

Chapter 1

1. Introduction

1.1 Background

Waste management is a worldwide problem dating back from early ages, which affects all living organisms on the earth. But in recent years, with waste escalation, it has become a very crucial issue that has required robust strategies to be put in place, in order to intervene with as well as eradicate the problem. Its dependence on increasing population size has made it rather difficult or even impossible to regulate, as people are the main contributors to waste production (with other organisms such as animals only playing a minor contribution).

Waste contributes to crises such as land, water and air pollution, resulting from increased dumping, contamination of surface and ground water supply as well as the burning of the solid wastes [1-5]. Unlike other global crises this is an unavoidable topic, particularly because it is an ongoing problem which results from the incline in living standards of man in the course of economic development. In order to efficiently manage and/or eradicate this problem, an understanding of the quantities and characteristics of the waste being generated needs to be acquired. Some developed countries, like the USA, have a much better understanding of this problem and hence have put robust plans in place to manage a large range of wastes [6-11].

Systems that have been implemented have involved the collection and transferral of waste to selected areas for appropriate disposal, according to their nature i.e. the extent of their toxicity and degradability. There have been a variety in waste collection methods used, which have included door to door collection as well as indirect collection (where containers such as bins have been used) [12]. These systems have been very expensive, time consuming and have required a lot of labour. Hence management of waste in most parts of the world, especially those in less developed countries and communities, has remained a crisis. This is especially significant in areas with small populations, where there has been a land or space shortage and where little to no option for waste disposal has existed [12]. Hence in these

cases mentioned above it has become vital to recover, reuse and recycle these waste materials.

Sources of wastes range from: household, agricultural, commercial, industrial, construction and institutional. These may be in the form of solids, liquids and gases and include items such as: glasses, fuels, plastics, tyres, hazardous chemicals and methane. In the case of waste rubber, used automobile tyres have rapidly become sources of solid waste as there has been a worldwide increase in the number of cars [12]. However, little has been done to eradicate this type of solid waste material. Waste tyres, are used tyres that have been worn down or have had damage to their sidewalls and have ultimately become unsuitable for road or any other type of use. Due to the nature of this bulky, stiff and chemically cross-linked material, waste tyres have been difficult to dispose of. These properties have made waste tyres near impossible to crush, compress or fold, like most other waste materials (e.g. metal cooldrink cans) in order to make them smaller for easier management. Similarly, the tightly bound long polymer chains associated with rubber, which are not easily degradable, has been another factor which has made used tyres difficult to dispose [12-13]. Hence shredding methods have been used for their disposal [14]. However, these have involved a number of mechanical operations and have thus tended to be expensive. For this main reason many companies have stopped using these infeasible methods [13-14]. Unfortunately this has resulted in large quantities of waste tyres being disposed of by illegal dumping [14]. These illegally disposed tyres have in turn piled up and become an environmental problem in many other ways. One of these has been the trapping of rain water, which has resulted in their habitation by mosquitoes and other viral hosts with the potential to cause diseases, such as malaria [14]. In addition, when waste synthetic rubber materials, such as styrene-butadiene rubber (SBR), have been illegally disposed of this way, the numerous hazardous components contained therein (such as: copper, cadmium, zinc, etc.) have been known to be able to leach into the environment [14-15]

Of all the waste rubber materials dumped world-wide (Figure 1.1), styrene-butadiene rubber (SBR), is one the largest components [16]. Hence it is vital to investigate and study its properties, in order to implement ways of recycling and/or reusing products containing it, like waste car tyres.



Figure 1.1. Waste tyres disposed of on open land [16].

1.2. Motivation

1.2.1 Setting the scene

Considering the huge impact that waste tyres have had on the environment, the purpose of this study was to examine whether an alternative approach could be developed to utilise pure SBR polymer (the main component in used car tyres) to synthesize a reinforced composite material. Due to their ideal physical properties (which will be discussed in detail later) doped and undoped micro and nanocarbon materials were chosen to be studied as fillers for these SBR polymers. In this way it was hoped that the lessons learned through this study, could then be directly applied to waste rubber tyres for possible future applications such as: low cost building materials in the housing industry. The sections which follow, briefly describe the backgrounds associated with components of the composite material proposed and the aims and objectives behind this study.

1.2.2 The reinforcement of rubber polymers by fillers

The reinforcement process of rubber has been referred to as the improvement of its elastic modulus, failure resistance (tensile and tear strength), as well as the related properties of its vulcanizates [17]. In order to achieve high strength in rubber composite structures, a rubber matrix has to be filled with a material of high strength and surface area. The higher the surface area and the strength of the filler applied, the more reinforcement gained [17]. The main reason for filler addition in polymeric materials like rubber has been to improve their flexibility and eliminate disadvantageous properties like stiffness [17]. Structure and surface characteristics, especially the particle size and chemistry, have been some of the most important factors which have controlled the reinforcing ability of fillers [17].

The presence of filler materials has been known to modify the polymer behaviour depending on the cure process [18]. The cure process has typically involved cross-linking (the making of bridges between individual polymer chains) of the loosely hanging, freely moving polymer chains, to make the resultant material more rigid [18]. Two ways this has been achieved have been through adding elements like sulphur and by mixing the components at high temperatures [18].

Fillers also have been known to form barriers/coatings that have significantly reduced the permeability and thus the absorption of liquids/gases in these composite materials. This in turn has improved the fire resistance of some composites by restricting the supply of oxygen to the combustible areas [19]. Likewise these barriers have hindered the access of water vapour or chemical solutions and have thus prevented cracking as well as peeling of the polymer. Hence by providing thermal stabilisation, increased hardness and reduced permeability, fillers have been successfully used to extend the lifespan of an original polymer [19-24].

Carbon nanomaterials (like carbon nanotubes (CNTs)) are assumed to be some of the best reinforcement materials for polymer matrix composites, because of their high aspect ratio, specific surface area and Young modulus [25]. Furthermore these nanomaterials have been shown to enhance the electrical properties of the polymer matrix that they have been added into [25]. The introduction of foreign elements (often called ‘doping’), such as nitrogen or boron, into the lattice of carbon nanotubes (CNTs) and carbon nanospheres (CNSs) has been shown to tune their electronic and chemical properties by changing the number of electrons

on the surface [26]. This, in conjunction with surface functionalisation (a technique used in this study to add sulphonate moieties onto carbon microspheres (CMSs)), has been shown to enhance the preparation of reinforced composites by increasing their dispersion in the polymer matrices, as well as improving their bonding within the polymer matrix by reducing CNT agglomeration [27].

1.2.3 The possible uses of nano and microcarbon reinforced rubber polymers

Due to the abundance of solid waste rubber in South Africa [27] and the potentially good mechanical, thermal and electrical properties that could arise from the synthesis of composites reinforced with nano and micro-sized carbon nanomaterials, these may become suitable for use in a wide range of applications, including low cost housing materials (i.e. for insulation, roofing, etc.).

An example to show that utilising waste tyres for such an application is possible comes from the company: Euroshield [28]. This company has made roof tiles (Figure 1.2) comprised mainly of recycled waste tyres, as an economic and environmentally friendly building material. These tiles mimic the normal thick slate roof tile but have been shown to be more durable, thus making them a good investment for a house owner. In the process used by Euroshield, waste tyre-walls have been removed and the tread sections cut off into large pieces. The tile has then been made by heating these large pieces into shape [28].



Figure 1.2. Roofing tiles made from waste tyres by Euroshield [28].

Shelter, in the form of housing, is essential to all human beings, just like food and water. Of particular importance locally is that about 1.8 million South African families (in the middle to lower income groups) live in rented accommodation, as opposed to the approximately 5.2 million families that own property [29]. Hence there is a need for housing, which the Department of Human Settlements aims to address, especially for the poor who are living in shacks/informal settlements and rural areas. The Government has stated that it aims to improve well-located informal settlements and provide proper houses by 2014 [32]. In this regard, over 6 000 hectares of well-located public land will be allocated for low-income and affordable housing [30]. On the other hand there is worldwide interest in the disposal of scrap tyres [30]. Hence it is a worthwhile endeavour to explore ways of producing building materials (bricks, roofing, wall insulators, etc.) out of these waste tyres. These building materials should theoretically be much cheaper, with the potential to make it easier to realise the dream of millions of South Africans of owning a proper house at a lower cost. This approach may also be one of the ways that could be used to promote the recycling of rubber, which is a sustainable solution that is recognised and encouraged by the South African government [31]. Likewise should such waste tyre recycling facilities arise, they could potentially reduce the environmental impact of this solid waste, as well as offer significant profit potential both in the informal and formal sectors.

1.2.4 The rationale for the choice of materials used

Although the eventual aim of the overall project to be conducted in this area is to examine the properties of waste rubber composites reinforced with micro and nanocarbon materials, a number of reasons guided the decision to start simply with pure SBR (which could easily be obtained from KarboChem Ltd) and micro and nanocarbon materials (which could be synthesized under controlled conditions in the laboratory). The main reasons for this were:

1. The components added to each of the various blends of rubber used in the car tyre industry in South Africa are numerous. The effects of each of these on the synthesis of such a composite would be unknown and untestable, since the identification of these components constitutes the violation of intellectual property (IP) owned by each company.

2. Use of waste tyres from any of these blends would suffer a similar problem with the added complication of contaminants that have now been entrained in the rubber during the lifetime of the tyres.
3. The lack of crushing equipment to make rubber chips from selected waste tyres that would be sufficiently small for use in composite synthesis.

For these reasons a decision was then made to utilise pure SBR (the main component of car tyres) and study its interactions with micro and nanocarbon material fillers, as a preliminary study for this dissertation, in order to offer knowledge for similar work on waste tyres in the future.

1.3. Aims and objectives of the study

The aims of the project were to:

1. Synthesise by the chemical vapour deposition (CVD) method and then purify a variety of micro and nanocarbon materials for use as fillers in SBR including: undoped CNTs, N-doped CNTs (NCNTs), carbon microspheres (CMSs) and N-doped microspheres (NCMSs).
2. Synthesise by the hydrothermal method and purify functionalised CMSs with sulphonate moieties (SOCMSs) and unfunctionalised CMSs for use as fillers in SBR for comparison with those synthesised by the CVD method.
3. Prepare a range of composites (with the same filler volume fraction) comprising SBR with: undoped CNTs, NCNTs, CMSs and NCMSs as well as SOCMSs.
4. Evaluate the chemistry and the mechanical behaviour (tensile strength) of the various SBR/micro and nanocarbon composites.
5. Characterise the various micro and nanocarbon materials synthesised and the reinforced composites by a range of techniques including: transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), fourier transform infrared spectroscopy (FTIR), laser Raman spectroscopy, Brunauer Emmet and Taller (BET) surface area analysis.
6. Perform mechanical tests (tensile strength measurements) on the reinforced composite to establish the strengths of these materials.

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Chapter 2

Literature Review

2.1 Rubber Materials

2.1.1 Introduction

Rubber is a sticky elastic polymer called an ‘elastomer’. The word is believed to be derived from the properties such materials possess i.e. their elasticity and the fact that these kinds of materials are long chain molecules called polymers; so the combination of these gives rise to the name elastomer [1]. Elastomers are highly flexible and stable with a 3-dimensional chemical structure which is able to withstand an external force exerted upon it to induce deformations (Figure 2.1). These materials can be subjected to repeated stresses by stretching them to at least twice their normal length. It is these properties (durability, modulus and tensile strength) that lead rubber materials to be used for their specific applications such as in shock absorbers and tyres.

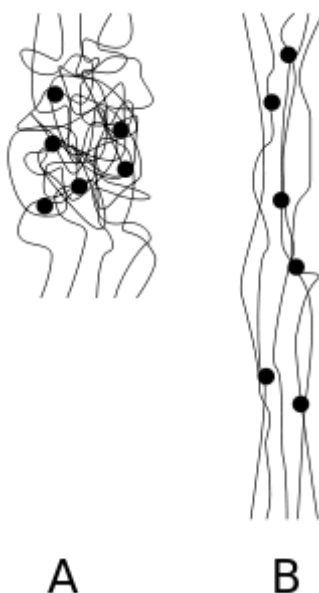


Figure 2.1. A schematic representation of unstressed polymer chains (A) and the same polymer chains under stress to form (B) [2].

In ancient times latex or modern-day ‘poly-isoprene’ was the only natural rubber material known to man [3]. Then, as is still done now, latex was harvested by ‘tapping’, a process whereby a cut was made in the bark of a rubber tree (without destroying it) and the sap (or latex) collected in a bucket below the cut [3]. Although tapping is still used as a source of poly-isoprene today, the majority of rubber produced in the world is synthetic. This is due to the ability to control its quality and quantity by chemical processes. However, the original contents of the rubber material (natural and synthetic) have been found to be sticky when hot and brittle at lower temperatures; this has made their direct application difficult [3]. Hence, through the process of vulcanisation, where chemical bonds between the long chain molecules have been formed by the addition of substances like sulphur or peroxide, rubber has been made to return to its initial shape after any type of strain has been applied to it [3]. In this way rubber’s elasticity has been increased and damage caused by strain from sunlight, oxidation, abrasion, cold, heat resistance, etc. have been minimised or eliminated.

Synthetic rubber that is used today has numerous advantages over natural rubber, including higher thermal stability and purity. The controlled synthesis of rubber has also allowed for co-polymerisation of various monomers which has further enhanced its physical, mechanical and chemical properties. The number of different synthetic rubbers that now exist include: chloro isobutylene isoprene, polyether urethane, vinyl methyl silicone, etc. However, in this study, the focus was specifically on a synthetic rubber called styrene butadiene rubber (SBR).

2.1.2 Styrene butadiene rubber (SBR)

SBR is one of the most widely used synthetic rubbers and has many applications that include: automotive tyres, sidewalls, cover strips, wires, cables, footwear, roofing barriers and sporting goods [4]. This wide range of applications exists because of the high fracture elongation of rubber. As a result, these applications contribute to the enhancement in the quality of life and contribute to a better economy in the different uses of this material. SBR (see Figure 2.2) is formed from the polymerisation of the monomers: styrene and 1,3-butadiene, in a reactor through heating [5].

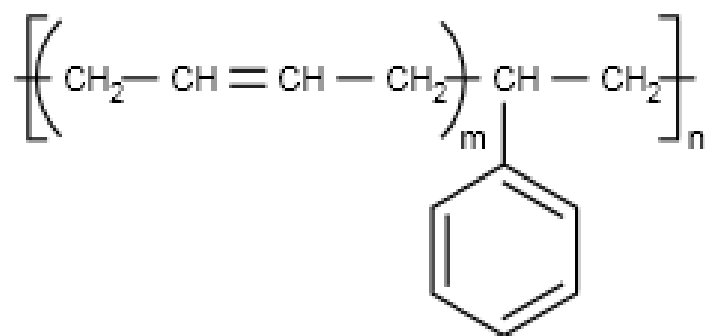


Figure 2.2. A diagram showing the structure of styrene butadiene rubber (SBR). Adapted from [6].

This copolymer (Figure 2.2) can be produced by two different processes: 1) solution (S) or S-SBR (i.e. ionic polymerisation) or 2) emulsion (E) or E-SBR (i.e. free radical polymerisation) [6]. The former process uses lithium alkyl, where each initiator molecule forms a single polymer chain. The lack of acidic solvents (chain terminators) in the system, results in the polymer chain continuing to grow as long as the initial material is provided. This process also involves two methods of initiating polymerisation, namely: direct and seeded. In the direct method all ingredients (solvent, monomer and initiator) are mixed directly with one another. However, in the seeded method the solvent and the initiator are mixed with only a small proportion of the monomer [6-7]. The process is then allowed to continue until all the monomer is used up, thereafter the remaining monomer is added [6-7]. In the latter process, there is a wide variety of E-SBR types that can be synthesised based upon: the styrene content, polymerisation temperature, staining or non-staining antioxidants as well as oil and filler content.

SBR is amorphous and lacks the self-reinforcing qualities of natural rubber. This causes it have low elastic modulus and durability [7]. Thus to SBR, as in other synthetic polymers, additives may be added to improve these properties. Typical additives may include: 1) vulcanisation agents such as sulphur or peroxide which are used to enhance polymer cross-linking, Figure 2.3, 2) fillers such as carbon black which are used to reinforce the rubber material, 3) plasticizers such as minerals oils and paraffins which are used to improve the flow of the material, 4) accelerators such as tert-butyl-2-benzothiazole sulphonamide (TBBS) to help increase the rate of complex formation (cross linking), 5) activators like zinc oxide and stearic acid which are used to trigger the vulcanisation process, 6) antioxidants or anti-

degrading agents which are used to shield against radicals formed from ozone and oxygen [7]. These supplementary chemicals have proven to be vital in achieving the required properties of the product, but have also been able to compromise the strength and stability of the final material to some degree if they were not controlled [7].

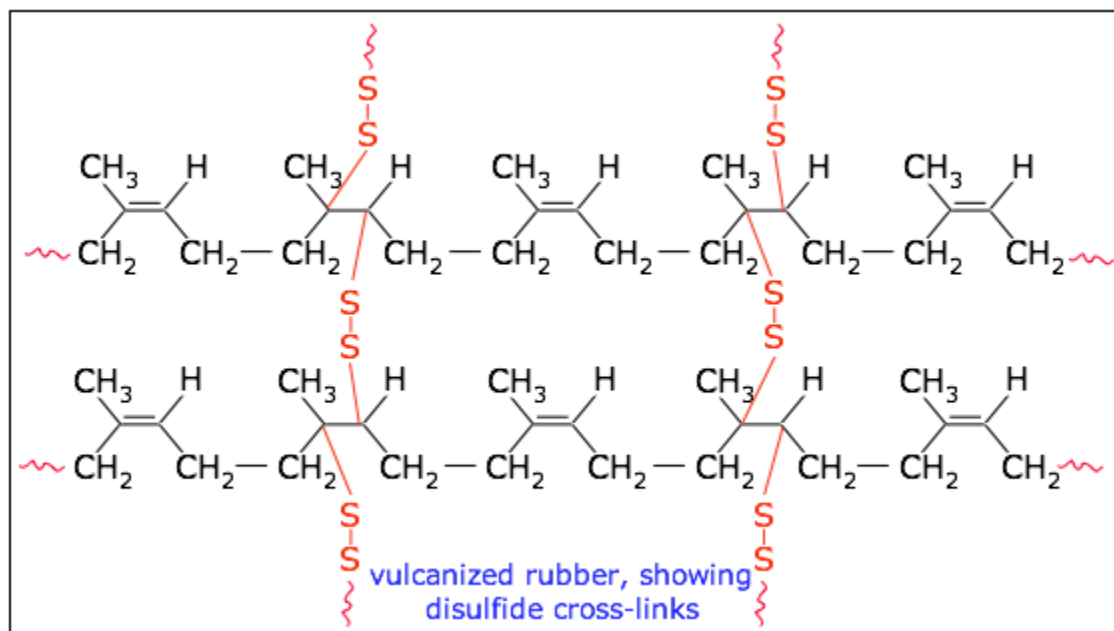


Figure 2.3. A schematic diagram showing the crosslinking of polymer chains by disulfide in vulcanized rubber [7].

The reinforcement of synthetic rubber using materials called fillers has been achieved by the formation of strong interactions and bonds between the fillers and the polymer. Thus the durability of the rubber material has been enhanced within the regions where the fillers were situated [8-9]. However, the reinforcement effects of these fillers have depended on the structure, surface characteristics, dispersion and particle size of the fillers. Larger particle sized fillers have been prone to deterioration due to poor polymer-to-filler interactions [9]. It has also been established that vulcanizates of SBR contain lower tensile properties [9]. On the other hand the tensile properties of E-SBR vulcanizates have depended in great measure on the type and quantity of filler that was added to the compound. Cured gum stocks for instance, have displayed tensile strengths of up to 27.6 MPa [10].

With regard to the curing of SBR, as previously indicated, a number of systems including sulphur (accelerators and sulphur), peroxides and phenolic resins have been used [10]. Likewise processing of SBR compounds has been performed in mills, internal mixers or

mixing extruders. SBR compounds have also been cured in a variety of ways, which have included: compression, injection moulding, hot air or steam autoclave, hot air oven, microwave ovens or combinations of these techniques [10].

Other properties of SBR have tended to vary. For instance, SBR (a non-polar polymer) and its vulcanizates have been shown to be poor conductors of electricity [10]. While the electrical properties of E-SBR have been shown to depend on the quantity and sort of emulsifier and coagulating agents that were used [10]. As far as resistance to solvents has been concerned, although E-SBR vulcanizates have prevented the chemical attack of many polar solvents (such as dilute acids and bases), they have been found to swell considerably when in contact with fuel, oil and fats [10]. Due to this limitation, SBR cannot be used in applications that require resistance to swelling in contact with hydrocarbon solvents.

2.1.3 SBR and its composites

A composite is formed when two or more materials are bound together to form a unit that has unique properties which the building blocks themselves don't have, or that enhances the properties of one of the materials by another [11]. Each of the components forming the composite still has their specific characteristics. The two important parts of a composite are the: matrix and the dispersed or 'reinforcing' phase. For a composite to be effective, the interaction between these two parts should be strong. Large surface area materials with high aspect ratios such as carbon nanotubes, nanofibers, flakes etc. are preferred as they offer better interaction of the two parts of the composite. Carbon black and silica have been used a great deal over the years as reinforcing phase components (which includes rubber) to enhance their initially low modulus and durability [11-12].

Polymer (rubber)/carbon nanomaterial composites have been prepared in a number of ways including: solution processing, melt mixing, *in situ* polymerisation, etc. [12-15]. Of these, solution processing has been found to be the most non-ideal for industries, due to its time consumption as well as usage of large amounts of solvents to dissolve the polymer (rubber) material. On the other hand, melt mixing has been preferred because of its speed and simplicity [12, 16-17].

However, even when melt mixing has been used, it has been noted that the manner in which this has occurred has also been important. For instance, depending on whether all the starting materials were mixed in an open mill or as a batch in an internal mixer, this has determined the characteristics of the final material. In the former case, an open mill with two heat controlled counter rotating rolls has resulted in the recovery of a sheet of rubber after mixing. In the latter, an internal temperature controlled mixer with two counter rotating rotors has mixed the rubber with the additives to make a kind of rubber ‘dough’ which could then be processed further.

In addition to this, the shapes of these materials need to be considered in different applications. These have been achieved through moulding. Depending on their intended final purpose, there have been a number of ways in which rubber materials have been formed into their desired shape, including: compression, transfer and injection moulding [18]. For instance, in compression moulding two preheated split moulds with cavities containing pre-weighed amounts of rubber have been used. Here when the moulds have been made to come together to firmly press against their contents they have given rise to the desired shape [19]. In these cases curing has been induced by applying heat and pressure to make the material take the shape of the mould cavity. While in transfer moulding, uncured material has typically been placed on a plate **above** the cavity. This is unlike in compression moulding where it was placed directly **in** the cavity of the mould. The contents were then pushed into the cavity, via a gate, in order to be vulcanised. Lastly, in injection moulding, in a manner similar to transfer moulding, a screw-in process rather than a push-in one was used. Of the three processes, injection moulding is the most preferred. This is because the repeatability and consistency of the technique has allowed for a high volume of production [19-23].

2.1.4 Properties of SBR

Rubber is not only an elastic material but a good electrical insulator and is a waterproof [23]. This material has shown good physical and chemical properties for centuries now as applications would suggest. These properties are further categorised into mechanical, thermal, electrical, optical and process or physical properties. Mechanical properties include tear strength, tensile strength, tensile modulus or modulus of elasticity, stretching

(elongation) and impact strength (toughness). Thermal properties are glass transition temperature, conductivity and expansion. Electrical and optical properties include resistivity, permittivity, refractive index and light transition. Process and physical properties include process temperature, density, viscosity, melting and absorption of water. In order to compare the different characteristics of these materials standardised tests are used [23-25].

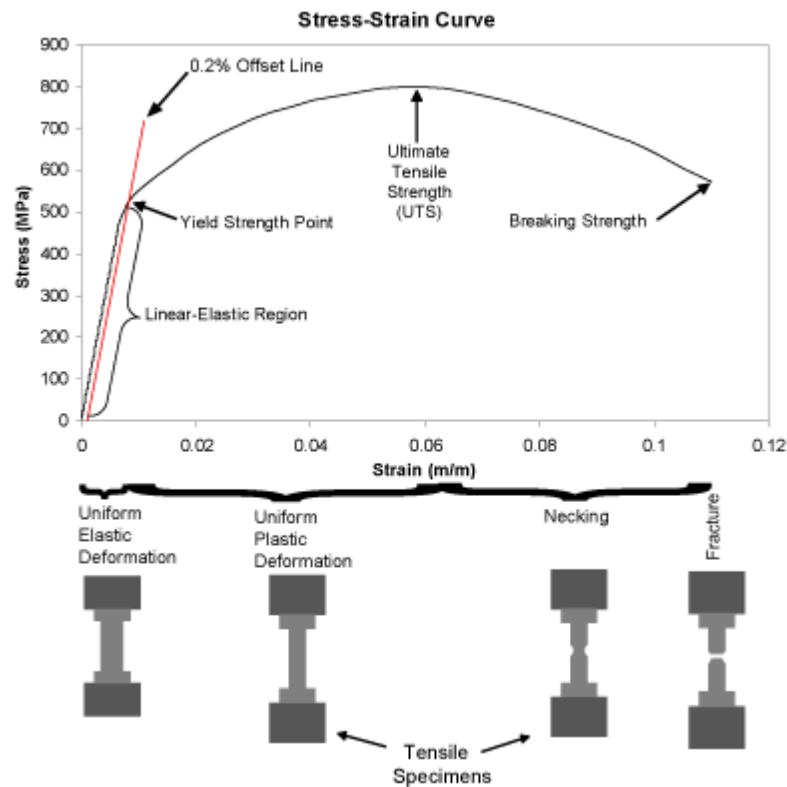


Figure 2.4. A schematic representation of the stress versus strain curve with related specimen deformation, accompanied by the applied stress [26].

Each material has a data sheet where results are provided by the International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM). Accordingly the most important properties associated with the character of a material are defined as (see Figure 2.4):

- Specific gravity: defined by the composition of the material (ISO 2871, ASTM D 1817) and is measured by weighing the specimen in air and water.
- Hardness: defined as the elasticity of a material (ISO 48, ISO 1400, ISO 1818, ASTM D 2240, ASTM 1415) and is measured using a durometer which uses a pointed

indenter that presses against the specimen and an IRHD tester where a dead-load is used to determine the specimen hardness from the indentation.

- Tensile strength-elongation: defined as the maximum stress reached when stretching a material in testing (ISO 37, ASTM D 412). A flat dumb bell shape specimen is usually used in this case, by stretching it to its breaking point.
- Compression: defined as the deformation between the original and final dimensions of a material (ISO 815, ASTM D 395). Cylindrical disks are used in this case and compressed such that the compression is 25% of the normal height at a specific temperature. After cooling, the thickness of the specimen is re-measured and the difference from initial to final thickness gives the level of compression.
- Resistance to heat aging: defined by testing the changes to physical properties under heat to also determine how long the material can last (ISO 188, ASTM 573). Tests are done in an air oven or in a pressure chamber.
- Resistance to weathering: defined as the deterioration of the physical properties of a material when exposed to weather (cracking, peeling, etc.) (ISO 1431/1, ASTM D 1149). The specimen is taken through a number of weather related conditions including: exposure to sunlight, oxygen and moisture.
- Resistance to liquids: defined as the absorption of a liquid by the material, causing swelling that affects the original structure (ISO 1817, ASTM 1817). The degree of swelling is measured by calculating the change in volume of the specimen before and after a liquid is absorbed [27].

