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CHEMICAL MODIFICATION OF POLYMER SURFACES USING SULFONATION TO IMPROVE ADHESION PROPERTIES

By

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ABSTRACT

CHEMICAL MODIFICATION OF POLYMER SURFACES USING SULFONATION TO IMPROVE ADHESION PROPERTIES

BY

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The nature of chemical changes occuring on the surface of polymers has been investigated in the thesis. Polypropylene and polystyrene were investigated in this study. XPS and FTIR Spectroscopy were used in conjunction with each other to determine the quantitative and qualitative changes occuring on the surface due to sulfonation.

It was observed that the surfaces of both polymers reach a saturation limit. Polypropylene is saturated in almost 3 minutes and polystyrene in the first minute itself. The polypropylene data indicates the formation of several chemical species which mainly includes sulfonic acid as well as a conjugated system of doubly bonded carbons in the backbone. On the other hand polystyrene mainly results in sulfonic acids at the para position of the aromatic ring along with some unsaturation in the aliphatic carbons in the backbone.

Dedicated to my family who put me on the right path and guided me through all this inspite of being half a world away

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Introduction

Chapter 1

Adhesion is defined as the state in which two dissimilar surfaces are held together by interfacial forces. Since it is an interfacial phenomenon the forces on the surface play a very important role in determining the nature and strength of adhesion.

1.1 NATURE OF INTERFACIAL FORCES

The forces at the interface system may be *Long Range Forces* or *Short Range Forces*. It has been shown that most of the inter-atomic forces are short range forces. If it were not so then the energy of a given portion of a system would depend on its macroscopic size as well [1]. However, there are several forces which are long range. These forces can act across the interface and are decisive in determining the adhesive strength. Broadly these forces may be classified as follows:

- Van-der Waals forces.
- Polar forces.
- Electrostatic forces.

1.1.1 Van-der Waals Forces

Van der Waals forces account for the general attractive interaction between atoms in the neutral state [1,2]. The van der Waals interactions are a result of three different contributions which are related to each other. A neutral molecule at any given time is in a state of agitation which leads to randomly orienting dipole-dipole interaction. These interactions were first described by Keesom and are called *Keesom Interactions*. They vary inversely as the sixth power of the distance between the dipoles and are described by the following equation [1].

$$\epsilon(\mu,\mu)_{av} = -\frac{2\mu^4}{3kTx^6}$$

where, μ is dipole-dipole interaction, units of Debye

T is the temperature of the system, units of Celsius

x is the separation between the entities, units of cm.

ϵ is the potential energy, units of ergs.

Another possible interaction in an atom is due to a randomly oriented dipole and an induced dipole (if the atom or molecule is polarizable). These were described by Debye and are called *Debye Interactions*. They also vary inversely as the sixth power of the distance between the dipole and induced dipole . The equation describing them is as follows [1]

$$\epsilon(\mu,\alpha) = -\frac{\alpha\mu^2}{x^6}$$

where, μ is the dipole-moment in units of Debye.

α is the polarizability in units of cm^3.

x is the separation in units of cm.

As has been pointed out, for *Keesom and Debye Interactions,* it is important that the molecules have permanent dipole moments. All the forces account for attractive (or repulsive) interactions in molecules which can be polarized. However, it is a universal observation that there is a general attractive interaction which exists in atoms and molecules which are not inherently charged and do not have a dipole moment associated with them. London, in 1930 showed the existence of a more general kind of electrical force between molecules which is always attractive and arises due to the fact that (even) neutral atoms and molecules constitute a system of oscillating charges. The positive necleus and the negative electron cloud result in a fluctuating dipole which leads to fluctuating dipole-induced dipole interactions. These are called *London-van der Waals or Dispersion* Interactions and are described by the following equation [1]

$$\epsilon(x) = -\frac{3}{2}\,\frac{\alpha_1\alpha_2}{x^6\,[(1/h\nu_1)+(1/h\nu_2)]}$$

where, $h\nu_1$ and $h\nu_2$ are the characteristic energies of atoms 1 and 2.

α_1 and α_2 are polarizability of atoms 1 and 2 in cm^3

Like the *Debye and Keesom Interactions* these also vary inversely as the sixth power of the distance between the molecules. To sum up, the interactions are characterised by the general equation as follows.

Debye, Keesom, Dispersion Interactions α d^{-6}

Where d is the distance between the molecules.

1.1.2 Polar Forces

Another class of forces which contributes to adhesion is *Polar Interactions* [1,2]. These are result of an actual electron(ic) reconfiguration of the species involved in adhesion. Interactions of the Hydrogen-bonding type are also included in this class of forces. To encompass all interactions which are of electron acceptor-electron donor type, the term Polar Interactions along with other acceptor-donor interactions are called *Lewis Acid-Base Interactions.* These are specific in nature vis-a-vis the chemical species under consideration and are essentially asymmetrical. The interactions of this class are short-range in comparison to the Dispersive forces which have been discussed previously which are a result of Long-Range Interactions.

1.1.3 Electrostatic Forces

Electrostatic Interactions play an important role in Polar media where it can be said with confidence that there are very few entities which do not carry a surface charge of electrical origin [2]. A charged surface experiences a force in an electric field similar to the situation when a field is induced by the relative motion of such a surface. In both cases there is a slip between the layer and the medium [1] the result of which may be measured in terms of the charge density. The extent of Electrostatic Interactions is indicated by the *Electro-Kinetic Potential* or *ζ-Potential.* It is the potential of entities measured at the slipping plane by electro-kinetic methods. The *ζ-Potential* is not directly related to the non-polar component of the surface energy. Also, it should be kept in mind that *ζ-Potential* is developed entirely within the fluid region. Electrophoresis and electro-osmosis are among common applications of Electrostatic Interactions. The mathematical expression for *ζ-Potential* or *Helmholtz potential* is as follows [18].

$$\zeta = \frac{4\pi\eta\mu}{\epsilon_r}V$$

where, η is the fluid viscosity

ϵ_r is the dielectric constant of the fluid

μ is the electrophoretic mobility of the particle.

The nature of *Electrostatic Interactions* is different from *Dispersive Interactions*. Pauling has classified Electrostatic interactions as a broad class of bonding. They include ion-ion, ion-dipole, ion-induced dipole etc kind of interactions [44]. In this class of interactions, an actual transfer of electrons within the atomic species involved. For e.g., in NaCl (sodium chloride or common salt) the metallic sodium ion actually donates the electron to the non-metallic chlorine atom. The main point to note in electrostatic interactions is that the interaction of an atom of a definite electronic structure is independent of the proximity of other atoms around it. Usually, there is an appreciable difference in the electronegativities of the atomic species involved in this kind of interaction.

1.2 MECHANISM OF ADHESION

As has already been pointed out earlier, adhesion is the resistance to separation of a joint by application of external force. The magnitude of adhesion is a function of several factors like the interfacial forces manisfested as the surface energy, work of adhesion, bulk and surface layer mechanical properties, joint geometry etc. [3,4]. Several theories have been proposed to explain the mechanism of adhesion [3]. They can broadly be classified as follows.

- Chemical Reaction Theory
- Mechanical (Hooking) Theory
- Electrostatic Theory
- Diffusion Theory

All the forces outlined above play an important role in determining the levels of adhesion.

1.2.1 Chemical Reaction Theory

The Chemical Reaction Theory proposes that the strength of joints is determined mainly by interfacial reactions. Whenever there is an actual chemical reaction across the interface the probability of forming a bond of high strength is large. The presence of polar groups at or across the interface contributes to the bond strength as it can lead to an actual electronic exchange. However, if only the van-der Waals forces act across the interface a joint of a lower strength is produced because electron exchange is not possible. The main criticism of this theory is that it relies entirely on interfacial reactions to which there is little direct and evidence.

1.2.2 Mechanical Theory

The Mechanical (Hooking) Theory emphasizes the Interlocking of adhesive and the adherend at the interface. However, roughness cannot be the sole criterion for adhesion as there are systems which involve adhesion between very smooth surfaces. But, it may be an important mechanism in adhesion of porous materials.

1.2.3 Electrostatic Theory

The Electrostatic Theory is based on the premise that the adhesive joints act like a capacitor which becomes charged due to the contact of two different substrates. The electrical double layer of the capacitor imparts strength to the joint. The main evidence of this phenomenon is in case of pressure-sensitive adhesives where electron emission can occur when a joint is broken. However, the main argument against this explanation is that the phenomenon of fracture is used to explain the phenomenon of joining. In most cases the nature of the original uncharged surfaces is not necessarily the same as that of charged fractured surfaces. The theory also does not explain the adhesion of conductive materials.

1.2.4 Diffusion Theory

The Diffusion Theory is especially applicable to polymers. It postulates that adhesion is not a result of surface contact alone. There is (inter)-diffusion of polymers across the interface which imparts joint strength to the system. However, this cannot explain adhesion in the broadest sense as in most non-polymeric solids where the probability of diffusion will be very low at the temperatures and time frame under consideration.

None of the mechanisms outlined above offers a complete picture of adhesion independently. For a holistic understanding it is important that each possible mechanism evaluated and then understood. However, one fact that clearly emerges is that forces at the surface play a crucial role in adhesion. If we can control or at least modify these surface forces then we can tailor a surface to our adhesion requirements. Several surface modification techniques are available towards this end.

1.3 WORK ON POLYMER SURFACES

Work on polymer surfaces assumes an important academic and industrial application because of the increasing application of polymers. The most common parameter used to define this work is the *Thermodynamic or Reversible Work of Adhesion* [46]. It is most commonly denoted by W_A and is defined as the change in free energy when the materials are brought in contact and is same under equilibrium conditions as the energy change when material interface is disrupted. However, the situation is far from a real situation where inelastic deformations occur during breaking of a joint resulting in loss of energy. Thus, at best one can get a direct correlation between the thermodynamic work of adhesion and the practical work of adhesion [46]. One of the earliest equation proposed for work of adhesion is due to Young. The equation is a force balance on a liquid drop placed on a solid surface as shown in Figure 1.1.

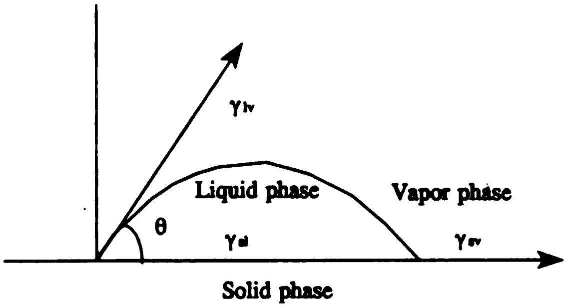


Figure 1.1: The figure illustrates a liquid drop resting on a solid surface. *θ* is the contact angle.

The equation is as follows.

$$W_A = \gamma_{LV} (1 + \cos\theta)$$

There have been attemps for a long time to quantify and separate the various components of work of adhesion based on the forces responsible for them. Approximately, there are two components, the dispersive and non-dispersive (or polar) component. The work related to this area has mainly been empirical in nature. The following equation was widely used by Hansen and Kaelble in their work.

$$\begin{aligned} W_A &= W_A{}^d + W_A{}^p \\ &= 2(\gamma_s{}^d\gamma_l{}^d)^{1/2} + 2(\gamma_s{}^p\gamma_l{}^p)^{1/2} \end{aligned}$$

There was agreement on the dispersive component of the work of adhesion but there were various schools of thought which did not agree entirely with the non-dispersive component termed polar in the above equation. One of the latest theory prevalent is due to Fowkes [47]. He proposed that besides the dispersive component all the other interactions are of acid-base types. That is, there is an interaction which actually involves the electrons in the system. The equation was modified as follows.

$$\begin{aligned} W_A &= W_A{}^d + W_A{}^{A-B} \\ &= W_A{}^d + f(-\Delta H_{AB})N \end{aligned}$$

where,

f is factor which converts enthalpy to free-energy.

N is the number of accessible functional sites.

$-\Delta H_{AB}$ is the exothermic enthalpy per mole of acid-base adduct formation at the interface.

However, there is controversy on this equation too regarding the interpretation and the various assumptions which are valid while using this equation. For e.g., Fowkes used the value of f as unity in all his work while several investigators do not agree on this assumption [47]. Thus, at present the work of adhesion on polymer surfaces is still not well understood. More work at the fundamental level needs to be done before the nature of polymer surfaces can be well understood and yield a better understanding about the nature of work on polymer surface.

Surface Modification Techniques

Chapter 2

2.1 AVAILABLE TECHNIQUES

There are several commercial and laboratory-scale techniques available for altering the surface in order to enhance adhesion capabilities. However, it must be remembered that none of the techniques can be applied universally. The detailed discussion here shall be limited to polymer surfaces . Each has its own limitations and thus the choice of the surface modification technique is of utmost importance. Some of the currently available techniques available currently are :

- Flame treatment
- Acid-etching
- Corona discharge and Plasma treatment
- Chemical treatment

Before each of them is discussed individually, it is important to familiarise ourselves with two interrelated concepts which play an important role in Adhesion Science. They are the concept of *Weak Boundary Layer* and *The Interphase* [4].

In the most general sense an adhesive joint is referred to as a three layered structure. Two adherend layers enclosing a layer of an adhesive. However, it may be that the adherends and the adhesives individually consist of more than one layer (each) [5]. This complicates the problem several fold, as now the interface between layers will play a role in determining the adhesion strength. The extent of adhesion also depends on the mechanism of stress transfer. This is governed by the stress concentration profile between any two adjoining layers. For maximum adhesion the stress transfer should be as smooth as possible. However, if we have multiple interfaces then there will be multiple stress concentration profiles which implies that the problem is complicated extensively. This surface region whose characteristics are different from the bulk is termed as *The Interphase*.

It was proposed by Bikerman that even though the failure may appear to occur interfacial, in reality the failure always occurs cohesively in a weak layer on one of the species involved in adhesion [23]. This weak layer where the bond fails is the *Weak Boundary Layer*. He further proposed that WBLs are associated with each kind of material. Bikerman's proposition was based on empirical observations. He said that a crack can propogate either between two molecules of the adhesive or two molecules of the substrate or between the substrate molecule and adhesive molecule. Thus, the probability of the crack propagating along the interface is 1/3 ! The above reasoning shows that based on purely statistical grounds it is improbable that the crack propogates along the interface only.

Weak Boundary Layers are associated with all classes of materials. On metals they are usually oxides while in polymeric materials they are usually low molecular weight chains which tend to migrate on the surface. The problem in polymers is complicated because of the impact of functional, structural and morphological factors [4]. The accepted view is that the mechanical properties of WBLs are poor in comparison to those of the bulk. Thus, it becomes important that for the purposes of adhesion all

WBLs be removed and work is carried out on a surface whose properties are as close to that of the bulk as possible. This also leads to simplification of the stress concentration profile. Some of the surface treatments affect the polymer surface to that end.

2.1.1 Flame Treatment

Flame treatment is a common surface modification technique which finds several applications in the industry. It consists of subjecting the polymer to an appropriate flame. The purpose is essentially to oxidize the top few layers of the polymer surface. The chemical effects of flame treatment have been studied by several investigators in detail [44,45]. It has been conclusively shown that a major impact of flame treatment is the enhancement of surface energy and polarity of the surface. The details and mechanism about the chemical changes are not very clear at this stage. The only conclusive fact which emerges from the literature is that oxidation of the surface is an important change. Various investigators have correlated the polarity to the differently oxidized chemical species on the surface. For e.g., Garbassi et.al. [44] have attributed the increase in polarity to the carbonyl functionality introduced on the surface. The reaction is supposed to proceed via a radical mechanism [44,45] which react and rearrange to form different chemical species. Briggs et. al have shown that the depth of modification is in the range $40 \text{ Å} < d < 90 \text{ Å}$. The overall impact of flame treatment is the improvement in adhesion properties of the polymer.

2.1.2 Acid-etching Treatment

Acid-etching is another method directed at removing the WBLs and in the process also modifying the chemical structure on the surface [6, 21]. A controlled mixture of sulfuric acid and chromic acid is often used to etch the polymer surface. It has been found that in the process of etching there is an actual chemical modification of the polymer surfaces as well. Mostly, it is characterised by the incorporation of sulfonic acid groups on the surface of the polymer attached to the carbon of the polymer chain. This leads to an enhanced polarity on the surface and thus increased adhesion. The main limitation of this technique is that it may lead to the destruction of surface of the polymer. The harsh environment of the acid treatment leads to chain scission and a modified topography. Investigation by Blais et al [21] shows that after treatment there is a marked surface roughness that appears on the surface. This can also be responsible for improved adhesion. The various sites on the polymer can react with the acid resulting in various chemical moieties. If these chemical moieties are stable in the given chemical, morphological and physical environment then a chain with a modified region is obtained. However, there are chances that the new chemical moities are unstable energetically which is the motivation for them to leave the system and thus they break away. These are the scission products which are mainly aldehydes and ketones [21]. This is also the reason that controlled modification is sometimes not possible in acid-etching.

2.1.3 Corona and Plasma Treatment

Corona discharge and plasma treatments lead to cleaning and chemical modification of the surface which leads to an enhanced adhesion [7]. The "Plasma" is defined as an ionized gas with an equal density of positive and negative charges. The highly energetic chemical environment produced by plasmas is utilized in chemical modifications of the materials. Free radical chemistry is the proposed mechanism of reaction. Plasmas may be generated from various gases depending on the specific requirement. Oxygen, Ammonia, Argon are some of the popular plasmas. However, due to the complex nature of the plasmas generated, at times it can be difficult to control chemistry on the surface. The main effects of plasma and corona treatment are [7]:

2.1.3a Cleaning

This is a major effect of Plasma on the surface. Most of the other processes leave behind a layer of contamination of organic nature. The main advantage of using Plasma is its capability to remove molecular layers from polymer surfaces. Since this is the actual layer of the polymer the complications arising due to Weak Boundary Layers are removed. Thus, this gives a reproducible surface and reproducible bonds.

The problem with using other cleaning techniques such as solvent wash is the non-volatile contents in them. It is almost impossible to obtain solvents without any non-volatile content in them. For purposes of adhesion it is well-known that even the slightest contamination can be detrimental.

2.1.3b Ablation

This is important for cleaning and removing contaminants and Weak Boundary Layers from the surface. These become a part of the surface during fabrication and handling procedures. Ablation is especially important because it generates a surface topography which can enhance adhesion due to mechanical bonding and increase the surface area for chemical interactions.

2.1.3c Cross-linking

Cross-linking is the observed phenomenon in Noble gas plasma when they are used in ultra-clean environment. the free radicals are created when the excited atoms attack the polymer surface resulting in the breakage of C-C, C-H bonds. These radical species combine with each other and form stable moieties. Due to the radical migration on the chain crosslinking, branching etc can occur. Crosslinking is known to give improved heat resistance and cohesive strength [7].

2.1.3d Surface Chemisry Modification

The chemical nature of the surface is modified such that its capability to interact with the adhesive is enhanced. This is achieved by using an appropriate plasma which can add polar groups on the surface. For example, it would be expeced that an Oxygen plasma would give a surface which has extensive oxygen functionalities. The new chemical moieties formed are more polar in nature which leads to improved adhesion. Due to these polar groups the polymer surface has an increased surface energy which leads to improved wetting and thus adhesion.

Studies have shown that the plasma treatment effects only the top 20 - 200 Å of the surface. This makes it important that the surface is clean before treatment which in turn demands that the treatment be long enough for removal of all kinds of Weak Boundary Layers.

2.1.4 Chemical Modification Techniques

Fluorination and Chlorination are two examples of chemical modification techniques. However, both of these have their limitations. Fluorination involves the attachement of a fluorine atom to the Carbon backbone of the polymer. Since fluorine is a highly electronegative element, this leads to bonds which have very high energies. This in turn leads to bond breakages and thus a loss in mechanical and barrier properties over a period of time. The final product in fluorination of organic polymers is formation of a fluorinated carboxylated product ($-FC=O$) [22,23] which are formed after exposure to oxygen. The process of Fluorination is hazardous as one of the by-products is Hydrofluoric acid which is highly corrosive. It involves exposing the polymer to a mixture of fluorine gas (0.1-20%) along with a carrier gas such as argon or nitrogen. Oxygen level has to be minimised as it leads to the undesirable carboxylated by-product. This is one of the main reason the the process has proven to be difficult to control [8]. On the other hand, chlorination is a slow reaction which can be promoted by Ultra-Violet light (UV). This makes it a difficult process to use at industrial level.

2.2 SULFONATION

One common factor that emerges from above discussion is that a chemical technique will be industrially attractive if it can offer a repeatable controlled reaction. Sulfonation as a surface modification technique has this potential. Moreover, unlike most other techniques it has an added advantage that it offers control over two adhesion parameters. One is the concentration of the chemical species and secondly the depth of modification achieved. These two variables in conjunction with each other offer a powerful tool to tailor the surface in a controlled manner. Sulfonation is also an attractive option for improving the *barrier properties, electrical (surface) properties and metallization of polymer surfaces* [8]. The barrier properties involve the reduction of permeability of polymers to liquids and gases. A detailed investigation can be obtained from reference [9]. For example, sulfonation has been successfully tested in fuel tanks where diffusion of gasoline out of tanks has been a major problem. It leads to a loss in shape due to swelling and ultimately the life of the tanks is reduced. For barrier against gases also sulfonation has been employed successfully.

2.2.1 Sulfonating Agents

There are several sulfonating agents in use. The most popular ones are the sulfurtrioxide complexes of organic compounds. The generic reason for the formation of comlex is that sulfur atom in SO_3 is a strong electron acceptor (Lewis acid) which has a strong tendency to combine with Lewis bases to form complexes [10]. The stability of the complex depends proportionally on the strength of the base used. At the time of sulfonation the complex dissociates and free SO_3 is released for sulfonation. The base forms a salt with the acid according to the following reaction.

$$RH + SO_3 \text{ --------> } RSO_3H.Base$$

Some of the common sulfonating agents which have been used for studying the chemistry of sulfonation have been briefly described below.

(2.2.1a) SO_3-pyridine complex.

This can be prepared in several ways. The most common being the direct reaction of SO_3 with pyridine. The complex is stable and insoluble in cold water and cold alkali but decomposes when the temperature increases [10].

