SURFACE MODIFICATION OF CARBON BLACK BY PLASMA POLYMERISATION

From Process to Performance in Elastomer Blend Systems

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From Process to Performance in Elastomer Blend Systems

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SURFACE MODIFICATION OF CARBON BLACK BY PLASMA POLYMERISATION

FROM PROCESS TO PERFORMANCE IN ELASTOMER BLEND SYSTEMS

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof.dr. W.H.M.Zijm,
on account of the decision of the graduation committee,
to be publicly defended
on Friday, 7 November 2008 at 13.15 hrs.

by

Tony Mathew

born on 5 August 1976
in Cheeramchira, India

This dissertation has been approved by:

Promotor : prof. dr. ir. J. W. M. Noordermeer
Assistant promotor : dr. R. N. Datta

To my parents

Table of Contents

Chapter 1

Introduction

This chapter gives a brief introduction into the topic of this research from a historical perspective. The aim of this research is stated and the structure of the thesis is presented.

1.1 INTRODUCTION

Rubber products have become so much part of our lives, that they are taken for granted. The valuable contributions from many scientists and the material itself helped the rubber industry to achieve this position. It is hardly possible to think of a world without rubber. The applications of rubber range from a simple rubber band to heavy duty tires, from roof sheeting to earth quake protections, from balloons to surgical gloves, etc. The developments of this industry happened through the ages. It has changed its face throughout the years to meet the demands and needs of the sector. However, in order to serve mankind in a better fashion and to meet the challenging demands, there is still a lot more to do and to understand in the field of rubber.

Mankind started using rubber in its rather basic form. Herodotus, the famous Greek historian, described in one of his narrations that he had seen natives from Zanzibar playing with balls which bounced high in the air[1]. This was in the fourth century BC. Maybe the first business using rubber, as noted in history, was for pencil erasers. In 1770, E. Nairne (U.K) started selling cubes of rubber from his artists shop as pencil erasers for three shillings. Priestley called it ‘India Rubber’, from where it came. More or less at the same time, in 1780 the first thesis or book solely on the subject of rubber was published from the University of Utrecht in the Netherlands. The major conclusion from this thesis was that the various Amazonian botanists were writing about more than just one ‘rubber’ tree. The author referred to many medical applications of rubber, including catheters.

The first ‘rubber factory’, to make elastic bands, was built near Paris in 1803. Subsequently, a few other rubber factories were started in other parts in Europe, as well as in the USA. The products manufactured at those times were catheters, rubber coated fabrics, gloves, shoes, etc. In 1839, although accidental, an important discovery in the field of rubber happened. Charles Goodyear left a mix of rubber, sulphur and white lead on a hot stove and he recognised that the resulting material was cured and was free from stickiness. This process was later named as vulcanisation by W. Brokendon in 1842.

With the discovery of vulcanisation, and the realisation that rubber products could actually have a reasonable life expectation, the demand for them began to grow. Since the raw material was expensive and short of supply, all possibilities to reduce the costs were sought for. The attempts included experiments with cheap fillers such as zinc oxide, magnesium oxide, silica, talc, clay, chalks, etc. But the advent of the motor car and the rise in demand for the quality of tires raised the requirement for more reinforcement of rubber. It is this requirement that paved the road for the entry of carbon black into the rubber industry.

Carbon black had been known for centuries for its use as a pigment by the Egyptians and Chinese. Goodyear and Hancock had used a type of black: lamp black, as a colourant and filler. In 1892 a process for producing a variant of lamp black called ‘channel black’ was invented in the USA by L. J. McNutt. In 1897 the commercial production of channel black started in the USA. In 1904 S. C. Moke (India Rubber, Gutta Percha and Telegraph Works) discovered that carbon black could be used to increase the mechanical strength of rubber vulcanisates. With this discovery carbon black gained an important position in the rubber field.

Later, newer methods for production of carbon black were discovered. In 1916 Brownlee and Uhlinger developed a method for producing carbon black with larger particle size, which were called ‘thermal blacks’. Another process was developed by the Columbian Carbon Company in 1922, which burnt gas in a furnace. The black obtained from this process was named ‘furnace black’. The combustion of acetylene gave another type of black called ‘acetylene black’, which is mainly used for electrically conductive applications. In 1923 it was realised that different types of blacks impart different physical properties onto rubbers. Carbon blacks produced by different routes and from different staring materials have different characteristics like particle size, structure and purity. Nowadays carbon black is available in many grades, which serve to produce different performance levels in rubber products.

In the mean time, attempts were made to produce rubber synthetically. In 1860, Williams correctly gave the elemental composition of rubber. In 1879 Bouchardat combined isoprene into a rubbery material, and in 1884 Tilden wrote of its possible industrial significance. In 1900 Kondakoff polymerised 2,3-dimethylbutadiene to obtain ‘methyl rubber’, which became the first commercial rubber when it was produced by Bayer in 1909. In 1910 the Russians managed to polymerise 1,4-butadiene to result in ‘butadiene rubber’ (BR). In 1920 Herman Staudinger proposed that these rubber materials are made up of molecules with very high molecular weights by chemically combining several simple molecules or monomers. This understanding became the fundamentals of Polymer Science. The increasing price of natural rubber and the shortage during Second World War fuelled the entry of various synthetic rubbers. Buna-S (styrene butadiene rubber, SBR) and Buna-N (butadiene acrylonitrile rubber, NBR) were produced on a laboratory scale in 1930. At the same time, Carothers and his team at DuPont synthesised poly-chloroprene, a rubber with oil resistance. This came into production in 1931 under the name ‘Neoprene’. In the early 1960s DuPont synthesised ethylene-propylene-diene rubber (EPDM), as the variants of the recently developed polyethylene and polypropylene thermoplastics.

It was only a natural development, that the rubber product manufacturers started to blend the synthetic elastomers with natural rubber to obtain a blend of elastomers.

Today many rubber products are made out of such a blend. Rubber articles usually have to meet a set of performance and process requirements, that are contradictory in nature. Blending of selected rubbers aids to meet the contradictory set of properties. Blending of rubbers usually generates a two phase morphology as it is uncommon to have a truly miscible elastomer blend system. The factors which are important in the case of elastomer blends are: 1) blend ratio; 2) phase morphology; 3) interfacial adhesion; 4) distribution of fillers between the phases and 5) distribution of crosslinks between the phases. The blend ratio is often decided based on the end use specifications. In a blend there always exists microheterogeneity as the solubility parameters of the different rubbers are not the same. The interfacial adhesion depends on the difference between the solubility parameter values. Further, each rubber requires its own specific set of fillers and vulcanisation ingredients for reinforcement and curing. Each rubber has its own affinity for the sort of filler and curatives. This mainly depends on the polarity difference between the filler and the rubber, the viscosity of the blend components and the mixing scheme. When rubbers with different levels of unsaturation/polarity are blended together, the reinforcing fillers and curatives mainly end up in one phase, leading to over-reinforcement and over-curing of one phase, leaving the other one less-reinforced and under-cured.

1.2 AIM OF THIS RESEARCH

The uneven distribution of fillers and curatives in an elastomer blend appreciably influences the morphology and physical properties of the blend. This has been the major problem restricting the commercial use of blends such as NR/EPDM, NR/NBR and tyre side wall compositions based on NR/BR/EPDM[2]. The present research considers one portion of this problem, which is the distribution of the filler carbon black. In the past, several approaches have been made to achieve uniform distribution of fillers in elastomer blends[2-5]. But these approaches were of limited success or ended up in additional mixing steps in processing. In the present research a novel route is attempted to solve this problem of non-uniform distribution of carbon black. The aim is to modify the surface of carbon black by a plasma polymerisation technique in order to match its surface energy with that of different rubbers. This may improve the wetting behaviour of the carbon black by low surface-energy rubbers, thereby improving the dispersion and distribution of the carbon black between the phases in an elastomer blend. The new plasma-coated carbon black could then be used as such in the blend, thereby eliminating additional mixing steps in the processing.

1.3 STRUCTURE OF THE THESIS

This thesis is divided into eight chapters as given below:

Chapter 2 gives an overview of the usage of carbon black in rubber. Special emphasis is put on the distribution of carbon black in rubber blends. An approach based on surface modification of carbon black is suggested to overcome the problem of non-uniform distribution. The chapter also gives an overview of the work done by others in the direction of surface modification of rubber ingredients by plasma polymerisation.

Chapter 3 discusses different plasma reactors for powder surface modification. Design aspects and major components of the reactors are described. Design and installation of a small scale vertical tubular plasma reactor are explained in this chapter.

In **Chapter 4** the initial attempts to modify the surface of carbon black by plasma polymerisation are described. Mechanistic aspects of the surface modifications of carbon black are also described in this chapter.

As regular rubber grade furnace carbon blacks are difficult to modify, a search for a new candidate from the carbon black family with good modification capability is carried out. Details of this search are described in **Chapter 5**. Several carbon blacks are selected for screening experiments based on the understanding obtained from the work described in Chapter 4. The search results in fullerenic carbon black as an ideal candidate for plasma surface modification.

Chapter 6 describes the scaling up of the plasma surface modification process for fullerenic carbon black. The state of the plasma-coating on the carbon black after mixing with rubber is studied using conductivity experiments as described in this chapter. The behaviour of the plasma-coated carbon black in various elastomers is measured and discussed.

Chapter 7 describes the behaviour of the plasma-coated carbon black in dissimilar elastomer blends. The understanding obtained from the behaviour of the plasma-coated carbon in single elastomers is utilised to explain the observations in these elastomer blends.

The thesis ends with a summary and concluding remarks in **Chapter 8**.

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Chapter 2

Carbon Black in Rubber, a Review

This chapter gives an overview of the usage of carbon black in rubber. Aspects like carbon black properties, mixing with rubber and reinforcement of rubber are discussed in the initial part. Usage of carbon black in rubber blends is described with special emphasis on the distribution of carbon black in rubber blends. An approach for obtaining a uniform distribution and dispersion of carbon black in rubber blends is suggested. Surface tailoring of carbon black by plasma polymerisation may be instrumental to direct the filler into the right phase, to which it has to arrive in the blend. Mechanistic aspects of plasma polymerisation and other details of the process are discussed. The chapter also gives an overview of the work done so far in the direction of surface modification of rubber ingredients by plasma polymerisation. The survey shows that plasma surface modification of rubber ingredients is still in its infancy and more scientific know-how is yet to be obtained by continued research in this direction.

2.1 INTRODUCTION

Carbon black is a fascinating material which has not only attracted the attention of those who are involved in the technology and application of this material, but also has inspired a large number of fundamental investigations in scientific laboratories around the world. The most known allotropes of carbon are amorphous carbon, graphite and diamond. Several other forms of carbon have been synthesised or discovered in recent years, which include fullerenes[1], carbon nanotubes[2], aggregated carbon nanorods, carbon nanofoams[3] etc. Carbon black is a form of amorphous carbon. It is widely used as a filler to modify the mechanical, electrical and optical properties of the medium in which it is dispersed. Its application plays a major role in elastomers, plastics and in paints and inks. The beneficial effects in rubber applications include increase in strength-related parameters (tensile strength, tear and cut growth resistance), abrasion resistance, stiffness (hardness and modulus), energy absorption characteristics, tyre traction and some other effects which are not directly related to reinforcement. Well known detrimental side effects are increased hysteresis properties and poor fatigue resistance as the stiffness of the polymer – black mixture increases. About 90% of the worldwide production of carbon black is used by the rubber industry.

2.2 CARBON BLACK PRODUCTION AND PROPERTIES

Carbon black meant for use in the rubber industry is produced by the incomplete combustion of hydrocarbons. The raw material is mineral oil, supplied by the petrochemical industry, is called the feedstock. The furnace black process is the most modern process for the manufacture of carbon black. This process uses the principle of oxidative decomposition. The process is continuous and is operated in closed reactors: Fig. 2.1

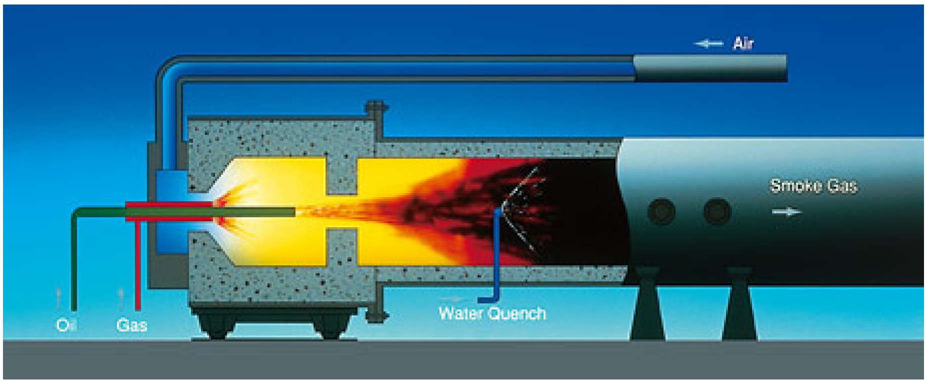

Fig. 2.1 Furnace black process[4]

During the process, the oil feedstock is pumped from the storage tank to the reactor via a preheater. Gas and preheated process air are also fed into the reactor. The incomplete combustion of oil into carbon black takes place in a flame lance of about 2000 °C. At a certain distance from the feedstock injection the thermal–oxidative reaction is quenched by injection of water, whereby the carbon black formation is stopped and the reactor off-gas is cooled. After further cooling in heat exchangers, the mixture of carbon black and off-gas is directed into filters where carbon black is separated from the off-gas. The filtered carbon black is then conveyed pneumatically to the pelletising section. Grit that may be present in the form of coarse particles is usually reduced to an acceptable size by the use of a hammer mill.

After separation and prior to the pelletising unit, the carbon black enters a surge bin or agitator tank, which acts as a material buffer for the pelletising unit and where some initial densification of the black takes place. Controlled amounts of black are then fed from the surge bin into a pelletiser or pin mixer and mixed with approximately the same amount of water. The wet pellets formed are subsequently dried in a rotary kiln drier which is heated by hot gases, preferably from the combustion of the off-gas. Carbon black dust carried off by the dryer exhaust gases is collected in a filter and recycled into the process. After leaving the dryer and before entering the storage silo, the carbon black pellets pass through powerful magnetic separators to remove any ferrous metal and rust contamination. The carbon black is conveyed to the storage silos by means of bucket elevators, conveyor belts and/or screw conveyors. From there it is discharged into the packaging units or directly to the bulk loading station. A separate storage facility serves as an off-spec silo and receives carbon black which does not meet the specifications. This may occur upon starting a production line or upon switching to a different grade. Depending on the type and extent of deviation, carefully controlled quantities of off-spec may be blended with material from subsequent production or eventually be used for applications not critical with respect to quality.

The most important process stages which are able to influence carbon black properties are the atomisation and vapourisation of the oil droplets in the reactor, the partial combustion and pyrolysis of the atomised feedstock and the secondary reactions between the carbon black particles and the components of the reactor off-gas. These stages are followed by the reaction of the carbon black with oxygen upon its first contact with air, mechanical treatment during the densification stage, further chemical modification depending on the conditions during drying and sometimes by the addition of additives. If the desired extent of the modification cannot be achieved during the process itself, specific chemical aftertreatment may also be carried out in a separate step following the actual manufacturing process.

The primary morphological properties of the carbon black are determined in the reactor and can only be changed to a very minor extent later in the process. Surface chemistry, on the other hand, can be influenced in the reactor, in the pneumatic handling system, during pelletisation and during drying. Additional specific changes in chemical surface properties may also be accomplished in separate chemical aftertreatment stages. The carbon black is formed and its morphological properties are determined after injection of the feedstock into the reaction zone. Major parameters which can be adjusted are the volume of combustion off gas, the amount of feedstock used and its chemical composition.

In the reaction zone, the gasified oil feedstock is subjected to very high temperatures of 2000 °C. This causes the molecules to decompose into fragments. On loosing hydrogen, these fragments combine with other fragments until they have reached a size where they are spontaneously precipitated from the gas phase as nuclei. The higher the temperature, the higher the rate of pyrolysis and the more frequent the formation of such nuclei. As pyrolysis proceeds, the new molecular fragments precipitate on to existing nuclei[5] which then continue to grow until all of the feedstock has been consumed. The higher the number of nuclei at any given amount of feedstock, the earlier the particles will stop growing since the amount of starting material is limited.

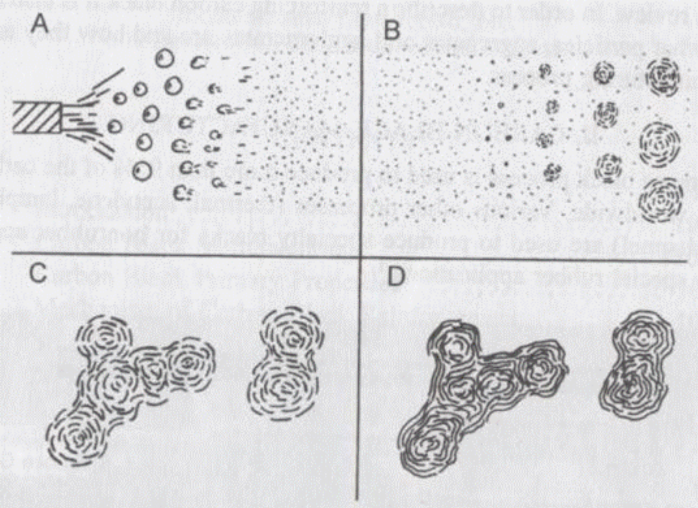

Fig. 2.2 Stages of carbon black formation[6]

Fig. 2.2 gives a fairly good representation of different stages of carbon black formation from atomisation of feedstock through the formation of fairly spherical (semi-solid) particles and subsequent collisions to form the so-called aggregates of particles. Time – temperature parameters and raw material flow rates determine the size of the ultimate particles, and the frequency of collisions of the particles under turbulent flow conditions determines the structure of the aggregates. Potassium salts may also be injected to reduce the amount of structure formation. Small particle reinforcing blacks are produced at higher temperatures and short residence times in the order of 10 – 100 milliseconds. Large particle (less reinforcing) blacks are produced at lower temperatures and slower rates.

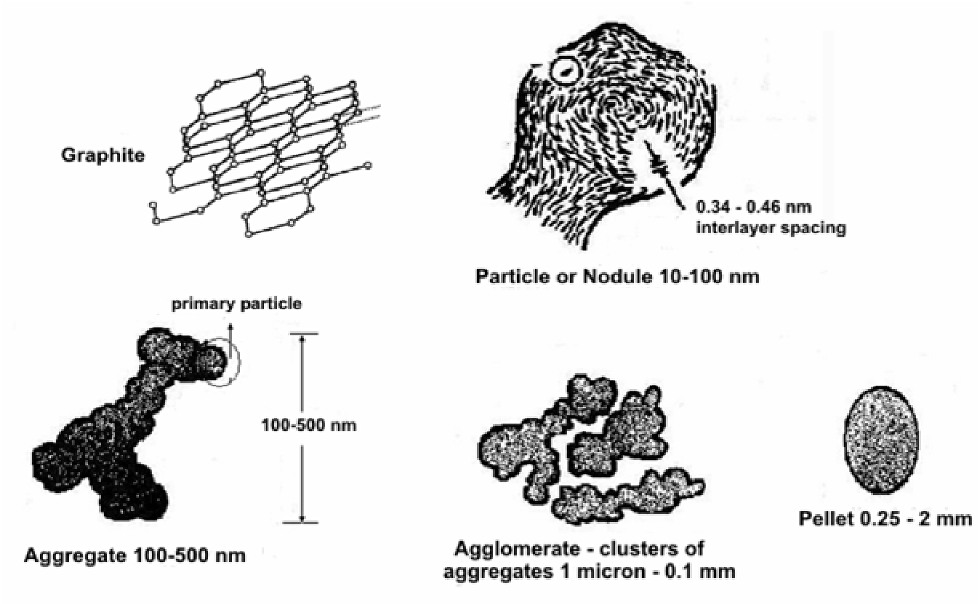

Fig. 2.3 Schematic representation of different states of aggregation of carbon black[6]

The primary particles of carbon black are made up of fairly concentric graphitic layers as illustrated in Fig. 2.3 A carbon black contains a number of these primary particles, also called nodules or nodes. A high structure black may consist of as many as 200 primary particles, while a low structure black may contain as low as 20 or 30. The aggregate is the primary reinforcing unit of the carbon black and is not easily broken down into smaller units. The aggregates are formed by collisions of semi–solid primary particles in the high temperature environment of the furnace. Fig. 2.4 shows the TEM image of an aggregate of carbon black. The carbon black shown here is a high structure variety.

The aggregates in-turn combine readily with neighbouring aggregates to form agglomerates as secondary structure. The final pellet-form that is produced to facilitate handling and to reduce dust, is a condensed form consisting of many agglomerates.

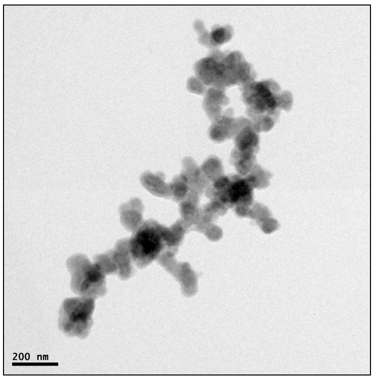

Fig. 2.4 TEM image of a high structure carbon black aggregate

2.2.1 Primary Properties of Carbon Black

The primary properties of carbon black that determine its behaviour in a polymer are:

a. specific surface area
b. structure and size
c. surface activity

a. Specific Surface Area

The surface area of the carbon black is one of the most used parameters to characterise carbon black. Usually surface area measurements include molecular adsorption and this phenomenon is influenced by the surface activity and surface energy of carbon black, which is inhomogeneous across the surface, due to the turbostratic crystalline structure of graphitic layers mixed with amorphous carbon. The most widely accepted and commonly used measurement technique for surface area is the Brunauer, Emmet and Teller (BET) method[7] (ASTM D3037 and D4820). It is based on the adsorption of nitrogen at liquid nitrogen temperatures. The results are expressed in m^2/g. It gives the total surface area of carbon black. One of the major assumptions for the BET-method is that monolayer coverage of the adsorbent can be achieved on an energetically homogeneous surface, which is not the case with carbon black. However, this characterisation technique has been widely accepted.

Another commonly used and widely accepted method is the surface area determination using cetyl trimethyl ammonium bromide (CTAB) (ASTM D3765). The CTAB-molecule is larger than a nitrogen molecule. Hence the surface area measured translates to the adsorption of this larger molecule. It means that, the CTAB surface area gives the surface area available for polymer chains and excludes external porosity. This value is more realistic for rubber applications. In general CTAB-values show good agreement with the BET-surface area. But for smaller particle size grades like N220, N110, the CTAB surface area is smaller than BET-value, the difference corresponding to porosity. Adsorption of CTAB from aqueous solution gives rise to a Langmuir adsorption isotherm, from which a monolayer coverage is determined. A calibration curve is generated using different weights of a standard carbon black of a given specific surface area (IRB3, 83 m^2/g as determined by BET), in order to determine a relationship between the amount of adsorbed CTAB and total filler surface. A given mass of an unknown sample is chosen such that the approximate surface area falls in the range of the experimental points of the calibration curve.

Another method was developed by de Boer[8] and recently popularised by Magee[9], named the Statistical Thickness Surface Area (STSA) (ASTM D3265). The STSA-method utilises a plot of the volume of adsorbed nitrogen as a function of the statistical layer thickness. According to Magee, it provides a more accurate assessment of external surface area compared to the CTAB-method.

The adsorption of iodine by carbon black is also used as a measure of the surface area and is probably the most commonly used procedure for manufacturing quality control of furnace blacks (ASTM D1510). The iodine-number is expressed in milligrams of iodine adsorbed per gram (mg/g) of carbon black and is not the true surface area. However, the concentration of the iodine solution has been adjusted so that the values are generally in good agreement with the nitrogen surface area for nonporous and nonoxidised carbon blacks. Surface impurities such as residual oil or oil used for beading depress the iodine number. The presence of high levels of surface oxygen functionality, which is typical for many carbon blacks used in paint and ink applications, will also cause a severe reduction in the iodine number. The oxygen groups on the surface of the carbon black actually react with the potassium iodide in the test solution, thereby causing release of free iodine which makes the surface area to appear lower. But for routine production control or quality assurance testing of known grades, the iodine test is widely used.

b. Structure

Structure is defined as the degree of aggregate irregularity or bulkiness of the carbon black. In general, high structure is associated with a large average number of primary particles per aggregate.

This parameter characterises the empty space between randomly packed primary particles in aggregates. In the test: ASTM D2414-08a, a moderately viscous liquid: oil is gradually added to dry carbon black in an internal mixer capable of measuring the torque as the mixing blades turn. An appreciable torque is not developed until the voids between the interstices between primary particles in the aggregates and agglomerates are filled with oil. The rise to a predetermined torque is taken as the endpoint.

The same oil absorption test can be run on a carbon black sample previously compacted: compressed OAN – ASTM D3493-07. In this measurement, carbon black is compressed four times in a cylinder at 165 MPa prior to testing in the Oil-absorptometer. This breaks the weak aggregates. Results from the compressed OAN-method are generally accepted as more indicative of the structure that remains after mixing.

The measurement of the void volume may also be done by measuring the compressed volume of known mass in a cylindrical chamber at a specific compression force in a test called Compressed Volume Index: ASTM D6086-97. In all these measurements it is assumed that the greater amount of voids per unit mass reflects greater departure of the aggregate from a spherical geometry leading to aggregates that will not pack as tightly. The structure as measured by the Oil-absorption test does not provide the actual information about the voids between aggregates of pelletised carbon black. Any work applied to the carbon black decreases the void volume measured by Oil- absorption. After mixing with rubber, the voids are filled with polymer chains and therefore will have a different size distribution, which may be very different from the one in the original carbon black. On the other hand, the crushed OAN-test, made on compacted pellets may have interaggregate voids distribution closer to that experienced after mixing in rubber. This test therefore may be of greater help for predicting rubber compound properties.

c. Surface Activity

This is a more descriptive term, which includes both physical and chemical aspects. In chemical sense, it is related to the reactivity of the functional groups on the carbon black surface. In a physical sense, it translates to the adsorptive capacity of the surface of carbon black. Compatibility, wettability, polarity and hydrogen bonding are important factors related to surface activity.

In the case of graphite, it has a highly ordered three–dimensional crystal structure composed of parallel layers of hexagonal rings of carbon atoms. It is a low energy state with low surface activity and low reinforcement in rubber. Whereas carbon black has a disordered surface structure. It is generally agreed that the carbon black surface consists of graphitic planes, amorphous carbon, crystallite edges and slit shaped cavities[10,11]. These sites give different energetic contributions towards the surface activity. The edges of the disorderly arranged graphitic planes form high energy sites on the surface of carbon black. Oxygen containing functional groups may be attached at these high energy sites. And it is agreed that polymer interaction in the form of physisorption or chemisorption happens at these highly energetic sites on the carbon black surface.

Recent studies[11,12] have shown that the concentration of different energetic sites on the surface of carbon black varies from grade to grade. Careful investigations using precise equilibrium gas adsorption measurements of ethene were carried out on different carbon black grades varying in particle size. The results demonstrate the existence of discrete energetic sites I – IV, with energies of 16 kJ/mol, 20 kJ/mol, 25 kJ/mol and 30 kJ/mol, respectively: Fig. 2.5. Site I relates to the graphitic planes, site II to amorphous carbon, site III to crystallite edges and site IV to slit shaped cavities.

In general, as particle size increases the fraction of these energetic sites per gram of the filler decreases dramatically, resulting in different surface activity and different reinforcing potentials. It is agreed that surface activity plays a key role in reinforcing capabilities of carbon black. Surface activity includes a) the surface roughness of small length scales, lower than the primary particle diameter, and b) the energy site distribution in relation to the primary particle microstructure and the specific reactivity of adsorption sites with a polymer. Recently it was demonstrated[13,14] by equilibrium gas adsorption measurements on carbon black, that the surface roughness characterised by its fractal dimension, is similarly graded for all carbon blacks, irrespective of their surface area and OAN numbers. These results confirm previous findings that all furnace carbon black grades absorb the same amount of polymer chains per unit surface area and lead to the conclusion that polymer chains of similar chemical nature are similarly decreasing their conformational entropy during adsorption on the carbon black surface. Therefore, the surface roughness cannot explain specific reinforcing effects caused by different carbon black grades, and more credit is given to energetic contributions of the surface activity in explaining both mechanical and processing effects of filled elastomers.

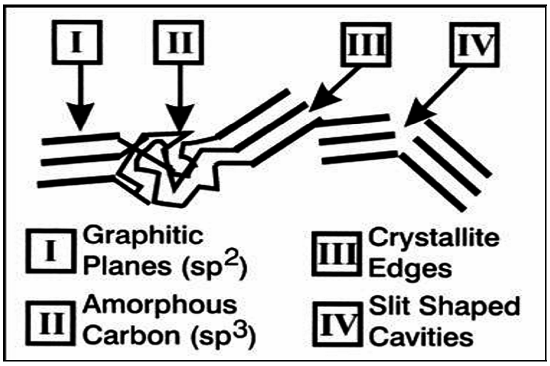

Fig. 2.5 Schematic representation of different energetic sites on the carbon black surface[10]

2.2.2 Mixing of Carbon Black into Rubber

Carbon black is generally incorporated into rubber by shear forces experienced in an open mill or an internal mixer. In mixing a batch of rubber, a number of elementary steps are involved[15-18]: Fig. 2.6.

1. ***Subdivision*** of larger lumps or agglomerates to smaller ones, suitable for incorporation into the rubber.
2. ***Incorporation*** of carbon black filler particles into rubber to form a coherent mass. During incorporation, encapsulation and wetting take place as the polymer breaks into small pieces and seals in the carbon black. Without incorporation, the ingredients are tumbled around in the mixer with little energy being spent while practically no mixing takes place.
3. ***Dispersion*** involves reduction of the size of agglomerates to their ultimate size; i.e., changing their physical state, while at the same time distributing the primary

aggregates formed. This is of special importance when adding carbon black. This phase is also called dispersive or intensive mixing.

4. ***Distribution*** involves the homogenisation of the mix by distributing the carbon black particles within the polymer matrix. This phase is also called simple mixing or extensive mixing.

5. ***Viscosity reduction*** by mechano-chemical breakdown of the polymer transforming it into a more easily deformable and less elastic state. This process further involves extension with oil.

In practice, the subdivision process causes problems. The same holds true for the incorporation stage, which can usually be manipulated by the sequence of feeding the ingredients to the mixer. Incorporation, however, may demand a considerable part of the total time in the mixer and may not be completely finished until the end of the cycle. Of the two remaining steps, the dispersion and distribution respectively, dispersion is the more difficult and therefore the rate determining step. Simple mixing and mastication: mechano-chemical breakdown of polymer chains, is determined mainly by the total accumulated shear deformation, while dispersion largely depends on the shear stress history during the mixing process. Below a particular shear stress, which is necessary to break down the agglomerates, no dispersive action takes place. It is a frequently cited practical experience that good dispersion requires high shear stresses.

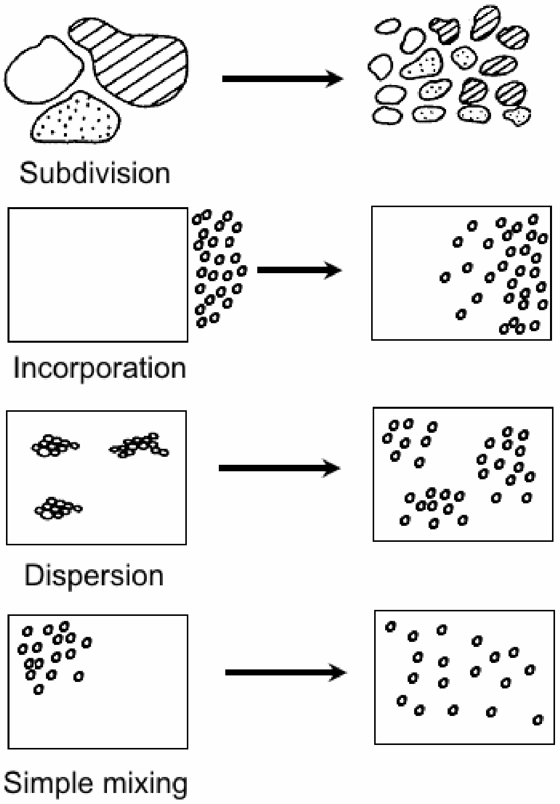

Fig. 2.6 Schematic representation of various stages of rubber mixing[14]

2.2.3 Reinforcement of Rubber by Carbon Black

The addition of carbon black significantly improves the physical and mechanical properties of elastomers, i.e. the modulus, tensile strength, tear strength, fatigue resistance and wear resistance. Such improvements resulting from the addition of carbon black are called carbon black reinforcement. This topic has been well discussed over many years[19-25]. But contrary to e.g. the reinforcement effect of fibres in polymers, a complete understanding of the reinforcement phenomena of carbon black is still lacking. There is a general agreement about the basic processes contributing to the stress-strain behaviour of filled elastomers. Besides the expected increase in modulus due to the inclusion of rigid particles in the soft matrix, another factor also contributes to reinforcement, which is the rubber-filler interaction. The incorporation of a rigid filler significantly changes the dynamic properties of the rubber. Filler networking formed by filler-filler interactions and the immobilised elastomeric layer on the filler surface contribute towards the dynamic response of the rubber.

Several theories and models have been proposed to explain the mechanisms involved in rubber reinforcement by carbon black. Before describing those theories and models, it is worth to say a few words about the contribution of the polymer network towards the total reinforcement effect. The crosslinked rubber network has a contribution towards the total modulus. This is strain independent and can be derived from network theories and is described by equation (2-1):

$$G = \nu\, k_b\, T \qquad (2\text{-}1)$$

where G is the shear modulus, ν is the concentration of elastically active network chains per unit volume, k_b is the Boltzmann constant and T is the absolute temperature.

Now we will discuss the factors that will describe the contribution from carbon black towards total reinforcement.

a. Hydrodynamic Effects

One of the most interesting phenomena generated by the addition of carbon black is the increase in modulus of an elastomer. Experimental results have generally indicated that the modulus of elastomers filled with carbon blacks can be described by the Smallwood[26] Guth[27] Gold equation[28]:

$$G_f = G_0\,(1+ 2.5\Phi +14.1\Phi^2) \qquad (2\text{-}2)$$

Where G_f is the shear modulus of the filled rubber, G_0 is the shear modulus of the pure rubber and Φ is the volume fraction of the filler. This is applicable in the case of low reinforcing carbon blacks, at low filler loading ($\Phi \leq 0.3$) and at low elongations. The above equation was derived with the assumption that the particles are spherical. A correction factor (f_s) for the non-spherical shape of the carbon black was added to the equation[29].

$$G_f = G_0 \left(1 + 0.67\, f_s \Phi + 1.62\, f_s^2 \Phi^2 \right) \qquad (2\text{-}3)$$

b. Filler-Polymer Interaction

The interactions of the carbon black filler with the rubber polymer can be divided into two main categories: physical and chemical interaction. The physical interactions contribute towards the immobilisation of polymer chains on the irregular carbon black surface. Chemical interactions arise from specific chemical bond formations between the rubber and the functional groups on the surface of carbon black. In the case of carbon black, as the concentration of functional groups on the surface is fairly low, their contribution towards filler–polymer interaction is small. But it does not mean that they can be totally neglected.

As a result of the interactions between carbon black and rubber, there exists a fraction of the rubber as a hard, glassy layer bound to the carbon black surface[30]. This is probably related to the phenomenon of bound rubber, being the fraction of unvulcanised rubber which cannot be extracted any more after having been mixed with the rubber. Both physical interactions such as adsorption of polymer chains, van der Waals interactions and various sorts of chemical interactions such as chemical bonds, bonding between free rubber radicals, all contribute to the formation of this bound rubber and glassy layer.

Medalia[31] proposed occlusion of rubber as the mechanism through which carbon black structure acts to reinforce compounds. Polymer chains are trapped inside the voids of the filler aggregates. They are immobilised and shielded from deformation and together with carbon black aggregate behave more like that of a rigid filler than like the polymer matrix. They do not contribute to the elastic behaviour of the matrix anymore, as their properties resemble the properties of the rigid filler particles rather than the properties of the flexible and elastic polymer chains. Occlusion of rubber further increases the effective volume of the filler with respect to its effect on the stress-strain behaviour.

c. Filler-Filler Interaction

Another major contribution comes from the network formed by the filler aggregates embedded in the matrix. This is a strain dependent phenomenon. Carbon black forms a secondary aggregate network held together by van der Waals forces. Payne[32-34] suggested that the commonly observed decrease of storage modulus of a filler reinforced rubber with strain is the result of the breakage of this secondary filler network. This effect is largely reversible, once the strain is released, and independent of the type of polymer; but dependent on the type of filler.

Combining the above factors, the total reinforcement effect created by the addition of a filler to a rubber matrix is an additive function of all the above mentioned factors. Fig. 2.7 shows a schematic representation of the typical behaviour of the complex shear modulus of filled rubber samples versus dynamic shear deformation.

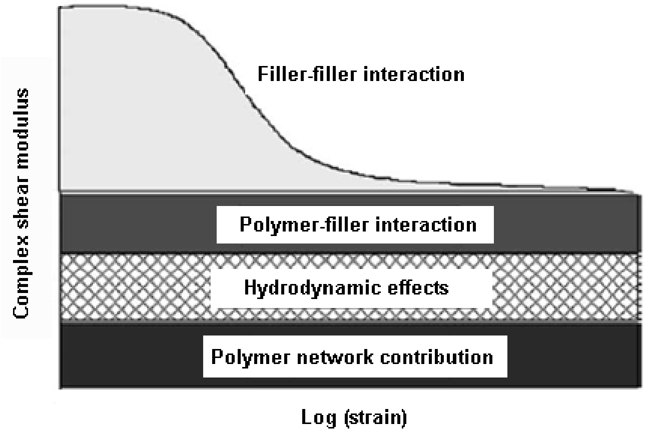

Fig. 2.7 A schematic representation of various factors contributing towards reinforcement

2.2.4 Length Scales in Filler-Polymer Interaction

Carbon black consists of spherical primary particles with a rough and energetically disordered surface, forming rigid aggregates in the range of 100 nm, with a fractal structure. Agglomeration of the aggregates on a larger scale leads to the formation of filler clusters and even a filler network at high carbon black concentration. These universal features are reflected in the corresponding universal properties of filled systems.

While considering the total reinforcement effects it is interesting to look at the length scales involved in the polymer-filler interaction. Considerable reinforcement can be achieved if the relevant scales of the filler particles coincide with those of the polymer matrix. Fig. 2.8 shows the interplay between the length scales by comparison of the relevant length scales between the monomer size, important for adsorption and chemical interaction[25]. The structures on larger scales such as aggregates do have similar scales with typical polymer coil radii. Phenomena like the hydrodynamic effect and the Payne effect can be attributed to the fractal nature of the filler and its network structure. Thus we may expect scale-dependent contributions to the modulus based on the interactions between polymer chains and filler particles.

In carbon black filled elastomers, the contribution to reinforcement on small scales can be attributed to the complex structure of the branched filler aggregates as well as to a strong surface polymer interaction. On larger length scales, the hydrodynamic aspect of reinforcement dominates. At macroscopic length scales the filler networking at large filler volume fractions plays the dominant role.

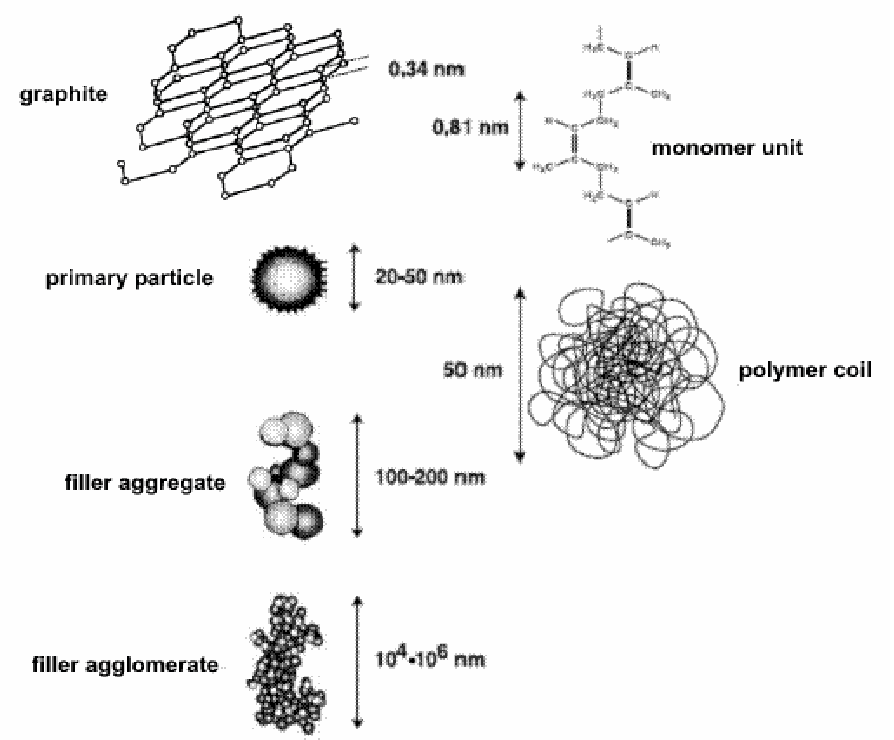

Fig. 2.8 Different length scales involved in rubber-filler interaction[25]

2.3 POLYMER BLENDS

After a relevant discussion on carbon black, a major filler used in rubber industry, the discussion further proceeds by describing the matrix into which it is being dispersed. For making a rubber article, a combination of rubbers is usually used, as a single rubber cannot provide the entire required property portfolio. Rubber articles have to meet a set of performance and process requirements that are often contradictory in nature. A tyre compound has to be soft and elastic in order to conform to the road surface and to function as a shock absorber. At the same time, it has to be stiff and strong in order to bear heavy load, and be abrasion resistant to provide long service life. Since different rubbers have different sets of properties, blending of selected rubbers has been practised to meet the contradictory set of properties. In the field of elastomers, blends are indeed much more established than in plastics – ever since the advent of synthetic rubbers after the Second World War, as the properties of Natural Rubber were superior to its synthetic counterparts. Blending of polymers is largely done with the aim to obtain a specific set of properties and at minimum cost.

2.3.1 Polymer-Polymer Miscibility

True miscibility is uncommon for polymer mixtures. The thermodynamic criterion for spontaneous miscibility is that the Gibbs free energy of mixing is negative[35]. The expression for the Gibbs free energy of mixing is given in eqn. (2-4):

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (2\text{–}4)$$

where ΔH_m is the change in enthalpy of mixing [J] and ΔS is the change in entropy of mixing. The change in enthalpy during mixing is the result of interaction energy and is mostly positive. The interaction energies arise due to hydrogen bonds, dipole interactions, van der Waals interactions, acid - base and coulombic interactions. For a mixture of polymers, the change in entropy is usually small due to constraints on the segmental mobility. Immiscibility then becomes much more likely for polymer mixtures than miscibility.

Generally, for predicting the miscibility of polymer systems, the concept of the solubility parameter (δ) is utilised. As a general rule, it can be stated that structural similarity favours miscibility. A quantitative measure of the cohesive properties of a substance is the cohesive energy. The cohesive energy (E_{coh}) of a substance in a condensed state is defined as the increase in internal energy (U) per mole of a substance if all the intermolecular forces are eliminated[36]. The cohesive energy per unit volume (V) is called the cohesive energy density. The solubility parameter is defined as the square root of the cohesive energy density.

$$\text{Cohesive energy density} = E_{coh} = \Delta U \qquad (2\text{–}5)$$

$$\text{Cohesive energy density, } e_{coh} = E_{coh}/V \qquad (2\text{–}6)$$

$$\text{Solubility parameter } \delta = \left(E_{coh}/V\right)^{\frac{1}{2}} = \left(e_{coh}\right)^{\frac{1}{2}} \quad [\text{MPa}]^{1/2} \qquad (2\text{–}7)$$

Solubility parameter values of typical rubbers are shown in Table 2.1[6]. In general, a difference of 0.1 or more in δ-values of the polymer pair can lead to immiscibility. Therefore, most elastomers form an immiscible blend.

Table 2.1 Solubility Parameter Values of Different Elastomers

Elastomer	Solubility parameter $[MPa]^{1/2}$
Styrene butadiene copolymer (SBR)	17.0
Acrylonitrile butadiene copolymer (NBR)	
18%	18.0
25%	19.0
30%	20.0
39%	21.0
Natural rubber (NR)	16.9
Polyisoprene (IR)	16.7
Polyisobutylene	16.5
Polyisobutylene-isoprene copolymer (IIR)	16.3
Polychloroprene (CR)	18.7
Ethylene – propylene copolymer (EPM)	16.6
Ethylene – propylene (norbornene) terpolymer (EPDM)	17.1
Ethylene vinyl acetate (EVA)	17.5
Polydimethyl siloxane elastomer (PDMS)	15.0

Schuster *et al.*[37] obtained accurate solubility parameter values of non polar rubbers. They applied gas–liquid–chromatography (GLC) for the determination of the polymer–solvent interaction parameters, solubility parameters and polymer–polymer interaction parameters (χ). There exists a relation between the polymer–polymer interaction parameter (χ) and the solubility parameter of the two polymers:

$$X_{12} = V_r(\delta_1 - \delta_2)^2 / RT \qquad (2\text{-}8)$$

where V_r is the average reference volume. The interfacial tension (γ) between the two polymers is given according to:

$$\gamma_{12} = (X_{12})^{1/2} \qquad (2\text{–}9)$$

From the values of the solubility parameters, the critical molecular weight above which phase separation occurs in a rubber blend can be estimated using the expression:

$$M_{cr} = 2\rho RT / (\delta_1 - \delta_2)^2 \qquad (2\text{–}10)$$

The molecular weights of technical rubber polymers are far above this critical molecular weight. The existence of a heterogeneous phase morphology in rubber blends and their interfacial tension can therefore be explained and calculated based on the solubility parameter values. As the solubility parameter difference between most rubber grades is larger than 0.1, they form a phase-separated system. The interfacial tension between the different polymers increases with an increasing difference between the solubility parameter values.