2.2 Carbon nanomaterials

Nanomaterials are small ‘not visible to the naked eye’ structures that can be assembled atom by atom, such that one or more dimension is of 100 nm or less. There are several types of these nanomaterials that are known and named according to the number of dimensions that conform to the range of 1-100 nm [28]. There are three classes of these materials, namely quantum wells, quantum wires and quantum dots. Quantum wells are two dimensional (2D) structures i.e. they have only one dimension confined to the nanometer range e.g. discs, prisms, films and plates [28]. Quantum wires on the other hand are one dimensional (1D) structures i.e. they have two dimensions that are confined to the nanometer range e.g. rods and wires [28]. Quantum dots are, however, zero dimensional (0D) structures i.e. they have

three dimensions confined to the nanometer scale e.g. spheres, cubes, and polyhedrons [29]. Typically it is found that materials with dimensions that are in the nanometer range are so small that they restrict electron movement along those dimensions. So for example in a 2D structure the electrons can only move along the two dimensions. This brings about enhancement in terms of optical, electrical and physical properties for this material as compared to the bulk or three dimensional (3D) material [29].

As a result of these desirable properties, nanomaterials have attracted a lot of interest. Carbon nanomaterials have been no exception to this trend. In 1985 Smalley and his co-workers were the first to synthesise and characterise carbon based quantum dots i.e. the C_{60} molecules which were later known as fullerenes [29]. Subsequently a great deal of research has been performed, to develop methods to synthesise, modify and utilise these nanomaterials. In particular carbon nanomaterials (e.g. nanotubes, nanospheres and nanofibers) due to their mechanical, thermal, magnetic and electrical properties have been exploited in research areas such as: catalysis (as catalyst supports), composite materials (to enhance the properties of an already existing material), medical research (drug delivery), energy research (for solar and fuel cell fabrication), electronics (in miniaturisation of devices such as cell phones and computers) and in water purification, etc. [30-37].

With the great reception of these materials came the exploration of the attractive properties displayed by the aforementioned carbon nanomaterials and their relatives, such as the good mechanical, thermal, magnetic, electrical properties. Carbon has four valence electrons which allow it to bond in various ways to form materials with different structures of various structural chemistry e.g. graphite and diamond which are the main allotropes of carbon, having sp^2 and sp^3 hybridisation respectively. This is owed to the fact that carbon has an ability to form multiple bonds with itself which gives it the many features associated with it [37].

2.2.1 Carbon nanotubes (CNTs)

CNTs together with graphite and diamond are regarded by many as a third allotrope of carbon [38]. They contain carbon atoms arranged in graphene sheets which are rolled together to form a seamless cylindrical tube [38]. CNTs are highly crystallised carbon filaments which are a few nanometers in diameter and a few microns long. Sumio Iijima

rediscovered CNTs in 1991 whilst using an electron microscope to study the carbonaceous deposit from an arc-discharge between graphite electrodes [38]. Since then, in addition to multiple tubes called multi-walled carbon nanotubes (MWCNTs), single tubes called single walled carbon nanotubes (SWCNTs) and double tubes called double walled carbon nanotubes (DWCNTs) have been discovered [38]. CNTs are divided into three types depending on the arrangement of the hexagonal rings in the graphene sheets as they roll up (or chiral angle) namely: armchair, zigzag and chiral [38]. An armchair CNT is associated with a 30° chiral angle and has a metallic conductor nature (which is characterised by a small bandgap between the conduction and valence bands) [38]. A zigzag CNT is also a metallic conductor but with chiral angle of 0° [38]. On the other hand a chiral CNT is a semiconductor with a chiral angle between 0 - 30° [38].

Although carbon is a light element, it has been shown to be very strong in its tubular form (just one sixth the mass of steel but at least a hundred times stronger [38]) with a Young's modulus of 1 TPa for SWCNTs [38]. Hence its broad application in the enhancement of the mechanical strengths of various materials [38], including the rubber-carbon nanomaterial composites investigated in this current study.

2.2.1.1 Production of CNTs

Well known techniques of synthesising CNTs include chemical vapour deposition (CVD), arc-discharge and laser ablation [39]. Laser ablation uses a laser pulse to heat the target surface containing graphite and the ground catalyst powder (nickel and/or cobalt) to create a vapour which is then rapidly cooled to form clusters as they condense [39]. These clusters then give rise to the tubular materials called CNTs. This process is, however, expensive because of the laser beam used. Arc-discharge on the other hand involves applying DC voltage power to create an arc between a graphite cathode and anode in a gas-filled space resulting in a high temperature to vaporise the precursor [39]. The CVD method is the most viable one for large scale production of CNTs because of its low cost and versatility [39]. Hence this technique was chosen for use in this study. Most CVD methods involve the use of a catalyst, but there are other non-catalytic CVD methods like direct pyrolysis. However in catalytic CVD the precursor gas (hydrocarbon) is passed through a high temperature furnace and the decomposition of a hydrocarbon gas which dissolves over the particles of a transition

metal such as cobalt, iron, etc. and precipitates out as CNTs in a CVD reactor and generate the required carbon.

In the production of MWCNTs acetylene is usually used as a source of carbon atoms at temperatures typically between 600 – 800°C [39]. To grow SWCNTs the temperature has to be significantly higher (900 – 1200°C) as compared to MWCNTs, due to the fact that they have a higher energy of formation. In the synthesis of SWCNTs, carbon monoxide or methane are used because of their increased stability at higher temperatures as compared to acetylene [40].

2.2.1.2 Doping of CNTs

Doping CNTs with desired chemical elements is an important way to improve their electronic and mechanical properties, by replacing carbon atoms in the CNTs for example with nitrogen or boron [41]. Recently nanotubes of other elements such as boron nitride, and boron and/or N-doped CNTs have attracted a great deal of interest [41]. Because of the difference in electronegativity between B and N atoms, boron nitride (BN) has been used in carbon allotropes in order to incorporate the desired elements to form BCN hybrids which by varying component ratios are believed to possess tuneable properties [41]. These properties include chemical reactivity and modified conductivity.

2.2.1.3 Functionalisation of CNTs

Undoped CNTs consist mainly of carbon atoms that are chemically inert. As a result they show a poor ability to be solubilised and processed [42]. In order to exploit their properties in potential applications, CNTs must therefore be chemically activated or functionalised [42]. Hence the functionalisation and solubilisation of CNTs has received much attention recently [45]. Consequently by attaching functional groups such as: –OH, –COOH, –S, etc. to their surfaces, it is possible to link up CNTs with other chemicals and polymers to tailor their properties [41-42].

2.2.2 Carbon spheres (CSs)

Graphite is formed from sheets of carbon called graphene. When a single sheet of graphene is formed into a sphere with 32 faces (20 hexagonal and 12 pentagonal) this constitutes a material commonly referred to as a buckyball or a fullerene [43]. The C_{60} buckyball is the most famous sphere but it is not the only one. In fact scientists have now discovered hundreds of different combinations of these interlocking pentagon/hexagon formations [43]. These carbon spheres (CSs) can either be nano or micro-sized and can be synthesised by methods similar to those that are normally used in the synthesis of CNTs. Among these methods are: electric arc-discharge techniques, catalytic CVD, catalytic pyrolysis of organic compounds, direct pyrolysis, high temperature hydrothermal (even low temperature syntheses have been reported), conversion from amorphous carbon and low temperature hydrothermal methods from a sugar solution [43-44]. While some of these techniques use a catalyst, the direct pyrolysis (in the absence of a catalyst) and the hydrothermal methods were the techniques of interest in this study.

2.2.2.1 Functionalisation

One of the best ways of incorporating functionalities into porous carbon materials like CSs (especially those that are micro-sized) is directly during their synthesis [45]. This can be achieved by nanocasting, chemical vapour phase infiltration or by direct methods [45]. For the direct synthesis of porous carbon materials, a very large variety of possible organic precursors for S, O and N functional groups have been used including: aromatics compounds such as acrylonitrile, hetero-aromatic compounds such as thiophene, furan and pyrrole [46-47].

In polymer composites two important aspects that need to be considered are the strength and the lifetime of the material e.g. in rubber-CNT composites, the rubber material alone has high fracture elongation and high deformability (elasticity) but has the disadvantage of forming cracks, while also having low elastic modulus durability [46-47]. On the other hand CNTs have high mechanical strength as well as thermal and electrical stability, so a composite of the two could overcome these disadvantages. These are some of the reasons why composites of CNTs/CSs and rubber were considered in this study. However, further details will be provided in the chapters which follow.

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Chapter 3: Experimental Procedures

3.1 Introduction

This chapter gives details of all the experimental procedures that were used for the synthesis of the catalyst (Fe-Co/CaCO₃), CNTs, NCNTs, CMSs, NCMSs, SOCMSs, and SBR/ Carbon material composites of each. The techniques that were used for their characterisation including: TEM, TGA, FT-IR, laser Raman Spectroscopy, BET, DSC, PXRD, Zeta potential and Tensile testing.

3.2 Chemicals and Materials

All the chemicals used in this work were 99% grade. The Fe(II) nitrate, Co(II) nitrate, CaCO₃, zinc oxide, stearic acid, antioxidant, sulphanilamide, and sulphur were all purchased from Sigma-Aldrich, South Africa. The N₂ gas and acetylene gas 99% were purchased from AFROX (South Africa).

3.3 CVD Synthesis of CNTs and NCNTs

3.3.1 Synthesis of the catalyst (10 wt% Fe-Co/CaCO₃)

Calculated amounts of the Fe(II) (3.617 g) and Co(III) (2.469 g) nitrates were mixed together, ground to a fine powder and dissolved in 30 mL of distilled water in a beaker. This solution was then added drop-wise to a CaCO₃ support (10 g) {99% obtained from sigma-Aldrich} while stirring and the mixture was left to stir for 30 min at room temperature (RT). The resulting metal-support mixture (i.e. Fe-Co/CaCO₃) was then filtered and the insoluble product was dried in an air oven at 120°C for 12 h, after which it was ground and finally screened through a 150 µm sieve. The catalyst powder was then calcined at 400°C for 16 h in a static air oven.

3.3.2. Synthesis of undoped CNTs or pristine CNTs

The 10 wt% Fe-Co/CaCO₃ catalyst was weighed into a quartz boat and placed in a quartz tube which was then placed in a tube furnace (Figure 3.1). The temperature of the tube furnace was then ramped at 10°C/min under N₂ (40 mL/min) from RT to 700°C. The flow rate was then increased to 240 mL/min and acetylene was introduced at 90 mL/min. After 1h, at 700°C, the acetylene flow was stopped and the nitrogen flow rate was reduced to 40 mL/min again as the tube furnace cooled down to RT. Thereafter the black product in the quartz boat was collected and weighed.

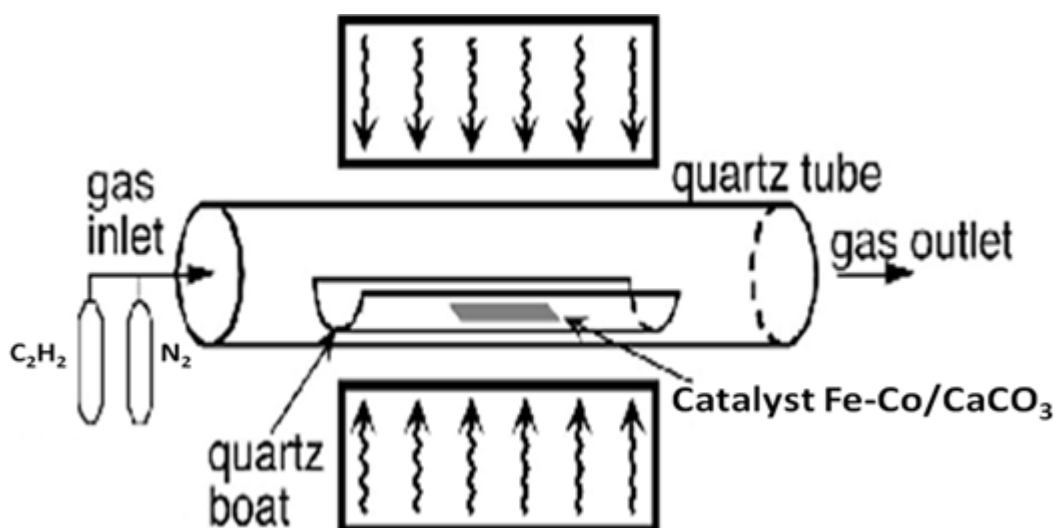


Figure 3.1. A schematic representation of the CVD set-up for the synthesis of undoped CNTs.

3.3.3 Synthesis of N-doped CNTs or NCNTs

The 10 wt% Fe-Co/CaCO₃ catalyst was weighed into a quartz boat and placed in a quartz tube which was then placed in a tube furnace connected to a bubbler containing acetonitrile, which was the nitrogen source (Figure 3.2). The temperature of the tube furnace was ramped at 10°C/min under N₂ (40 mL/min) flow from RT to 700°C. The flow rate was then increased to 240 mL/min and acetylene was introduced at 90 mL/min. After 1 h, at 700°C the acetylene was stopped and the nitrogen flow rate was reduced to 40 mL/min as the tube furnace cooled down to RT. The black product in the quartz boat was then collected and weighed.

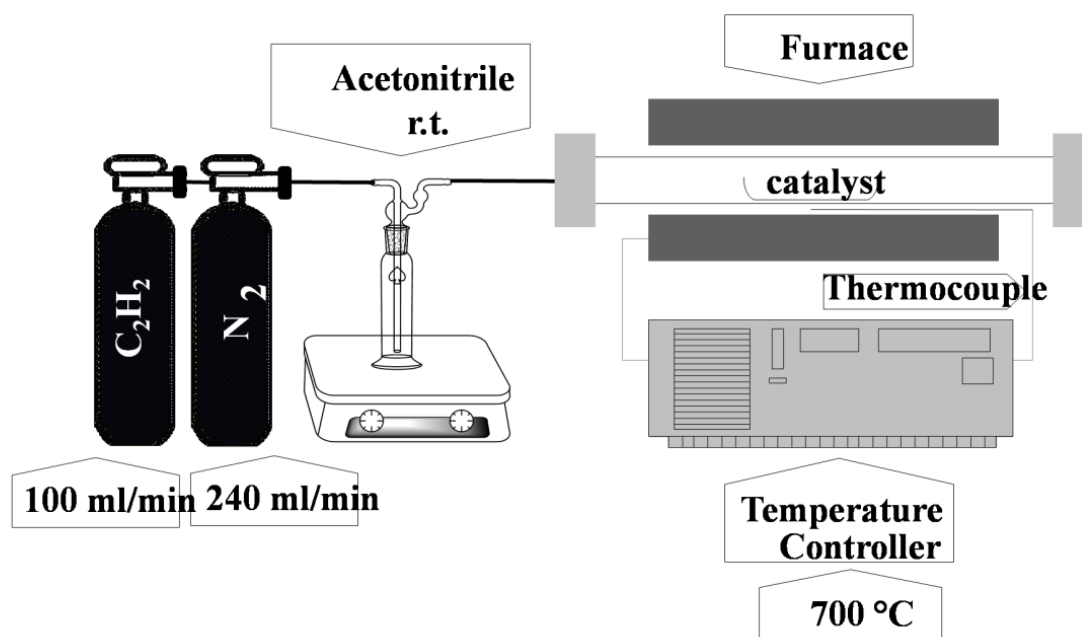


Figure 3.2. A schematic representation of CVD set up for the synthesis of N-doped CNTs.

3.3.4 Functionalisation of undoped CNTs and NCNTs

In order to functionalise the carbon materials a mass of 2.45 g product was placed in a round bottomed flask with 55% nitric acid and refluxed for 4 h at 110°C. After 4 h the mixture was cooled and 100 mL of distilled water was added to dilute the acid. This mixture was then suction filtered through a Buchner funnel until the water reached pH 7. The carbon materials were then dried overnight in a static oven at 120°C.

3.4 Uncatalyzed chemical vapour deposition (CVD) synthesis of carbon microspheres (CMSs) and N-doped carbon microspheres (NCMSs)

3.4.1 Synthesis of undoped CMSs (direct pyrolysis)

A quartz tube was placed in a tube furnace and the temperature was ramped at 10°C/min under N_2 flow of 40 mL/min from RT to 900°C. Once the tube furnace was stabilised at 900°C the nitrogen was stopped and acetylene was introduced at a flow rate of 100 mL/min for 1 h, where the decomposition (direct pyrolysis) of acetylene took place. After 1 h, at 900°C, the acetylene flow was stopped and nitrogen was re-introduced at 40 mL/min as the

tube furnace cooled down to RT. The black product that deposited in the inner lining of the quartz tube was then collected and weighed.

3.4.2 Synthesis of N-doped carbon microspheres (NCMSs) (direct pyrolysis)

A quartz tube connected to a bubbler with acetonitrile (the nitrogen source) was placed in a tube furnace and the temperature was ramped at 10°C/min under a N₂ flow rate of 40 mL/min from RT to 900°C. Once the tube furnace was stabilised at 900°C the nitrogen flow was stopped and acetylene was introduced at a flow rate of 100 mL/min for 1 h. After 1 h, at 900°C, the acetylene was stopped and nitrogen was reintroduced to the tube at a flow rate of 40 mL/min as the tube furnace cooled down to RT. The black product that deposited on the inner lining of the tube was then collected and weighed.

3.4.3 Functionalisation of CMSs and NCMSs

To functionalise the carbon materials, they were placed in a round bottomed flask with 55% nitric acid and refluxed for 4 h at 110°C. After 4 h the mixture was cooled and 100 mL of distilled water was added to dilute the acid and then the mixture was suction filtered by Buchner funnel. The wet product was then dried overnight in a static oven at 120°C.

3.5 Hydrothermal synthesis of CMSs and sulphonated CMSs (SOCMSs)

3.5.1 Hydrothermal synthesis of CMSs

In order to control the morphology and chemical properties of carbon spheres (CSs) such as the size, shape and graphitic nature, etc., carbon microspheres (CMSs) were synthesised using hydrothermal methods that involved heating a sucrose solution under pressure in an autoclave (Figure 3.3). The reaction temperature, ramping temperature/heating rate, reaction time and concentration of sucrose were varied. The materials so produced were characterised by TGA to ascertain their thermal stability and TEM to study their morphologies and sizes.



Figure 3.3. A representation of the type of stainless steel autoclave that was used in the hydrothermal synthesis of the carbon microspheres used in this study [1].

First 90 mL (using a 90% filling ratio) of a 0.3 M aqueous sucrose solution was added into a 100 mL stainless steel autoclave (Figure 3.3). The autoclave was fitted with heating elements around it and the temperature was ramped by 1.3°C/min from RT to 190°C. Thereafter the reaction was run at 190°C for 4 h, wherein the decomposition of the sugar solution under pressure occurred. After 4 h the reaction was cooled to RT. The black precipitate was filtered off using a suction Buchner funnel, washed with deionised water as well as ethanol and then dried overnight in a static oven at 120°C.

3.5.2 Hydrothermal synthesis of SOCMSs

Sucrose (10 g, 37×10^{-4} M) and 5 g of isenthoic acid (the sulphur source) were dissolved in 80 mL of deionised water and added into a 100 mL autoclave. The autoclave was fitted with heating elements around it and the temperature ramped from RT to 190°C in 3 h. After the temperature stabilised, the reaction was run for 4 h at 190°C and then cooled back down to RT. The black precipitate was then filtered off using a suction Buchner funnel, washed with deionised water as well as ethanol and then dried overnight in a static oven at 120°C.

3.6. Synthesis of SBR/ carbon composite materials

3.6.1 Preparation of the blank specimen

The SBR 1502 latex was supplied by Karbochem (Pty) Ltd Sasolburg, with 23.2% of bound styrene (Appendix A). Constituents for vulcanisation (listed in Table 3.1) were weighed out

in a beaker, to which 200 mL of toluene was added and stirred for 5 min. Thereafter 24.0 g of small pieces of SBR were dissolved in this mixture (i.e. 8.3 mL of toluene per 1 g of rubber) and stirred for 24 h. Because the SBR was obtained in bulk from Karbochem, small cutaway pieces were used as a way of reducing the bulk down to usable chips that could be dissolved (24 g of SBR in 200 mL toluene). A viscous white material was formed and added into an aluminium temperature controlled mould that had been designed and manufactured in the School of Mechanical and Aeronautical Engineering at the University of the Witwatersrand (Figure 3.4 (h)). Once the compartments were filled the open mould and its contents were dried for 12 h in a static oven at 60°C. Thereafter the mould was closed, connected to heating elements and subjected to a programmed heat treatment. Here the temperature was ramped successively to 60°C, 90°C and then 150°C over a period 12 h, 6 h and 3 h respectively. Finally the temperature of the mould was held at 150°C for 30 min and then left to cool to RT overnight.

Table 3.1. A list of the vulcanisation agents used in this study for SBR/ carbon material composite fabrication.

Composite constituent	Amount of constituents in 200 mL toluene Solvent (g)
SBR 1505	24.0
Zinc Oxide (activator)	4.0
Stearic acid (activator)	1.6
Anti-oxidant	0.8
Sulphanilamide (accelerator)	0.8
Sulphur (cure agent)	1.6

3.6.2 Preparation of the SBR/carbon composite materials

The carbon containing SBR composite was prepared by transferring 0.125% (m/m), 0.25% (m/m) or 0.50% (m/m) of the carbon material (CNTs, NCNTs, etc.) into a beaker together with 200 mL of toluene. This mixture was then stirred for 5 min in an ultrasonic bath. Constituents for the vulcanization (as listed previously in Table 3.1) were weighed out, added to the mixture and then stirred for another 5 min. A mass of 24.0 g of small pieces of SBR was then suspended in this mixture and the mixture was stirred for 24 h.

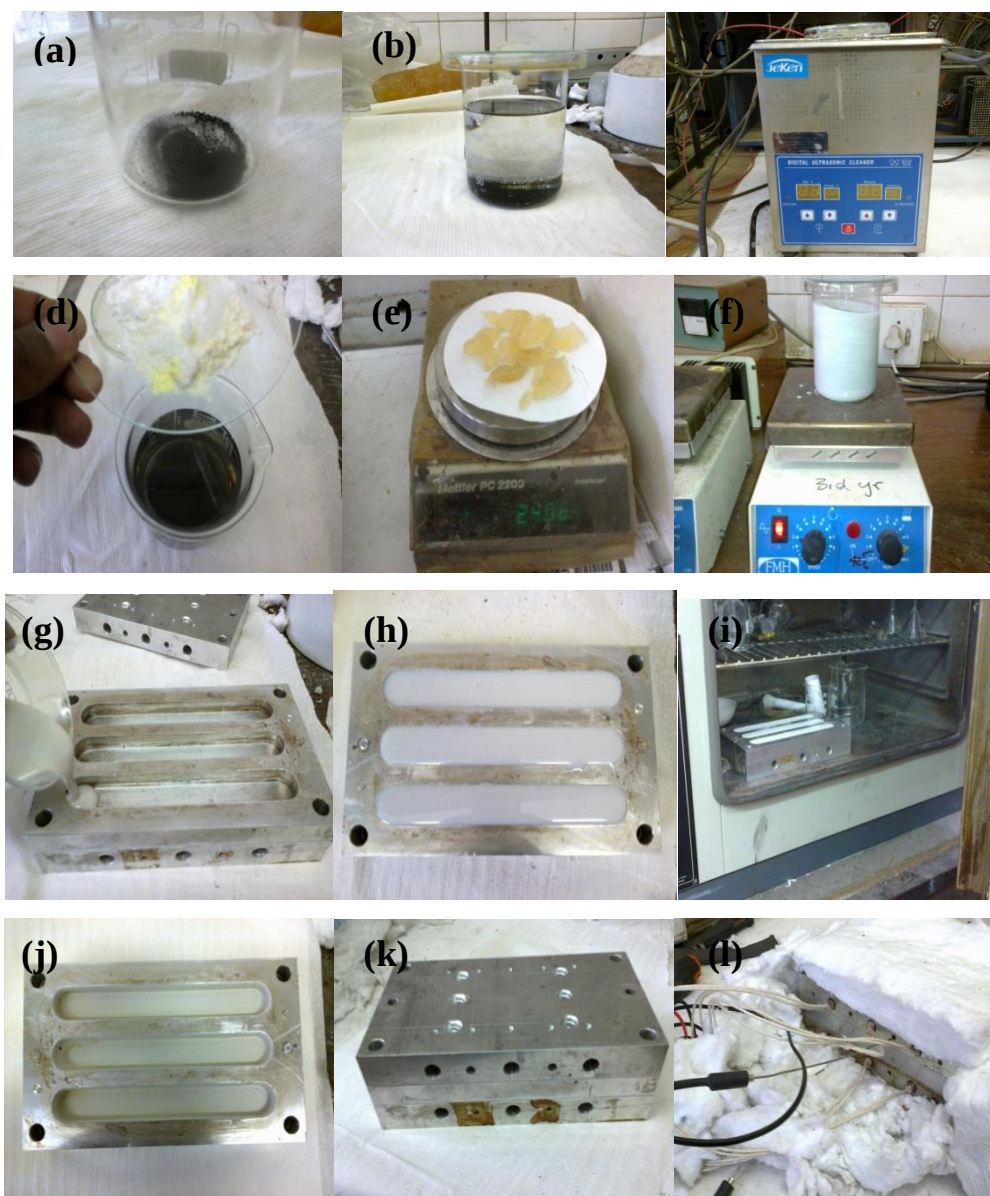


Figure 3.4. The SBR-carbon material composite specimen processing procedure: (a) a mass of carbon material was weighed into a beaker and (b) suspended in 200 mL toluene (c) stirred by ultrasonication for 5 min, (d) vulcanisates were added to the solution and stirred for 5 min, (e) 24 g of SBR pieces were added to the solution that was then left to stir for 24 h to form a viscous white suspension (f), the suspension was poured into the mould (g), (h) and then put in a static oven (i) maintained at 60°C for 12 h to evaporate the solvent. The mould was then closed, connected to heating elements, covered with fibre-glass and then subjected to the temperature programmed heating (j), (k) and (l).

3.7. Characterisation

3.7.1 Transmission electron microscopy

Transmission electron microscopy (TEM) is a technique that is used to produce images of a sample by illuminating the sample with a beam of electrons. The use of electron beams in TEM gives good resolution, allowing for imaging of samples at the nano-level. The information given by TEM is valuable in determining the morphology (size and shape), the arrangement and the distribution of particles in a sample. In this technique, sample preparation is important as the specimen under investigation has to be thin enough to allow an electron beam to pass through it allowing the transmitted electrons to produce an image of the sample [2].

The morphologies of the carbon nanomaterials synthesised in this study were determined using a Spirit transmission electron microscope (TEM) that was operated at 120 kV (Figure 3.5). Each sample was prepared by ultrasonication of a small amount of it in methanol to form a suspension. Thereafter a drop of each suspension was transferred onto a copper grid. Each copper grid was allowed to dry in air at room temperature before analysis. Image magnification was varied during analysis to obtain micrographs that were representative of each sample.