(2.2.1b) SO_3 -dioxane complex.

This is one of the earliest sulfonating agents to have been prepared and used to study the detailed chemistry of sulfonation [14]. There are several factors involved in synthesising this reagent [10] and the preparation should be a careful process. Care has to be taken that the adduct be prepared just before use as on long standing the solid can decompose violently even at room temperature. It has been employed largely for sulfonating alkenes and alcohols.

(2.2.1c) SO_3 triethyl phosphate.

The best way to prepare this complex is to add freshly distilled SO_3 to the phosphate at 15 °C. It is the electron-rich phosphoryl oxygen which reacts with SO_3 exothermically to make a 1:1 adduct. Other adducts are also possible depending on the extent of reaction [10]. Depending on the substrate to be sulfonated the ratio of SO_3 to phosphate has to be controlled.

(2.2.1d) Halosulfonic Acids.

The most common acid in this class is chlorosulfonic acid. This is a strong acid ($ClSO_3H$). In effect it is an HCl complex of SO_3 and more suitable represented as $SO_3.HCl$. It is prepared by direct reaction of the two compounds [10]. At the time of reaction SO_3 is freed as a chemical moiety and HCl is liberated as a gas. This is a popular reagent for sulfating alcohols.

(2.2.1e) Sulfuric Acid and Oleum

$H_2SO_4.xH_2O$ is the most popular sulfonating agents in practise. A comparison with respect to some important factors has been shown in Table 2.1 [10]. Although the commercial availability of both of these is great, the main shortcoming is the hazard which can be produced by them.

$$HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH \qquad HO-\overset{\overset{OH}{|}}{\underset{\underset{O}{\|}}{S}}=O$$

(A) **(B)**

Figure 2.1: Figure 2.1(A) illustrates the structure of Oleum while 2.1(B) illustrates the structure of Sulfuric acid. Oleum is Sulfuric acid saturated with Sulfurtrioxide.

Oleum and Sulfuric acid are extremely hygroscopic and react hygroscopically with water. Thus, any contact with water must be avoided. Due to their oxidising nature they should not be contacted with combustible materials.

Table 2.1: A comparison of Sulfuric acid versus Sulfurtrioxide as Sulfonating agents [10].

Factor Compared	Sulfuric Acid	SulfurTrioxide
Reaction Rate	Slow	Instantaneous
Heat Input	Requires heat for completion	Strongly exothermic reaction
Extent of reaction	Partial	Complete
Side reactions	Minor	Sometimes extensive
Viscosity of Reaction Mixture	Low	Sometimes High
Boiling Point	290-317 °C	42-44 °C
Solubility in halogenated solvents	Very low	Miscible

As is evident from the table above almost all the factors except heat side reactions and viscosity of reaction mixture make sulfurtrioxide a better and a more viable choice as the sulfonating agent. Moreover, if the reaction is carried out in a controlled manner then the abovesaid shortcomings can be overcome.

2.3 SULFURTRIOXIDE MOLECULE

The sulfurtrioxide molecule has a very complicated chemistry [10]. The complication arises from the fact that Sulfur is a strongly electron-deficient atom while oxygen is an electron-rich center. Thus, the molecule has a Lewis acid site as well as a Lewis base site. This imparts it an *Amphoteric Character.* The sulfur in SO_3 has a strong tendency to increase the number of electrons to eight, ten or even twelve at times [10]. The amphoteric character is also responsible for the ease with which it can polymerize and its behaviour as a sulfonating agent. The electron-deficient sulfur atom attacks the basic sites while the electron-rich oxygen atoms attack the acidic sites. Sulfurtrioxide can exist in *solid, liquid and gaseous forms.*

2.3.1 Solid Sulfurtrioxide

Sulfurtrioxide in the solid state has various polymeric forms which are *alpha, beta and gamma form.* The gamma form is the most desirable and exists when SO_3 is absolutely pure and anhydrous [11]. Alpha form is highly crystallized and difficult to work with. It has highly stable asbestos-like crystals which do not melt easily. A comparison of properties of the various polymeric forms is given in the table which follows [11].

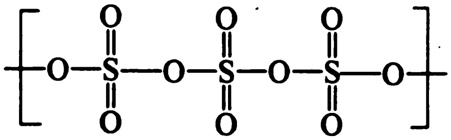


Figure 2.2: Polymeric form of solid SO_3

The β-form is the metastable form (m.p. 32.5°C) and is easy to melt. On the other hand α-form is highly stable (62.3°C). Solid samples do not have a well-defined melting point due to an undefined mixture of α-form and β-form. Attempts to melt this mixture without prior expertise can lead to a sudden increase in vapour pressure (of SO_3) which can be risky.

Table 2.2. Comparison of the properties of various polymeric forms of SO_3[11]

Description	**Gamma-form** **(Ice-like)**	**Beta-form** **(Asbestos- like)**	**Alpha-form** **(Asbestos-like)**
Equilibrium Melting point	16.8 °C	32.5°C	62.3°C
Heat of fusion	7.5 kJ/mol	12.1 kJ/mol	25.9 kJ/mol
Heat of Sublimation	49.8 kJ/mol	54.4 kJ/mol	68.2 kJ/mol
Vapor pressure			
0°C	45 mm Hg	32 mm Hg	5.8 mm Hg
25°C	433 mm Hg	344 mm Hg	73 mm Hg
50 °C	950 mm Hg	950 mm Hg	650 mm Hg
75 °C	3000 mm Hg	3000 mm Hg	3000 mm Hg

2.3.2 Liquid Sulfurtrioxide

In the liquid state sulfurtrioxide is available in the *stabilised and unstabilised forms*. The stabilised form contains very low quantities of chemicals which inhibit the formation of asbestos-like Beta (m.p. 32.5°C) form and Alpha (m.p. 62.3°C) crystals which are the high melting forms. Theoretically, in the stabilised form all the liquid SO_3 must be in the Gamma form. However, the presence of moisture destroys the inhibiting action of the stabiliser and with time straight-chain Beta form and the highly cross-linked stable Alpha form is formed. It is advisable that the liquid be stored at 35-41°C. Due to the possibility of formation of the different polymeric forms there is always a possibility of a sudden increase in vapor pressure on heating the liquid.

2.3.3 Gaseous Sulfurtrioxide

In gaseous state SO_3 exists as a monomeric form. Its proposed structure is planar, triangular and symmetrical. It is a resonance hybrid in which all the Oxygen atoms are equivalent. However, the exact distribution of electrons in a Sulfurtrioxide molecule is uncertain[10]. The possible canonical forms of SO_3 are shown in Figure 2.3 [10].

Figure 2.3: Possible canonical forms of SO_3.

2.4 OLEUM OR FUMING SULFURIC

An easier and more acceptable way to handle SO_3 is in the form of *Oleum.* Oleum is the term employed to describe fuming sulfuric acid and consists of SO_3 dissolved in 100% sulfuric acid. It is specified in terms of *percent strength.* Say, 20% oleum would mean 20% SO_3 dissolved in 80% sulfuric acid on a weight basis. On exposure to the atmosphere SO_3 tends to escape and combine with the moisture to form an acid mist, thus it must be avoided as much as possible. This has been the choice in the studies carried out in the presented thesis. The strength and operating conditions have been delineated in the context. Gaseous SO_3 was generated from oleum with a specially designed SO_3 generator, the details of which have been outlined in the following chapter.

Sulfurtrioxide Generator

Chapter 3

In order to use Sulfonation Process for surface treatment it is imperative that the generation of SO_3 is a controlled and a repeatable process. In keeping with the industrial norms it is important that it be a safe process. This chapter delineates the details of the Gas-phase SO_3 generator provided by Coalition Technologies Inc., Midland (Patent # 4,915,912, Figure 3.1a,b)

3.1 PRINCIPLE OF GENERATION

The source of pure gaseous SO_3 is the gas-phase generator provided by Coalition Technologies Limited, Midland [13]. The operation is based on the principle that if oleum (fuming sulfuric acid) is controllably agitated with air/nitrogen it will release its excess SO_3 . In the generator agitation is controlled and governed by forced-flow of air by means of a gas-pump which is operated when gaseous Sulfurtrioxide is required. The generator has several units which assist in controlled SO_3 production. The details of each individual component have been delineated in the following passages.

3.1.1 The Reactor

The reactor is the heart of the system. It is a Glass-vessel which has Raschig Ring packings and appropriate fitting arrangements on the cover to facilitate the flow of the reaction fluid. The reaction fluid is Oleum (of known concentration) which is pumped continously in a 3/8 inch steel tubing closed loop through the reactor vessel. For purposes of generating SO_3 gas, air is pumped into the reactor through a 1/2 inch steel tubing by the gas pump. The temperature is controlled by a heating jacket which in turn is controlled by a Series 965 Watlow Temperature Controller. The desired temperature for the reactor can be set and controlled from the Controller.

In order to minimise the contact of active Oleum with atmospheric moisture, the sealing arrangement on the reactor (and all other relevant components of the SO_3 generator) has been elaborately designed. The mouth of the (reactor) glass-vessel is covered by a steel-sheet with appropriate fittings for tubing arrangement. The whole assembly upper is made intact and leak free by a teflon ring held in place by an overlaying rubber ring and a hose clamp arrangement. This ensures that the concentration of oleum is not depleted due to intrusion of atmospheric moisture which tends to convert oleum into sulfuric acid. These features are also important for safety, handling and repeatibility during experimentation.

Since the reactor configuration demands maximum liquid-gas contact in order to enrich the gaseous phase in SO_3 , it has been provided with Raschig ring packings. The advantages of using packings are as follows [12].

- The packings are unaffected by the acid environments.
- The lower pressure-drop of a packed bed reactor reduces load on the liquid pump.
- Packings provide an increased surface area for attaining of gas phase equilibrium.
- Residence time of the liquid in the packed bed is short. This is particularly important in this case as the liquid is thermally sensitive.

The reactor is equipped with a pressure gauge which senses the pressure in the reactor. If at anytime there is an overpressure, a safety valve on the surge tank will release the pressure.

3.1.2 Vapor Filter

Inspite of the best efforts and arrangement to eliminate moisture leaking into the system, it is not possible to eliminate it completely. The SO_3-air mixture generated in the reactor has moisture content and other impurities associated with it. In order to purify the outgoing gas which has to be used for sulfonation a vapor filter has been provided in the generator. It consists of a glass vessel of the same dimensions as the reactor and is filled with fiber glass wool. The moisture and the particulate solids from the gas mixture are trapped by the wool and rendered clean.

3.1.3 Surge Tank

The outlet of the vapor filter is connected to a surge tank via a four-way valve which governs the direction of the flow of the gas mixture. The dimensions of the surge tank are same as the reactor and it is equipped with a pressure relief valve and a vent valve. In case of a minor over-pressure condition, the vent valve can be used to release the excess pressure. However, if due to an accident the pressure rises beyond control, the pressure relief valve will release the pressure to the enviroment. It is set at an overpressure limit of 3psi. The outlet of the surge tank is connected to the inlet of the gas pump.

3.1.4 Storage Tanks

The oleum is stored in three storage tanks which are provided in the generation unit itself. This facilitates the alteration in the concentration of active oleum in the reactor to the desired level. The stored oleum can be transferred to the reactor through 3/8 inch lines by a liquid pump. Also, it is possible to transfer oleum from the reactor to the storage tanks by an appropriate arrangement of the valves. There are three storage tanks in the unit which are of the same dimension as the reactor. A common inlet and an outlet line connects the liquid pump, reactor and storage tanks. Each tank is isolated from the main lines by a one-way valve. Since oleum can freeze under ambient conditions it has to be kept warm. The temperature of the storage tank area is maintained by a forced air heated convection system.

3.1.5 Piping and Valves

The generator unit has a relatively simple piping layout. Appropriate in-line valves 3/8 inch stainless steel tubing with compression fittings valves have been placed according to the requirements. The valves and the tube lines are color coded for the purposes of convenience and Chemical Engineering norms [13].

All the gas lines are 1/2 inch dia. and those handling liquids are 3/8 inch dia. The valves and lines which handle liquid oleum or SO_3 are color coded RED. For gas (mixture) the color is YELLOW. In addition valves on each storage tank are used to vent the gas mixture from the storage tanks when they are being filled or emptied of the liquid are coded BLACK.

On the surge tank there are two additional valves. There is a pressure relief valve which is set at fail open (FO) condition and there is a green vent valve. They can be used to release excess pressure which may develop in the system.

3.1.6 Pumps

The SO_3-generator unit has two pumps installed in it. One is a liquid pump and the other is a gas pump. The liquid pump is an *M-7 Micropump*. It has been designed such that all the parts which come in contact with oleum are made up of teflon. This allows a smooth operation and also significantly reduces maintenance costs due to the highly corrosive and reactive environment of SO_3 . To prevent contaminants from entering the pump a *140 micron filter* has been installed at the inlet port of the pump. The other pump is a *Metal-Bellows gas pump* with a capacity of 15 liters per minute. It has the capability of handling SO_3-air mixtures. Unlike the liquid pump it is not in continous operation and used used only when SO_3 is required for sulfonation.

3.1.7 Controls

There are three control panels on the SO_3 generator. They are the Temperature Control, Main Control and Pump Control [13]. The Temperature Controller allows control of the temperature of the reactor and the storage tanks area. The reactor temperature is especially important because it directly affects the concentration of SO_3 generated. As the temperature of the system is increased the amount of SO_3 generated also increases. The temperature of the cabinet must be maintained above the freezing point of the oleum stored (depending on the concentration of oleum). A j-type thermocouple is used in both the controls for temperature sensing.

The main control panel has all the operation controls of the generator. It consists of four push button switches and a timer (with display). Three of the push buttons control the operation of the pumps while the fourth controls the timer.

The pump control panel has a DC power supply and a relay that supplies power to the liquid pump. The mode of operation of the liquid pump (speed and direction) is also controlled from this panel. The pump can be operated in reverse as well as forward direction. The speed control knob allows the pumping rate to vary according to the needs.

A schematic flow-sheet of the lay out of generator has been presented in Figures 3.1a and 3.1b in the following pages. To facilitate the understanding of the diagram the flow-sheet has been split into two figures. The main unit which generates the gas has been shown in figure 3.1a and the unit with sulfonating chamber set-up is shown in figure 3.1b.

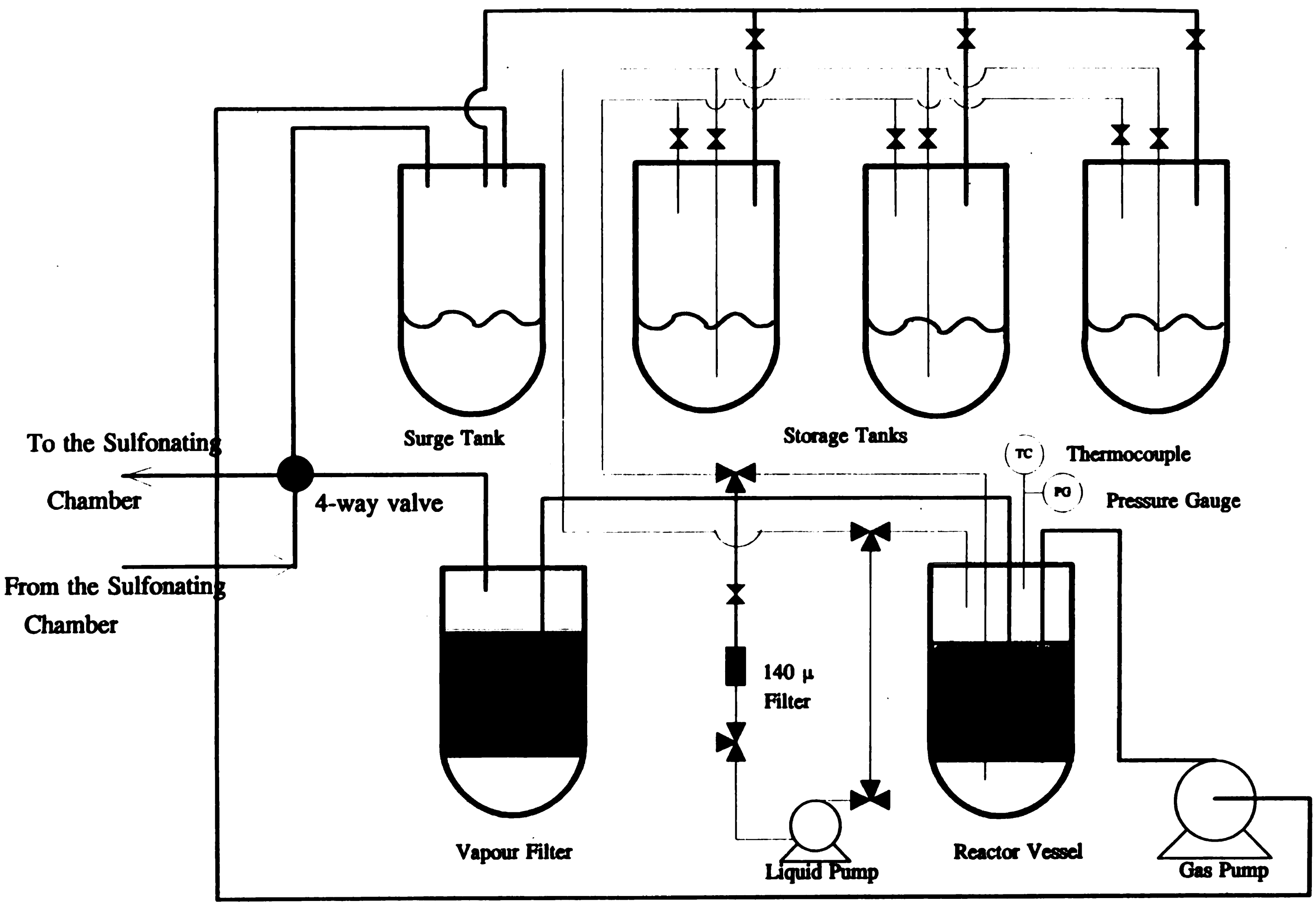


Figure 3.1a: Flow-sheet of the gas-phase SO_3 generator. (Contd. figure 3.1b)

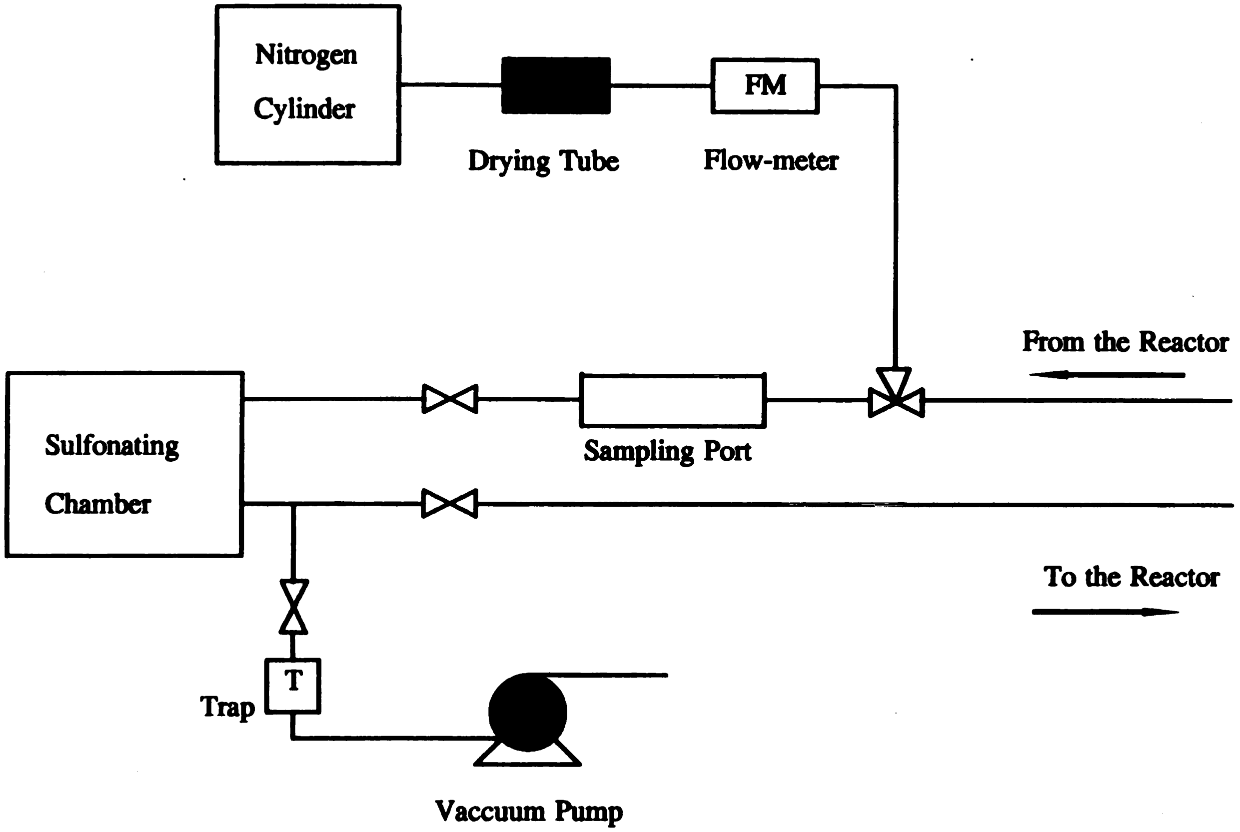


Figure 3.1b: Schematic showing the SO_3 flow pattern in the Sulfonating chamber. (Contd. from 3.1a)

3.2 OPERATION OF THE REACTOR

The main purpose of the reactor is to generate pure gaseous SO_3 under controlled conditions at a fixed level over a range of concentration. To achieve this it is important that in addition to the external conditions like temperature etc., the nature of the oleum producing SO_3 is always same.

3.2.1 Oleum Circulation Patterns

To maintain consistency of the gaseous mixture being generated the concentration and activity of the oleum source must be kept constant. To do this it is circulated continously. In the generator this is done by pumping the oleum (in a closed loop through the reactor) continously through the liquid pump via the 140 micron filter installed at the inlet of the pump. When SO_3 is required, the gas pump can be switched on to force air in the reactor which absorbs the excess SO_3 from the fuming sulfuric.

