silica and elastomer have limited the fracture process. Chemically modified silica has played a major role in the wear process. The higher degree of DIN abrasion resistance observed with the coupling silanes can be explained through higher tear strength and stronger elastomer-filler coupling, as shown in the stress-strain measurements. It appears that elastomer-silica coupling is not a crucial factor in controlling the Akron abrasion resistance, which is controlled more by the dispersion of the silica. This finding is consistent with a recent study that has provided evidence of poor correlation of Akron abrasion with on-the-road tyre wear testing.

Compound C1 (untreated silica) shows a large Payne effect due to the presence of a developed silica network. The results also indicated that the untreated silica network breaks down more compared to that of the silanised silicas. By comparing different kinds of silanised silica, the study showed that the Payne effect can be directly related to filler surface activities, which affect the deformation and reformation of the filler network. Compounds C6 and C7 with the bulky coupling silanes DTSPM and

TESPO/M, respectively, exhibit the smallest Payne effect, while compound C9, with the non-coupling OTES, has a larger Payne effect than the other compounds with coupling silanes. There appears to be a correlation between poor microdispersion and greater hardness, implying that silica networking is leading to higher hardness.

CHAPTER 9 CONCLUSIONS

9.1 Introduction

In this section, the thesis is summarised and some major points, research findings and challenges are highlighted. The aim of the research was to establish the role of silica surface chemistry and the effect of interactions between silica and the elastomer phase on the filled elastomer properties. A range of silanes were investigated, employing a systematic and detailed approach. These silanes include coupling and non coupling silanes. To characterise the grafted silanes on the silica surface, thermogravimetric analysis with infrared spectroscopy (TGA-IR), inverse gas chromatography (IGC), TEM-network visualisation analysis of dispersion, rheological and mechanical analysis techniques were employed. The results obtained from these techniques were evaluated, and the surface energies of the modified silica were correlated with the silica particle dispersion in the elastomer phase. The major findings of this study are as follows:

- i. Silanes with long alkyl chains reduce the surface energy of silanised silica the most and provide a relatively homogeneous dispersive surface energy.
- ii. A correlation between the silica work of cohesion and silica aggregate microdispersion in the elastomer phase.
- iii. Use of coupling silanes can further improve the silica aggregate microdispersion due to a small amount of silica-elastomer coupling occurring during mixing.
- iv. Strong bonds between silica and elastomer are important for improvement in the abrasive wear. Breakdown of the filler-elastomer coupling may play an

important part in the mechanism of tyre wear. Use of coupling silanes provides strong silica-elastomer bonds and limits the fracture process.

9.2 Overall Summary

The investigation of the silanes started with the evaluation of the effectiveness of silica silanisation process using a TGA-IR technique. Tyre reinforcing grade silicas as-received were studied to measure the density of physisorbed water and silanol groups on the silica surface. In TGA, the removal of water physisorbed on the silica surface occurred mainly between RT and 200 °C, and silanol groups dehydrated to siloxanes between 200 °C and 800 °C. The physisorbed water and surface silanol groups were taken into consideration when quantifying the amount of silane grafted on the silanised silica surface and the weight losses determined relative to dry silanised silica. The evolved gas from the TGA was analysed by FTIR to determine and identify the type of functional groups displaced from the modified silica surface. The TGA data showed that the efficiency of the silica silanisation process for 1 hr ranged between 29% and 78%, mainly at the upper end of this range with a median efficiency of 63%. The bulkier silanes, DTSPM and TESPO, showed lower grafting efficiencies, but probably similar or greater surface coverage. The study estimated that approximately 53% to 69% of silica silanised with TESPT and TESP is disubstituted or doubly bound to silica surface. The TGA-IR technique allows measurement of the silanised silicas and compares with untreated silica. The information gained is used to explain the silanised silicas surface thermodynamic characteristics and filled-elastomer properties. Ethanol is displaced to form siloxanes at moderately low temperatures.

The second approach as discussed in this thesis was to measure the changes of silica surface energy when the silica surface chemistry is modified. The aim is to establish the silica surface energy heterogeneity and the dispersion of the modified silicas in elastomer compounds. The surface energy profiles as a function of surface coverage, which include the dispersive and specific components, were correlated with the microdispersion of the untreated silica and silanised silica aggregates in the elastomer matrix. The first major finding, reported for the first time in this thesis, was the effect of long substituent chains in the bulkier silanes (DTSPM, TESPO and TESPO/M). The long chains silane significantly reduce the surface energy of silanised silica and provide a relatively homogeneous dispersive surface energy, even though the TGA results indicated lower silanisation efficiencies for the bulkier silanes. The silanised silicas with silanes that have similar chemical structure (TESPT and TESPD) exhibit similar dispersive surface free energy profiles.