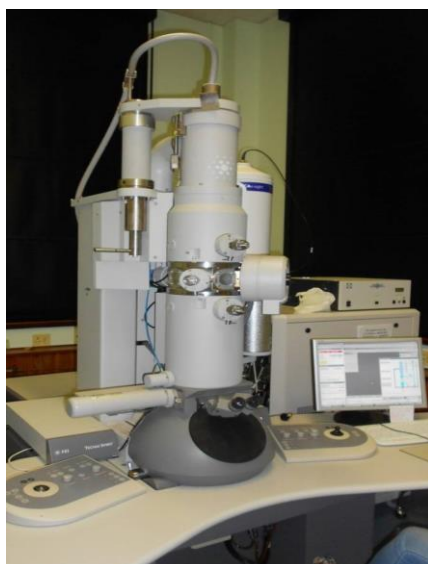


Figure 3.5. A photograph of the Spirit transmission electron microscope (TEM) that was used in this study.

3.7.2 Thermogravimetric analysis (TGA)

TGA is a thermal analysis technique that is used to measure changes in the mass of a sample as a function of temperature and/or time, in a controlled atmosphere (typically in N₂ or air). In TGA analysis, a predetermined mass of sample is loaded into an aluminium cup that is supported on an analytical balance, located outside the furnace chamber. The balance continuously weighs the sample as the sample cup is gradually heated, according to a programmed thermal cycle, to higher temperatures. The mass loss during the heating is recorded as a function of temperature. TGA data obtained in this way can be used to determine the degradation temperature of the sample material, absorbed moisture content and the amount of inorganic species or functionalities absorbed in or on a material [3].

In this study, TGA analyses were performed by using a Perkin Elmer, Pyris 1 TGA analyser (Figure 3.6) under air atmosphere in the temperature range between 25-1000°C at a heating rate of 10°C/min. Peak positions were recorded in units of degree Celsius versus weight loss percentage.

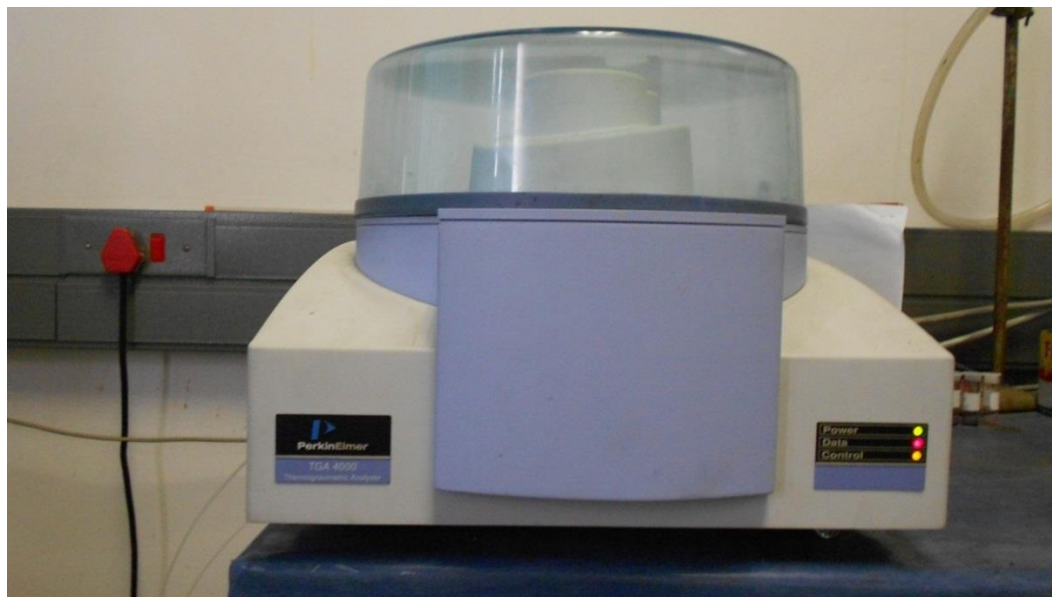


Figure 3.6. A photograph of the Perkin Elmer, Pyris 1 Thermogravimetric (TGA) analyzer that was used in this study.

3.7.3 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy is a technique that can be used to identify functional groups that are present in a molecule. The interaction of the sample material with the incident infrared radiation, initiates various twisting, bending, rotating and vibrational motions of atoms in a material. IR spectroscopy can be used to interpret these motions with relation to the incident radiation that is absorbed at particular wavelengths. This produces a highly complex absorption spectrum, which is uniquely characteristic of the functional groups constituting the material [4].

IR spectra of the different powdered carbon nanomaterials samples were recorded on a Bruker Tensor 27 Fourier transform infrared spectrometer (Figure 3.7). The percentage transmittance over the range of 400-4000 cm^{-1} was recorded for each sample.



Figure 3.7. A photograph of a Bruker Tensor 27 Fourier transform infrared spectrometer that was used in this study.

3.7.4 Laser Raman spectroscopy

Laser Raman spectroscopy is one of the oldest techniques that have been used extensively as a non-destructive technique to characterise carbon-based materials. In this technique, carbon materials (CNTs, CMSs, etc.) were generally characterised by looking at the response in two spectral regions, namely the tangential mode (G-band) and the disorder-induced mode (D-band) which correspond to the excitation of the related vibrational modes. The G-band, which is characterised by a peak at around 1580 cm^{-1} indicates graphitic features in the sample, while the D-band which is characterised by a peak around 1345 cm^{-1} , shows disordered features in the graphitic sample [5]. The structural quality of a carbon material can be determined by the I_G/I_D ratio, i.e. the ratio between the intensities (or areas) of the G and D peaks. The higher the I_G/I_D ratio, the more graphitic the structural quality of the material is [5].

Laser Raman spectra of the carbon nanomaterials synthesised in this study were recorded using a Bruker Senterra micro-Raman spectrometer which was operated at 20 mW power using a 532 nm laser (Figure 3.8). The spectra were recorded over a Raman shift wavelength ranging from $0\text{--}4000\text{ cm}^{-1}$.

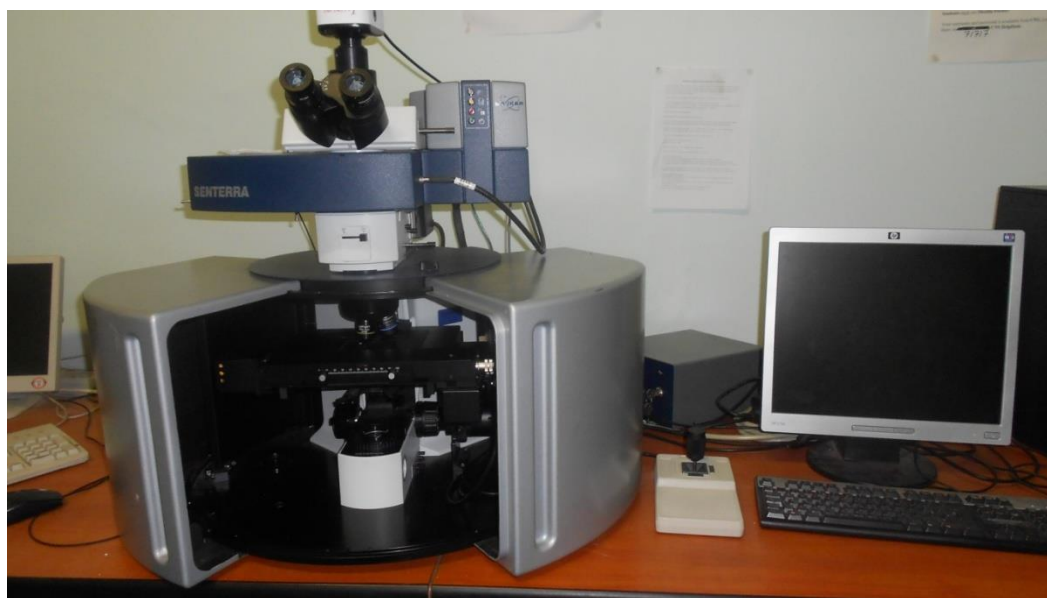


Figure 3.8. A photograph of the Bruker Senterra micro-Raman spectrometer that was used in this study.

3.7.5 Brunauer-Emmett-Teller method (BET) surface area analysis

The BET method is the most widely used technique to determine the surface area and porosity of a material. BET analysis gives information of the measure of the exposed surface (surface area), and porosity (including pore size and volume) of a solid sample, on the molecular scale. This information gives a useful prediction of how the materials will decompose, dissolve, adsorb, or react with other materials [6].

In the BET analyses that were performed in this study, 0.2 g of material are degassed under a flow of N₂ at 150°C for 5 h, using a Micromeritics Flow Prep 060 sample degas system, prior to analysis. The pore size distribution and specific surface areas were determined by means of N₂ adsorption/desorption according to the BET method, using a Micromeritics Tristar surface area and porosity analyzer (Figure 3.9).



Figure 3.9. A photograph of a Micromeritics Tristar surface area and porosity analyzer that was used in this study.

3.7.6 Differential scanning calorimetry (DSC) analysis

DSC is a thermo-analytical technique that is used to measure the temperatures and heat flow associated with phase transitions in materials. DSC data provides information about physiochemical properties of a material, by monitoring the amount of heat in the endothermic and exothermic processes, or changes in heat capacity that occur with every transition in the material. Thus by using this technique the properties of a material such as: the melting

temperature (T_m), crystallisation temperature (T_c), glass transition or softening temperature (T_g) and thermal stability can be determined [7].

A Mettler Toledo DSC 822e analyzer (Figure 3.10) was used to analyse the SBR-carbon material composites in this study. Composite materials (1-3 mg) were placed in an aluminium sample pan with a lid and analysed over a temperature range of (25-220°C). A heating rate of 5°C/min was used with a nitrogen flow of 60 ml/min. Peak positions were recorded in units of degree Celsius (°C).



Figure 3.10. A photograph of a Mettler Toledo DSC 822e analyzer which was used in this study.

3.7.7 Powder X-Ray Diffraction (PXRD) analysis

PXRD is one of the oldest and most frequently used bulk characterization techniques. It is used for the identification of crystalline phases, lattice structural parameters, and particle sizes of a material [8]. On a secondary basis PXRD can also be used to infer the presence of impurities and sample contamination [8].

PXRD measurements were performed on a Bruker D2 Phaser machine (Figure 3.11) using Co 260 radiation at 40 kV and 40 mA. The scan range used was $20^\circ < 2\theta < 100^\circ$. The diffraction patterns obtained were then contrasted with those of materials reported in the Diffrac^{plus} evaluation package using the EVA software package.

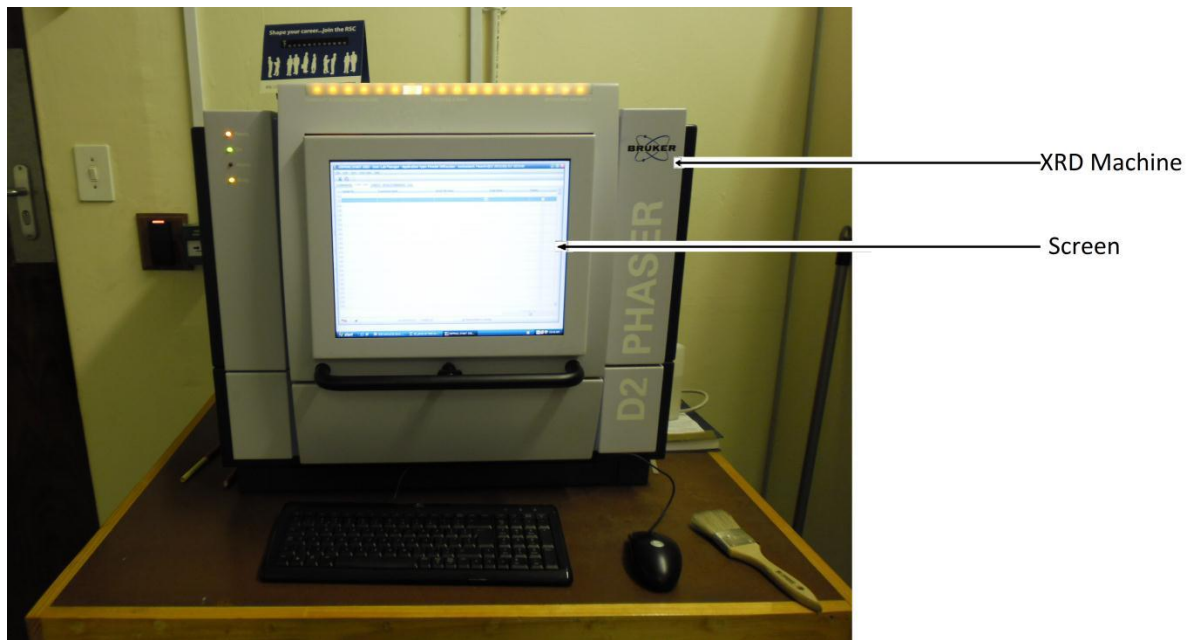


Figure 3.11. A photograph of the Bruker D2 Phaser powder X-Ray diffractometer which was used in this study.

3.7.8 Tensile strength testing

Tensile strength is a mechanical property of a material that measures the extent of the elasticity or the stiffness of a material. It is defined mathematically as the maximum force per unit area, also known as the maximum stress that the material can withstand when subjected to tensile load. In simpler terms, this refers to the maximum limit a material can be stretched before the material cross-sectional area starts to reduce and ultimately snaps or fails [9].

The tensile strength analysis technique provides data in a form of a graph of a load versus extension, when a specimen is extended due to stretching. However, an extension is dependent on the dimensions of the object, thus to get data that represents the whole material and not just the specimen, a curve of stress versus strain has to be deduced from the data as illustrated by Table 3.2.

Table 3.2. Information showing the relationship between stress and strain.

Stress is defined as the force per unit area of a material. Stress = force / cross sectional area:	Strain is defined as extension per unit length. Strain = extension / original length
$\sigma = \frac{F}{A}$ where, σ = stress, F = force applied, and A = cross sectional area of the object. Units of stress: Nm^{-2} or Pa.	$\varepsilon = \frac{e}{l_o}$ where, ε = strain, l_o = the original length e = extension = $(l - l_o)$, and l = stretched length Strain has no units

Tensile strength analyses of samples of SBR-carbon composite materials with thicknesses, widths and lengths of 1 mm, 20 mm and 145 mm respectively, were performed using a MX100K tensile testing machine (Figure 3.12). Each analysis was performed by the tension test method, using a 500 N load cell at a test speed of 5 mm/min.



Figure 3.12. A photograph of a MX100K tensile testing machine that was used in this study.

3.7.9 Zeta Potential Measurements

Zeta potential analysis uses the concept known as electrophoresis, where the mobility of the ions is measured. An electrical double layer is formed by introducing ions of the opposite charge, as counter ions, close to the surface of a particle. A net charge that results from that interaction is called the zeta potential. From the magnitude of the zeta potential, the nature of the functionalities on the surface of a material can be determined [10].

The functionalities present on the surface of the carbon materials synthesised in this study were analysed by a Malvern Zeta sizer machine (Figure 3.13). The pHs of the samples in the range of 2-12, in increments of 2, were adjusted by using 0.10 M NaOH and 0.10M HCl solutions. The zeta potential measurements of these materials were recorded over the above mentioned pH range at room temperature.



Figure 3.13. A photograph of a Malvern Zeta sizer machine that was used in this study.

3.8 References

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Chapter 4: Results and discussion

The results in this chapter will be presented in the following order: First an optimisation study of the synthesis of carbon microspheres (CMSs) by the hydrothermal technique, showing the effect of reaction parameters such as: concentration, temperature and reaction time on characteristics such as: morphology, outer diameter and the extent of graphitisation (defined hereafter as graphicity) will be presented. Thereafter through a comparison study of the properties/characteristics of the nano and micro carbonaceous materials (i.e. CNTs and CMSs) synthesized by the CVD and hydrothermal methods (as presented by using data obtained by: TGA, TEM, laser Raman, PXRD, zeta-potential and BET surface area measurements) will be given. Finally tests conducted with these nano and micro carbonaceous materials when added to styrene-butadiene rubber (SBR) for their ability to enhance the mechanical strength thereof will conclude the chapter.

4.1 A study of the effect of synthesis parameters (i.e. concentration, temperature and time) on the formation of carbon microspheres (CMSs) by the hydrothermal method

A study which investigated the effect of synthesis parameters on the morphology, outer diameter and graphicity of the CMSs that were formed by the hydrothermal method was conducted. CMSs were synthesised using a sucrose solution as the carbon source, which was heated in an autoclave under pressure (see Chapter 3 section 3.5.1). A number of conditions were varied in this study, namely: the concentration of sucrose (C) (0.1 – 0.3 M), the reaction temperature (T) (175–210°C) and the reaction time (t) (2 – 8 h).

4.1.1 A study on the effect of sucrose concentration (C) on the formation of CMSs at fixed temperature (i.e. 190°C) and reaction time (4 h).

Hydrothermal syntheses are generally reactions of aqueous solutions conducted under various temperatures and pressures. As compared to other methods such as CVD, where hydrocarbons are routinely reacted at temperatures that can range between 600°C and 900°C, the hydrothermal method (which was used in this study to synthesize CMSs) took place at relatively low temperatures (i.e. 190°C) with sugar solutions as the carbon source. The characteristics of these CMSs such as: outer diameter and graphicity were believed to be affected by the reaction parameters such as the concentration (C), temperature (T) and reaction time (t). Hence the influences of these reaction parameters were experimentally

studied, by varying each parameter (one at a time), to achieve suitable reaction conditions for the synthesis of CMSs. In the first section, the concentration of sucrose (C) was varied between (0.1 – 0.3 M). The reaction temperature (T) was maintained at 190°C; based upon previous observations that orange red viscous solutions were formed at lower temperatures, which indicated that instead of having synthesised nano/micro carbonaceous products, some aromatic compounds and oligosaccharides had been formed [1]. The reaction time was fixed at 4 h.

The results that follow represent the TEM and TGA analyses of the carbonaceous products that were formed.

4.1.1.1 TEM analysis of carbonaceous products formed by hydrothermal syntheses for C= 0.1-0.3 M, T=190°C and t= 4 h.

It was observed that nucleation only occurred when supersaturation had been reached, and the solution had turned a dark-brown to nearly black colour at the end of the reaction. At low sucrose concentrations (C's) (e.g. C = 0.1 M and 0.2 M), chain-like conglomerations consisting of ill-defined or irregular CMSs were formed (Figures 4.1 (a) and (b)) which indicated that sufficient nucleation had not taken place. By comparison large individual, properly formed CMSs were formed when the sucrose concentration was 0.3 M (Figure 4.1 (c)). The carbonaceous products formed under these conditions contained irregularly or fully formed CMSs whose outer diameters increased (ranging from 0.5-1 μm for the 0.1 M, thereafter 1-1.5 μm for the 0.2 M and finally 1.5-2 μm for the 0.3 M solution) as did their abundance, as the sucrose concentration (C) was increased (Figure 4.2).

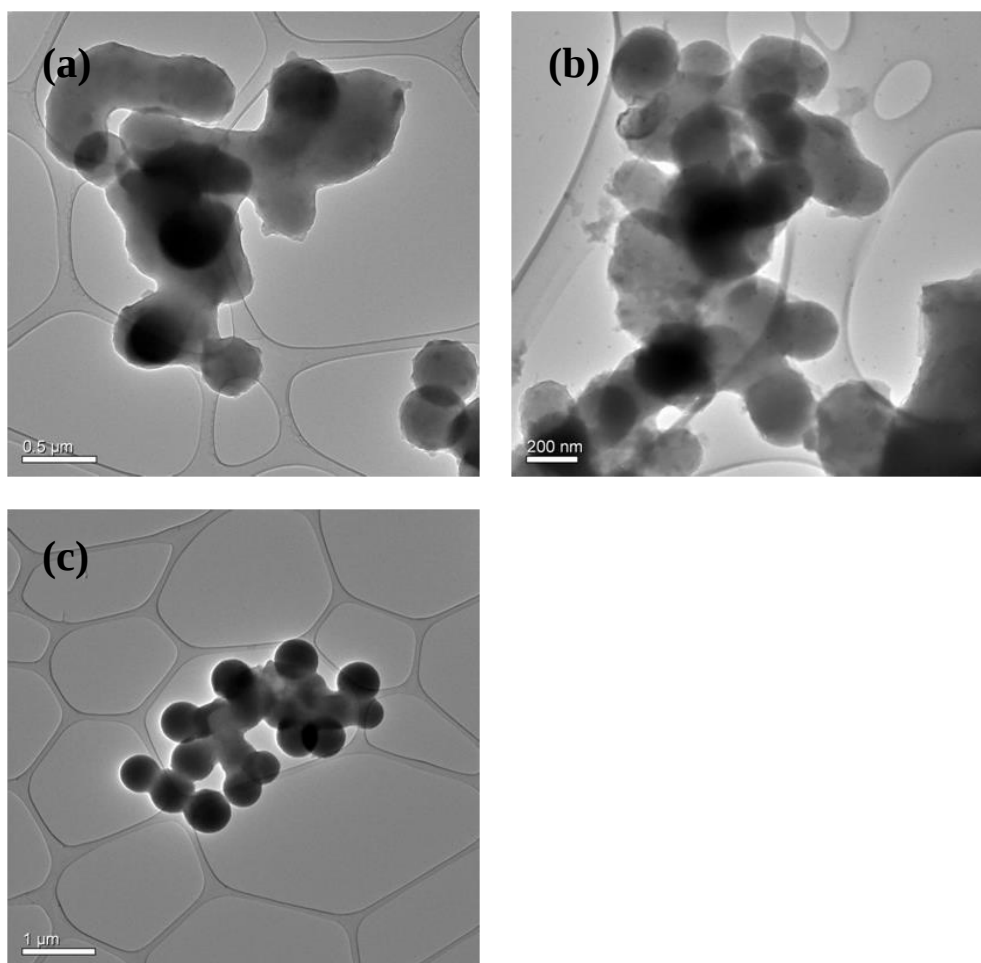


Figure 4.1. TEM images of hydrothermally formed CMSs with varied concentrations of sucrose solution i.e. (a) 0.1 M, (b) 0.2 M and (c) 0.3 M at 190°C for 4 h.

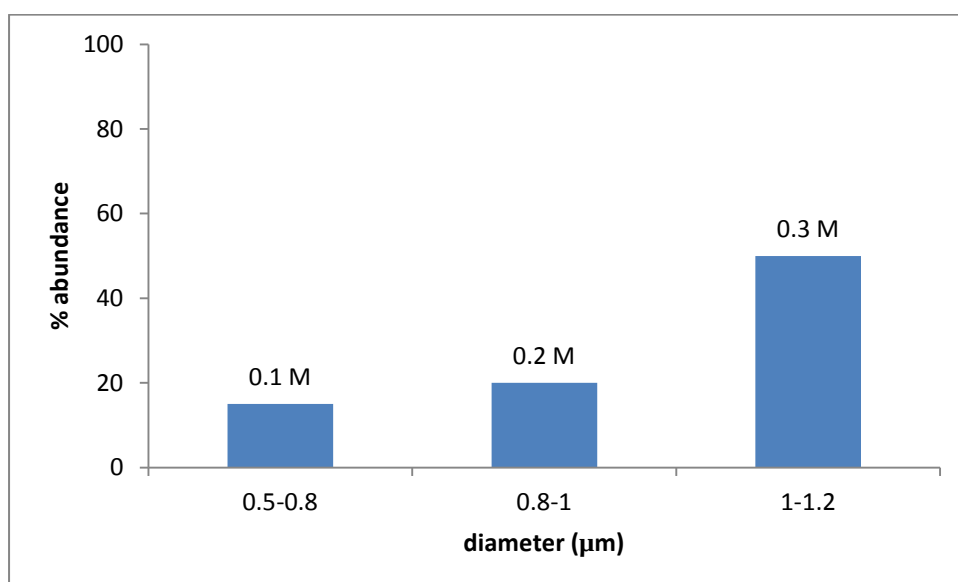


Figure 4.2. Size distribution graphs of hydrothermal CMSs with varied concentrations of sucrose solution (0.1-0.3 M) at 190°C for 4 h.

4.1.1.2 TGA analysis of carbonaceous products formed by hydrothermal syntheses for C= 0.1-0.3 M, T=190°C and t= 4 h.

Subsequent to the TEM observations mentioned previously, TGA analyses were performed on all three carbonaceous products (Figures 4.3 and 4.4). Based upon these results, it could be observed that all three carbonaceous products were non-uniform in size, type and quantity, as multiple combustion peaks were present in each case (Figure 4.4). Additionally the data obtained from these analyses were consistent with the TEM results which showed that there was a high content of irregularly formed CMSs in the carbonaceous products that were formed, when the concentration of sucrose used was between 0.1 M- 0.2 M. Here ca. 60% of the carbonaceous materials formed were combusted between RT and 400°C, with maximal combustion temperatures for the 0.1 M and 0.2 M sucrose solutions having been observed at 517°C and 527°C respectively. Similarly, evidence that better graphitized (i.e. more well-defined) CMSs were present at a higher sucrose concentration (0.3 M) was identified by TGA, as these materials combusted at the highest temperature (628°C) of all three products.

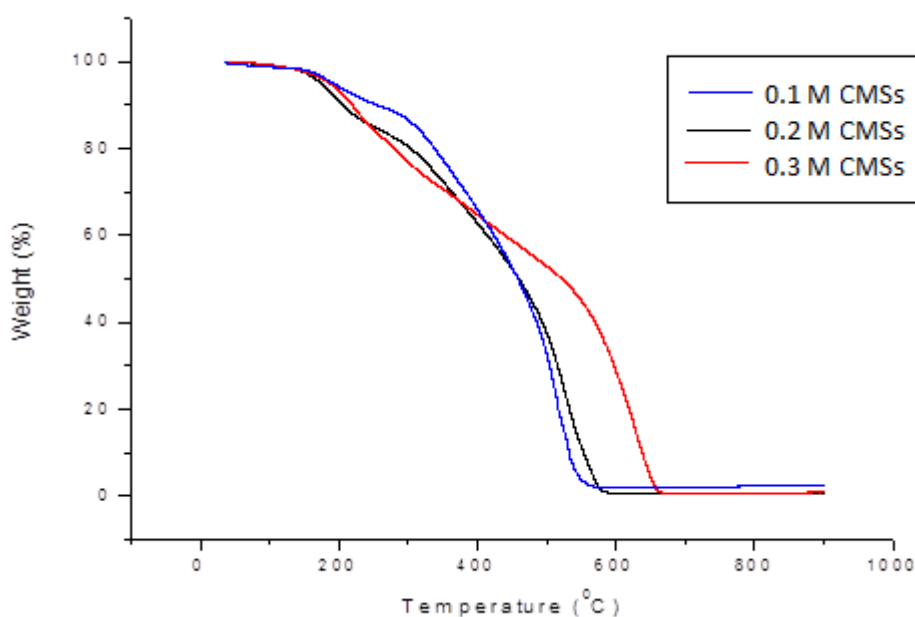


Figure 4.3. TGA profiles of CMSs formed by hydrothermal synthesis with varied sucrose concentrations (0.1 M - 0.3 M) at 190°C for 4 h.