3.2.2 SO_3 Gas Circulation Patterns

As has been discussed above, in order to generate SO_3, air in the lines is pumped into the reactor containing active oleum. The pumping operation results in release of SO_3 from fuming sulfuric acid. The gas mixture generated is stripped of impurities (including moisture) by the vapor filter. The gas then goes into the surge tank from where it is recycled into the reactor via the gas pump. This process is continued until an SO_3-saturated gas mixture is obtained. This cycle is called *Internal Circulation*. The gas line connecting the vapor filter to the surge tank has a 4-way valve which can be positioned to direct the flow of SO_3 into the sulfonating chamber which lies in-between the vapor filter and the surge tank. It is in this chamber that the substrate under investigation is sulfonated. During sample sulfonation, gas flows from the vapor filter into the surge tank through the sulfonating chamber and is said to be in *External Circulation*. There are distinct advantages of using SO_3 in external circulation mode as against a one point usage and disposal of the excess. Firstly, there is conservation of the unused portion of the gas. This is recycled into the system and in subsequent contact with oleum it is saturated again. Secondly, it is easier to maintain a constant concentration of the product gas in this manner. This results in constant experimental conditions. The major shortcoming of this procedure is the moisture carryover in the system during sulfonation.

3.3 SULFONATING CHAMBER

The sulfonating chamber is a stainless steel parallelopiped box with manifolds at two of its narrow sides. The dimensions of the box are 15 x 15 x 1.75 inches and the

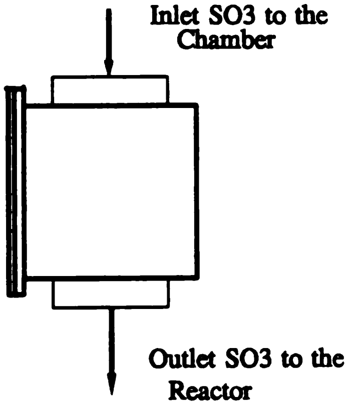


Figure 3.2: A schematic figure of the sulfonating chamber showing positions of the manifolds.

steel is 1/4 inches thick. Both the manifolds are welded to the narrow sides of the box and are made of stainless steel. All the fittings on the manifolds are 1/ 2 inch swagelok stainless steel fittings. Figure 3.2 is a sketch of the manifold showing a lay out of the inlet and outgoing tubes.

The sheet to be sulfonated is placed inside the chamber on a support which ensures that the sheet is not touching the sides of the chamber. The sheet must be as taut as possible so that the flow of gas mixture is maintained uniform ensuring that sulfonation conditions do not change while in the middle of the run. The open side of the chamber through which the sheet and the support is placed inside is a highly machined surface. The lid which closes the side is also highly machined and has a Buna -N rubber O-ring which comes in direct contact with the opening on the box. This has proved to be a good arrangement for creating and maintaining a vacuum (of 300 microns) in the chamber before sulfonating.

The inlet line to the sulfonating chamber carries the SO_3 gas mixture from the reactor via the vapor filter in a 2 inch teflon line braided with stainless steel. Teflon is an inert material and thus does not degrade in contact with SO_3. Stainless steel braiding provides strength to the tube assembly. The same port is also the inlet for nitrogen gas which is used to create an inert atmosphere in the chamber before sulfonating and purge the system after sulfonation is over. Also located on the main lines which carry SO_3 (or nitrogen) into the sulfonating chamber is a sampling port for monitoring the SO_3 concentration (see Figure 3.3). The sampling port is made up of stainless steel. Silicon septum (coated with teflon on one side) is inserted in the port and made secure by a teflon stopper. An air-tight syringe with 18 gauge needle is used for sampling purposes.

The gas mixture is pulled out of the lines while sulfonating. The contents of this syringe are then released into an erlenmeyer fitted with a glass adaptor. The erlenmeyer contains water. The SO_3 of the gas mixture reacts with water to form acid. The strength of this acid is indicative of the strength of the gaseous mixture.

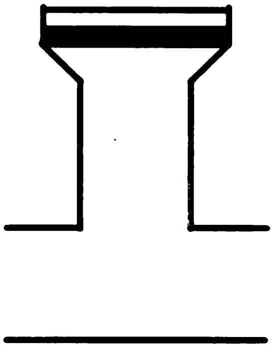


Figure 3.3: Schematic of the sampling port for SO_3 gas.

The second manifold is the outlet line of the sulfonating chamber and it recycles the gas mixture back into the reactor. At this port a T-arrangement has been installed, one arm of which is connected to the manifold and the other arm to the vacuum Pump. The rubber hose connecting the vaccuum pump to the manifold (through the 1/2 inch ball-valve) has a Liquid nitrogen trap. The installation of this trap system is for the purpose of trapping any contaminants, especially residual SO_3 from going into the pump and to prevent back streaming of pump oil into the system.

The successful operation of the generator has been verified by checking as to whether it can generate SO_3 in a controlled and repeatable manner. For achieving this end the first requirement is that one must have a confident method of measuring the gas concentration. This is the topic of discussion of the following chapter.

Measurement And Control of Sulfurtrioxide

Chapter 4

The process of surface treatment using sulfonation in order to be industrially and commercially viable must have strict control over the amount of SO_3 generated under a given set of conditions. The gaseous product should be of constant composition and must be repeatable under the stated conditions. However, considering that SO_3 (and Oleum) are highly reactive chemical species the system has to be so designed that the influence of external parameters is minimised while offering maximum control on the parameters that control the amount of SO_3 generated.

4.1 EXTERNAL PARAMETERS AFFECTING SO_3 CONCENTRATION

There are several external parameters which strongly affect SO_3 concentration. The most important is moisture which is extremely detrimental to the concentration of measurable SO_3. Moisture immediately combines with SO_3 to form sulfuric acid when brought in contact with Oleum or SO_3. Thus, even trace amounts of moisture must not be admitted into the system. In order to achieve this, the storage tanks were blanketed with dry nitrogen gas. The surge tank and the vapor filter were also flushed with nitrogen. In order to minimise the damage due to moisture during actual use of the machine, all the lines, manifolds, valves etc. were heated up to 110 °C for at least 5 hours to remove all the moisture absorbed on the surface. The sulfonating chamber was subjected to a vaccuum of 300 microns to reduce moisture from the polymer film being sulfonated.

Another important parameter which controls the amount of SO_3 generated is the temperature at which the oleum is maintained. The vapor pressure of gaseous SO_3 generated is highly sensitive to the temperature of the oleum reactor. In order to maintain a constant temperature, the reactor has been provided with a heating jacket and a controller through which the required temperature can be maintained (± 1°F).

4.2 TECHNIQUES USED TO MEASURE SO_3 CONCENTRATION

An accurate and reproducible method to measure the concentration of SO_3 in the gas mixture is a prerequisite for the successful operation of the process. The details of the technique used are described in the following discussion.

4.2.1 Volumetric Gas Sampling

This technique is based on the principles of chemical titration. That is, at the end-point of the titration reaction, the numbers of equivalents of both species reacted is same. Now, it is known that SO_3 is highly susceptible to reaction with water to form sulfuric acid. Thus, if we assume a complete reaction between SO_3 gas and water the concentration of the resulting acid should be identical to the concentration of SO_3 gas. This principle has been used in the present study in order to quantify the SO_3 gaseous concentration.

The SO_3-gas mixture was trapped in a specially designed glass tube called a Volumetric Gas Sampler (VGS) of 210 ml by installing it in the external lines just before the sulfonating chamber. All the lines and valves were heated to 110°C to drive out all the absorbed moisture before being used. In order to minimise the effect due to external moisture the lines were thoroughly flushed with dry nitrogen at a rate of 34 l/min for 2 minutes so that all the atmospheric air was replaced with dry nitrogen. At this stage the 4-way valve was switched to the external loop mode so that SO_3 gas could be introduced in the gas sampler. After 5 minutes the gas flow was stopped, stop-cock on the gas sampler shut off and the VGS removed from the system. In order to create a slight vaccuum for facilitating the introduction of water the sampler was placed in freezer for 10 minutes. Deionised water was introduced in the sampler gradually by the action of vaccum. The amount of deionised water supply was always in excess so that air could not enter the system and also so that all the SO_3 molecules react. As soon as water entered the gas sampler it became cloudy due to sulfuric acid mist. The reaction is as follows.

$$SO_3 + H_2O \text{ ------> } H_2SO_4$$

The glass sampler was shaken thoroughly to carry out the reaction to completion and to ensure that all the SO_3 molecules are reacted. The resultant acid was transferred to a flask and titrated against sodium hydroxide (NaOH) of known concentration with phenolphthanalein as an indicator. The neutralisation reaction resulted in formation of a salt. The proposed reaction sequence is as follows.

$$H_2SO_4 + 2\ NaOH \text{ -----> } Na_2SO_4 + 2H_2O$$

The reaction end-point was determined as soon as the reaction mixture achieved a pink coloration. Also, at the end-point the number of equivalents of NaOH reacted equals the number of equivalents of H_2SO_4 reacted.

Or, in other words

$$N_1V_1 = N_2V_2$$

where, N_1 is the normality of NaOH, V_1 is the volume of NaOH used and

N_2 is the normality of H_2SO_4, V_2 is the volume of H_2SO_4 used.

Now, notice that according to the stoichiometric relation two moles of NaOH are used for each mole of H_2SO_4 employed. Thus, the following relationship can be derived.

$$\text{Volume of } SO_3 = (N_{NaOH}\, V_{NaOH}/2)\ (22.4\ \text{l/g-mol})$$

Thus, $$\text{Percentage volume of } SO_3 = (\text{Volume of } SO_3)/(\text{Volume of VGS})$$

4.3 THE pH MODEL

There are certain inherent limitations in the technique outlined above. Firstly, introducing water to carry out its reaction with SO_3 to make an acid was difficult and user dependent. The SO_3 vapour had a tendency to escape from the gas sampler thus giving erroneous results. Also, the VGS, gas lines etc had to be washed and dried out each time they were used. To reduce the sampling time and to ensure a stricter control over repeatability, the pH of the resulting acid was measured instead of carrying out actual titrations each time. The theoretical derivation of the equation to be employed is based on the definition of pH. The pH of a reagent is defined as the negative log (base 10) of the hydrogen ion concentration of the system. The reagent in the system under consideration is sulfuric acid which was prepared by reacting DI-water with SO_3 gas. The details of the relation are as follows.

$$SO_3 + H_2O = H_2SO_4$$

$$H_2SO_4 = 2H^+ + SO_4^{-2}$$

$$[H_2SO_4] = [H^+]/2$$

Now, $$[H^+] = 10^{-pH}$$

Thus, $[SO_3] = [H_2SO_4] = [H^+]/2 = 10^{-pH}/2$

$$\text{Number of moles of } SO_3 = [SO_3] \text{ (Volume of acid)}$$

$$\text{Number of moles of } SO_3 = [SO_3] (V_{H2O})$$

$$\text{Volume of } SO_3 = (22.4 \text{ l/g-mole}) (V_{H2O}) 10^{-pH}/2$$

$$\text{Percentage } SO_3 = (\text{Volume of } SO_3)/(\text{ Total Volume of gas mixture})$$

Now, volume of water employed was kept constant in each run (20ml) and the total volume of gaseous mixture was constant at 100 ml. Therefore,

$$\textbf{Percentage } \mathbf{SO_3} = \mathbf{(224)10^{-pH}}$$

The pH was measured using Corning Model M-250 pH/ISE meter which had an accuracy of ±0.001.

Now, the amount of SO_3 released from a given concentration of SO_3 is dependent on the temperature. Figure 4.1 shows the variation of vapor pressure of SO_3 and oleum with respect to temperature. The oleum in the reactor was known to be of 30% strength. The plot of experimentally calculated vapour pressures and the actual vapour pressures shown in Figure 4.2 indicate a variable difference between the experimental values and actual values [25]. Thus, this method although time saving and reproducible did not prove to be accurate.

4.4 RELATION BETWEEN pH AND VGS MODELS.

Although the VGS model was time consuming it was accurate. On the other hand the pH method was time saving and reproducible but inaccurate. Thus, an attempt was made to relate pH values to the VGS values [25]. The results are shown in Figure 4.3 [25]. This served as the master curve for all the work presented in this thesis.

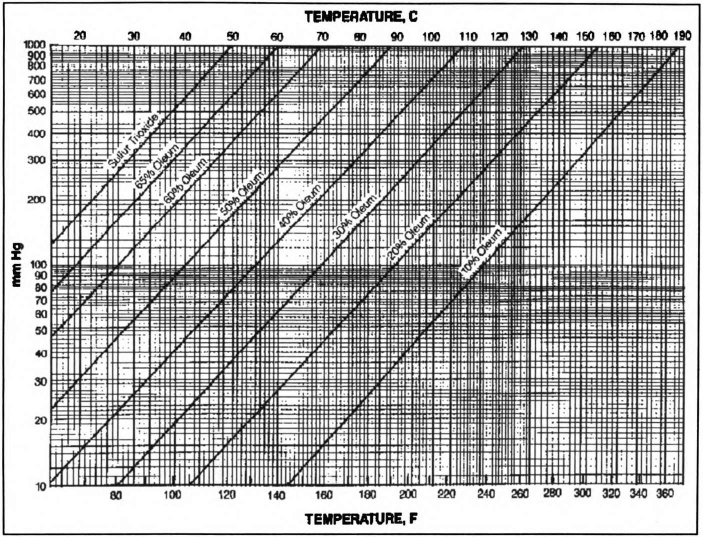


Figure 4.1: The figure illustrates the variation of vapor pressure of SO_3 and Oleum with respect to temperature [11].

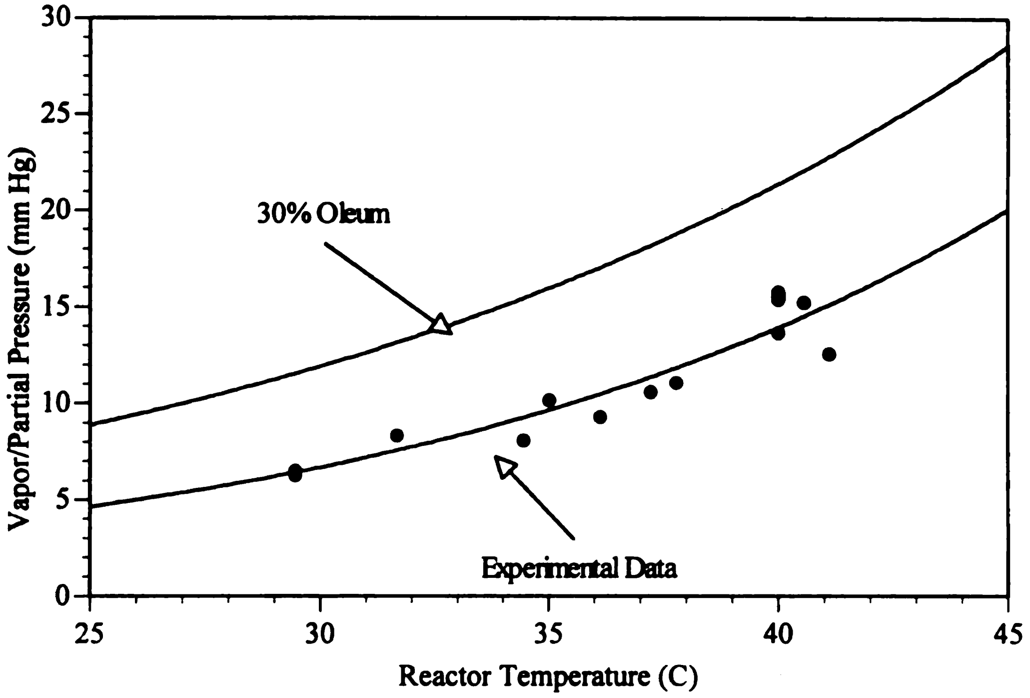


Figure 4.2: The figure illustrates the experimentally determined vapor pressure and the actual vapor pressure of SO_3 in the reactor [25].

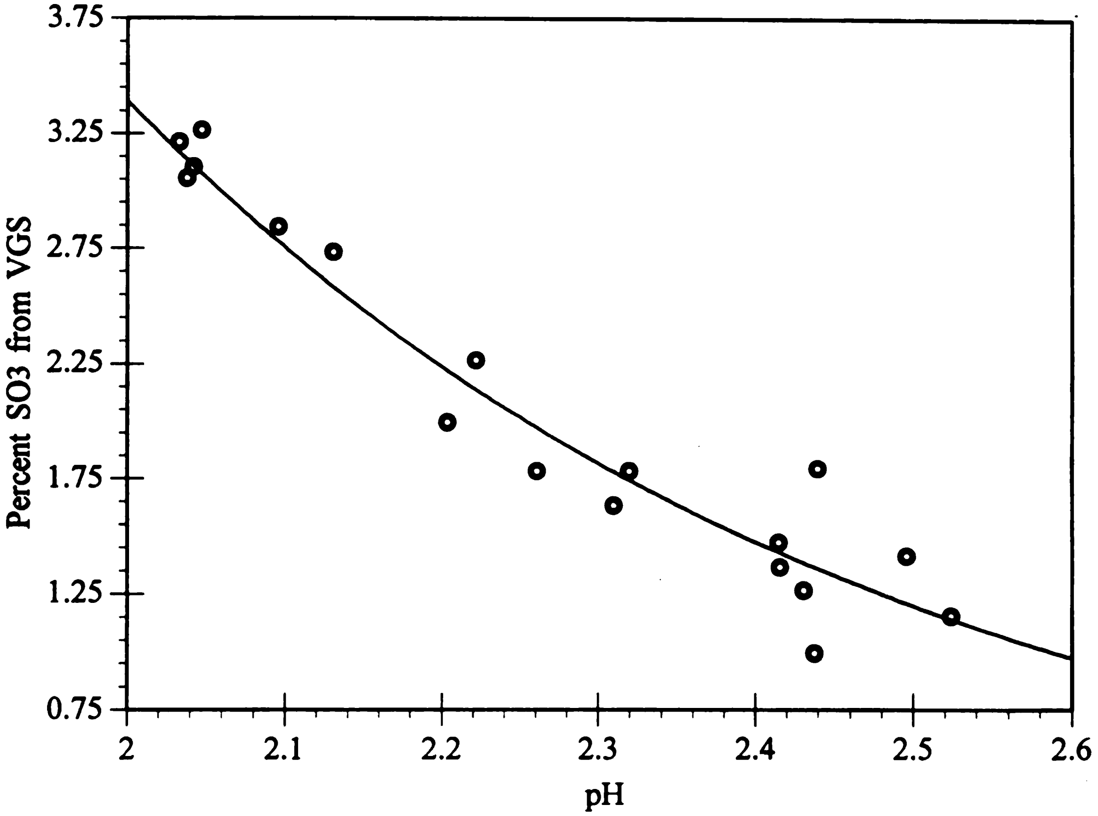


Figure 4.3: The calibration curve showing the relationship between pH and percentage SO_3 obtained from VGS [25].

Experimental Methods and Protocols

Chapter 5

The characterisation of the surface of modified polymers is of utmost importance to determine the chemical changes occuring on the surface. Several spectroscopic techniques were employed for this purpose. Also, in order to ensure that the modified surface is essentially identical in every run, or in other words for repeatability of the experiments strict experimental protocols were followed. This chapter delineates the spectroscopic methods and the experimental protocols followed.

5.1 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray Photoelectron Spectroscopy is a surface-sensitive technique which is finding increasing applications in surface analysis of polymers. The technique is powerful because besides giving qualitative atomic information it can provide quantitative data and chemical information. For example, typically a complete data set would consist of the kinds of atoms present on the surface, percentage of each of them and also the chemical environment of the atoms. That is, the oxidation state of each of the element present in the system.

X-rays are the primary beam which are impinged on the surface of the material being analysed under ultra-high vaccuum conditions. The interaction of X-rays with the atoms of the material causes the ejection of the core electron(s) imparting them kinetic energy in the process. This is called *the Photo-ionization* process. The binding energy of the core electrons is characteristic of the element from which they originate and since the X-ray photons are non-energetic, the kinetic energy of the photo-electrons is also unique to each element (and its corresponding oxidation state). The governing equation for XPS in its simplest form is an energy balance.

$$E_K = h\nu - E_b$$

where,

E_K is the kinetic energy of the photo-electron

$h\nu$ is the energy of the primary beams

E_b is the binding energy of the core electrons

The photo-electrons are collected and sorted according to their energy, thus yielding the spectrum. However, there are certain inherent limitations of this technique. The most important one being the requirement of Ultra-high vaccuum (UHV). The signal quality and quantity is greatly reduced in the absence of UHV as the photo-electrons collide with gas phase molecules on their way to the detector thus distorting the signal. Another major problem, especially with polymers is charge build-up on the surface. As the electrons leave the surface of the sample, there is a net charge build-up due to decreasing number of electrons on the sample causing an increasing resistance to the electrons from leaving the surface. This can shift the signal substantially. One way to alleviate this problem is to flood the sample with low-energy electrons which do not affect the signal character. The third problem is that the X-rays are difficult to focus. This may lead to an unacceptable spatial resolution of the sample under investigation. The maximum depth from which the signal is collected can range from 2-5 nm. A detailed explanation of the process is given in reference [15].

All XPS experiments were carried out on a Perkin-Elmer PHI 5400 XPSA system using an Al Kα (1486.6 eV) monochromatic source (PHI 10-410). Spectra were collected at a base pressure of approximately 10^{-9} Torr and electron take-off angle of 65° using a position sensitive detector on a 180° hemispherical analyser set at 89.9 eV for wide scan and 35.5 eV for narrow scans of the elemental regions.

5.2 FOURIER TRANSFORM INFRA-RED SPECTROSCOPIC ANALYSIS

Fourier Transform Infra-red Analysis involves the use of Infra-red region of Electro-magnetic spectrum to analyse the chemical information about the species under investigation. The infra-red region of the spectrum lies at wavelengths longer than visible light and less than microwaves. That is, $400 \text{ nm} < \lambda_{IR} < 800 \text{ nm}$ ($1 \text{ nm} = 10^{-9}\text{m}$).