2.3.2 Morphology Development

In practice, rubber polymer blending is carried out in an internal mixer or on a mill. In general, the development of morphology in a rubber blend system is influenced by the blend ratio, the viscosity of blend components and the mixing parameters. It is known that the dispersed phase breaks down progressively with mixing time, which is related to the stress exerted on the droplets of the dispersed component by the flowing continuous component. The breakdown process never reaches the molecular level, even with increased mixing intensity. Detailed investigations about the morphology development in rubber blend systems were carried out by Avgeropoulos *et al.*[38] and Tokita[39]**.** Avgeropoulos *et al.*[38] studied incompatible blends of EPDM and BR. They showed that, with a single pair of polymers, it is possible to obtain either EPDM or BR as the continuous phase or both polymers as co-continuous phases. This was achieved by manipulating the viscosity of the blend components. However, there exists a dependence of the morphology on the blend ratio also, as achieved during mixing. Competition will thus exist between the compositional and rheological parameters.

Tokita[39] has also evaluated the morphology formation in an elastomer blend. For a typical NR-EPM blend system, it was shown that: 1) low Mooney EPM shows larger domain size and clearly a spherical shape; 2) high Mooney EPM shows irregular shapes and a wide range of sizes at short mixing times. The distribution becomes narrower and the shape of the domains tends to become spherical, with increased mixing time. The larger domain sizes for low Mooney EPM are due to low stress levels. For blends of NR with various rubbers like BR, high vinyl – BR, E-SBR, S-SBR a linear relationship between average domain size and difference in solubility parameters is observed. More incompatible blends based on EPDM or Chloro-Butyl rubber (C-IIR) with the polydienes obey the equation:

$$d = 1260\,(\Delta\delta - 0.204) \qquad (2\text{–}11)$$

where d denotes average domain size in nanometers [nm]. As long as the chemical nature and molecular weight of the constituents are kept constant, the shear rate employed during mixing dominates the domain size reduction. Accordingly, it might be assumed that the domain size is larger at higher temperatures. But Tokita showed that at higher temperatures, the domain sizes decrease. A probable explanation for this observation is that the interfacial tension reduces with increasing temperature.

This generalisation about the morphology however, does not directly translate to filled rubber systems. In the presence of a filler, the polymer incompatibility and the shear rate exhibit effects of the same order of magnitude. The influence of shear rate becomes predominant when the filler is present above the percolation threshold (usually 30 phr of filler, where the electrical conductivity suddenly increases due to carbon black aggregates coming in close contact).

2.3.3 Factors Affecting Blend Properties

In addition to the normal factors in compounding a recipe of a single elastomer for a particular end use – such as filler type and loading, its dispersion, type and amount of curing system, and antidegradants – there are a number of other factors which play a role in the case of elastomer blends. This is primarily because of the fact that there will be two phases corresponding to the blend components. As stated before, it is uncommon to have a truly miscible elastomer blend system. The following factors are important while considering the compounding of an elastomer blend for an end use:

- blend ratio;
- phase morphology;
- interfacial adhesion;
- distribution of fillers between the phases;
- distribution of crosslinks between the phases.

The blend ratio is often decided based on the end use specification and can be well controlled. However, the control of phase morphology is difficult. The majority of controlling factors are in the blend preparation step. In general, the higher the shear used in mixing, the smaller the phases obtained. But the domain size obtained also depends on the types of polymers and the blend ratio. In rubber blend systems with fillers above the percolation threshold (in most cases) the shear will be higher, leading to smaller domain sizes. But for most rubber applications miscibility into a single homogenous phase is not a strict requirement for optimum performance. Homogeneity to a fairly good level can produce optimum performances and some degree of micro-heterogeneity will help in preserving the individual properties of the blend components. However, for the achievement of good rubber properties, interfacial adhesion between the phases is important. In case of blends of general purpose rubbers such as NR, SBR, BR, IR the difference in solubility parameters is quite low and hence they form a relatively homogenous blend. Even in those cases a certain level of micro-heterogeneity exists. But, the state of miscibility can be stabilised to some extent by crosslinking at higher temperatures. Whereas in the case of blends with wider differences in solubility parameter values, the heterogeneity obtained is large and the interfacial interactions are poor. In this case the possibility of phase miscibility stabilisation at higher temperatures by crosslinking is also less, as there is little adhesion between the phases.

The remaining factors relate to the distribution of different ingredients between the polymer phases of the blend. Rubbers are mixed with reinforcing fillers, non-reinforcing fillers, plasticisers, processing aids, antioxidants and vulcanisation ingredients to achieve the required mechanical properties and to bring about an optimal level of vulcanisation. In contrast, thermoplastics are mixed with few ingredients such as fillers, stabilisers and processing aids. The viscosity of thermoplastics during the processing stage is low, whereas rubber compounds generally possess a high viscosity. This makes the dispersion and distribution of ingredients in a rubber matrix difficult. The situation is more complex for elastomer blends. Each rubber requires its own specific set of vulcanisation ingredients and fillers for curing and reinforcement. Also each rubber has its own affinity for the sort of filler, which mainly depends on the polarity difference between the filler and the rubber, the viscosity of the blend components and the mixing scheme. The vulcanisation packages are also specific for each rubber, usually determined by the amount of unsaturation in the rubber.

When rubbers with different levels of unsaturation/polarity are blended together,

1. reinforcing fillers mainly end up in one phase, leading to over-reinforcement of one phase and under-reinforcement of the other;
2. vulcanisation ingredients end up more in one phase, resulting in overcuring of one phase and under-curing of the other.

This uneven distribution of fillers and curatives appreciably influences the morphology and physical properties of the blend. This has been the major reason restricting the commercial use of blends such as NR/EPDM, NR/NBR, NR with epoxidised natural rubber and tyre side wall compositions based on NR/BR/EPDM. Since rubber vulcanisation occurs over a longer period of time compared to thermoplastic processing, it is likely that the curatives migrate to a phase where they have the highest affinity. Partition of the vulcanisation chemicals and other intermediate species formed during the crosslinking reaction happens between the polymer phases, where there is a mechanism for preferential solubility. Carbon black filler also locates itself in a phase with higher unsaturation/polarity, leaving behind the lower unsaturation/polar phase unreinforced. The non–uniform distribution of fillers and curatives in a rubber blend is a serious problem known to the rubber industry from its beginning. Extensive studies have been carried out to understand the problem in detail in attempts to solve the problem.

2.3.4 Carbon Black Distribution in Rubber Blends

The distribution of filler particles between the separate phases of an elastomer blend is affected by various factors like unsaturation of the rubber components, their viscosity, polarity and mixing procedure. The surface of carbon black consists primarily of carbon atoms. There are small concentrations of oxygen containing chemical functionalities on the surface. In a blend, carbon black dominates in one of the two polymers. This is particularly apparent when the difference in unsaturation between the elastomers is large. In such cases the bulk of the carbon black is always found in the highly unsaturated polymer.

The work of Walters and Keyte[40] indicated that, in addition to the heterogeneity observed in elastomer blends, the ingredients are also not distributed proportionally between each polymer phase. Studies on carbon black distribution, however were limited to fairly low loadings. Considerable progress in the study of carbon black distribution was reported by Callan, Topcik and Ford[41] in their studies on blends of IIR and EPDM. They used both phase-contrast light microscopy and electron microscopy to classify polymer zone size and the relative location of carbon black between the two phases. Blends containing carbon black loadings up to 50 phr were examined in the electron microscope via ultramicrotomy of frozen specimen blocks. However, good interzone contrast became increasingly difficult as black loadings were raised above 20 phr. One of the most significant findings of this work was that IIR showed a considerably lower affinity towards carbon blacks than EPDM. On this basis, it was possible to explain certain abnormalities in the mechanical properties of black loaded blends of these elastomers.

Similar variations in the relative affinity of polymers for carbon black were reported by Hess, Marsh and Eckert[42], who worked with carbon black loaded blends of cis-polybutadiene and synthetic polyisoprene. With loadings up to 20 phr, a large percentage of the carbon black appeared to be in the polybutadiene phase. Studies on stocks with higher carbon black loadings were hampered, because of the inability to cut suitably thin specimens for this particular polymer combination. With high black loadings, zone boundaries were generally quite diffuse and the location of filler particles could not be determined with sufficient accuracy. Microscopy has thus proven to be very useful for studying elastomer blend heterogeneity. However, when fillers were added to a blend, particularly at high loadings, resolution of zone boundaries and interzone contrast became relatively poor.

Hess and coworkers[43] developed improved techniques based on microscopy for resolving elastomer zone boundaries. Vulcanisates were embedded and swollen in a specific monomer system, which was subsequently polymerised. Specimens were then sectioned with an ultramicrotome and examined in the electron microscope. Good contrast between polymers was obtained in examination of blends of natural rubber with several other elastomers. The homogeneity of the blend was shown to be influenced by the mixing procedure and polymer characteristics such as viscosity and various interaction effects. Differences in filler location in elastomer blends were detected. They demonstrated that carbon black normally locates preferentially in the BR component of a NR/BR 50:50 blend. This affinity was shown to depend on polymer viscosity and could be varied.

Further work[44] indicated that carbon black can migrate from an NR solution masterbatch to BR under specific mixing conditions. Marsh[45,46] recognised the existence of unequal filler distribution in elastomer blends but was unable to verify carbon black transfer during mixing. This discrepancy has been largely resolved by further investigations by Callan[47] using techniques such as DTA, GPC and Quantimet Image Analysing Computer in combination with electron microscopy. The incorporation of carbon black into a 50:50 elastomer preblends indicated that carbon black affinity decreased in the order BR > SBR > CR > NBR > NR > EPDM > IIR. In addition, carbon black transfer during blending was observed from a mechanically mixed IIR masterbatch to a high-unsaturation gum rubber but not from a NR masterbatch. Transfer thus appears to be limited to those situations in which the adsorptive capacity of the filler has not been fully realised. This may occur if the polymer-filler master batch has minimum thermal or mechanical history (such as a solution master batch) or involves low molecular weight or low unsaturation elastomers, situations in which bound rubber formation is minimised. The accumulation of carbon black in the BR phase of a NR/BR blend has also been confirmed by Vohwinkel[48]. IIR and CIIR gave comparable results in blends with other polymers, and ranked lowest in their relative response to carbon black. In blends of these two polymers with EPDM, a preference of the carbon black for EPDM was observed.

Natural rubber appears to occupy a unique position in its response to carbon black in that it falls midway between low unsaturation elastomers and elastomers such as BR, SBR, CR and NBR. In blends of NR with these elastomers the carbon black affinity decreases in the order, CR > NBR > BR > SBR > EPDM > IIR/CIIR. In blends of CR and NBR with carbon black, there appeared to be some preference of the black for the CR phase. The trends changed when oxidised carbon black was mixed into preblends of these elastomers. Here, the more polar elastomers, CR and NBR, appeared to show a black preference in blends with BR and SBR. No particular preference was observed in the CR/NBR blend containing oxidised carbon black. In summary, SBR and BR appeared to have the strongest affinity for a standard carbon black in blends with the other rubbers. They are followed by CR, NBR, NR, EPDM, IIR and CIIR.

In addition to electron microscopy techniques, carbon black distribution was also investigated using other techniques such as differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), pyrolysis gas chromatography and dynamic mechanical analysis (DMA). The DSC technique is based on a method developed by Fouche and McGill[49]. They used DSC to show that the crystallisation temperature of cis-1,4-polybutadiene increases with carbon black loading. Based on this, they determined the carbon black distribution in IR/BR blends. A similar technique was also used in the study of a NR/BR/N550 carbon black system[50]. But these kinds of measurements are restricted to blends which contain cis-1,4-polybutadiene or any other crystalline polymer, which gives a distinct crystallisation peak in DSC.

There are some reports[47,51] on the use of pyrolysis gas chromatography for the determination of carbon black distribution in elastomer blends. The technique is based on the analysis of bound rubber. The analysis is based on the assumption that the distribution of carbon black among the separate zones is unchanged during an extraction process. The results so obtained must be corrected for the differences in reactivity of carbon black with the individual polymers. The rubber sample is pyrolysed at a high temperature. The pyrolysed products are analysed using a gas chromatograph. The analytical peaks are selected by running samples of pure polymers. The resolution of this technique is sufficiently good to identify two clearly separated peaks due to the degradation products of blend components.

Another quantitative method for the determination of carbon black distribution in elastomer blends was developed by De and coworkers[52]. This method is based on the determination of the mechanical damping properties of gum (unfilled) and filled rubber vulcanisates. This gives quantitative and reproducible results within a short time and is applicable also at higher filler loadings. The authors studied the distribution of carbon black and silica in a 50:50 blend of NR and ENR. In the 50:50 blend of NR/ENR, silica resides mainly in ENR phase. At 10 phr loading, the NR phase contains 12% filler, which gradually increases to 35% at 40 phr loading of silica. When silica is replaced by carbon black in blends of NR/ENR, the filler in NR phase increases to 30% of black from 18% of silica at 20 phr loading, due to better polymer-filler interaction in the case of carbon black. But this method has been applied so far only to very few blend systems such as NR/ENR and BR/NBR[53].

Another approach based on dynamic mechanical analysis was put forward by M. Klüppel *et al.*[54]. The method is based on the influence of phase morphology and carbon black distribution on energy storage and dissipation during dynamic excitations of rubber blends. The differences in the local stiffness of the phases in the glass transition regime of unfilled blends lead to characteristic deviations of the local strain from the externally applied strain amplitude. These deviations are governed by a critical phenomenon due to the formation of a phase network above a critical blend ratio. As a result, a strongly nonlinear dependence of the glass transition maxima of the loss modulus on the volume fraction of the phases is observed. By counting the elastically effective bonds of the phase network, the local strain amplitude is estimated by purely geometrical arguments. Based on a consideration of the phase network, the distribution of carbon black in the different phases of the filled blends is estimated from the height of the local maxima of the loss modulus in the glass transition regime. Thereby, a linear increase of the maximum value of the loss modulus with rising carbon black concentration is exploited that relates the enhanced energy dissipation of filled rubbers to the interfacial friction of the filler particles. Results on EPDM/BR/N550 carbon black blends indicate that carbon black is preferably located in the BR phase. A somewhat higher concentration of carbon black in the SBR phase is found in the case of NR/SBR/N330 carbon black blends.

Radusch and coworkers[55] used online measurement of the electrical conductance during mixing as a measure of carbon black dispersion and distribution in rubber blends. Carbon black causes electrical conductivity in a normally insulating matrix, if they are loaded above the percolation threshold. The gap between conductive carbon black aggregates is of the order of 15-100 Å[56]; the electrons must overcome a potential barrier to get out of the carbon black aggregate and cross the gap: tunneling. Kohjiya[57] visualised carbon black networks and stated that the insulating rubber gap is of 3nm. When the infiltration of carbon black into the rubber molecules takes place the conductance increases. The conductance reaches the maximum at black incorporation time (BIT), when the infiltration process seems to be complete. In the case of blends, the dispersion curve presents two plateaus at mixing times corresponding to the BITs of the blend components. The measurement is based on the observation that the BITs of the two blend components shift to a longer mixing time in comparison to the BITs of the corresponding single components. The shift of the BIT is obviously related to the fact, that the CB infiltration process of one component in the rubber blend is inhibited due to the presence of the second component. A typical 50:50 blend of SBR/NR showed a conductance curve with two BITs, which are obviously related to the blend components. Due to the high infiltration rate of SBR, CB is fast infiltrated by SBR. As a result, the first BIT in the conductance curve was related to the dispersion of carbon black in SBR. After a certain mixing time, the second component NR began to infiltrate the carbon black. This process was the reason for the appearance of the second BIT. The correlation between the value of conductance measured at the BIT of the single SBR mixture and its carbon black distribution could be used for the estimation of the carbon black distribution in a blend.

Recently, people have started using Atomic Force Microscopy (AFM) as a tool to visualise the morphology of rubber blends and to understand the filler distribution. In these cases of AFM measurement[58-61], different techniques like force modulation (FM), tapping mode and non-contact or intermittent contact mode are utilised. In the case of a rubber blend, differences of the mechanical properties, the elastic moduli of the separate components cause changes of the tip-sample interaction force: the amplitude or phase shift of cantilever oscillation varies in response to the mechanical properties of the sample surface. In the AFM-tapping phase image mode, harder materials show as lighter phase and hence the filler particles look brighter, whereas the rubber matrix is dark.

2.3.5 Approaches Towards a Uniform Distribution of Filler

Several approaches have been attempted in the past by various researchers to achieve a uniform distribution of filler in a dissimilar rubber blend. They include modifications in the mixing sequence, modification of low unsaturated rubber to increase its polarity, etc[62-64]. These steps were of limited success or ended up in additional mixing steps in processing.

Very recently a new plasma polymerisation technique has been developed for modifying the surfaces of various substances, including those of powders. The plasma modification technique can change the surface properties of the powders in terms of surface energy, functional groups, wettability, interaction with polymers, dispersion in polymers etc. Thus it is possible to tailor the surface of fillers and curatives hydrophobic or hydrophilic, as required to match the polarity characteristics of the rubbers in a blend. This may direct the fillers and curatives to the respective phase where it has to arrive during the mixing operation. Hence, surface modification of fillers and curatives to direct them to the right phase in a rubber blend is a novel approach to control their distribution in the blend.

2.4 PLASMA POLYMERISATION

Plasma polymerisation is a recent technique to modify the surfaces of various substrates. It is a thin film forming process, where these films deposit directly on surfaces of the substrates. In this process the growth of low molecular weight monomers into high molecular weight polymer networks occur with the aid of plasma energy, which involves activated electrons, ions and radicals. This process is very different from a conventional polymerisation process. Before going into details of plasma polymerisation, it is worth to give a brief introduction into plasma technology in general.

A plasma is a mixture of electrons, negatively and positively charged species, neutral atoms and molecules. A plasma is considered as being a state of materials, which is more highly activated than in the solid, liquid or gas situation. Sir William Crooks suggested the concept of the ‘fourth state of matter’ (1879) for electrically discharged matter and Irving Langmuir[65] first used the term ‘plasma’ to denote the state of gases in discharge tubes. The state of plasma can be created by a variety of means. In general, when a molecule is subjected to a severe condition, such as intense heat, ionisation of the molecule takes place. At temperatures higher than 10,000 K, all molecules and atoms tend to become ionised. The sun and other stars of the universe have temperatures ranging from 5000 K to 70,000 K or more, so they consist entirely of plasma.

In the laboratory, plasma is generated by combustion, flames, electric discharge, controlled nuclear reactions, shocks etc. Because a plasma loses energy to its environment mainly by radiation and conduction to walls, energy must be supplied as fast as it is lost in order to maintain the plasma state continuously in a laboratory apparatus. Of the various means of maintaining the plasma state continuously for a relatively long period of time, the most obvious and most common method is the use of an electrical discharge. For this reason, most experimental work, particularly in the study of plasma polymerisation, was carried out using some kind of electrical discharge. There are many types of electrical discharges, all characterised by the presence of free electrons and/or an electric field. Among the many types of electrical discharges, glow discharge is by far the most frequently used in plasma polymerisation.

Plasma states can be divided into two main categories: Hot Plasma (near-equilibrium plasmas) and Cold Plasmas (non-equilibrium plasmas). Hot plasmas are characterised by very high temperatures of electrons and heavy particles, both charged and neutral and which are close to maximal degrees of ionisation. Cold plasmas are composed of low temperature particles (charged and neutral molecular and atomic species) and relatively high temperature electrons and they are associated with low degrees of ionisation. Hot plasmas include electrical arcs, plasma jets of rocket engines, thermonuclear reaction generated plasmas, etc.; while cold plasmas include low-pressure direct current (DC) and radio frequency (RF) discharges, discharges from fluorescent (neon) illuminating tubes. Corona discharges are also considered as cold plasmas.

Hot plasmas have an extremely high energy content, which induces fragmentation of all organic molecules to atomic levels and as a consequence, these plasmas can only be used for generating extremely high caloric energy or to modify thermally stable inorganic materials. Hot plasma approaches for materials processing have been created with the use of plasma arc heaters, and later on, three distinct application areas emerged: synthesis, melting and deposition. Progress in thermal plasma processing has been limited by an unsatisfactory understanding of the extremely complex reactions kinetics, transport properties, heat transfer and particle dynamics during gas-solid and gas-gas interactions. As a result thermal plasma processing has only in a few instances progressed beyond laboratory and pilot scale stages.

Low pressure non-equilibrium discharges, cold plasmas, are initiated and sustained by DC, RF or microwave (MW) power transferred to a low pressure gas environment, with or without an additional magnetic field. Ultimately, all these discharges are initiated and sustained through electron collision processes under action of specific electric or electromagnetic fields. Accelerated electrons induce ionisation, excitation and molecular fragmentation processes leading to a complex mixture of active species. The work described in this thesis is carried out by a cold plasma process.

The glow discharge is formed by exposing the gaseous monomer at low pressure (< 10 Torr) to an electric field. Energy is transferred by the electric field to free electrons which collide with molecules, electrodes and other surfaces. Inelastic electron collisions with molecules generate more electrons, as well as more ions, free radicals and excited state molecules. Although the degree of ionisation is low, charged particles play an important role in determining both the deposition rate and the chemical structure of the plasma polymer film. All fragments are very reactive with surfaces exposed to the plasma and with other fragments. The average electron energy in a low pressure discharge is in the range of 2-5 eV[66]. The electron energy distribution in a low pressure discharge follows a Maxwellian-Druyvesteyn distribution. There is a high energy tail, which means that there are some high energy electrons (8-14 eV), but of lower concentration, which have a significant impact on the overall reaction rates in the plasma.

At low pressures, the electron temperature is much higher than the temperature of the gas, $T_e >> T_{gas.}$ The temperature of an electron with an energy of 2 eV will be 23200 K. Even though the electrons are really hot, the system or gas remains at ambient conditions. Because of the very low density and very low heat capacity of the electrons, the amount of heat transferred to the gas and to walls of the container is very small. Thus the term “cold plasma” derives its meaning from the small amount of heat transferred to the gas or solids in contact with it.

2.4.1 Mechanism

Chemical reactions that occur under plasma conditions are generally very complex[67] and consequently are nonspecific in nature. Such reactions are of merit when special excited states of molecules are required as intermediate states and cannot be achieved, or can only be achieved with great difficulty, by conventional chemical reactions. Thus, plasma polymerisation should be recognised as a special means of preparing unique polymers that cannot be made by other methods, rather than as a special way of polymerising monomers. The capability of plasma polymerisation to form ultra thin films with minimum flaws is unique.

Plasma polymers are deposited on surfaces contacting a glow discharge of organic or organometallic monomers in the form of a thin film and/or as a powder. Such films find potential applications as surface modifiers and in applications where the bulk properties of extremely thin films are desirable.

The following are some important characteristics of plasma polymers.

1. Plasma polymer films can be easily formed with thickness of 500 Å to 1 micron.
2. Such films are often highly coherent and adherent to variety of substrates including conventional polymers, glass and metal surfaces.
3. The films are pinhole free and highly crosslinked.
4. Multilayer films or films with grading of chemical or physical characteristics are easily made by this process.

For the most practical coating process, the monomer flows into the plasma reactor continuously, while the glow discharge is in progress, and is wholly or partially consumed in the conversion to plasma polymer. In such a set up, gaseous by-product and unconverted monomer are continuously pumped out of the reactor.

In a plasma polymerisation process, the growth of low molecular weight monomer species to high molecular weight plasma polymer takes place. In a chemical sense, plasma polymerisation is different from conventional polymerisations such as radical or ionic. The term *radical polymerisation* means that propagating reactions of monomers are initiated by radical species at polymer chain ends; *ionic polymerisation* means chemical reactions propagating by ionic species in the polymerisation step. Therefore, the adjectives *radical* and *ionic* signify a kind of species propagating polymer chains in the polymerisation step. The term *plasma* means an energy source to initiate polymerisation reactions. Polymers formed by plasma polymerisation are entirely different from those formed by ionic or radical polymerisation. The monomer structure is not retained in a plasma polymer. The polymer formed in this case is a highly crosslinked three dimensional network. A schematic representation of a plasma polymer is shown in Fig. 2.9. This uniqueness results from the reaction mechanism of the polymer-forming process.

Based on various investigations, scientists proposed different mechanisms for the plasma polymerisation process. An ionic mechanism was proposed by Williams and Hayes[69], Haller and White[70], Westwood[71], Thompson and Mahayan[72], separately. A radical mechanism was proposed by several other investigators[73-76]. The argument for a radical mechanism was based on: 1) the magnitude of energy required to form radicals (3-4 eV) is considerably less than that required to form ions (9-13 eV); 2) the average electron energy in a low pressure discharge is typically 2-5 eV; 3) the radical concentration in discharge (10^{-2} – 10^{-1} of the neutral species) is much higher

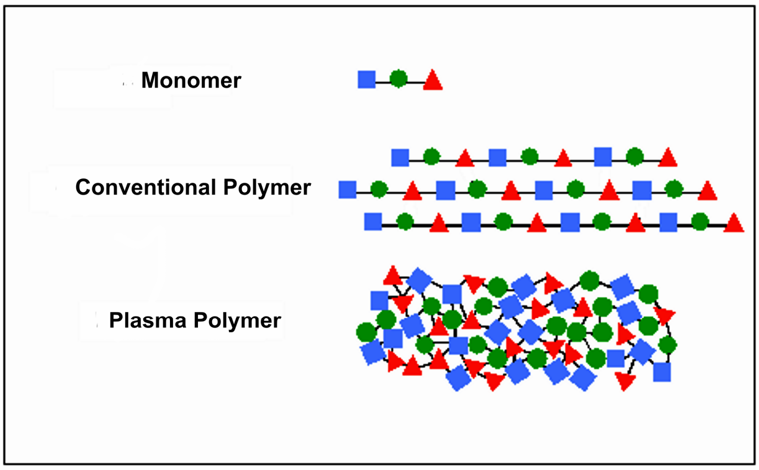

Fig. 2.9 Schematic representation of a plasma polymer[68]

than the ion concentration (10^{-6} – 10^{-5} of the neutral species); 4) there is no correlation between polymer deposition rate and the ionisation potential of the used monomer; 5) a considerable amount of radicals remains in the deposited polymer.

Yasuda explained the plasma polymerisation process by a new concept of atomic polymerisation[77]. In a plasma, monomer molecules gain high energy from electrons, ions and radicals, and are fragmented into activated small fragments and in some cases into atoms. These activated fragments recombine, sometimes accompanied by rearrangement, and the molecules grow to large molecular weight in the gas phase or at the substrate. The repetition of activation, fragmentation and recombination leads to polymer formation. This concept is essentially different from the mechanism of conventional polymerisation. In that case, monomers are linked together through chemical reactions without alteration of the chemical structure of the monomer or in some cases, with small alterations by loss of small fragments from two monomers. Therefore, the chemical structure of the formed polymer chains can be well predicted from the chemical structure of the monomer. However, the chemical structure of the plasma polymer can never be predicted based on the structure of the monomer used, because fragmentation and rearrangement of the monomers occur in the plasma. The concept of atomic polymerisation is well accepted among various investigators, and it allows to interpret features of the plasma polymerisation process and the chemical and physical properties of the formed polymers.

Because fragmentation and recombination occur in a plasma, starting molecules for plasma polymerisation are not restricted to unsaturated compounds, but saturated compounds can also be transformed into polymers. The rate constant of the process will be slightly higher for unsaturated ones. The propagation reaction in plasma polymerisation is not a chain reaction through double bonds, but stepwise reactions of recombination of biradicals that are formed from fragmentation of the starting compounds by the plasma.

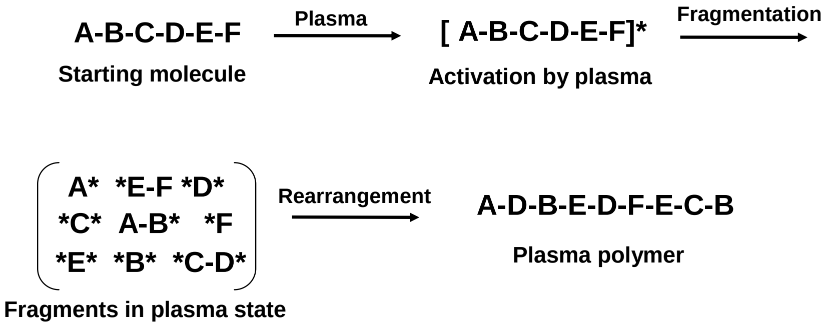

Fig. 2.10 Schematic representation of plasma polymerisation

In an extreme case, the monomer molecule is fragmented into atoms and restructured into large molecules; therefore, the sequence of the formed polymer chains is not identical to that of the monomer molecule. How the starting molecules are fragmented into activated small fragments depends on the level of plasma and the nature of the monomer molecules. This is a reason why plasma polymers possess different chemical composition when the plasma polymerisation is operated at different conditions such as monomer flow rate, RF power and pressure of the reaction chamber, even if the same starting materials are used for the plasma polymerisation.

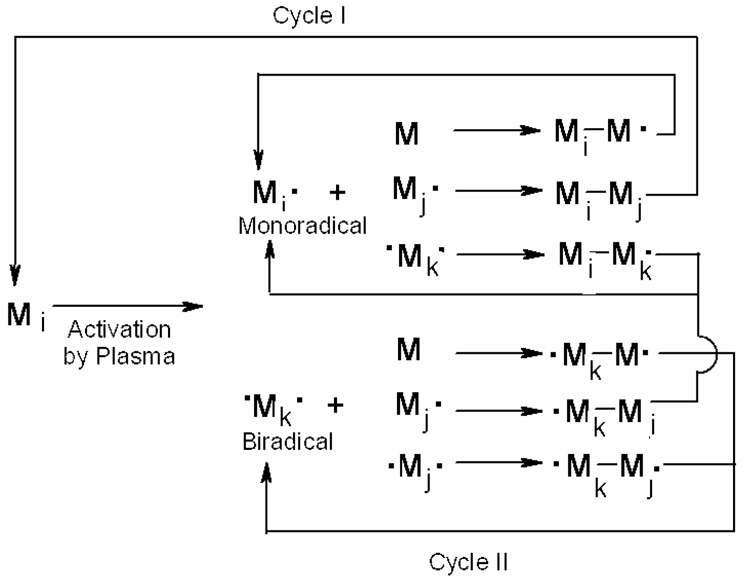

Fig. 2.11 Overall plasma polymerisation mechanism

The fragmentation of starting molecules in a plasma is represented by two types of reactions: the elimination of hydrogen atoms and C-C bond scission. Hydrogen elimination is considered to contribute greatly to the polymer forming process in plasma polymerisation. Actually, the gas phase of a closed system after plasma polymerisation of hydrocarbons (converted to polymers at yields of 85-90%) is mainly composed of hydrogen, and the amount of hydrogen eliminated by plasma (hydrogen yield per monomer molecule) in the gas phase increases by increasing the number of hydrogen atoms in a hydrocarbon[78]. Therefore, it seems probable that hydrogen atoms are eliminated from monomer molecules by plasma to form monoradicals and biradicals and then, the addition of the radicals to a monomer and the recombination between two radicals proceed to make large molecules with or without a radical. Fig. 2.11 shows an essential polymer forming process in plasma polymerisation, which was proposed by Yasuda[79]. The stepwise reaction may be predominant in the polymer forming process. Chain reactions of the radicals M_i* and $*M_k*$, via double bonds and triple bonds to form polymers, will occur infrequently because of a lower ceiling temperature ($T_{ceiling}$). The Gibbs free energy of polymerisation by chain reactions is:

$$\Delta G = \Delta H - T\Delta S \quad (2\text{-}11)$$

As the reaction temperature is raised, the magnitude of $- T\Delta S$ increases. When the reaction temperature is raised to $T_{ceiling,}$ where the magnitude of $- T\Delta S$ is equal to ΔH, the Gibbs free energy is zero; therefore at $T_{ceiling}$ the reaction is in equilibrium between polymerisation and depolymerisation and this temperature is called ceiling temperature of polymerisation. Above $T_{ceiling}$ the polymerisation never proceeds spontaneously. The ceiling temperature is a function of pressure, and most monomers at low pressure show lower ceiling temperatures than at 1atm. Thus the $T_{ceiling}$ is too low to expect appreciable polymer formation by the chain reactions. Also, because of the very small number of molecules available in a vacuum, the relatively slow polymerisation process based on the step growth polymerisation of molecules (not reactive species) fails to explain the rather rapid formation of polymers that is found in plasma polymerisation. Thus, the most acceptable mechanism for plasma polymerisation taking place in a vacuum, is the one given by Yasuda.

2.4.2 Operational Parameters

The activation of monomers and reactivation of the recombined molecules by plasma are due to the fragmentation: hydrogen abstraction and bond scission by plasma. The fragmentation process depends on how much electrical energy (RF power) is supplied to maintain the plasma, how much monomer is introduced into the plasma, and where the monomer molecules interact with activated species of the plasma. Yasuda proposed a controlling parameter or W/FM value, where W, F, and M were RF power [J/s], the monomer flow rate [mol/s], and the molecular weight of the monomer [kg/mol], respectively[80]. The W/FM parameter is an apparent input energy per unit of monomer molecules [J/kg]; therefore, the magnitude of the W/FM parameter is considered to be proportional to the concentration of activated species in the plasma. The polymer formation rate, polymer deposition rate, increases by increasing the W/FM parameter in the operational condition, where the activated species have a far lower concentration than monomer molecules in the plasma: the monomer sufficient region; afterwards, the polymer formation rate levels off: competition region, and over that region, the polymer formation rate decreases with increasing the W/FM parameter because of lack of monomer molecules: the monomer deficient region. The domains of plasma polymerisation are schematically illustrated in Fig. 2.12.

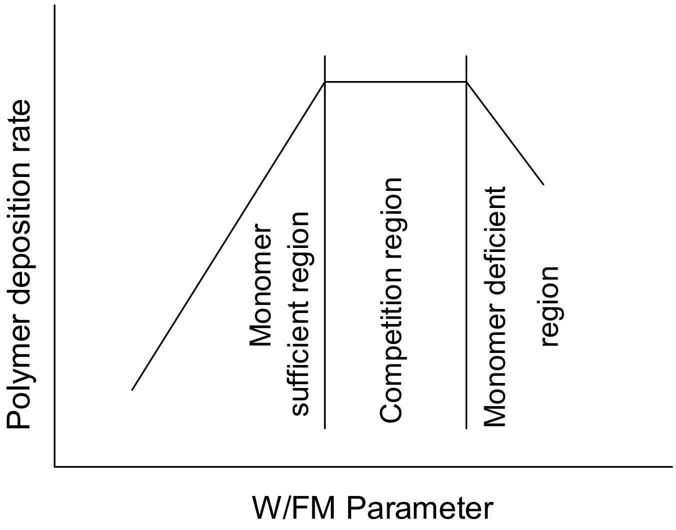

Fig. 2.12 Domain of polymer deposition

In the monomer-sufficient region, monomer molecules are subjected to less fragmentation to be plasma–polymerised, and plasma polymers with little rearrangement and little loss of groups such as hydrogen, hydroxyl groups and carbonyl groups are formed. In the monomer-deficient region, monomer molecules are subjected to heavy fragmentation, and plasma polymers with much rearrangement and a large loss of some groups are formed. Usually, plasma polymerisation is operated in the monomer-sufficient region. The monomer flow rate is also a factor to control plasma polymerisation. At a constant level of RF-power, increase of the monomer flow rate results in a decrease of the W/FM parameter. As the monomer flow-rate increases, the domain of plasma polymerisation changes from the monomer-deficient region to the monomer-sufficient region.

The hydrodynamic factor that influences the plasma polymerisation process is a complicated problem and is of importance in the application of plasma for thin film coating. When two reaction chambers with different shapes or sizes are used and when plasma polymerisation of the same monomer is operated under the same operational conditions as RF power, monomer flow rate, pressure in the reaction chamber etc., the two plasma polymers formed in the two reaction chambers are never identical, because of the differences in the hydrodynamic factor. In this sense, plasma polymerisation is a reactor dependent process. Yasuda and Hirotsu[81] systematically investigated the effects of hydrodynamic factors on the plasma polymerisation process. They studied the effect of monomer flow pattern on the polymer deposition rate in a tubular reactor. Polymer deposition rate is a function of the location in the chamber. The distribution of the polymer deposition rate is mainly determined by the distance from the plasma zone and the direction of pumping flow. The direction of monomer flow gives less influence on the distribution of the polymer deposition rate. These results emphasise the importance of: 1) the diffusional transport of the energy carrying species, electrons, ions, radicals of plasma; 2) the flow of monomer and product gas, fragments generated by plasma; and 3) the diffusional transport of polymer-forming species, radicals.

A similar investigation of the hydrodynamic effect on the polymer deposition rate using a bell-jar type reactor was done by Kobayashi[82]. The experimental data using two reactors with different shapes indicate that the polymer deposition rate does not become uniform at any spot of the reactor, even if the patterns of the diffusional transport of the energy carrying species of plasma, of the flow of monomer and product gas, and of the diffusional transport of the polymer forming species are changed. This means that a certain degree of thickness variation always exists when a plasma polymer is deposited on a stationary substrate in a reactor. The thickness variation can be avoided by moving the substrate when plasma polymers deposit in the reactor. Inagaki and Yasuda[83] designed a special reactor in which a moving substrate plate was positioned mid way between two parallel electrodes and was rotated at 60 rpm in and out of the plasma zone, repeatedly. The polymer deposition rate at any place on the moving substrate was very uniform. This uniformity achieved by the relative position of the polymer deposition may be due to changing the direction of the diffusional transport of the energy-carrying species, of the flow of monomer and product gas, and of the diffusional transport of polymer forming species. This aspect is applicable to tubular type reactors.

2.4.3 Plasma Generation

To reach the plasma state of atoms and molecules, energy for the ionisation must be absorbed by the atoms and molecules from an external energy source. Further, the plasma state does not continue at atmospheric pressure, but at a low pressure of $1 – 10^{-2}$ Torr. The essential items for plasma generation are: 1) an energy source for the ionisation; 2) a vacuum system for maintaining a plasma state; and 3) a reaction chamber.

Generally, electrical energy is used as the energy source for the ionisation of atoms and molecules because of the convenience of handling. Direct current (DC), commercial alternating current of a frequency of 50 or 60 Hz, and an alternating current (AC) with a high frequency of more than 60 Hz, for example: 10 or 20 KHz (audio frequency), 13.56 MHz (radio frequency), or 2.45 GHz (microwave frequency) are applicable for electrical energy. These electric powers are basically supplied to atoms and molecules in the reaction chamber from a pair of electrodes placed in the reaction chamber in a capacitative coupling manner with the electric generators. An inductive coupling manner is also possible for electric generators with a high frequency of more than 1MHz.

A vacuum system composed of a combination of a rotary pump and an oil diffusion pump is frequently used. Although use of a rotary pump alone can reach low pressures of 1 – 10^{-2} Torr, use of both rotary and oil diffusion pumps is desirable because of less gas remaining in the reaction chamber.

The reaction chamber is usually designed based on the substrates to be irradiated with plasma. A bell jar or tubular chamber made of glass or stainless steel is frequently used as a reaction chamber. A bell jar type chamber is convenient for massive substrates, and a tubular type chamber is better for long substrates like fibers. The reactor contains two electrodes and a substrate stage, which is midway between the electrodes. Using a rotatory substrate stage it is possible to obtain a homogenous deposition of plasma polymer.

2.5 PLASMA SURFACE MODIFICATION OF POWDER SUBSTRATES

Plasma treatment of powder substrates is difficult compared to that of a flat substrate. The main reason for this is the agglomeration of powders and large surface area per unit mass of the powder. In order to modify the surface, each powder particle must be exposed to plasma. Unexposed regions are seldomly modified. Therefore, the plasma surface modification of powder substrates has to be dealt differently.

One of the important aspects is the surface exposure of powder substrates during the plasma modification process. For this, the aggregation of the powders should be destroyed. A fluidised bed is a way to expose all the powder particles to plasma. In this case powder is placed on a porous plate in the reactor, which is positioned vertically, and a gas is injected from the bottom of the reactor. The gas passes through the bed of powder. At more than a critical flow rate of the gas stream, the pressure drops, and the drag on individual powder particles increases. As a result, the powder starts to move and become suspended in the fluid. This is called fluidisation, which is the condition of fully suspended particles. Using a reactor with a fluidised bed, all surfaces of each powder can be exposed to plasma. Thus, effective surface modification of powders is possible.

Another possible technique for the plasma treatment of powders is based on tumbling of the powder[84]. In these type of reactors powders are treated remotely from the plasma i.e., away from the most intense glow. These types of reactors can handle powders in the range of 300-500g.

The major differences between plasma polymerisation on a flat substrate and that on a powder substrate are: 1) Powders are characterised by a large surface area per unit mass. The specific surface area for 1 g powder with average particle size 20 μm and density 2000 kg/m^3 is around 0.15 m^2, which is two orders of magnitude larger than that of a flat substrate[85]. Therefore, for the same plasma polymerisation condition and the same total amount of film deposited per unit time, the thickness of the film deposited on powders will be much smaller than that on a flat substrate. 2) There is a difference in the length of time during which the substrate surface is exposed to the plasma. During a plasma polymerisation process, a flat surface is exposed to plasma throughout the process. Whereas a powder surface exposes part of its surface periodically to plasma depending on the shape and mixing efficiency. 3) Since the nature of treatment of powdered materials involves mixing the particles to continuously refresh the surfaces exposed to the plasma, the stability of the plasma in the chamber is affected by interactions between the particles and the plasma. 4) Exhaustion of monomer close to the powder surface is another important factor affecting the film deposition rate. Due to the large surface area, the monomer concentration around the powder substrate is much lower compared to that around a flat substrate, assuming the deposition conditions are the same. The growth of the plasma polymer on powder surfaces is slowed down because the monomer and radicals around the particle surface are depleted and exhausted. Hence, plasma polymerisation on a powder substrate proceeds in a monomer deficient region. Therefore, plasma polymerisations on powder substrates are to be carried out at an ample supply of monomer.

The first attempt to modify powder substrates by plasma polymerisation was done by Inagaki[86]. He reported the modification of polyethylene and magnetite powder surfaces by a plasma polymerisation process in a fluidised bed reactor. The monomer used for the process was tetrafluoroethylene. Later, Piskin and Atac[87] reported controlled release of antibiotic ciprofloxacin using RF – glow discharge plasma deposition. The technique of plasma coating of powder substrates has been utilised in the field of coatings also. Corrosion inhibitive paint pigments like tolyltriazole, benzotriazole and 1,2,4 triazole are soluble in water and therefore cannot be used in paints, as they would cause blistering of organic coatings when in contact with moisture. The pigments were encapsulated in a plasma polymerised thin film to serve as slow release pigments[85].

Thin organic films were deposited on polymethylmethacrylate powder particles by combining the techniques of plasma polymerisation and vacuum fluidisation[88]. Monomer hexamethylene disiloxane was used for modifying the surface of these PMMA powders. A thin film of plasma polymerised pyrrole was deposited on the surfaces of alumina nanoparticles[89]. The nanoparticles ranged from 10-150 nm in spherical shapes. The particles were treated in a plasma reactor consisting of a Pyrex glass column. The particles were vigorously stirred at the bottom of the tube in order to expose the full powder surface to plasma. The deposited plasma polymer on the surface of alumina nanoparticles was about 2 nm thick. The surfaces of carbon nanotubes were also modified using a plasma polymerisation technique[90]. Pyrrole was again used as the monomer for the modification process. Hydroxyapatite (HA) powders were modified by the plasma polymerisation technique in order to improve its water dispersibility for biomedical applications. Acrylic acid was used as the monomer for the process[91].

2.5.1 Plasma Modification of Fillers for Rubber Applications

In the process of plasma polymerisation a highly crosslinked polymer is deposited on the surface. By a careful selection of monomers, a particular substrate can be made hydrophobic or hydrophilic. The deposited plasma polymer changes the surface properties of the substrate dramatically. It modifies the surface of the powders in terms of surface energy, functional groups, wettability, interaction with polymers and dispersion in polymers. This technique of modifying powder surfaces has received the attention of scientists in the field of rubber technology. The dispersion of fillers in a rubber matrix is a difficult task. The reinforcement of rubber by fillers depends on the degree of rubber–filler interaction. Akovali and Ulkem[92] reported the surface modification of carbon black by plasma polymerisation of styrene and butadiene. The effect of such plasma coated carbon black was studied in a SBR matrix. A slight increase in the tensile strength was observed for plasma polymerised styrene-coated carbon black. This was explained by a decrease in the interfacial tension, as result of the similarities between the treated filler and the matrix at the interface. They also concluded that the plasma coating obtained on carbon black is so thin, that no blockage of the pores occurred and that there was no decrease in the original absorptive capacity. However, these claims were not justified by any means of scientific investigation.

Another attempt by Tricas *et al*. to modify the surface of carbon black was by the plasma polymerisation of acrylic acid[93]. The treatment with acrylic acid made carbon black hydrophilic. Plasma coated carbon black was mixed with natural rubber and showed increased filler-filler interaction. The bound rubber content was reduced after the surface treatment of the filler. The authors also concluded that the surface of carbon black was completely covered by the plasma polymer film, preventing the carbon black surface to play any role in the polymer matrix.