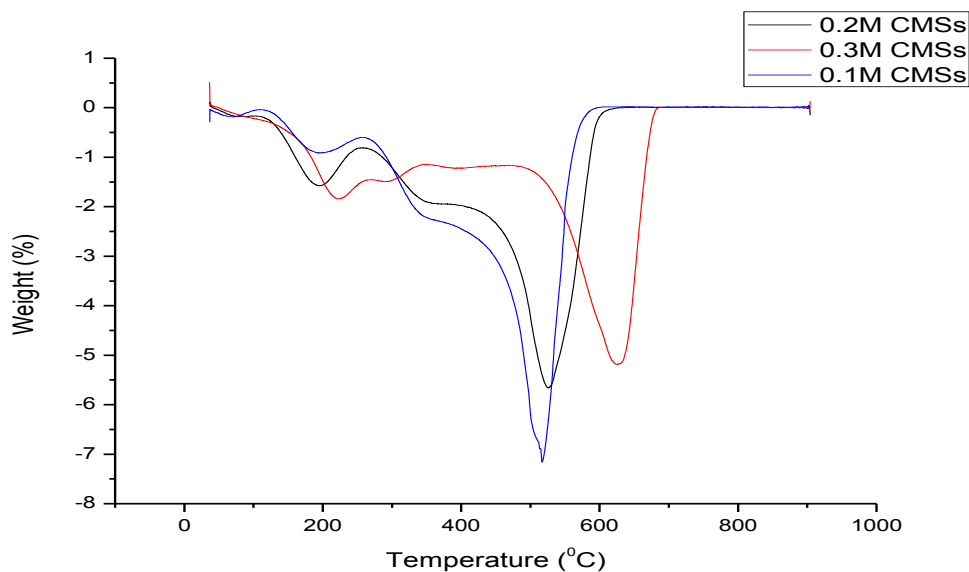


Figure 4.4. A plot of the first derivatives for the TGA profiles of the CMSs formed by hydrothermal synthesis with varied sucrose concentrations (0.1 M - 0.3 M) at 190°C for 4 h.

4.1.1.3 Summary of TEM and TGA analyses of the carbonaceous products formed by hydrothermal synthesis for C= 0.1-0.3 M, T=190°C and t= 4 h.

Based upon the results obtained in this study, it could be concluded that when the temperature and reaction time were kept constant, the higher the sucrose concentration used in the hydrothermal reaction, then the carbonaceous products synthesised were: 1) more well-defined and individualized as spheres, 2) larger in outer diameter, and 3) more graphitic (as seen by the higher combustion temperatures). Hence the follow-up study in this optimisation process was conducted using the optimal concentration of sucrose i.e. 0.3 M.

4.1.2 A study on the effect of temperature (T=175-210°C) on the formation of CMSs at fixed sucrose concentration (C=0.3 M) and reaction time (t=4 h).

4.1.2.1 TEM analysis of carbonaceous products formed by hydrothermal synthesis for T=175-210°C, C= 0.3 M and t= 4 h.

Hydrothermal syntheses (at a fixed sucrose concentration and reaction time) were conducted at temperatures ranging from 175-210°C. The carbonaceous products that were formed were

analysed by TEM and are displayed in Figures 4.5 (a), (b) and (c). As in the case where lower concentrations of sucrose produced irregularly formed CMSs, a similar trend was observed at lower temperatures. For instance, it was noted that no spheres were formed at 175°C (Figure 4.5 (a)), while the spherical shape only started to form as the temperature was increased as observed in Figures 4.5 (b) and 4.5 (c). This can be attributed to the fact that insufficient pressure was built up inside the closed autoclave, at lower temperatures, in order to facilitate the formation of spheres.

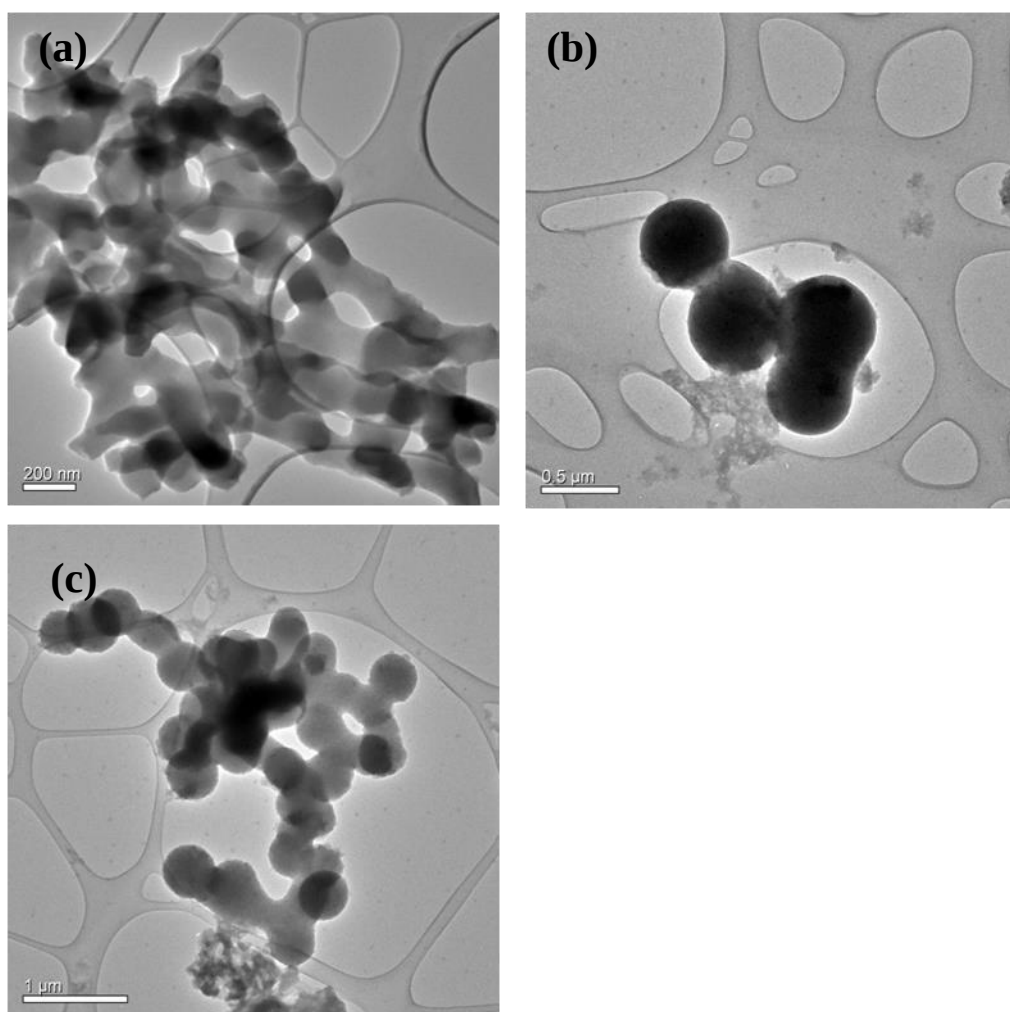


Figure 4.5. TEM images of hydrothermal CMSs formed with varied reaction temperature i.e. (a) 175°C, (b) 190°C and (c) 210°C at 0.3 M for 4 h.

4.1.2.2 TGA analysis of carbonaceous products formed by hydrothermal synthesis for T=175-210°C, C=0.3 M and t=4 h.

TGA analyses of the carbonaceous products (Figures 4.6 and 4.7) confirmed that at 175°C and 190°C a large portion of the sample had been burned off (i.e. ca. 65% and 60%) between RT and 400°C. Again, it was observed that all three carbonaceous products were non-uniform in size, type and quantity, as multiple combustion peaks were present in each case (Figures 4.6 and 4.7). As in the previous study (section 4.1.1.) the data obtained from these analyses were consistent with the TEM results, which showed that there was a higher content of irregularly formed CMSs at lower temperatures (i.e. 175°C and 190°C), where their maximal temperatures of combustion were 511°C and 519°C respectively. Similarly, the maximum combustion temperature for carbonaceous products formed at 210°C was much higher (i.e. 625°C) than those formed at lower temperatures which indicated a higher graphiticity (Figure 4.7) as compared to those formed at lower temperatures. This too was consistent with the TEM results, from which it could be observed that these products had become more well-defined spheres.

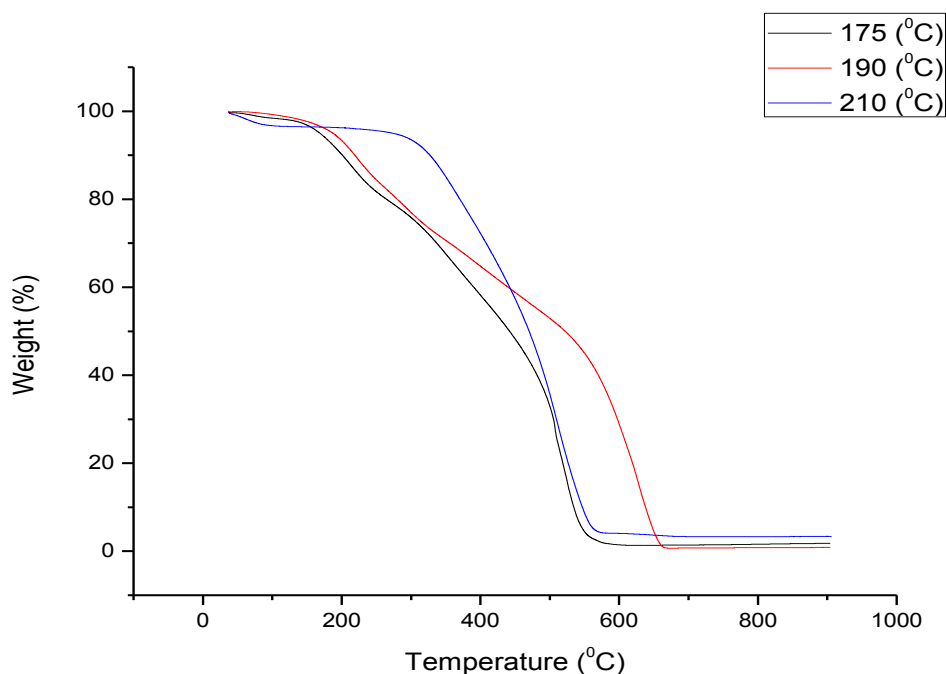


Figure 4.6. TGA profiles of hydrothermal CMSs formed at varied reaction temperature (175-210°C) at 0.3 M for 4 h.

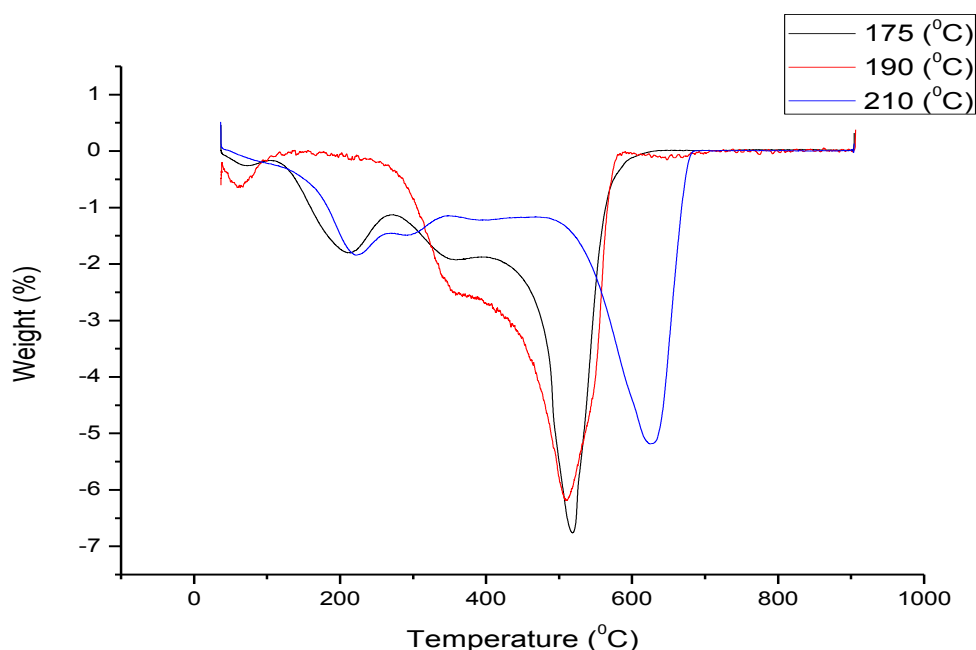


Figure 4.7. A plot of the first derivatives for the TGA profiles of hydrothermal CMSs synthesised under varied reaction temperatures (175-210°C) at 0.3 M for 4h.

4.1.2.3. Summary of TEM and TGA analyses of carbonaceous products formed by hydrothermal synthesis for T=175-210°C, C= 0.3 M and t= 4 h.

Based upon the results obtained in this study, it could be concluded that when the sucrose concentration and reaction time were kept constant, the higher the reaction temperature used in the hydrothermal reaction, then the carbonaceous products synthesised were: 1) more well-defined and individualized as spheres and 2) more graphitic. Hence the follow-up study in this optimisation process was conducted using the optimal temperature (i.e. 210°C) as well as concentration of sucrose (i.e. 0.3 M).

4.1.3 A study on the effect of reaction time (t=2-8 h) on the formation of CMSs at fixed sucrose concentration (C=0.3 M) and reaction temperature (T=210°C).

4.1.3.1 TEM analysis carbonaceous products formed by hydrothermal synthesis for t=2-8h, C=0.3 M and T=210°C.

Hydrothermal syntheses (at a fixed sucrose concentration and reaction temperature) were conducted for reaction times ranging from 2- 8 h to establish what effect/s reaction time had

on the morphology, outer diameter and graphicity on the CMSs formed. As can be observed in the TEM micrographs displayed in Figures 4.8 (a), (b) and (c), the reaction time appeared to have a much lower effect on the morphology of CMSs as compared to the sucrose concentration or the reaction temperature, since spheres were formed under all three reaction times. However, as in the previous two studies, less well-defined spheres were observed at lower reaction times. As discussed previously, it was found (both in this study and in others) that reaction time was important in the nucleation of carbon and appeared only to have occurred sufficiently for $t > 2$ h [1-5]. Thereafter it appeared that subsequent to nucleation, the diameters of the CMSs grew with time (Figure 4.9), from 0.5-0.8 μm for the 2 h (Figure 4.8 (a)), thereafter 0.8-1 μm for the 4h (Figure 4.8 (b)) and finally 1-1.2 μm for the 8 h samples (Figure 4.8 (c)).

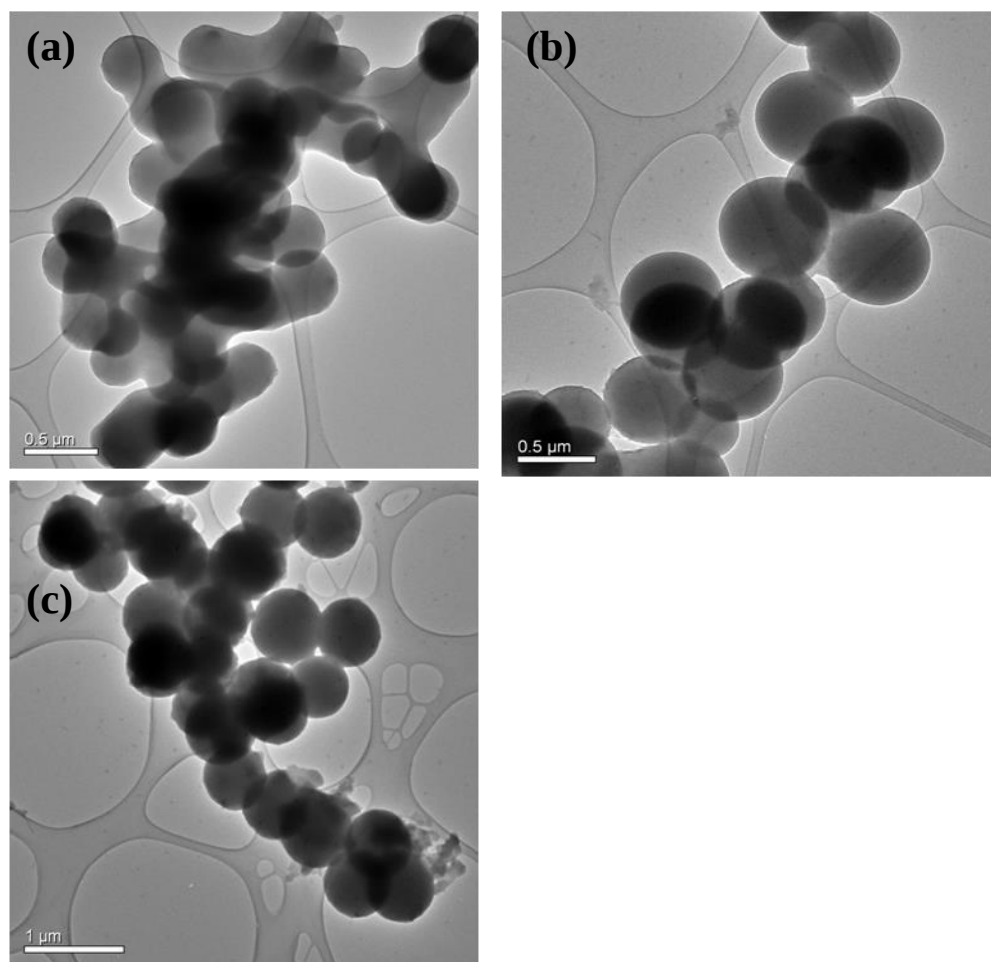


Figure 4.8. TEM images of hydrothermal CMSs with varied reaction time i.e. (a) 2 h, (b) 4 h and (c) 8 h at 0.3 M and 210°C.

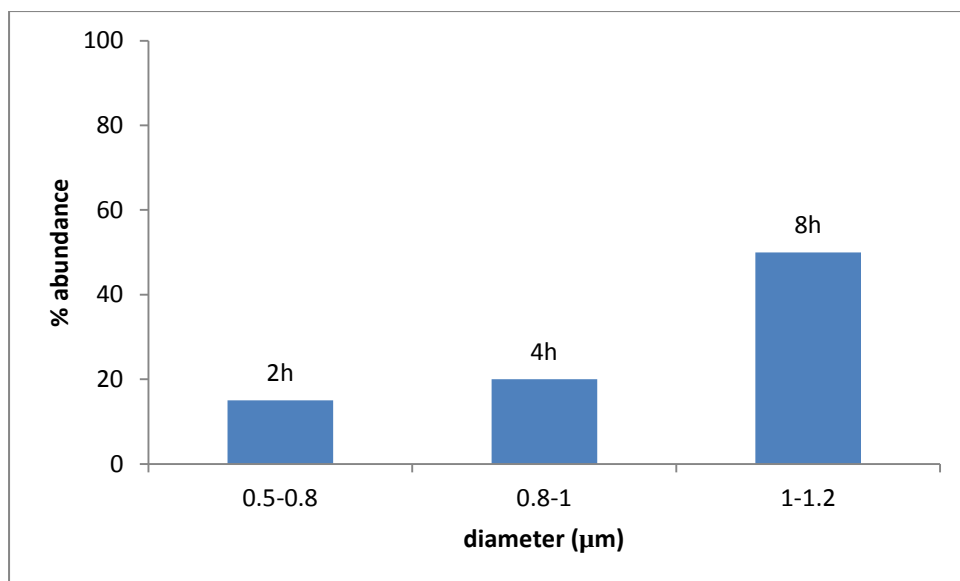


Figure 4.9. A plot of the size distribution of hydrothermal CMSs formed with varied reaction time (2-8h) at 0.3 M and 210°C.

4.1.3.2 TGA analysis of carbonaceous products formed by hydrothermal synthesis for t=2-8h, C=0.3 M and T=210°C.

TGA analyses of the carbonaceous materials synthesised in this study (Figures 4.10 and 4.11) once again showed that all three carbonaceous products were non-uniform in size, type and quantity, since multiple combustion peaks were present in each case. Likewise, as in the two previous studies (sections 4.1.1 and 4.1.2) the data obtained from these analyses were consistent with the TEM results, which showed that there was a higher content of irregularly formed CMSs at the lowest reaction time (i.e. 2 h), which corresponded with the lowest combustion temperature (i.e. 495°C). In contrast to these previous studies, there appeared to be very little difference between the CMSs produced at 4 h and 8 h (i.e. combustion temperatures of 518°C and 519°C respectively were observed). However, CMSs synthesised at 4 h and 8 h both appeared to have higher graphicity than those synthesised at the shortest reaction time.

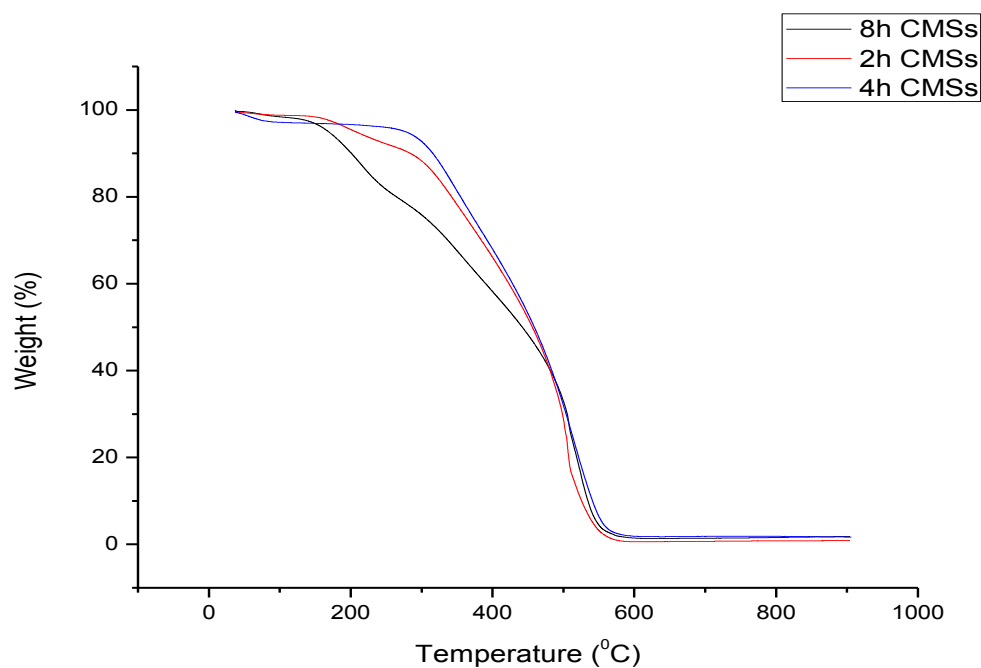


Figure 4.10. TGA profiles of hydrothermal CMSs formed with varied reaction time from 2-8h at 0.3 M and 210°C.

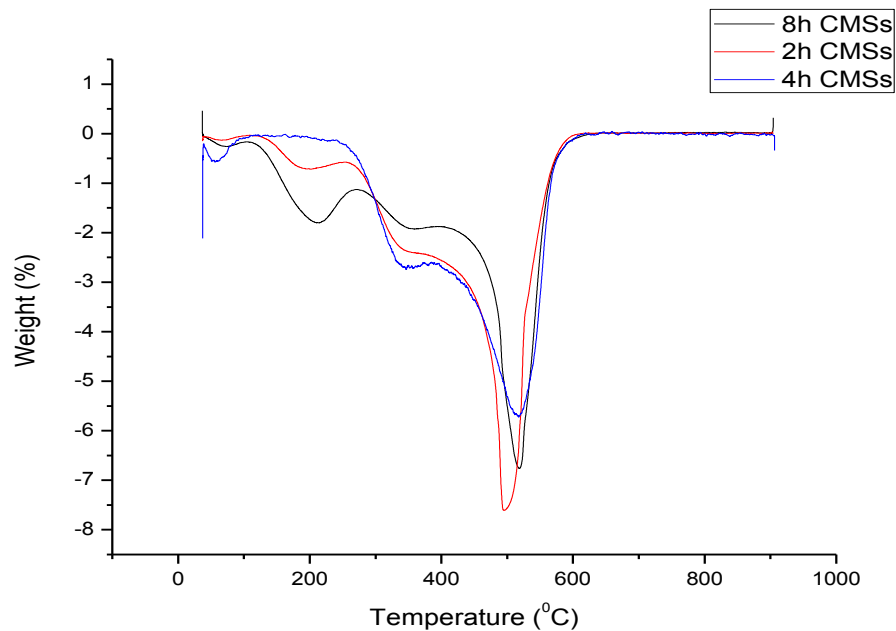


Figure 4.11. A plot of the first derivatives for the TGA profiles of hydrothermal CMSs formed with varied reaction time from 2-8h at 0.3M and 210°C.

4.1.3.3 Summary of TEM and TGA analyses of carbonaceous products formed by hydrothermal synthesis for C=0.3 M, t= 2-8h and T =210°C.

Based upon the results obtained in this study, it was observed that when the concentration of sucrose and the reaction temperature were kept constant (at 0.3 M and 210°C respectively), the longer the reaction time used in the hydrothermal reaction, then the carbonaceous products synthesised were generally: 1) more spherically well-defined, 2) larger in outer diameter and 3) more graphitic.

4.1.4 Overall summary for studies 4.1.1 - 4.1.3

Based upon the data gathered from these studies it was noted that suitable C's, T's and t's were essential to attain well-defined, larger diametered, individual CMSs with higher graphitic content (i.e. more thermally stable). Evidence from the TEM and TGA data that were acquired in these studies showed that higher sucrose concentrations, reaction temperatures and reaction times were required to meet these requirements. Hence, it could be concluded that the ideal conditions for the synthesis of CMSs using the hydrothermal technique in these studies were: C=0.3 M, T=210°C, and t=8h. Apart from a variance in the temperature (which may be due to the autoclave design), this conclusion is consistent with earlier publications that have reported that the optimal conditions for the hydrothermal synthesis of CMSs by sucrose were C=0.3 M and T=190°C and t=8h [6-9].

4.2 A comparison of the properties/characteristics of carbon materials synthesized by CVD and hydrothermal techniques

As mentioned previously in this and in earlier chapters, the carbon materials (CNTs and CMSs) that were studied were synthesized by two different methods i.e. by CVD and by the hydrothermal method. The hydrothermal method was used by means of the reaction of an aqueous sugar solution under temperature and pressure to synthesize CMSs (see sections 4.1.1-4.1.3) and SOCMSs (see section 3.5.1). The CVD method on the other hand used gaseous acetylene and/or acetonitrile (as a source/s of carbon and/or nitrogen) and a catalyst Fe/Co in a quartz boat under temperatures of 700-900°C to synthesize CNTs, NCNTs, CMSs and NCMSs. In the sections which follow, the CNTs synthesized by CVD were compared first, with the expectation that the differences in undoped and N-doped carbonaceous

materials would bring about the required properties for reinforcement in the SBR composites that were planned (as discussed in the earlier chapters). Thereafter the CMSs synthesized by the hydrothermal and CVD methods were compared.

4.2.1 A comparison of the properties/characteristics of undoped CNTs and N-doped (NCNTs) synthesised by CVD

The first comparison that was made was between undoped CNTs and N-doped CNTs that were synthesized by CVD. CNTs are assumed to be some of the best reinforcement materials for polymer matrix composites, because of their high aspect ratio, specific surface area and Young modulus [10]. Similarly, the introduction of foreign elements such nitrogen into the lattice of CNTs has been shown to tune their electronic and chemical properties by changing the number of electrons on the surface [11]. Hence a comparison of the two types, intended as reinforcing materials in SBR, was made.

4.2.1.1 Thermal properties of undoped CNTs and N-doped (NCNTs) synthesised by CVD

TGA analyses of undoped CNTs (or pristine carbon nanotubes (CNTs)) and N-doped CNTs (NCNTs) showed that the introduction of the nitrogen heteroatom into the CNTs appeared to reduce the thermal stability of such CNTs (Figures 4.12-4.13). Here decomposition peaks were observed at 70°C, 450°C and 600°C (Figure 4.13). The 1st peak was attributed to the moisture absorbed by the sample, where about 5% of the material was lost [12]. The 2nd peak was due to the removal of the functionalities present on the surface of the NCNTs [12], while the third the removal of graphitic carbon [12]. On the other hand for the undoped CNTs there was little to no moisture content and the main decomposition took place at ca. 494°C (Figure 4.12 and 4.13), which could be attributed to the removal of graphitic carbon [12].