The principle of operation involves the absorption of energy by molecules/chemical entities which promotes them to a higher energy state. All compounds which have covalent bonds absorb energy at various frequencies of electromagnetic radiation in the IR region. The absorption of energy is a quantized process. The energy absorbed (8.36-41.8 kJ/mole) puts the molecule in a higher energy state which increases the amplitude of the stretching, bending vibrational motions of the bonds in molecules. However, since the presence of dipole-moments is a prerequisite for energy absorption not all molecules can absorb IR energy.

Each molecule has a different set of bonds. That is, a single kind of bond may be present in two different molecules but the fact that they do not have the same chemical environment implies that the natural frequency of this bond will be different. Thus, no two structures can have exactly the same IR absorption pattern/ IR spectrum. This is the reason that IR can be used to quantify molecular information.

IR rays impinging on a sample can be reflected, absorbed, transmitted or scattered. Mathematically, this is expressed as,

$$I_0 = I_r + I_a + I_t + I_s$$

where, I_0 intensity of the incident beam.

I_r is intensity of the reflected beam.

I_a is intensity of the absorbed beam.

I_t is intensity of the transmitted beam.

I_s is intensity of the scattered beam.

Any of the above beams can be the sampling beam for the purposes of analysis, the final choice depending on the nature of sample, geometry of the sample etc. For opaque samples where polymer sample has a low transmittance Internal Reflectance Spectroscopy (or Attenuated Total Reflectance) is used. This technique is a contact sampling method involving a crystal with a high refractive index and low IR absorption. The main advantage of IRS is that spectra of opaque samples can be obtained. In the present study KRS-5 (Thallium Bromide-Iodide) crystal was used with angle of analysis being 45°. ATR MTCN mode with MCTN detector was employed. The depth of penetration of the beam is given by the following equation.

$$D_p = \left(\frac{\lambda}{2\pi}\right) \left(n_1^2 \sin^2\theta - n_2^2 \right)^{-\frac{1}{2}}$$

where, D_p is the depth of penetration in microns.

λ is the wavelength in microns.

n_1 is refractive index of the crystal.

n_2 is the refractive index of the material.

θ is the angle of the face of the crystal.

IR spectra were recorded on a Perkin-Elmer 1800 FTIR Spectrometer with MCTN detector. The sample chamber was purged with dry and carbon dioxide removed air for 10 minutes before spectra were recorded. An ATR attachment with KRS-5 crystal (Thallium Bromide-Iodide) internal reflectance element was used for analysis. The crystal had 45° endface angles and 50x50x2 mm dimension. The sample strips were placed on either side of the crystal and flushed securely with pads. The sample signal was ratioed against KRS-5 crystal reference. 500 scans were collected for each sample.

In order to study the material degraded by sulfonation polypropylene samples were prepared with noninfrared absorbing KBr matrix. The material was scraped off the surface of polypropylene with a clean razor blade. This was thoroughly mixed with KBr and a disk made out of it under high pressure.

5.3 CONTACT ANGLE ANALYSIS

Contact Angle is a measure of degree of wettability of liquid on a solid surface. The concept of contact angle is widely employed to estimate the trends in wettability and thus adhesion. A contact angle of 0° indicates spontaneous wetting while 180° indictes non-wetting condition. That is, if the angle is 0° the situation is most favourable for adhesion while 180° is the most unfavorable.

For the present work, contact angle analysis was used to complement the information provided by XPS and observe the trends on the nature of changes occuring on the surface. The angles were measured using a Rame-Hart Goniometer Model 100-00. Water was used as the probe liquid. 5 μL drops were placed manually on surface of the polymer under investigation with a Precision Microliter Pipette (Pipetteman). The angle was read from the calibrated eye-piece.

5.4 MATERIALS

One of the main objectives of the present work was to characterise the effect of sulfonation on an aliphatic polymer and on an aromatic polymer. For this purpose, polypropylene was chosen as the model for aliphatic system and polystyrene was chosen as a model for aromatic system. Both the polymers were 0.03 inches thick films and used as available from a commercial source.

The repeating unit of polypropylene is shown in Figure 5.1. As is clear from the figure, it is characterised by primary, secondary as well as a tertiary carbon. Tertiary carbon is the most probable site for sulfonation due to the highly electrophilic nature of sulfonation reaction. Details will be discussed in Chapter 6 (Sulfonation of

Polypropylene)

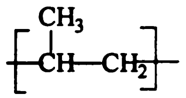


Figure 5.1: The figure illustrates the repeating unit for polypropylene.

The repeating unit for polystyrene has been depicted in Figure 5.2. It is characterised by two secondary carbons of aliphatic nature and a phenyl ring. Due to the high electron density on this ring ortho and para position are the most probable sites for sulfonation. More details on this aspect have been presented in Chapter 7 (Sulfonation of Polystyrene).

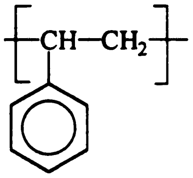


Figure 5.2: The figure illustrates the repeating unit for polystyrene polymer.

Gaseous sulfurtrioxide of known concentration was generated from a specially designed generator the details of which have already been given in Chapter 3. The concentration of SO_3 used in the following work was 1% (± 0.2%) SO_3-air mixture.

5.5 REACTION CONDITIONS AND SCHEME

All the reactions were carried out under ambient conditions. To clean the surface of the polymers prior to sulfonation, they were treated with a commercially available detergent 'Micro'. All the sheets were washed and rinsed in deionised water thoroughly and the samples were then air-dried. In order to minimise the effect of moisture and to ensure the repeatability of the reaction , the following procedure was followed in each run.

- Micro-washed sheets thoroughly washed in DI-water and air-dried were placed in the sulfonating chamber and flushed with dry Nitrogen (34 l/min) for 5 minutes
- A vaccuum of about 300 microns was applied to the sulfonating chamber (with the sheet placed inside) for 10 minutes. This removes the moisture to the maximum possible extent. However, it is not possible to remove the monolayer of water which is adsorbed on the surface of the polymer.
- The vaccuum was broken by purging and flushing the system with dry nitrogen (34 l/min) for 5 minutes for bringing it to atmospheric conditions again. The unit cannot be operated at sub-atmospheric conditions, since a vaccuum on the reactor will seriously disturb the SO_3equilibrium in the reactor.
- The sheets were sulfonated for the desired time.

- The system was then flushed with dry nitrogen (34 l/min) for 5 minutes before opening the sulfonating chamber. This ensures that all the residual SO_3/H_2SO_4 is purged out of the system through the vent tube.
- The sheets were neutralised in 5% aqueous solution of Ammonium Hydroxide (NH_4OH). This was prepared by mixing the commercially available 1 part volume of 30% NH_4OH with 6 parts volume of DI- water.
- The neutralised sheets were placed in excess of DI-water for 5 minutes.
- The sheets were then washed thoroughly in running DI-water and air-dried.

The details of the reactions and chemical changes occuring on the surface are presented in the following Chapters (6 and 7).

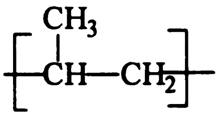
Sulfonation of Polypropylene

Chapter 6

Polypropylene has wide ranging industrial and daily life applications. However, like most thermosplastics polypropylene also has a low-energy surface. It has been shown by investigators that surface modification of polypropylene using sulfonation is a viable technique to improve its adhesion properties [25]. The focus of present discussion is to follow the chemical changes that occur on the surface of polypropylene as a result of sulfonation.

6.1 NATURE OF POLYPROPYLENE

Polypropylene is an aliphatic polymer. In other words, it does not have any phenyl rings in its structures. The repeating unit of polypropylene is shown in Figure 6.1.



$$-\left[\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\mathrm{CH_2}\right]-$$

Figure 6.1: The figure illustrates the repeating unit of polypropylene.

As can be seen in Figure 6.1 it is characterised by primary, secondary as well as a tertiary carbon atom. Thus, if this system can be characterised as to its reactivity to sulfonation, then predictions about other polymer systems which contain these kind of carbons can be made.

It has been documented in the literature sulfonation is an electrophilic reaction. The sulfur in sulfurtrioxide behaves as a Lewis acid and oxygen atoms behave as a Lewis base. The molecule is planar, triangular and symmetrical [10]. The S-O bond is short (1.4198 Å) and all the oxygen atoms have been shown to be equivalent indicating a resonance hybrid structure. The high reactivity of sulfurtrioxide is due to the electron deficient nature of sulfur which tries to increase the number of electrons in its outermost shell to ten or even twelve [10] thus supporting the electrophilic nature of the reactions of sulfurtrioxide.

Due to the highly electrophilic mechanism of sulfonation, the tertiary carbon is most susceptible to attack during sulfonation followed by secondary and primary respectively. This is because tertiary carbon is bonded to three other carbons secondary to two and primary to a single carbon atom. This makes the electron density on tertiary carbon maximum which will drive the reacting SO_3 molecule preferentially towards this site. However, sulfurtrioxide is such a reactive species that reaction with secondary or primary cannot be ruled out.

To investigate the nature of chemical species various analytical techniques were employed the details of which are in the preceding chapter. The following results are for polypropylene sulfonated with 1% SO_3-air mixture (by volume) followed by neutralisation with 5% aqueous solution of ammonium hydroxide unless stated otherwise. The observations and results from each of them will be discussed in detail in the following passages.

6.2 FTIR-SPECTROSCOPY OBSERVATIONS.

Several investigators have used Infra-red technique to determine the chemical species on the top 1-2 μm of the sulfonated surface [26-30]. Based on work by Ihata et. al. [30], Cameron et. al. [28,29], Gibson et. al. [35] and reference 31 and 34 the following table has been compiled for ready reference in the following discussion.

Table 6.1: The table shows the wavenumbers and the probable chemical species responsible for their presence.

Peak Position (cm^{-1})	Possible chemical species
1110	-CHOH
1167	O=S=O stretch
1045	O=S=O stretch
1385	-NH of ammonium
1425	O=S=O stretch
~ 1600	Conjugated C=C stretch
1680-1620	Unconjugated C=C stretch, water
1700-1750	-C=O (ketones, carboxylic acid)
3030	-CH=CH- stretch
3220	-NH of NH_4
3450	-OH (water, alcohol, acid)

Figure 6.2 shows the IR spectra (in transmission mode) of Polypropylene sulfonated from 1 thru 5 minutes in 1% SO_3-air mixture followed by neutralisation with ammonium hydroxide. Figure 6.3 is the spectra of polypropylene subtracted from sulfonated polypropylene (in absorbance mode) which shows the changes occuring on the surface as treatment time is increased from 1 minutes to 5 minutes. The major bands observed after sulfonation are the bands that appear in 1170 cm^{-1} region, a band in 1350 cm^{-1} region, a band in 1450 cm^{-1} region, a band in 1600-1750 cm^{-1}region, band in 3400 cm^{-1} region and in 3200 cm^{-1} region.

Bands at 1170 cm^{-1} and 1450 cm^{-1} are attributed to S=O vibrations . The exact location and nature of these bands depends on the groups attached [31]. Also, in the region 1390-1430 cm^{-1} the contribution can be from -NH of NH_4^{+1} [34]. As the time of sulfonation is increased not only the the intensity of these bands increase but also subtle changes start to occur within the envelope. There is a possibility that additional peaks start emerging in this region. The essential nature of the compounds which yield peaks in this region is the same, i.e. they contain S=O linkage but the nature of group which carries this chemical species starts to vary which leads to the belief that certain other compounds besides sulfonic acids are being formed [31]. Also, the intensity of each of these bands increases as the time of sulfonation is increased.

A review of the past literature work shows that formation of sulfonic acids is the major chemical change effected due to sulfonation on the polymer surfaces [26-30]. Sulfonic acids are characterised by two peak positions. One is a strong band near 1175 cm^{-1} and the other is a medium intensity band near 1055 cm^{-1} [31]. In the present work these band positions have been fixed at 1167 cm^{-1} and 1045 cm^{-1}. But, since changes

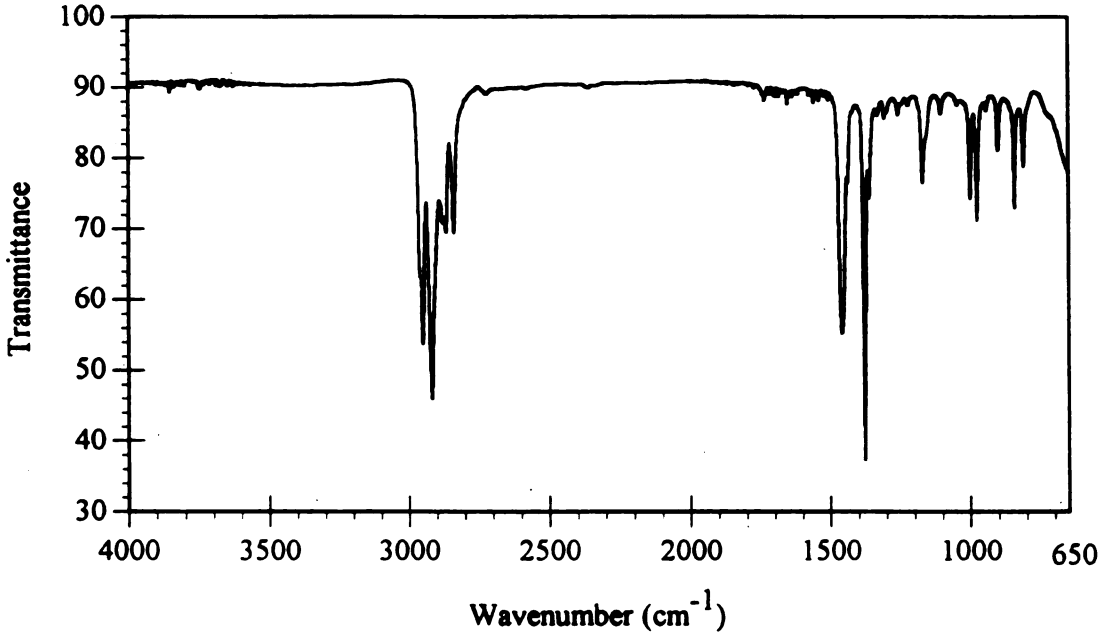


Figure 6.2a: The figure illustrates the IR spectrum of unsulfonated polypropylene.

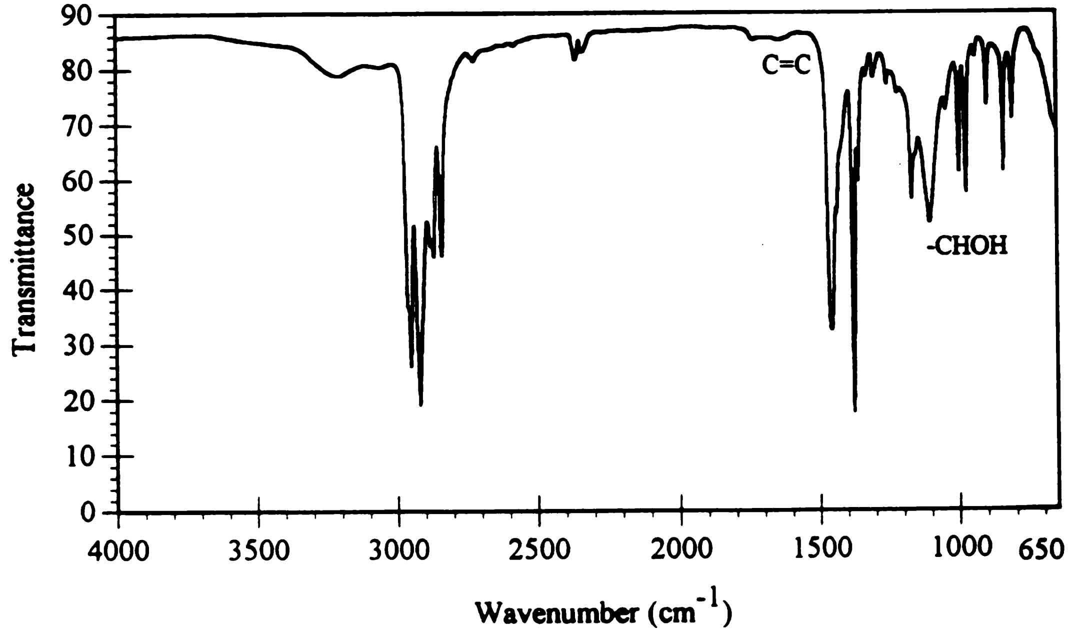


Figure 6.2b: The figure illustrates the IR spectrum of polypropylene sulfonated for 1 minute followed by neutralisation with ammonium hydroxide.

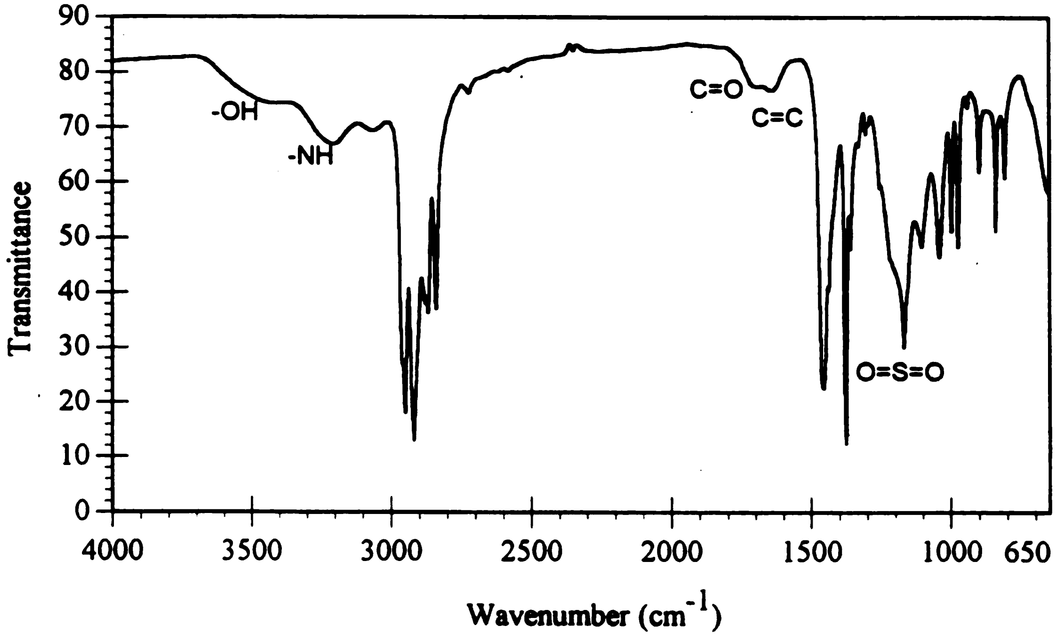


Figure 6.2c: The figure illustrates the IR spectrum of polypropylene sulfonated for 2 minutes followed by neutralisation with ammonium hydroxide.

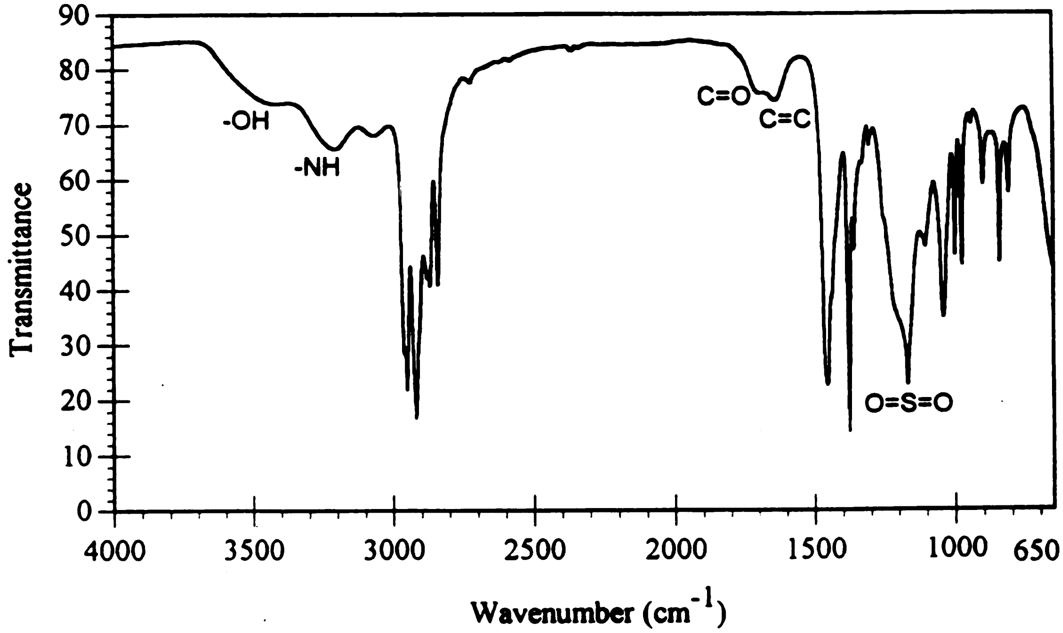


Figure 6.2d: The figure illustrates the IR spectrum of polypropylene sulfonated for 3 minutes followed by neutralisation with ammonium hydroxide.