Later, Kang *et al*.[94] reported surface modification of carbon black using various monomers like acetylene, acrylic acid, butadiene and oxygen. They concluded that it is possible to manipulate the surface properties of carbon black using plasma polymerisation of various monomers.

Surface modification of silica, another filler used in rubber industry, has been reported by Nah *et al.*[95,96]. The silica surface was modified by plasma polymerisation of acetylene. The modified silica was mixed with SBR to study its performance. They observed an increase in reinforcement with the plasma modified silica and hence better mechanical properties. They also observed an improvement in the dispersion properties for the plasma coated silica. The authors explained the observed improvement in properties by a mild cross linking between plasma polymerised acetylene and the butadiene part of the SBR matrix.

Sulphur, the main crosslinking agent used in the rubber industry, has a problem of poor miscibility with rubbers. During storage of a mixed compound before vulcanisation, sulphur tends to bloom to the surface. This migration can create sulphur bloom and spots on the surface that affect the compounds tack properties. Vidal-Escales *et al.*[97] modified sulphur by the plasma polymerisation technique to change its surface polarity. Pyrrole, acetylene and perfluorohexane were used as the monomers for plasma polymerisation. This modification changed the sulphur accessibility and consequently the vulcanisation kinetics. Using N-cyclohexyl benzothiazole sulphenamide (CBS) accelerator, squalene vulcanisation seemed to be affected by the plasma treatment. This is, because after the plasma treatment sulphur is encapsulated in a plasma polymer shell, and it has to escape out of the shell in order to take its role in the crosslinking reaction.

Vidal *et al.*[98] reported plasma modification of CBS with different monomers: acrylic acid, acetylene and perfluorohexane. It was found that by plasma polymerising appropriate monomers onto the surface of accelerator particles, the onset of its accelerating effect during vulcanisation could be controlled. Rheometer testing clearly showed that scorch times were affected by the plasma polymerised monomers on the CBS surface, but final crosslink densities of the cured rubbers were almost identical. In the case of CBS with acrylic acid coating, the scorch time was reduced compared to that of unmodified CBS. Whereas in the case of CBS with plasma polymerised acetylene and perfluorohexane, the scorch time was found to be longer.

2.6 SUMMARY AND DIRECTION OF PRESENT RESEARCH

In previous pages, a review on the usage of carbon black in rubber, rubber blends, factors affecting the properties of rubber blends and a novel route for the surface modification of powder substrates was given. Uneven distribution of fillers and curatives influences the morphology and physical properties of rubber blends appreciably. This has been the major reason to restrict the commercial use of blends such as NR/EPDM, NR/NBR, NR with epoxidised natural rubber and tyre side wall compositions based on NR/BR/EPDM. In a recent paper it has been mentioned that the influence of filler distribution probably plays a much more important role than the degree of crosslinking[99].

Plasma polymerisation has emerged as a surface modification technique for powder substrates. Advantages of surface modification by plasma polymerisation are

- The modification is limited to a very thin layer at the surface, and hence the alteration of bulk properties of the substrate is minimal.

- By a careful selection of type and nature of the gas to be used for plasma treatment, a particular substrate can be made hydrophobic or hydrophilic. Thus it is possible to tailor the surface characteristics of the substrate in a desired manner.

- The process as such does not require any solvents, making it a clean process.

Progress of research in this area lead to the development of a bench-scale size tumbler RF plasma reactor for surface modification of powder materials in quantities of 300-500 g[100]. Even though a wide interest in this area is observed among scientists and industry, the scientific knowledge about the surface modification of powders is still not very well advanced. This novel technique of surface modification of powders can be utilised to meet the technical difficulties that occur during blending of different rubbers. If it is possible to match the surface characteristics of carbon black particles to that of different rubbers, ideally a homogenous distribution of carbon black between the phases in the blend can be achieved.

During mixing of carbon black with rubber, after incorporation, distributive and dispersive processes control the dispersion quality. After an initial breakdown of the macroscopic filler pellets, the wettability of the filler and its interaction with the rubber play an important role in achieving a good dispersion state. The wettability of a filler particle by a polymer chain can be quantified in terms of surface energy. The surface energy of a filler in turn depends on the physico-chemical composition of its surface. In order to have a good compatibility, the surface energy difference between the filler and rubber should be low. With a large surface energy difference between filler and rubber, filler-filler interaction prevails, which has a negative influence on the stability of the dispersion state attained during mixing. In the case of carbon black, its surface energy is high compared to that of various elastomers like Styrene-Butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene-Propylene-Diene rubber (EPDM). Reducing the surface energy of carbon black may aid in improved wetting of this filler by different rubbers and their blends.

There are a few reports on the surface modification of carbon black by plasma polymerisation. But the reported investigations are not very conclusive about the modification aspects and its behaviour with rubber. Moreover, the previous investigators were mainly focusing towards increasing the surface polarity of carbon black. In the present work, a reduction of surface energy of carbon black is aimed at in order to facilitate better wetting by low surface energy rubbers.

The present work has an important area of application, the incorporation of EPDM in tyre side wall compositions. The presence of EPDM can improve the ozone resistance of tyre side walls. The commonly used antiozonants such as N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), do discolour or stain the side wall. The use of EPDM allows to eliminate the antiozonants from the tyre side wall formulation. With this end application in mind, during the present research the effect of plasma modified carbon black in rubber blends containing EPDM will be investigated. Two different rubber blends SBR/EPDM and NBR/EPDM are selected for this study. Both these systems differ in the level of unsaturation and polarity. Hence this forms a good system to study the distribution of carbon black.

As mentioned in the beginning of this review, carbon black is available in the form of pellets for its usage in the rubber industry. During mixing of carbon black in rubber, these pellets break down to agglomerates and aggregates. If the carbon black is plasma coated in this state of the material, during mixing, the plasma coated carbon black pellets will break down and there will be more fresh uncoated surface than coated surface. Then the effect of plasma coating may therefore be not identifiable. Hence, it is very important to choose the proper state of carbon black for the plasma surface modification process. We chose the agglomerate state, the fluffy carbon black for the plasma coating purpose. This is the state of carbon black just before pelletisation. The material was collected from the carbon black manufacturer before the pelletisation stage.

The following points will be considered during this research project:

- Installation of a small scale RF plasma reactor for the treatment of powders;
- Development of a novel surface modification technique for carbon black by plasma polymerisation;
- To understand the state of plasma coated carbon black in rubber and its effect on rubber properties;
- To study the effect of plasma coated carbon black in rubber blends with respect to its distribution between the phases in the blend.

The initial work on surface modification of carbon black was carried out at the University of Cincinnati, USA, utilising their RF plasma tumbler reactor facility. After the initial studies, in the second phase, a small scale RF plasma reactor was installed at the University of Twente for carrying out screening experiments and for the treatment of small scale samples. In the third phase, the surface modification process of carbon black was scaled up at the University of Cincinnati. And in the fourth phase, the effect of plasma coated carbon black in rubber and rubber blends was studied.

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Chapter 3

Plasma Reactors for Powder Surface Modification

Plasma surface modification of a substrate can alter its surface characteristics to a few atomic layers without affecting the bulk properties. Plasma reactors for powder surface modification are custom made and are designed based on specific requirements. This chapter discusses different plasma reactors for surface modification of powder substrates. Design aspects and the major components of a plasma reactor are described. Details of a tumbler plasma reactor which is capable of treating about 300–500 g of powder are described. Design and installation of a small scale vertical tubular plasma reactor are explained in this chapter. Optimisation of experiments was carried out in this vertical tubular plasma reactor to find out suitable positions for coil and monomer inlet to carry out surface modification experiments. The plasma polymer formed from acetylene is characterised using Thermogravimetric analysis and X-ray photoelectron spectroscopy.

3.1 INTRODUCTION

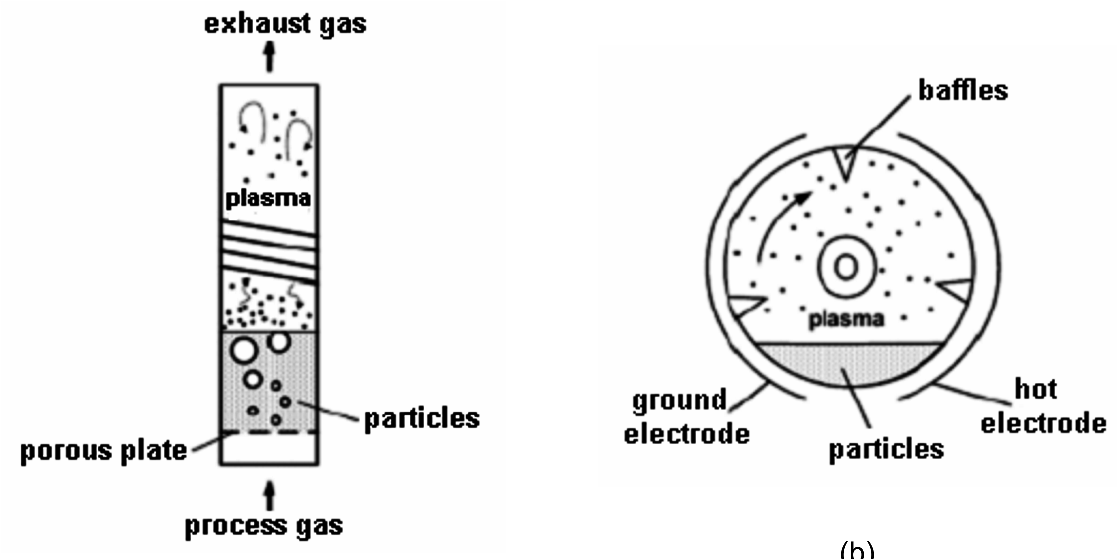
During the last decade plasma technology has been extensively investigated due to its possible application in technology, synthesis and processing of polymeric and other materials. The selection of a material for a particular application is usually a compromise of bulk versus surface properties. If the surface of a plastic, powder, rubber, metal, etc. can be non-destructively altered down to a depth of a few molecules, it can make a large difference in the material's suitability for a broad range of applications[1-4]. Using a cold gas plasma reactor to tailor the surface of a material by just a few nanometers is a very energy efficient, clean and environmentally safe method. The possible effects of plasma treatment on a particular surface are alteration of wettability, increased chemical activity, improved surface interactions, cleaning etc.

For the surface modification of flat solid materials, conventional plasma reactors are available[5]. However, such plasma reactors are often unsuitable for powder materials due to the lack of facilities for solid mixing. In such cases, custom made plasma reactors are designed based on the particular requirements. This chapter will give an overview of different type of reactors for powder surface treatment, aspects in designing, details of a custom made plasma reactor, etc.

3.2 REACTORS FOR POWDER SURFACE MODIFICATION

The design of a plasma reactor for surface modification of powder materials has to take into account the properties of the particles, in particular their size, shape, chemical and physical nature. Intimate mixing and homogeneity of the treatment or modification are the primary criteria for plasma treatment of powder materials. For uniform surface modification of each powder particle, the powder surface has to be exposed to the plasma. Because of severe agglomeration and aggregation of powder materials, the duration for which a particular powder surface is exposed to plasma is very low when compared to that of a flat surface. Therefore, an optimal contact between the powder surface and gas plasma phase is necessary for uniform surface modification.

In recent years, four main types of plasma treatment systems for powder materials have been presented in the literature. The four types are: a) a plasma fluidised bed reactor (PFBR); b) a plasma circulating fluidised reactor (PCFBR); c) a plasma rotating drum reactor (PRDR) and d) a plasma batch reactor (PBR).



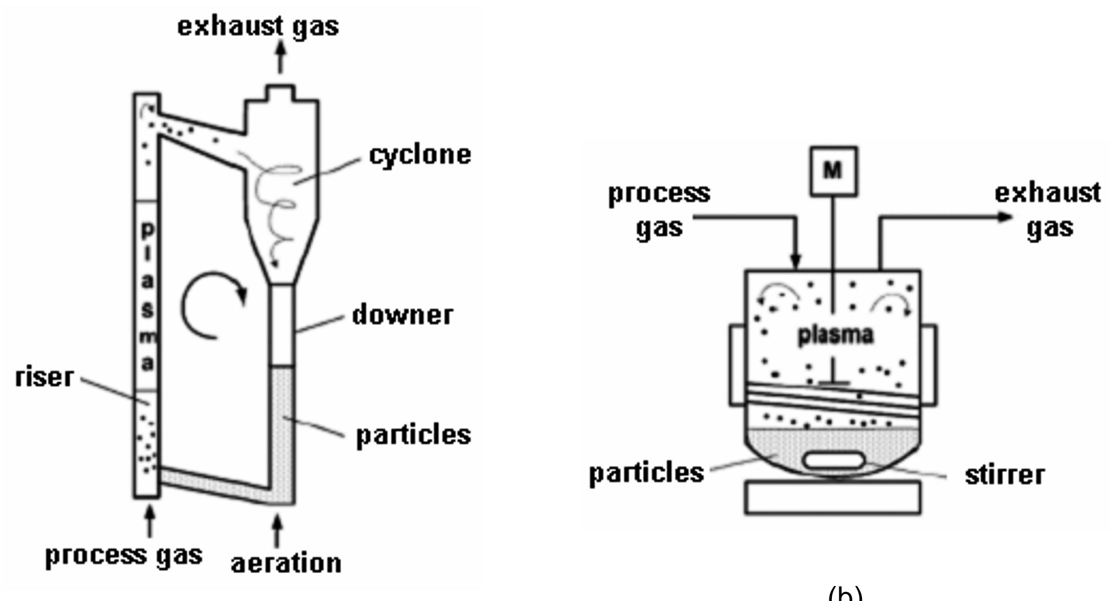
(a)

(b)

Fig. 3.1 Reactor configurations for: a) Plasma fluidised bed reactor (PFBR); and b) Plasma rotating-drum reactor (PRDR)[10]

The most common plasma reactor for powder treatment is the fluidised bed reactor (PFBR)[6-10]. The process gas carries a minimal fraction of particles from the bubbling fluidised bulk of powder into the gas phase. The advantage of this reactor type is the intense mixing of the small amount of powder with the plasma species, while only marginally affecting plasma properties. A disadvantage is that uniform treatment of the entire bulk of the powder is difficult. An approach to increase the transfer efficiency is the use of agitating reactors such as rotary drums. The so-called plasma rotating-drum reactor (PRDR)[11-13] has the advantages of high powder load and high batch wise throughput, but dispersion is not satisfactory in the case of fine powders. Furthermore, no uniform treatment can be obtained in a batch mode because particles in the bulk are less exposed to the plasma than particles at the surface of the bulk. To overcome this effect, long treatment times in the order of hours, and/or strong physical mixing of the particles by means of internal moving baffles is generally necessary. Nevertheless, a PRDR is still the only commercially available reactor, which can treat up to 70 kg of powder in 20-25 minutes.

A less common reactor type is the plasma batch reactor (PBR)[14]. Because of the disadvantages of nonuniform treatment such reactors require longer treatment times.



(a)

(b)

Fig. 3.2 Reactor configurations for: a) plasma circulating fluidised bed reactor (PCFBR); and b) plasma batch reactor (PBR)[10]

In order to obtain a narrower residence time distribution, the plasma circulating fluidised bed reactor (PCFBR) has been developed. The PCFBR circulates the entire powder bulk through the plasma zone in a riser tube[15,16]. An intense plasma contact of all the particles can be achieved. A statistically uniform treatment can be obtained by cycling the powder several times. The PCFBR is used for the deposition of very thin coatings on powders[17].

Another development is the plasma downer reactor (PDR). This reactor combines plasma low-temperature processing technology and the downer reactor principle in a single process for short-time plasma surface modification of powder materials, e.g., polymer powders. The downer reactor is an appropriate reactor for very fast reactions, e.g., fluid catalytic cracking reactions[18]. Low temperature plasma processing enables surface modification, in an ecologically benign way without changing the bulk properties of the solid. The downer reactor principle enables advantageous flow characteristics and high reaction rates coupled with intense particle gas contact. The main principle is to directly feed the polymer powder continuously into a plasma environment for a short time plasma powder reaction. A similar reactor design has been described in the US patent 5 234 723[19]. The most essential element in the process is a vertical glass tube, in which low temperature plasma is generated. Fig. 3.3 illustrates the configuration of the pilot PDR. The particles are accelerated in a nozzle device and are distributed over the reactor cross-section concurrently with the process gas through the plasma treatment zone, where the powder interacts directly with the reactive plasma species. The powder passes through the plasma zone once only. The residence time of a polymer particle in the plasma is very short, typically 0.1 s and depends on the plasma glow volume, the process pressure and the gas flow rates. The plasma treated particles leave the temperature zone and pass into a solid collecting vessel. A minor part of the powder passes into the cyclone separator where the residual powder is separated from the gas stream. The plasma treated powder is finally recovered in the solid collecting vessels.

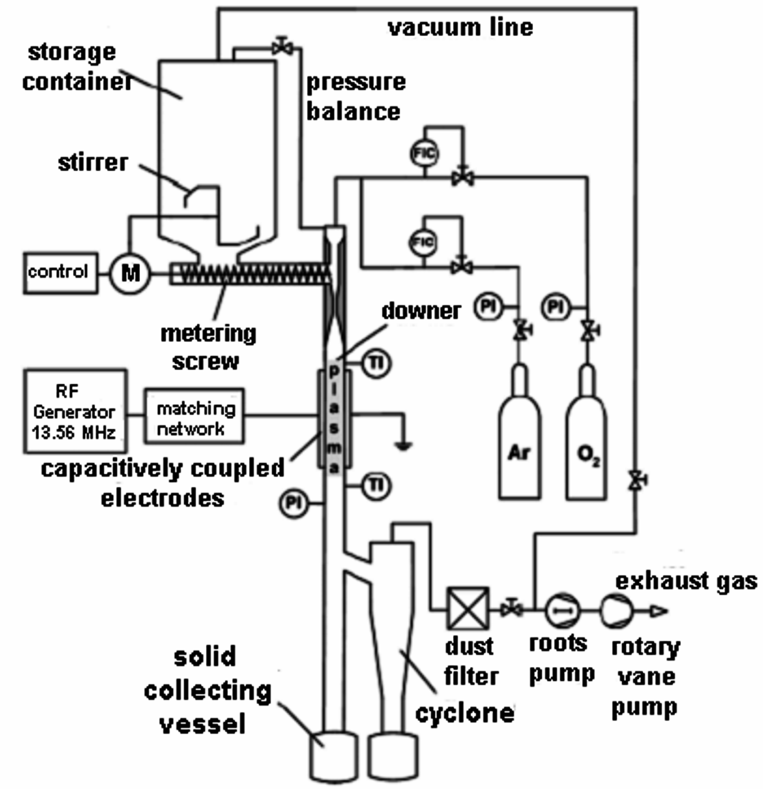


Fig. 3.3 Configuration of the plasma downer reactor (PDR)[10]

Another plasma reactor[20] for the treatment of powder substrates is shown in Fig. 3.4 with the aim of modifying of superficial physico-chemical characteristics of polymer nanoparticles or powders, meant for plastic materials, inks, paints, rubber etc. On this installation, it is possible to achieve an uniform plasma treatment of powders with 0.1-1 g/cm^3 density. The main component is a glass vessel having a rotor attached inside. The rotation of the rotor is achieved from outside the reactor through a magnetic coupling. When the pressure attains the proper value for the plasma treatment, the RF discharge is striken and the powder treatment is achieved.

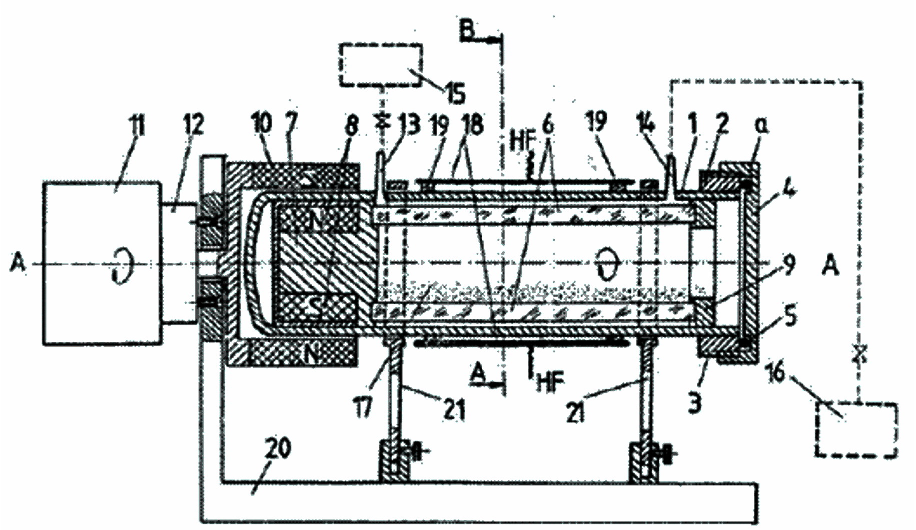


Fig. 3.4 Cold plasma installation for powder treatment[20]*: 1- reactor, 2- ring shaped piece, 3-thread, 4- metallic lid, 5- silicone rubber mounting, 6- glass rotor, 7- teflon muff, 8- permanent magnets, 9- teflon ring, 10- electromagnetic training head, 11- electric motor, 12- revolution variator, 13,14- rigid connections, 15- vacuum unit, 16- gas recipient, 17- polymer powder, 18- semi cylindrical electrodes, 19- teflon mounting, 20- metallic support, 21- gliding rods.*

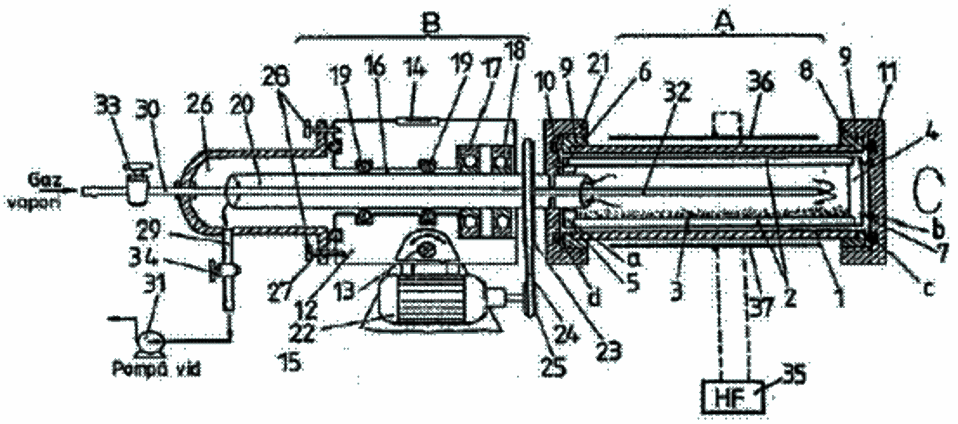


Fig. 3.5 Plasma reactor for powder surface treatment[20] *: A- reactor, B- rotational training system, 1- thermoresistant cylinder, 2- longitudinal pallets, 3- polymer powder, 4,5- annular teflon pieces, 6- training pin, 7- helical arch, 8- entrance lid, 9- metallic rings, 10,11- silicone rubber mounting, 12- parallelepiped metallic body, 13- horizontal axle, 14- plump line, 15- metallic support, 16- cylindrical profile, 17,18- bearings, 19- tightness rings, 20- metallic tubular piece, 21- clamping-training head, 22- electric motor, 23,24- wheel transmission device, 25- driving belt, 26- distributing chamber, 27- rubber mounting, 28- bolts, 29,30- connections, 31- vacuum pump, 32- admission coupling, 33,34- faucets, 35- RF generator, 36,37- semicylindrical electrodes.*

An installation for polymer powder treatment in RF plasma in a gas or vapour atmosphere is presented in Fig. 3.5. This reactor allows a homogenous mixing of larger quantities of polymer powder and with different densities. The powder is plasma treated in the presence of low pressure gases or vapours in a horizontal cylindrical reactor from thermo-resistant glass, connected with longitudinal pallets and situated between two cylindrical electrodes connected to the variable voltage generator. A convenient way of uniform stirring is achieved by the rotation of the reaction vessel.

3.3 DESIGN OF A PLASMA REACTOR

The major parts of a plasma reactor are a power supply (AC or DC), a matching network, vacuum chamber, mass flow controller, pressure gauge and a pumping system. A schematic representation of a low pressure plasma reactor is shown in Fig. 3.6. In the following sections each part will be discussed in detail.

3.3.1 Power Supplies

The plasma state can be produced in the laboratory by raising the energy content of matter regardless of the nature of the energy source. Thus plasmas can be generated by mechanical, thermal or chemical reactions, high energy electromagnetic radiation, nuclear and electrical energies and by combinations of them. Plasmas lose energy to their surroundings through collision and radiation processes. Therefore, energy must be supplied to the system in order to maintain the plasma. The easiest way to sustain plasma in a continuous manner is with electrical energy and that is the reason why electrical discharges are used for making man-made plasmas.

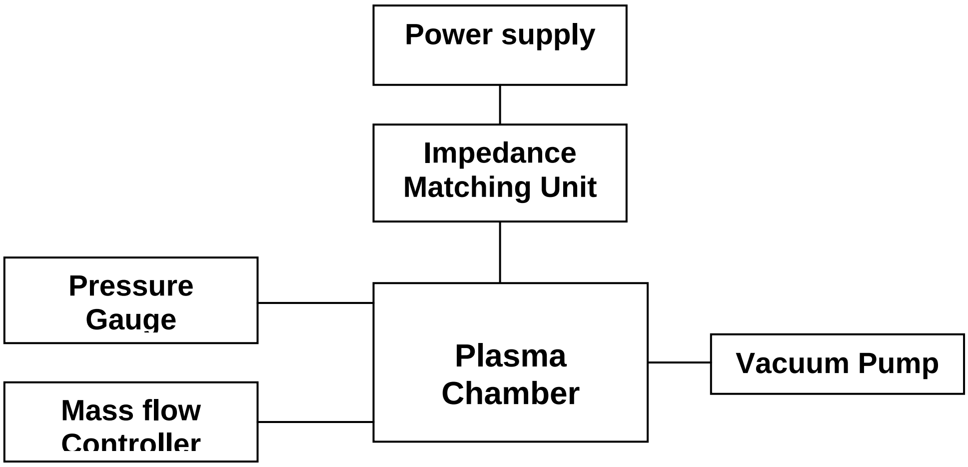


Fig. 3.6 Scheme of a low pressure plasma reactor

As the work described in this thesis is a non-equilibrium cold plasma, the discussion will mainly be focused on such systems. Direct current (DC), alternating current (AC) of a frequency of 50 or 60 Hz, alternating currents with frequencies of more than 60 Hz, for example: 10 or 20 KHz (audio frequency), 13.56 MHz (radio frequency), or 2.45 GHz (microwave frequency), are applicable for electrical energy. Low-pressure non-equilibrium discharges are initiated and transferred to a low-pressure gas environment, with or without an additional electric or magnetic field. Ultimately, all these discharges are initiated and sustained by electron collision processes under the action of the specific electric or electromagnetic fields. Accelerated electrons induce ionisation, excitation and molecular fragmentation processes leading to a complex mixture of active species.

3.3.1.1 DC Discharges

DC glow discharges are generated in a low-pressure gas environment (10^{-2} – 10^{2} Torr) between two conductive electrodes connected to a power supply, with an electrode voltage usually in the range of 10^{2}-10^{3} V. Most DC reactors are made of cylindrical glass tubes and are provided with two disc shaped electrodes at the ends of the chamber. The discharge is initiated when the free electrons in the low-pressure gas environment are accelerated by the electric field to energy levels at which ionisation and excitation processes occur through inelastic collision mechanisms. At low voltages, elastic collisions characterise the system and the electrons lose only a negligible part of their kinetic energy. At high voltages, electrons gain enough energy to ionise, and a discharge is created. The pressure in the discharge tube, the geometrical shape and the dimensions of the discharge tube, and the gap between the electrodes significantly influence the distribution and dimensions of the luminous and dark areas. Changing the gap between the electrodes will result in the spatial and dimensional rearrangement of the specific plasma zones.

3.3.1.2 High Frequency Plasmas

Discharges excited and sustained by AC, and more specifically high frequency electromagnetic fields are of increasing interest for technical and industrial applications. RF-discharges gain their name from the frequency range, which is employed to produce plasma: 1 kHz – 1 GHz. Most RF-installations involve the standard 13.56 MHz frequency in order to avoid interference with communication networks. These discharges are characterised by low degrees of ionization and operate in low pressure environments (10 - 500 mTorr). Electrons absorb power from the RF-field, and transmit the power through elastic and inelastic collisions. RF-power supplies are usually connected to the discharge chamber through a matching network. This is required to increase the power transfer and to protect the generator by matching the impedance of the plasma reactor to that of the power supply. The power coupling in RF-discharges can be accomplished in different ways, as:

1. capacitively coupled discharges,
2. inductively coupled discharges.

In the case of a capacitively coupled plasma reactor, the chamber contains electrodes inside the chamber which are separated by a distance of a few centimeters. They may be in contact with the discharge or they may be insulated from it by a dielectric. In the case of insulating chamber walls, outer electrodes are sometimes used. In a capacitively coupled RF-discharge, the electron density is in the range of 10^9 – 10^{10} cm^{-3} and densities up to 10^{11} cm^{-3} are possible at higher frequencies.

An inductively coupled plasma (ICP) is excited by an electric field generated by a transformer from a RF-current in a conductor. The changing magnetic field of this conductor induces an electric field in which the plasma electrons are accelerated. There are two types of ICP-geometries: planar and cylindrical. In planar geometry, the electrode is a coil of flat metal wound like a spiral. In cylindrical geometry, it is like a helical spring. When a time-varying electric current is passed through the coil, it creates a time varying magnetic field around it, which in turn induces azimuthal electric current in the gas leading to break down and formation of plasma. ICPs can achieve high electron densities in the range of 10^{12} – 10^{15} cm^{-3} at low ion energies.

Microwaves are also utilized for the generation of plasma. A characteristic frequency for a microwave discharge is 2.45 GHz. Microwave discharges are also characterised by high electron densities.

3.3.2 Impedance Matching Unit

Impedance matching is the practice of attempting to make the output impedance of a source equal to the input impedance of the load to which it is ultimately connected. This process is carried out in order to minimize the reflections from the load and maximize the power transfer. Electrical impedance extends the concept of resistance to AC circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. Impedance (Z) is a complex quantity.

$$Z = R + j\,X \qquad (3\text{-}1)$$

where R is resistance and X is reactance. In simple cases, such as low frequency or direct current power transmission, the reactance is negligible or zero and the impedance can be considered a pure resistance. The SI unit for impedance is Ohm, the same as that for resistance. Putting impedance in Ohms law:

$$V = I.Z = I.Z_0 e^{j\theta} \qquad (3\text{-}2)$$

The magnitude of impedance acts just like resistance, giving the drop in voltage amplitude across an impedance for a given current I. The phase factor tells us that the current lags the voltage by a phase θ.

Impedance matching to minimize the reflections and maximize power transfer over a relatively large bandwidth is the most commonly used. To prevent all reflections of the signal back into the source, the load must be matched exactly to the source impedance. This is the case for a resistive load and resistive source. In a low frequency or DC system, or a system with purely resistive sources and loads, the reactance is zero. In this case maximum power transfer occurs when the resistance of the load is equal to the resistance of the source.

There are a variety of devices that are used between source of energy and load that perform impedance matching. To match electrical impedance, engineers use combinations of transformers, resistors, inductors and capacitors.

3.3.3 The Vacuum Chamber

The design of the chamber is usually empirical. The design usually depends on the requirements of the process. In the case of powder surface modification the mixing of powder substrate is very important. Hence this aspect has to be included in the design of the chamber. This limits the use of electrodes inside the chamber and hence the use of DC sources for plasma generation. The most preferred sources are then high frequency systems with electrodes outside the system, such as an inductively coupled plasma reactor. The design also takes into account the amount of powder to be treated. Different mixing techniques can be utilized in the design in order to expose and refresh the powder surface to the plasma environment. In the simple case, a magnetic stirrer is utilized to mix the powder particles. For better mixing, a fluidized bed or any other technique which provides good contact of powder surface and plasma can be utilized.

3.3.4 Mass Flow Controller

A mass flow controller (MFC) is used to measure and control the flow of gases. A mass flow controller is designed and calibrated to control a specific type of gas at a particular range of flow rates. The MFC can be given a set point from 0 to 100 % of its full scale range, but is typically operated in the range of 10 – 90 % of its full scale where the best accuracy is achieved. MFCs can be either analog or digital. A digital flow controller is usually able to control more than one type of gas, whereas an analog controller is limited to the gas for which it was calibrated. All mass flow controllers have an inlet port, an outlet port, a mass flow sensor and a proportional control valve. The MFC is fitted with a closed loop control system which is given an input signal by the operator (or an external circuit/computer) that it compares to the value from the mass flow sensors and adjusts the proportional valve accordingly to achieve the required flow. The flow rate is specified as a percentage of its calibrated full scale flow and is supplied to the MFC as a voltage signal. MFCs require the supply gas to be within a specific pressure range. Low pressure will starve the MFC of gas and it may fail to achieve its set point. High pressure may cause erratic flow rates. The heart of a mass flow controller is a thermal sensor. It consists of a small bore tube with two resistance thermometer elements wound around the outside of the tube. The sensor tube is heated by applying an electric current to the elements. A constant proportion of the gas flows through the sensor tube, and the cooling effect creates a temperature differential between the two elements. The change in the resistance due to the temperature differential is measured as the electric signal.

3.3.5 Pressure Gauge

A pressure sensor is required to measure the pressure inside the chamber. Any type of pressure measurement system can be used for this purpose: a pressure transducer or a capacitance manometer.

3.3.6 Vacuum Pump

A vacuum pump is required for generating vacuum inside the chamber. The selection is usually based on factors like: required vacuum level, working pressure range, type of monomers used, etc. As the plasma modification process uses different gaseous chemicals, it will always be good to have a pump that withstands these harsh environments. In addition to this, a particulate and chemical trap aids in preventing transfer of particulate matter and gaseous chemicals to the pump. Small tricks in the pump operation can also help in preventing particulate transfer to the pump. Usually, during the initial stages of vacuum generation, there is viscous flow inside the chamber. And it is during viscous flow that any particulate material is carried to the pump. When the pressure drops below 10^{-1} – 10^{-2} [Torr], there is molecular flow inside the chamber. During molecular flow, no particulate transfer happens. Having a control valve at the pump inlet and its gradual opening aids in preventing particulate transfer to the pump to a certain extent.

3.4 TUMBLER REACTOR

In this section, a tumbler reactor, which is used for plasma surface modification of powders in a relatively large scale, will be discussed. The work described in this thesis was partly carried out in this reactor. It was designed and installed in the Material Sciences Department of the University of Cincinnati, USA. The idea behind the construction of this reactor was to build a plasma reactor for the surface modification of powders, in which a satisfactory contact between the powder and plasma is maintained and also allows treatment of at least 300 g – 500 g of powder[20]. A schematic representation of the tumbler reactor is shown in Fig. 3.7.

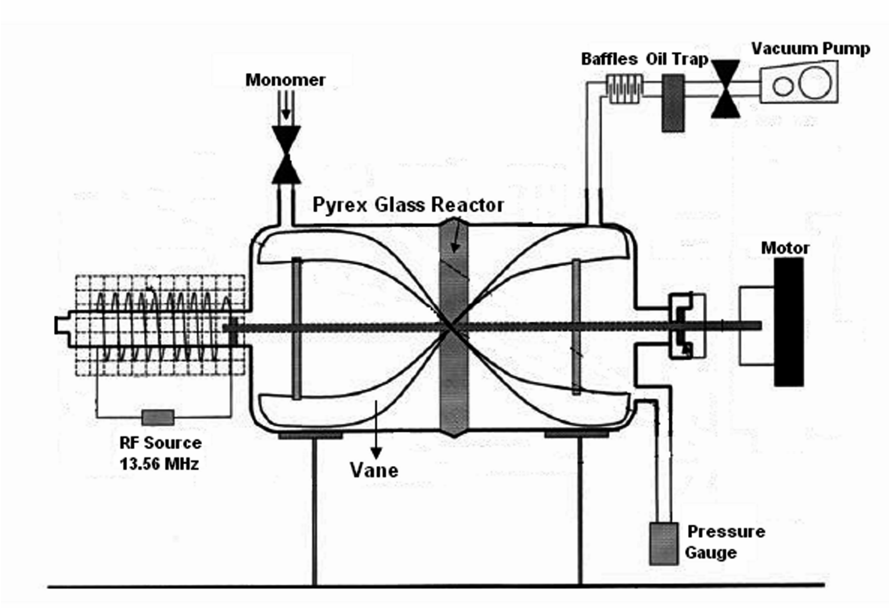


Fig. 3.7 Schematic representation of plasma tumbler reactor[21]

In the tumbler reactor, the powder materials are exposed to RF-plasma in which an organic monomer in injected. The low temperature glow discharge will result in a cold deposition of the monomer onto the material in the form of a polymerised coating. The powders are treated remotely, i.e., away from the most intense glow.

The reactor essentially consists of a Pyrex cylinder chamber of 40 cm length and 20 cm diameter. The powdery materials to be coated are placed at the bottom of the chamber. The plasma is generated through the RF copper coils with 5 – 6 turns rolled over one module of the chamber and is maintained by Radio Frequency energy generated by a Kenwood Transceiver 530 SP (power range from 0 – 100 W) with matching network. Thus, the powders are treated in the remote plasma zone to avoid direct plasma exposure. Carrier gas (can be used optionally) conveys the plasma energy to the deposition area where the reactions with the monomer molecules take place, essentially within the Pyrex cylinder chamber.

Across the centre of the chamber, there is a motor–driven shaft, which can be rotated at variable speed controlled by the motor. Two vanes running in opposite direction are attached to the shaft. As the shaft rotates, these two vanes whirl up the powders at the bottom of the chamber and let the powders fall down gradually, thereby continuously refreshing the powder surfaces to the plasma environment. The vanes are designed in such a way that they not only mix the powders up and down in the chamber, but also push the powders back and forth, hence, increase the mixing efficiency. Since the vanes are conductive and non-sticky to the powders, almost all powder particles fall down before the vanes reach the top of the chamber, where the pumping port is located. This avoids the risk of sending powders to the pump. A powder trap is placed between the pump and the reactor in order to effectively trap any powder particles from going into the pump. The filter is rated from 5 μm particles and has a pressure drop of 6.5 – 13.3 Pa under normal conditions.

Appropriate shielding using a metal mesh outside the chamber is set up to improve the deposition rate of the plasma polymer film by increasing the plasma density within the chamber and to achieve uniform coating on the particles by controlling the plasma shape. Since the metal mesh is conductive, it interferes with the electric field and changes the distribution of the plasma within the chamber.

Facilities in this reactor include monomer introduction for both gases and vapours, a pressure transducer (MKS 627AO1TAC) which can read pressures between 0 and 1000 mTorr, and mass flow controllers from Cole Parmer with a 0 – 100 standard cubic centimeters per minute (sccm) range for air. Airtight O-rings are used at the point where shaft goes into the chamber in order to avoid any leakage. A nylon brush is attached to the edges of the vanes in order to avoid contact problems with the chamber wall.

Characterisation of this tumbler reactor was carried out via the deposition rate measurement of plasma polymer film deposited on silicon wafers under different conditions. Longitudinally, the deposition rate decreases significantly when the plasma moves from the central plasma zone to the remote plasma zone, while remaining constant in the remote plasma zone. With appropriate shielding, the decay in deposition rate in the longitudinal direction can be effectively reduced and a uniform plasma distribution is achieved within the chamber where powders are treated. Radially, at a particular level, the deposition rate on the shaft is generally higher than that on the chamber wall. However, since during the process, powder particles are mixed by the vanes up and down as well as to and fro, hence the opportunities for each particle to visit at different radial positions are almost the same. Therefore, the radial difference in deposition rate will not appreciably affect the homogeneity of the plasma polymer film on the powder surfaces.

3.5 VERTICAL TUBULAR REACTOR

In this section, the development of a vertical tubular reactor at the University of Twente is described. The purpose of this development was to have a plasma facility capable of treating powders at a small scale, in order to perform some screening experiments. For this purpose a basic design of the vertical plasma reactor from the University of Cincinnati was adopted. But some design changes and improvements were made from this basic model. A schematic representation of the vertical tubular reactor is shown in Fig. 3.8.

The reactor essentially consists of a round bottom flask, and attached to it is a long tubular region. The powder particles are kept at the bottom of the round bottom flask. The powders can be stirred with the help of a magnetic stirrer. In order to facilitate good mixing a brush is attached to the magnet so that it helps in mixing the particles thoroughly. An outlet is given from the round bottom flask for the connection to the vacuum pump. Attached to the round bottom flask is a long cylindrical tube. A copper coil of 5 turns is wound over the long tubular region. The coil is kept inside a faraday cage in order to prevent electromagnetic radiation. The coil is further connected to a RF generator via an impedance matching unit. There are two ports on the top of the tubular region. These are slots for connections to the monomer source and for the pressure gauge. The top portion of the tubular part is closed using a glass cover with a vent.

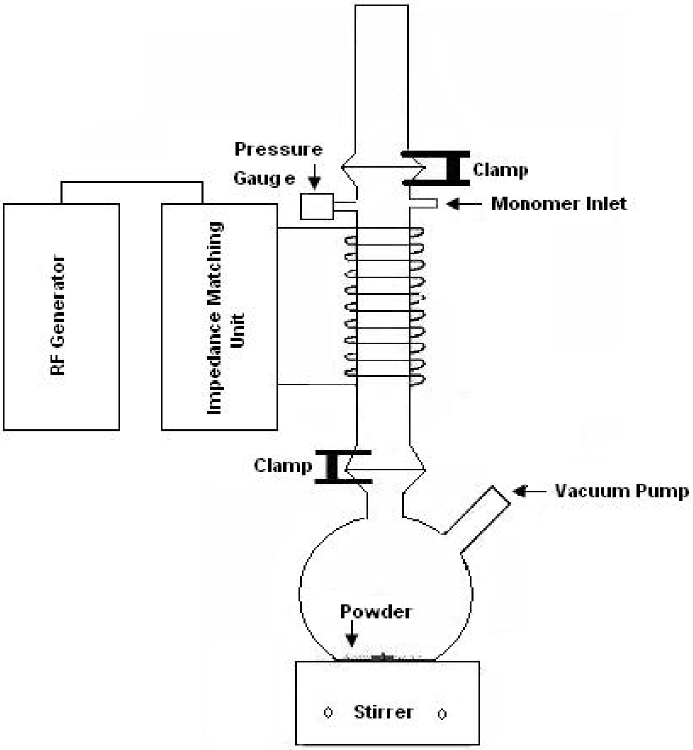


Fig. 3.8 Schematic representation of vertical tubular reactor

3.5.1 Components and Specifications

a. RF Generator

The RF generator is from MKS/ENI, type ACG-3B-01. The specifications are AC-input 100 - 240 V, 50 - 60 HZ, power output 0 - 300 W and frequency 13.56 MHz. The generator has a display with the forward and reverse power levels.

b. Impedance Matching Unit

The impedance matching unit is also from MKS/ENI, type MWH-5.01. This is a digitally controlled impedance matching network for plasma applications. With an accurate auto-tune as well as a fully manual tuning capability, the matching unit ensures controlled RF-power transfer between the RF-generator and the plasma chamber. The matching network operates over a power range of 40 – 500 W at 13.56 MHz. A wide 10- 600 Ω tuning range ensures that the chamber's varying impedance can be matched to the generator's 50 Ω working impedance. The matching network is capable of handling up to 5000 VA of continuous RF-power. The MWH-5.01 consists of two separate assemblies: a tuner unit and a controller unit. The tuner unit contains the matching network whose output impedance is varied by two motor controlled capacitors and a fixed inductor. The controller unit drives the tuner motors in response to the signals from the remote interface or RF-sensors in the tuner unit. The MWH-5.01 uses a microprocessor based control circuit for improved accuracy and tuning precision. For better transfer of power, the unit has to be mounted close to the chamber and connected with short cables. The matching unit requires a 24 V DC-power supply for its working.

c. Plasma Chamber

The chamber is made of Pyrex glass. The round bottom flask has a length of 15 cm. The tubular region is of length 34 cm, with an outer diameter of 10 cm and thickness 5 mm. An outlet for the vacuum pump is available in the round bottom flask. Similarly, two ports are positioned on the long tubular region, one for monomer inlet and the other for the pressure gauge. A vent is arranged at the top portion of the chamber in order to facilitate safe opening of the chamber after the process.

d. Mass Flow Controller

The mass flow controller used in the set up is also from MKS, model 1179B. It incorporates an advanced flow sensor, a control valve and an optimized bypass. The flow controller measures and controls the gas flow rate according to a given set point signal, which may be an analog signal or a digital command. The control range is from 2 % to 100 % full scale. The controller on supply is capable of measuring in the range of 20 – 200 sccm. But this was retuned at MKS lab to the range of 2 – 200 sccm in order to meet our specific process requirements. Upon entering the flow controller, the gas stream passes first through the metering section of the instrument for its mass flow to be measured. The gas moves on through the control valve for its rate of flow to be regulated according to the given set point, and then exits the instrument at the established flow rate. The metering section consists of a sensor tube for ranges $\leq$ 10 sccm (N_2-equivalent) and another sensor tube and parallel by pass for ranges > 10 sccm (N_2-equivalent). The control valve is a specially designed solenoid driven valve. The armature is suspended by two radial springs. This design provides frictionless movement and thus precise control. The control valve is normally closed. The sealing material of the valve plug is typically viton or teflon. The 1179B is connected to a control unit PR 4000, which facilitates control and display of the gas flow to the plasma chamber.

e. Pressure Gauge

A MKS Baratron® type 627B absolute pressure transducer is used for pressure measurements in the plasma reactor. The instrument operates with ± 15 V DC-input at ≤ 250 mA, and provides 0 – 10 VDC output linear with pressure. The 627B transducer permits the use with corrosive or dirty gases and eliminates contamination of the process with transducer materials. Measurements are independent of gas composition. Protection from RF-interference (RFI) and noisy electrical environments is increased by the use of a metal case, by internal design elements and by the use of RFI-filtering on all inputs and outputs. The 627B unit controls its temperature at 45 °C, thereby minimizing the effects of ambient or process temperature variations typically in process line environments. The transducer unit is connected to a display unit PR 4000, which displays the pressure measurements.

f. Display Unit

The mass flow controller and pressure transducer are connected to a 2 channel power supply and read out unit. This is also from MKS, type PR 4000 F. This unit can be used for giving a set point for gas flow, which in turn opens the control valve in the flow controller giving precise control over the process. The unit has two channels and therefore both pressure transducer and flow controller can be connected to it. The unit has a two-line display, which displays the measurements from channel 1 & 2, respectively.

g. Vacuum Pump

A DuoSeal vacuum pump from Welch vacuum is used in the system to generate vacuum, model number 1402 B. This type of vacuum pump has a large oil reservoir to dilute contaminants, coupled with a low pump rotation speed to reduce friction and wear.