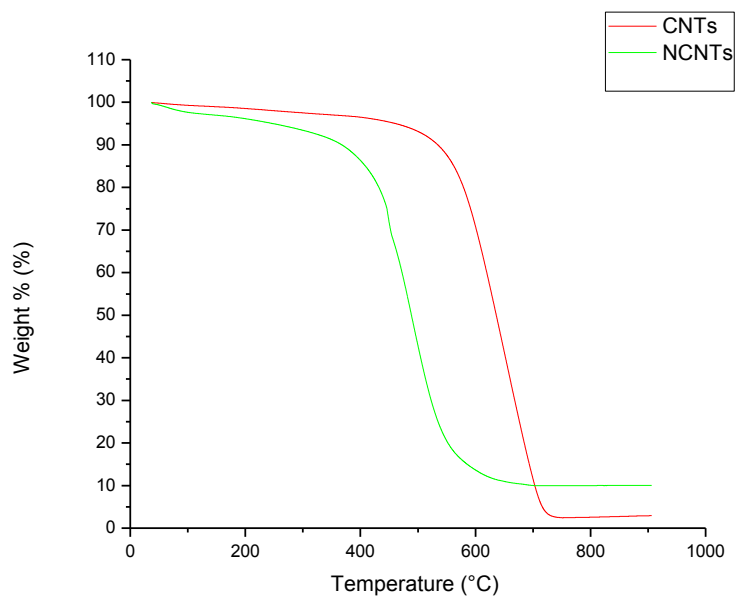


Figure 4.12. TGA profiles of CVD undoped CNTs and N-doped CNTs (NCNTs).

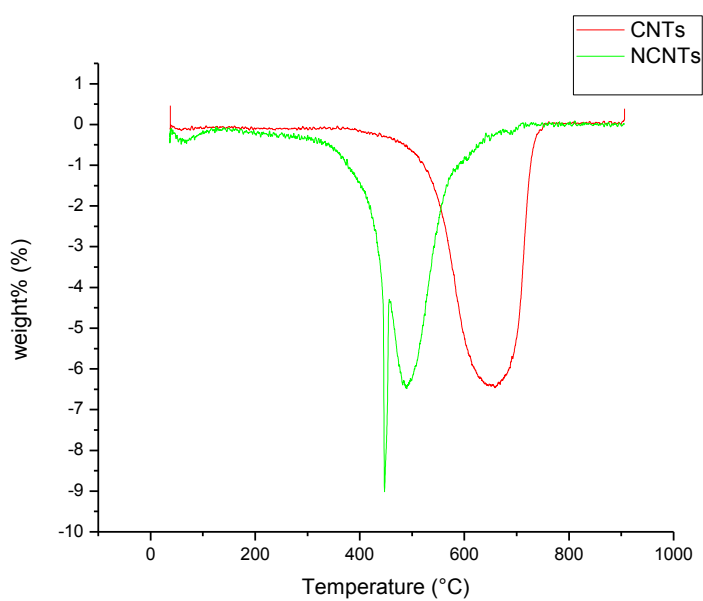


Figure 4.13. A plot of the first derivatives for the TGA profiles of CVD synthesised undoped CNTs and NCNTs.

4.2.1.2 Morphological and size properties of undoped CNTs and N-doped (NCNTs) synthesised by CVD

The morphologies of undoped CNTs and NCNTs, synthesised by CVD, were studied using TEM. The TEM micrographs of these materials (Figures 4.14 and 4.16) revealed that they were of high purity and tubular. Measurements obtained from these micrographs showed that the diameters obtained varied for each type of CNT (Figures 4.15 and 4.17). It was noted that for the undoped CNTs the diameters were predominantly between 15-30 nm (Figure 4.15) and the CNTs were hollow inside (Figure 4.14). However, in some cases metal particles (remnants from the catalyst; see arrow) were embedded in small portions of the tube (Figure 4.14). The NCNTs on the other hand had larger diameters, which ranged between 30-45 nm (Figure 4.17). Unlike the undoped CNTs, the inner cavity of the NCNTs was compartmentalised (Figure 4.16) due to the inclusion of nitrogen [12]. Since acetylene and acetonitrile were used to synthesise NCNTs, and acetonitrile acted as a nitrogen source as well as a carbon source, the amount of carbon supplied in this case was higher than in the undoped CNTs. Hence the diameters of the NCNTs were bigger [12].

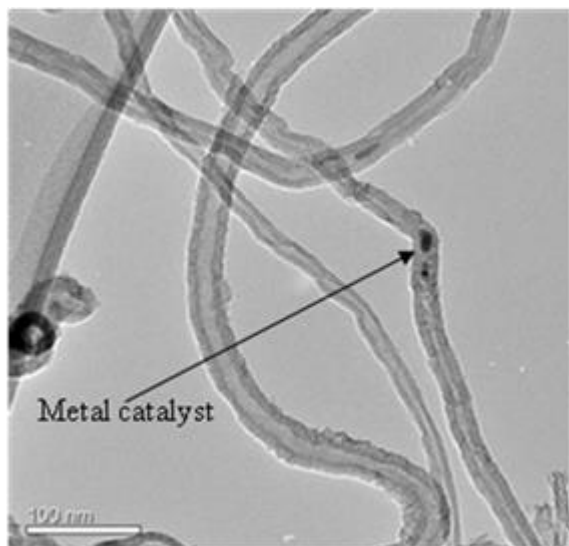


Figure 4.14. A TEM image of undoped CNTs synthesised by the CVD method (arrow showing the metal catalyst precursor from which the tubular material was grown).

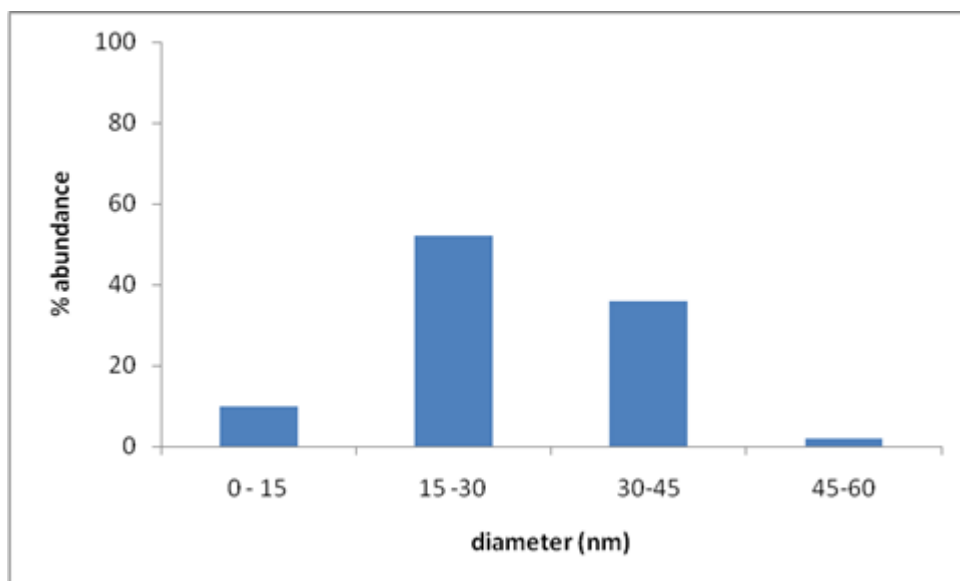


Figure 4.15. A plot of the size distribution of undoped CNTs synthesised by CVD.

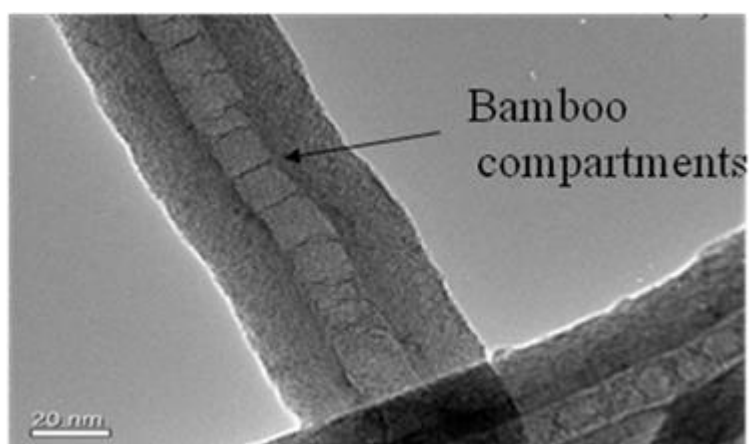


Figure 4.16. A TEM image of NCNTs synthesised by the CVD method (arrow showing bamboo compartments formed by nitrogen incorporation).

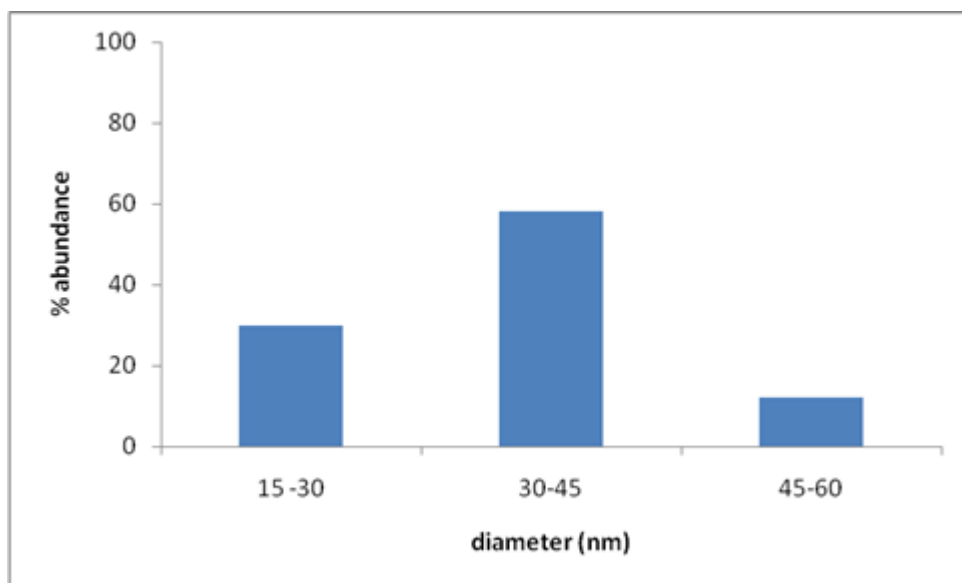


Figure 4.17. A plot of the size distribution of NCNTs synthesised by CVD.

4.2.1.3 Laser Raman characteristics of undoped CNTs and N-doped (NCNTs) synthesised by CVD

Laser Raman analyses (Figures 4.18-4.19) of the undoped and N-doped CNTs synthesised by CVD were performed. In the former case well pronounced D and G peaks with similar intensities i.e. the $I_G/I_D = 1.1$ (Table 4.1) were observed in the laser Raman spectrum (Figure 4.18). This indicated that the undoped CNTs consisted of sp^2 carbon which had some defects [13]. In the latter case (Figure 4.19), a reduction in the intensity ratio of the G and D peaks i.e. the $I_G/I_D = 1.0$ (Table 4.1) in the laser Raman spectrum of the NCNTs was observed. In addition the absence of a clear 2D peak implied that the incorporation of nitrogen had decreased the crystalline nature of the CNTs [13]. Both of these results were consistent with the TEM observations and TGA analyses (sections 4.2.1.1 and 4.2.1.2) of the undoped and N-doped CNTs.

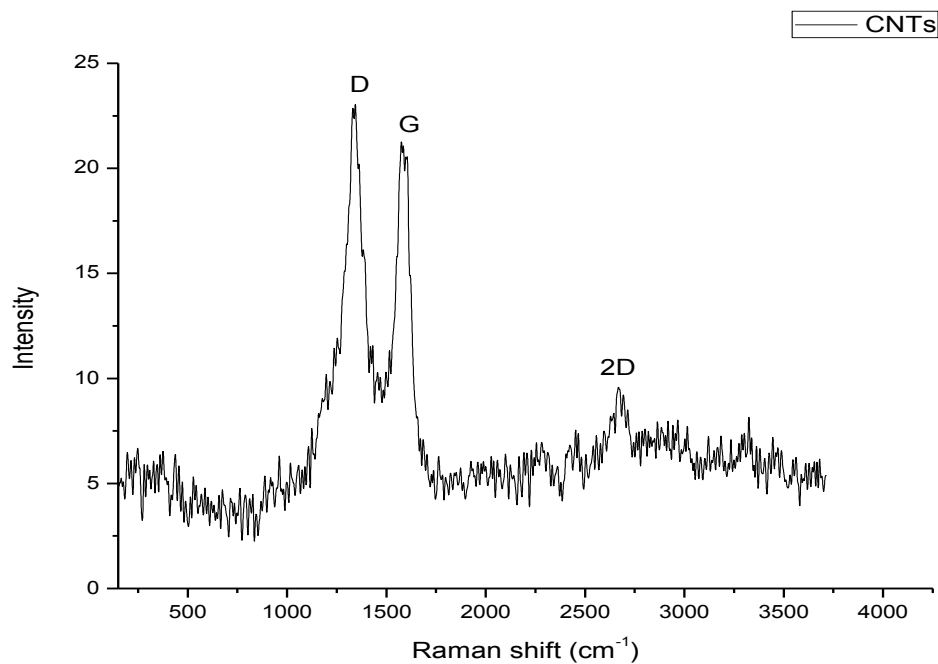


Figure 4.18. A laser Raman spectrum of undoped CNTs that were synthesised by the CVD method.

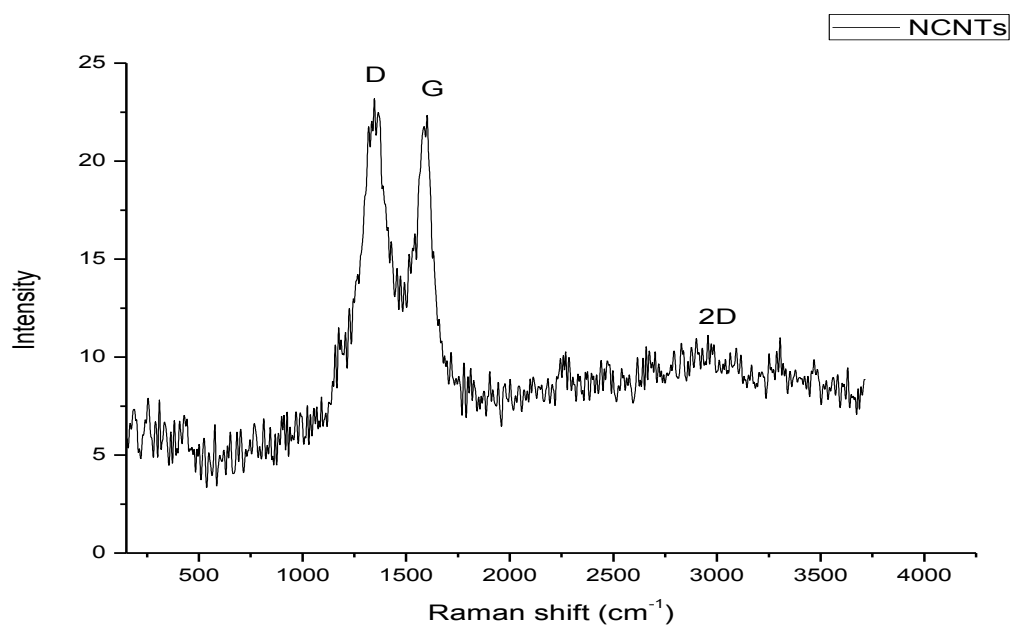


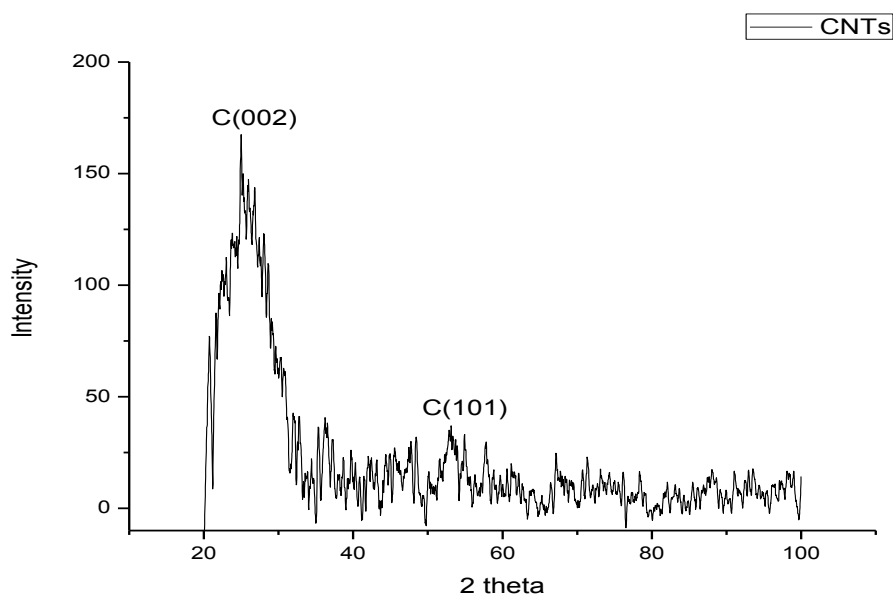
Figure 4.19. A laser Raman spectrum of N-doped CNTs (i.e. NCNTs) that were synthesised by the CVD method.

Table 4.1. Raman shifts for undoped and N-doped CNTs that were synthesized by CVD.

Carbon material	Raman shift (cm^{-1})		I_D/I_G
	D	G	
CNTs	1355	1588	1.1
NCNTs	1366	1601	1.0

4.2.1.4 PXRD characteristics of undoped CNTs and N-doped (NCNTs) synthesised by CVD

Power X-ray diffraction (PXRD) analyses were carried out on the undoped and N-doped CNTs to establish their crystallinity and purity. With respect to carbon materials, there are two peaks of significance to look for when dealing with hexagonal graphite. These peaks are: 1) a large broad peak at 25° (i.e. the (002) plane) and 2) a smaller peak in the range between $45\text{--}60^\circ$ (i.e. the (101) plane) [13]. Both of these peaks were present and broad in the undoped and N-doped CNTs (Figures 4.20 and 4.21). This suggested that there was a low degree of graphitisation with the possible presence of amorphous carbon (as confirmed by the TGA as well as the laser Raman analyses). Since no other peaks were observed, this also suggested that the materials were relatively free of other impurities [13]).

**Figure 4.20.** A PXRD diffractogram of undoped CNTs that were synthesised by the CVD method, which showed the characteristic (002) and (101) peaks of carbon.

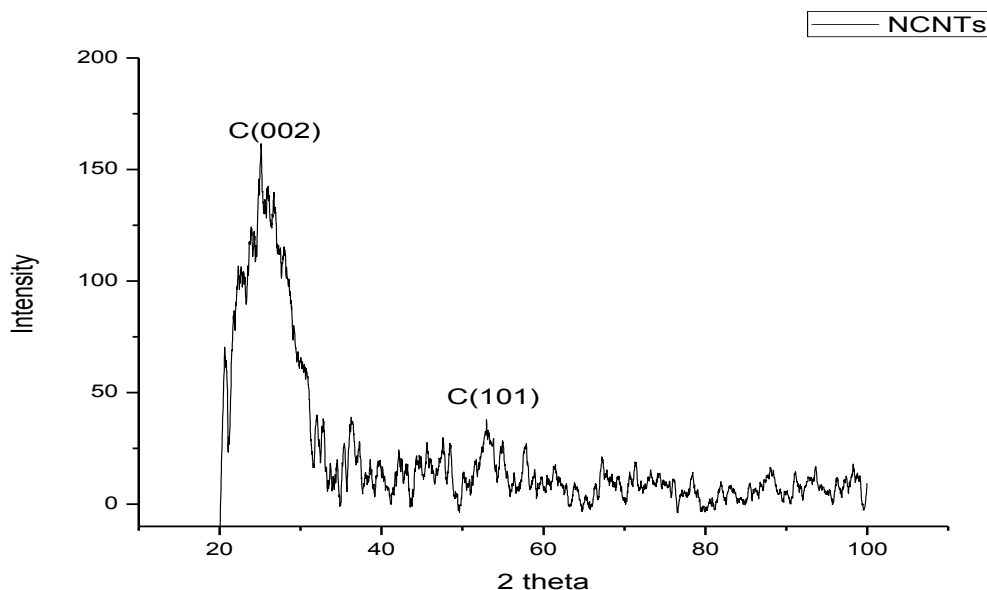


Figure 4.21. A PXR D diffractogram of NCNTs that were synthesised by the CVD method, which showed the characteristic (002) and (101) peaks of carbon.

4.2.1.5 Zeta-potential properties of undoped CNTs and N-doped CNTs (NCNTs) synthesised by CVD

In order to verify the presence of acid functional groups on the carbonaceous materials, samples were titrated with [0.1 M] NaOH and HCl solutions so that the pH was varied from 2 to 12. The results were useful in giving insight on the surface functionalities by giving the potential difference (charge) of these materials in the medium (in that case water). Undoped CNTs were observed to have had a positive charge (zeta potential) in the pH range between 2 and 4 (Figure 4.22). However as the pH was increased the surface of the materials became more negative. At around pH 5 a point called the isoelectric point was observed. This was the point of zero charge for the undoped CNTs and this continued decreasing to a negative charge as the pH was increased [14]. This was attributed to the number of acid groups on the surface and how much base was needed to neutralise them. The same trend was observed for NCNTs however, the point of zero charge was at a lower pH than the undoped CNTs. This was believed to be due to the electron rich nitrogen atoms that were introduced on the surface of the NCNTs [14]. These results suggested that the NCNTs possessed a higher degree of functional groups as compared to the undoped CNTs. As such their dispersion in solution or polymer blends (such as SBR) was expected to be better than that of undoped CNTs.

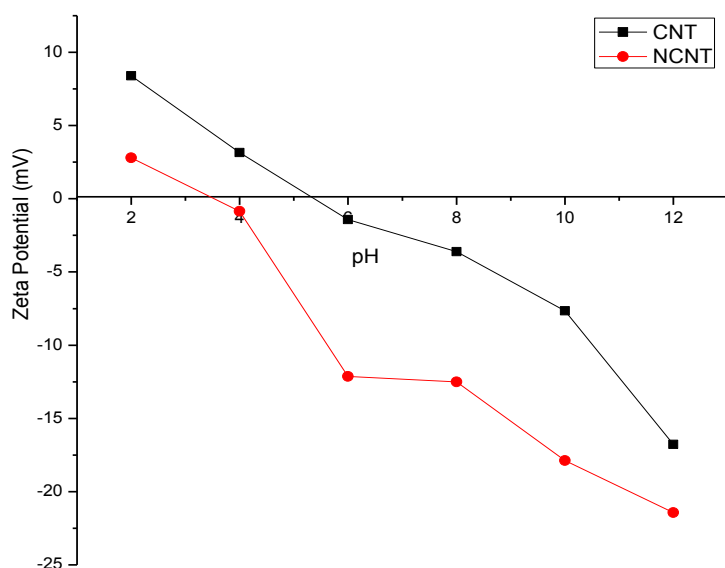


Figure 4.22. A plot of the Zeta-potentials of undoped CNTs and N-doped CNTs that were synthesised by CVD.

4.2.1.6 BET surface area properties of undoped CNTs and N-doped (NCNTs) synthesised by CVD.

BET surface area and pore volume analyses of the undoped and N-doped CNTs were performed. Results from these analyses (Table 4.2) indicated that the undoped CNTs possessed a higher surface area ($80 \text{ m}^2/\text{g}$) than NCNTs ($62 \text{ m}^2/\text{g}$). The lower surface area of the NCNTs could well be attributed to the introduction of nitrogen in the CNTs, as its incorporation generated a tube that had compartments [15].

Table 4.2. BET surface areas for undoped CNTs and NCNTs synthesized by CVD.

Samples	Average Surface Area (m^2/g)
CNTs	80
NCNTs	62

4.2.1.7 A summary of the comparison of the properties/characteristics of undoped CNTs and N-doped CNTs synthesised by CVD.

Based upon the data gathered from these studies, it could be concluded that the incorporation of nitrogen into CNTs: 1) lowered their thermal stability, 2) increased their external tube

diameter, 3) decreased their crystallinity, 4) added more surface functionalities, 5) lowered the pH at which they reached the point of zero charge, 6) increased their negative surface charge at higher pH's and 7) decreased their surface area.

4.2.2 A comparison of the properties/characteristics of undoped and N-doped CMSs synthesised by CVD.

A second comparison was made between undoped CMSs and N-doped CMSs (or NCMSs) that were synthesized by CVD. Like CNTs, the CMSs are believed to have good mechanical and electrical properties due to their interlocking pentagonal/hexagonal graphene-like arrangements [16]. Just as was the case with CNTs, the introduction of foreign elements, such as nitrogen, into the lattice of CMSs was expected to tune their electronic and chemical properties [16].

4.2.2.1 Thermal properties of undoped CMSs and N-doped (NCMSs) synthesised by CVD

TGA analyses of undoped CMSs and NCMSs, synthesised by CVD, were performed. In these results, one very small and then two main peaks were observed for the CMSs (Figures 4.23-4.24). The very small peak was observed at around 100°C. This was most likely due to a small quantity of moisture. The other two main peaks, at higher temperatures, suggested that at least two different types of carbon were present in the products. The first of these peaks was observed at 634°C and could either be attributed to less graphitic carbon (amorphous carbon) or to the removal of surface functionalities (Figures 4.23 - 4.24) [16-17]. While the second of these peaks, at around 848°C, could be attributed to the removal of graphitic carbon [16-23]. Clearly, these CMSs were more thermally stable than the CNTs/NCNTs (section 4.2.1) or the CMSs produced by the hydrothermal method (section 4.1), as their final decomposition temperature was much higher than all three of the others (compare Figures 4.7 with 4.13 and 4.24). Hence it appeared that the CMSs synthesised by the CVD method produced carbonaceous products which had higher graphitic content. This was most likely due to better ordering of the synthesised material due to the higher reaction temperature used [16], i.e. 900°C for CMSs by CVD, 700°C for CNTs/NCNTs and 210°C for CMSs by the hydrothermal method. A similar trend was also observed for the NCMSs (Figures 4.23-4.24),

however the addition of N to the CMSs, as with NCNTs, slightly lowered their thermal stability as compared to the undoped CMSs [17-23].

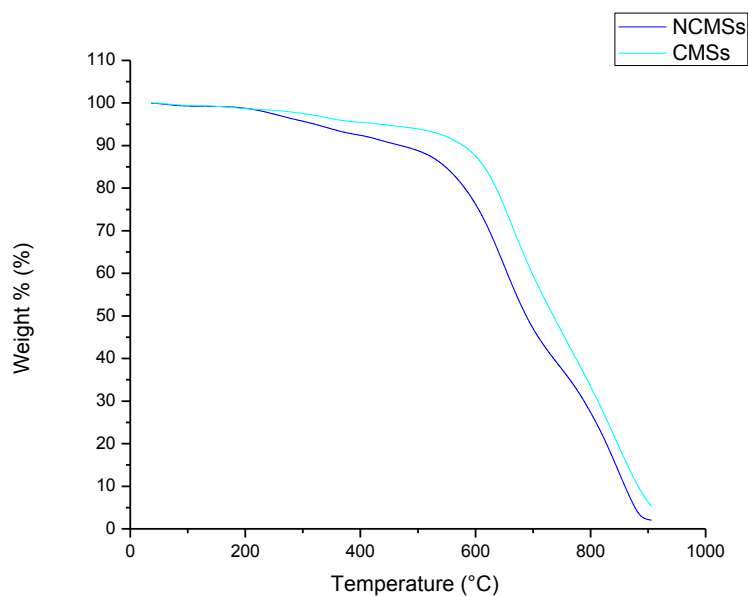


Figure 4.23. TGA profiles of undoped CMSs and N-doped CMSs synthesized by CVD.