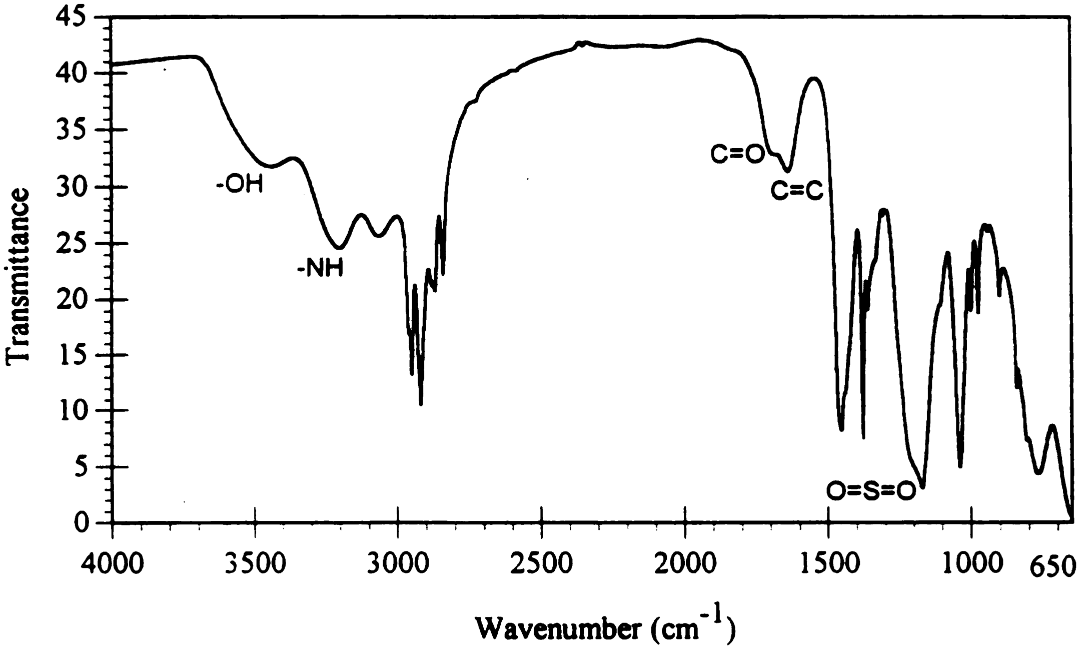


Figure 6.2e: The figure illustrates the IR spectrum of polypropylene sulfonated for 4 minutes followed by neutralisation with ammonium hydroxide.

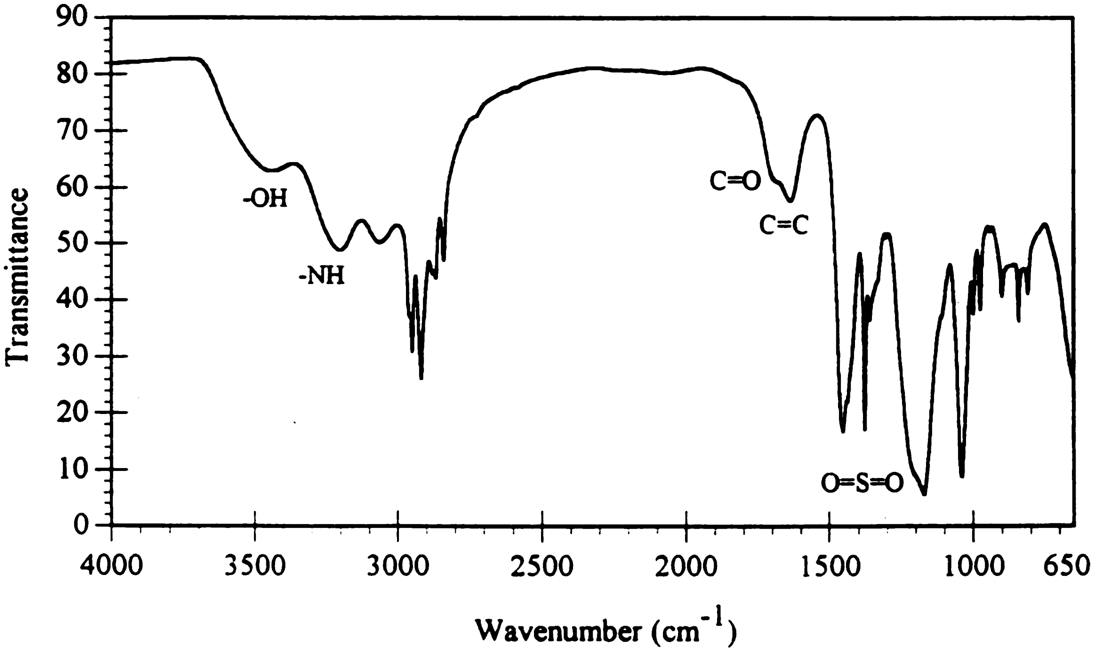


Figure 6.2f: The figure illustrates the IR spectrum of polypropylene sulfonated for 5 minutes followed by neutralisation with ammonium hydroxide.

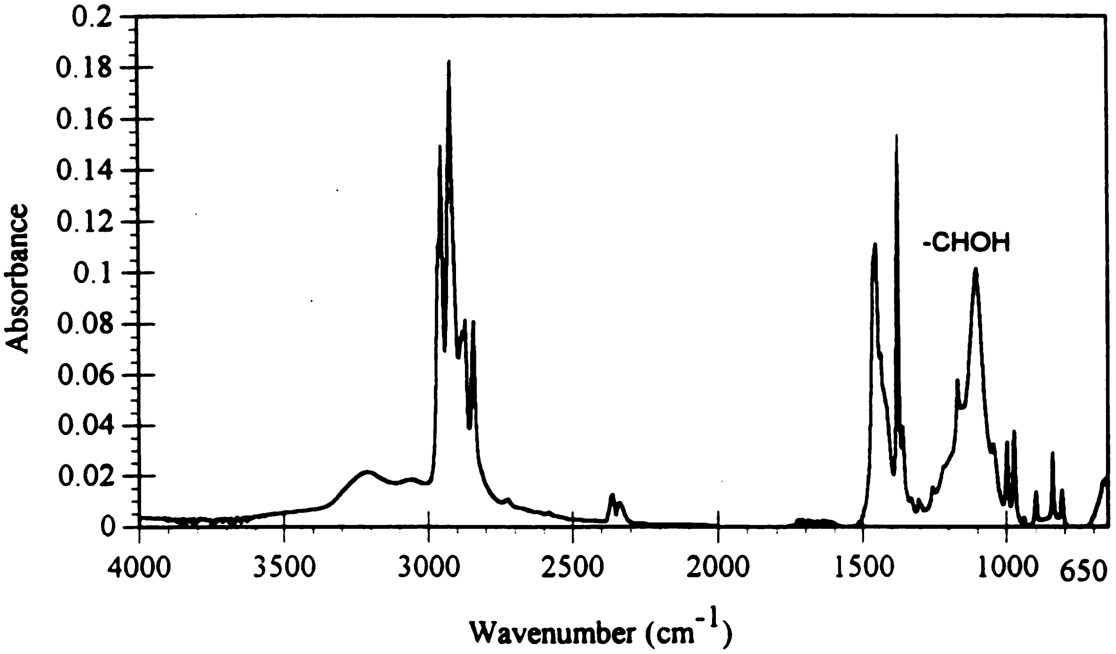


Figure 6.3a: The difference spectra between 1 minute sulfonated polypropylene and unsulfonated polypropylene.

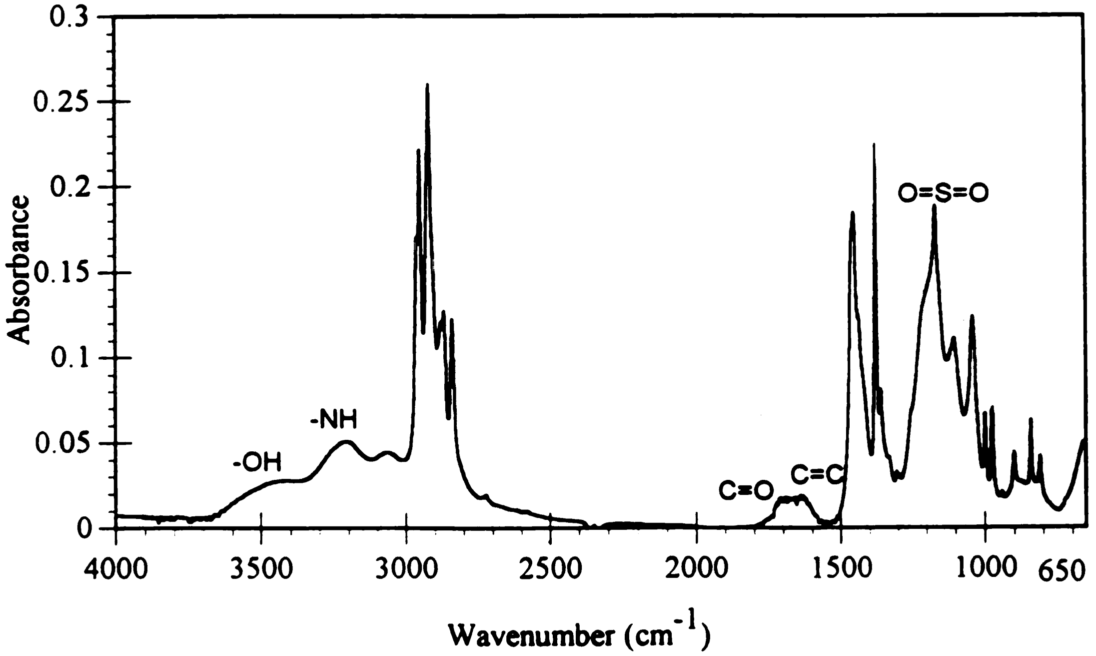


Figure 6.3b: The difference spectra between 2 minute sulfonated polypropylene and unsulfonated polypropylene.

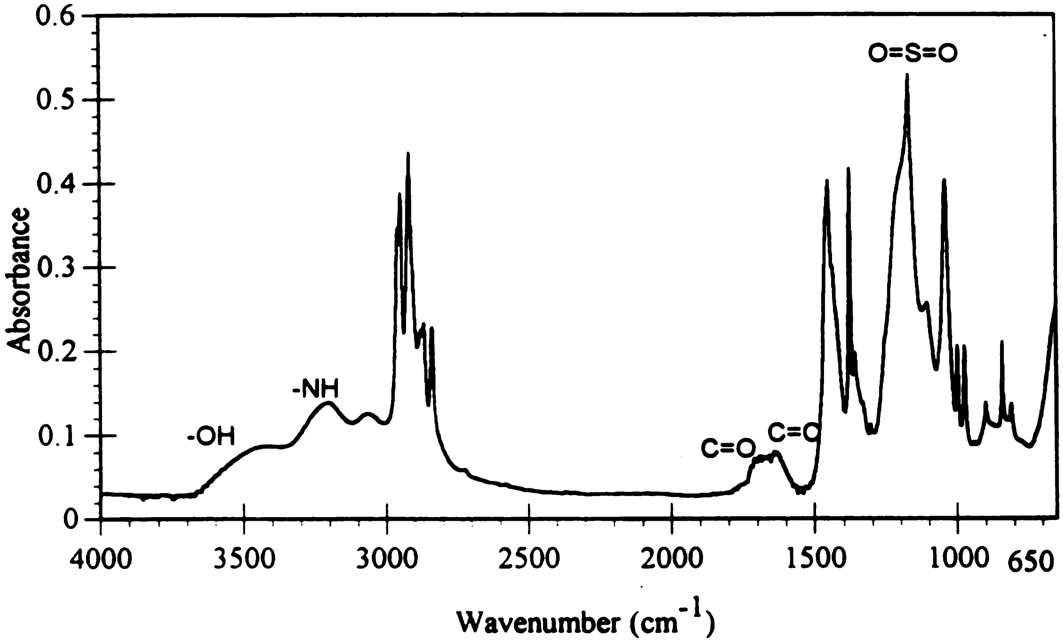


Figure 6.3c: The difference spectra between 3 minute sulfonated polypropylene and unsulfonated polypropylene.

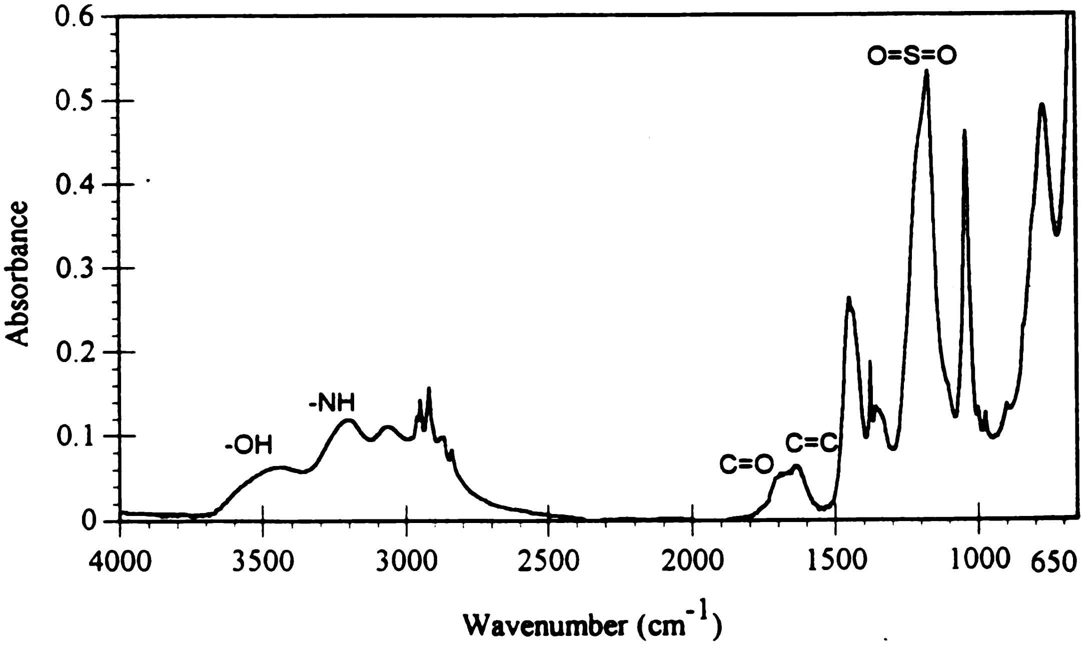


Figure 6.3d: The difference spectra between 4 minute sulfonated polypropylene and unsulfonated polypropylene.

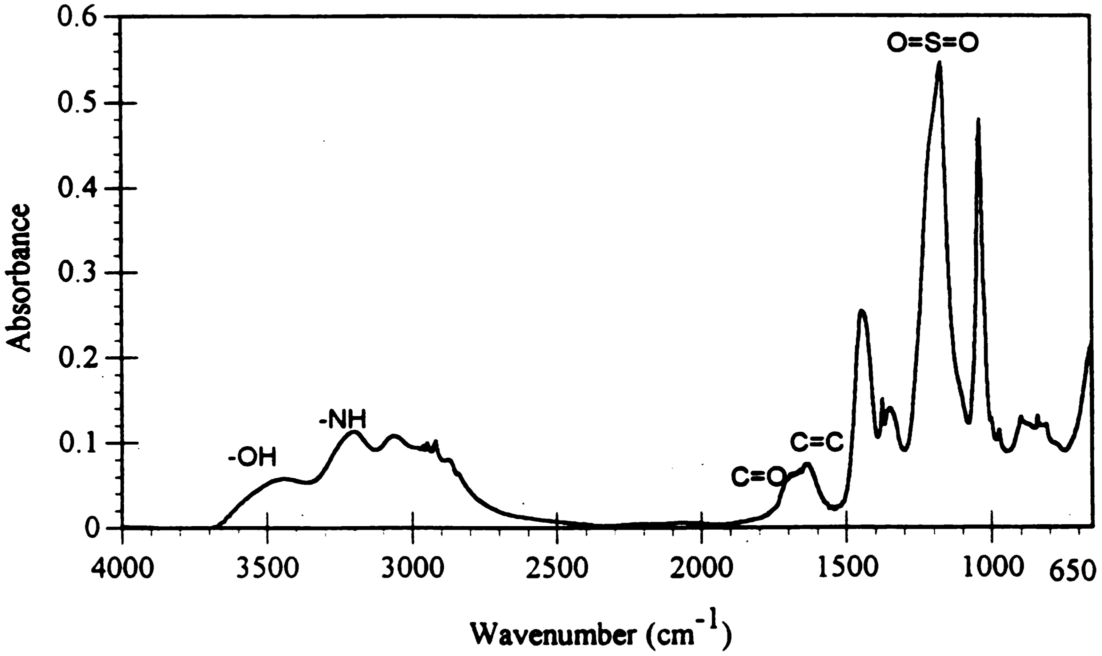


Figure 6.3e: The difference spectra between 5 minute sulfonated polypropylene and unsulfonated polypropylene.

occur within the stated envelopes it could be that besides sulfonic acids there are several other species containing S=O linkage also being formed.

The other region which shows a change is 1600-1750 cm^{-1}. This peak position is characteristic of C=C vibrations (1600-1680 cm^{-1}) and C=O linkage (1720 cm^{-1}). The intensity of this composite band also increases as time of sulfonation is increased. The peak position however remains almost unchanged as time of sulfonation is changed. Between 3000-3600 cm^{-1} three peaks appear. These peaks are clearly separated which can be seen from the subtracted spectra for higher times of sulfonation. The peaks are positioned in 3100 cm^{-1} region, 3200 cm^{-1} region and 3450 cm^{-1} region. The 3450 cm^{-1} band is a broad and is attributed to -OH species. 3200 cm^{-1} is attributed to -NH linkage and the peak in 3100 cm^{-1} is attributed to =C-H linkage [31].

6.3 FTIR RESULTS.

The present section discusses the probable chemical species responsible for the bands observed above. Each region has been discussed separately.

6.3.1 Band Region 1170 cm^{-1} and 1450 cm^{-1}

Two band regions are attributed to S=O vibrations and contributions from -NH of the NH_4^{+1}. Within this envelope the main sulfonic acid peaks fixed at 1167 cm^{-1} and 1045 cm^{-1} are also located. A careful inspection of the peaks in this region shows that as the time of sulfonation increases not only does the intensity increase but there is an apparent change in the peak growth pattern. It appears that additional peaks are growing within the same envelope in 1170 cm^{-1} region. This leads us to believe that possibly there is the formation of additional chemical species besides sulfonic acids.

The literature shows that besides formation of sulfonic acids there is a possibility of formation of sultones, alkene disulfonic acids, alkene sulfonic acids and ketones in the system [30, 32, 33]. The contribution in 1390-1430 cm^{-1} region can also be from -NH of NH_4^+ [31] besides S=O vibrations. Due to a lack of pertinent literature, it is difficult to make a conclusion as to the exact nature of this band or which compounds will yield the specific bands. Suffice it to say that it does support the conclusion that species other than sulfonic acids which contain S=O kind of bonds. Various vibrations in the 800-1000 cm^{-1} can be attributed to S-O-C kind of linkage [31]. Thus, it can be concluded that as a result of sulfonation the system contains the following species:

- S=O kind of linkages.
- S-O-C kind of linkages.
- NH kind of linkages.

6.3.2 Band Region 1600-1750 cm^{-1}

The band region 1600-1680 cm^{-1} is attributed to alkene kind of structures (C=C linkages) and the band at 1720 cm^{-1} is linked to the C=O structure which can be a ketonic, aldehyde, ester or a carboxylic acid species [34]. A review of the literature shows that as a result of sulfonation, the formation of a conjugated system of double bonds is probable. Literature values fix bands due to conjugation near 1600 cm^{-1} and for unconjugated system the region has been identified at 1680-1620 cm^{-1} [34]. Observation of the subtracted spectra shows the appearance of a broad peak in this region as a result of sulfonation which implies that there is an arrangement of conjugated as well as unconjugated carbons in the system under investigation. The band at 1720 cm^{-1} attributed to C=O grows along with the band attributed to C=C linkage.

6.3.3 Band region 3000-3500 cm^{-1}

An inspection of the spectra shows the appearance of three bands in this region as sulfonation is carried out. The three bands can approximately be fixed at 3030 cm^{-1}, 3220 cm^{-1} and 3450 cm^{-1}. Each of these is attributed to specific chemical species. The band at 3030 cm^{-1} can be attributed to -CH=CH- stretching [34]. 3220 cm^{-1} is attributed to -NH stretching vibration from $-NH_4^{+1}$ [34] and the broad band located at 3450 cm^{-1} is attributed to -OH linkage. Also, it can be concluded that this -OH linkage is not free -OH kind because the band attributed to free -OH appears in 3650-3590 cm^{-1} region [34, short course]. From the preceding discussion it can be concluded that the following kinds of chemical linkages are also present as a result of sulfonation:

- S=O linkages.
- C=C linkages.
- -OH, -NH linkages.
- C=O linkages.

6.4 DISCUSSION OF RESULTS.

Sulfonation of polymer surfaces has been investigated by several workers and the chemical changes have been documented. The general consensus has been the formation of sulfonic acid groups on the surface. For e.g Ihata et. al [30] sulfonated polyethylene and proposed that the final product contains sulfonic acids having highly conjugated C=C unsaturated bonds. Cameron et. al. [29] have proposed that the most significant chemical changes on the surface is olefinic conjugation leading ultimately to carbonisation.

In both the instances the investigators proposed that desulfonation via expulsion of Sulfurous acid (or $SO_2 + H_2O$) is a dominating step in the whole reaction scheme. This is in agreement with the present work. However, Ihata's as well as Cameron's work does not focus on the fact that once the double bond is formed then this itself becomes a potential site for attack by SO_3 due to the high electron density at this site. This is an important focus of the present work. Cameron et. al. have proposed that formation of β-sultone is a possibility in the scheme of reaction but they concluded that β-sultone would desulfonate to yield diene as a final product. However, this is not always the case as it is well-documented that besides desulfonation there are other reaction products which can be formed with B-sultone as the starting point [10,32,33]. These include alkene sulfonic acid, C-sultone, D-sultone, alkene disulfonic acid, ketones etc. Also, there is a probability of formation of pyrosultone which can rearrange to give several other products.

6.4.1 Proposed Reaction Scheme

As soon as Polypropylene is subjected to reaction with SO_3 the tertiary carbons are the most probable to be attacked due to their high electron density. However, it has been well-established in the literature that the resulting sulfonic acid tends to desulfonate by extracting hydrogen from the neighbouring carbon and expelling sulfurous acid by the following mechanism.