A block diagram showing all the connections is shown in Fig. 3.9. A picture of the whole set up is shown in Fig. 3.10. The copper coil is kept inside a faraday cage in order to prevent RF-radiation. As per the original configuration, the power transfer from the RF-generator was not good and therefore plasma generation was difficult. The impedance matching unit was not able to tune in the required tune range. The power generated in the RF-generator was reflected back. Hence the tuning range of the impedance matching unit had to be readjusted to the present configuration. For that purpose a communication was established between a computer and the impedance matching unit. The matching unit was changed into a manual mode of tuning. Then the capacitors inside the matching unit were changed between the positions 0 – 90 using software ENIDS and the forward and reverse power levels were monitored. The optimum values for the capacitors were found in order to have maximum forward power and zero reflected power. The matching unit was switched back to auto tune mode upon which it was able to transfer power from the RF-generator to the coil with zero reflected power. The whole chamber is kept inside a metal box (not in Fig. 3.10) in order to prevent any electromagnetic radiation. This also provides additional safety for the situations arising due to eventual implosion of the pyrex glass chamber.

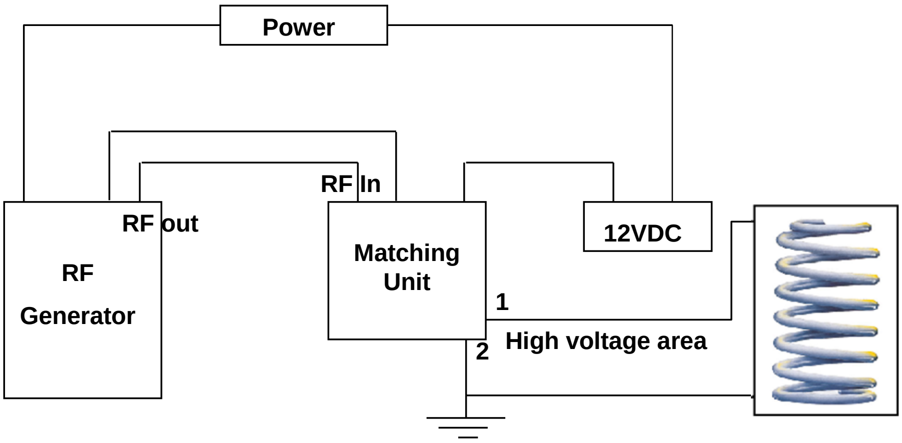


Fig. 3.9 Block diagram showing the connections in the RF vertical tubular plasma reactor

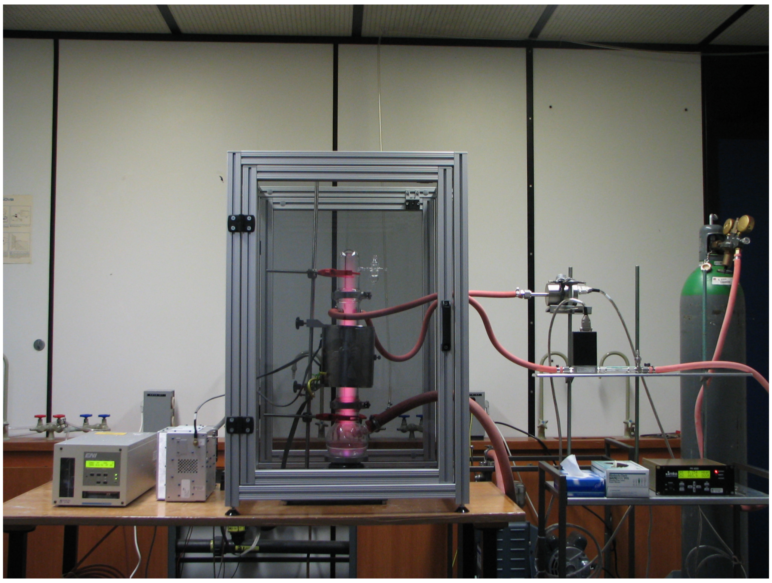


Fig. 3.10 Vertical tubular plasma reactor

3.5.2 Optimisation Experiments

The chamber geometry, position of the coil and monomer inlets, has an influence on the modification process happening inside the reactor. The powder is kept at the bottom of the round bottom flask and is stirred. In order to identify the optimum position of coil and monomer inlet, to obtain good depositions in the area where the substrate is kept, a few optimization experiments were carried out with monomer acetylene. Plasma polymerisation of acetylene yields a brown film on the surface of the substrate. In order to identify the deposition at different locations inside the reactor, a glass strip was put inside the reactor covering the whole length of the chamber. By looking at the deposition obtained at different regions on the glass strip, the position of coil and monomer inlet could be optimized. The process was carried out at 250 W RF-power and at 150 mTorr monomer pressure for 30 min.

***Positions 1 & 2*:**

An initial attempt was made to fix the position of the coil. The possible options were: either it can be placed away from the powder (position 1) or it can be placed close to the powder (position 2). The position of the monomer inlet was kept unchanged during these experiments. For position 1, where the coil is kept away from the substrate, not much deposition was found in the areas close to the substrate. Some deposition was found at the bottom of the chamber. In other areas of the round bottom flask only slight deposition was observed. Hence this is not a good position for the process. For position 2, where the coil is positioned close to the substrate, good deposition was observed throughout the chamber. All areas of the round bottom flask were covered with deposition. Hence keeping the coil close to the substrate would be a better position for carrying out plasma surface modification of the powders.

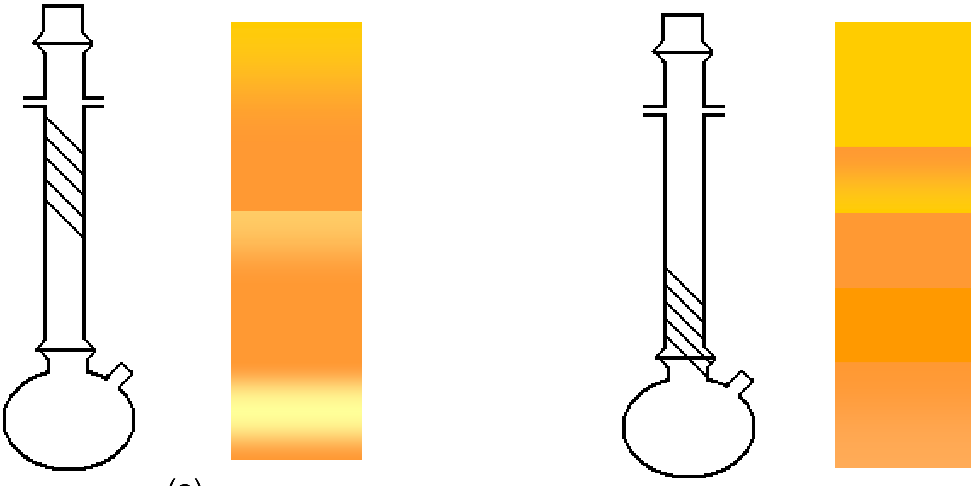

(a)
(b)

Fig. 3.11 Optimisation experiments: a) position 1; and b) position 2

Positions 3, 4 & 5:

After fixing the position of the coil close to the substrate, experiments were carried out to find out the optimum position for the monomer inlet. The options were keeping the monomer inlet as in position 2, monomer inlet below the coil (position 3), monomer inlet above the coil (position 4) and monomer inlet in an intermediate position between 2 & 4. In the case of position 3, during the initial stages of the process itself, plasma polymerised acetylene started to deposit in the form of powder. Some amount of film deposition was also observed along with the rapid powder formation. Powder formation in plasma polymerisation is not new. Several reports mention powder formation in a plasma polymerisation process[2,3]. Powder is formed in a plasma by the reaction in the gas phase, as opposed to reaction at the interface of gas and surface for film formation. Conditions which promote powder formation include intermediate pressure, high flow rate, long residence times, high power, monomers with a rapid reaction rate and conditions that suppress ionic bombardment of surfaces. However, the exact reason for the powder formation in the present case was not investigated, as it was outside the scope of the work. The relevant information for the present case is that this particular position is not suitable for plasma surface modification.

In the case of position 4, the situation was already better. More film deposition was observed during the process. However, a small amount of powder formation was still observed. For that reason this particular position was also not considered appropriate for carrying out further experiments.

In the case of position 5, good film deposition was observed throughout the length of the chamber except on the top part. Neat film deposition was observed in the region of the round bottom flask. Hence this is the best position for carrying out the plasma surface modification process.

Based on these experiments two positions: positions 2 & 5, were identified as suitable positions for carrying out the plasma surface modification of powder substrates in the vertical tubular reactor.

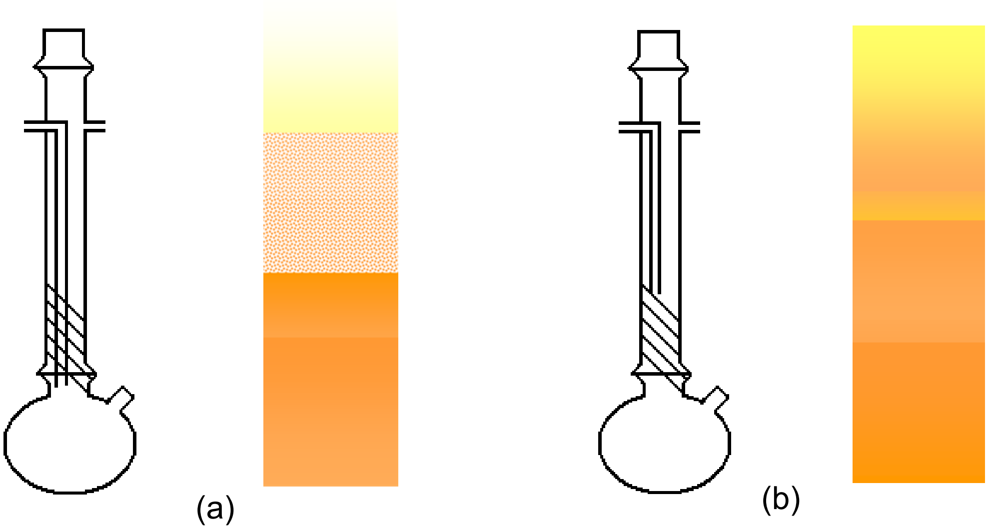


Fig. 3.12 Optimisation experiments: a) position 3; and b) position 4

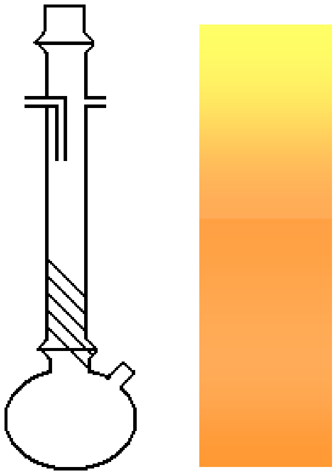


Fig. 3.13 Optimisation experiment position 5

3.6 CHARACTERISATION OF ACETYLENE PLASMA POLYMER

The plasma polymer formed from acetylene monomer was characterised using Thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The TGA-data provide the thermal behaviour of the neat plasma polymerised acetylene and XPS provides the chemical composition.

3.6.1 Thermogravimetric Analysis

A Perkin Elmer TGA was used for thermogravimetric analysis of the samples. The samples were heated from 50 °C to 800 °C at 10 °C/min in an air atmosphere. The TGA-thermogram of pure plasma-polymerised acetylene is shown in Fig. 3.14. Pure plasma-polymerised acetylene starts to decompose at 265 °C and the decomposition is complete at 600 °C.

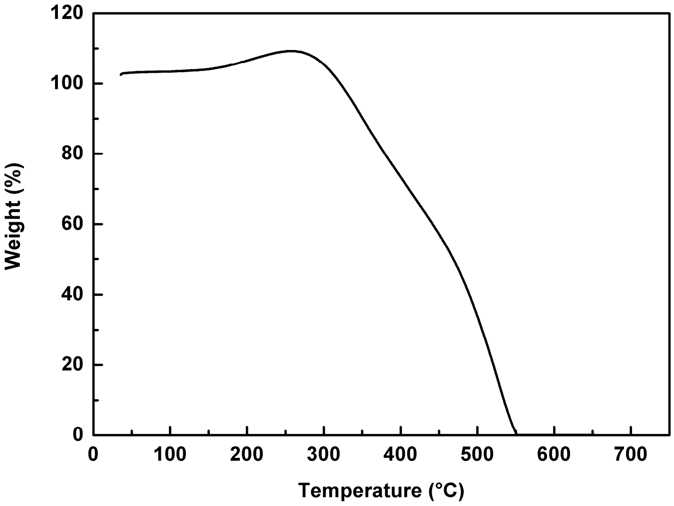


Fig. 3.14 TGA thermogram of plasma polymerised acetylene

3.6.2 X-ray Photoelectron Spectroscopy

XPS-analysis was performed on a Quantera XPS from Physical Electronics equipped with an Al Kα X-ray source (1486.6 eV). The plasma polymer powder samples were deposited onto an indium foil, which was then loaded onto the sample holder. Pass energy for the survey scans was 224 eV and that for the elemental scans was 55 eV. The XPS-spectrum for pure plasma-polymerised acetylene is shown in Fig. 3.15. The spectrum shows the presence of carbon as a peak at binding energy value 284.5 eV. In addition, an oxygen peak is observed at binding energy value 532.4 eV. The atomic concentration of carbon was 87.83 % and that of oxygen was 12.17 %. This means that oxidation of the plasma-polymerised acetylene has taken place after the process. This is possible due to the presence of radical sites on the surface of the plasma polymer film. This of course is one of the important characteristics of a plasma polymer[2]. Large quantities of radicals are trapped in the polymer during the process. Although the amount varies with the type of monomer and the conditions of the plasma polymer, it is always safe to consider that plasma polymers contain a certain amount of trapped radicals on their surface. The plasma polymers when exposed to normal conditions after the process, give rise to the presence of oxygen containing functionalities on their surface as evidenced from the XPS data.

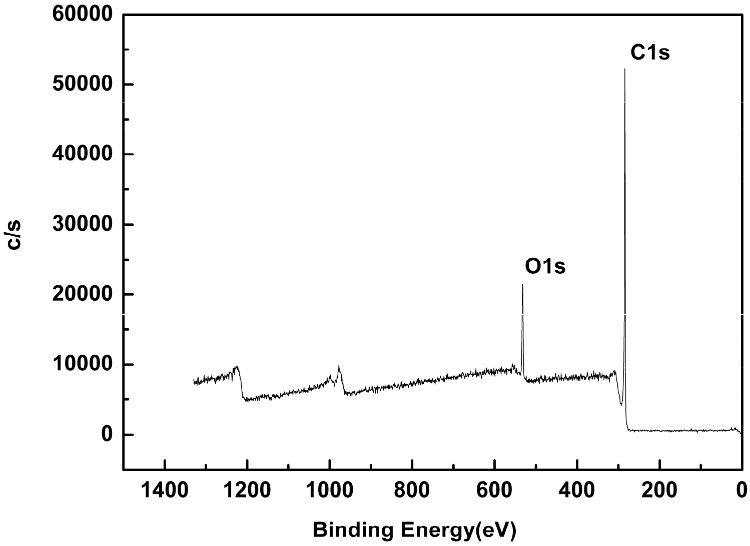


Fig. 3.15 XPS-spectrum of pure plasma-polymerised acetylene

3.7 CONCLUSIONS

The design of a plasma reactor for surface modification has to take care of the mixing of powder substrates so as to expose and refresh the powder surface to the plasma environment. A vertical tubular reactor for powder surface modification on a small scale was successfully installed and tested. Optimisation experiments carried out show that positions 2 and 5 are suitable for carrying out surface modification experiments. The plasma polymer formed during the process is thermally stable. On exposure to atmospheric conditions the plasma polymer is easily oxidised, resulting in oxygen functionalities on its surface.

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Chapter 4

Surface Modification of Carbon Black by Plasma Polymerisation*

Carbon black is widely used as an active filler in the rubber industry to improve the physical properties of rubber. The surface energy of carbon black is high compared to various elastomers like Styrene – butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene – Propylene Diene rubber (EPDM). The work aims at reducing the surface energy of carbon black by modifying its surface for applications especially in rubber blends. Experiments are carried out to look into the possibilities of using plasma polymerisation as a surface modification technique for carbon black and are described in this chapter. Thermogravimetric analysis (TGA), wetting behaviour with liquids of known surface tension and time – of – flight secondary ion mass spectroscopy (ToF-SIMS) are used to characterise the carbon black before and after modification. The study shows that surface modification of carbon black by plasma polymerisation is difficult in comparison with silica, unless treated for long duration. The mechanistic aspects of surface modification and the importance of active sites on the carbon black surface for effective modification are discussed in this chapter.

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* The work presented in this chapter has been published in Plasma Chemistry and Plasma Processing 28, 273 (2008).

4.1 INTRODUCTION

Carbon black is widely used as an active filler in the rubber industry to improve the physical properties of elastomers[1]. Dispersion and distribution of carbon black in the rubber matrix are important factors for achieving optimum physical properties. The behaviour of carbon black in rubber depends mainly on the particle size, surface area, aggregate structure and size, nature of the surface and its activity. Filler-filler and filler-polymer interaction are important factors involved in the dispersion of the filler and reinforcement of the rubber by the filler. A higher filler-filler interaction is marked by a poor dispersion state. The affinity of carbon black towards different elastomers determines the polymer–filler interaction.

During mixing of carbon black with rubber, after incorporation, distributive and dispersive processes control the dispersion quality. After an initial breakdown of the macroscopic filler pellets, the wettability of the filler and its interaction with the rubber play an important role towards achieving a good dispersion state. The wettability of a filler particle by a polymer chain can be quantified in terms of surface energy. The surface energy of a filler in turn depends on the physico-chemical composition of its surface. In order to have a good compatibility, the surface energy difference between the filler and rubber should be low. With a large surface energy difference between filler and rubber, the filler-filler interaction increases, which in turn has a negative influence on the stability of the dispersion state attained during mixing. In the case of carbon black, the surface energy is high compared to that of various elastomers like Styrene-Butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene-Propylene-Diene rubber (EPDM). It is also worth to mention that the surface energy of silica, another filler used in the rubber industry, is even higher than that of carbon black, which corresponds to an even stronger filler-filler interaction than for carbon black[2].

It is possible to tailor the surface properties of a filler. Plasma polymerisation has emerged as a surface modification technique for metals, polymers and powders. The technique involves electric field bombardment of monomer molecules, thereby creating active monomer species, which then react with the surface to form a film over the substrate. As a result, the surface properties of the substrate change dramatically. By suitable selection of monomers, a substrate can either be made hydrophobic or hydrophilic. Plasma polymerisation can be carried out at ambient temperature and does not require any solvents for the process, making it a clean process.

Contrary to the vast amount of information available on plasma deposition on flat surfaces[3,4], there are only a few reports on the deposition on powder substrates. Powders are difficult to handle in plasma treatment, mainly because of aggregation and the large surface area per unit mass of the powder. Inagaki *et al.*[5] reported surface modification of polyethylene powders using a fluidised bed. Later, van Ooij *et al.*[6-8] reported surface modification of various powder substrates using different reactors, which included a vertical tubular reactor, a tumbler reactor and a fluidised bed reactor.

The extension of plasma polymerisation as a surface modification technique for fillers like carbon black and silica for application in rubber happened quite recently. Nah *et al.*[9,10] reported plasma polymerisation on silica and its effect on rubber properties. Borros *et al.*[11,12] reported modification of various curatives like sulphur and cyclohexylbenzothiazole sulphenamide. Donnet *et al.*[13] have reported on the plasma treatment of graphitised carbon black using reactive gases. Their study showed that after plasma treatment the graphitised surface appeared to be more like that of regular carbon black than that of graphite. Akovali *et al.*[14] and Tricas *et al.*[15,16] reported the modification of carbon black by plasma polymerisation. The monomers used for the process were styrene, butadiene, and acrylic acid. Their findings led to the conclusion that carbon black was modified successfully, with the coating covering all sites on the surface. Kang *et al.*[17] also reported on the modification of carbon black by plasma polymerisation and concluded that it is possible to manipulate the surface properties.

The present work looks into the possibilities of plasma polymerisation as a surface modification technique for carbon black, with the aim of reducing its surface energy, by applying a hydrophobic coating over the surface. The monomer chosen for this purpose is acetylene. The modified filler is characterised by thermogravimetric analysis (TGA), wetting behaviour with various liquids of known surface tension and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In this paper we report on the mechanistic aspects of surface modification and on the importance of active sites on the surface of carbon black for an effective surface modification by plasma polymerisation. For reason of comparison some experiments on a silica sample are included.

4.2 EXPERIMENTAL

4.2.1 Materials

The type of carbon black chosen for the modification process was carbon black N330 in the fluffy state, as supplied by Degussa AG, Germany. The surface area of the N330 carbon black was 83 m^2/g (BET-nitrogen adsorption surface area). The type of silica used in the comparative experiments was a rubber grade - Hi Sil 233, as obtained from PPG, USA, for which the surface area was 152 m^2/g. The monomer used for plasma polymerisation was acetylene (99.6% purity), as supplied by Matheson tri gas, USA.

4.2.2 Methods

4.2.2.1 Plasma Polymerisation

Plasma polymerisation was carried out in a Radio frequency (RF) plasma tumbler reactor at the University of Cincinnati, Ohio, USA[6]. A schematic representation of this reactor is shown in Fig. 4.1. After introduction of the powder, the chamber was evacuated to a pressure of 10 Pa. Then monomer was injected into the reaction chamber under steady flow conditions, maintaining the monomer pressure inside the chamber at 20 Pa. Subsequently, RF-power was applied. The frequency was 13.56 MHz. The conditions of the process were varied as given in Table 4.I. The powder samples were mixed inside the chamber with the help of two vanes running in opposite directions on a shaft inside the chamber. This aids in exposing the powder particles to the plasma, in order to obtain uniform modification all over their surface.

Table 4.1 Experimental Conditions Employed for the Plasma Polymerisation

Sample Code	RF Power (W)	Monomer Concentration (Pa)	Treatment Time
N330-1	30	20	1 hr
N330-2	60	20	1 hr
N330-3	90	20	1 hr
N330-4	90	40	1 hr
N330-5	90	40	4 hr
Silica	90	40	1 hr
Metal Plate	60	20	15 min

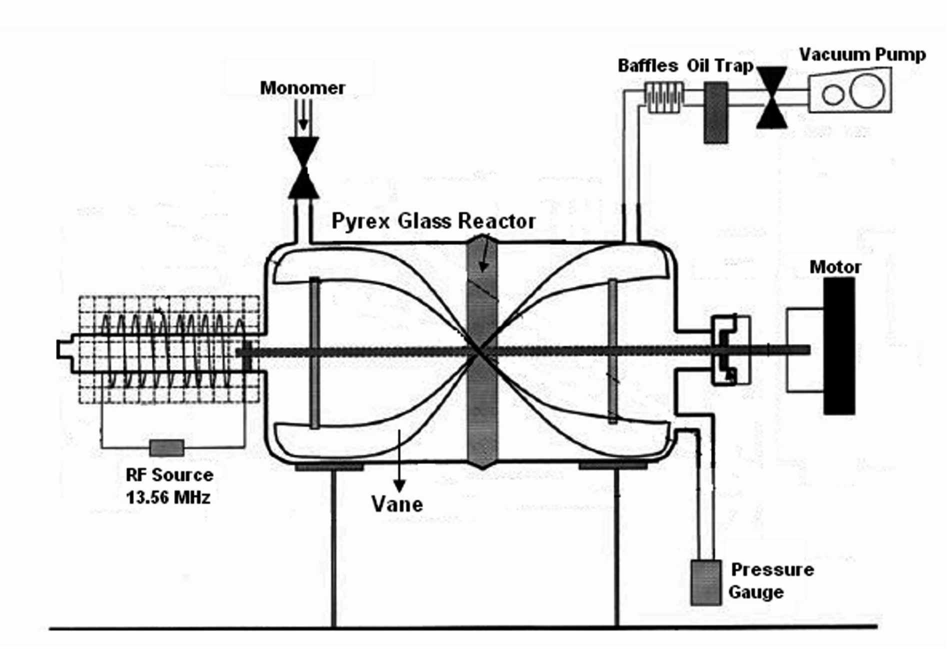


Fig. 4.1 Schematic representation of tumbler reactor

4.2.2.2 Thermogravimetric Analysis

A Perkin Elmer TGA was used for thermogravimetric analysis of the samples. The samples were heated from 50 °C to 800 °C at 10 °C/min in an air atmosphere. The thermal degradation behaviour of pure plasma polymerised acetylene was first studied. Acetylene plasma-polymer powder obtained in one of the optimisation experiments (described in chapter 3) was used for this purpose. Pure plasma polymerised acetylene starts decomposing at 265 °C and the decomposition is complete at 600 °C. Based on this, the weight losses for the coated and uncoated carbon blacks were calculated in this region of decomposition of plasma polymerised acetylene. The difference in weight loss between the coated and uncoated samples corresponds to the amount of coating deposited on the surface of the carbon blacks.

4.2.2.3 Wetting Behaviour with Liquids of Known Surface Tension

Wetting behaviour of the modified and unmodified powders with liquids of known surface tension was observed in order to semi-quantitatively characterise the degree to which modification had taken place. For this purpose, 50 ml of liquid was put in a glass beaker and 1-2 g of sample was added to the liquid. Depending on the surface energy of the powder, it will either sink or float on the liquid. The wetting behaviour gives an idea about the range over which surface energy has been reduced.

4.2.2.4 Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

In order to study the surface composition of the coated carbon blacks, ToF-SIMS measurements were carried out. ToF-SIMS is a very sensitive surface analysis technique, which especially looks at the uppermost layers of the surface. The measurements were carried out in an Ion-Tof Cameca ToF-SIMS IV machine. The carbon black powder samples were deposited on an indium foil, which was then loaded on to the sample holder. The system vacuum was maintained at between 10^{-7} and 10^{-9} mbar. Monoisotopic Gallium (^{69}Ga) ions were used as the primary ion source and the primary ion source energy was 25 kV. The ion current was kept in the range 1.5-2.5 µA. The total integrated ion dose was ≈ 10^{10} ions/cm^2.

4.3 RESULTS

The plasma reactor is based on the tumbling of powders in a cylindrical chamber into which an organic monomer is introduced to produce low temperature plasma, which results in the deposition of plasma polymerised film on the powder surface. Powders are treated in the remote plasma zone i.e., away from the most intense glow. In the remote plasma zone there will be more radicals than electrons and ions, because of the life time differences. In a pioneering work, characterisation of this tumbler reactor has been carried out via the deposition rate measurements of plasma polymer film deposited on silicon wafers under different conditions[18]. Longitudinally, the deposition rate decreases significantly when it moves from the central plasma zone to the remote plasma zone, while remaining constant in the remote plasma zone. With appropriate shielding, the decay in the deposition rate in the longitudinal direction can be effectively reduced and a uniform plasma distribution is achieved within the chamber where powders are treated. Radially, at a particular level, the deposition rate on the shaft is generally higher than that on the chamber wall. However, since during the process powder particles are mixed by the vanes up and down as well as to and fro, hence the opportunities for each particle to visit at different radial positions are almost the same. Therefore, the radial difference in deposition rate will not appreciably affect the homogeneity of the plasma polymer film on the powder surfaces.

The TGA thermogram of plasma polymerised acetylene is shown in Fig. 4.2. The decomposition starts at 265 °C and is complete at 600 °C. The TGA thermograms of the various coated and uncoated carbon black samples are shown in Fig. 4.3. The weight loss in the region of decomposition of plasma polymerised acetylene was calculated from the thermograms of the coated and uncoated carbon blacks. The difference in weight loss of the coated and uncoated carbon black samples corresponds to the weight of the plasma polymerised acetylene film deposited on the surface of carbon black. The calculated weight losses of various treated carbon black samples are mentioned in Table 4.2. The 1hr treated samples show only a little amount of deposition. The 4 hr treated carbon black sample shows an increased weight loss, indicating that there is a more than proportional deposition as treatment time is increased.

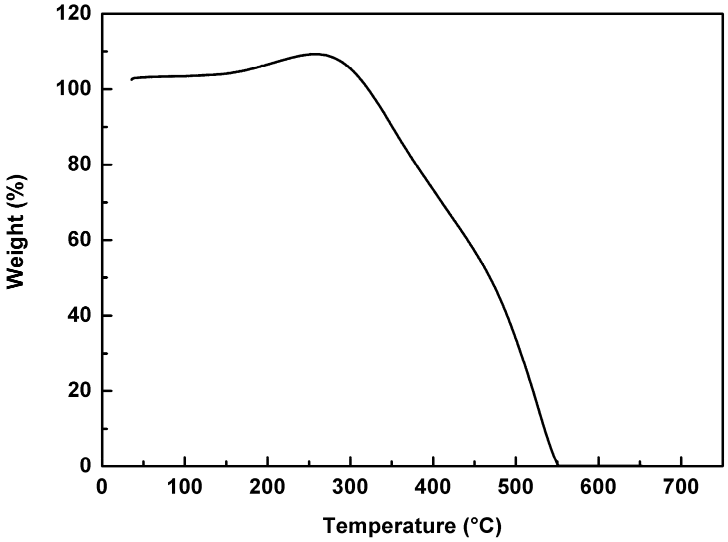


Fig. 4.2 TGA thermogram of pure plasma polymerised acetylene

Table 4.2 Calculated Weight Losses for Various Powder Samples

Sample Code	Weight Loss (%)
N330-1	1.02
N330-2	1.37
N330-3	0.35
N330-4	2.32
N330-5	17.6
Silica	5.12

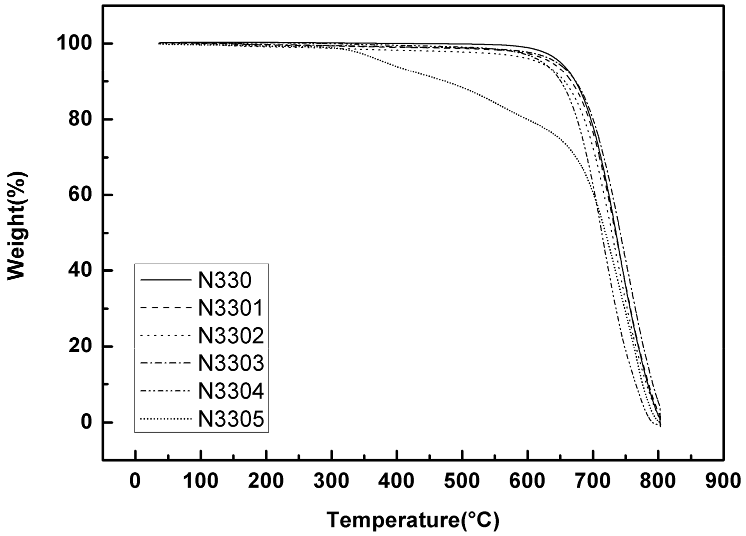


Fig. 4.3 TGA thermograms of plasma coated and uncoated carbon black samples

For a liquid to wet a particular surface, the surface energy of the liquid has to be lower than that of the substrate. The wetting behaviour of carbon black samples in liquids of known surface tension gives an indication about the range over which the surface energy has been reduced. The wetting behaviour of coated and uncoated carbon black samples are summarised in Fig. 4.4. After the formation of the plasma polymerised acetylene film, the surface of carbon black should show characteristics corresponding to the formed acetylene film: a lower surface energy**.** This also depends on the surface coverage of the film. All 1hr treated carbon black samples show a slight reduction in surface energy, without differences amongst the separate samples. The 4 hr treated carbon black shows an appreciable reduction in surface energy, which corresponds with the substantial deposition as already evident from the TGA results.

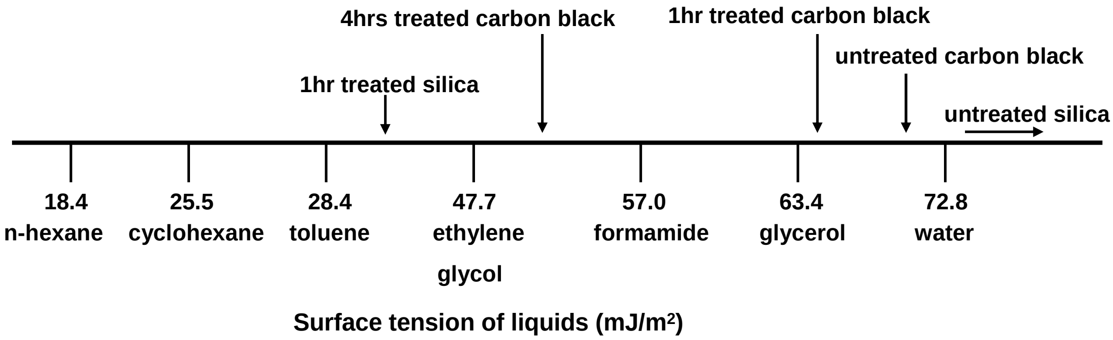


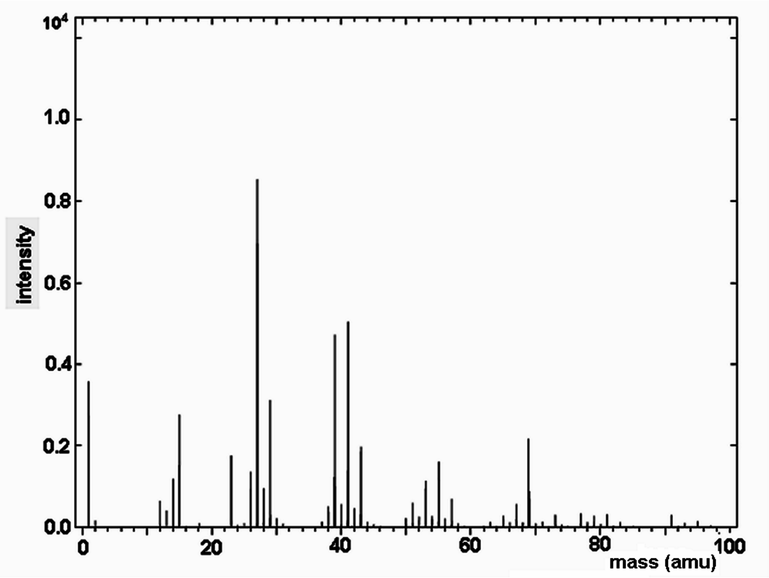
Fig. 4.4 Schematic representation of wetting behaviour of treated carbon blacks and silica

Plasma polymerisation of acetylene will result in the formation of a crosslinked hydrocarbon film. In a positive ToF-SIMS spectrum, such a hydrocarbon must show a cluster pattern of mass fragments, especially in the higher mass fraction regions[19]. The ToF-SIMS spectrum of untreated carbon black is shown in Fig. 4.5. The SIMS spectrum of untreated carbon black displays some hydrocarbon peaks and a signal corresponding to Na^+. This is characteristic of a carbon black surface. Detailed studies of carbon black surface using ToF-SIMS have been reported earlier by Poleunis *et al*[20]**.** A ToF-SIMS spectrum of a representative 1hr treated carbon black sample (N330-2) is shown in Fig. 4.6. For comparison purposes, acetylene was plasma polymerised on to a metal plate under the same conditions as used for carbon black and the ToF-SIMS spectrum of such a film was also taken: Fig. 4.7. Peak assignments for some significant peaks are listed in Table 4.3[21]. The spectrum obtained for the plasma polymerised acetylene film shows the presence of highly intense peaks corresponding to the hydrocarbon composition. Also in the higher mass fraction regions, the spectrum shows a cluster pattern of mass fragments typical of hydrocarbons, thereby confirming the formation of a neat hydrocarbon film on the surface of the metal plate.

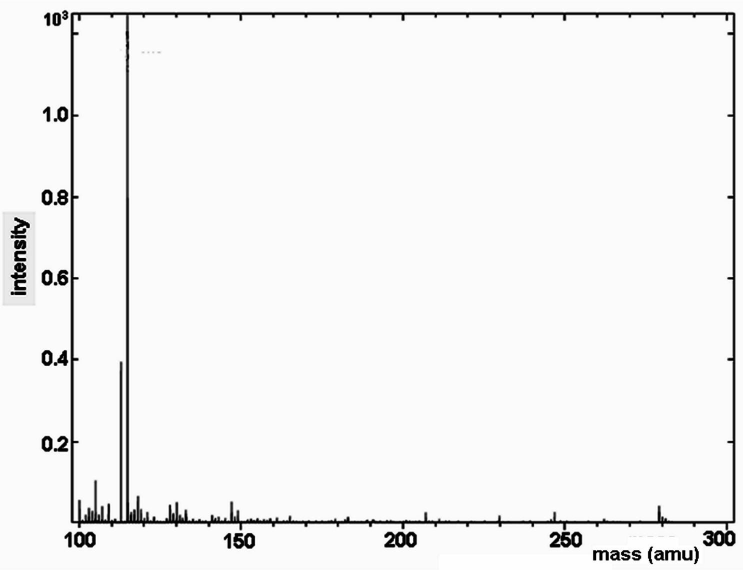
Table 4.3 Ion Fragments in Positive ToF-SIMS Spectra

Mass (amu)	Composition
1^+	H^+
15^+	CH_3^+
26^+	$C_2H_2^+$
27^+	$C_2H_3^+$
29^+	$C_2H_5^+$
39^+	$C_3H_3^+$
41^+	$C_3H_5^+$
43^+	$C_3H_7^+$
55^+	$C_4H_7^+$
69^+	Ga^+
91^+	$C_7H_7^+$
114^+	In^+

The ToF-SIMS spectrum of the 1hr treated carbon black shows less intense hydrocarbon peaks and shows only a small extent of cluster patterns in the higher mass fraction regions. This, combined with the lower deposition levels as seen from TGA results and only a slight reduction in surface energy from wetting behaviour, points towards the fact that deposition may have happened only locally without formation of a complete film over the surface.



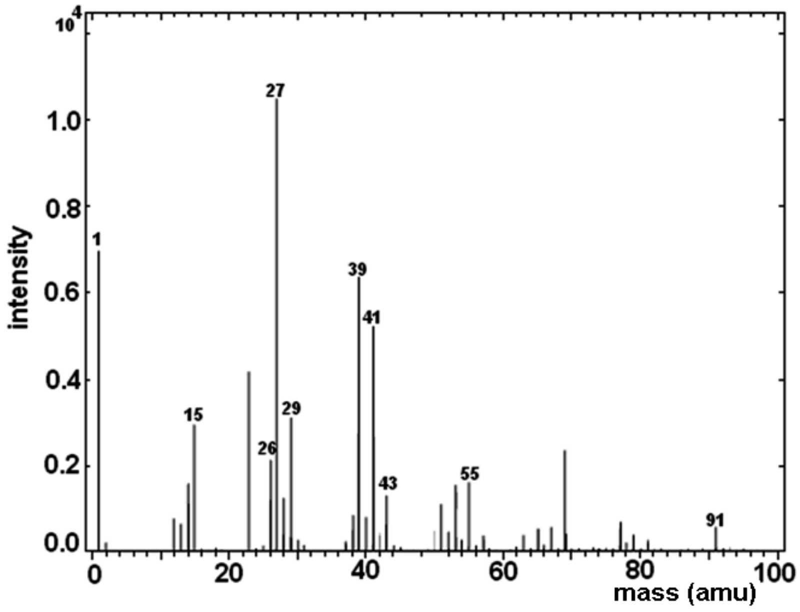
(a)



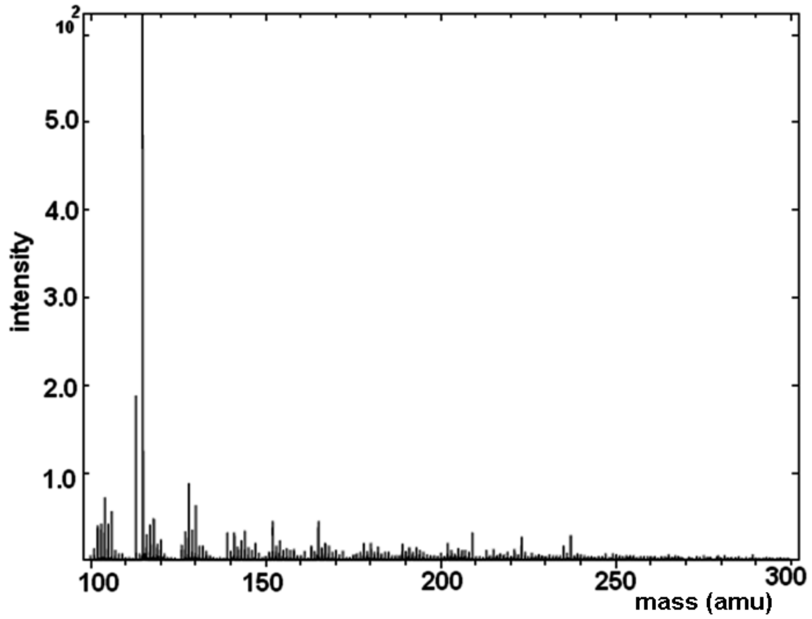
(b)

Fig. 4.5 ToF-SIMS Spectrum of untreated carbon black (N330); a) mass range 0-100 (amu); b) mass range 100-300 (amu).

Plasma polymerisation on powder substrates is usually different from that on a flat surface. Factors like the higher specific surface area of the powder and duration of surface exposure to plasma contribute to this difference. Due to the large surface area, the monomer concentration around the powder surface is much lower compared to that around a flat surface. The growth of the plasma polymer on powder surface is slowed down because the monomer and radicals around the powder surface are depleted and exhausted. Hence the plasma polymerisation on powder substrates proceeds in a monomer-lean region. Therefore, two more experiments were carried out on carbon black at a higher monomer concentration and at longer treatment time. The conditions for the processes are mentioned in Table 4.1.

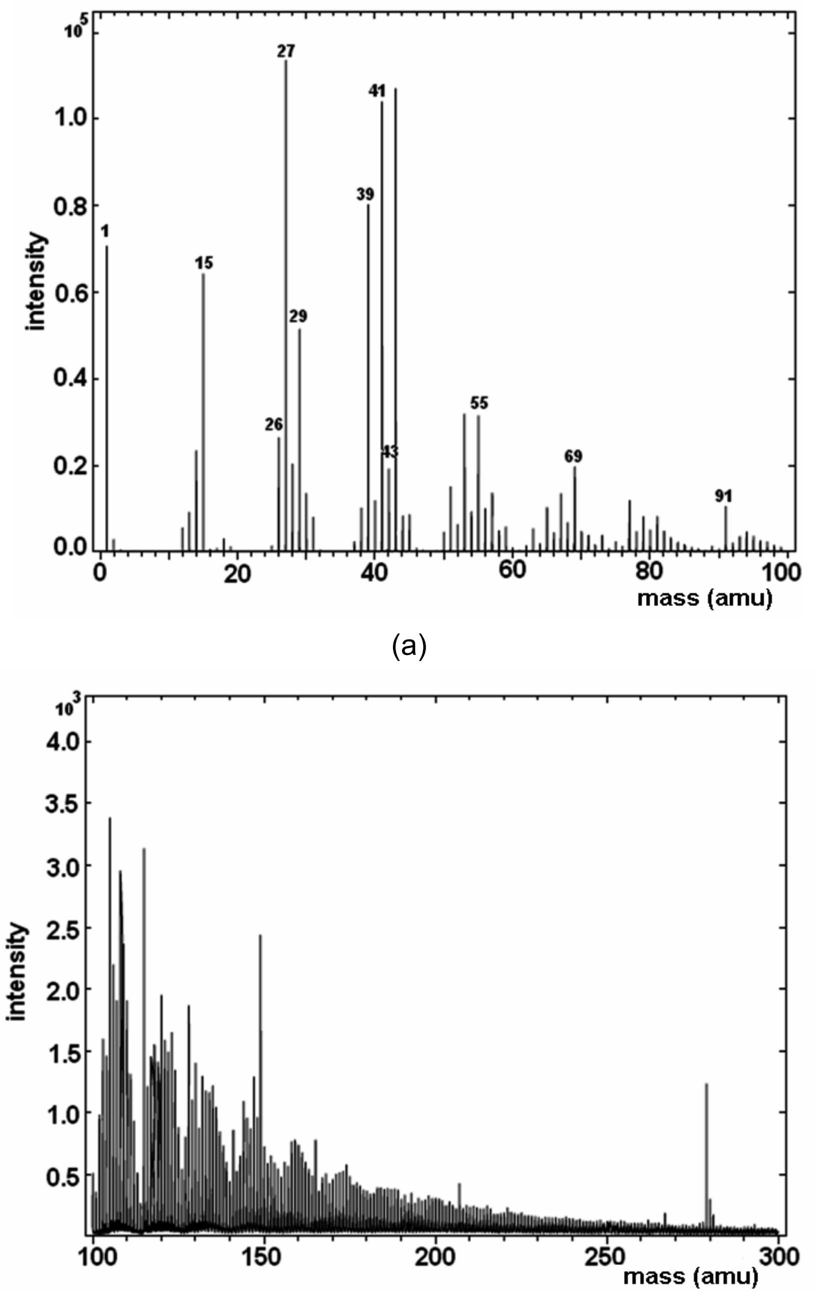


(a)



(b)

Fig. 4.6 Positive ToF-SIMS spectrum of representative carbon black treated for 1hr (N330-2) a) mass range 0-100 (amu); b) mass range 100-300 (amu).