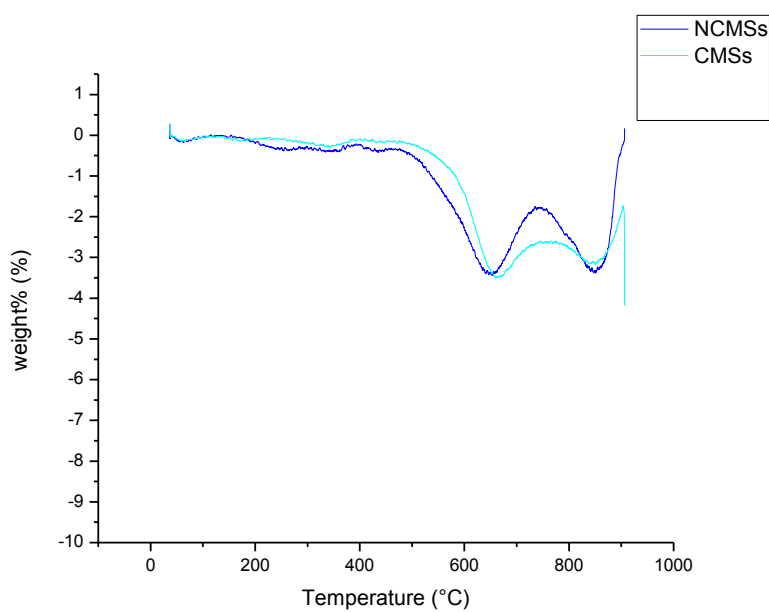


Figure 4.24. The first derivatives of the TGA profiles for undoped CMSs and N-doped CMSs that were synthesized by CVD.

4.2.2.2 Morphological and size properties of CMSs and NCMSs synthesised by CVD

The morphologies and sizes of CMSs and NCMSs that were synthesised by CVD were studied by using TEM. The TEM micrographs (Figures 4.25 and 4.27) showed that both types of materials were spherical and tended to agglomerate. This agglomeration was due to the Van der Waals forces between the spheres. The undoped CMSs had an average outer diameter of 1 μm (Figure 4.26), while the incorporation of nitrogen increased the average outer diameter of NCMSs i.e. 1.5 μm (Figure 4.28). It was also observed that as the CMSs grew bigger in size they tended to stand individually, without agglomeration (Figure 4.27).

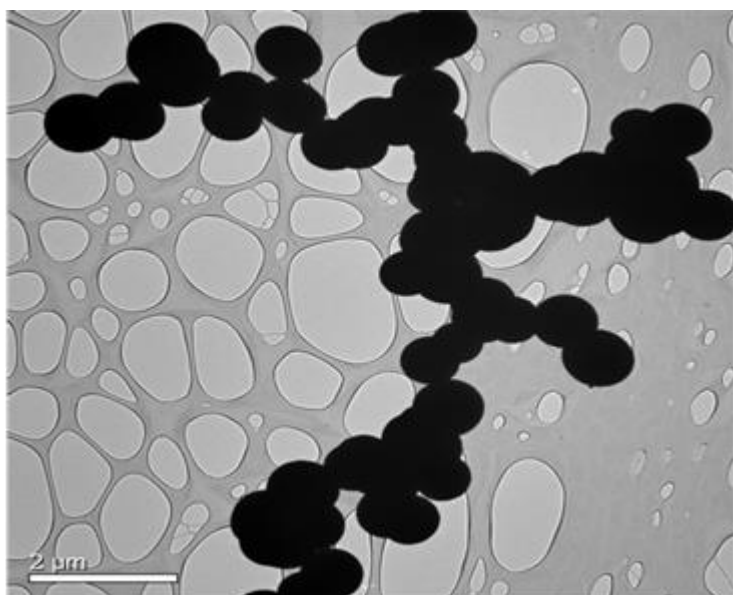


Figure 4.25. A TEM image of undoped CMSs synthesised by the CVD method.

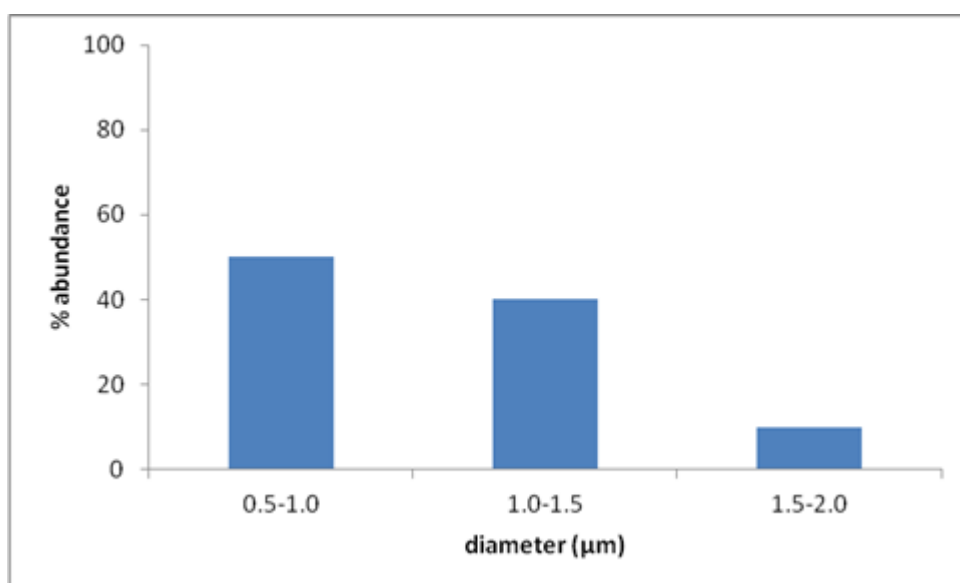


Figure 4.26. A plot of the size distribution of undoped CMSs synthesised by CVD.

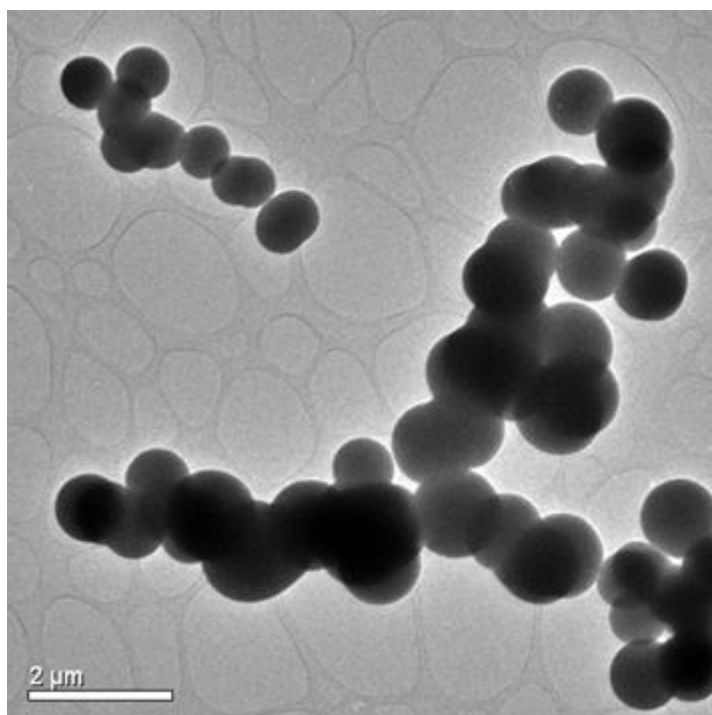


Figure 4.27. A TEM image of NCMSs synthesised by CVD method.

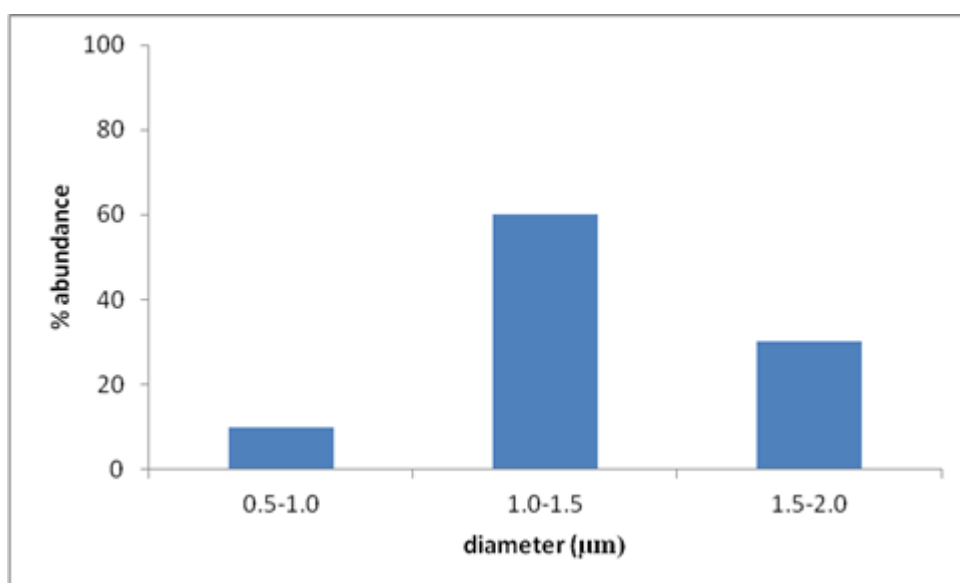


Figure 4.28. A plot of the size distribution of NCMSs synthesised by CVD.

4.2.2.3 Laser Raman characteristics of CMSs and NCMSs synthesised by CVD

Laser Raman analyses (Figures 4.29-4.30) of the undoped and N-doped CMSs synthesised by CVD were performed. In the laser Raman spectrum of undoped CMSs, displayed in Figure 4.29, the characteristic D and G peaks were once again observed. As expected from the higher reaction temperature (i.e. 900°C), a higher intensity ratio of these peaks i.e. $I_G/I_D=1.2$ was observed for undoped CMSs as compared to the NCMSs i.e. $I_G/I_D=1.1$ (Figures 4.29-4.30 and Table 4.3). However, by comparison with functionalised multi-walled carbon nanotubes ($I_D/I_G=1.54$) the I_D/I_G ratio was lower and showed a higher degree of defects [24]

It was also observed that this intensity ratio decreased with the introduction of nitrogen into the structure of the CMSs, probably due to defects introduced into the carbon packing structure. Once again this could have been due to the high reaction temperature (900°C) used to synthesise the CMSs and NCMSs. This high temperature may have minimised defects by surface reconstruction or through the removal of impurities (glassy carbon) [24]. These results were consistent with those observed in the TGA analyses (Figure 4.24).

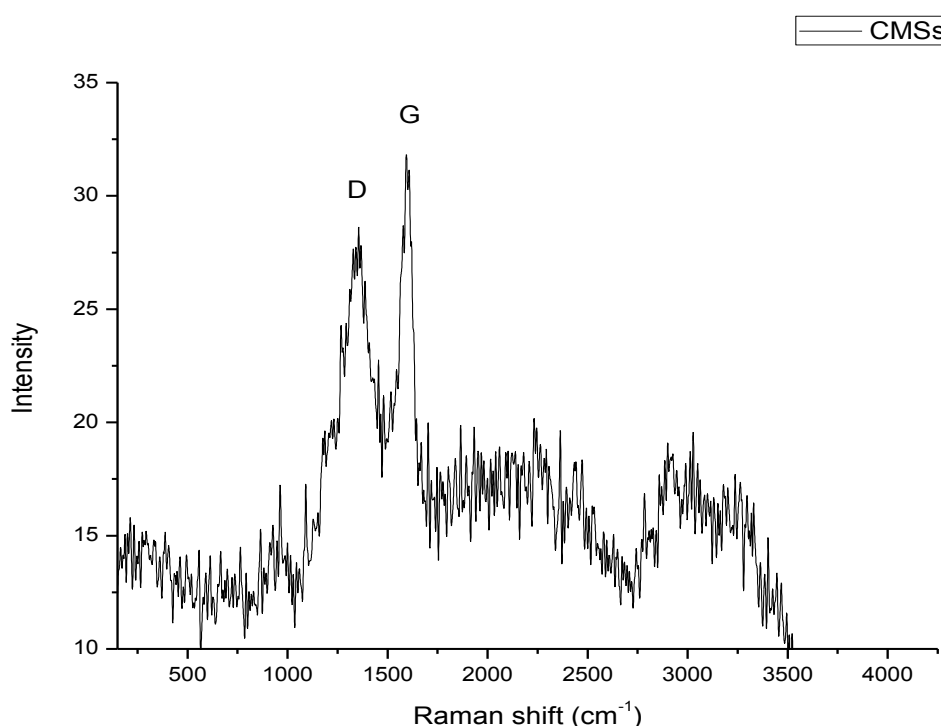


Figure 4.29. A laser Raman spectrum of CMSs synthesised by CVD.

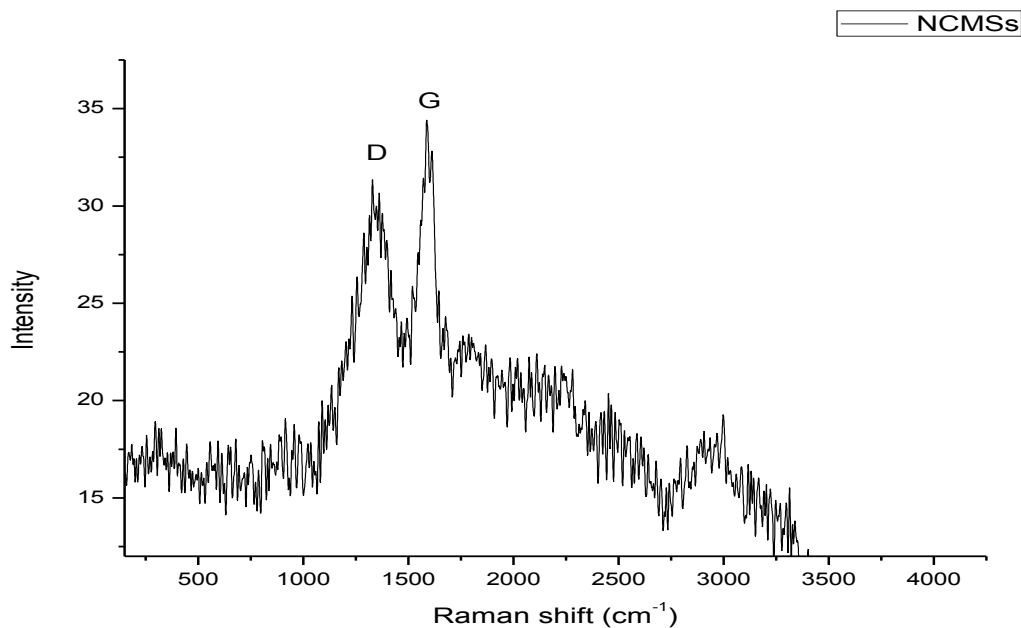


Figure 4.30. A laser Raman spectrum of NCMSs synthesised by CVD.

Table 4.3. Raman shift of CMSs and NCMSs synthesized by CVD

Carbon material	Raman shift (cm ⁻¹)		I _G /I _D
	D	G	
CMSs	1348	1578	1.2
NCMSs	1370	1590	1.1

4.2.2.4 PXRD characteristics of CMSs and NCMSs synthesised by CVD

PXRD analyses were carried out on the undoped and N-doped CMSs to establish their crystallinity and purity. As noted previously (section 4.2.1.4) both forms of hexagonal graphite were observed (i.e. the broad (002) plane and the smaller (101) plane) at 25° and 45-60° respectively (Figures 4.31 and 4.32) in the CMSs and the NCMSs. Since two main types of combustion peaks for carbon (of approximately equal magnitude) were observed in the TGA data (Figure 4.24), these results confirmed the possible presence of amorphous carbon and suggested that the overall degree of graphitisation of both of these materials was low. This was consistent with the laser Raman results (Table 4.3).

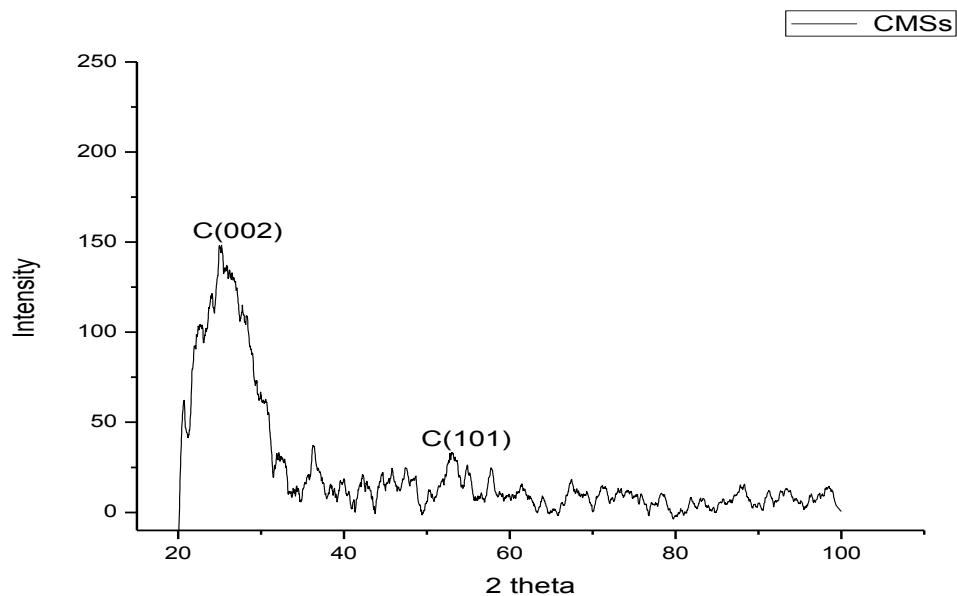


Figure 4.31. A PXRD diffractogram of undoped CMSs synthesised by the CVD method showing the characteristic (002) and (101) C peaks.

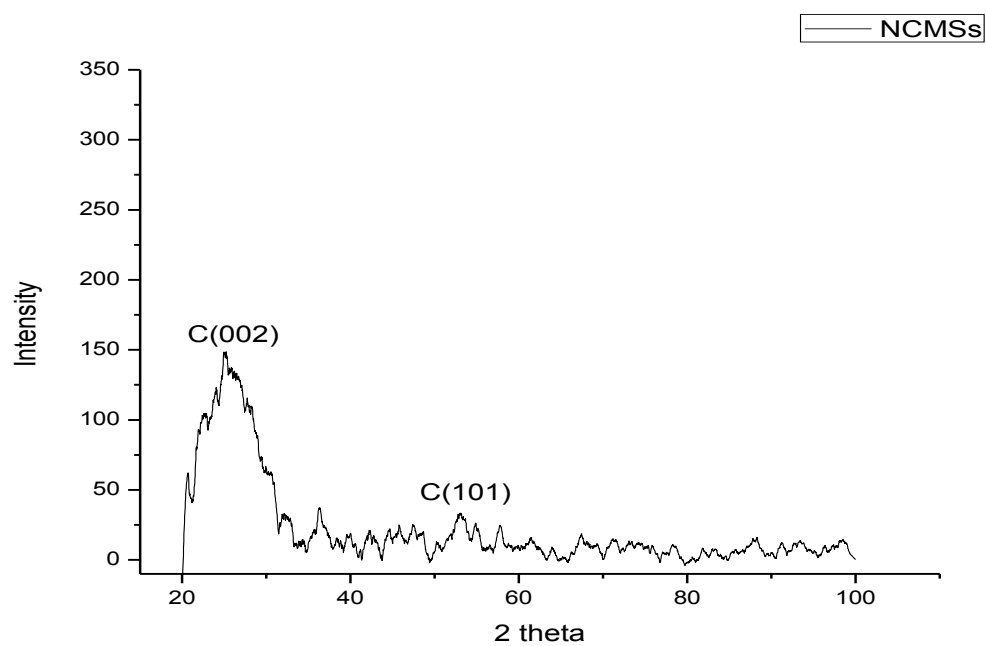


Figure 4.32. A PXRD diffractogram of NCMSs synthesised by the CVD method showing the characteristic (002) and (101) C peaks.

4.2.2.5 Zeta-potential properties of CMSs and NCMSs synthesised by CVD

As before, the presence of acid functional groups on these carbonaceous materials was verified by samples of each which were titrated with [0.1 M] NaOH and HCl solutions, ranging in pH from 2 to 12. In the case of the undoped CMSs it was observed that the point of zero charge occurred at pH 2 (Figure 4.33) and the Zeta-potential became increasingly more negative as the pH increased. However, the negative surface charge was substantially less than that of undoped CNTs (Figure 4.22). By contrast it was observed that the surface charge of NCMSs was initially positive between pH 2-4, presumably as the incorporated nitrogen was protonated. Here the point of zero charge was observed to occur at pH 5.5 which was approximately one pH unit above that of NCNTs (Figure 4.22). As with NCNTs, the surface charge generally tended to become more negative (Figure 4.22).

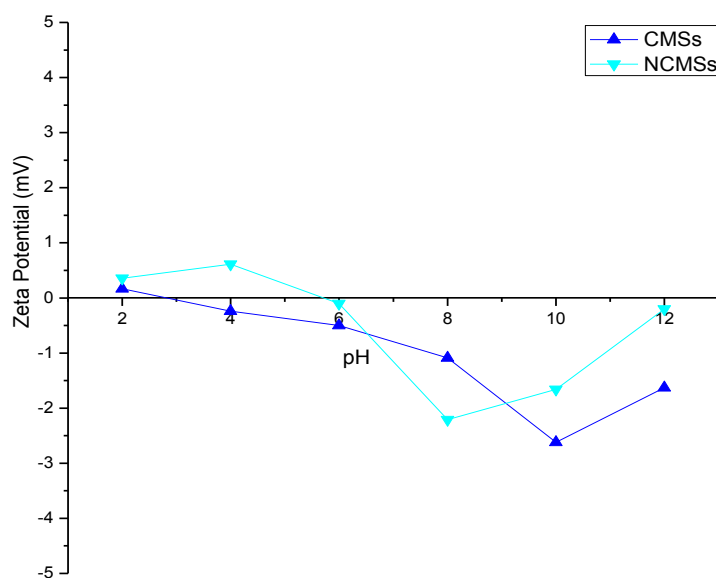


Figure 4.33. A plot of the Zeta-potentials of undoped CMSs and N doped CMSs that were synthesised by CVD.

4.2.2.6 BET surface area properties of CMSs and NCMSs synthesised by CVD

BET surface area analyses of the undoped and N-doped CMSs were performed. As with undoped CNTs and NCNTs the results from these analyses (Table 4.4) indicated that the surface area of the undoped CMSs ($2.4 \text{ m}^2/\text{g}$) were slightly higher than that of the NCMSs ($2.0 \text{ m}^2/\text{g}$). However, these values were between 30 to 35 times less than those of the CNTs and NCNTs. This is most likely due to the porosity of these materials i.e. 1–2 μm for CMSs

and NMCSs by comparison with between 15-45 nm for CNTs and NCNTs. In general, it would have been expected that larger carbon materials would have had fewer atoms exposed on the surface of the material and hence have exhibited a lower surface area [24]. In this case, consistent with this expectation, it was observed that the bigger NCMSs had slightly lower surface than the smaller undoped CMSs (Figures 4.26 and 4.28).

Table 4.4. BET surface areas of CMSs and NCMSs synthesized by CVD

Samples	Average Surface Area (m ² /g)
CMSs CVD	2.4
NCMSs CVD	2.0

4.2.2.7 A summary of the comparison of the properties/characteristics of undoped CMSs and N-doped CMSs synthesised by CVD.

Based upon the data gathered from these studies, it could be concluded that the incorporation of nitrogen into CMSs: 1) slightly lowered their thermal stability, 2) increased their external diameter, 3) slightly decreased their crystallinity, 4) raised the pH at which they reached the point of zero charge, 5) increased their negative surface charge at pH's > 6 and 6) decreased their surface area. Based on this data, especially the lower surface area and surface charge it was expected that undoped CMSs would make slightly better reinforcing materials when making composites with SBR.

4.2.3 A comparison of the properties/characteristics of non-functionalised and functionalised CMSs synthesised by hydrothermal techniques.

Before all of these carbonaceous materials were tested as potential reinforcing materials in composites with SBR, one last comparison was made between CMSs and SOCMSs that were synthesized by the hydrothermal method. Unlike in the CVD method, here CMSs were formed from the carbonisation of a sugar solution under temperature and pressure. Also, unlike in the previous study (section 4.2.2), oxygen rich groups (including the sulphonate group) were expected to be found on the surface of these CMSs (consistent with earlier publications [25-26]). Hence a thorough comparison of the CMSs and SOCMSs was then made.

4.2.3.1 Thermal properties of CMSs and SOCMSs synthesised by hydrothermal method.

TGA analyses of unfunctionalised CMSs and SOCMSs synthesised by the hydrothermal method were performed. For both the unfunctionalised CMSs and the SOCMSs three decomposition peaks were observed (Figures 4.34-4.35). The first peak at 70°C was most likely due to a small quantity of moisture in the products, as well as alcohol which was used to clean the CMSs. The second peak at 350°C was most likely due to the removal of amorphous carbon as well as some of the oxygen-bearing functional groups on the surfaces of these spheres. The last peak at 510°C was most likely the combustion of graphitic carbon. Based upon the data that was obtained it appeared that only minor differences between the two types of CMSs produced by the hydrothermal method could be observed, with a marginal improvement of the thermal properties having occurred when the CMSs were sulphonated (Figures 4.34 and 4.35). However, their thermal stability appeared to be very much lower than CMSs produced by CVD (see Figure 4.24). This observation is most likely due to the large difference in their reaction temperatures i.e. 900°C for CVD and 210°C for the hydrothermal method. Thus these CMSs would be expected to be more amorphous and hence less thermally stable.

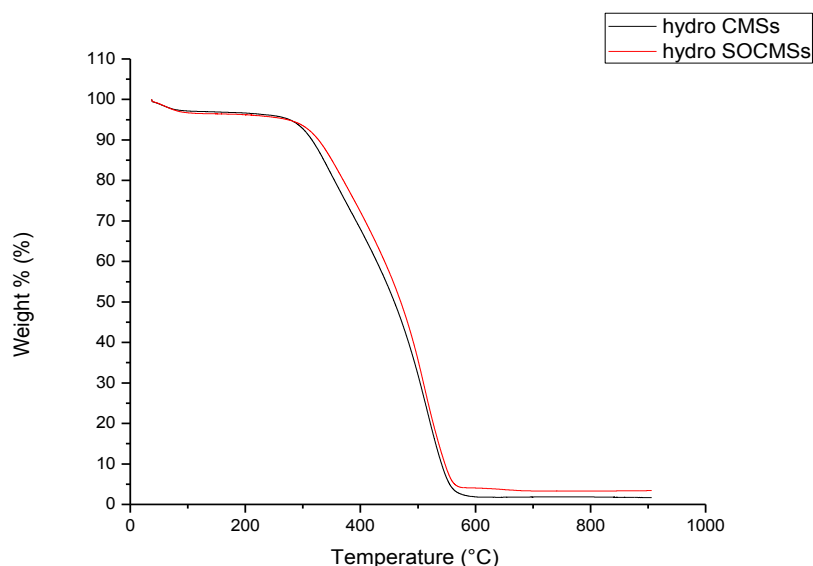


Figure 4.34. TGA plots of CMSs and SOCMSs that were synthesised by the hydrothermal method.