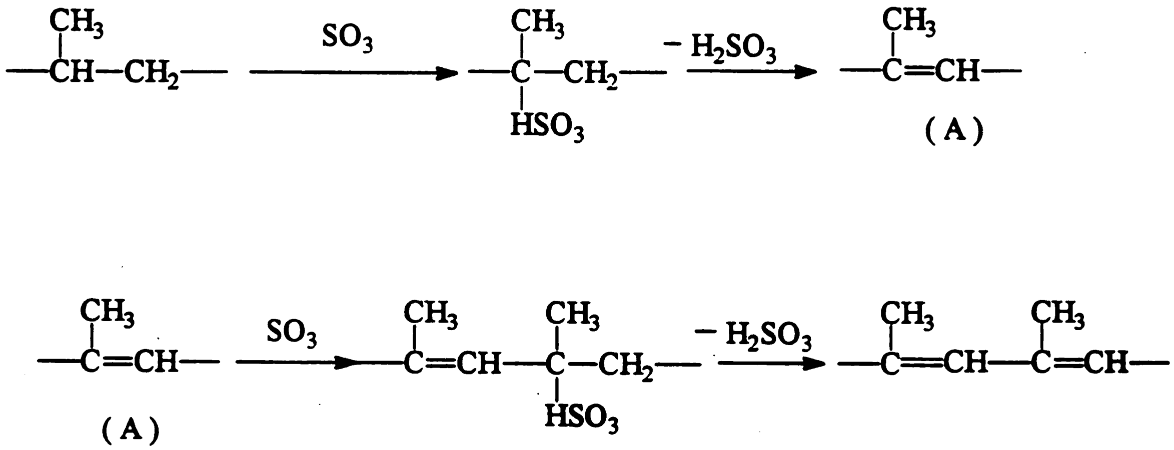
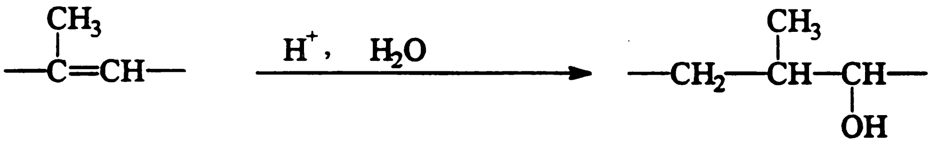


Figure 6.4: The figure illustrates the formation of conjugated system of double bonds as a result of sulfonation.

This reaction mechanism continues until there is a system of conjugated carbons which are formed due to desulfonation. Now, these double bonds in turn become potential sites for attack by SO_3 resulting in formation of B-sultones in the first step followed by several other products.

It is worthwhile to take a closer look at the subtracted spectra of 1 minute treated sample. The main change in all the other samples has been depicted by the sulfur species band at 1170 cm^{-1}. But, in 1 minute sample the main band is stationed at 1110 cm^{-1}. This is the band location for secondary alcohol. That is, the main effect of sulfonation in the first minute is formation of an alcohol and not a sulfonated species. An indication of a similar effect is seen in the XPS and contact angle data also which will be discussed shortly. There is a possibility of formation of alcohol species with alkene as the starting point as in Figure 6.5 [40]. The H^+ can come from the residual acid in the system, while water is available from the aqueous ammonium hydroxide solution used to neutralise the sulfonated polymer.



$$-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}- \xrightarrow{\mathrm{H^+},\ \mathrm{H_2O}} -\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}-$$

Figure 6.5: The figure shows the formation of secondary alcohol species in the first minute of treatment. The incorporation of the sulfonic acids starts after the second minute of sulfonation.

6.4.1a Formation of C,D-sultones.

The mechanism of formation of C,D-Sultones has been delineated in Figure 6.6. B-Sultone is an unstable chemical species thus the reaction is driven towards the formation of C and D-sultones. Work carried out by Herman de Groot shows the formation of these species [32]. Further there is a possibility that the B-Sultone may desulfonate to yield a double bond structure as proposed by Cameron et. al. [29].

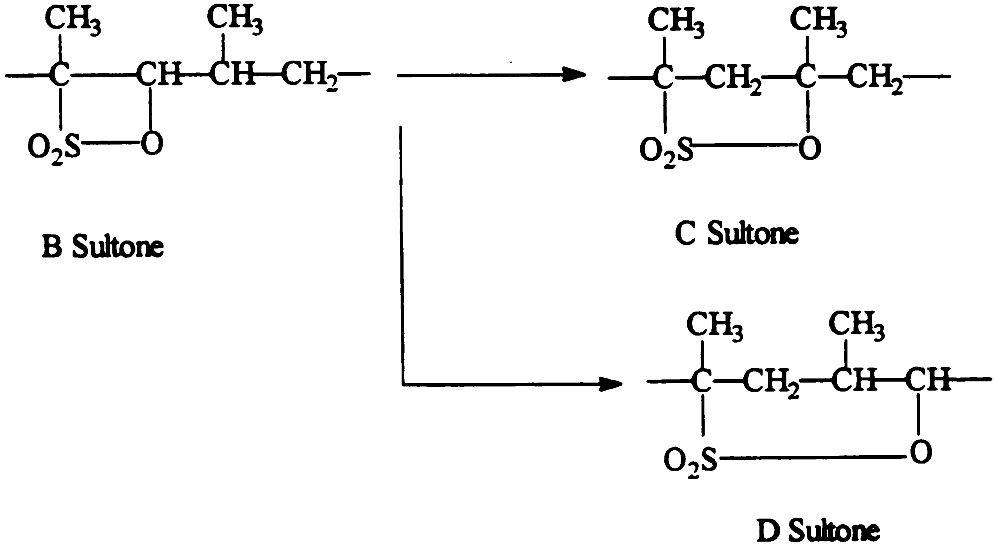


Figure 6.6: The figure illustrates the rearrangement of B-Sultones to C,D-Sultone.

6.4.1b Formation of Alkene Sulfonic Acids.

Alkene sulfonic acids are compounds which contain sulfonic acid group as well as a doubly bonded carbon [10, 32]. The reaction scheme for formation of alkene sulfonic acids has been delineated below.

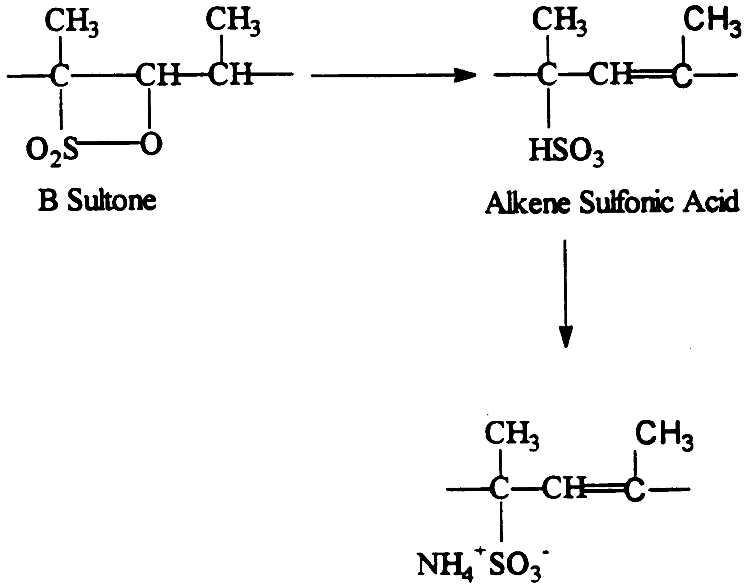


Figure 6.7: The figure illustrates the rearrangement of B-Sultone to alkene sulfonic acids followed by neutralisation with ammonium hydroxide.

6.4.1c Formation of Hydroxysulfonic Acids.

In presence of water molecules the B-Sultone can make hydroxy sulfonic acids. The reaction path is delineated in Figure 6.8.

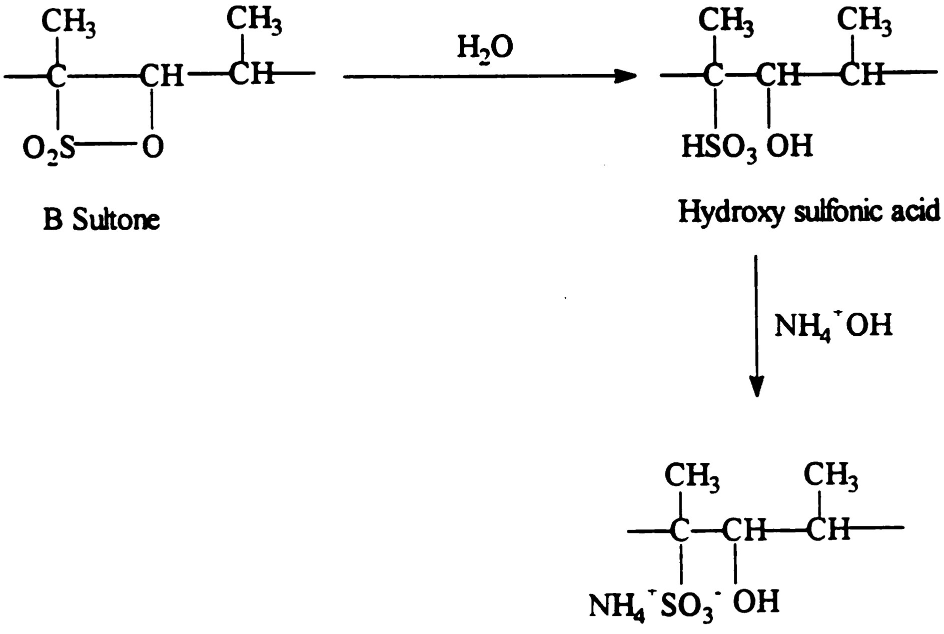


Figure 6.8: The figure shows the rearrangement of B-Sultone to hydroxysulfonic acid.

6.4.1d Reaction of B-Sultone with SO_3.

It has been shown above that B-Sultone can rearrange to yield a variety of different products. However, besides rearrangement there is a possibility that it may further react with more SO_3 to give pyrosultone. But, eventually pyrosultone decomposes or rearranges to give C-Sultone, D-Sultone, alkene sulfonic acid or hydroxy sulfonic acid. The conversion of B-Sultone to pyrosultone and then to hydroxysulfonic acid is illustrated in the figure below. As can be seen, in the last step of the reaction sulfuric acid is formed which can further sulfonate a potential site in the chain.

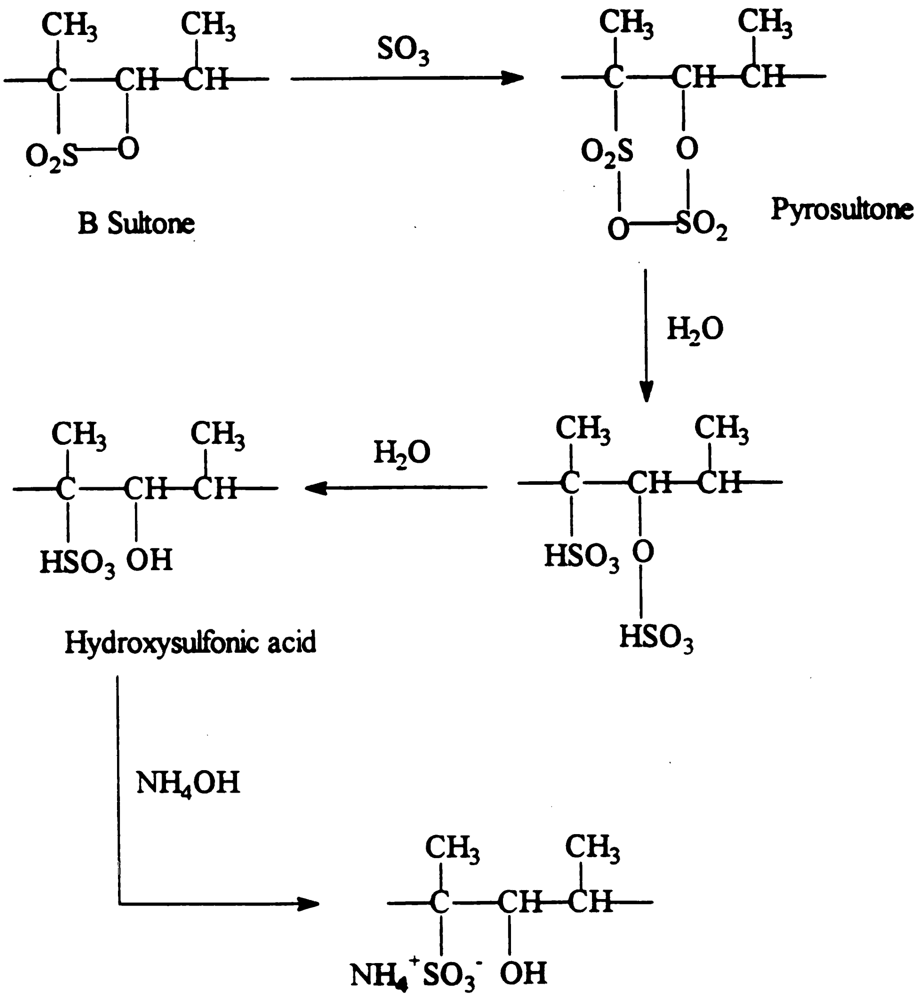


Figure 6.9: The figure shows the reaction of SO_3 with B-Sultone to make pyro sultone. This can rearrange to give several products. Rearrangement to hydroxy sulfonic acid has been shown above.

6.4.1e Formation of Ketone

The peak position at 1720 cm^{-1} is characteristic of the C=O of structure. There is a possibility of the formation of such a structure in the system under investigation. This has been shown by Ihata et. al [36]. The reaction sequence proposed in that work was based on the cleavage of C-S bond due to VIS light. However, the following reaction sequence is also possible and proposes the product based on chemistry only.

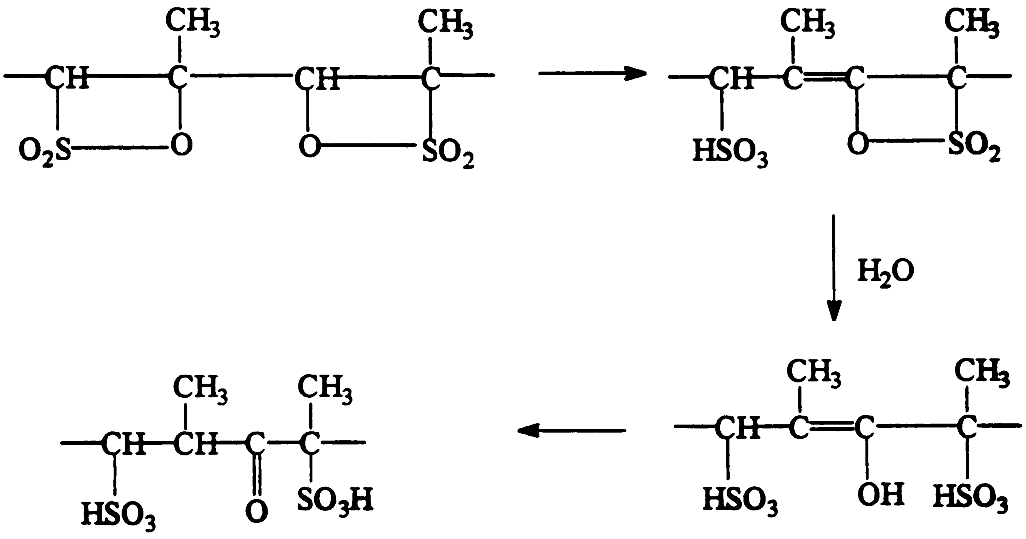


Figure 6.10: The figure shows the possible route of formation of ketone species. The formation of ketone was explained by Ihata et.al. on the basis degradation due to VIS light.

6.5 XPS OBSERVATIONS AND RESULTS

X-Ray Photoelectron Spectroscopic Analysis (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a surface sensitive technique, analysing the top 50-60 Å of the surface. In the previous section IR results were analysed. IR is not a purely surface sensitive technique as its depth of analysis is 1-2 μm (1μm = 10^4 Å). In this section the results obtained from ESCA shall be analysed and conclusions about the chemical changes occuring on the top few layers of the surface hall be made. Quantitaitive changes occuring on the surface can also be made using this technique. Thus, it will also aid in quantifying the "amount of change" which occurs on the surface and at the same time if there is a pattern of change on the surface. Besides quantitative changes ESCA can also yield qualitative results about the nature of chemical bonding on the surface.

6.5.1 Quantitative Analysis of ESCA Results.

The following table gives the atomic concentrations of the different elements in percentage terms. In some of the samples contaminants were detected which have been mentioned.

Table 6.2: The table shows the data for atomic concentration for polypropylene sulfonated for 1 thru 5 minutes as obtained from XPSA.

Sample	Carbon	Oxygen	Sulfur	Nitrogen	Others
0 minute	95.7±0.53	3.55±0.72	0.57±0.06	-	Silicon
1 minute	93.4±0.6	5.4±0.9	1.0±0.1	-	Fluorine
2 minute	69.8±3.6	22.4±3.0	4.6±0.3	2.8±0.7	Calcium
3 minute	64.8±0.5	25.0±0.2	5.7±0.4	4.2±0.4	Calcium
4 minute	59.3±1.8	28.2±0.9	7±0.5	5.4±0.4	-
5 minute	59.0±0.6	29±0.4	6.8±0.01	5.1±0.2	-

The following conclusions can be made from the data in the table.

(i) The percentage composition of the untreated sample and the 1 minute sample is not very different. Also, nitrogen is absent in the 1 minute sample although this was neutralised in NH_4OH. However, the adhesion results show that the adhesion of the 1 minute treated sample did improve over the untreated sample [25]. This means that some change has occured on the surface in the first minute of treatment albeit not of the nature of sulfonation. IR data also shows that the net impact of the first minute of sulfonation is formation of an alcoholic species rather than induction of sulfonic acids in the system.

(ii) There is a marked change in atomic compositions from 1 minute to 2 minute sample and subsequent treatment times. It can be concluded that an effective chemical reaction starts after the first minute of treatment.

(iii) The magnitude step of atomic concentration change of the various elements is very small after 2 minute through 5 minute treatment. All the values seem to be reaching a saturation value. This implies that there is a maximum amount of sulfonation that can be carried out without extensively damaging the surface.

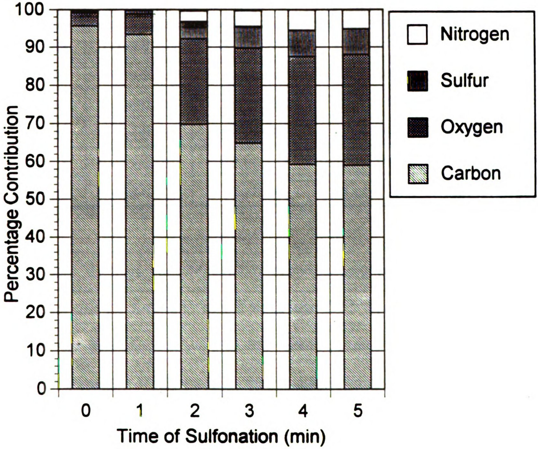


Figure 6.11: The plot shows the contribution of different elements as sulfonation progresses. The contribution of carbon decreases as sulfonation time increases.

In order to visualise the chemical changes that have occured on the surface it is helpful to determine the changes in terms of ratios of the various elements which has been tabulated below.

Table 6.3: The data presented above shows the respective atomic ratios using the data from table 6.2. Notice the saturation levels reached at 4 minutes.

Sample	O/C	S/C	S/O	N/S
0 minute	0.04±0.007	0.005±0.001	0.16±0.014	-
1 minute	0.06±0.009	0.01±0.001	0.18±0.003	-
2 minute	0.34±0.058	0.08±0.020	0.22±0.035	0.61±0.130
3 minute	0.38±0.007	0.09±0.006	0.23±0.014	0.73±0.117
4 minute	0.48±0.032	0.12±0.011	0.25±0.008	0.78±0.008
5 minute	0.49±0.012	0.12±0.001	0.24±0.005	0.76±0.035

Theoretically, the impact of sulfonation is the formation of sulfonic acid species (-HSO_3) This means that the S/O ratio should be around 0.33 (or, O/S should be almost 3). However, the data above shows that S/O rests around 0.25-0.16 This implies that besides the formation of sulfonic acids there is a probability of other oxygen compounds (not containing sulfur) being formed. The probable species are ketones, carboxylic acids, aldehydes, alcohols etc. There was an indication of these species in the IR data too. Another important observation to be made from the above data set is that in the 1 minute sample no nitrogen was detected although these samples were neutralised in ammonium hydroxide. The following reaction sequence should have occured.

$$R\text{-}SO_3H + NH_4OH \text{ -----> } R\text{-}(SO_3^{-1})(NH_4^{+1})$$

However, the data shows absence of nitrogen. Also, for 1 minute sample there is a very small increase in the atomic concentrations (and the respective ratios) of other elements. The reaction above also shows that S/N ratio should be theoretically one if complete neutralisation occurs. It can be observed that this is not the case in any of the samples. This leads to the belief that besides steric factors probably some of the sulfur containing species is not available for neutralisation. The important requirement for neutralisation with ammonium Hydroxide is the availability of hydrogen which can be replaced with ammonium ion (NH_4^+). As was proposed in the IR results there is a possibility of C,D-sultones in the system. In the structure of C,D-sultones the hydrogen which can exchange with ammonium is not available which implies that these centers cannot be neutralised. This reinforces the proposed presence of sultones species in the system. Another argument which reinforces the proposition that there is a possibility of other compounds containing oxygen besides sulfonic acids is the fact that in the idealised case when sulfonic acids are the only products O/N ratio should be around 3. However, the data presented indicates that the ratio is much higher than 3 (between 5.0-6.0). Thus, there is a possibility of oxygen compounds which neither contain sulfur nor nitrogen. IR data clearly indicates that presence of alcohols, ketones groups etc is a viable option which lead to higher numbers for O/N and O/S ratio than proposed theoretically.