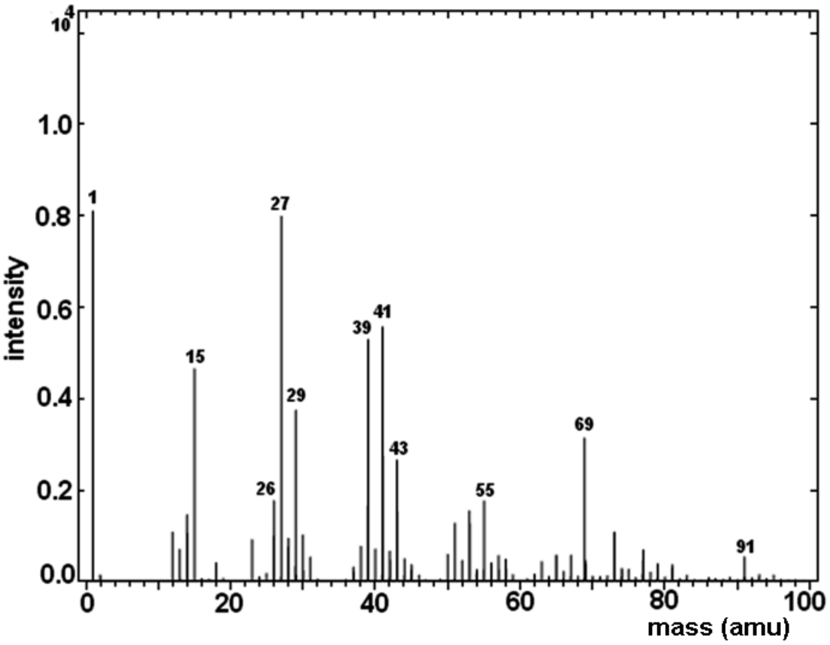


(a)

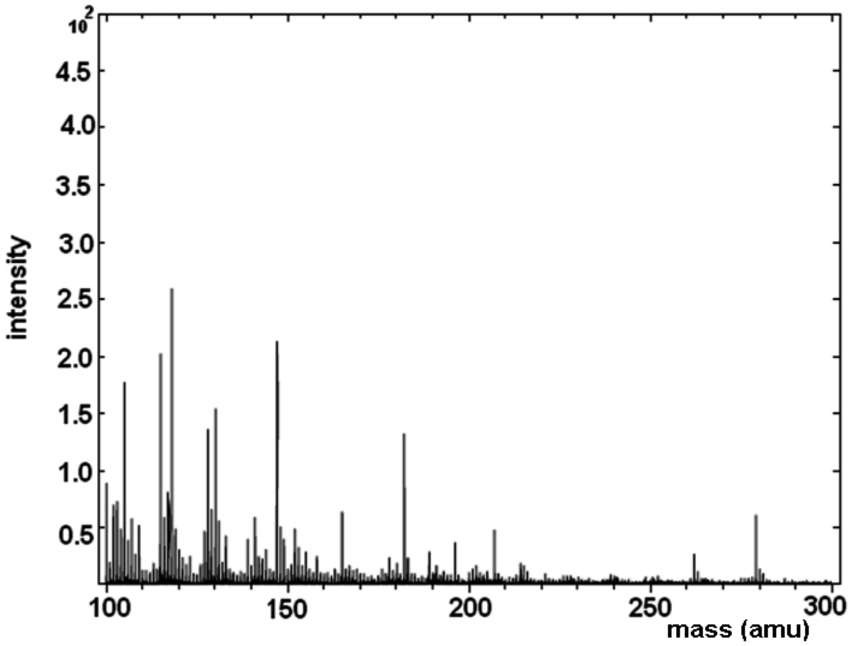
(b)

Fig. 4.7 Positive ToF-SIMS spectrum of plasma polymerised acetylene on a metal plate; a) mass range 0-100 (amu); b) mass range 100-300 (amu).

The ToF-SIMS spectrum of the carbon black treated at a higher monomer concentration is shown in Fig. 4.8: no significant improvement in the cluster pattern behaviour can be observed. The spectrum of the 4-hr treated carbon black (N330-5) is shown in Fig. 4.9. It shows a clearer cluster pattern, indeed indicating a better coverage of the plasma polymer on the surface than for the 1hr treated sample. However, the development of a cluster pattern as seen in Fig. 4.7 is still in no way achieved. A siloxane contamination in a ToF-SIMS was observed on the carbon black surfaces, especially on the 4-hr treated sample: Fig. 4.9. Peaks at 73 amu ($C_3H_9Si^+$) and 147 amu ($C_5H_{15}OSi_2^+$) corresponds to the siloxane contamination.



(a)



(b)

Fig. 4.8 Positive ToF-SIMS spectrum of carbon black treated for 1hr at a higher monomer concentration (N330-4); a) mass range 0-100 (amu); b) mass range 100-300 (amu).

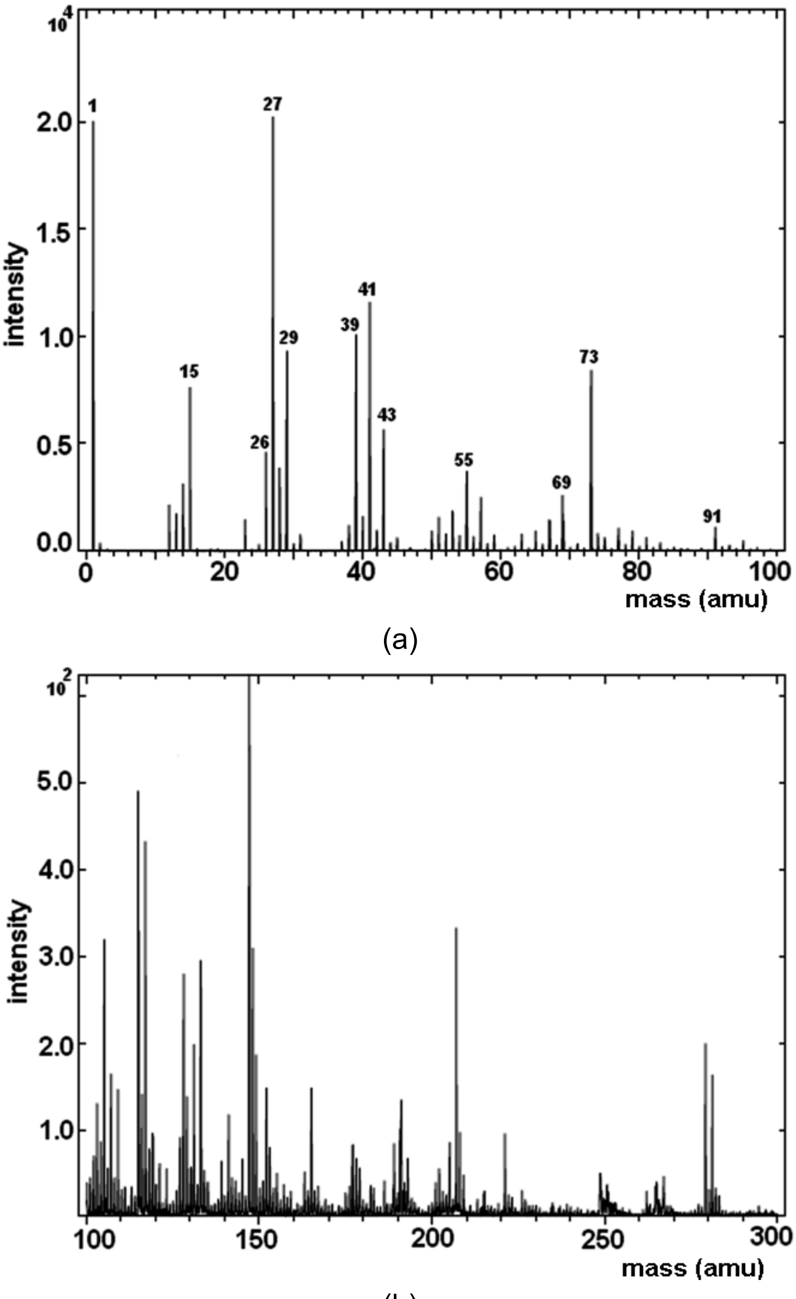
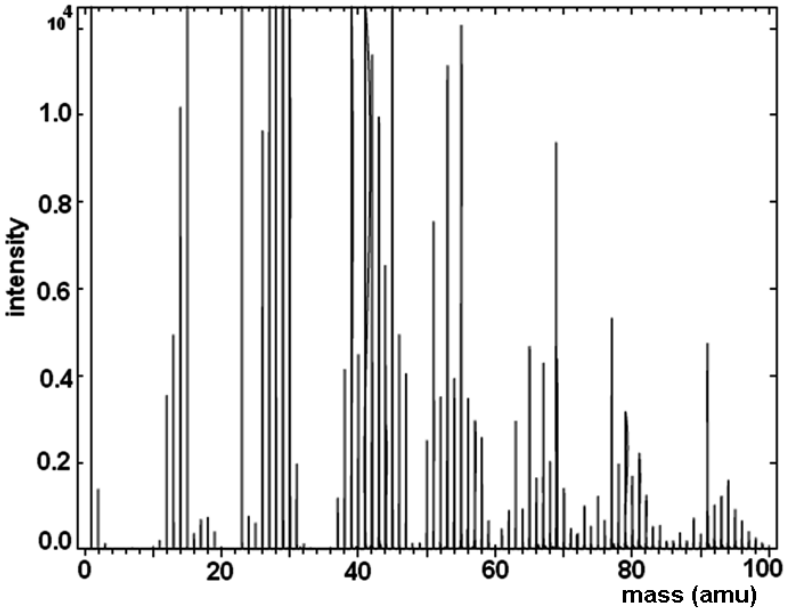
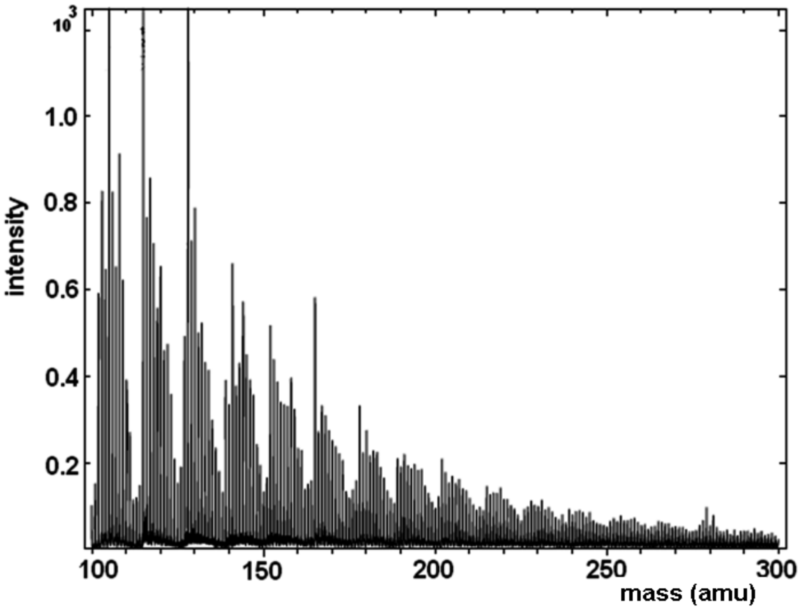


Fig. 4.9 Positive ToF-SIMS spectrum of carbon black treated for 4-hr (N330- 5); a) mass range 0-100 (amu); b) mass range 100-300 (amu).

Based on the above observations it is clear that carbon black shows a low tendency for plasma polymer deposition on its surface. In order to quantify this in more detail, a comparative experiment was carried out on the behaviour of silica, another filler commonly used in rubber. The experiment was carried out on silica under the conditions mentioned in Table 4.1. A 1hr treatment on silica gave an appreciable reduction in surface energy, as seen in the wetting behaviour of this sample shown in Fig. 4.4. The ToF-SIMS data also support a strong modification, by the observation of very good cluster pattern, especially in the higher mass fraction regions of the SIMS spectrum: Fig. 4.10.



(a)



(b)

Fig. 4.10 Positive ToF-SIMS spectrum of silica treated for 1-hr; a) mass range 0-100 (amu); b) mass range 100-300 (amu).

4.4 DISCUSSION

It may be concluded that some modification has occurred on the surface of carbon black by deposition of plasma polymerised acetylene, but the extent of modification is very little in comparison with the ease with which silica could be modified. The ToF-SIMS results show that silica, which has a surface area of 152 m^2/g, double the amount of experimental carbon black N330 (83 m^2/g), under similar conditions of plasma polymerisation gives much better modification. The wetting behaviour of the silica sample shows an appreciable reduction in surface energy. It clearly shows that a plasma polymerised acetylene film with a good coverage is formed on the surface of the silica.

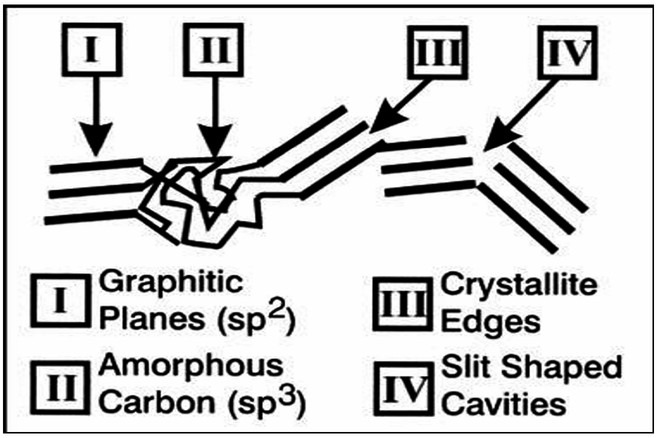


Fig. 4.11 Schematic representation of carbon black surface[22]

The surface of carbon black is known to consist of graphitic planes (site I), amorphous carbon (site II), crystallite edges (site III) and slit shaped cavities (site IV)[22]: Fig. 4.10. The conduction electrons associated with the graphitic structure play an important role in the amount of energy associated with these sites. Recently, Schröder *et al.*[22-24] quantified the different energies at these sites on the surface of carbon black by analysing adsorption isotherms of various molecules. According to their analysis, particularly the crystallite edges (III) and slit shaped cavities (IV) on the surface of carbon black are the sites of high concentration of π-electrons. These sites are most important with respect to rubber-filler and filler-filler interaction. Furthermore, the surface of carbon black is also covered with functional groups like carboxyl, phenol, lactones and quinonic groups[25]. These are preferably located at the edges of the graphitic basal planes or at the crystallite edges. For furnace carbon blacks, the concentration of these active sites (II-IV) varies between 5-20% on the surface, and the other 95-80% contribution is from graphitic planes (site I). Furnace carbon blacks with higher specific surface area and lower primary particle size has more fractions of these energetic sites (sites II-IV): Fig. 4.10. As the surface area reduces and particle size increases, the fraction of these sites decreases. Carbon black N330 has approximately 10% of type II, III and IV sites and the remaining 90% of the surface consists basically of graphitic planes.

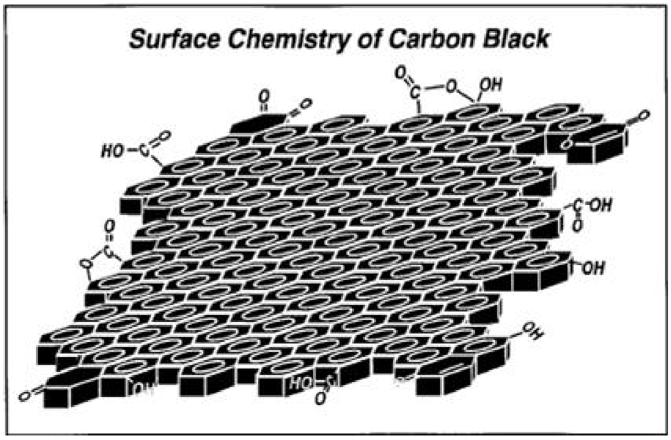


Fig. 4.12 Schematic representation of Carbon black surface[25]

The excitation of gaseous molecules in the plasma generates active species like electrons, protons, excited molecules, ions etc. The energy required for the formation of a free radical is 3-4 eV, whereas the energy required for the formation of ions is 9-13 eV. The average electron energy in a low pressure discharge is in the range of 2-5 eV [26,27]. This energy is sufficient to break almost all types of bonds. Typical bond energies are given in Table 4.4. As soon as a plasma is generated, the substrate or any other surface around it acquires a negative charge relative to the plasma. This accelerates positive ions towards the substrate and causes bond breakage, generating active radical sites on the surface. Thus surface activation of the substrate takes place. Onto these surface active sites monomer active species can attach and grow from there to a plasma-polymer.

Therefore, when carbon black is exposed to plasma, the following processes can happen:

1. C-C bond breakage in the graphitic planes.
   Due to breakage of these C-C bonds, radicals are generated on the graphitic planes. However, the graphitic structures are stabilised by resonance. As soon as radicals are generated, they will reform the bond and return to their stable state upon which the radical functionality will migrate to the edge of the graphitic plane. In the present case, acetylene was used which generates radicals of carbon. So the system will favour restructuring itself to its original state or to another favourable state by rearrangement. This reduces the chances of attaching a monomer active species on to the graphitic planes.
2. The breakage of C-O bonds and other functional groups, located at the crystallite edges. As soon as a C-O bond or another functional group located at the crystallite edges is broken, monomer active species can attach on to these sites, which is more favourable.

The thermodynamic feasibility of these processes can also be made clear on basis of the bond energy values: Table 4.4. The active sites formed on the graphitic basal planes are extremely short lived, so that they revert to their original state before the attachment of monomer active species has happened. Successful attachment of the monomer active species only happens at the sites generated at the crystallite edges, the sites generated by the bond breakage of the functional groups or from the migration of the radicals away from the planes. These sites represent somewhat higher bond energy, and cannot easily stabilise their radical nature by resonance. So it is from these low concentrations of sites on the surface of carbon black that the plasma polymer can grow. That is the reason why so little plasma polymer coverage happens in the first place, to continuously increase with further treatment time.

Table 4.4 Bond Energy Values of Typical Bonds

Bond Type	Bond Energy (kJ/mol)	Bond Energy (eV/mol)
C-C	346	3.56
C=C	602	6.23
C≡C	835	8.65
C-O	358	3.70
C-F	458	4.73
C-H	411	4.25
C-S	272	2.80
Si-O	452	4.68
Si-C	318	3.28

In the case of silica, on the contrary, the plasma polymer is easily formed on the surface. For silica, Fig. 4.13, densily occurring siloxane and silanol linkages may be broken, and on to these sites successful attachment of monomer active species may happen. The feasibility of the attachment of monomer species on to the active sites on silica is clear from the bond energy values: Table 4.4. Once these monomer species are attached they can grow further from these sites. Also, due to the fact that the distribution of functional groups on the surface of silica is very dense, growing chains from neighbouring sites are linked chemically, hence giving a good coverage within a short time, with low energy.

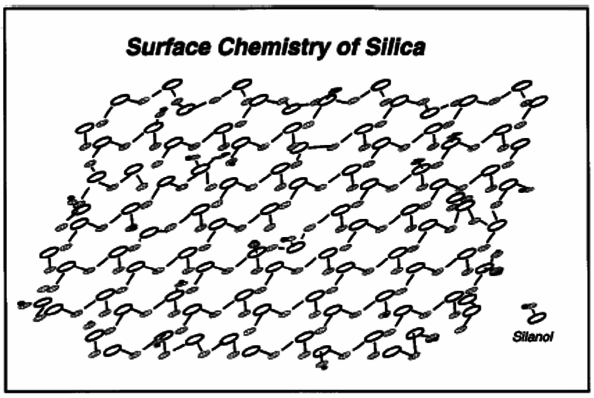


Fig. 4.13 Schematic representation of silica surface[25]

4.5 CONCLUSIONS

Plasma polymerisation on carbon black and silica was attempted using acetylene as monomer. TGA, wetting behaviour with different liquids of known surface tension and ToF-SIMS were used as characterisation techniques for the degree of modification. Under the conditions applied, the amount of plasma polymer formed on the surface of carbon black was very little, in comparison with silica, unless treated for very long duration. The thermodynamic feasibility of attachment was explained on the basis of energy values of the various bonds involved. Successful attachment of the monomer active species on the carbon black surface happens only at the crystallite edges, i.e., the very low concentration of sites generated due to bond breakage of functional groups at these locations or due to the migration of radicals away from the graphitic planes. Active sites formed on the graphitic planes are extremely short lived, so that they return to their original state because of resonance stabilisation before attachment of monomer active species can take place. In the case of silica, the much higher concentration of functional groups and their random distribution all over the surface aids the easy formation of a plasma polymer film over its surface.

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Chapter 5

Investigation on Different Carbon Blacks for their Behaviour during Plasma Surface Modification[*]

Reducing the surface energy and matching its surface chemistry to that of various rubbers aids in compatibilising carbon black with different rubbers. Obtaining a significant reduction in surface energy on regular rubber grade furnace carbon black by plasma polymerisation is a difficult task. Hence a search for an ideal candidate from the carbon family was carried out. This chapter provides the details of that search. Different carbon blacks were selected based on the understanding obtained from our previous work. Thermogravimetric analysis (TGA), X-ray photo electron spectroscopy (XPS), wetting behaviour with liquids of known surface tension, time–of–flight secondary ion mass spectroscopy (ToF-SIMS) and Transmission electron microscopy (TEM) were used to characterise the carbon black samples before and after modification. The study shows that the extent of modification obtained on different carbon black samples is little in comparison with the ease with which fullerenic carbon black can be modified. The fullerenic structures on its surface act as growth sites for the plasma polymer.

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[*] A part of the work presented in this chapter has been published in Rubber Chemistry and Technology vol. 81, 209 (2008). Another part has been submitted to journal Carbon.

5.1 INTRODUCTION

Plasma technology has emerged as a surface modification technique for various substrates like metals, polymers and powders. The method allows tailoring the surface of a substrate without affecting the bulk properties. The process as such does not require any solvents, making it a clean technology. Altering the surface characteristics makes the material suitable for a wide range of application. The possible effects of plasma treatment are alteration of wettability, induced chemical activity, improving surface interactions, cleaning, etc.

The surface characteristics of carbon materials have a major influence on their behaviour in various matrices. Carbon black is widely used as a reinforcing filler in the rubber industry[1]. It is also used as conductive filler and as pigment in the ink industry. Several attempts were made earlier to modify the surface characteristics of carbon black by a plasma technique. Most of the reported attempts used plasma technology to increase the chemical functionality on the surface of carbon black, expecting to increase the interaction with the matrix[2-10]. Tricas *et al.*[7] reported that it is possible to alter the surface characteristics of carbon black using air and nitrogen plasma. Depending on the treatment, different pH levels and acidity values were obtained. The modification also had a positive influence on the bound rubber. Takada *et al.*[8] showed that microwave oxygen plasma can considerably change the carbon black surface chemistry and raise the surface oxygen functionality. Donnet *et al.*[9] reported that air and ammonia plasma treatment can alter the surface characteristics of carbon black. Loh *et al.*[10] reported that plasma modified carbon blacks and carbon fibers have the potential to improve the properties of composites by achieving appropriate levels of adhesion between filler and matrix through physical compatibility and/or chemical bonding.

The above mentioned reports are on the surface modification of carbon black by plasma treatment without deposition of a film. For surface modification with a thin film deposition, a plasma polymerisation process is utilised. This gives the opportunity to alter the surface to hydrophobic or hydrophilic. Surface modification of carbon black by plasma polymerisation has been tried by few researchers in the past. Akovali *et al.*[11] and Tricas *et al.*[12] reported the modification of carbon black by plasma polymerisation. The monomers used for the process were styrene, butadiene and acrylic acid. Their findings led to the conclusion that carbon black was modified successfully, with the coating covering all sites on the surface. Kang *et al.*[13] also reported the modification of carbon black by plasma polymerisation and concluded that it is possible to manipulate the surface properties. But it is clear from our own previous studies[14], as described in Chapter 4 of this thesis, that surface modification of carbon black by plasma polymerisation is a difficult task. This is very prominent when a significant reduction in surface energy is required. In order to have an appreciable effect on the dispersion or distribution of carbon black in an elastomer matrix, a significant reduction in surface energy is required. In the case of dissimilar elastomer blends, carbon black has a tendency to occupy the highly unsaturated/polar phase leaving behind the saturated/apolar phase. All commercial elastomers have a surface energy lower than that of carbon black. Reducing the surface energy of carbon black to the range of various rubbers may aid in compatibilising the filler. This may also aid in directing the filler into the phase into which it has to arrive during the mixing operation.

In order to show appreciable reduction in surface energy, the surface coverage of the deposited plasma polymer film is important. Sufficient active sites on the surface are a pre-requisite for successful plasma coating deposition all over the surface. The crystallite edges and amorphous carbon areas are the active sites on the surface of carbon black for growth of the plasma polymer. In the case of furnace blacks, it has been shown by Schröder[15] that the fraction of these active sites varies between 5-20 % at the surface. It is from these 5–20 % active sites that the plasma polymer has to grow. Hence, it is a difficult task to attain a good coverage on the surface of furnace carbon blacks in a realistic treatment time.

This understanding gave a strong impetus for the search for new candidates in the carbon black family which can give sufficient surface modification by plasma polymerisation. With this aim, a series of carbon black samples were selected for testing. Carbon blacks with more functionality and those which can generate stable active sites during plasma surface modification were considered for this purpose. This chapter will provide information regarding the search for a new carbon black which can give sufficient surface modification by plasma polymerisation. If the search is successful, the particular carbon black can be used for further studies to understand their behaviour in rubber systems. Details of sample selection are provided in section 5.2 under materials. Thermogravimetric analysis (TGA) will be used to calculate the amount of plasma polymer deposited on the surface of the carbon black. X-ray photo electron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (ToF-SIMS) are used to understand the surface chemical composition of the surface of these samples. Transmission electron microscopy (TEM) is utilised to visualise the plasma coating on the surface of the carbon material.

5.2 EXPERIMENTAL

5.2.1 Materials

The selection of samples from the carbon black family was based on the understanding obtained from the previous work as mentioned in Chapter 4. Carbon blacks with more functionality and blacks which can generate stable active sites during plasma surface modification were selected. The first option was a furnace carbon black with more chemical functionality. One of the available options from the market was an oxidised furnace black: SP 350, from Degussa AG, Germany. The trade name and characteristics of all samples are provided in Table 5.1. The pH of SP 350 is 4.1, which indicates more polar functionality on the surface. The next variety of carbon black was a Gas Black. This grade is similar to Channel black. Both these blacks are produced by thermal oxidative decomposition operated in an open system, where the carbon black is formed in diffusion flames. Air has free access to the system resulting in surface oxidation, thus producing acidic sites on the blacks. To note, it was with channel blacks that the reinforcing effect of carbon black in rubber was first discovered. The type of gas black used in the present case is also from Degussa with trade name CK3. The pH of this grade is 4.4. An oxidised gas black: FW 200, was also obtained from Degussa.

Another variety of black is a hybrid material, which is called carbon silica dual phase filler: CSDPF[16-20]. This was supplied by Cabot Corporation, USA. These carbon-silica hybrid fillers are produced by simultaneous combustion of low molar mass polydimethylsiloxane and mineral oil under carefully controlled conditions in a furnace system that is otherwise used to produce conventional furnace carbon blacks. By varying the level of dimethylsiloxane in the feed it is possible to vary the silica-content of the CSDPF. From our previous studies we know that silica responds positively to surface modification by plasma polymerisation. These carbon silica dual phase fillers with varying silica content will then provide an excellent transition from pure carbon black to silica and also help to understand the effect of chemical functionality and their coverage on the surface of the substrate. Two different types of CSDPF's were used in our experiments, CSDPF 2124 (9% silica surface coverage) and CSDPF 4210 (55% silica surface coverage). It has been shown by L. J. Murphy and co-workers, that the silica domain-surfaces show characteristics similar to fumed silica and posses silanol-groups[18]. The carbon phase of CSDPF has also been shown to have higher oxygen content than for equivalent furnace blacks[19].

Another sample which is called active carbon black was obtained from Timcal Graphite & Carbon company, Belgium. The development of plasma technology has paved the way for cleaner ways of producing new varieties of carbon materials[21-23]. Being highly flexible, the thermal plasma technology allows the exposure of a wide range of carbonaceous feedstock (solid, liquid or gases) to very high temperatures with enthalpy densities unreachable in a normal combustion process. New plasma technology has been extended for the production of fullerenes and carbon nanotubes[24,25]. The system comprises of 3 phase AC plasma generator allowing the injection of carbonaceous feedstocks into a high temperature zone and a tail filter unit to separate the solid carbon products obtained from the gaseous flow components. The set up of the reactor is shown in Fig. 5.1

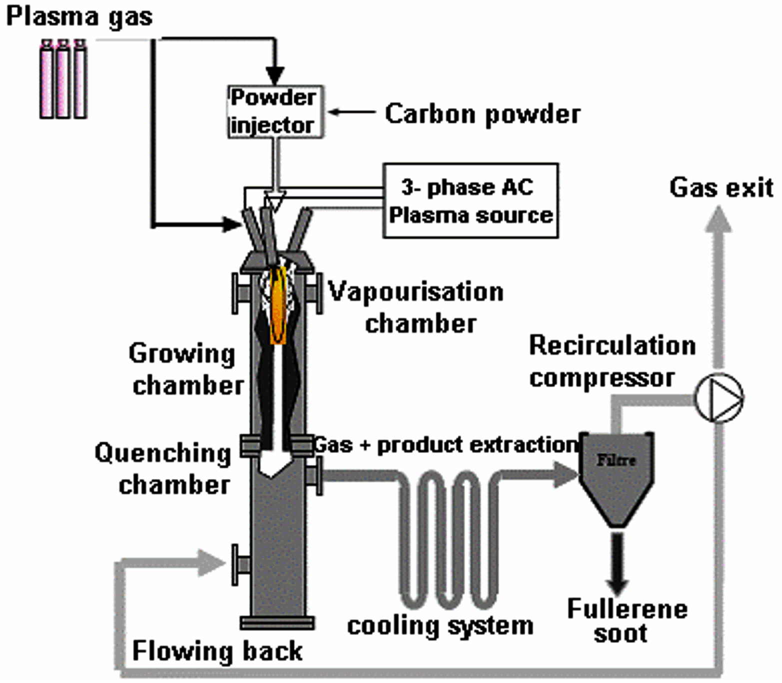


Fig. 5.1 Schematic representation of a plasma facility for the production of fullerenes and other carbon nanomaterials[24]

A thermal plasma is generated by an arc discharge between three graphite electrodes placed in the upper part of the reactor. A special powder injection system is employed to mix a solid carbonaceous precursor (powder) with a suspending gas to transport the mixture into the reactor. The aerosol then flows across the arc reaching the high temperature region (> 4000 K) in the reactor. Due to the high enthalpy density obtained, the solid carbon is vapourised. The high temperature gas is then quenched in a predetermined position, is cooled down rapidly to the conditions chosen for the production of fullerenes and carries the resulting product from the reactor. The gas is filtered and a part of it is recirculated into the reactor.

During the above mentioned process, vapourisation of carbon precursor takes place and recondenses as fullerenes. Part of the carbon vapour recondenses on the carbon precursor. The fullerenes are extracted. The remaining precursor material then consists of the original precursor in its core and on its surface it contains recondensed fullerenes or fullerene fractions. The yield of the fullerene production process is about 5%. Therefore, the major left over after the production of the fullerenes is the precursor having fullerene and fullerene-like residues on its surface. The precursor is then a highly reactive material[26]. In principle, the precursor could be carbon black, graphite or any other carbon allotrope or mixture

Table 5.1 Carbon Black Samples and Characteristic Properties

Sample	Category	Surface area	Other characteristics	Supplier
SP 350	Oxidised furnace black	BET : 65 m^2/g	pH = 4.4	Degussa
CK3	Gas black	CTAB: 88 m^2/g	pH = 3.5	Degussa
FW 200	Oxidised gas black	BET: 550 m^2/g	-	Degussa
CSDPF 2124	Carbon silica dual phase filler	BET : 171 m^2/g	9 % Silica coverage	Cabot corporation
CSDPF 4210	Carbon silica dual phase filler	BET : 154 m^2/g	55 % silica coverage	Cabot corporation
EP-P434	Fullerene soot	BET : 70 m^2/g	Carbon black with fullerenic active sites	Timcal graphite and carbon
E-250G	Conductive carbon black	BET : 65 m^2/g	-	Timcal graphite and carbon
EMM131	Graphitised E-250G	-	-	Timcal graphite and carbon

of those. The properties of the materials will most probably be affected by their original morphology; however their reactivity should be comparable.

An activated carbon black with fullerenic active sites was provided by Timcal Graphite and Carbon. The sample code is EP-P434. The carbon precursor for this material was a conductive carbon black E-250G. In addition to this, a graphitised version (heated above 2000 °C in an inert atmosphere) for E-250G was also obtained from Timcal for completing the series.

All these samples were tested for their behaviour during surface modification by plasma polymerisation. The monomer used for plasma polymerisation process was acetylene (99.6% purity), as supplied by Praxair, the Netherlands.

5.2.2 Methods

5.2.2.1 Plasma Polymerisation

Plasma polymerisation on carbon samples was carried out in a Radio Frequency (RF) plasma vertical tubular reactor. A schematic representation of the reactor is shown in Fig. 5.2. The reactor consists of a round bottom flask attached with a long tubular region. The powders are kept at the bottom of the chamber and stirred with the help of a magnetic stirrer in order to expose the powder particles uniformly to plasma. The system is evacuated to a pressure of 4 Pa. The monomer is injected into the reaction chamber under steady flow conditions. The monomer flow is monitored by a mass flow controller (MKS-1179A) and the system pressure by a temperature regulated capacitance manometer (MKS-627B). Plasma is generated with the help of a 13.56 MHz Radio frequency (RF) plasma generator (MKS–ENI ACG 3B). When sufficient monomer pressure is attained, RF power is applied. All carbon black samples as mentioned in Table 5.1 were tested in the plasma reactor for their behaviour during surface modification. The conditions applied for the surface modification process are 27 Pa monomer pressure, 250W RF power and a treatment time of 1hr.

5.2.2.2 Thermogravimetric Analysis

A Perkin Elmer TGA was used for thermogravimetric analysis of the samples. The samples were heated from 50 °C to 800 °C at 10 °C/min in an air atmosphere. The thermal degradation behaviour of pure plasma polymerised acetylene was first studied. Pure plasma polymerised acetylene starts to decompose at 265 °C and the decomposition is complete at 600 °C. Based on this, the weight losses for the coated and uncoated carbon blacks were calculated in this region of decomposition of plasma polymerised acetylene. The difference in weight loss between the coated and uncoated samples corresponds to the amount of coating deposited on the surface of the carbon blacks.

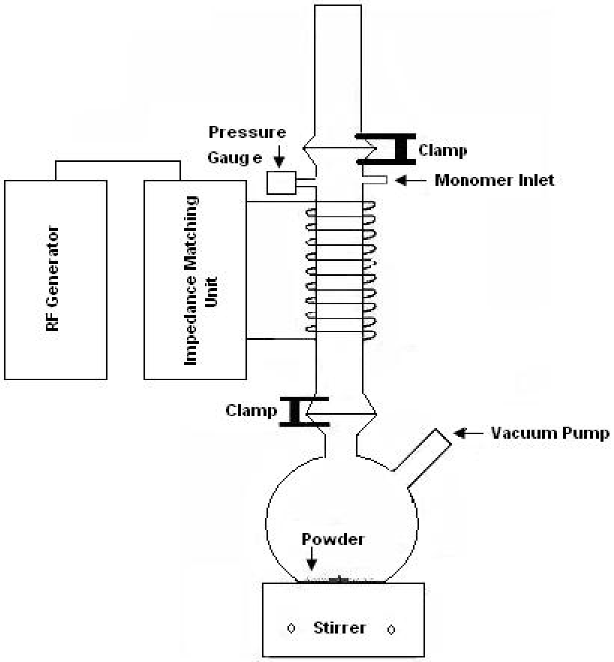


Fig. 5.2 Schematic representation of Vertical Tubular Plasma Reactor

5.2.2.3 X-ray Photoelectron spectroscopy (XPS)

Surface analysis was performed on a Quantera XPS from Physical Electronics equipped with an Al Kα X-ray source (1486.6 eV). The powder samples were deposited on to an indium foil, which was then loaded on the sample holder. Pass energy for the survey scans was 224 eV and that for the elemental scans 55 eV.

5.2.2.4 Wetting behaviour with liquids of known surface tension

Wetting behaviour of the modified and unmodified powders with liquids of known surface tension was observed in order to semi-quantitatively characterise the degree to which the modification had taken place. For this purpose, 50 ml of liquid was put in a glass beaker and 1-2 g of sample was added to the liquid. Depending on the surface energy of the powder, it will either sink or float on the liquid. The wetting behaviour gives an idea about the range over which surface energy has been reduced.

5.2.2.5 BET surface area measurement

A micrometrics model 2280 nitrogen adsorption surface area analyser was used to determine the BET surface area of the fullerenic carbon black sample before and after modification. Procedures according to ASTM D-3037 were followed during the measurements.

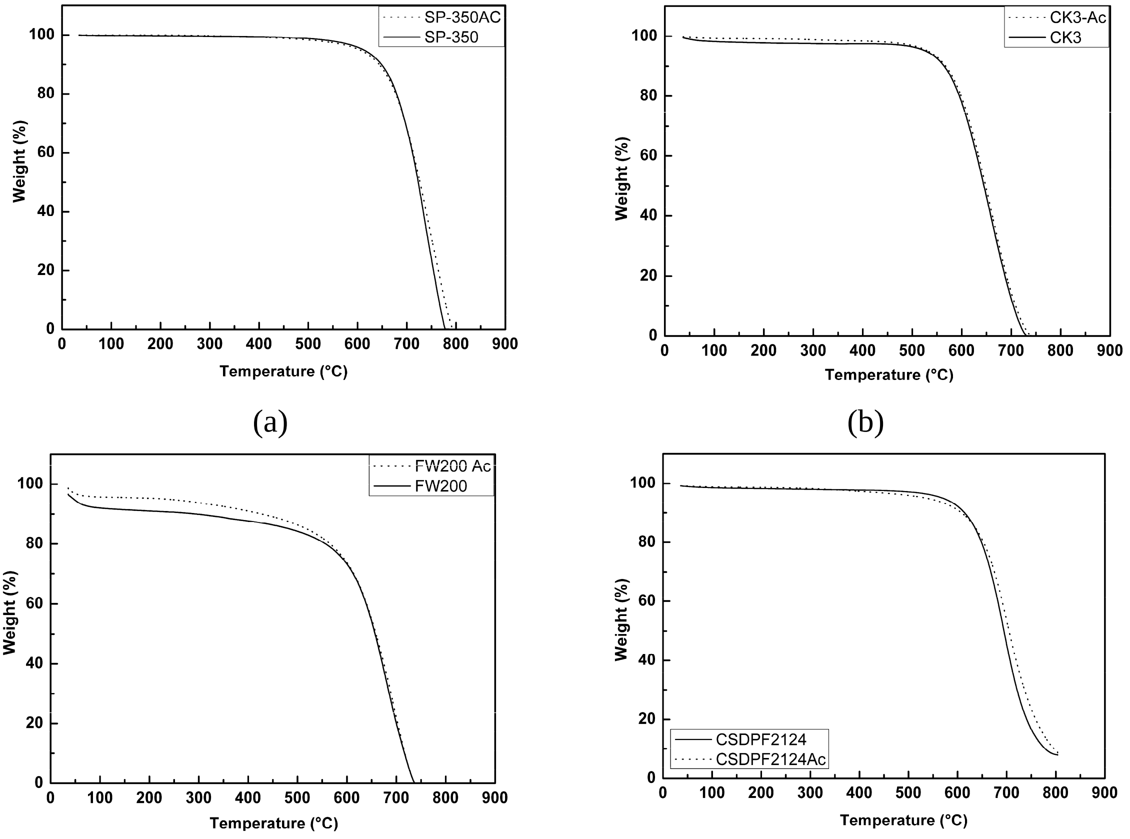
5.2.2.6 Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

In order to study the surface composition of the coated carbon blacks, ToF-SIMS measurements were carried out. ToF-SIMS is a very sensitive surface analysis technique, which specially looks at the uppermost layers of the surface. The measurements were carried out in an Ion-Tof Cameca ToF-SIMS IV machine. The carbon black powder samples were deposited on an indium foil, which was then loaded on to the sample holder. The system vacuum was maintained at between 10^{-7} and 10^{-9} mbar. Monoisotopic Gallium (^{69}Ga) ions were used as the primary ion source at an energy of 25 keV. The ion current was kept in the range 1.5-2.5 µA. The total integrated ion dose was ≈ 10^{10} ions/cm^2.

5.3 RESULTS

The TGA-thermograms of the coated and uncoated carbon black samples are shown in Figs. 5.3 and 5.4. The decomposition of pure plasma polymerised acetylene starts at 265 °C and is complete at 600 °C. The difference in weight loss of the coated and uncoated carbon black samples corresponds to the amount of plasma polymerised acetylene film deposited on the surface. The calculated weight losses for all treated carbon black samples are tabulated in Table 5.2.

The oxidised carbon black (SP350) and gas black (CK3) show only a little amount of deposition. The oxidised gas black (FW200) gives a higher amount of deposition than SP350 and CK3. The carbon silica dual phase filler samples show a deposition in relation to the silica coverage on their surface. The sample with 55% silica surface coverage gives a higher amount of deposition than the one with 9% silica surface coverage. On the other hand the carbon black with fullerenic active sites: EP-P434 after a 1 hr treatment under similar conditions gave 14 wt % deposition of plasma polymerised acetylene, indicating a substantial amount of deposition on its surface. The precursor E-250G gave a deposition of 2.4 wt % deposition of plasma polymerised acetylene. The graphitised sample EMM131 also gave a similar amount of deposition to that of E-250G.



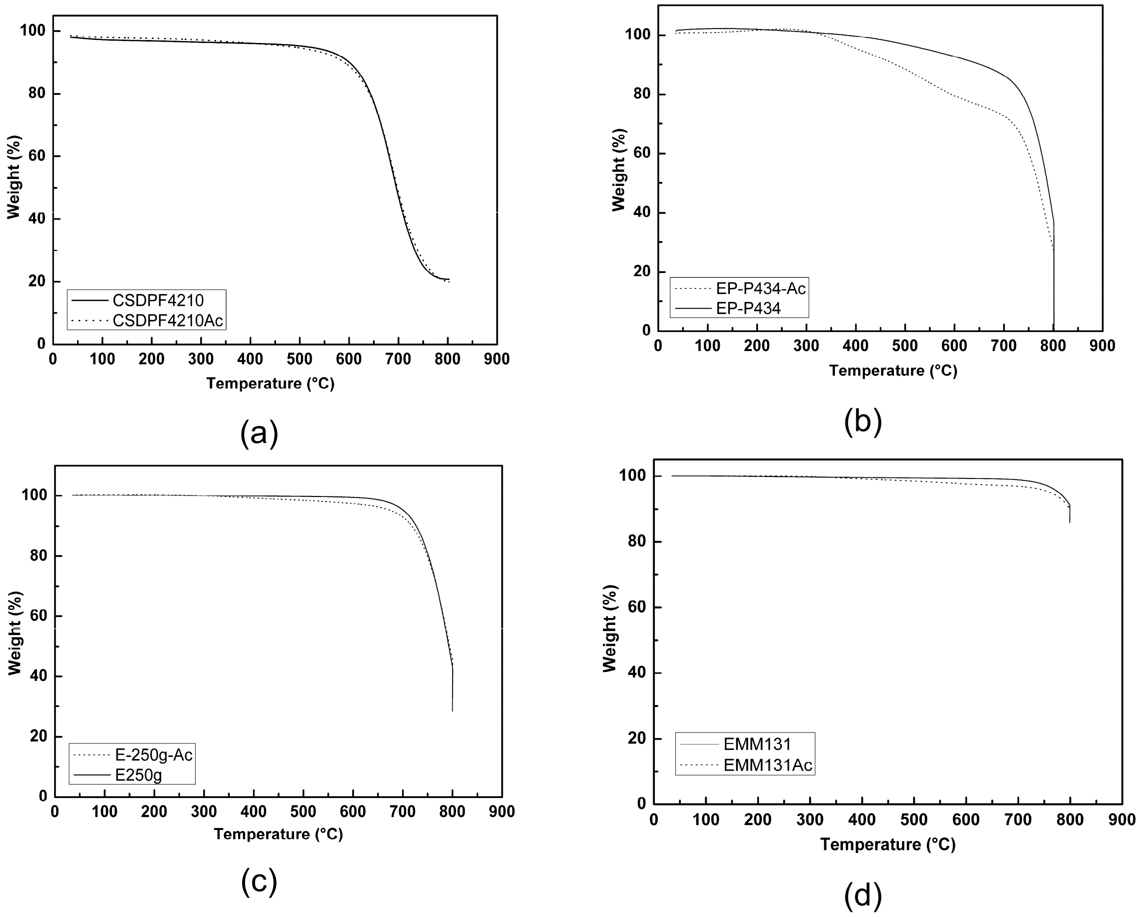
(a) (b)

(c) (d)

Fig. 5.3 TGA- thermograms of coated and uncoated samples of a) SP-350; b) CK3; c) FW200 and d) CSDPF 2124.