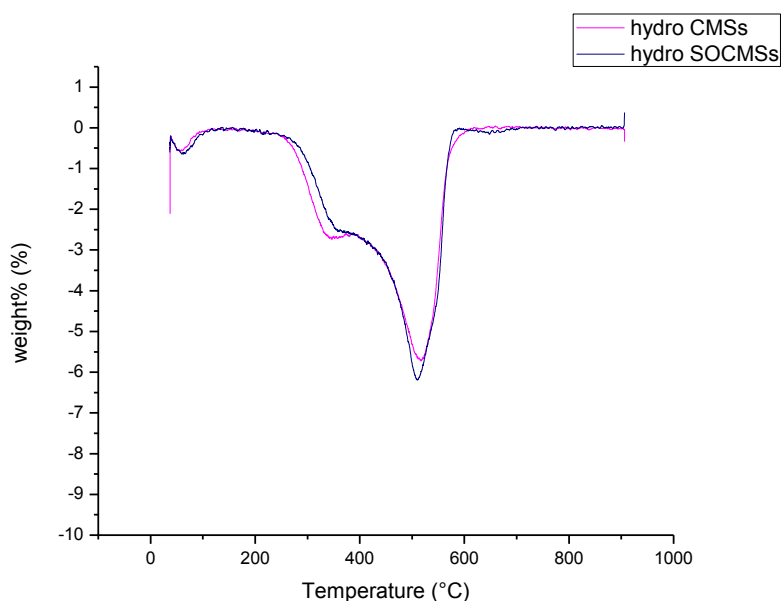


Figure 4.35. The first derivatives of the TGA profiles for undoped CMSs and SOCMSs that were synthesised by the hydrothermal method.

4.2.3.2 Morphological and size properties of CMSs and SOCMSs synthesised by hydrothermal method.

The morphologies and sizes of CMSs and SOCMSs that were synthesised by the hydrothermal method were studied by using TEM. The TEM micrographs (Figures 4.36 and 4.38) revealed that both types of materials were spherical with some tendency to agglomerate. Similarly, the outer diameters of these spheres ranged from 1.5-2 μm for CMSs but from 1.5-2.5 μm for SOCMSs (Figures 4.37 and 4.39). Hence it appeared that the introduction of sulphonic acid ($-\text{SO}_3\text{H}$) functionalities on these spheres resulted in an increase amounts of surface functionalities as compared with unfunctionalised CMSs [27]. This result is consistent with research which has suggested that flake-like compartments, formed on the surfaces of such spheres, allowed functionalities to bind in between them and hence cause an increase thereof [28-39].

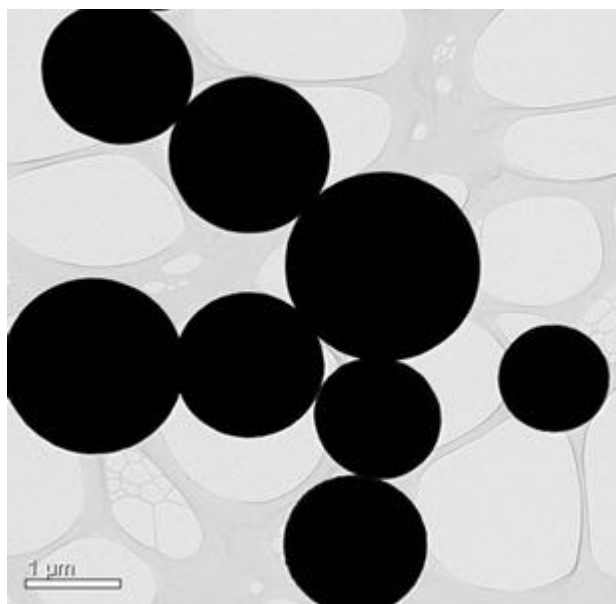


Figure 4.36. A TEM image of CMSs synthesised by the hydrothermal method.

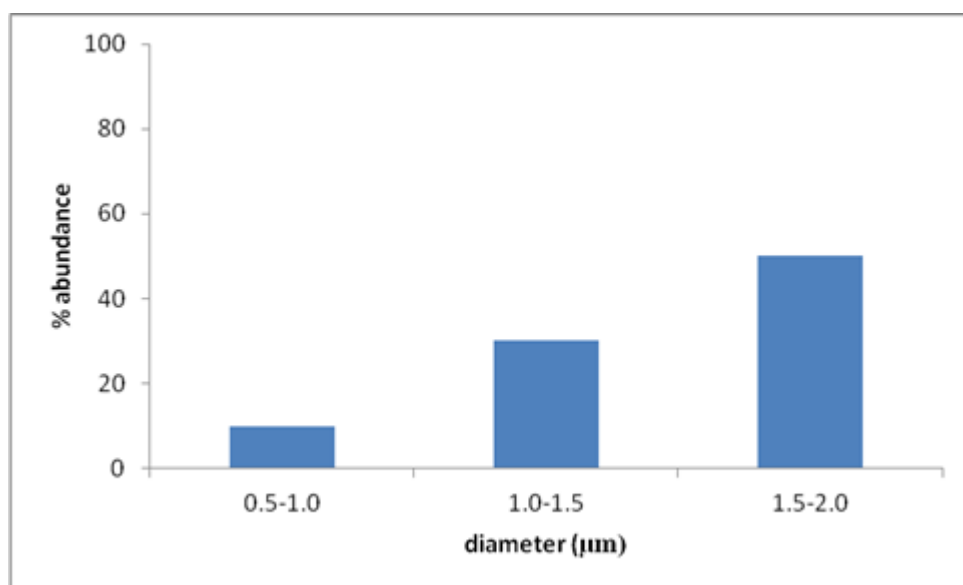


Figure 4.37. A plot of the size distribution of CMSs synthesised by the hydrothermal method.

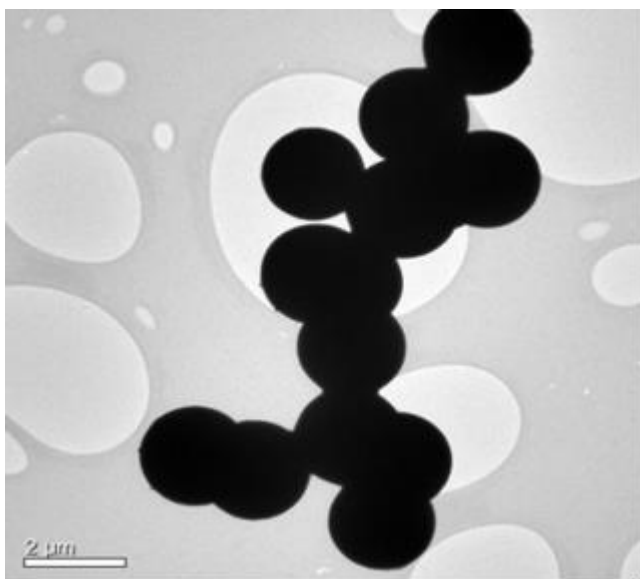


Figure 4.38. A TEM image of SOCMSs synthesised by the hydrothermal method.

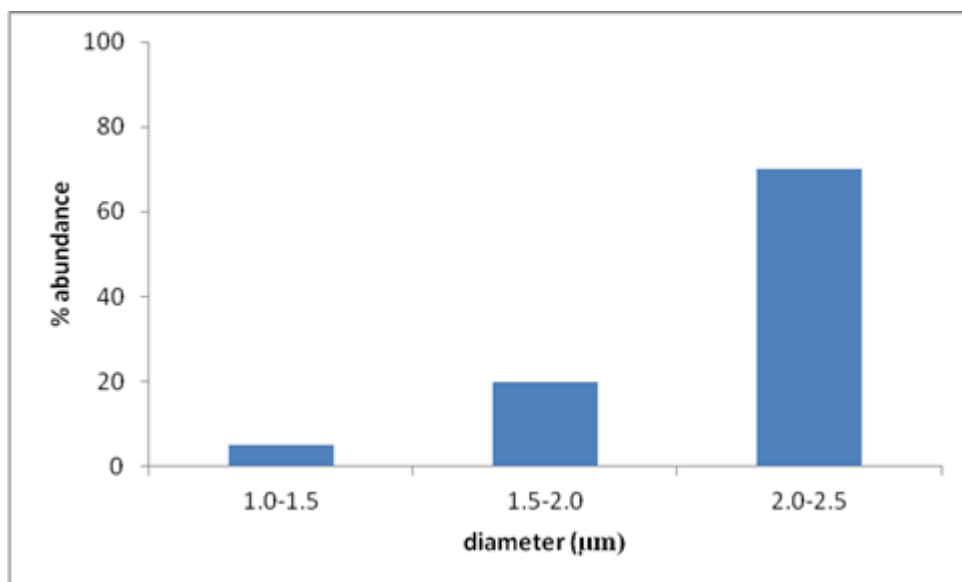


Figure 4.39. A plot of a size distribution of SOCMSs synthesised by the hydrothermal method.

4.2.3.3 FTIR characteristics of CMSs and SOCMSs synthesised by hydrothermal method.

4.2.3.3.1 FTIR Analysis of carbonaceous products formed by hydrothermal method.

The functionalities present on the surface of the CMSs and SOCMSs, that were synthesised by the hydrothermal method, were studied by using fourier transform infrared (FTIR)

spectroscopy (FTIR). It has generally been found to be difficult to observe IR peaks of carbon materials using IR, due to their black colour. In an attempt to establish the presence/absence of functionalities on the surface of carbonaceous materials synthesised by the hydrothermal technique, dilutions of these materials were made with distilled water to overcome this problem. Bands in the FTIR spectrum (Figure 4.40) at 1675-1715 cm^{-1} and 1625 cm^{-1} were attributed to C=O and C=C vibrations respectively for the undoped CMSs. Traces of the O-H band were also observed in the 3000-3500 cm^{-1} region. The presence of the C=O and O-H peaks confirmed that the surfaces of the CMSs were functionalised. In the case of the SOCMs (Figure 4.41), while the O-H band was more visible, the presence of the S=O in ca. 750 cm^{-1} region confirmed that the surface of the CMSs was functionalised with the sulphonic acid group ($-\text{SO}_3\text{H}$).

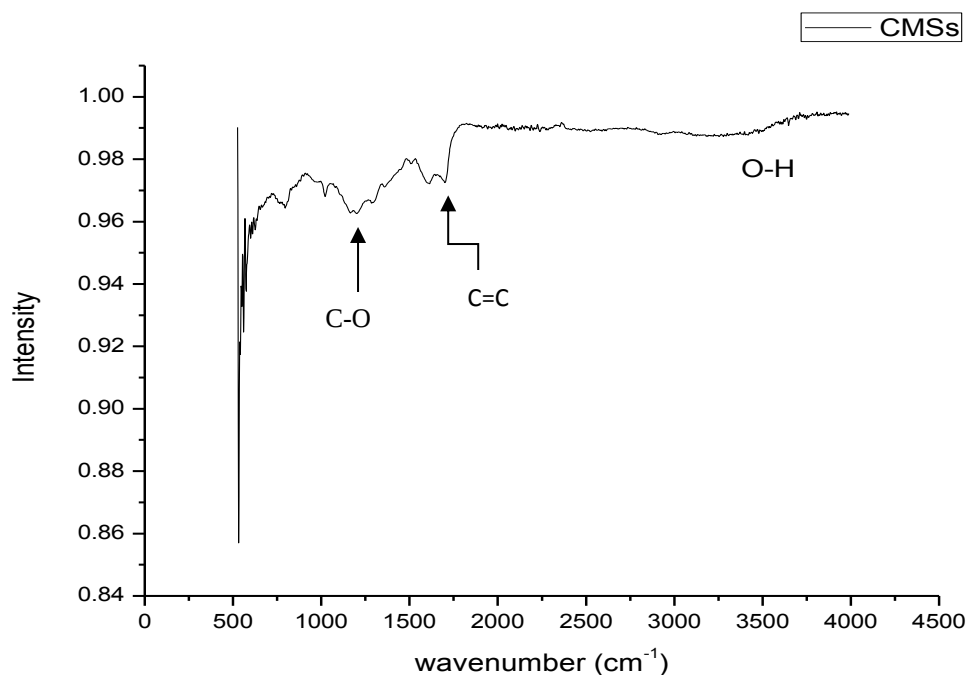


Figure 4.40. A FTIR spectrum of hydrothermal CMSs.

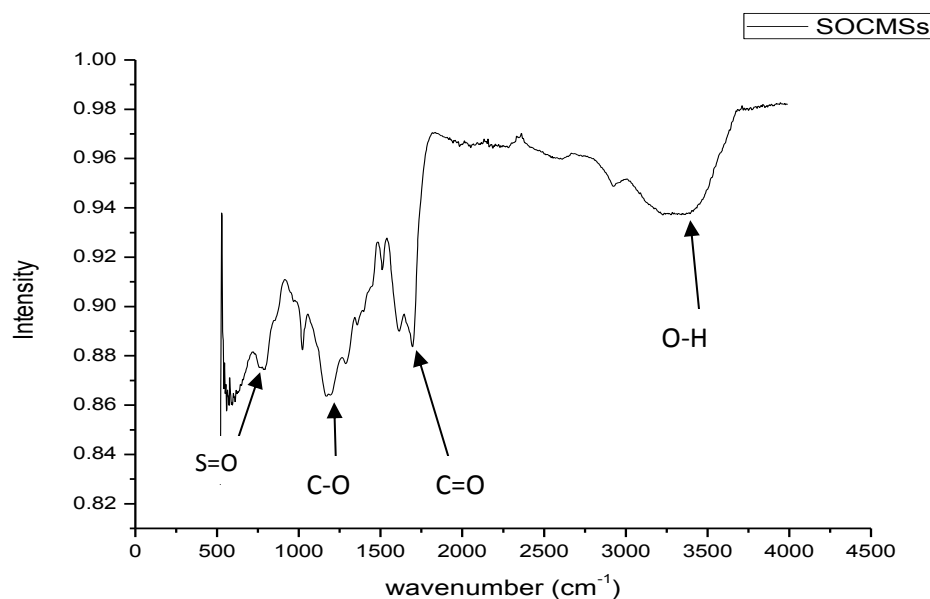


Figure 4.41. A FTIR spectrum of hydrothermal SOCMSs.

4.2.3.4 Laser Raman characteristics of CMSs and SOCMSs synthesised by the hydrothermal method.

Laser Raman analyses (Figures 4.42-4.43) of the unfunctionalised CMSs and SOCMSs synthesised by the hydrothermal method were performed.

In both cases the CMSs were found to be very disordered as seen by their low I_G/I_D ratios (Table 4.5). This was most likely due to the low temperatures that were used to synthesise these materials (i.e. less than 200°C). As expected, due to the introduction of the sulphonic groups on the carbonised structures, the SOCMSs were more disordered than the unfunctionalised CMSs (i.e. $I_G/I_D=0.75$ for CMSs versus $I_G/I_D=0.59$ for SOCMSs).

Table 4.5. Table of Raman shift for CMSs and SOCMSs synthesized by hydrothermal method

Carbon material	Raman shift (cm ⁻¹)		I_G/I_D
	D	G	
hydro CMSs	1344	1567	0.75
hydro SOCMSs	1356	1595	0.59

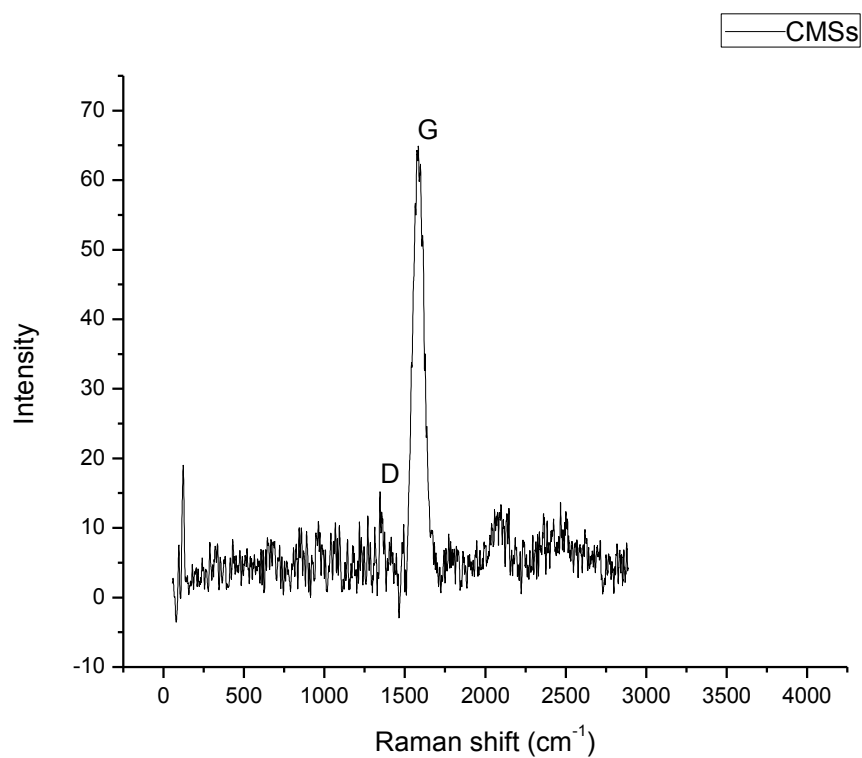


Figure 4.42. A laser Raman spectrum of CMSs synthesised by the hydrothermal method.

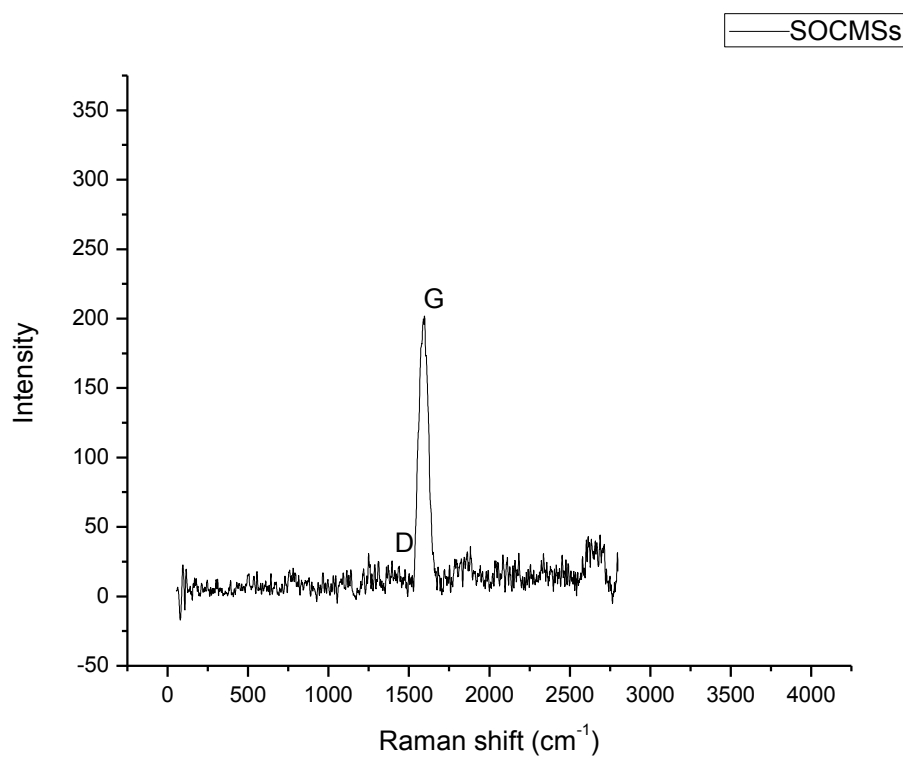


Figure 4.43. A laser Raman spectrum of SOCMSs synthesised by the hydrothermal method.

4.2.3.5 PXRD characteristics of CMSs and SOCMSs synthesised by hydrothermal method.

PXRD analyses were carried out on the unfunctionalised CMSs and SOCMSs to establish their crystallinity and purity. As noted previously (section 4.2.2.4) both forms of hexagonal graphite were observed (i.e. the broad (002) plane and the smaller (101) plane) at 25° and 45-60° respectively (Figures 4.44 and 4.45) in the CMSs and the SOCMSs. Similarly, since two main types of combustion peaks for carbon (of approximately equal magnitude) were observed in the TGA data (Figure 4.35), these results once again confirmed the possible presence of amorphous carbon as well as suggested that the overall degree of graphitisation of both of these materials was low. This was consistent with the laser Raman results, where the I_G/I_D ratios were found to be low (Table 4.5). Once again, no other peaks were observed, which suggested that the materials were relatively free of impurities after purification and functionalisation.

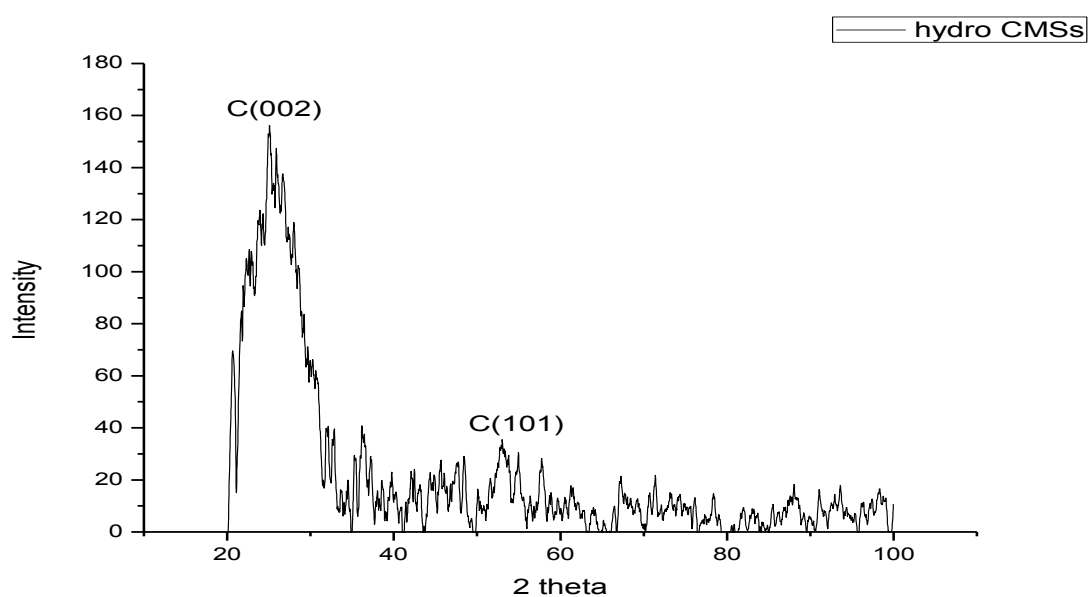


Figure 4.44. A PXRD diffractogram of CMSs synthesised by the hydrothermal method showing the characteristic (002) and (101) C peaks.

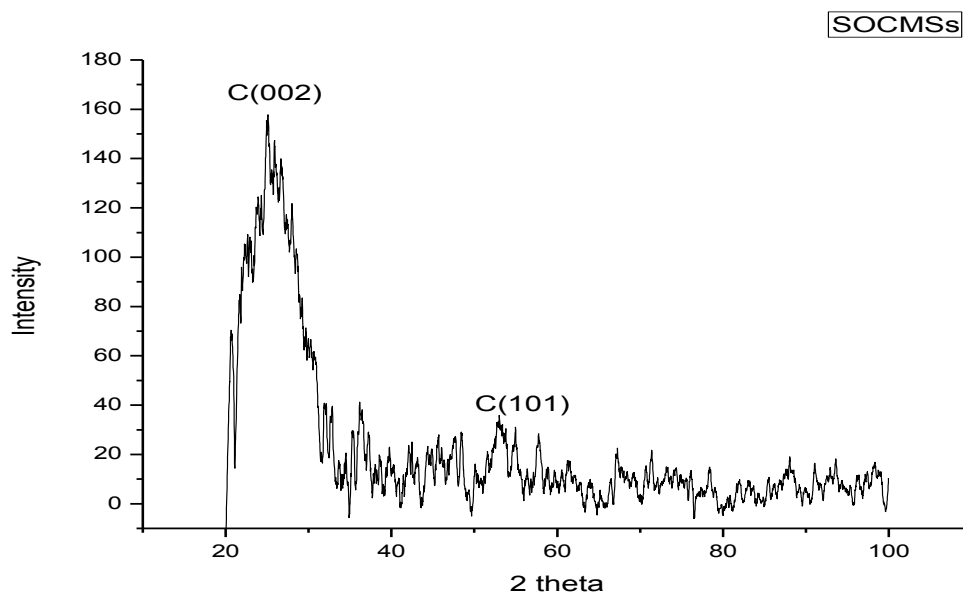


Figure 4.45. A PXRD diffractogram of SOCMSs synthesised by the hydrothermal method showing the characteristic (002) and (101) C peaks.

4.2.3.6 Zeta-potential properties of CMSs and SOCMSs synthesised by hydrothermal method

The presence of acid functional groups on these carbonaceous materials was ascertained by Zeta-potential measurements as before (Section 4.2.2.5). In both cases it was observed that the point of zero charge would most likely have occurred at a $\text{pH} < 2$ (Figure 4.46). Similarly in both cases the Zeta-potential became increasingly more negative as the pH increased. This is in direct contrast with the CMSs and NCMSs synthesised by CVD (see Figure 4.33). The presence of: S=O, C-O, C=O and O-H groups on the surfaces of the CMSs synthesised by the hydrothermal method (Figure 4.41) may have been the reason for this observation [25-26].

It was also observed that the negative surface charge for unfunctionalised CMSs, synthesised by the hydrothermal technique, appeared to be substantially higher than that for the SOCMSs for $\text{pH}'\text{s} > 8$ (see Figure 4.46). Since there should have been more functional groups which contained oxygen on the surface of SOCMSs (by the addition of the sulphonyl group), the reverse would have been expected. It was not clear why this trend was observed.

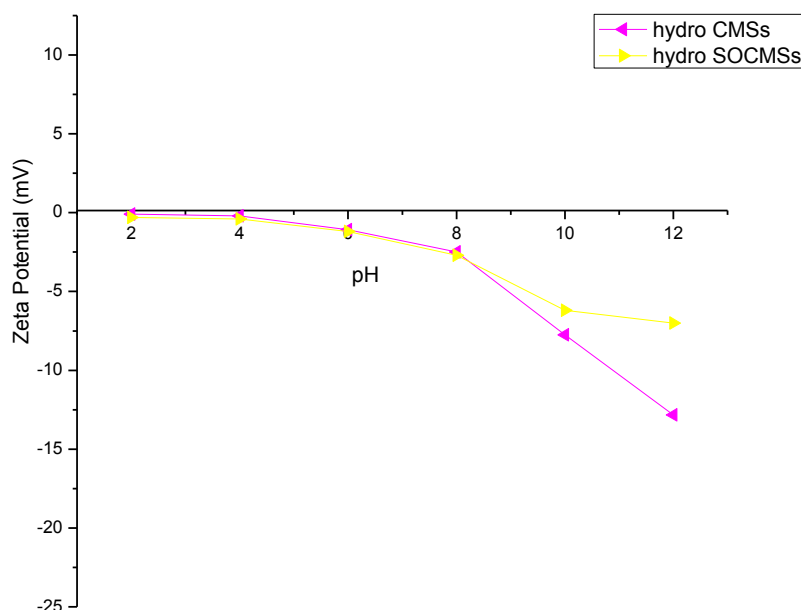


Figure 4.46. A plot of the Zeta-potentials of unfunctionalised CMCs and SOCMSs that were synthesised by the hydrothermal method.