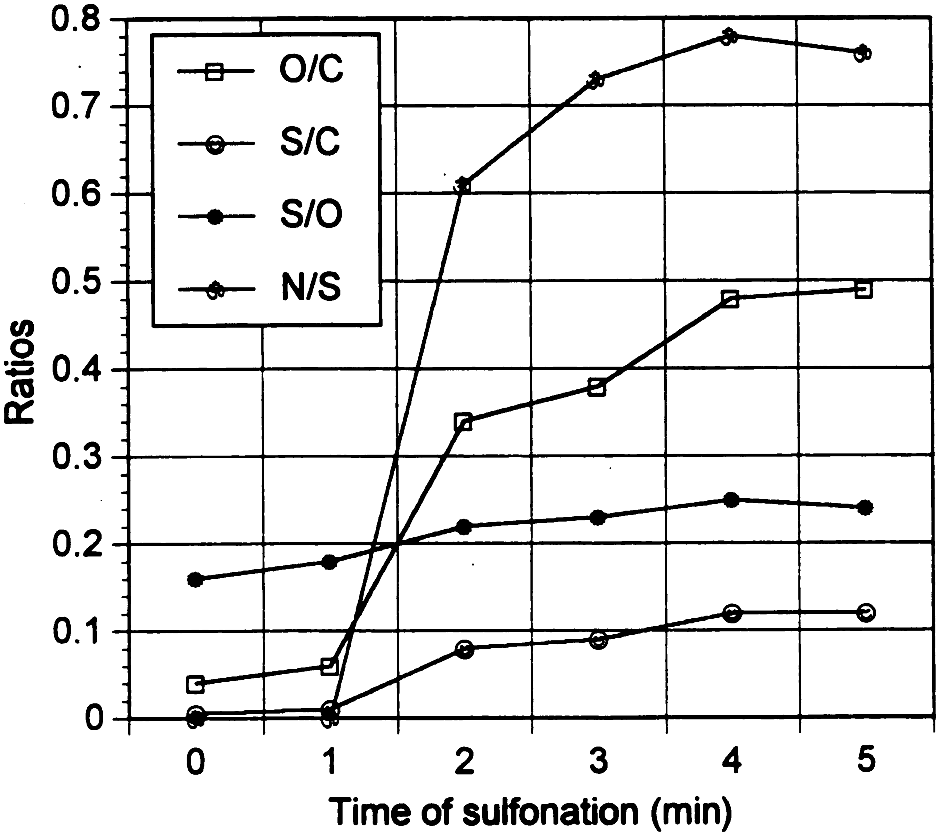


Figure 6.12: The ratios achieve a saturation value at almost 3 minutes treatment.

6.5.2 Qualitative Analysis of XPS Results.

Qualitative analysis of XPS data to determine the chemical information like nature of bonding etc. is based on the principle that the peak obtained from the narrow scan (also called multiplexing) can be mathematically resolved into its constituents. Each peak individually represents a specific chemical species. This process is called deconvolution of the peak. In the present discussion deconvolution of the peaks obtained from sulfonated polypropylene shall be carried out.

The data clearly indicates that C-C/C=C/C-H linkages are the most abundant chemical linkages in the system. Thus, the carbon peak was shifted to 284.6 eV from its original position. The peaks for the other elements in the system (O1s, S2s, N1s) were also shifted by the same amount respectively. The new peak positions assumed by each of the elements for different treatment times turned out to be the same. The oxygen peak assumed a position of 531.8 ± 0.16, sulfur at 167.6 ± 1.63 and nitrogen at 401.8 ± 0.2 (no nitrogen detected in 1 minute treated sample). For 1 minute treated sample the sulfur peak did not always show a change. It was closer to sulfur seen in untreated signal. This indicates that in the first minute probably the chemical change is not being effected significantly. The peak position of oxygen is consistent with the literature values. Briggs et. al. [39] obtained their oxygen peak at 532.0 eV after chromic acid etching of polymers. Most of the oxygen in the system under investigation is bonded to sulfur as in ammonium salt of sulfonic acid (NH_4^{+1} SO_3^{-1}). The other linkages are O-C, O=C, and -COOH. The peak position of sulfur at 167.6 is consistent with the work done by Seigbahn et. al. where the peak position for R-SO_2OR kind of compounds was fixed at 167.5 eV. In the system under investigation also all the sulfur is bonded to carbon on one side and oxygen on the rest of the sites. The nitrogen peak position at 401.8 eV is in consonance with the value of 401.3 eV for $(NH_4)_2SO_4$ [41].

Since carbon is the main constituent of the system and undergoes maximum chemical changes this shall be analysed first. Before sulfonation essentially there are two kinds of carbon in the system. They are C-H and C-C. Due to the presence of oxygen there is a possibility of some C-O/C=O kind of linkage also. For purposes of XPS C-H linkage is same as C-C linkage. So, it can be concluded that there are two kinds of carbon in the system. However, after sulfonation chemical changes occur on some of the carbon atoms. The new kinds of carbon based on IR results which appear are as follows.

(i) C-S linkage from sulfonic acid, sultones.

(ii) C-OH linkage from hydroxysulfonic acids.

(iii) C=O linkage from ketones and -COOH from acids.

The energy position for each of these types of carbon has been fixed empirically. However, the value for C-S in the system under investigation is not well documented (C-S as in sulfonic acids, sultones etc).

The deconvolution of the peak shows the presence of four peaks after sulfonation. In the present work the 'goodness of fit' of the data had to be sacrificed because of extensive sample charging problems. The position of these peaks is highly mobile. The region of movement is as high as 0.8eV. Approximately, the peak positions can be fixed in 284.3-284.6, 285.0-286.0, 286.0-287.0, 288.0-289.0 region. All the peaks were manually shifted to 284.6 eV (C1s). Due to the nature of the sample under investigation a high degree of sample charging was observed as is normally associated with polymers. Probably this is an important factor contributing to the peak mobility. Thus, definitive conclusions about exact nature of the peaks or their growth pattern cannot be made. However, it is clear that the contribution due C1s peak fixed at 284.6 eV decreases progressively as treatment time increases. The data has been presented in the following table.

Table 6.4: The table shows the percentage contribution of the different peak regions after deconvolution of the C1s peak. Notice that the contribution from the peak in 284.3-284.7 region decreases as treatment time increases.

Sample	284.3-284.7	285.0-286.0	286.0-287.0	288.0-289.0
0 minute	99.0 ± 0.28	0.62 ± 0.9	-	0.42 ± 0.60
1 minute	98.5 ± 1.09	1.14 ± 1.61	-	0.36 ± 0.52
2 minute	86.0 ± 86.0	9.9 ± 8.0	2.13± 1.54	1.9 ± 0.48
3 minute	77.4 ± 7.88	10.5 ± 5.1	9.6 ± 2.48	2.5 ± 0.28
4 minute	72.0 ± 3.50	13.3 ± 3.13	11.9 ± 0.72	2.8 ± 0.34
5 minute	57.0 ± 1.72	28.7 ± 2.8	11.5 ± 0.58	2.8 ± 0.49

The position of C-C/C=C linkage is empirically fixed at 284.6 eV, C-O at ~ +1.5eV, C=O at ~ +3.2eV and -COOH at ~ +4.2eV. As can be observed from the table above, it is not possible to fix the position of the peaks based on the above empirically fixed positions and conclude about the nature of peak growth and patterns. The problem is complicated by the fact that there is no documented evidence about the position of C-S bond as present in the system under investigation. Earlier work by Briggs et.al. on chromic acid etching of polymers where sulfonic acids are introduced [37] shows that the shift due to C-SO_3H linkage should be ~ 1-2 eV. Their investigation also reports the introduction of the different kinds of carbon listed above. In the presented data it is not possible to assign fixed positions to the respective linkages conclusively due to the absence of past literature values. The major conclusion which can be made is that the contribution due to C-C/C=C/C-H linkage goes down progressively. In other words, the contribution due to C-S, C-O, C=O, -COOH goes up. This means that as sulfonation time is increased more sulfur and oxygen compounds are introduced in the system. It is also possible that the mobility of the peaks is not an experimental artifact but indicates that there actually is no strict control over the kinds of chemical species that are introduced into the system. This is possible because the surface undergoes degradation as it is sulfonated. There is no control over the nature of substance degraded as it is dependent upon several factors beyond control.

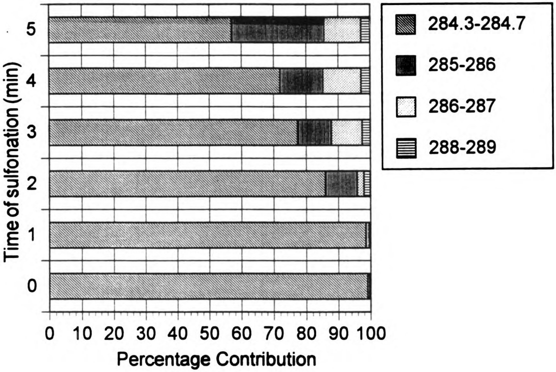


Figure 6.13: The figure shows the contribution of different peaks in the C1s envelope. The contribution of C-C linkage decreases with increasing time.

Oxygen is the next most abundant element in the system after carbon. The IR data shows that it will be available as oxygen doubly to sulfur (sulfonic acids, sultones) oxygen singly bonded to sulfur (sultones), singly and doubly bonded to carbon (hydroxyls, ketones, carboxylic acids). The values for sulfur species are not available.

But, on the basis of first principles it can be concluded that the values will be in the same range as carbon since the Pauling electronegativity of carbon and sulfur is the same. Deconvolution of the oxygen peak yields the following results. The percentage contribution of the different peaks has been shown in Table 6.5.

Table 6.5: The table illustrates the peaks resulting due to deconvolution of oxygen peak. The contribution of the 531.8-532.5 eV region is maximum. This is also the region where most of the O=S signal falls.

Sample	530.5-531.5 eV	531.8-532.5 eV	533.0-533.6
0 minute	17.4 ± 2.45	53.7 ± 2.94	28.9 ± 5.40
1 minute	23.3 ± 17.74	55.9 ± 14.8	20.8 ± 2.92
2 minute	15.2 ± 0.57	62.0 ± 3.8	22.8 ± 3.23
3 minute	17.3 ± 3.6	62.2 ± 6.66	20.4 ± 3.07
4 minute	19.6 ± 0.92	63.9 ± 0.47	16.5 ± 1.34
5 minute	12.9 ± 2.02	69.4 ± 7.42	17.6 ± 5.40

As the above data shows, the peak region 531.8-532.5 eV contributes maximum towards the peak. Most of the oxygen in the system is linked to sulfur (sulfonic acids, sultones etc). Thus, this region can be assigned to this kind of oxygen. This is in consonancewith work done by Clark et. al. [38]. They estimated that the oxygen of polysulfone would lie around 532.5 eV. The other carbons present in the system are of the kind O-C, O=C, -COOH. In the same work Clark et. al. fixed the value for singly and doubly bonded oxygen in 533.5 eV region. The envelope 533.0-533.6 eV can be assigned to these kinds of linkages. The lowest energy envelope (530.5-531.5) is difficult to assign due to a lack of relevant literature. Probably, this is a result of charging as is generally associated with polymers.

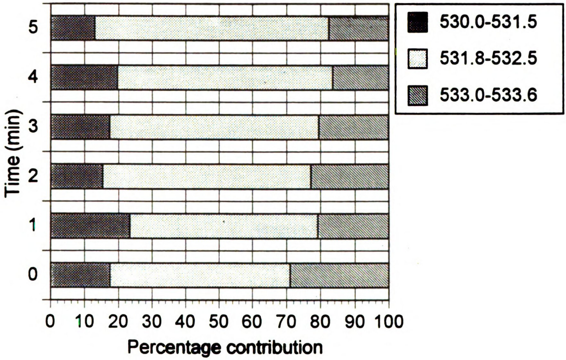


Figure 6.14: The figure illustrates the contribution of the different deconvoluted peaks in the O1s peak.

6.6 CONTACT ANGLE RESULTS

The contact angle results are important to study changes occuring on the top most surface. For the present work, contact angles were measured directly using a Rame-Hart Goniometer Model 100-00 with deionised water as the probe liquid. 5 μL drops were manually placed on the surface and the contact angle measured through a calibrated eye-piece. 15-20 drops were measured for each sample. The results are presented below.

Table 6.6: The table shows the contact angle obtained on sulfonated polypropylene using water as a probe liquid. Note that at 1 minute treatment the contact angle does not change significantly.

Sample	Contact Angle (θ) (degrees)	cosine θ
0 minute	90.7 ± 5.4	-0.012
1 minute	82.8 ± 5.9	0.125
2 minute	14.5 ± 5.7	0.968
3 minute	20.8 ± 5.3	0.935
4 minute	18.6 ± 3.9	0.948
5 minute	18.3 ± 4.9	0.949

There are certain important observations which were made in the process of measuring these results. Some drops tended to spread as soon as they were placed on the surface. They tended to assume a random shape and spread unevenly. At times this spreading was time dependent. That is, the drop would stay static for sometime and then start to spread (within 30-45 seconds). This made the data collection difficult. If the drops were not sufficiently far apart then these drops would tend to merge with each other. This points to the chemically uneven surface that may have resulted due to sulfonation and uneven degradation. The data clearly indicates that the first minute of treatment does not change the surface appreciably. This is also supported by the ESCA data where the percentage change in atomic concentration of the respective elements is insignificant and IR data where the nature of chemical change is formation of additional oxygen compounds and very small sulfonation. The surface tends to reach a saturation state which is indicated by the constant contact angle achieved (18.5°).

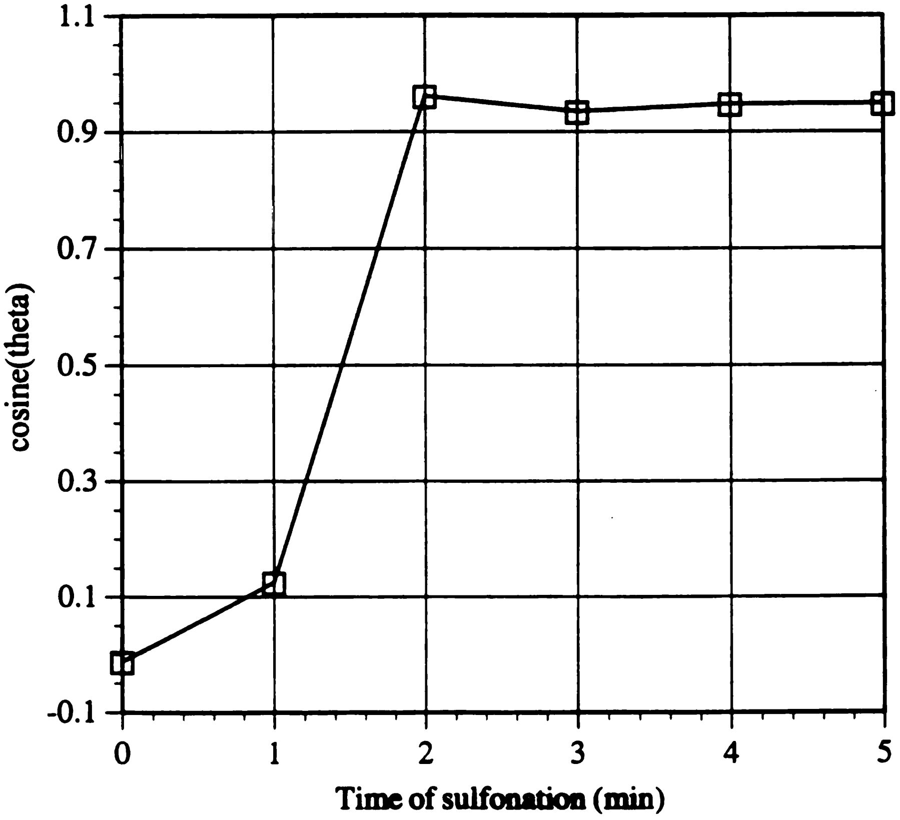


Figure 6.15: The figure shows the change in contact angle of water on polypropylene with increasing time of sulfonation. Note the saturation reached on the surface at about 2 minutes.

6.7 DEGRADATION OF POLYPROPYLENE.

It was observed that due to sulfonation the surface of polypropylene would discolour to brown. This layer would slough off during neutralisation in ammonium hydroxide. This was especially true for higher times of sulfonation. The phenomenon of discolouration has been reported in earlier works by other investigators also. But, there is no documented evidence about the nature of the degraded material. For e.g. Cameron et. al. concluded that it may be a completely carbonised layer of polypropylene. To investigate the nature of this brown degraded material, it was collected from the surface of the degraded polypropylene by scratching the surface with a razor blade prior to neutralisation. This was then air-dried and a KBr disk was made with it to carry out an IR analysis. The results are shown in Figure 6.16. The figure clearly indicates that the degraded material is not a plain carbonised layer. It has several species the most dominant of which is the broad sulfur compounds peak located at 1176 cm^{-1}. The peak at 1630 cm^{-1} shows the presence of -C=C- kind of linkage. Also, there is a shoulder in this composite peak at 1700 cm^{-1} which indicates the C=O kinds of species from ketones, carboxylic acids etc. The broad peak at 3400 cm^{-1} is attributed to -OH kind of linkages. Notice the absence of the -NH peak which has been seen in all the samples that have been neutralised with ammonium hydroxide. All the above information shows that the degraded material consists of a mixture of several kinds of sulfur compounds along with olefinic carbons, ketones etc.

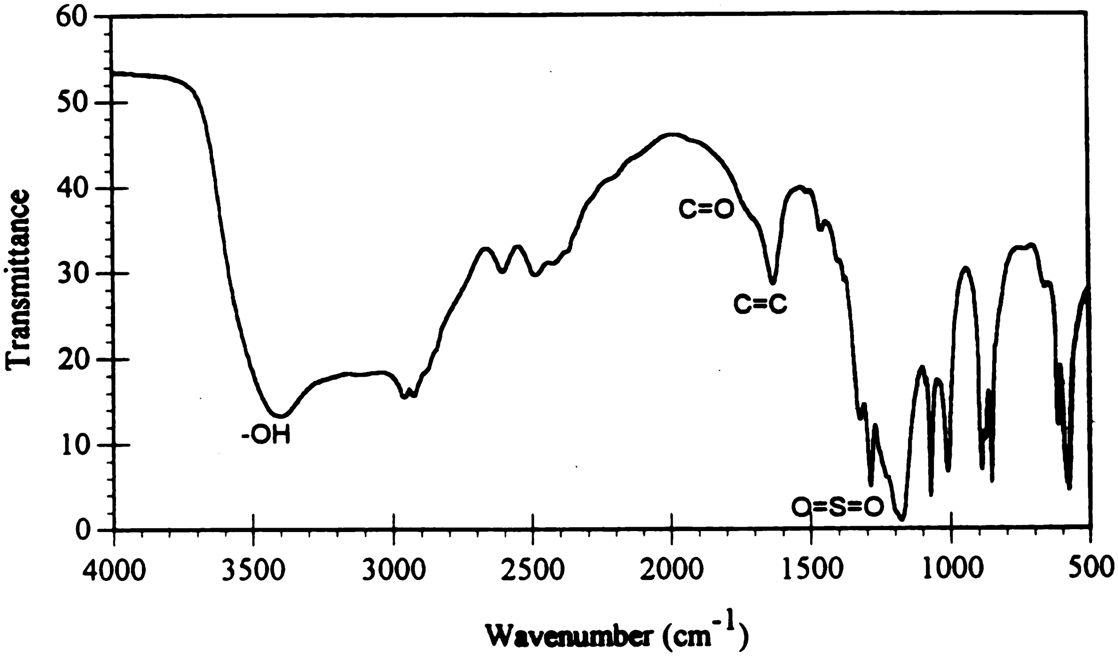


Figure 6.16: The figure illustrates the IR spectra of degraded polypropylene. The spectra was collected by preparing a KBr disk with degraded material scraped off the surface of sulfonated polypropylene.

6.8 DISCUSSION

The data presented above clearly shows that major changes occur on the surface of the polymer as a result of sulfonation leading to a more polar surface. A comparison of the atomic concentrations of untreated polymer with 1 minute polymer shows that chemical change on the surface has not been significant. The contact angle also shows that the drop in contact angle values is insignificant and the IR data indicates that sulfonation is not the major impact of treatment in the first minute. The deconvoluted ESCA peaks of the untreated and 1minute treated sample indicates that the nature of carbon has essentially remained same. But, the adhesion values clearly show a marked improvement [25]. This means that some other effect besides chemical modification contributes towards adhesion. In the case under investigation it seems that the impact of 1 minute treatment has been the removal of the Weak Boundary Layer on the surface of untreated polymer besides addition of some oxygen species probably in form of alcohols (as shown in IR data). The removal of this layer leaves behind a chemically pure surface which leads to improved adhesion.

To test the efficacy of sulfonation over other available techniques, polypropylene was flame treated and acid etched as these are the most popular techniques. The ESCA results were compared with untreated and 1 minute sulfonated sample. The atomic concentration values are tabulated below.

Table 6.7: The data shows the atomic concentration comparison of flame treated, acid etched, 1 minute sulfonated and untreated polypropylene. Note that the major impact of flame treated and acid etching has been oxidation of the surface.

Sample	Carbon	Oxygen	Sulfur	Nitrogen	Others
Untreated	95.7	3.55	0.57	-	Si
1 minute	93.4	5.4	1.0	-	F
Flame etch	82.7	16.4	-	-	Cl, P
Acid etch	91.0	8.6	0.5	-	-

The data shows that the net impact of flame treatment and acid etching has been oxidation of the process. The adhesion results point that it has also helped in removal of the Weak Boundary Layer. These two factors together contribute towards increased adhesion [25].

However, after the first minute of treatment there is a distinct change in the chemical nature of the surface. This is mainly characterised by the increase in oxygen and sulfur levels as detected by XPS. As was discussed in earlier sections, the nature of data points to the formation of species other than sulfonic acids. They include alkene sulfonic acids, sultones, ketones, carboxylic acids, hydroxy sulfonic acids etc. It cannot be determined at present as to the nature of growth of each of these individual species. Extensive careful and controlled work is required in this area due to the highly reactive nature of SO_3. The deconvoluted XPS data also shows that oxygen containing species increase on the surface as sulfonation time is increased until a state of saturation is reached when no more sulfur - oxygen species can be placed on the surface without extensively damaging the surface. This proposed state of saturation is also reinforced by the contact angle data. After 2 minute treatment the contact angle assumes almost a constant value of about 18°. As the surface is being chemically saturated a competitive phenomenon is also occuring simultaneously. That is of degradation. Sulfonation is an extremely exothermic reaction. The energy released can contribute towards disrupting the surface. Also, as was shown in earlier discussion, sulfonation of the different sites leads to a complex mixture of rearranged products the exact nature of which cannot be commented upon. This requires chain movement which coupled with the fact that the new chemical groups ($-HSO_3$, $NH_4^{+1}SO_3^{-1}$, -OH, sultones) are bulky leads to concentrated strains on the backbone chain of polypropylene contributing towards disruption. The IR data of the degraded material clearly shows that carbonisation is not the dominating effect as was proposed by Cameron et.al. Various chemical species are being formed dominated by the S=O kind of linkages. These include sultones, alkene sulfonic acids etc. In the process SO_2 and CO_2 are released.