Table 5.2 TGA Weight Loss for Various Carbon Black Samples

Sample	TGA weight loss (%)
SP 350	0.4
CK3	0.3
FW 200	3.0
CSDPF 2124	1.5
CSDPF 4210	2.6
EP-P434	14
E-250G	2.4
EM-M131	2.3



(a)

(b)

(c)

(d)

Fig. 5.4 TGA- thermogram of coated and uncoated samples of a) CSDPF 4210; b) EP-P434; c) E-250G and d) EMM131.

XPS can be used to study the surface composition of materials. Elemental scans were carried out on each sample: the atomic concentrations of various elements are given in Table 5.3. The surface of unmodified N330 furnace black shows carbon, oxygen and sulphur peaks (binding energies of 284.4 eV, 533.2 eV and 164 eV, respectively). The presence of oxygen comes from various functional groups on the surface of carbon black and the presence of sulphur in small quantities is already known[27]. The small amount of oxygen refers to the low fraction of functional groups present on the surface of carbon black. One of the criteria for the selection of the different carbon samples was the concentration of oxygen on their surface. Information about its distribution over the surface of the carbon blacks was not available. However, all selected carbon black samples have a higher concentration of oxygen on their surface than N330, as is clear from the XPS data. The increased concentration of oxygen can contribute to improve their

Table 5.3 Atomic Concentrations of Various Elements on Different Filler Samples
(-Ac is the acetylene plasma modified version of each sample)

Sample	Carbon 1s (%)	Oxygen 1s (%)	Sulphur (%)	Silicon 2p (%)	O/Si ratio
N330	98.49	1.19	0.32	-	-
N330-Ac	98.01	1.70	0.29	-	-
SP 350	97.92	2.08	-	-	-
SP 350-Ac	97.28	2.72	-	-	-
CK3	96.41	3.59	-	-	-
CK3-Ac	96.17	3.83	-	-	-
FW 200	90.98	9.02	-	-	-
FW 200-Ac	91.58	8.42	-	-	-
CSDPF 2124	87.65	9.13	-	3.22	2.84
CSDPF 2124-Ac	89.86	8.18	-	1.96	4.17
CSDPF 4210	59.98	29.25	-	10.77	2.72
CSDPF 4210-Ac	64.07	26.62	-	9.31	2.86
EP-P434	97.36	2.64	-	-	-
EP-P434-Ac	92.62	7.38	-	-	-
E-250G	98.81	1.19	-	-	-
E-250G-Ac	96.95	3.05	-	-	-
EMM131	98.46	1.54	-	-	-
EMM131-Ac	96.58	3.42	-	-	-

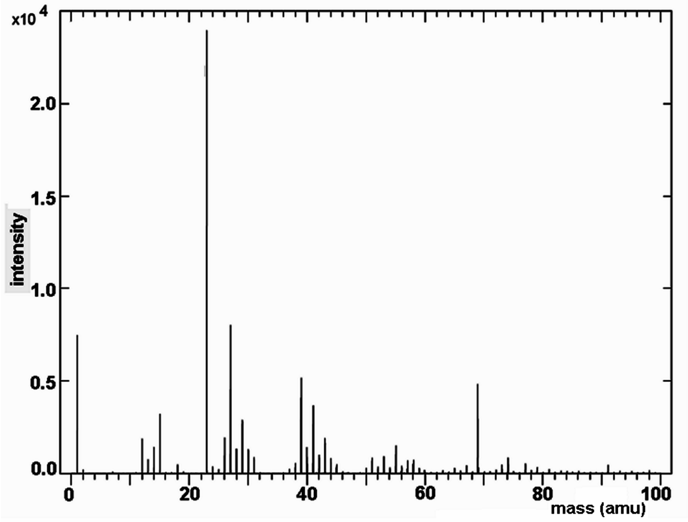
capability for surface modification. The oxidised furnace black SP350 and gas black CK3 have a relatively higher concentration of oxygen on their surface than the regular furnace black N330. The oxidised gas black FW 200 shows even a higher concentration of oxygen on its surface.

Upon modification by plasma, a hydrocarbon plasma polymer film is deposited on the surface of the carbon samples. It is worth to note that a plasma-polymer contains an appreciable amount of trapped radicals, and after the process the plasma polymer can get easily oxidised under atmospheric conditions, giving rise to the presence of oxygen on its surface. The oxidised furnace black SP350 and gas black CK3 did not show an appreciable variation in their carbon and oxygen concentration after plasma modification. This is in correspondence with the TGA data. The oxidised gas black FW 200 which has a relatively higher oxygen concentration, shows some variation in carbon and oxygen concentrations after modification. In fact, it has to be admitted, that the suitability of this technique for the present purpose is a bit questionable, as we are depositing a hydrocarbon film over a carbon substrate. However, the technique is more suitable in the case of filler samples of the dual phase type.

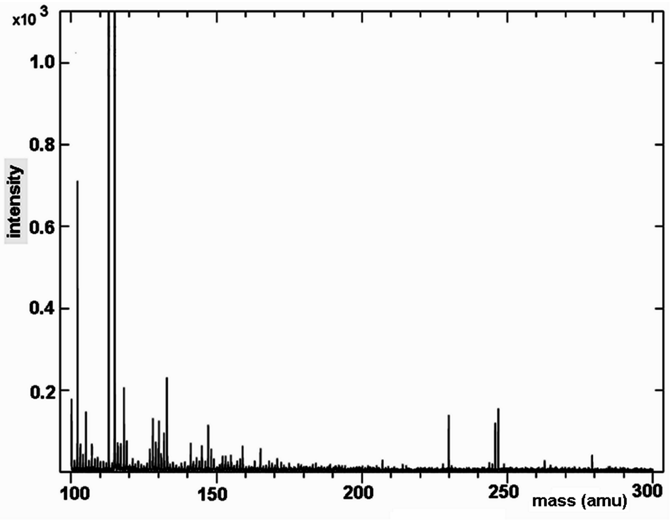
The surface of unmodified carbon silica dual phase filler shows the presence of silicon (Si2p – 103.6 eV and Si2s – 154.8 eV) in addition to carbon and oxygen peaks. This is in accordance with the reported surface composition of these materials[19]. The O/Si ratio for these carbon silica dual phase filler samples matches the silica coverage of those samples. After the plasma surface modification the dual phase filler samples show an increase in concentration of carbon on their surface. This increase in concentration of carbon is proportional to the silica coverage of the samples. The higher the silica coverage, the more is the increase in carbon concentration. This also substantiates the data obtained from TGA.

The fullerenic carbon black EP-P434 shows an appreciable difference in carbon and oxygen concentrations after the plasma surface modification. The trapped radicals on the surface of the deposited film are the cause for the increased oxygen concentration on the sample. The TGA-data also indicate a significant amount of deposition on its surface. The samples E-250G and EMM131 show some increase in carbon and oxygen concentrations after plasma surface modification, in correspondence with the much lower amount of plasma polymer deposited on their surface.

It is clear that carbon black with fullerenic active sites behaves very different from the rest of the samples. The plasma polymer is readily formed on the surface of carbon black with fullerenic active sites. In order to substantiate this in more detail, more analysis was carried out on the carbon black with fullerenic active sites.



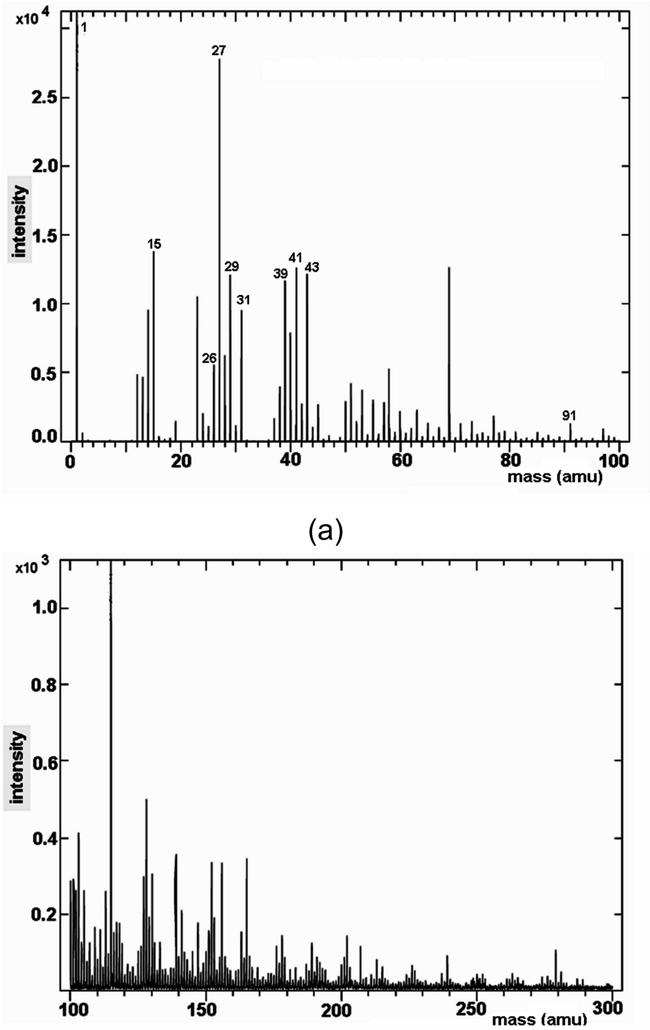
(a)



(b)

Fig. 5.5 ToF-SIMS spectrum of carbon black with fullerenic active sites: a) mass range 0-100 (amu); b) mass range 100-300 (amu).

Plasma polymerisation of acetylene will result in the formation of a crosslinked hydrocarbon film. In a positive ToF-SIMS spectrum, such a hydrocarbon must show intense hydrocarbon peaks and a cluster pattern of mass fragments especially in the higher mass fraction regions[28]. The ToF-SIMS spectrum of carbon black with fullerenic active sites is shown in Fig. 5.5. Traces of Na^+ (23 amu) and a small amount of hydrocarbon peaks is visible in the spectrum of untreated fullerene soot. The presence of these chemical compositions on the surface of carbon black is already known[27,29]. After the plasma treatment, the ToF-SIMS spectrum (Fig. 5.6) shows intense hydrocarbon peaks and also hydrocarbon clusters in the higher mass fraction regions especially in the mass range of 100-300 amu. This gives a clear indication for the presence of a hydrocarbon film over the surface of the fullerenic carbon black.



(a)

(b)

Fig. 5.6 ToF-SIMS spectrum of carbon black with fullerenic sites after plasma surface modification with acetylene: a) mass range 0-100 (amu); b) mass range 100-300 (amu).

The wetting behaviour of the samples with liquids of known surface tension will give an idea about the range to which the surface energy has been reduced. The wetting behaviour of the coated and uncoated carbon black sample with fullerenic active sites is shown in Fig. 5.7. After the formation of the plasma polymerised acetylene film, the surface of the carbon black should show characteristics corresponding to the formed acetylene film: a lower surface energy. The 1 hr treated fullerenic soot EP-P434-Ac shows an appreciable reduction in surface energy, which corresponds to the deposition of a film with good surface coverage.

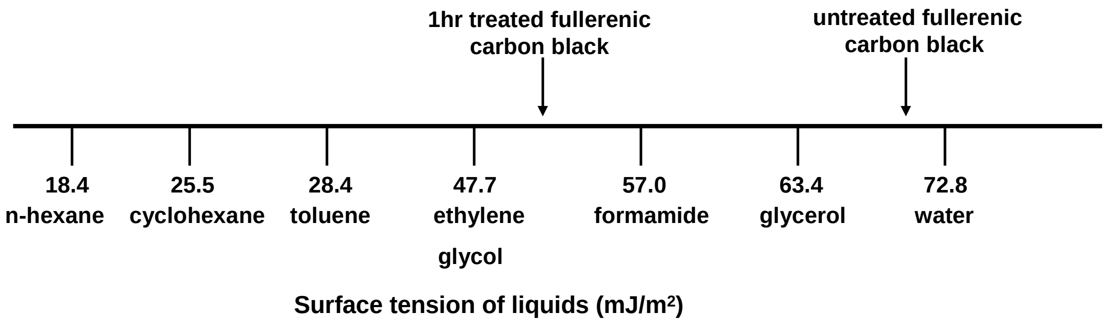


Fig. 5.7 Schematic representation of wetting behaviour of untreated and plasma coated fullerene soot

In order to understand whether the plasma coating affects the specific surface area, the BET surface area of the coated and uncoated fullerene soot was measured. Before modification the fullerene soot had a surface area of 69 m^2/g, whereas after the plasma polymer deposition, it reduced somewhat to 63.7 m^2/g.

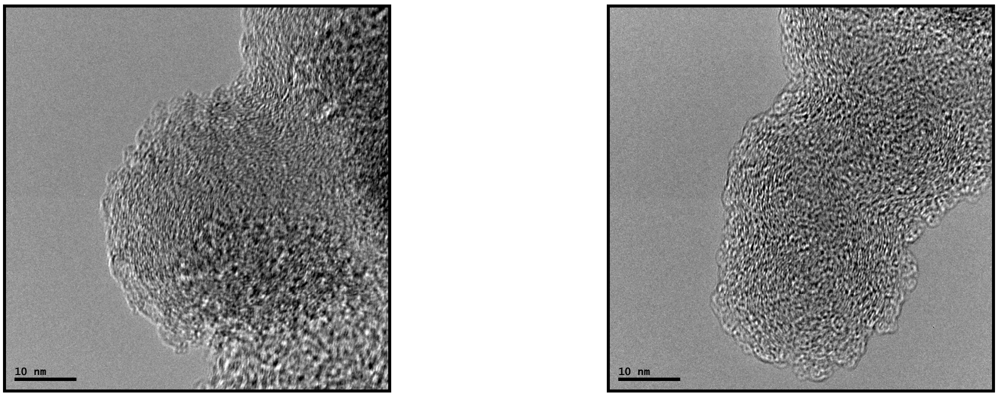


Fig. 5.8 TEM image of fullerenic carbon black

TEM-images were taken in order to visualise the plasma polymer coating on the surface of carbon black with fullerenic active sites. Fig. 5.8 shows the TEM image of an uncoated fullerenic carbon black. The image clearly reveals the surface with fullerenic nanostructures, as reported by Goel et al[30]. The fullerenic structures are recondensed at the surface of the carbon black during the production of the fullerenes, while towards the core the orginal structure is retained. The TEM-image of the plasma coated fullerenic carbon black is shown in Fig. 5.9. It clearly shows the existence of the plasma polymer film over its surface. The average thickness of the coating was characterised to be in the range of 3-5 nm. In some regions, the thickness was in the range of 8-10 nm. These are areas which are more exposed to plasma, during the modification process. The TEM-image also shows that the total carbon black aggregate is encapsulated in the plasma polymer shell. It demonstrates that it is possible to deposit a plasma polymer film on irregular structures such as that of carbon black.

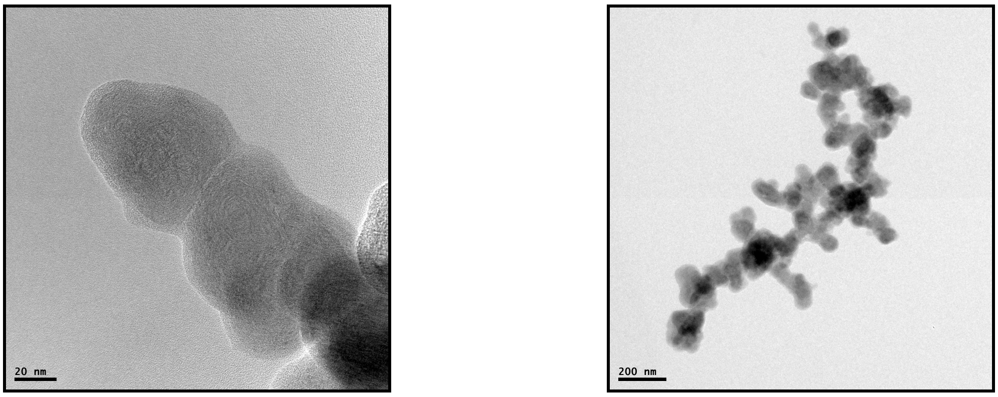


Fig. 5.9 TEM image of plasma coated fullerenic carbon black

5.4 DISCUSSION

From the results obtained, it is clear that some surface modification has happened on all carbon black samples. In the case of oxidised gas black, the increase in oxygen functionality increased its capability to be modified. Similar is the case with carbon silica dual phase fillers. TGA- and XPS-data clearly show that, the higher the silica content on the surface, the higher is the amount of plasma polymer deposited. This proves that chemical functionality and its distribution over the surface plays an important role in the surface modification by plasma polymerisation. But the extent of modification of the above mentioned carbon black samples are limited in comparison with the ease with which fullerenic carbon black could be modified. The fullerenic carbon black after modification shows a substantial amount of plasma polymer deposition and an appreciable reduction in surface energy, as evidenced by the wetting behaviour with liquids of known surface tension. The ToF-SIMS spectrum clearly shows the presence of intense hydrocarbon peaks and a cluster pattern of mass fragments in the higher mass fraction region, which proves the presence of a hydrocarbon film over the carbon black surface. The TEM-image also clearly reveals that the whole carbon black aggregate is encapsulated in the plasma polymer shell.

This wide difference in behaviour arises due to the various surface characteristics of the carbon blacks. The surface of oxidised furnace blacks, gas blacks and oxidised gas blacks contains more oxygen functionality on the surface than a normal rubber grade furnace black (e.g. N330). This is clear from the XPS- data. Similarly, on the surface of the dual phase fillers, silanol groups are present, while the experimental samples vary in their distribution over the surface. In the case of fullerenic carbon black, the surface contains fullerenes and fullerene-like structures. In fullerenes and fullerene-like structures, the double bonds present are localised and weakly conjugated[31]. This is due to the strong deviation from planarity of the curved surfaces of these molecules (pyramidalisation). Fullerenes and higher homologues have an unusually high electron affinity and have been defined as free radical sponges. The presence of these highly active moieties on their surface makes fullerenic carbon black very reactive.

As was discussed in the previous chapter, the excitation of gaseous molecules in the plasma generates active species like electrons, protons, excited molecules, ions, etc. When the filler particles are exposed to the plasma atmosphere, positive ions are colliding on its surface and are capable of breaking bonds at the surface. This creates radical active sites on the surface onto which monomer active species can attach and further grow from there. The active sites formed on the graphitic planes of carbon black are extremely short lived, so that they revert back to their orginal state before attachment of monomer species has happened. Successful attachment of monomer species happens at the sites generated by bond breakage of functional groups. Even though there is an increased concentration of oxygen functionality on the surface of the oxidised furnace blacks and gas black samples, the extent of modification is relatively low compared to that obtained on fullerenic carbon black. This may be due to the fact that the distribution and concentration of these functional groups are still not sufficient enough to give a good coverage of the plasma polymer film. The fact that carbon silica dual phase fillers show an increased amount of deposition and carbon concentration with increase in silica coverage is a direct proof for the importance of distribution of the functional groups on the surface.

In the case of fullerenic carbon black, fullerenic structures are present all over the surface. Hence, during exposure to plasma more stable active sites are formed. On to these sites monomer active species can attach and further grow from there. Also due to the fact that the stable active sites are formed all over the surface, the growing plasma polymer from neighbouring sites can link chemically, giving a good coverage within a short time.

The results of this study open the possibilities of fullerenic carbon black to be an ideal candidate for plasma surface modification. The next step should then be the scaling up of this modification process at least to an extent of 100 g per batch. This will provide sufficient samples for studying the behaviour of plasma coated carbon black mixed into rubber. For the scaling up and rubber testing a few practical difficulties exist. The fullerenic carbon black obtained from Timcal company is in a highly fluffy form, which is unsuitable for mixing with rubber. So before mixing with rubber it has to be subjected to a granulation process. The carbon black used for the plasma coating process must still be in the fully form. A question is whether, after the plasma coating process, the coating will withstand the granulation process and the shear forces involved in a rubber mixing operation. This question will be addressed in the next chapter. In principle, for the fullerene soot production, any carbon precursor can be used. Practically, for the time being, the regular conductive carbon blacks from Timcal company have only been used as fullerene precursors. In order to extend the applicability of this surface activation process, it is important that regular rubber grade furnace blacks can also be used. We hope to address this issue in a later stage of this research.

5.5 CONCLUSIONS

Surface modification of different categories of carbon blacks by plasma polymerisation was attempted using acetylene as monomer. Under the conditions applied, the amount of plasma polymer formed on the surface of different carbon black samples is little in comparison with fullerenic soot. The experiments show that the distribution and concentration of functional groups is an important aspect for the surface modification by plasma polymerisation. In the case of fullerenic carbon black, there is an abundant amount of fullerenic active sites all over the surface. Hence, successful attachment of monomer species takes place on to these sites. Also due to the fact that stable active sites are formed all over the surface, the growing plasma polymer from neighbouring sites are linked chemically giving a good coverage of the plasma polymer film over the total carbon black surface. This makes fullerenic carbon black an ideal choice for surface modification by plasma polymerisation.

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Chapter 6

Properties of Plasma Acetylene-Coated Carbon Black in Elastomers

The surface energy of carbon black is high compared to various elastomers like Styrene–Butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene–Propylene Diene rubber (EPDM). Reduction in surface energy of carbon black was achieved by modifying its surface by plasma polymerisation of acetylene. A fullerenic carbon black was used for the modification process. The surface modification process was scaled up to a batch size of 100 g. Thermogravimetric analysis (TGA), wetting behaviour with liquids of known surface tension and time–of–flight secondary ion mass spectroscopy (ToF-SIMS) were used to characterise the carbon black before and after modification. The state of the plasma-coated carbon black in rubber was studied by electrical conductivity measurements. The behaviour of the plasma- coated filler in the various rubbers was studied using the Payne effect and stress-strain properties. Due to the low surface energy of the plasma-coated carbon black, it shows low filler-filler interaction in various rubber matrices compared to the uncoated version. The filler-polymer interaction remains unaffected in unsaturated rubber matrices such as SBR or NBR, while in a saturated rubber such as EPDM, it is found to decrease.

6.1 INTRODUCTION

Carbon black is an essential component in rubber formulations. Dispersion and distribution of carbon black in a rubber matrix are important factors to achieve optimum physical properties[1]. The structure of carbon black, wettability of the filler by the rubber, rubber-filler interactions all have a major influence on the resultant properties of the rubber compound. During the incorporation process of carbon black into the rubber matrix, wetting of carbon black with rubber and squeezing out of entrapped air takes place. The wettability of a filler particle by a polymer chain can be quantified in terms of surface energy. The surface energy of a filler in turn depends on the physico-chemical composition of its surface. In order to have a good compatibility, the surface energy difference between the filler and the rubber should be low.

In the case of carbon black, the surface energy is high compared to that of various elastomers like Styrene-Butadiene rubber (SBR), Butadiene rubber (BR) and Ethylene-Propylene-Diene rubber (EPDM). In order to have an appreciable influence on the dispersion and distribution properties of carbon black in rubber, there should be a significant reduction in surface energy of the filler. Surface modification by plasma polymerisation can tailor the surface characteristics of the filler, as described in the previous chapters. In order to obtain a significant reduction in surface energy, the surface coverage of the plasma-polymer film is important. To achieve a good coverage of the plasma-polymer film in a realistic treatment time, there should be sufficient active sites on the surface of the filler for growth of the plasma polymer[2].

From our previous studies[2,3] it is clear that normal rubber grade furnace carbon blacks are difficult to modify by a plasma polymerisation technique. The search for a new candidate from the carbon black family with good modification capability resulted in fullerenic carbon black. It gave a very good surface modification compared to other, different carbon black samples. The fullerenic carbon black used for the plasma surface modification process was in the fluffy form. But this form as such could not be used in rubber mixing, as it is very difficult to handle during mixing. Hence, the plasma-coated carbon black was first granulated and then used for rubber mixing.

It is important to understand the state of the plasma coating after mixing the coated carbon black in rubber. Before being incorporated into rubber, the plasma-coated fluffy carbon black is subjected to a granulation process and to all sorts of shear and compression forces during the rubber mixing operation. It is known that during mixing, carbon black agglomerates are broken down into aggregates and other smaller fractions. It is well possible that the plasma-coating over the surface of the carbon black gets damaged during these processes.

To understand this in detail, a concept from carbon black testing was utilised. The structure of carbon black that remains after the mixing and dispersion process determines the contribution to the reinforcement of rubber. The resultant structure after mixing is difficult to determine and is hard to predict from measurements made on the carbon black itself. Therefore, to simulate the structure that remains after mixing, a Compressed OAN test (ASTM D3493-07) is used. In this test (also called "Crushed OAN or 24M4 OAN), carbon black is compressed four times in a cylinder at 165 MPa (24,000 psi) prior to testing in the Oil absorptometer. This breaks down some of the agglomerates. Results from the Compressed OAN method are generally accepted as more indicative of the structure that remains after mixing.

In order to understand the state of the plasma coating after mixing, electrical conductivity measurements were utilised as an alternative characterisation method. These measurements were carried out according to the procedures mentioned by Grivei and Probst[4]. The intrinsic conductivity of carbon black originates from carbon-carbon contacts. A plasma-polymer film deposited over the surface of carbon black has a major influence on the intrinsic conductivity of carbon black. The electron now has to tunnel through the plasma polymer layer. This depends on the thickness of the plasma-polymer film. Moreover, the deposited plasma-polymerised film has a low surface energy, which tends to keep the carbon particles separated. Hence, the deposition of a plasma-polymerised acetylene film over the surface of carbon black will have an influence on its intrinsic conductivity. Measuring the conductivity before and after plasma coating (in the fluffy state) provides an indication of the effect of plasma coating on the intrinsic conductivity of carbon black. Before mixing into rubber, the plasma-coated carbon black undergoes a granulation procedure, a proprietary technique. Measuring the conductivity of the plasma-coated granulated carbon black and comparing it with fluffy coated carbon black then gives an impression of the state of the plasma coating after the granulation procedure. Also, during the conductivity measurements pressure is applied onto the carbon black sample. Hence, the conductivity values after the granulation of the plasma-coated carbon black at different pressures will give an impression of the state of the plasma coating after the granulation process. This may also be taken as indicative for the state of the plasma-coated carbon black that remains after mixing.

Scaling up of the plasma coating process was carried out in a RF plasma tumbler reactor to a batch size of 100 g. The conditions were optimised based on the amount of plasma-polymer deposited on the surface. The coated carbon black was then granulated and mixed with rubber. In the present chapter the behaviour of the plasma-coated carbon black in single rubber systems will be described. The filler-filler interaction is studied using the Payne effect and the stress-strain properties using tensile tests.

6.2 EXPERIMENTAL

6.2.1 Materials

The fullerenic carbon black in the fluffy form was obtained from Timcal Graphite and Carbon, Belgium. The sample code is RP-P579. The BET specific surface area of the fullerenic carbon black is 66.8 m^2/g. The monomer used for plasma polymerisation was acetylene (99.6% purity) as supplied by Matheson Trigas, Ohio, USA.

The rubbers used for the experiments were a solution Styrene-Butadiene-Rubber (S-SBR), Acrylonitrile-Butadiene-Rubber (NBR) and an Ethylene-Propylene-Diene rubber (EPDM). S-SBR was supplied by Lanxess Corporation, Germany: Buna VSL 5025-0HM with Mooney viscosity ML (1+4)100 °C: 65, vinyl content 50 wt%, styrene content 25 wt%. NBR was also supplied by Lanxess Corporation, Germany: Perbunan NT 3446 with Mooney viscosity ML (1+4)100 °C: 45, acrylonitrile content 34.7±1 wt%. EPDM rubber was supplied by DSM Elastomers B.V. the Netherlands: Keltan 4703 with Mooney viscosity ML (1+4)125 °C: 65, ethylene content 48 wt% and ethylidene norbornene content 9.0 wt %.

Two compound codes are used in the rubber data of this chapter. Rubber compounds with fullerenic carbon black will be denoted as FS and that with the plasma-coated fullerenic carbon black will be denoted as PCFS.

6.2.2 Methods

6.2.2.1 Plasma Polymerisation

Plasma polymerisation was carried out in a Radio-frequency (RF) plasma tumbler reactor at the University of Cincinnati, Ohio, USA. After introduction of 100 g of carbon black, the chamber was evacuated to a pressure of 10 Pa. Then monomer was injected into the reaction chamber under steady flow conditions, maintaining a pre-determined monomer pressure inside the chamber. Subsequently RF-power was applied. A frequency of 13.56 MHz was applied. The powder samples were mixed inside the chamber with the help of two vanes running in opposite direction on a shaft inside the chamber. This aids in exposing the powder particles to the plasma, in order to obtain uniform modification all over their surface. The conditions of the process were varied as given in Table 6.1, in order to find an optimised condition for the process based on the amount of plasma-polymer deposited on the surface of the carbon black.

Table 6.1 Experimental Conditions Employed for the Plasma Polymerisation onto Carbon Black

Sample Code	RF Power (Watts)	Monomer Concentration (Pa)	Treatment time (hr)	TGA weight loss (%)
RP-P579-1	80	20	1	1.72
RP-P579-2	100	40	1	2.15
RP-P579-3	100	40	2	4.01
RP-P579-4	100	50	2	3.9
RP-P579-5	100	50	2.5	5.06
RP-P579-6	100	40	2.5	5.5

6.2.2.2 Thermogravimetric Analysis

A Perkin Elmer TGA was used for thermogravimetric analysis of the coated carbon black samples. The samples were heated from 50 °C to 800 °C at 10 °C/min in an air atmosphere. The thermal degradation behaviour of pure plasma polymerised acetylene was first studied. Pure plasma polymerised acetylene starts decomposing at 265 °C and the decomposition is complete at 600 °C. Based on this, the weight losses for the coated and uncoated carbon blacks were calculated in this region of decomposition of plasma polymerised acetylene. The difference in weight loss between the coated and uncoated samples corresponds to the amount of coating deposited on the surface of the carbon blacks.

6.2.2.3 Surface Energy Measurements

The surface energy for the two rubbers, S-SBR and EPDM was determined using contact angle measurements according to Young's equation:

$$\left(\gamma_s^D \gamma_l^D\right)^{1/2} + \left(\gamma_s^P \gamma_l^P\right)^{1/2} = \gamma_l\,(Cos\theta + 1)/2 \qquad (6\text{-}1)$$

where γ_s^D and γ_s^P are the dispersive and the polar component of the surface energy of the solid, γ_l^D and γ_l^P are the dispersive and polar components of surface tension of the liquid and θ corresponds to the contact angle. The liquids chosen for the measurement were water with a surface tension of 72.8 and di-iodomethane with 50.8 [mJ/m^2]. For the contact angle measurements unfilled, uncured rubber samples were used. The contact angle measurements were carried out on a VGA 2000 contact angle measuring instrument.

Wetting behaviour of the modified and unmodified powders with liquids of known surface tension was observed in order to semi-quantitatively characterise the degree to which the modification had taken place. For this purpose, 50 ml of liquid was put in a glass beaker and 1-2 g of sample was added to the liquid. Depending on the surface energy of the powder, it either sinks in or floats on the liquid. The wetting behaviour gives an impression about the range over which surface energy has been changed.

6.2.2.4 Surface Area Measurements

The BET and CTAB surface areas of the plasma-coated and uncoated carbon blacks were determined. The BET surface area was measured according to the procedure mentioned in ASTM D3037, and the CTAB surface area was determined according to ASTM D3765.

6.2.2.5 Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

In order to study the surface composition of the coated carbon blacks, ToF-SIMS measurements were carried out. ToF-SIMS is a very sensitive surface analysis technique, which specially looks at the uppermost layers of the surface. The measurements were carried out in an Ion-Tof Cameca ToF-SIMS IV machine. The carbon black powder samples were deposited on an Indium foil, which was then loaded on to the sample holder. The system vacuum was maintained at between 10^{-7} and 10^{-9} mbar. Monoisotopic Gallium (^{69}Ga) ions were used as the primary ion source and energy was 25 keV. The ion current was kept in the range, of 1.5-2.5 µA. The total integrated ion dose was ≈ 10^{10} ions/cm^2.

6.2.2.6 Conductivity Measurements

The electrical conductivity experiments were performed in a set-up as shown in Fig. 6.1. Approximately 1 g of sample was mounted into an electrically insulated mould with an internal cross section of 1 cm^2. The experiments were carried out at room temperature in the pressure range of 0.1 MPa to 0.35 MPa. The bottom of the mould as well as the piston are made of copper and are electrically connected to a Keithely 2000 digital multimeter in order to measure the electrical resistance of the sample. Both the height and the electrical resistance of the samples are measured at a given pressure after waiting for about 30 sec in order to stabilise the sample.

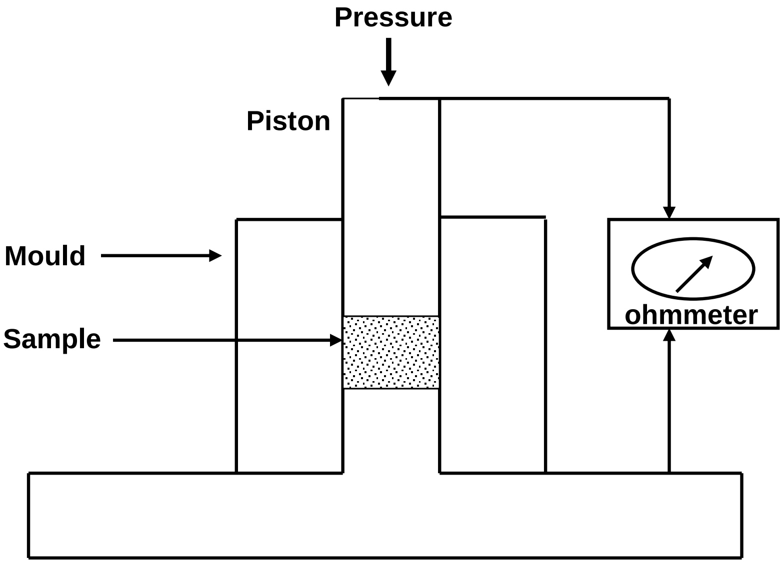


Fig. 6.1 Experimental set up for conductivity measurements[4]

6.2.2.7 Rubber Mixing and Curing

Rubber compounds with carbon black samples were prepared according to the formulations given in Table 6.2. The mixing was carried out in a Brabender Plasticorder internal mixer with a chamber volume of 390 ml. The mixing procedure employed is mentioned in Table 6.3. The starting temperature was 50 °C. The mixing conditions were optimised to obtain a mixing energy smaller than 500 MJ/m^3. This was done to obtain a situation comparable with that of industrial scale mixing. The rotor speed was 50 rpm. After mixing, the compound was discharged and was sheeted out on a two roll mill. The addition of sulphur and accelerators was carried out on a two roll mill as well.

After the addition of curatives, the curing properties of the compound were determined using a RPA 2000 from Alpha Technologies. The optimum vulcanisation time t_{90} and scorch time t_{s2} were determined. The compounds were subsequently cured in a Wickert laboratory press at 160 °C and 100 bar pressure.

Table 6.2 Compound Formulations in phr

Component			
SBR, NBR or EPDM	100	100	100
Carbon black	20	30	40
Zinc oxide	4	4	4
Stearic acid	2	2	2
TMQ	1	1	1
Sulphur	2.5	2.5	2.5
CBS	1.98	1.98	1.98
TOTAL	131.5	141.5	151.5

Table 6.3 Mixing Scheme

Time (min)	Action
0.00	Open ram, add rubber
0.00-1.30	Rubber mixing
1.30-2.10	Add ZnO, Stearic acid,TMQ and ½ Carbon black
2.10-3.10	Mixing
3.10-3.50	Add ½ carbon black
3.50-5.50	Mixing
5.50	Dump

6.2.2.8 Strain Sweep Measurements

Strain sweep measurements of uncured compounds were performed on the RPA 2000. The storage modulus G' was measured in the range of 0.56 % - 100.04 % strain. The temperature and frequency were kept constant at 60 °C and 0.5 Hz.

6.2.2.9 Stress Strain Properties of Cured Compounds

The stress-strain properties of the cured compounds with the carbon black samples were measured according to ISO 037. The measurements were carried out on a Zwick Z 1.0/TH1S tensile tester.

6.3 RESULTS

This section is divided into three sub sections which will discuss the characterisation of the plasma-coated carbon black, the state of the plasma-coating in rubber and the behaviour of the plasma-coated carbon black in rubber, separately.

6.3.1 Characterisation of the Plasma-Coated Carbon Black

Optimisation of the conditions for the scaling up of the plasma surface modification process was carried out based on the amount of plasma-polymer deposited on the surface of the carbon black. The conditions were varied as mentioned in Table 6.1. 100 g of sample was used in each experiment. The TGA-thermograms of the various coated and uncoated carbon black samples are shown in Fig. 6.2. Pure plasma-polymerised acetylene starts to decompose at 265 °C, which is complete at 600 °C. The weight loss in the region of decomposition of plasma-polymerised acetylene was calculated from the thermograms of the coated and uncoated carbon black samples. The difference in weight loss between coated and uncoated carbon black gives the amount of plasma-polymer deposited on the surface. The calculated weight losses are tabulated in Table 6.1. Based on the TGA-data, RP-P579-6 gave the highest amount of plasma-polymer deposition and those conditions were used for the batch-wise large scale preparation of plasma-coated fullerenic carbon black.

For large scale production, 100 g of sample were used in each batch, whereas in the screening experiments as mentioned in previous chapters only a few grams of sample were used. Hence, as the amount of sample increases the treatment time also needs to be adjusted to achieve appreciable surface modification. 100 g of the sample occupied approximately 3 liters by volume. Hence, sufficient treatment time is necessary to expose and refresh all particle surfaces to plasma and to achieve a uniform surface modification.

Under the conditions mentioned for RP-P579-6, approximately 1.75 kg of plasma-coated carbon black was produced. All the samples from the individual batches were characterised for the amount of plasma-polymer deposited on their surface. The amount of plasma-polymer obtained on carbon black in the various batches varied in the range of 5.5 ± 0.6 weight %.

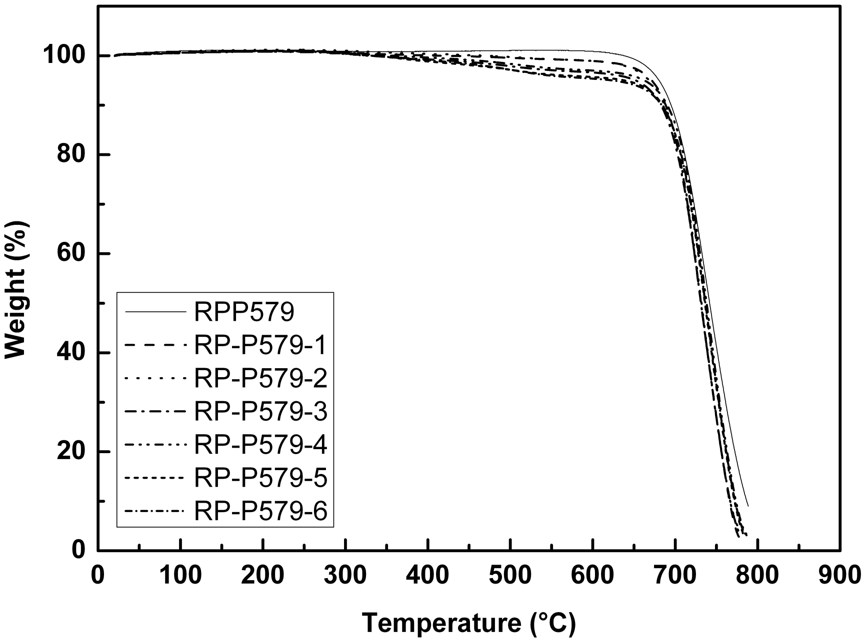


Fig. 6.2 TGA thermograms of uncoated and various plasma- coated carbon black samples

The surface energy of the two rubber samples is shown in Table 6.4. In order to understand the surface energy reduction of the modified filler, the wetting behaviour of the filler with liquids of known surface tension was observed. The wetting behaviour of carbon black samples in liquids of known surface tension gives an indication about the range over which the surface energy has been reduced. The wetting behaviour of coated and uncoated fullerenic carbon black is shown in Fig. 6.3. After the formation of the plasma-polymerised acetylene film, the surface of carbon black should show characteristics corresponding to the formed film: a lower surface energy. After the plasma coating, the fullerenic carbon black shows an appreciable reduction in surface energy and is closer to that of the different rubbers.

This indicates a substantial coverage of the plasma-polymer film over the surface of the fullerenic carbon black.

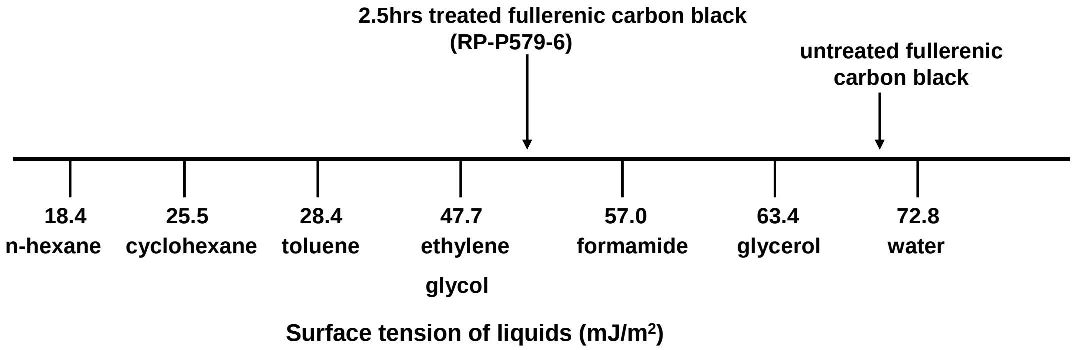


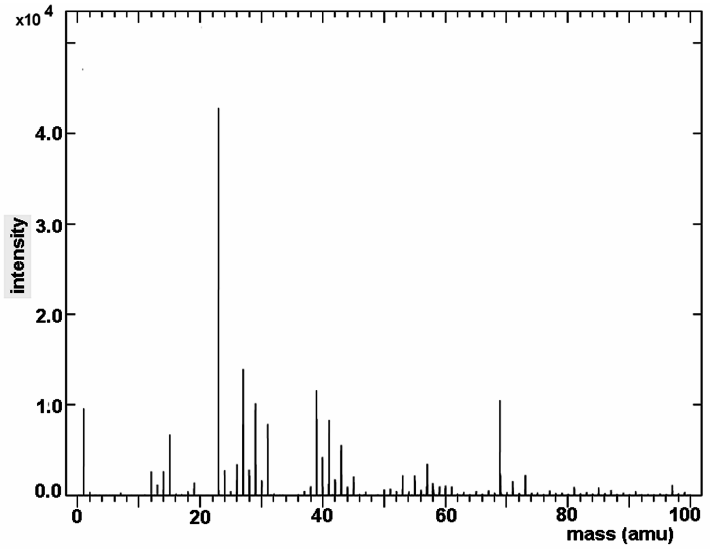
Fig. 6.3 Schematic representation of wetting behaviour of carbon black samples

Table 6.4 Surface Energy Values of Rubbers

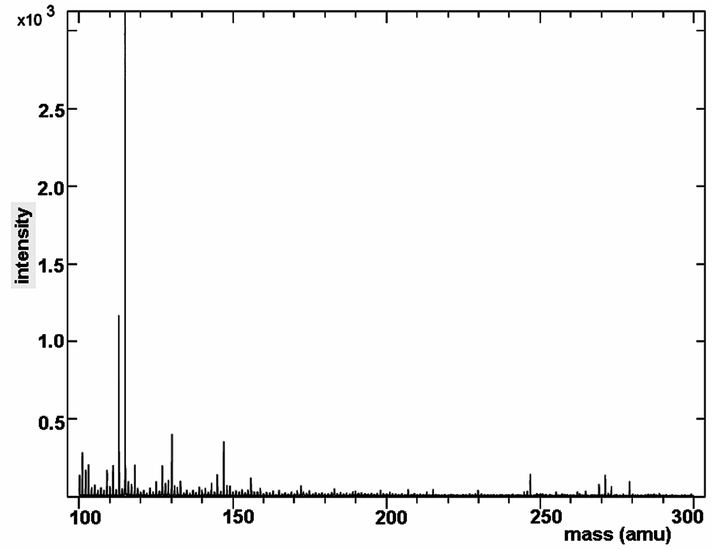
Rubber	Contact angle		Surface energy (mJ/m^2)		
	water	**Di-iodomethane**	**Dispersive component**	**Polar component**	**Total**
S-SBR	78.5	77.2	18.94	9.7	28.64
EPDM	88.26	77.77	18.65	5.0	23.65

In order to understand how the plasma coating affects the surface area of carbon black, the BET and CTAB-surface areas were determined. The BET-surface area gives the total surface area including porosity and the CTAB-surface area gives the available surface area of the carbon black without pores. As far as rubber reinforcement is concerned, the CTAB- surface area is more important, because it gives the surface area which is available for interaction with polymer chains. The BET-surface area of the fullerenic soot reduces from 66.8 m^2/g to 63.1 m^2/g after the deposition of plasma-polymerised acetylene. The CTAB-surface area of the fullerenic soot reduces from 79.6 m^2/g to 69.3 m^2/g after the modification. This reduction in surface area substantiates the formation of plasma coating over the surface and indicates that it has some influence on surface area.