The second major finding was the correlation between the work of cohesion of silica and the microdispersion of the aggregates in the elastomer phase. The work of cohesion, W_{coh} , of silica was determined through the IGC analysis. The TEM micrographs, obtained by a network visualisation procedure, have provided a good estimation of silica aggregate microdispersion in the elastomer matrix. Bound rubber results showed that silanising silica using coupling silanes normally provides a limited degree of coupling between the silica and the elastomer chains during mixing at normal dumping temperatures (above 155 °C). This premature silica-elastomer coupling leads to a further improvement in the silica microdispersion.

The Mooney viscosities of compounds containing untreated silica show the hydrophilic nature of the silica surface and the development of a strong silica network. Silanisation suppresses the silica aggregates' work of cohesion and reduces re-agglomeration after mixing. The bulkier silanes provide more surface coverage and consequently exhibit the lowest Mooney viscosities. These observations are in good agreement with the low and homogenised surface energy characteristics measured through IGC. The compounds with silanes containing trimethoxy- or triethoxy-silyl groups display smaller viscosity decreases during the Mooney test at 100 °C. This is attributed to hydrolysis of the additional alkoxy groups leading to siloxane bonding and silica-silane-silica bridges.

The cure kinetics analysis showed that silanised silica-filled elastomer compounds exhibit lower M_H compared to compound filled with untreated silica. In the case of the coupling silanes, there appears to be an inverse correlation between the torque rise and the expected reactivity of the sulfur-containing group within the silane towards the elastomer. The third major finding is that the limited degree of coupling between the silica and the elastomer chains, occurring during mixing, is a key factor in shielding the silica surface and limiting silica networking during the cure. This observation is supported by TEM microdispersion analysis. Thus, silica silanised with coupling silane prevents the re-agglomeration of silica aggregates and improves the microdispersion in the elastomer matrix.

Another key point is that strong coupling between silica particles and elastomer chains are crucial in elastomer vulcanisates for improvement of the abrasive wear. The abrasion of elastomer composites, appears to involve breakdown of the interaction between filler and elastomer. With coupling silanes the coupling between silica and elastomer chains increase the tear strength and reduce the fracture process.

To further study the effect of silica surface chemistry modification, dynamic mechanical analysis was performed from 0.01% to 100% and reversed to 0.01% at a frequency of 1 Hz. The study showed that the Payne effect can be directly related to filler surface activities, which affect the deformation and reformation of the filler network. Compound C9 with OTES, a non-coupling silane, exhibits the smallest Payne effect. This provides evidence that the Payne effect arises from silica networking rather than from silica-elastomer adsorption and desorption.

The results presented in this thesis, provide an insight into the importance of silica surface chemistry and of strong interaction between the silica and elastomer chains for improving the reinforcing of an elastomer, especially for tyre applications.

9.3 Future Work

Future work should centre around the following matters: the implications of particle surface chemistry in other elastomers such as natural rubber; the implications of silica surface chemistry in large-scale reactive mixing in the rubber industry; investigation of the performance of silanised silica-filled elastomers tyre compounds under actual road service conditions.

The amount of physically adsorbed water on a silica surface is a common challenge faced by rubber component manufacturers. The presence of water molecules on the silica surface contributes to the formation of silica networks. Modification of the silica surface with the appropriate silane would certainly be a step forward in improving the silica microdispersion in various elastomers or blends of elastomers. This can be extended to other coupling silanes and using elastomers other than sSBR and BR.

Large scale mixing, such as 100 kg or more per batch, in a rubber processing plant may face different challenges to meet the designated vulcanisate mechanical application. Developing an approach for large scale silanisation is important as this study has showed the importance of silica surface chemistry for the reinforcement of elastomers.

The road and weather conditions in different regions have effects on the performance of tyres during service. The modified silica might have different implications in different road conditions. An investigation of the impact on surface

properties of large-scale silanisation and on the resulting performance in tyre tread compounds would be useful.

9.4 Final Remarks

Modification of silica with different silanes enabled the direct investigation of the effect of silica surface chemistry through IGC analysis and TEM-network visualisation, on the silica microdispersion in the elastomer phase as well as of the effects on compound properties. This work has successfully exemplified the importance and the role of silica surface chemistry in the characteristics of silica-reinforced elastomers. The hypothesis that silica surface modification with a coupling silane enhances the mechanical performance has been shown here. It is certainly worthwhile to apply these new findings to the engineering of silica-filled elastomer compounds for tyre applications and perhaps other applications.

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