4.2.3.7 BET surface area properties of CMCs and SOCMSs synthesised by hydrothermal method

BET surface area analyses of the unfunctionalised and SOCMSs were performed. As with the CMCs and NCMSs synthesised by CVD (see Table 4.4) the surface areas for the CMCs and SOCMSs were very low (Table 4.6).

Table 4.6. BET surface areas for all carbon materials synthesised by hydrothermal method.

Samples	Average Surface Area (m ² /g)
Hydro CMCs	1.7
Hydro SOCMSs	1.3

As before it also appeared (Table 4.4) that the surface area of the unfunctionalised CMCs (1.7 m²/g) were slightly higher than that of the SOCMSs (1.3 m²/g) (see Table 4.6). However, these values were between 40 to 60 times less than those of the CNTs and NCNTs (see Table 4.2). This is most likely due to the porosity of these materials i.e. 1–2.5 μ m for CMCs and

SOCMSs by comparison with between 15-45 nm for CNTs and NCNTs as discussed previously.

4.2.3.8 A summary of the comparison of the properties/characteristics of unfunctionalised CMSs and SOCMSs synthesised by hydrothermal method.

Based upon the data gathered from these studies, it can be concluded that the functionalisation CMSs with sulphonyl groups by the hydrothermal method: 1) marginally improved their thermal stability, 2) increased their surface functionalities, 3) decreased their crystallinity, 4) increased their porosity and 5) increased their negative surface charge by comparison with CMSs produced by CVD.

4.3 Tensile strength

Composites of the SBR and the various carbon materials previously mentioned were synthesised (Section 3.6.2). Specimens of each of these composites were then tested for their tensile strengths at room temperature (Section 3.7.8). The cured specimens (before testing) are displayed in Figure 4.47. As can be seen, six samples were tested for each loading. This was done so that the average of the tensile strength for each loading and each carbonaceous filler could be obtained.



Figure 4.47. A photograph of a typical group of six specimens shown before being analysed for their tensile strengths.

After each specimen was analysed for its tensile strength it was observed (for the blank SBR and all SBR composite materials) that the break point generally occurred at the same place i.e. at the grip point (Figure 4.48). However, this should typically have occurred in the middle of the specimen and not at the grip point.



Figure 4.48. A photograph of a typical group of six specimens shown after being analysed for their tensile strengths. Notice the consistency of their break points.

There are a number of reasons why these break points may have been inconsistent with where they ought to have been:

1. It may have been possible that the grip (the region where each specimen was mounted) had cut into the specimen and hence under stress had broken each specimen at the same point every time.
2. Since it was difficult to remove the solvent (toluene), which was used to dissolve the SBR bulk rubber in order to create an homogenous slurry with the carbon materials, this could have played a role in the reduction of the strength of the final composite.
3. Despite the enormous effort that was put in to generate specimens of the same size, shape and thickness (with a special mould that was manufactured for this study), specimens were not always uniform (as can be seen in Figures 4.47 and 4.48). These variations may have affected the final measurements.
4. Despite attempts to thoroughly disperse the various carbonaceous materials through the viscous SBR when dissolved in toluene, agglomeration of these materials (due to

Van der Waals forces) could not be entirely eliminated. This may well have resulted in a reduction in the strengths of the final composites.

4.3.1 A comparison of the mechanical properties of undoped CNTs and NCNTs synthesised by the CVD method.

Analyses of the composite specimens formed by the incorporation of undoped CNTs in the SBR were performed at three different loadings (i.e. 0.125%, 0.250% and 0.500% (m/m)). The stress-strain curves of the blank SBR and SBR/undoped CNTs composites were then plotted (Figure 4.49). Each curve corresponded to the average (or mean value) of all 6 samples tested in each loading category. Thereafter the ultimate tensile strengths and Young's moduli of all the materials were calculated (see Section 3.7.8). Based upon this data it was observed that SBR incorporated with all three loadings of CNTs (Table 4.7) had higher tensile strengths than the blank specimen (i.e. 2.20 MPa), showing that the inclusion of CNTs had strengthened the SBR.

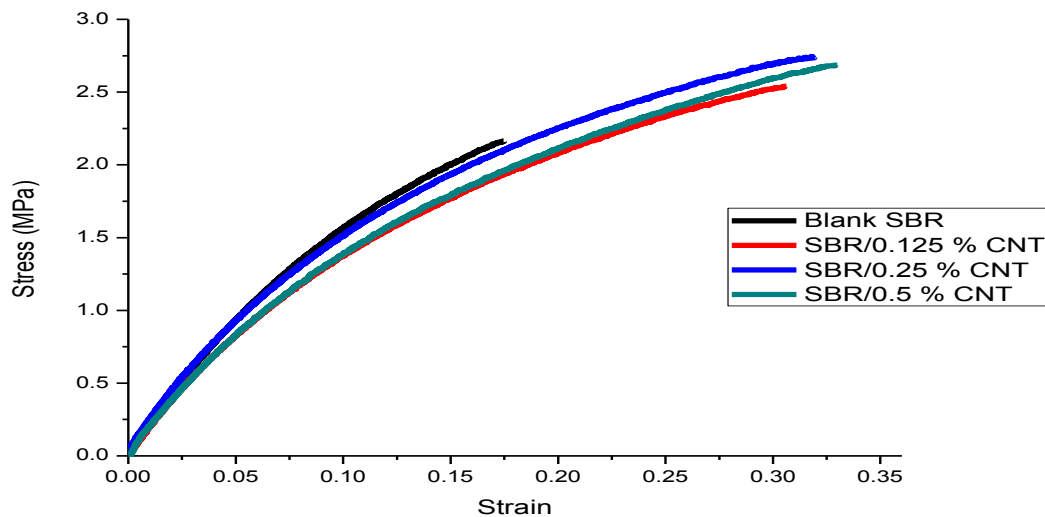


Figure 4.49. Stress vs. strain curves of undoped CNTs synthesised by CVD at different loading in comparison with the blank SBR specimen.

It was also observed that the tensile strength increased to a maximum loading (at the 0.250% (m/m)) and then dropped off slightly thereafter (see Figure 4.49 and Table 4.7). Similarly it was observed that the best loading of undoped CNTs into SBR was c.a. 0.250% (m/m), which

was supported by the highest Young's modulus by comparison with the blank SBR (i.e. 29.74 MPa by comparison with 22.18 MPa) as noted in Table 4.7. It was also noted that the Young's modulus for 0.125% and 0.500% loading were less than that of the blank SBR. This may be related to the four possible reasons mentioned previously.

Table 4.7. Table of ultimate tensile strengths and Young's moduli for SBR filled with different loadings of undoped CNTs (synthesised by CVD).

Loading % (m/m))	Filler in SBR	Tensile strength (MPa)	Young's modulus (MPa)
0.000	None	2.20	22.18
0.125	CNTs	2.54	19.85
0.250	CNTs	2.74	29.74
0.500	CNTs	2.69	19.50

Thereafter analyses of the composite specimens formed by the incorporation of nitrogen doped CNTs or NCNTs in the SBR were performed at the same three loadings as before (i.e. 0.125%, 0.250% and 0.500% (m/m)). The stress-strain curves of the blank SBR and SBR/NCNTs composites were then plotted (Figure 4.50).

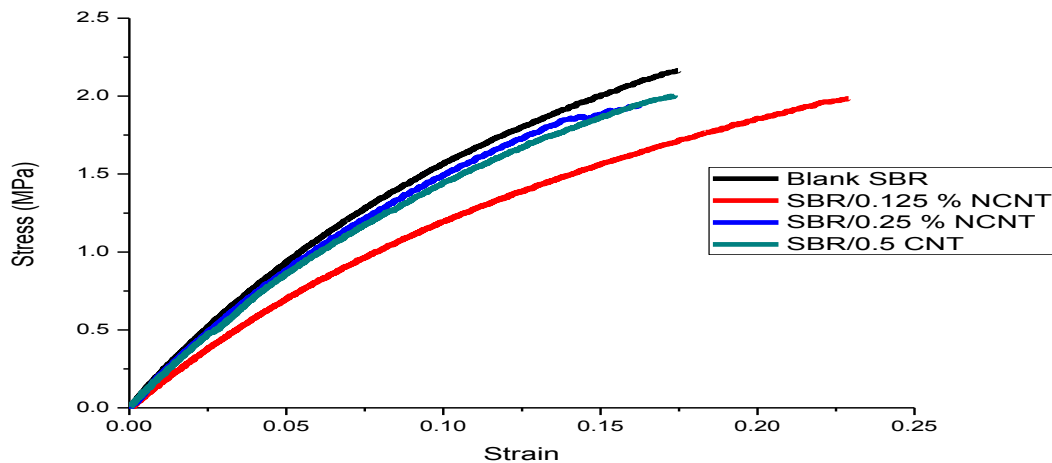


Figure 4.50. Stress vs. strain curves of NCNTs synthesised by CVD at different loadings in comparison with the blank SBR specimen.

As before the ultimate tensile strengths and Young's moduli of all these materials were calculated (see Section 3.7.8) and were represented in Table 4.8.

Table 4.8. Table of ultimate tensile strengths and Young's moduli for SBR filled with different loadings of NCNTs (synthesised by CVD).

Loading % (m/m))	Filler in composite	Tensile strength (MPa)	Young's modulus (MPa)
0.000	None	2.20	22.18
0.125	NCNTs	1.99	15.54
0.250	NCNTs	1.95	21.65
0.500	NCNTs	2.01	21.00

However, the tensile strengths and Young's moduli for all loadings were lower than those of for blank SBR. This was also observed in most cases for SBR/CNTs. Unlike the case with CNTs incorporated into SBR, no maximum loading with NCNTs was observed. It therefore appeared that inclusion of nitrogen into the CNTs reduced both the tensile strength and Young's modulus of the resultant composite. Hence SBR incorporated with undoped CNTs appeared to make stronger composites. This was an observation that was consistent with previous findings [39].

Unlike previous predictions (section 4.2.1.5) that the incorporation of NCNTs into SBR may have improved the strength of the resultant composites, the reverse was observed. At this stage it is difficult to be certain exactly what may have caused this, but several factors (previously noted in Section 4.2.1.7) may have contributed to this: 1) the larger external tube diameters of NCNTs, 2) the lower surface areas of NCNTs and perhaps very importantly 3) the increased negative surface charge of NCNTs at higher pH's.

4.3.2 A comparison of the mechanical properties of four different types of CMSs synthesised both by the CVD and the hydrothermal methods.

Analyses of the composite specimens formed by the incorporation of undoped CMSs and NCMSs (by the CVD method) as well as CMSs and SOCMSs (by hydrothermal method) into SBR were performed at three different loadings (i.e. 0.125%, 0.250% and 0.500% (m/m)). The stress-strain curves of the blank SBR and the various SBR/undoped CMSs (CVD and hydrothermal), NCMSs and SOCMSs composites were then plotted (Figures 4.51-4.54).

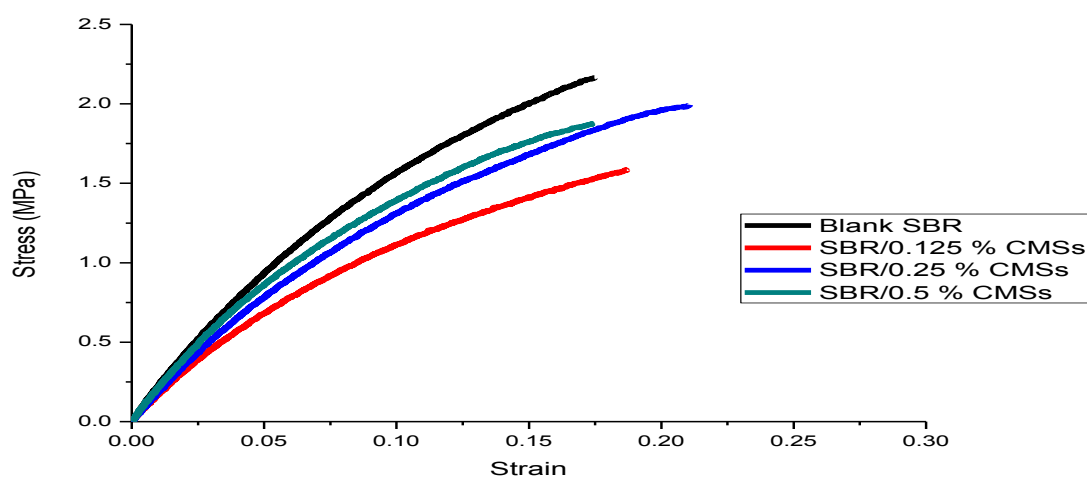


Figure 4.51. Stress vs. strain curves of CMSs synthesised by CVD at different loadings in comparison with the blank SBR specimen.

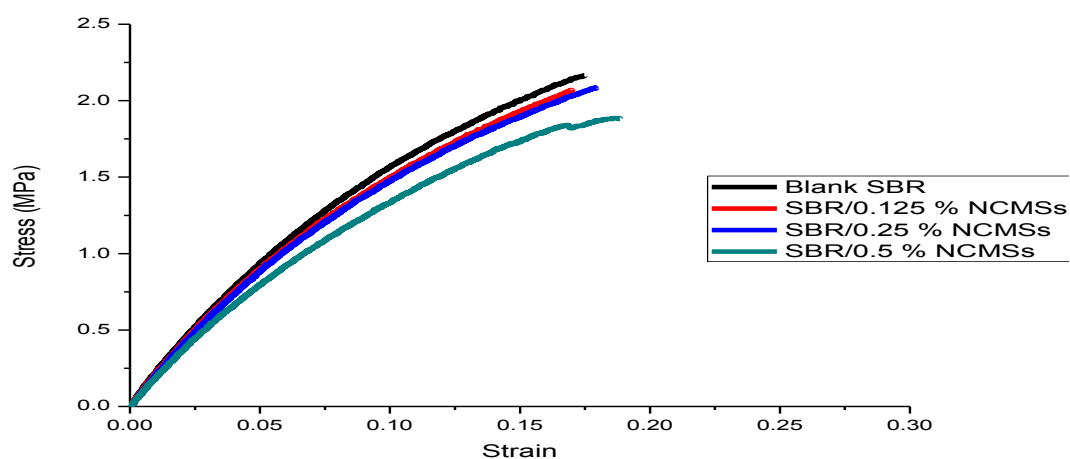


Figure 4.52. Stress vs. strain curves of NCMSs synthesised by CVD at different loading in comparison with the blank specimen.

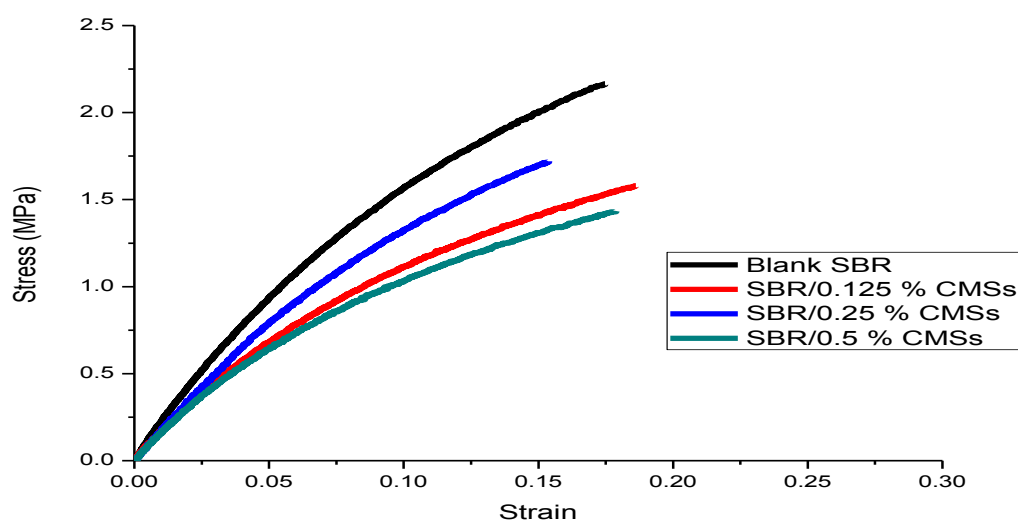


Figure 4.53. Stress vs. strain curves of CMSs synthesised by the hydrothermal method at different loadings in comparison with the blank SBR specimen.

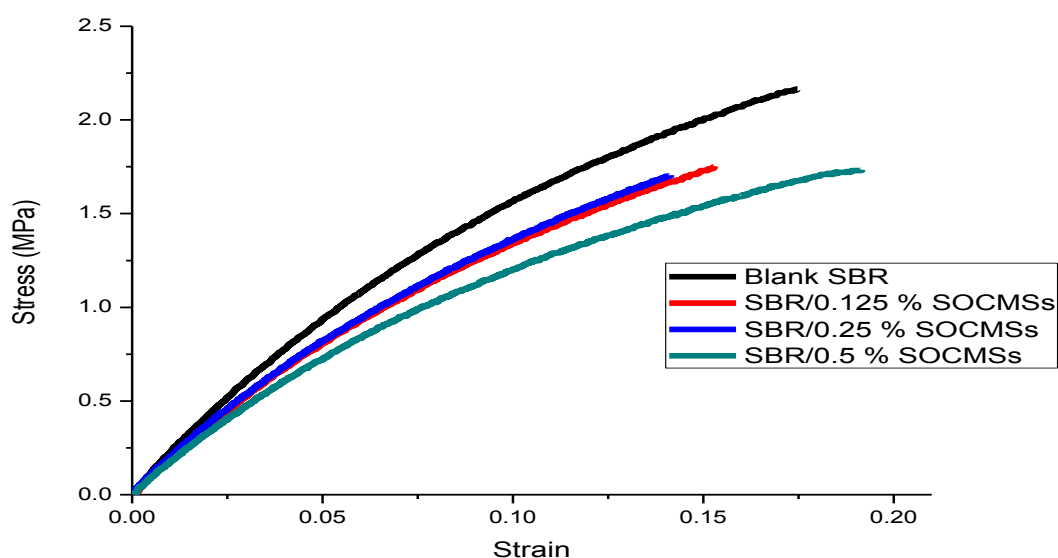


Figure 4.54. Stress vs. strain curves of SOCMSs synthesised by the hydrothermal method at different loadings in comparison with the blank SBR specimen.

Each curve corresponded to the average (or mean value) of all 6 samples tested in each loading category. Thereafter the ultimate tensile strengths and Young's moduli of all the materials were calculated (see Section 3.7.8) and were represented in Tables 4.9-4.10.

Table 4.9. Table for ultimate tensile strengths for SBR filled by various CMSs synthesised by the CVD and hydrothermal methods at different loadings.

	Tensile strength (MPa)			
Loading % (m/m))	SBR/CMSs (CVD)	SBR/NCMSs (CVD)	SBR/CMSs (Hydro)	SBR/SOCMSs (Hydro)
0.125	1.59	2.09	1.58	1.76
0.250	2.00	2.09	1.72	1.71
0.500	1.88	1.88	1.44	1.74
Tensile strength for the blank SBR was 2.2 MPa				

Table 4.10. Table of Young's moduli for SBR filled with different loadings of various CMSs synthesised by the CVD and hydrothermal methods.

	Young's modulus (MPa)			
Loading % (m/m))	SBR/CMSs (CVD)	SBR/NCMSs (CVD)	SBR/CMSs (Hydro)	SBR/SOCMSs (Hydro)
0.125	17.39	21.99	17.39	18.70
0.250	17.69	20.45	16.97	20.63
0.500	21.54	19.46	17.26	18.14
Young's modulus for the blank SBR was 22.18 MPa				

An examination of the data in Table 4.8 showed that composites formed by the incorporation of CMSs and NCMSs synthesised by CVD had higher tensile strengths than those formed by the hydrothermal method. This too was corroborated by their higher Young's moduli as compared to composites formed with CMSs and SOCMSs by the hydrothermal method (Table 4.9). However, contrary to the prediction made in Section 4.2.2.7, it appeared that NCMSs had both higher strengths and Young's moduli at every loading than any other kind of CMS no matter what method was used to synthesise it. This contrasts with what was observed with the SBR composites with CNTs, where SBR/NCNTs composites had lower tensile strengths and Young's moduli than SBR/CNTs composites. This observation may have been to the lower negative surface potential of the NCMSs by comparison with that of NCNTs (see Figure 4.46 and Figure 4.22).

Although the presence of the sulphonic acid functional group appeared to enhance the Young's moduli of SBR/SOCMSs composites, a slight reduction in their tensile strengths was observed. Since the properties of CMSs and SOCMSs synthesised by the hydrothermal method were fairly similar, the reasons for this observation were not known at this stage.

However, of greater importance was the observation that none of the SBR composites with CMSs (synthesised by either technique) had tensile strengths and Young's moduli greater than the blank SBR specimen. This implied that the addition of the CMSs actually reduced the mechanical strength of SBR.

Equally, it was observed that in the majority of the cases the SBR composites with CMSs (synthesised by either technique) had tensile strengths and Young's moduli less than any SBR composites formed either with CNTs or NCNTs. It is speculated that the main reasons for this were: 1) the higher surface area of CNTs/NCNTs (Table 4.2 vs Tables 4.4 & 4.6), 2) the small diameters of CNTs/NCNTs (Figures 4.15 & 4.19 vs Figures 4.26, 4.28, 4.37 & 4.38), and 3) the shapes of the two types of materials used in these studies.

4.4 References

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Chapter 5: General conclusions and recommendations

5.1 Conclusions

The main aim of this study was to synthesize and characterise (by TEM, TGA, FTIR, laser Raman, BET and PXRD) different carbonaceous materials (CNTs, NCNTs, CMSs, NCMSs, hydrothermal CMSs and SOCMSs) and compare the extent of their reinforcement in a SBR rubber matrix using a tensile testing machine. These aims were successfully achieved and the following conclusions were drawn.

- Four different carbon materials were synthesised by the CVD method (using a Fe-Co/CaCO₃ catalyst, gaseous acetylene as a carbon source, nitrogen gas as carrier gas and acetonitrile as nitrogen source), namely: CNTs, NCNTs, CMSs and NCMSs. These were then characterised by: TEM, TGA, FTIR, laser Raman, BET and PXRD.
- The incorporation of nitrogen into either type of carbonaceous material (CNTs or CMSs) increased their diameters: for CNTs from an average of 15-30 nm in un-doped CNTs to 30-45 nm for NCNTs, while in un-doped CMSs < 1.5 μm to NCMSs to > 1.5 μm .
- Two different carbon materials were able to be synthesised by the hydrothermal method (CMSs and SOCMSs) by using an autoclave, a sucrose solution as a carbon source and sulphonic acid as a sulphur source. All of the reaction parameters studied had significant effects on the stability, shape and texture of the carbon microspheres that were formed. The optimum conditions for these studies were found to be 0.3 M sucrose, 4 h reaction time and 190°C reaction temperature.
- CMSs synthesised by the CVD method produced materials of higher graphitic content. Most likely this was due to higher reaction temperature (i.e. 900°C) in the CVD method as compared with those in the hydrothermal one (i.e. 190°C-210°C).

Un-doped CNTs had a highest surface area (80 m²/g) when compared to the other carbonaceous materials.

- Reinforced composites were able to be formed by dissolving SBR rubber specimens in toluene and adding various loadings of different types of carbonaceous materials as fillers.
- Composites formed from SBR and un-doped CNTs displayed a better tensile strength and Young's modulus as compared to a blank SBR material and all other SBR-carbon material composites that were made. It appeared that a small quantity (as low as 0.125% m/m) of un-doped CNTs was enough to improve the mechanical properties of SBR when compared with the other carbon materials that were synthesised.

5.2 Future Recommendations

It is recommended that the following may be areas of future research:

1. Examine the effect of the ratios of the curing agents used in order to lessen the defects in SBR rubber even before carbon materials are added.
2. Investigate various methods of mixing SBR with various carbonaceous materials to establish if better specimens for analysis can be produced.
3. A better mould be designed or used to form dumb-bell shaped specimens that are in alignment with the ASTM standards of rubber.
4. Investigate the use of a melt mixer (as opposed to using the solvent mix method that was used in this study) in order to establish better dispersions of carbonaceous materials.
5. Synthesise smaller carbon spheres from both the CVD and hydrothermal method.

Appendix A.



KARBOCHEM

KARBOCHEM (Pty) Ltd
MARKETING
Eastgate Office Park, Block A
South Boulevard, Bruma, 2198
P O Box 581, Bruma 2026
South Africa
T +27 11 601 1660
F +27 11 616 6651

SASOLBURG SITE
Bunsen Street
PO Box 19
Sasolburg 1947
South Africa
T +27 16 970 1911
F +27 16 976 2672

NEWCASTLE SITE
Karbochem Road
Private Bag X6600
Newcastle 2940
South Africa
T +27 34 370 1111
F +27 34 312 1577

www.karbochem.co.za

DIRECTORS Dr AJ Brink, PJ Steenkamp, DT Blackburn, DW Kydd Reg. No. 2002/015590/07

CERTIFICATE OF ANALYSIS

CUSTOMER CODE

TRADE NAME:

AFPOL 1502

PRODUCED BY:

KARBOCHEM

LOT No.:

1407192D1

SKID No

REV:

07/2010-19

PLANT:

SASOLBURG

PRODUCTION DATE:

19-Jul-14

TEST DATE:

20-Jul-14

PHYSICAL PROPERTIES:	TEST METHOD	SPECIFICATION	RESULTS
Mooney Viscosity, ML1+4 @ 100°C (i) mean	ASTM D1646	47 - 53	49
Stats on mooney: (ii) sample size		-	21
(iii) Cpk-value		-	1.37
(iv) S.D.			0.63
Tensile Strength, @ 145 °C (35'), MPa	ASTM D412	22.6 min	23.1
Elongation @ 145 °C (35'), %	ASTM D412	340 min	360
300% Modulus @ 145 °C (35'), MPa	ASTM D412	15 - 21.2	19.1
CHEMICAL PROPERTIES:			
Volatile Matter, mass %	ASTM D5668	0.50 max	0.36
Ash content, mass %	ASTM D5667	0.5 max	0.10
Extractables, mass %	ASTM D5774	6 - 10	7.4
Organic acid (mixed) %	ASTM D5774	5.0 - 7.0	6.0
Bound styrene (% of polymer chain)	ASTM D5775	22.3 - 24.7	23.2
RHEOMETER MDR 2000:			
(160 °C, 0.5° Arc, 100 CPM) Lab Banbury mix	ASTM D3185		
ML, dN.m	ASTM D5289	2.0 - 3.2	2.4
MH, dN.m	ASTM D5289	18.5 - 23.5	20.8
t' 1, minutes	ASTM D5289	1.4 - 3.8	2.6
t' 25, minutes	ASTM D5289	4.4 - 6.2	5.1
t' 50, minutes	ASTM D5289	5.6 - 8.4	7.3
t' 90, minutes	ASTM D5289	11.9 - 15.3	13.1

IBR 7

THIS MATERIAL IS FREE OF NITROSAMINES AND NITROSAMINE GENERATING SUBSTANCES
THE SHELF LIFE OF THIS MATERIAL IS TWO YEARS FROM DATE OF MANUFACTURING

SIGNED:

[Signature]
576822
Q C LABORATORY