Plasma polymerisation of acetylene will result in the formation of a crosslinked hydrocarbon film. In a positive ToF-SIMS spectrum, such a hydrocarbon film must show intense hydrocarbon peaks and a cluster pattern of mass fragments especially in the higher mass fraction regions of the spectrum[5]. The ToF-SIMS spectrum of untreated RP-P579 is shown in Fig. 6.4. This spectrum displays some hydrocarbon peaks and a peak corresponding to Na^+ (23). This is characteristic of a carbon black surface[6,7]. The ToF-SIMS spectrum of the plasma-coated fullerenic carbon black (RP-P579-6) is shown in Fig. 6.5. The spectrum shows intense hydrocarbon peaks and a cluster pattern of mass fragments especially in the mass range 100-300, thereby confirming the formation of a neat hydrocarbon plasma polymerised film over its surface.

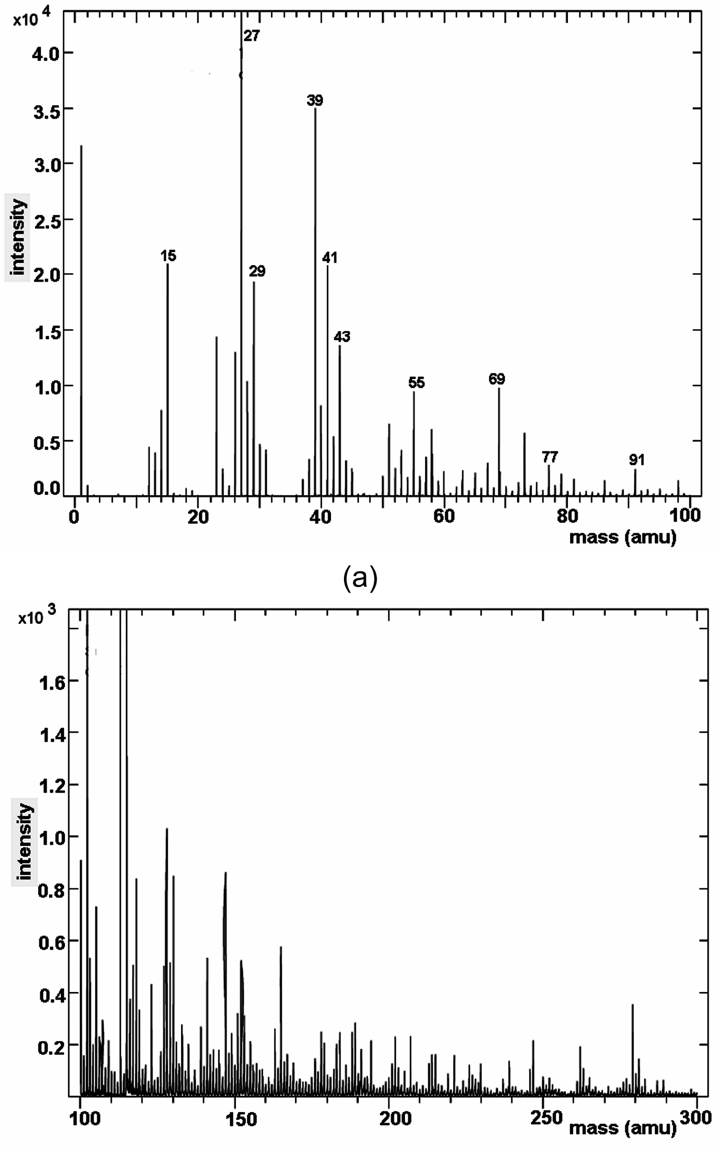


(a)



(b)

Fig. 6.4 ToF-SIMS spectrum on untreated fullerenic carbon black: a) mass range 0-100 (amu), b) mass range 100-300 (amu)



(a)

(b)

Fig. 6.5 ToF-SIMS spectrum of plasma-coated fullerenic carbon black: a) mass range 0-100 (amu); b) mass range 100-300 (amu)

6.3.2 State of Plasma Coating in Rubber

As stated before, during the rubber mixing operation the carbon black is subjected to shear and compressive forces, which may damage the plasma coating. Conductivity measurements were carried out on the uncoated and the plasma-coated carbon black, both in fluffy and granulated form. Fig. 6.6 shows the variation of electrical volume resistivity with density of various carbon black samples.

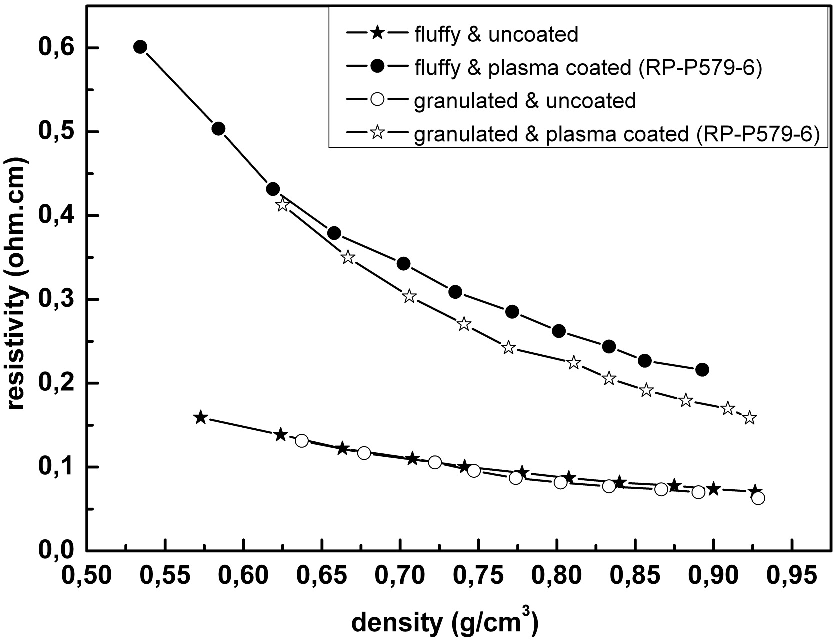


Fig. 6.6 Variation of resistivity with density on various carbon black samples

To note some initial observations, the amount of sample required for occupying a certain volume in the equipment differed for various carbon blacks. Plasma-coated carbon black took relatively less sample by weight, to fill the same volume compared to the uncoated version. This means that the plasma-coated carbon particles tends to occupy more volume than the uncoated version. This is due to the low surface energy of the plasma-polymer layer over the surface of the carbon black.

Fig. 6.6 clearly shows, that the resistivity of fluffy carbon black increases substantially after the deposition of plasma coating. This directly translates to less carbon-carbon contacts in the plasma-coated state. For application in rubber, the fluffy carbon black was granulated. The conductivity measurements carried out on the granulated sample also show an increased resistivity relative to the uncoated version. Compared to the fluffy plasma-coated carbon black, there is some reduction in resistivity, especially at higher compacted densities. Still, the resistivity, values are substantially higher than the uncoated version. This means, that even after granulation there is still a significant amount of plasma coating on the surface of carbon black, which indicates good adherance of the coating.

6.3.3 Behaviour of Plasma Coated Carbon Black in Rubber

In order to understand the behaviour of plasma-coated carbon black in rubber, it was mixed with the different rubbers SBR, NBR and EPDM. The mixing energy was optimised to be smaller than 500 MJ/m^3.

The Payne effects of the plasma-coated carbon black at various filler loadings in SBR, NBR and EPDM are shown in Figs. 6.7, 6.8, 6.9, respectively. The difference in G' value at 0.56 % strain and 100.04 % strain can be represented as the Payne effect. The Payne effect is usually used to obtain information regarding the filler-filler interaction in a rubber matrix[8]. The higher the storage modulus (G') value at lower strains, the higher is the filler-filler interaction. During the strain sweep measurement, the storage modulus value decreases due to breakdown of the filler-filler network to obtain similar G' values at high strains, irrespective of the filler-filler interaction to begin with at low strain.

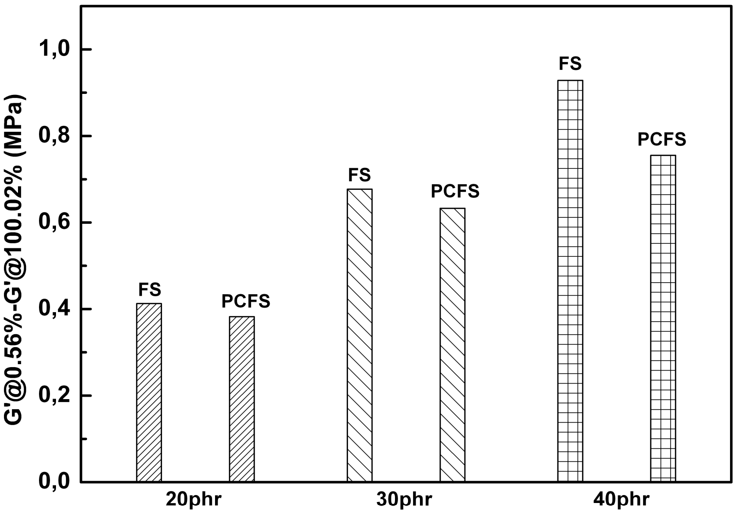


Fig. 6.7 Payne effect in SBR at various carbon black loadings

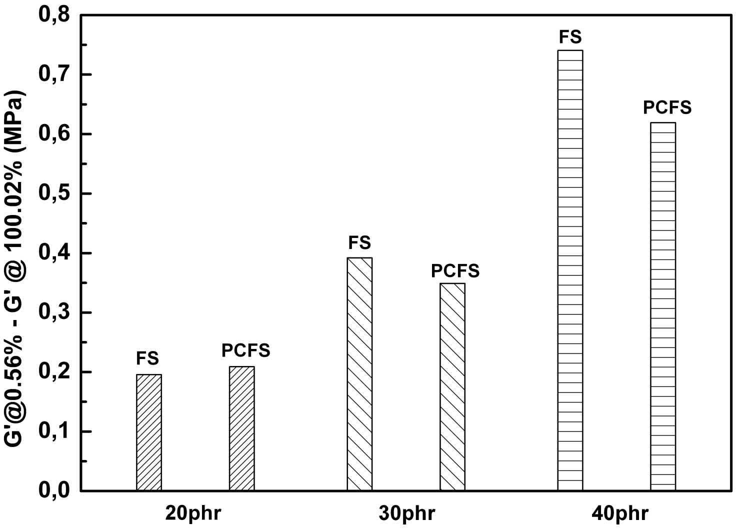


Fig. 6.8 Payne effect in NBR at various carbon black loadings

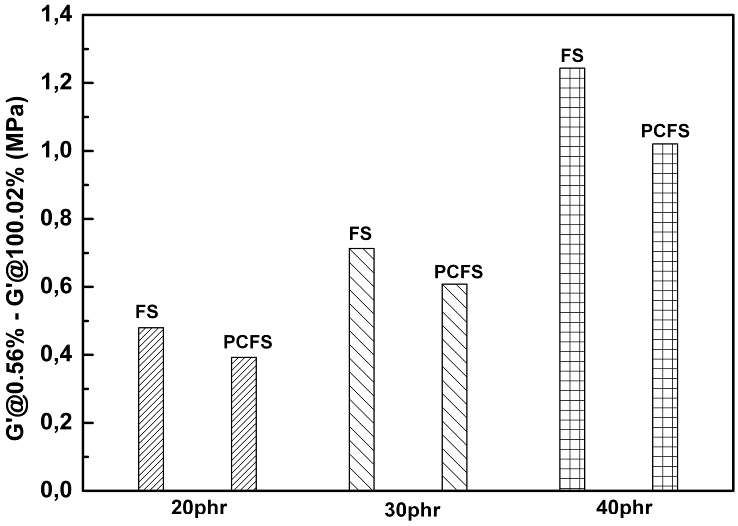


Fig. 6.9 Payne effect in EPDM at various carbon black loadings

The Payne effect is usually employed for rubber compounds with filler contents above the percolation threshold, which depending on the specific grade of carbon black is usually in the range of 30 phr. But in this case, as we have used a high structure carbon black, the data for 20 phr is also given. The plasma-coated carbon black shows a lower Payne effect in all rubber compounds and at all filler concentrations. The difference in Payne effect value becomes more prominent at higher filler loadings.

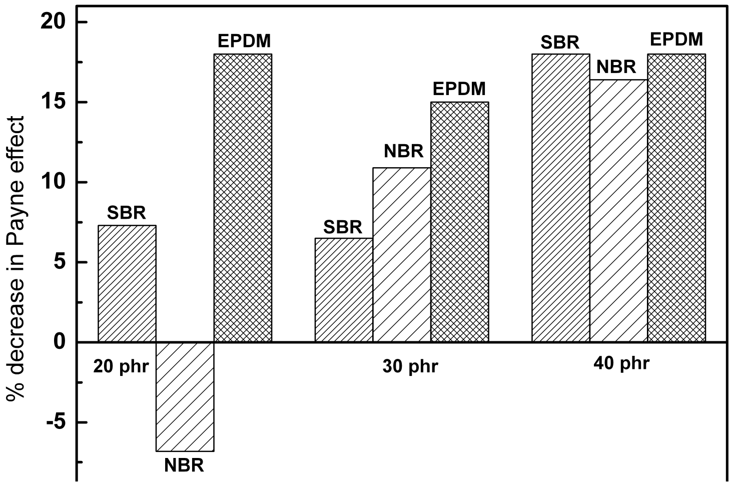


Fig. 6.10 Percentage reduction of Payne effect in different rubbers

The relative decrease of the Payne effect in different rubbers is shown in Fig. 6.10. It clearly shows that at lower filler loadings (20 and 30 phr), the decrease of the Payne effect is most prominent in EPDM rubber. But at higher filler loadings the effect is almost the same for the different rubber samples.

The stress-strain curves of vulcanisates of SBR, NBR and EPDM with 40 phr filler loading are shown in Figs. 6.11, 6.12 and 6.13, respectively. SBR with plasma-coated carbon black shows a slight improvement in tensile strength. In the case of NBR, no significant improvement is observed. In the case of EPDM, there is an appreciable reduction in tensile strength, accompanied by an improvement in elongation at break. Carbon black can interact chemically and physically with elastomers and thus contribute to the reinforcement of the elastomer. It is widely accepted to use the carbon black-rubber interaction parameter to denote the interaction between rubber and carbon black[9]. It is commonly referred to as the slope of the stress-strain curve in a relatively linear region, typically within the range of extension ratios from 100 to 300 %.

$$\text{Carbon black-rubber interaction parameter } \sigma = \frac{\sigma_b - \sigma_a}{\lambda_b - \lambda_a} \qquad (6\text{-}1)$$

Where σ_b and σ_a are the stresses at corresponding strains λ_b and λ_a: 300 and 100 respectively. The modulus development at these elongations has been shown to depend on strong adhesion between the carbon black surface and the polymer[10,11]. While comparing different carbon blacks, the slope of the stress strain curve was found to be a better indicator of the polymer-filler interaction than the individual modulus values[12].

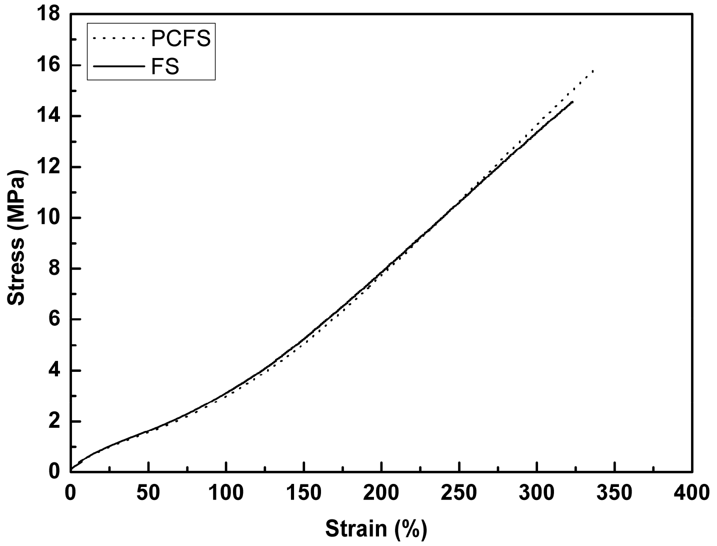


Fig. 6.11 Stress-strain curve of SBR with 40phr carbon black

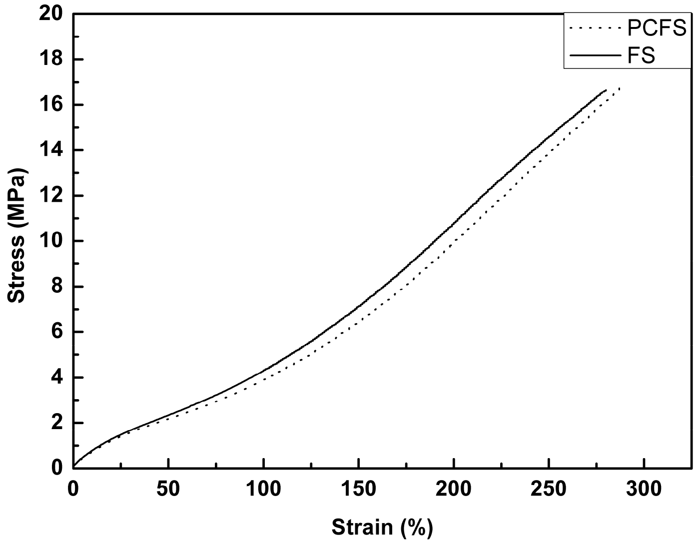


Fig. 6.12 Stress-strain curve of NBR with 40phr carbon black

The calculated σ–values are tabulated in Table 6.5. In the case of SBR and NBR a slight increase in σ–value is observed, whereas in the case of EPDM a significant reduction in carbon black–rubber interaction is observed.

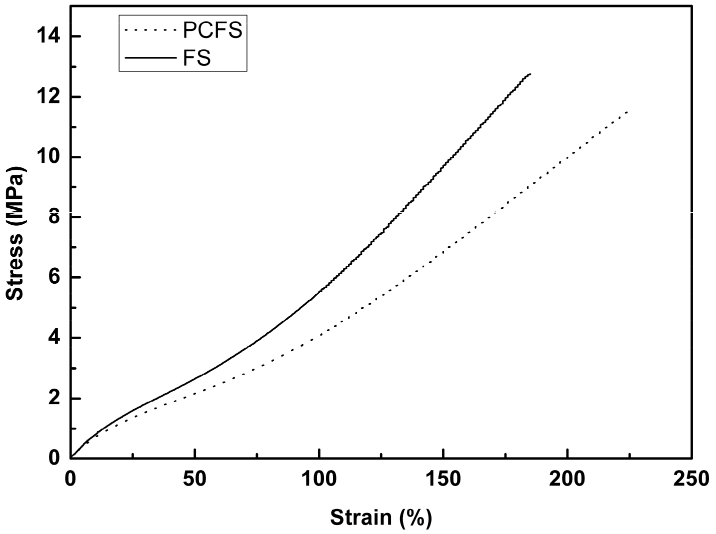


Fig. 6.13 Stress-strain curve of EPDM with 40phr carbon black

Table 6.5 Carbon black–rubber interaction parameter for different systems

Sample	FS	PCFS
SBR	5.5	5.8
NBR	7.5	7.8
EPDM	8.5	5.8

6.4 DISCUSSION

The plasma surface modification process of fullerenic carbon black with acetylene has successfully been scaled up in the tumbler reactor with batch size of 100 g. The TGA-data show an appreciable amount of deposition of plasma-polymerised acetylene over the surface. The TGA-data of individual batches also gave consistent results. The wetting behaviour of the treated fullerenic carbon black shows appreciable reduction in surface energy, again indicating a good coverage by the plasma-polymer film. The ToF-SIMS spectrum of the plasma-coated fullerenic carbon black also confirms the deposition of a hydrocarbon plasma-polymer film over its surface.

The electrical conductivity measurements provide a good understanding on the influence of plasma-coating on the conductivity of carbon black. The measurements carried out on the granulated samples also give an indication about the state of the plasma-polymer film in the rubber matrix. The large increase in electrical resistivity of the fluffy plasma-coated carbon black clearly proves the formation of the plasma-polymer shell over its surface. The increase in resistivity can be attributed to two factors: 1) electrons have to tunnel through the plasma-polymer layer for conduction; 2) the low surface energy of the deposited plasma- coating tends to keep the particles separated. The presence of the plasma-polymer layer on the carbon black surface reduces the carbon-carbon direct contact. This can be considered as low filler-filler interaction in its free-standing state. The fact that the plasma-coated carbon black occupies a higher specific volume than the uncoated version substantiates this observation.

Before mixing with rubber, the plasma-coated fullerenic carbon black had to be subjected to a granulation process. The granulated plasma-coated carbon black also shows an increased electrical resistivity relative to the uncoated version, but somewhat less than that of the coated fluffy version. During the granulation process and conductivity measurements under pressure two things can happen: 1) structure breakdown of the carbon black itself, creating fresh carbon surfaces; 2) damage of the plasma coating creating new surfaces. Both can contribute to a reduction of resistivity after granulation. In the present case, there is a higher probability for structure breakdown of the carbon black during granulation and conductivity measurements, than damage of the plasma-polymer film. The significantly higher resistivity of the granulated version compared to the uncoated version can be taken as an indication that the plasma-polymer layer, being chemically attached on to the surface, can withstand shear and compression forces during a mixing operation to a good extent and hence, stays on the surface of carbon black in the rubber matrix.

In order to judge the effects of plasma-coating of the carbon black in the various rubber systems, it is important to define the different factors which may influence the reinforcing power of carbon black:

a. the primary particle size, as reflected in the BET and/or CTAB specific surface areas;
b. the spatial arrangement of the primary particles in the aggregates, what is commonly denoted as the ‘structure’;
c. the amount of filler-filler interaction;
d. the amount of filler-polymer interaction, whether chemical or physical of nature.

Admittedly, the plasma-coating may have an effect on all four, which in rubber matrices may turn positive in some, negative in other cases; in again other cases balancing each others effects.

The plasma-coated carbon black shows less filler-filler interaction in all rubber compounds as evidenced by the Payne-effect data. Apart from 20 phr filler in NBR a lower filler-filler interaction was observed for all other rubber systems. The reduction in Payne-effect is more prominent at higher filler loadings. The reduction in filler-filler interaction is obviously due to the lower surface energy of the plasma-coated carbon black. The wetting behaviour of the plasma-coated carbon black clearly showed an appreciable reduction in surface energy towards the range of the different rubbers. The surface energy closer to that of the elastomers aids in better wetting of the filler particles by the elastomer matrices[13,14].

Considering the relative decrease of the Payne-effect in the different rubbers, the reduction is most prominent in EPDM rubber, wherein carbon black is less compatible compared to SBR and NBR. The difference shows most clearly at lower filler loadings. At higher filler loadings the percentage reduction in filler-filler interaction is almost the same for all three rubbers. At higher loadings, a good carbon-carbon network is formed in all rubber systems and hence the reduction in filler-filler interaction is similar, irrespective of the matrix in which it is dispersed.

The stress-strain behaviour of SBR is slightly affected by the presence of the plasma-coated carbon black. A slight improvement in the tensile strength and elongation at break is observed. In the case of NBR, no significant improvement is observed. In the case of EPDM, there is some reduction in tensile strength, accompanied by an improvement in elongation at break.

On deposition of the plasma-polymer layer, the primary particle size of carbon black increases corresponding to the thickness of the layer. There are no signs that the “structure” of the carbon black is significantly changed by the coating. The surface area measurements show, that there is a slight decrease in surface area after the deposition of the plasma-polymer. Furthermore, deposition of the plasma-polymer layer makes the orginal carbon black surface unavailable for direct interaction with rubber; or in other words the plasma-polymer layer alters the surface activity of carbon black. It makes the plasma-coated carbon black less reinforcing compared to the uncoated version for all rubbers. In the case of SBR we observe a slight increase in tensile strength and elongation at break. It has been reported[15], that plasma-polymerised acetylene contains some amount of unsaturation. Peaks in the ToF-SIMS spectrum at positions 27($C_2H_3^+$), 39($C_3H_3^+$), 41($C_3H_5^+$), 43($C_3H_7^+$), 53($C_4H_5^+$), 55($C_4H_7^+$) [amu] indicate the presence of unsaturated fragments in the plasma-polymerised film[16-18]. There are some aromatic peaks present too on the surface of the plasma-polymer film. Peaks at positions 77, 91, 105, 115, 128 [amu] etc. correspond to aromatic peaks. During ion bombardment structural rearrangements of unsaturated organics can occur forming these cyclic aromatic ions[16-18]. The level of unsaturation is usually determined by comparing the intensities of certain hydrocarbon peaks. This is based on the fact that in a saturated polymer like polyethylene, the saturated $C_2H_5^+$ peak at 29 [amu] is larger than the unsaturated peak at 27 [amu]. On the other hand, in polymers with unsaturated carbon-carbon bonds like polyacetylene the intensity of peak 27 [amu] dominates[18]. In the case of plasma-coated carbon black, the presence of the intense $C_2H_3^+$ peak at 27 [amu] indicates the occurrence of unsaturation in the plasma-polymerised acetylene film: Fig. 6.5. There are also peaks at 39, 41, 43, 77, 91, 105, 115 and 128 [amu] showing the presence of unsaturation in the plasma-polymerised acetylene film. Tsai and coworkers[19,20] carried out an investigation on the reactions between model rubber systems and plasma-polymerised acetylene films. They compared a saturated model: squalane, and an unsaturated model: squalene, for their reactions with plasma-polymerised acetylene. They found that some sort of crosslinking-reaction happened between the squalene model system and plasma-polymerised acetylene through intermediates formed during vulcanisation. However, there was no evidence for a direct reaction of the curing system with the squalane and for crosslinking between the squalane and plasma-polymerised acetylene.

So, even though it has not been explicitly investigated in the present case, it seems most probable that the observed effects in the various rubbers have to be viewed in the light of the possible interactions between plasma-polymerised acetylene and the unsaturations in these polymers through crosslinking intermediates. A slight increase in the rubber-carbon black interaction parameter may also be an indication of this effect. Admittedly, the observed improvement in the present case is not very substantial. In the case of EPDM-rubber, a substantial decrease in rubber-carbon black interaction parameter is observed. As noted previously and proven by model compound studies[19,20], there is no reaction taking place between plasma-polymerised acetylene and a saturated rubber system. EPDM being a main-chain saturated polymer, there is therefore little chemical interaction possible between the plasma-polymerised acetylene and the rubber. This is the reason for the substantial decrease in rubber-carbon black interaction parameter. However, there was still a substantial reduction in the filler-filler interaction. This is due to the lower surface energy of the plasma-coated carbon black. Exhibiting a surface energy closer to that of the matrix, will aid in better wetting of the filler particle by the elastomer matrix. This in turn will lead to an improvement in dispersion of the filler in the matrix, even though at the same time the plasma-polymerised acetylene film reduces the interaction possibilities between the carbon black filler and the EPDM rubber. For an unsaturated rubber, there is still a possibility to improve the interaction by manipulating the level of unsaturation of the plasma-polymerised acetylene film. The fact that there is no reduction in the rubber-filler interaction after the incorporation of the plasma-coated carbon black in SBR and NBR point towards this possibility.

6.5. CONCLUSIONS

The plasma surface-modification process for the fullerenic carbon black has successfully been scaled up in a tumbler reactor for a batch size of 100 g. TGA, wetting behaviour with liquids of known surface tension and ToF-SIMS measurements clearly prove the formation of a plasma-polymer layer with good surface coverage. Electrical conductivity measurements show that the plasma-polymer layer reduces the carbon–carbon direct contacts. The granulated sample still has a substantially higher resistivity than the uncoated version. This indicates that the plasma-polymer layer stays on the carbon black even after mixing with rubber. The plasma-coated carbon black shows low filler–filler interaction in the different rubber systems compared to the uncoated version. This is due to the low surface energy of the plasma-coated carbon black. The filler-polymer interaction remains unaffected in unsaturated rubber matrices, while in a saturated rubber, it is found to decrease. EPDM-rubber shows a decrease in tensile properties due to a substantial decrease of interaction between the plasma-polymer film and the polymer due to its saturated nature. Whereas in SBR and NBR, the properties remain more or less unaffected due to possible interactions remaining between unsaturations left in the plasma-polymer layer and unsaturations in these rubbers.

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Chapter 7

Effect of Plasma Acetylene-Coated Carbon Black in Dissimilar Elastomer Blends

Carbon black tends to be preferentially located in one phase of a rubber blend. A novel approach to overcome this is attempted, as described in this chapter. A plasma-coated carbon black is tested in dissimilar SBR/EPDM and NBR/EPDM rubber blends for its distribution between the phases. The Payne effect, transmission electron microscopy (TEM) and stress-strain properties are used to characterise the blend system with the acetylene plasma-coated and uncoated carbon black. The results show that the plasma-coated carbon black is better dispersed in the blend. However, the expected improvement in mechanical properties due to the better dispersion is not visible from the results obtained. This is most probably due to the less reinforcing effect of the plasma-coated carbon black. However, the less reinforcing effect of the plasma-coated carbon black is balanced by the positive effects arising from the better dispersion of the plasma-coated carbon black.

7.1 INTRODUCTION

Non-uniform distribution of carbon black in elastomer blends is a known problem to the rubber industry from its beginning. The problem is prominent in the case of blends of dissimilar elastomers, i.e. blends of an unsaturated rubber and a saturated rubber. In such cases, carbon black has a tendency to partition in the unsaturated phase, leaving behind the saturated phase. This leads to an over-reinforcement of the unsaturated phase and to a low degree of reinforcement of the saturated phase. This uneven distribution of filler appreciably influences the morphology and physical properties of the blend. This is the major reason which restricts the commercial use of blends such as NR/EPDM, NR/NBR, NR with epoxidised natural rubber and tyre side wall compositions based on NR/BR/EPDM.

Several investigations have been carried out on the topic of non-uniform distribution of carbon black in rubber blends[1-7]**.** Most of these were on different methodologies for the determination and visualisation of the distribution of carbon black between the phases in the blends. Electron microscopy is one of the most commonly utilised and accepted techniques for this purpose. Several other techniques like dynamic mechanical analysis[5,6], electrical conductivity measurements[7] etc. have also been utilized for this purpose. But the application of those techniques has been limited to certain blend systems.

The distribution of filler particles between the phases of an elastomer blend is affected by various factors like unsaturation of the rubbers, their viscosity and polarity, and the mixing sequence. Several approaches have been attempted in the past to achieve a uniform distribution of filler in a dissimilar rubber blend. They include modifications in the mixing sequence, modification of the low unsaturated rubber to raise its polarity, etc[8-11]**.** But these steps were of limited success or ended up in additional mixing steps in the processing.

One approach to improve the distribution and dispersion of carbon black in rubber blends is to improve the wetting behaviour of carbon black by the low surface energy rubbers. For this purpose, the surface energy of carbon black has to be matched to that of the different rubbers in the blend. A surface energy closer to that of the matrix will aid in better wetting of the filler by the matrix. From the previous chapters its clear, that plasma polymerisation on carbon black using acetylene as monomer can appreciably reduce the surface energy of carbon black[12,13]. Upon addition of the plasma coated carbon black to the rubber blend, low surface energy rubbers could wet the filler surface better as is clear from its behaviour in single rubbers, which is described in Chapter 6. Thus use of plasma coated carbon black may be able to direct the filler to the phase into which it has to arrive in the blend, achieving a uniform distribution of the filler in the blend. Attempts in this direction are presented in this chapter. Two different rubber blend systems are investigated: SBR/EPDM and NBR/EPDM. As these two systems widely differ in their level of unsaturation and polarity, they form an ideal system to investigate the behaviour of plasma coated carbon black. The distribution aspect is studied using transmission electron microscopy (TEM) as the major tool. The plasma-coated fullerenic carbon black, as described in Chapter 6, is also used for the experiments described in this chapter.

7.2 EXPERIMENTAL

7.2.1 Materials

The fullerenic carbon black was obtained from Timcal Graphite and Carbon, Belgium and was obtained in the fluffy form. The sample code is RP-P579. The specific surface area: BET surface area of the fullerenic carbon black is 66.8 m^2/g. The monomer used for plasma polymerisation was acetylene (99.6% purity) as supplied by Matheson trigas, Ohio, USA.

The plasma coated carbon black was granulated at Timcal Graphite and Carbon, Willebroek, Belgium.

The rubbers used for the experiments were a solution Styrene-Butadiene-Rubber (S-SBR), Acrylonitrile Butadiene Rubber (NBR) and an Ethylene-Propylene-Diene rubber (EPDM). S-SBR was supplied by Lanxess Corporation, Germany: Buna VSL 5025-0HM with Mooney viscosity ML (1+4)100 °C: 65, vinyl content 50%, styrene content 25%. NBR was also supplied by Lanxess Corporation, Germany: Perbunan NT 3446 with Mooney viscosity ML (1+4) 100°C: 45, acrylonitrile content 34.7±1. EPDM rubber was supplied by DSM Elastomers, the Netherlands: Keltan 4703 with Mooney viscosity ML (1+4)125 °C: 65, ethylene content 48 wt% and ethylidene norbornene content 9.0 wt %.

Two sample codes are used in the rubber data of this chapter. Rubber compounds with fullerenic carbon black will be denoted as FS and that with plasma-coated fullerenic carbon black will be denoted as PCFS.

7.2.2 Methods

7.2.2.1 Plasma Polymerisation

Plasma polymerisation was carried out in a Radio Frequency (RF) plasma tumbler reactor at the University of Cincinnati, USA. Details of the process are described in Chapter 6 under section 6.2.2.1. The optimised condition for the process was 100W RF power, 40 Pa monomer pressure and 2.5 hrs of treatment time. The characterisation of the plasma-coated carbon black was carried out as described in Chapter 6.

7.2.2.2 Rubber Mixing

Rubber compounds with carbon black samples were prepared according to the formulation given in Table 7.1. The mixing was carried out in a Brabender Plasticorder internal mixer with a chamber volume of 390 ml. The mixing procedures employed are mentioned in Table 7.2. The starting temperature was 50 °C. The rotor speed was 50 rpm. The mixing conditions were optimized to a mixing energy < 500 MJ/m^3. This was done to have a comparable situation with that of industrial scale mixing. After mixing, the compounds were dumped and sheeted out on a two roll mill. The addition of sulphur and accelerators was carried out in a second step on the two roll mill.

After the addition of curatives, the curing properties of the compound were determined using a RPA 2000 from Alpha Technologies. The optimum vulcanization time t_{90} and scorch time t_{s2} were determined. The compounds were cured in a Wickert 1600 laboratory press at 160 °C and 100 bar pressure till the t_{90}.

Table 7.1 Compound Formulations in phr

Component	phr	phr	phr	phr	phr
S-SBR	100	-	-	50	-
NBR	-	100	-	-	50
EPDM	-	-	100	50	50
Carbon black	40	40	40	40	40
ZnO	4	4	4	4	4
Stearic acid	2	2	2	2	2
TMQ	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5
CBS	1.98	1.98	1.98	1.98	1.98
TOTAL	151.5	151.5	151.5	151.5	151.5

Table 7.2 Mixing Scheme

Time (min)	Action
0.00	Open ram, add rubber
0.00-1.30	Rubber mixing
1.30-2.10	Add ZnO, Stearic acid,TMQ and ½ Carbon black
2.10-3.10	Mixing
3.10-3.50	Add ½ carbon black
3.50-5.50	Mixing
5.50	Dump

7.2.2.3 Strain Sweep Measurements

Strain sweep measurements of uncured compounds were performed on the RPA 2000. During the measurement the storage modulus was measured as a function of strain in the range of 0.56 % - 100.04 %. The temperature and frequency were kept constant at 60 °C and 0.5 Hz, respectively.

7.2.2.4 Morphological studies by TEM

The morphology of the blend samples was studied using transmission electron microscopy (TEM). Ultrathin sections (70 nm) of the blend samples were cut using a diamond knife at -130 °C. The sections were then vapour stained with OsO_4. The staining time was 10 min. The TEM studies were performed on a Philips CM 30 transmission electron microscope.

7.2.2.5 Stress Strain Properties

The stress-strain properties of the compounds with carbon black samples were measured according to ISO 037. The measurements were carried out on a Zwick Z 1.0/TH1S tensile tester.

7.3 RESULTS

The plasma coated carbon black was characterised using different techniques as described in Chapter 6. The data showed the formation of a hydrocarbon plasma polymer over the surface of carbon black. The behaviour of the plasma-coated carbon black in dissimilar elastomer blends is discussed below.

7.3.1 SBR/EPDM blend

The difference in G' value at 0.56 % strain and 100.04 % strain can be represented as the Payne effect. The Payne effect is usually used to obtain information regarding the filler-filler interaction in a rubber matrix[14]. The higher the storage modulus (G') value at low strains, the higher is the filler-filler interaction. During the strain sweep measurement, the storage modulus value decreases due to breakdown of the filler-filler network. The Payne effects in SBR, EPDM and their 50:50 blends loaded with 40 phr carbon black are shown in Fig. 7.1.

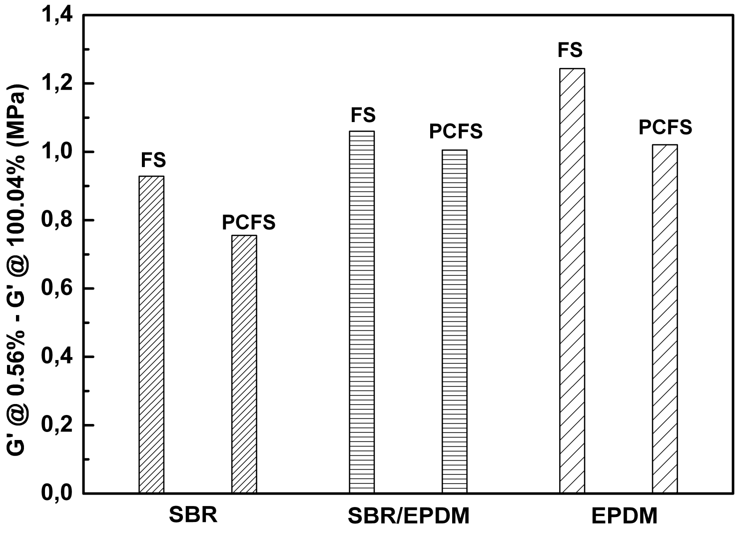


Fig. 7.1 Payne effect in SBR, EPDM and 50:50 SBR/EDPM blend

The data show that the plasma-coated carbon black has less filler-filler interaction in SBR and EPDM matrices. This is because of the lower surface energy of the plasma-coated carbon black. The Payne effect has not been used in the case of a dissimilar blend to study the distribution of filler in the blend. However, it may still be possible to get some indications about the dispersion and distribution of the plasma-coated carbon black from this data. With the uncoated carbon black, the Payne effect in the SBR/EPDM blend places itself in between pure SBR and EPDM. In a dissimilar blend carbon black is preferentially located in the highly unsaturated phase, in this case the SBR-phase. Compared to the situation in a SBR matrix with 40 phr filler, in the 50:50 blend of SBR and EPDM, the filler has approximately only half the volume to occupy, as the filler has more affinity towards the SBR-phase. Naturally, the filler-filler interaction would then be higher in the blend than in the case of a straight SBR compound. This is clear from the present data. The SBR/EPDM blend with the plasma-coated carbon black however, shows a Payne effect similar to that of straight EPDM-rubber with plasma coated carbon black. This might well be an indication that the EPDM-phase is more populated with plasma coated carbon black and hence the blend shows behaviour similar to the EPDM rubber. Moreover, the Payne effect value of the SBR/EPDM blend with the plasma-coated carbon black is lower than that with the uncoated version. This can be taken as an indication that the coated filler is better dispersed in the blend than the uncoated version, i.e. the EPDM-phase is more populated with the plasma-coated black and the coated filler in the SBR-phase is better dispersed than the uncoated version.

A morphological investigation of the blend may give a better idea about the distribution of the filler between the phases. Transmission electron microscopy was used to study the morphology of the filled blend system. For this purpose, thin sections of the SBR/EPDM blend were stained with vapour of OsO_4. Initially for optimizing the measurement, a 70:30 and a 30:70 blend were stained for 15 min and observed through the microscope. The images obtained are shown in Fig. 7.2.

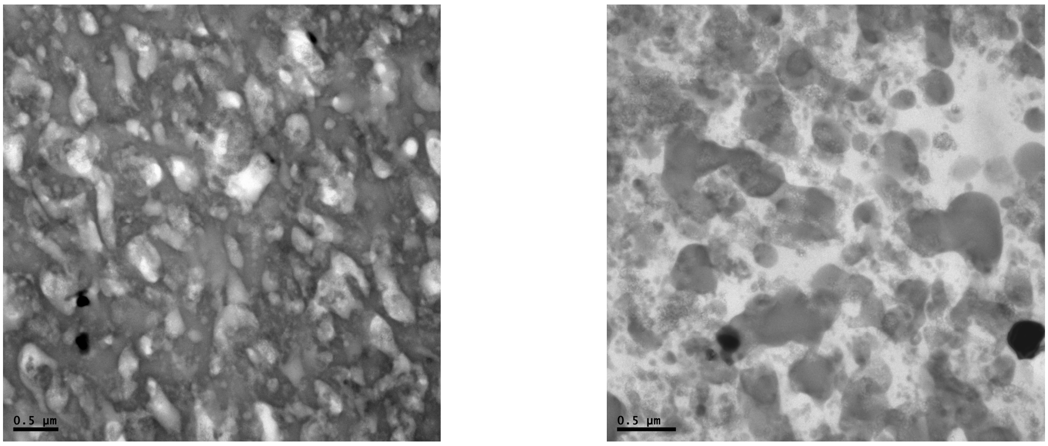


Fig. 7.2 TEM images of SBR/EPDM blends with 20 phr uncoated carbon black a)70:30; b)30:70

The image clearly shows a two phase morphology. The unsaturated phase: SBR, has selectively been stained and appears dark in the image. The saturated phase: EPDM appears lighter in the image. In the 70:30 blend, the stained portion forms the continuous phase and the unstained EPDM forms the discontinuous phase. The image of 30:70 blend clearly shows a phase inversion. But in both cases the carbon black is not properly visible. This is because most of the carbon black is located in the stained SBR-phase which appears dark. Hence the staining time in the next experiments was reduced to 10 min.

Another technique adopted in this context was that all the measurements were carried out a bit out-of-focus. This helps to identify the boundary of any solid particle and hence the location of the carbon black particles. Fig. 7.3 shows an image taken out-of–focus. The carbon black particles are clearly visible. In all further experiments, a slight out-of–focus was used in order to identify the carbon black. In addition to this technique, both stained and unstained sections were compared. This also provides a good impression about the distribution of the carbon black in the blend.

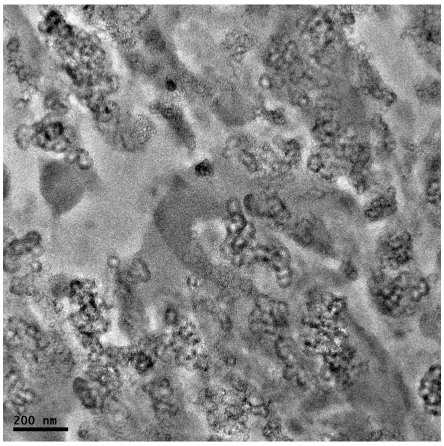
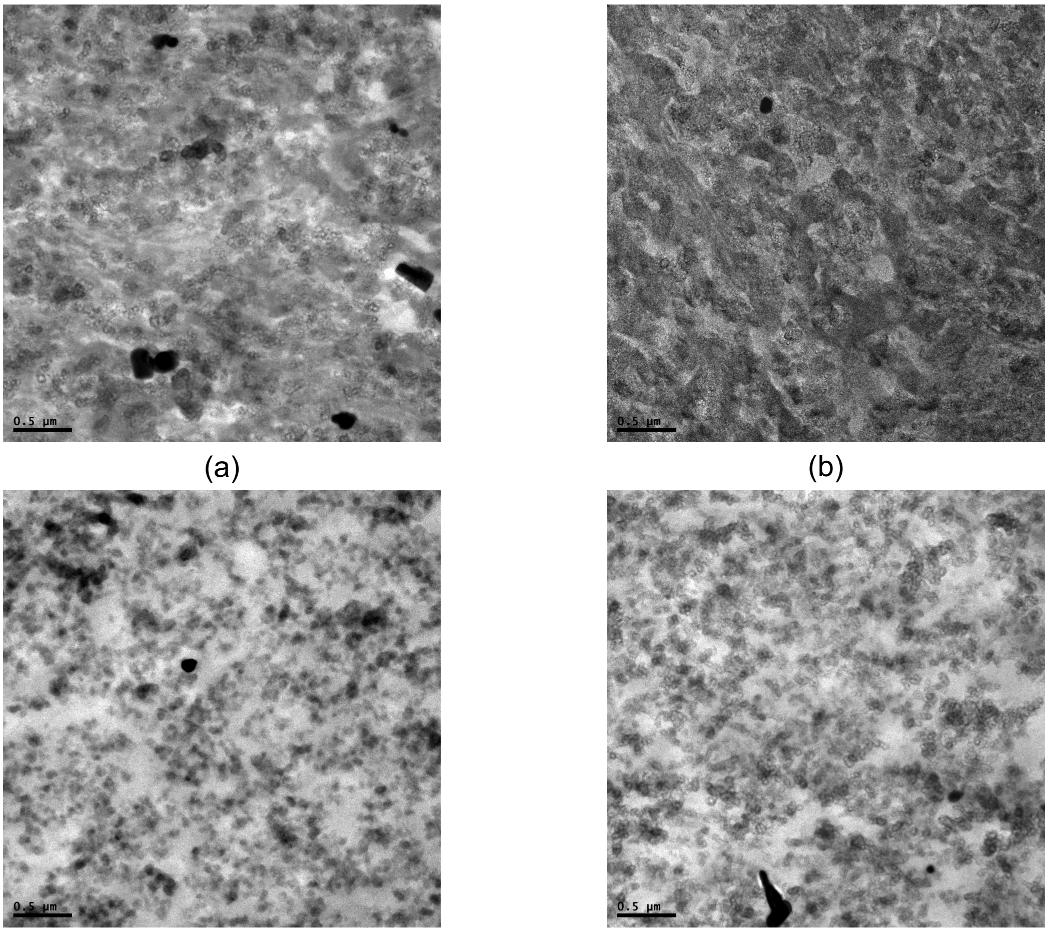


Fig. 7.3 TEM image of a carbon black filled rubber blend taken out-of- focus

Fig. 7.4 shows the TEM-images of SBR/EPDM 50:50 blend with 40 phr carbon black. The image shows that the fullerenic carbon black is preferentially located in the SBR-phase. The unstained section shows occupied and unoccupied areas with carbon black. Comparing the stained and unstained sections, it is clear that the unoccupied areas in the unstained section are those of EPDM. The TEM-image of the blend with the plasma-coated carbon black shows that the filler is better dispersed in the matrix. The unstained section reveals that there are less unoccupied areas, which means that the EPDM-phase is also populated with the plasma-coated carbon black. Admittedly, there are still unoccupied EPDM areas in the blend. However, the addition of plasma-coated carbon black has improved the overall dispersion of the filler in the blend and also between the phases.

The stress-strain curve for the SBR/EPDM blend with uncoated and plasma-coated carbon black is shown in Fig. 7.5. The blend with plasma-coated carbon black shows a slightly higher stress development in the stress-strain curve. This may be due to the better filled EPDM-phase in the blend.



(a) (b)

(c) (d)

Fig. 7.4 TEM images of a SBR/EPDM 50:50 blend with: a) 40 phr fullerenic carbon black; b) plasma coated fullerenic carbon black; c) unstained section with fullerenic carbon black; d) unstained section with plasma coated fullerenic carbon black

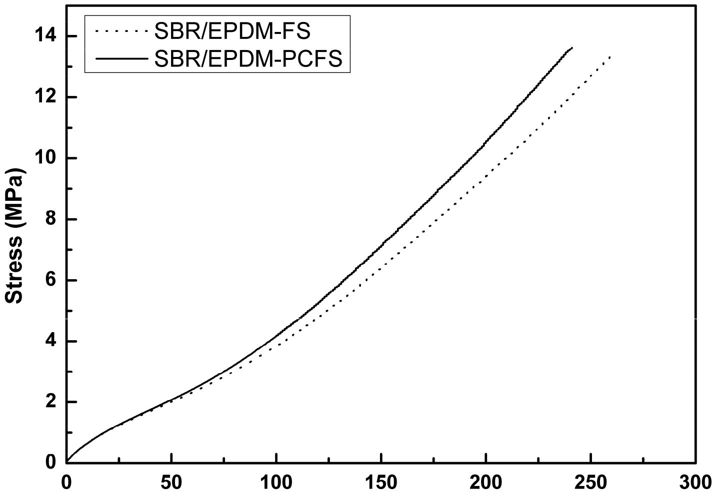


Fig. 7.5 Stress-strain curve of the SBR/EPDM 50:50 blend with 40 phr carbon black

7.3.2 NBR/EPDM blend

Fig. 7.6 shows the Payne effect in NBR, EPDM and their 50:50 blend filled with 40 phr carbon black. Plasma-coated carbon black shows a lower Payne effect in the NBR and EPDM single rubber systems. The blend system with uncoated carbon black shows a Payne effect similar to that of NBR. After the incorporation of plasma-coated carbon black, the blend also shows a lower Payne effect than the uncoated version. This may be an indication that the plasma-coated carbon black is better dispersed in the blend.

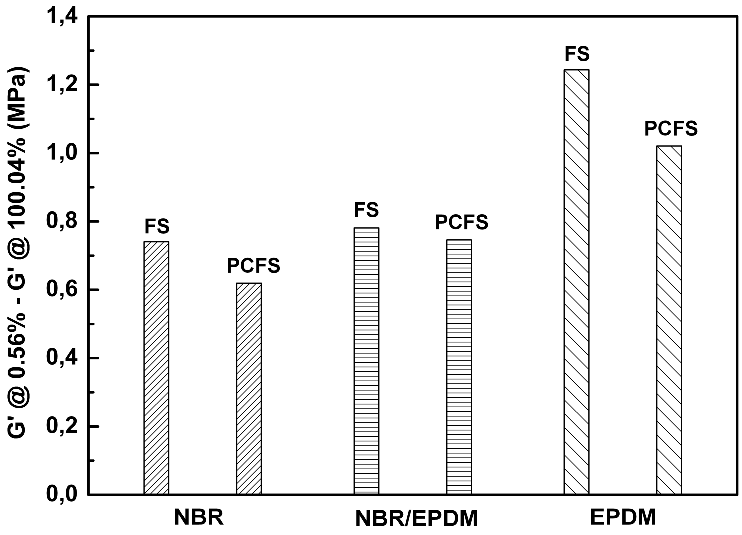
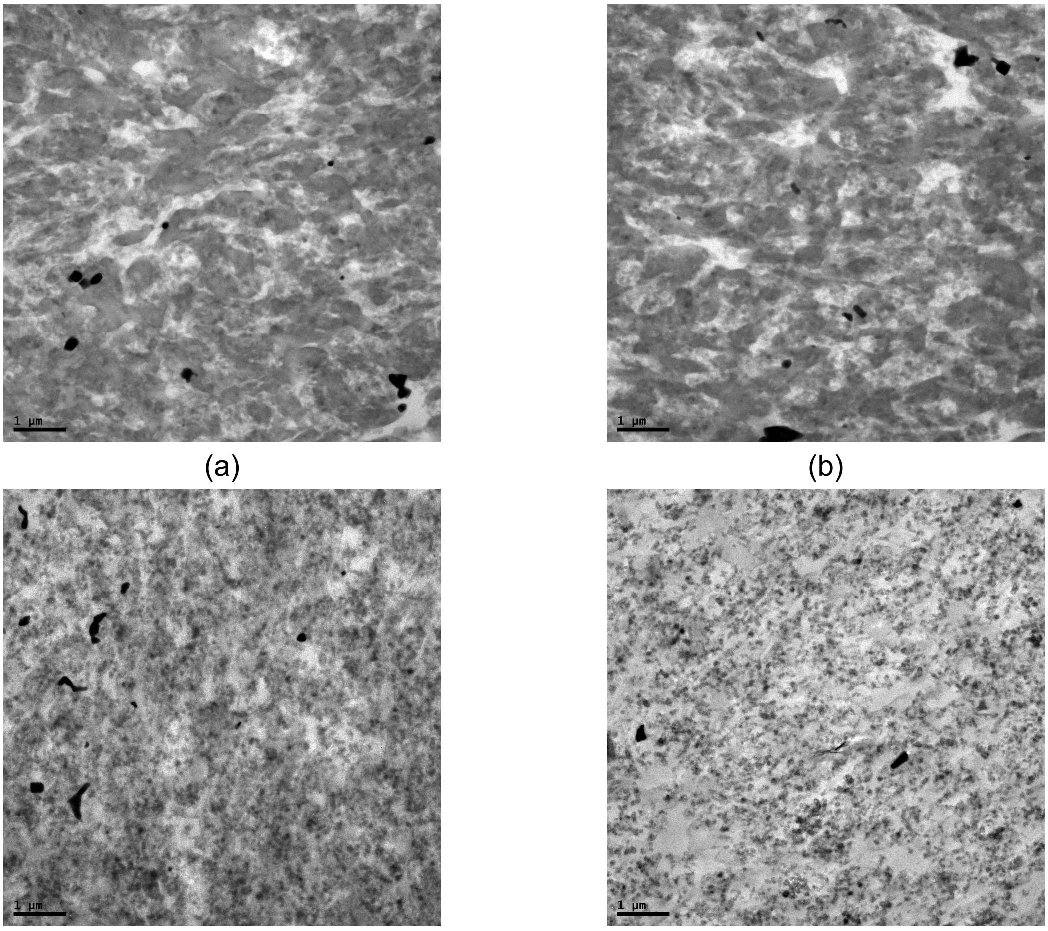


Fig. 7.6 Payne effect in NBR, EPDM and 50:50 NBR/EPDM blend with 40phr carbon black

TEM images of the NBR/EPDM blends with 40 phr carbon black are shown in Fig. 7.7. The information which the images provide is a bit different from that of the SBR/EPDM blend. Here in the uncoated state itself, we see some amount of carbon black located in the EPDM-phase. This was not an expected observation. It may be attributed to the behaviour of the fullerenic carbon black. After the incorporation of the plasma-coated carbon black, as the TEM images reveals, the dispersion of carbon black in the whole matrix is improved.

The stress-strain curve of the NBR/EPDM blend is shown in Fig. 7.8. A major difference in behaviour is not observed between the compounds with coated and uncoated carbon black.



(a) (b)

(c) (d)

Fig. 7.7 TEM images of the NBR/EPDM 50:50 blend with 40 phr of: a) fullerenic carbon black; b) plasma-coated fullerenic carbon black; c) unstained section with fullerenic carbon black; d) unstained section with plasma-coated fullerenic carbon black

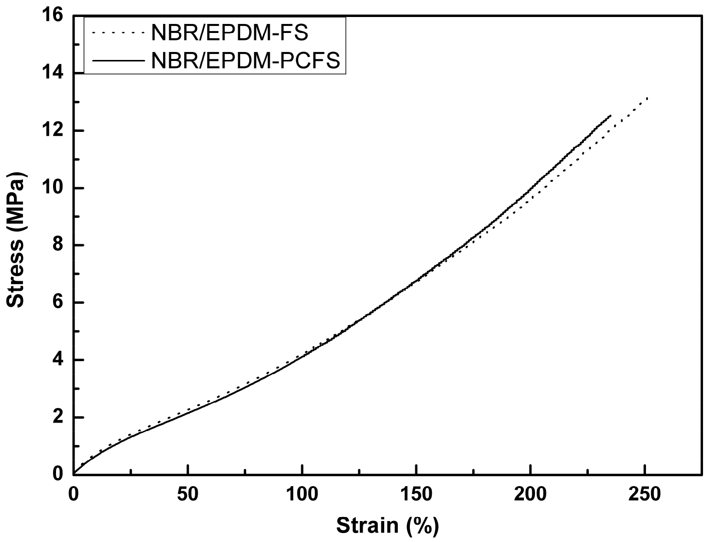


Fig. 7.8 Stress-strain curve of the NBR/EPDM 50:50 blend with 40 phr carbon black

7.4 DISCUSSION

The results show that the plasma-coated carbon black tends to be better dispersed in the blend matrices. The Payne effect data gives indications that the EPDM phase might well be more populated with the plasma-coated carbon black. The TEM image of the SBR/EPDM blend with the plasma-coated carbon black (both stained and unstained), shows that there is more carbon black in the EPDM-phase than in the case of uncoated black. The lower amounts of unoccupied areas in the unstained section also indicate that the EPDM-phase is more populated than with uncoated black. The better dispersion and distribution of carbon black in the blend matrix is due to the fact that the plasma-coated carbon black is better wetted by both SBR and EPDM. As a result the carbon black is better dispersed in the SBR-phase and a higher amount of carbon black is also found in the EPDM-phase.

However, the expected improvement in properties due to better dispersion is not visible from the results obtained. The SBR/EPDM blend with the plasma-coated carbon black shows a slightly higher stress development in the stress-strain curve. This may be due to the better filled EPDM-phase in the blend. But the improvement is not substantial. The observations point towards the fact, that the positive effects due to improvement in dispersion are suppressed by some other effects caused by the incorporation of the plasma-coated carbon black. In order to understand this in more detail, we have to recall the discussion in Chapter 6 about the interaction of the plasma-polymer film with unsaturated and saturated rubbers. The deposition of the plasma-polymer layer on the surface carbon black makes the carbon black less reinforcing. However, there are interactions possible between the unsaturations in the rubber and the remaining unsaturations in the plasma-polymer film. In the case of SBR, a slight improvement in the tensile strength and elongation at break was observed. In the case of NBR, no significant improvement was observed. In the case of EPDM, there was some reduction in tensile strength, accompanied by a clear improvement in elongation at break.

Now in the blend, the total effect of the plasma-coated carbon black will be a combination of the effects of the plasma-coated carbon black in the individual rubbers in the blend. In the SBR/EPDM blend, a combination of the previously mentioned effects could be expected. Both phases wet the plasma-coated carbon black. The SBR-phase contributes by having an interaction with the remaining unsaturations in the plasma-polymerised acetylene film. The EPDM-phase also shows a modulus improvement, because the phase is more populated with carbon black. The stress-strain behaviour of the SBR/EPDM blend points towards this effect. Since the plasma-coated carbon black does not have any interaction with a saturated rubber, it might well be possible that some portion of the plasma-carbon black that arrived in the EPDM-phase could transfer to the SBR-phase during vulcanisation. However, we do not observe a reduction in any of the properties measured after the incorporation of the plasma-coated carbon black. This might be due to the fact that the less reinforcing effects of the plasma-coated carbon black are well counter-balanced by the positive effects due to the interactions between the unsaturated rubber and the plasma-polymer film, respectively by the slightly better dispersion and distribution of the plasma-coated carbon black between the phases in the blend.

The behaviour of the NBR/EPDM blend is contrary to what was expected. In the uncoated state of the carbon black, an appreciable amount was found to be located in the EPDM-phase. This may be attributed to the specific behaviour of the fullerenic carbon black again. Upon addition of the plasma coated carbon black, the dispersion of the filler is improved as revealed by the TEM images. In the blend, however, no significant difference in tensile behaviour was observed.

To summarise, the effect of the plasma-coated carbon black in a dissimilar rubber blend is a combined effect of individual contributions from the rubbers in blend. The plasma-coated carbon black improves the dispersion in single rubber systems and their blends. But the overall mechanical properties are also influenced by the interaction between the plasma-coated carbon black and the individual rubbers. The difference in behaviour in this respect of saturated and unsaturated rubbers is reflected in the overall stress-strain behaviour. The less reinforcing effects of the plasma-coated carbon black are balanced by the positive effects arising from the incorporation of plasma coated carbon black. The positive effects will become more significant, if it is possible to chemically link the plasma-coated carbon black arriving in the saturated rubber phase. This might probably reduce the filler transfer and will increase the contribution of the EPDM-phase towards the total properties of the blend.

It has to be realised, that this blend study is still very limited. It cannot be excluded that in the case of more realistic rubber compounds, including oils and higher filler loadings, the effects of the plasma-coating of the carbon black may become more significant.

7.5. CONCLUSIONS

Plasma-coated carbon black has been used in dissimilar rubber blend systems in an attempt to improve the dispersion and distribution of carbon black in the blends. The studies show, that the dispersion and distribution of the plasma-coated carbon black is better than of the uncoated version in the blend. The plasma-coated carbon black is better wetted by both the phases in the dissimilar blend. However, the expected property improvements due to better dispersion and distribution were not visible in the properties of the blends. This arises due to the less reinforcing effects of the plasma-coated carbon black. The overall effect of the plasma-coated carbon black in a dissimilar blend is a combined effect of individual contributions from the rubbers in the blend. The mechanical properties are also affected by the interaction between the plasma-coated carbon black and the individual rubber. The difference in behaviour in this respect of saturated and unsaturated rubbers is reflected in the overall stress-strain behaviour. The less reinforcing effects of the plasma-coated carbon black are counter-balanced by the positive effects due to the increased interaction between the unsaturated rubber and the plasma-polymer film, and by the better dispersion and distribution of the plasma-coated carbon black between the phases in the blends.

7.6. REFERENCES

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Chapter 8

Summary and Concluding Remarks

The work described in this thesis is summarised in this chapter. The chapter begins with the motivation for this research. The work described in each chapter is summarised and evaluated. The chapter ends with some concluding remarks and possibilities for further research.

8.1 MOTIVATION

The primary motivation for this research is a problem existing in rubber products, which is the non-uniform distribution of carbon black between the phases in an elastomer blend. Uneven distribution of carbon black appreciably influences the morphology and physical properties of the blends. As most rubber products are made from blends and carbon black is one of the major reinforcing fillers used, there exists a need for finding a solution for this problem. Several approaches have been attempted in the past to achieve a uniform distribution of fillers in dissimilar rubber blends. They include modifications in the mixing sequence, modification of low unsaturated rubber to raise its polarity, etc. But these approaches were either of limited success or ended up in additional mixing steps in the processing. In the present research a novel route is attempted in an effort to solve the problem of non-uniform filler distribution. The concept utilised here, is to try to match the surface energy of carbon black with that of different rubbers. This may improve the wetting behaviour of carbon black by low surface energy rubbers, thereby improving the dispersion and distribution of the carbon black between the phases in an elastomer blend.

The technique used for bringing the surface energy of carbon black to the range of different rubbers is to modify its surface by plasma polymerisation. This generates a new type/grade of carbon black: the plasma-coated carbon black. The ultimate aim of such a type of carbon black is to use it as such in the rubber blend, thereby eliminating additional mixing steps in processing. But, before going to the application in a large-scale practical rubber blend system, the concept has to be proved in a lab-scale set-up. This is attempted in this research. The introduction of a new type of carbon black also gives rise to several questions concerning its characteristics, performance etc. Attempts are also made to address at least some of them.

8.2 SUMMARY

The initial attempt was to produce a new type of carbon black: the plasma-coated carbon black. Before starting the modification process, a proper selection of the state of carbon black for modification was made. During mixing with rubber, filler pellets break down to agglomerates and aggregates. If carbon black is plasma-coated in this state of the material, during mixing the plasma-coated carbon black pellets will break down and there will be more freshly uncoated surfaces than coated surface. Then the effect of plasma-coating may be unidentifiable. Hence, the agglomerate state of fluffy carbon black was chosen for the surface modification process. This is the state of carbon black just before pelletisation.

Surface modification of regular rubber grade furnace carbon black was carried out at the University of Cincinnati, Ohio, USA. The studies as described in Chapter 4, show that surface modification of regular rubber grade carbon black is a difficult task, especially when aiming for a significant reduction in surface energy. A mechanistic investigation was carried out based on this observation. This gave more insight into the surface modification aspects of powder substrates by plasma polymerisation. The surface characteristics of the substrate have a major role to play in the surface modification. The substrate should provide sufficient active sites during the modification process for the attachment of monomer active species in the plasma. A comparative study with another powder substrate, silica showed that there are not enough active sites on the surface of carbon black for the attachment of the monomer active species. The surface of carbon black mostly contains graphitic planes, which are resonance stabilised. The active sites generated on the graphitic planes are extremely short lived and hence successful attachment of the monomer species is not happening on these planes. The successful attachment of monomer species on the surface of carbon black happens only on the small percentage sites where functional groups and amorphous carbon are located. Hence it is concluded that it is difficult to deposit a plasma-polymer on the surface of regular rubber grade furnace carbon black, unless treated for an unrealistically long duration.

This understanding gave a strong impetus for the search for a new candidate from the carbon black family, with good modification capability. This requirement raised another practical problem of the accessibility of a plasma reactor, for testing different carbon black samples. Hence, it was decided to build a small scale plasma facility at the University of Twente, in order to carry out screening experiments. The basic design of the vertical tubular plasma reactor at the University of Cincinnati was considered for this purpose. The details of this equipment and its installation are described in Chapter 3. Optimisation experiments were carried out and optimum positions for the coil and monomer inlet were found for carrying out the practical experiments.

Once the vertical tubular plasma reactor was successfully installed, screening experiments were carried out in order to find out an ideal carbon black candidate for plasma surface modification. The details of this search are described in Chapter 5. Several carbon black samples were selected and tested for their modification capability. The selection was carried out based on the understanding obtained from the work described in Chapter 4. Carbon blacks with more chemical functionality and those which can generate stable active sites during plasma surface modification were considered for the testing. The screening experiments gave an ideal candidate for plasma surface modification: fullerenic carbon black. The modification capability of this sample lies in the fact that it contains stable active sites, remaining from fullerene production and available for plasma modification, and these sites are distributed all over the surface. TEM-imaging clearly revealed the presence of a nice plasma-coating over the surface of fullerenic carbon black. The screening experiments also provided valid information about the importance of the spatial distribution of active sites on the surface. If the active sites are distributed homogenously all over the surface, a plasma-polymer coating can be formed in a relatively short time.

Once an ideal candidate for plasma surface modification was identified, the next step was to scale-up the modification process, at least to a batch size of 100 g. This provided sufficient samples for studying their behaviour in rubber. But for scaling-up and rubber testing a few practical difficulties exist. The fullerenic carbon black obtained from Timcal Company was in highly fluffy form, unsuitable for direct mixing with rubber. This was solved by granulating the sample. The carbon black used for the modification process was still in the fluffy form. Details of the scaling-up of the modification process are given in Chapter 6.

At the same time, it raised a question about the state of plasma-coating on carbon black once it was mixed into rubber, i.e. whether the plasma coating withstands the granulation process and the shear forces involved in the rubber mixing operation. Electrical conductivity measurements were carried out on fluffy and granulated samples in order to get an impression about the state of the plasma-coating on carbon black in rubber. The details of this are also described in Chapter 6. The results give strong indications that there exists a significant amount of plasma-coating on the surface of carbon black even after the granulation process. This also points towards a strong adherence of plasma-coating on the surface of the black.

After the successful scaling-up of the modification process, the plasma-coated carbon black was mixed with different rubber systems. These were studied using the Payne effect and stress-strain properties. The results are also described in Chapter 6. The results show that the plasma-coated carbon black behaves differently towards different types of rubbers. To explain this behaviour, the characteristics of the plasma-coated carbon black were critically evaluated with respect to the factors responsible for the reinforcement of rubber. The primary factors responsible for reinforcement of rubber by carbon black are: 1) primary particle size; 2) specific surface area; 3) filler-filler interaction; and 4) polymer-filler interaction (physical and chemical). The evaluation lead to the conclusion that the presence of plasma-coating makes the carbon black less reinforcing. However, if mixed into unsaturated rubbers such as SBR and NBR, no reduction in properties was observed. In fact, in the case of SBR a slight increase in tensile strength, accompanied with an improvement in elongation at break was observed. Whereas in the case of a saturated rubber such as EPDM, some reduction in tensile strength was observed. These observations point towards some other effects associated with the plasma-polymer coating which act positively in the case of unsaturated rubbers. Analysis of the plasma-coated carbon black gave indications for the presence of some unsaturation left in the plasma-polymer film. Even though it has not been explicitly investigated in the present case, it seems most probable to consider the observed effects in the light of possible interactions between unsaturations in the plasma-polymer film and the unsaturation in rubbers such as SBR and NBR. Tsai and coworkers had already proved the existence of such an interaction between unsaturations in a plasma-polymer film and squalene through crosslinking intermediates. At the same time, there is no such interaction occurring between a saturated model, squalane and the unsaturations in the plasma-polymer film. This substantiates the observation in EPDM rubber. EPDM being a main-chain saturated polymer, there are no unsaturations available for an interaction with the plasma polymer film.

After understanding the behaviour of plasma-coated carbon black in individual rubbers, its behaviour in dissimilar rubber blends was studied. The distribution aspect was studied using the Payne effect, transmission electron microscopy and stress-strain properties. The details are described in Chapter 7. Two blend systems: SBR/EPDM and NBR/EPDM were analysed. The results show that the coated carbon black is better dispersed in the rubber blend than the uncoated version. Both phases wetted the carbon black better than the uncoated version and hence, more carbon black arrived in the EPDM-phase, respectively the carbon black in the SBR-phase is better dispersed. However, the expected improvement in properties due to the improvements in dispersion and distribution were not visible in the mechanical properties. The SBR/EPDM blend with the plasma-coated carbon black shows a slightly higher stress development in the stress-strain curve, but the improvements are not substantial. This might be due to the fact, that the positive effects arising from the better dispersion and distribution are suppressed by the less reinforcing effects of the plasma-coated carbon black. The results given in Chapter 6 show that after plasma-coating, the carbon black has become less reinforcing. Naturally, a decrease in properties can be expected after the incorporation of the plasma-coated carbon black. Neither a reduction in properties nor substantial improvements in properties were observed in the blends analysed. Hence it is most probable, that the less reinforcing effects of the plasma-coated carbon black are balanced by interactions occurring between the unsaturations in the rubbers and remaining unsaturations in the plasma-polymer film, respectively due to better dispersion and distribution of carbon black between the phases.

8.3 CONCLUDING REMARKS

The research described in this thesis started with the aim of solving the problem of non-uniform distribution of carbon black in rubber blends. But, as the work progressed a deviation in direction had to be taken due to the fact that regular rubber grade furnace carbon black could not be modified in the required way. A substantial part of this research had to be devoted to understanding the problem with regular rubber grade carbon black, identifying a new candidate from the carbon black family and the installation of a plasma reactor facility. The work regained track after the identification of fullerenic carbon black as an ideal candidate for the plasma surface modification. The effect of the plasma-coated carbon black was first studied in single rubber systems and the nature of their behaviour was elucidated. The studies then extended to rubber blend systems, to give indications for better dispersion and distribution of carbon black in blends. It has to be mentioned, that the rubber studies were carried out in a formulation which is not commercially used. Oil was excluded from the formulation in order to avoid its influence on the dispersion properties of the carbon black. Further research has to include oil in the system.

In retrospect, the studies carried out in rubber blend systems was rather limited. The studies could provide some explanations for the mechanisms involved in the behaviour of the plasma-coated carbon black. Extensive investigations in rubber blend systems has to be carried out to get more insights into the phenomena involved. It seems that, in addition to the reduction in surface energy, a chemical attachment of the carbon black with the saturated phase in the dissimilar blend could enhance positive effects of the plasma-coated carbon black.

The plasma coating was carried out on a specialty carbon black which is having a high structure. This is not a regular rubber grade carbon black. Hence, there is a need for studying the activation of regular rubber grade furnace blacks via the production of fullerenes and so activating their surface for plasma-coating. Though an initial step in this direction was carried out, it did not reach a stage to be included in this thesis. I hope that in a later stage, regular rubber grade carbon blacks can also be activated by the afore-mentioned technique, which in principle is possible. Once that is accomplished, they can be plasma-coated and used for studies in commercial rubber blend systems. This generates the need for a much larger scale production of the plasma-coated carbon black, i.e. to the stage of a pilot plant plasma reactor.

Samenvatting en afsluitende opmerkingen

Het werk beschreven in dit proefschrift is samengevat in dit hoofdstuk. Het hoofdstuk begint met de motivatie van dit onderzoek. Het werk beschreven in elk hoofdstuk van dit proefschrift wordt samengevat en geëvalueerd. Dit hoofdstuk eindigt met enkele afsluitende opmerkingen en mogelijkheden voor verder onderzoek.

MOTIVATIE

De onderliggende motivatie voor dit onderzoek is een probleem dat optreedt bij rubber produkten: de ongelijkmatige verdeling van roet tussen de verschillende componenten in een mengsel van meerdere rubbers. Een ongelijke distributie van roet beïnvloedt in aanzienlijke mate de morfologie en de fysische eigenschappen van de mengsels. Omdat de meeste rubber produkten zijn samengesteld uit mengsels en omdat roet als een van de belangrijkste versterkende vulstoffen wordt gebruikt, is er een sterke behoeft aan een oplossing voor dit probleem. In het verleden zijn verschillende manieren uitgeprobeerd om een uniforme verdeling te krijgen van vulstoffen in mengsels van verschillende rubbers. Onder andere wijzigingen in de volgorde van mengen, modificatie van de laag onverzadigde rubber om de polariteit te verhogen, enz. Maar deze aanpakken waren of weinig succesvol, of leidden tot extra mengstappen. In het huidige onderzoek is een nieuwe aanpak uitgeprobeerd in een poging het probleem van niet-uniforme vulstof-verdeling op te lossen. Het gebruikte concept is het aanpassen van de oppervlakte-energie van roet aan die van de verschillende rubbers. Dit zou het bevochtigingsgedrag van roet door rubbers met lage oppervlakte energie kunnen verbeteren, en daardoor ook de dispersie en de onderlinge distributie van de roet tussen de afzonderlijke fasen in een mengsel van verschillende rubbersoorten.

De toegepaste techniek om de oppervlakte energie van roet op het niveau te brengen van de verschillende rubbers is oppervlaktemodificatie door middel van plasma-polymerisatie. Dit genereert een nieuw type roet: plasma-gecoate roet. Het uiteindelijke doel van zulk een roet is om deze als zodanig te gebruiken in het rubber mengsel en daardoor extra mengstappen overbodig te maken. Voordat op grote schaal gekeken kan worden naar praktische rubber mengsels, moet dit concept bewezen worden op laboratorium-schaal. Het introduceren van een nieuw type roet roept vragen op met betrekking tot de eigenschappen, prestaties, enz. Er worden pogingen ondernomen om enkele van deze vragen te beantwoorden.

SAMENVATTING

Een eerste poging was het aanmaken van een nieuw type roet: plasma-gecoate roet. Voordat begonnen kon worden met de modificatie, moest er een goede keuze gemaakt worden ten aanzien van de hoedanigheid van de roet tijdens het modificatie-proces. Tijdens mengen van roet met rubber breken roet-pellets (1-3 mm) af tot agglomeraten (1-10 µm) en vervolgens tot aggregaten 100 – 300 nm). Indien de roet met plasma zou worden behandeld in de pellet-toestand, dan zouden deze pellets gedurende het mengen opbreken en zou er meer vers ongecoat oppervlak ontstaan dan gecoat. Het effect van de plasma-coating zou dan niet waarneembaar zijn. Daarom is ervoor gekozen om roet te modificeren in de agglomeraat of fluffy toestand. Dit is de staat waarin de roet verkeert vlak voordat het commerciëel in pellets wordt geperst.

De oppervlakte-modificatie van standaard furnace-roet voor rubber-doeleinden is uitgevoerd aan de universiteit van Cincinnati, Ohio, VS. De studie beschreven in Hoofdstuk 4 laat zien, dat oppervlakte-modificatie van standaard rubber-roet erg moeilijk verloopt, vooral wanneer wordt geprobeerd om een verlaging in oppervlakte energie te bewerkstelligen. Een mechanistisch onderzoek is uitgevoerd op basis van dit gegeven. Dit resulteerde in meer inzicht in de diverse aspecten van oppervlakte-modificatie van poedervormige substraten door middel van plasma. De oppervlakte-eigenschappen van het substraat spelen een grote rol in de oppervlakte-modificatie. Het substraat moet voldoende actieve plekken bezitten tijdens het modificatie-proces, zodat de actieve monomeren in de plasma zich daaraan kunnen hechten. Een vergelijkend onderzoek met een ander poedervormig substraat: silica, toonde aan dat er onvoldoende actieve plekken op roet voorhanden zijn voor de hechting van actieve monomeren. Het roet-oppervlak bestaat vooral uit grafiet-lagen, welke gestabiliseerd worden door resonantie. De actieve plekken die ontstaan op deze grafiet-lagen hebben een extreem korte levensduur en daarom treedt er geen succesvolle hechting van monomeren op deze plekken op. Succesvolle hechting van monomeren aan het oppervlak van roet gebeurt alleen op de weinige locaties waar functionele groepen en amorf koolstof aanwezig zijn. Derhalve wordt geconcludeerd dat het aanbrengen van plasma-polymeer op het oppervlak van standaard furnace-roet voor rubber een moeizame zaak is, tenzij de roet wordt behandeld gedurende een onrealistisch lange tijd.

Dit gegeven gaf een sterke impuls voor een zoektocht naar een nieuwe kandidaat van de roet-familie, geschikt voor gemakkelijke modificatie. Dit leidde tot een praktisch probleem: de beschikbaarheid van een kleinschalige plasma reactor om verschillende roet-typen te kunnen testen. Daarom werd besloten om op kleine schaal een plasma-faciliteit te bouwen op de universiteit Twente, teneinde verkennende experimenten te kunnen uitvoeren. Als basisontwerp werd de verticale buisvormige plasma-reactor van de universiteit van Cincinnati genomen voor dit doel. De details van de apparatuur en de inwerkingstelling zijn beschreven in Hoofdstuk 3. Optimalisatie experimenten zijn uitgevoerd en de optimale positites voor de electrische spoel en de monomeren-inlaat zijn vastgesteld voor het uitvoeren van latere experimenten.

Toen de verticale plasma reactor succesvol was geïnstalleerd, zijn verkennende experimenten uitgevoerd om de ideale roet-kandidaat te vinden voor plasma oppervlakte-modificatie. De details van deze zoektocht zijn beschreven in Hoofdstuk 5. Verscheidene roet-monsters zijn geselecteerd en getest op hun geschiktheid voor modificatie. De keuze is gemaakt op basis van de resultaten verkregen uit het werk beschreven in Hoofdstuk 4. Roeten met veel chemische functionaliteiten en met duurzaam actieve plekken op hun oppervlak zijn getest. De verkennende experimenten resulteerden in een ideale kandidaat voor plasma-modificatie: fullereen-roet. De modificatie-eigenschappen van dit monster zijn gebaseerd op het feit dat het duurzaam actieve plekken bevat op het oppervlak, die zijn overgebleven na de fullereen-productie en beschikbaar zijn voor plasma-modificatie. De actieve plekken liggen verdeeld over het gehele roet-oppervlak. TEM-analyse liet duidelijk zien dat een goede plasma-coating over het oppervlak van fullereen-roet kon worden aangebracht. De verkennende experimenten resulteerden ook in informatie betreffende de significantie van de ruimtelijke verdeling van de actieve plekken op het oppervlak. Wanneer de actieve plekken homogeen over het oppervlak verdeeld zijn, kan een plasma polymeer-coating in een relatief korte tijd worden aangebracht.

Toen de ideale kandidaat-roet voor plasma oppervlakte-modificatie eenmaal was gevonden, was de volgende stap het opschalen van het modificatie-proces, op zijn minst naar een batchgrootte van 100 gram. Dit was voldoende om het gedrag van de gemodificeerde roet in rubber te onderzoeken. Maar er waren enkele praktische problemen bij het opschalen en testen in rubber. De fullereen-roet verkregen van het bedrijf Timcal in België was in een erg fluffy vorm, ongeschikt om direct te mengen met rubber. De roet werd in fluffy vorm onderworpen aan het plasma-modificatie proces. Daarna werd het monster gegranuleerd. Details van de opschaling van het modificatie proces zijn weergegeven in Hoofdstuk 6.

Tegelijkertijd kwam de vraag naar voren over de toestand van de plasma-coating op de roet, wanneer het eenmaal in rubber is gemengd; met andere woorden: verdraagt de plasma-coating het granuleringsproces en de afschuifkrachten tijdens het inmengen in rubber? Electrische geleidbaarheids-metingen zijn uitgevoerd op de fluffy en gegranuleerde monsters om een indruk te krijgen van de staat van de plasma coating op de roet in de rubber. De details hiervan zijn ook beschreven in Hoofdstuk 6. De resultaten geven een sterke aanwijzing, dat er een significante hoeveelheid plasma coating aanwezig is op de roet zelfs na het granuleringsproces. Dit duidt op een sterke hechting van de plasma coating op het oppervlak van de roet.

Na de succesvolle opschaling van het modificatie-proces, is de plasma-gecoate roet gemengd met verschillende rubber systemen. Deze zijn onderzocht middels het Payne-effect en de trek-rek eigenschappen. De resultaten zijn eveneens beschreven in Hoofdstuk 6. Zij laten zien dat de plasma-gecoate roet zich verschillend gedraagt jegens verschillende types rubber. Om dit te verklaren, zijn de eigenschappen van de plasma-gecoate roet kritisch geëvalueerd op die faktoren, die verantwoordelijk zijn voor de versterking van rubber. De hoofdfaktoren verantwoordelijk voor het versterken van rubber door roet zijn: 1) elementaire deeltjesgrootte; 2) specifiek oppervlak; 3) vulstof-vulstof interactie; 4) polymeer-vulstof interactie (fysisch en chemisch). De evaluatie leidde tot de conclusie, dat door de aanwezigheid van de plasma-coating de roet een minder versterkende werking heeft. Wanneer het echter gemengd wordt in sterk onverzadigde rubbers zoals SBR en NBR is er geen afname waargenomen in de eigenschappen. In het geval van SBR wordt zelfs een lichte stijging in treksterkte en rek bij breuk waargenomen. In het geval van verzadigde rubbers zoals EPDM, wordt een daling in treksterkte waargenomen. Deze waarnemingen duiden op effecten die geassociëerd kunnen worden met de plasma-coating, die positief uitwerken in het geval van onverzadigde rubbers. Analyse van de plasma-gecoate roet gaf indicaties dat er onverzadigde bindingen zijn achtergebleven in de plasma polymeer-film. Ook al is het in dit kader niet expliciet onderzocht, het lijkt waarschijnlijk dat de waargenomen effecten verklaarbaar zijn door mogelijke interacties tussen de onverzadigde bindingen in de plasma polymeer-film en de onverzadigde bindingen in rubbers als SBR en NBR. Tsai en medewerkers hebben een dergelijke interactie tussen onverzadigde bindingen en een plasma-film al aangetoond in squaleen, met behulp van crosslinking intermediates. Tegelijkertijd hebben zij geen interactie waargenomen tussen een verzadigde model-verbinding, squalaan, en de onverzadigde bindingen in de plasma polymeer-film. Dit ondersteunt de waarneming in EPDM rubber. EPDM heeft een verzadigde moleculaire hoofdketen en er zijn praktisch geen onverzadigde bindingen beschikbaar voor interactie met de plasma polymeer-film.

Nadat het gedrag van de plasma-gecoate roet in individuele rubber werd begrepen, is het gedrag in mengsels van ongelijke rubbers bestudeerd. Het distributie-aspect is bestudeerd door middel van het Payne-effect, transmissie electronen microscopie en trek-rek eigenschappen. De details zijn beschreven in Hoofdstuk 7. Twee blend systemen zijn onderzocht: SBR/EPDM en NBR/EPDM. De resultaten tonen aan, dat de gecoate roet homogener verdeeld is in de rubber blend dan de ongecoate versie. Beide fasen benatten de plasma-gecoate roet beter dan de ongecoate versie en daardoor komt er meer roet in de EPDM-fase terecht en wordt ook de roet in de SBR-fase beter gedispergeerd. De verwachte verbetering in de eigenschappen door de betere dispersie en verdeling worden echter niet teruggevonden in de mechanische eigenschappen. De SBR/EPDM blend met de plasma-gecoate roet laat een iets hogere spanningsontwikkeling zien in de trek-rek curve, maar de verbeteringen zijn niet substantieel. Dit kan veroorzaakt zijn door het feit dat de positieve effecten van een betere dispersie en distributie onderdrukt worden door een verminderd versterkend effect van de plasma-gecoate roet. De resultaten in Hoofdstuk 6 laten zien dat roet na de plasma-behandeling inderdaad minder versterkende eigenschappen heeft. Hierdoor zou een afname in eigenschappen verwacht kunnen worden nadat de plasma-gecoate roet is ingemengd. Geen verlaging in eigenschappen maar ook geen substantiele verbetering zijn waargenomen aan de geanalyseerde blends. Daarom is het waarschijnlijk, dat het verlaagde versterkende effect van de plasma-gecoate roet wordt uitgebalanceerd door de interactie tussen de onverzadigingen in de rubbers en de overgebleven onverzadigingen in de plasma polymeer-film, en door de verbetering in dispersie en distributie van de roet tussen de onderscheiden fasen.

AFSLUITENDE OPMERKINGEN

Het onderzoek beschreven in dit proefschrift begon met als doel het oplossen van de ongelijkmatige verdeling van roet in mengsels van verschillende rubbers. Maar gaandeweg moest worden afgeweken van deze richting, omdat standaard roet zich niet liet behandelen volgens de gewenste plasma-methode. Een groot deel van dit onderzoek is gewijd aan het probleem met standaard roet, het identificeren van een nieuwe kandidaat van de roet-familie en het installeren van een plasma-reactor. Het onderzoek ging weer in de oorspronkelijke richting nadat fullereen-roet was gevonden als de ideale kandidaat voor plasma oppervlakte-modificatie. Het effect van plasma-gecoate roet werd eerst bestudeerd in systemen met één soort rubber om meer inzicht te krijgen in het gedrag. De studie werd vervolgens uitgebreid naar rubber meng-systemen. Er moet vermeld worden dat de rubber studies uitgevoerd zijn in een niet-commerciële mengsel-samenstelling. Er werd geen olie toegevoegd aan de mengsels om de invloed op de dispersie-eigenschappen van roet uit te sluiten. Verder onderzoek zal uitgevoerd moeten worden met olie in het systeem.

Achteraf zijn de onderzoeken uitgevoerd uitgevoerd aan rubber blends wat beperkt. De studies kunnen verklaringen geven voor de mechanismen, die een rol spelen in het gedrag van plasma-gecoate roet. Meer diepgaande onderzoeken zullen uitgevoerd moeten worden in rubber blend-systemen om meer inzicht te krijgen in de fenomenen, die een rol spelen. Het lijkt erop dat, naast de verlaging van de oppervlakte-energie, een chemische binding van de roet met onverzadigde functionaliteiten in ongelijke rubber-blends het positieve effect van plasma-gecoate roet kan versterken.

De plasma-coating is aangebracht op een speciale roet met een hoge ruimtelijke structuur. Dit is geen standaard roet. Daarom is een onderzoek noodzakelijk naar de activering van standaard roet via de productie van fullerenen om het oppervlak zo geschikt te maken voor plasma-modificatie. Een eerste stap is gemaakt in het kader van het onderhavige onderzoek, maar het heeft niet het stadium bereikt om in dit proefschrift te kunnen worden opgenomen. Ik hoop dat in een later stadium standaard roet geactiveerd kan worden via de hierboven genoemde methode, die in principe goede mogelijkheden biedt. Als dat eenmaal is gelukt, kan deze plasma-gecoat worden en gebruikt worden in commerciële rubber blend-systemen.

Hierdoor kan de behoefte ontstaan aan productie van plasma-gecoate roet op grotere schaal: het stadium van een pilot-plant plasma-reactor.

Symbols and Abbreviations

Symbols and abbreviations	Description
ν	Concentration of elastically active network chains per unit volume
Φ	Volume fraction of filler
δ	Solubility parameter
Ω	Electrical resistance (Ohm)
χ	Polymer-polymer interaction parameter
γ	Interfacial tension
ΔG_m	Gibbs free energy by mixing
ΔH_m	Change in enthalpy by mixing
ΔS_m	Change in entropy by mixing
Å	Angstrom
AFM	Atomic force microscopy
amu	Atomic mass unit
ASTM	American society for testing of materials
BET	Brunauer, Emmet and Teller specific surface area
BIT	Black incorporation time
CBS	N-cyclohexylbenzothiazole sulphenamide
CR	Polychloroprene rubber
CSDPF	Carbon silica dual phase filler
CTAB	Cetyl trimethyl ammonium bromide specific surface area
d	Average domain size
DBP	Dibutyl phthalate
DC	Direct current
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_{coh}	Cohesive energy density
EPM	Ethylene propylene rubber
EPDM	Ethylene propylene diene rubber
EVA	Ethylene vinyl acetate
E-SBR	Emulsion styrene butadiene rubber
eV	Electron volts
F	Monomer flow rate (mol/s)

FS	Fullerene soot
G_f	Shear modulus of filled rubber
G_0	Shear modulus of unfilled rubber
G’	Storage modulus
GLC	Gas liquid chromatography
GPC	Gel permeation chromatography
ICP	Inductively coupled plasma
IIR	Isobutylene-isoprene rubber
ISO	International standarsiation organisation
K_b	Boltzmann constant
keV	Kilo electron volt
M_{cr}	Critical molecular weight
MFC	Mass flow controller
MW	Microwave
NBR	Acrylonitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
OAN	Oil adsorption number
PDMS	Poly dimethyl siloxane
phr	Parts per hundred rubber
psi	Pounds per square inch
R	Resistance
RF	Radio frequency
S-SBR	Solution styrene butadiene rubber
sccm	Standard cubic centimeters per minute
STSA	Statistical thickness surface area
TEM	Transmission electron microscopy
$T_{ceiling}$	Ceiling temperature
T_e	Temperature of electron
T_g	Temperature of gas
TGA	Thermogravimetric analysis
ToF-SIMS	Time of flight secondary ion mass spectroscopy
TMQ	2,2,4-trimethyl 1,2-dihydroquinoline
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide

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PATENT APPLICATION

1. Production of plasma polymer film coating on carbon particles and usage thereof.

Curriculum vitae

Tony Mathew was born on 5th August, 1976 in Cheeramchira, Kerala, India. He obtained his Bachelor of Science (B. Sc.) in 1997 and Master of Science (M. Sc.) degree in 2000 from Mahatma Gandhi University, Kerala, India. After that he worked (2001-2002) in the R&D Centre of Speciality Coatings Division of MRF Ltd, as R&D Chemist in Chennai, India. Later he did Master in Technology (M. Tech.) in Polymer Technology at Cochin University (2002-2004). As a part of his M. Tech thesis, he worked at National Chemical Laboratory (NCL), Pune, India. The topic of his research was “Melting and crystallization behaviour of binary aliphatic polyamide blends”.

In July 2004, he started his Ph.D under the supervision of Prof. Dr. Ir. J. W. M. Noordermeer at the University of Twente, the Netherlands. The topic of his research was “Surface modification of carbon black by plasma polymerisation and its effect in elastomer blend systems”. The research was funded by Dutch Technology Foundation (STW). The results of this research are described in this thesis. From June 2008, the author started working at Teijin Aramid BV, Arnhem, the Netherlands as Senior R&D coworker in the Finishes department.

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