6.9 CONCLUSIONS.

It has been shown above that sulfonation of polypropylene leads to a mixture of various kinds of compounds besides sulfonic acids. The surface is a complex arrangement of conjugated and unconjugated carbons, various kinds of sultones, hydroxy sulfonic acids, carboxylic acids and ketone moieties. There is a ceiling on the amount of sulfonation that can be carried out on the surface as indicated by contact angle and XPSA data. At higher times of sulfonation the polymer surface tends to scission leading to degradation.

Sulfonation of Polystyrene

Chapter 7

In the previous chapter the effect of sulfonation on polypropylene was discussed. Polypropylene is an aliphatic polymer with no phenyl rings in its structure. In order to study the effect of sulfonation on a polymer system containing phenyl rings in its backbone, polystyrene was chosen. Polystyrene is used in a wide range of applications varying from industrial to daily life. In applications where adhesion is important, the surface properties of polystyrene are critical. Sulfonation is a surface modification technique which enhances the adhesion capabilities by incorporating polar groups on the surface, thereby resulting in improved wetting. Investigations into adhesion properties of (sulfonated) polystyrene have been studied by other investigators [25]. The present discussion will focus on the chemical changes which occur on the surface of the polystyrene as treatment time is varied.

7.1 NATURE OF POLYSTYRENE

Polystyrene contains phenyl rings in its backbone. The repeating unit of polystyrene has been shown in Figure 7.1 . As can be seen in the figure, polystyrene is characterised by a phenyl ring bonded to a secondary carbon. The repeating unit does not have a primary carbon as in the case of polypropylene discussed in the previous chapter. The reactivity of this carbon should be similar for all polymers which contain phenyl rings in their backbone.

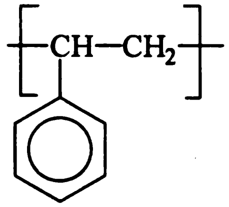


Figure 7.1: The figure illustrates the repeating unit for polystyrene.

The probability of sulfonation at the phenyl ring as compared to the aliphatic carbons is much greater due to the fact that sulfonation is a highly electrophilic reaction. In addition the concentration of carbons in the phenyl ring compared to aliphatic carbons is also much higher. The reaction at aliphatic carbons does take place however. Phenyl ring has a resonance structure. It can be seen from the structure of polystyrene that the phenyl ring is bonded to -CH. Due to the ortho and para directing influence of -CH (-CH is electron donating) these are the probable sites for sulfonation [40]. Also, since sulfonic acid is a bulky group, steric hinderance will make the para position more susceptible to attack as compared to ortho position. Thus, it would be expected that during sulfonation, ortho and para positions will be the most probable sites for attack with para position as the most favoured site. It is well-documented in the literature that benzene ring has an extremely stable structure due to the extra stability provided by the delocalised electrons. Due to this reason the phenyl ring (paralleled from benzene) stays intact in the presence of powerful oxidants like nitric acid and sulfuric acid [43]. Aliphatic compounds do not have this ability to stay intact due to absence of delocalised electrons which makes them more susceptible to degradation in presence of such a harsh chemical environment. This was discussed in the previous chapter while focussing on the sulfonation of polypropylene. In order to investigate the nature of chemical changes effected due to sulfonation of polystyrene, several analytical techniques were used. The observations and details from each of them will be discussed in the following sections. The following results are for polystyrene micro-washed and treated with 1% (±0.2) SO_3-air mixture for 1 thru 5 minutes followed by neutralisation with ammonium hydroxide.

7.2 FTIR-SPECTROSCOPY RESULTS

Several changes occur on polystyrene as a result of sulfonation. The main peaks and bands have been tabulated in the Table 7.1. Figure 7.2 illustrates the IR data of sulfonated polystyrene (in transmission mode) and Figure 7.3 illustrates the subtracted spectra (in absorbance mode, sulfonated minus unsulfonated) which highlights the changes due to sulfonation [31,34,35].

Table 7.1: The table illustrates the relevant peak positions and the probable chemical species associated with them.

Peak Position (cm^{-1})	Possible Chemical Species
696,748	Monosubstituted benzene
1008,1034	Monosubstituted benzene
1450	C=C skeletal in-plane vibration
1620-1680	C=C, water
1040	O=S=O str.
1168	O=S=O str.
3200	-NH of ammonium
3400	-OH of alcohol, phenol, water and
3000-3100	-CH vibrations of phenyl ring

The major bands that appear after sulfonation are as follows.

- A sharp band at 1040 cm^{-1}.
- A broad band at 1170 cm^{-1}.
- A broad band in 1400-1500 cm^{-1} region which encompasses two peaks.
- A broad band at 3200 cm^{-1}.

The bands at 1040 cm^{-1} and 1170 cm^{-1} can be attributed to O=S=O str. vibrations [31]. These are associated with sulfonic acid groups. The exact nature of chemical species in the system under investigation will be discussed in the following sections. The band region around 1430 cm^{-1} can be a contribution from -NH of ammonium and also S=O vibrations [31]. This band although broad does not extend into the 1700-1800 cm^{-1} region showing the absence of C=O kind of species. The broad band in 1620-1680 cm^{-1} is attributed to water (absorbed by the hygroscopic sulfonic acids) and/or C=C kind of linkages. There are two notable bands to the left of 3000 cm^{-1}. The band at 3200 cm^{-1} is attributed to -NH of NH_4^{+1} [34]. Note the extremely low intensity of the peculiar band at around 3030 cm^{-1} which was found in polypropylene. This was attributed to -C=C- kind of linkages. There is also a broad band at 3500 cm^{-1} which can be attributed to -OH resulting from water and phenol/alcohol. The exact nature of this band will be decided in the following discussion. Thus, from the above it can be concluded that the following chemical species are present in the system under investigation.

- O=S=O kind of chemical linkages.
- -OH kind of chemical linkages.
- -NH kind of chemical linkages.
- -C=C- kind of chemical linkages.

7.3 DISCUSSION OF RESULTS

The results listed above agree with the literature available on sulfonation of polystyrene [35]. The formation of sulfonic acid species is the main effect of sulfonation on polystyrene. Also, note that unlike polypropylene, the nature of spectrum the is almost same throughout for 1 minute through 5 minute sulfonation. This indicates that most probably all the chemical changes occur on the surface in the first minute thereby leading to a saturated surface. This proposition is also supported by the XPS and contact angle data which will be discussed later.

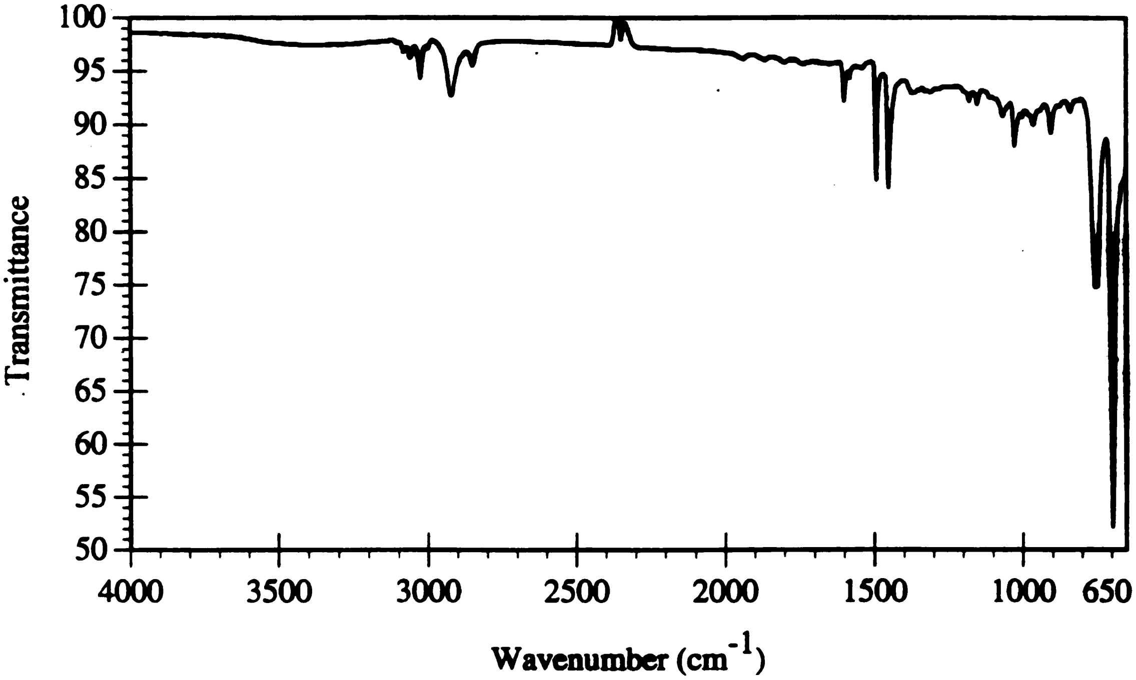


Figure 7.2a: The figure illustrates the IR spectrum of unsulfonated polystyrene.

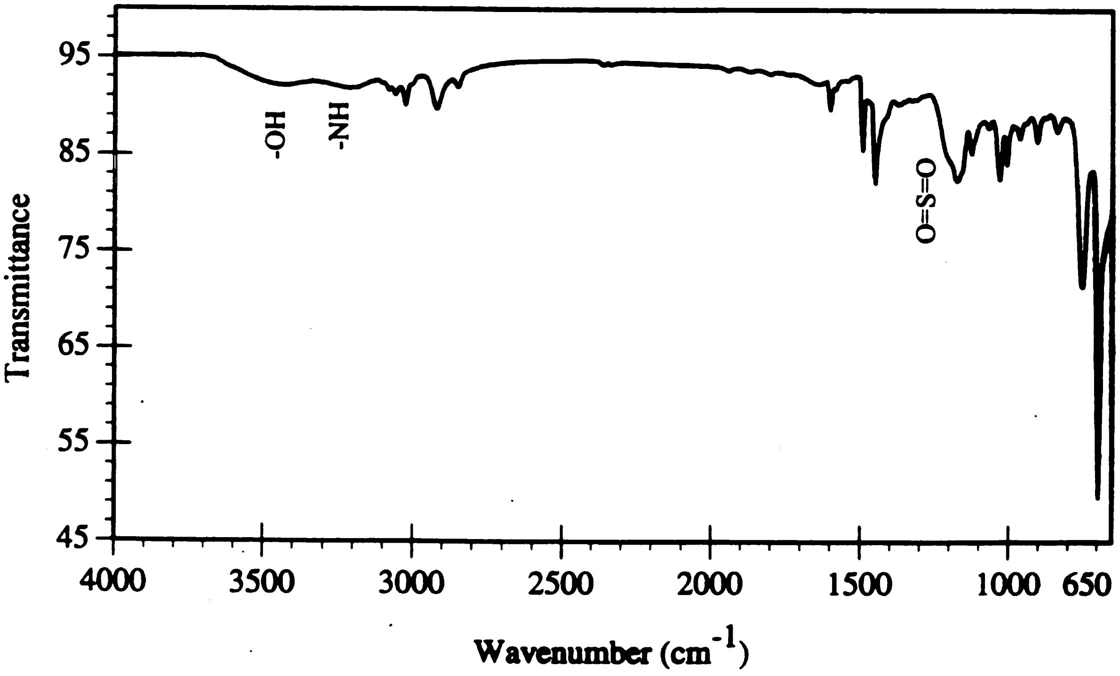


Figure 7.2b: The figure illustrates the IR spectrum of polystyrene sulfonated for 1minute followed by neutralisation with ammonium hydroxide.

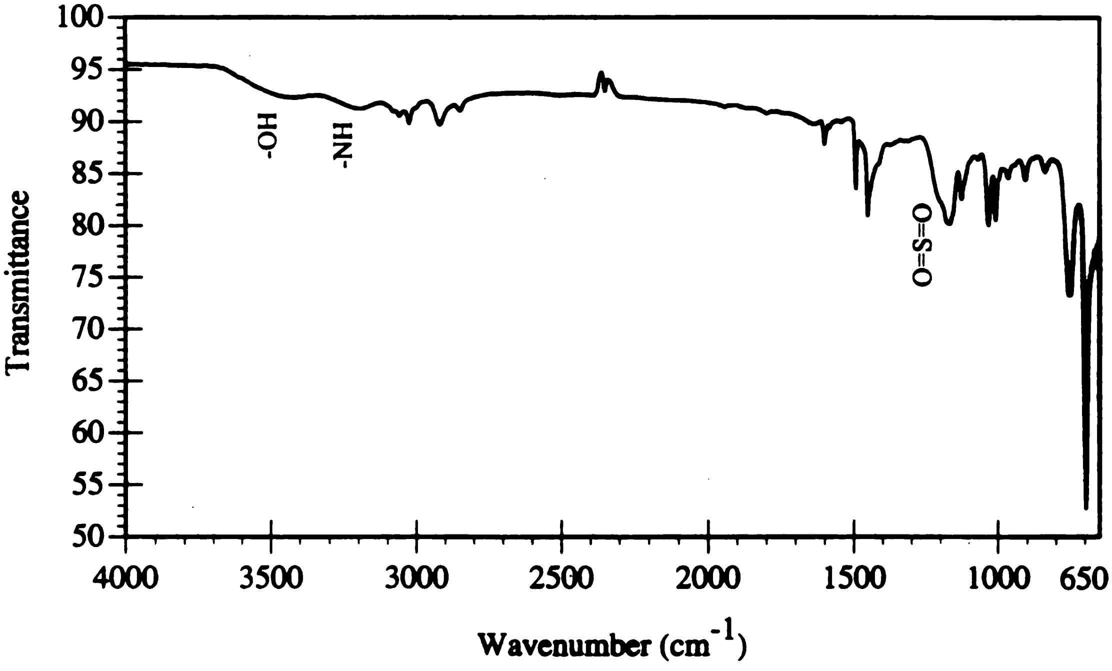


Figure 7.2c: **The figure illustrates the IR spectrum of polystyrene sulfonated for 2minutes followed by neutralisation with ammonium hydroxide.**

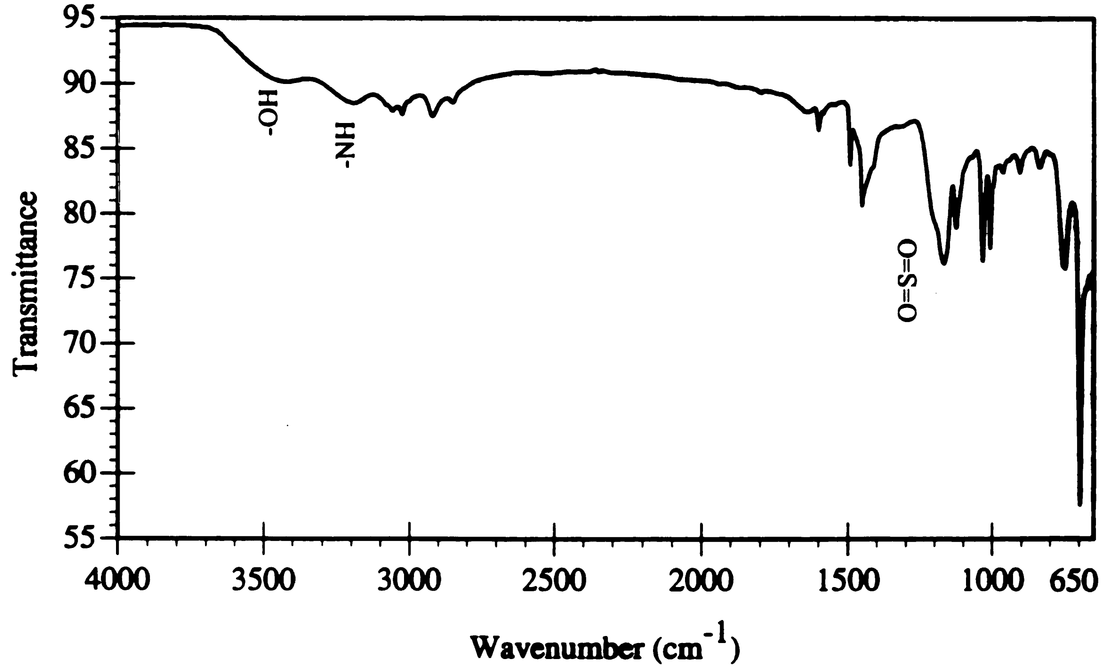


Figure 7.2d: **The figure illustrates the IR spectrum of polystyrene sulfonated for 3 minutes followed by neutralisation with ammonium hydroxide.**

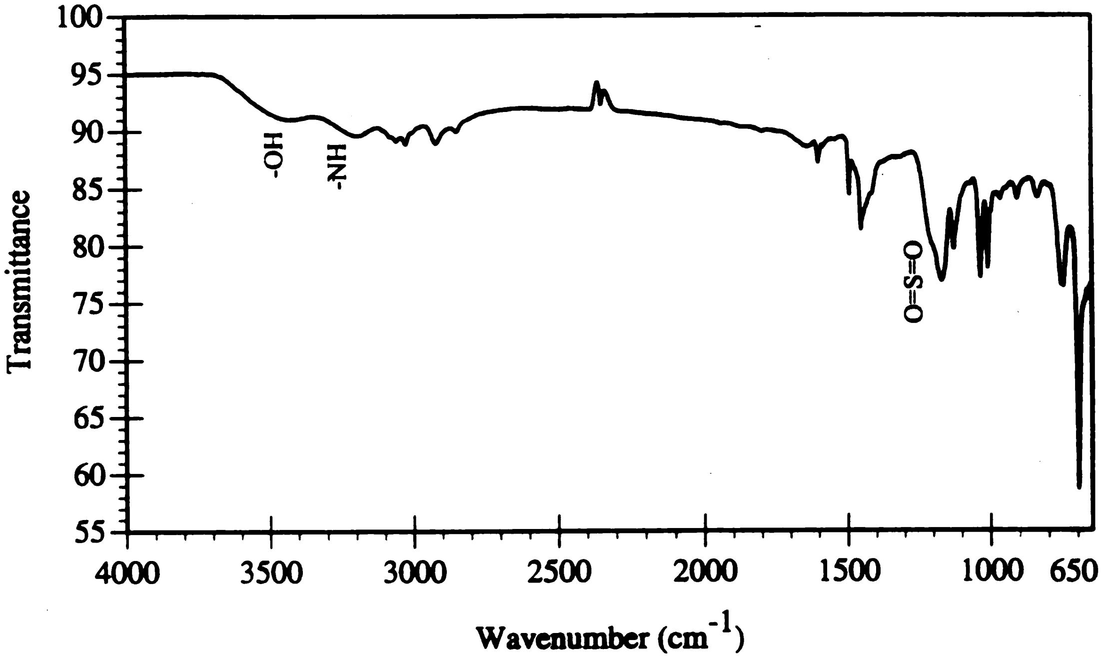


Figure 7.2e: The figure illustrates the IR spectrum of polystyrene sulfonated for 4minutes followed by neutralisation with ammonium hydroxide.

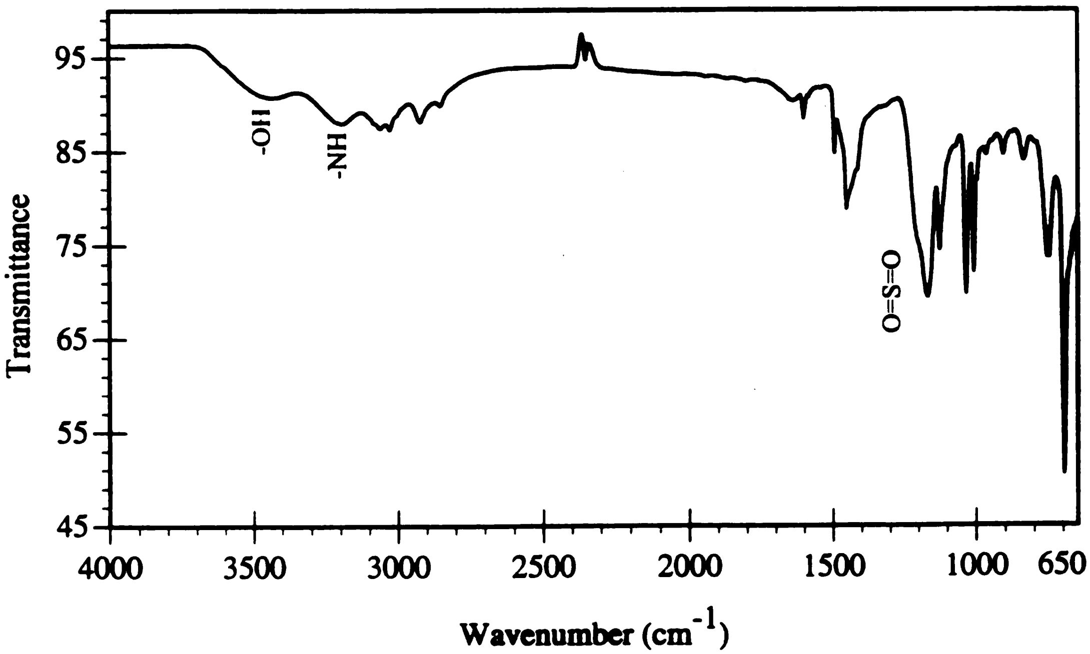


Figure 7.2f: The figure illustrates the IR spectrum of polystyrene sulfonated for 5 minutes followed by neutralisation with ammonium hydroxide.

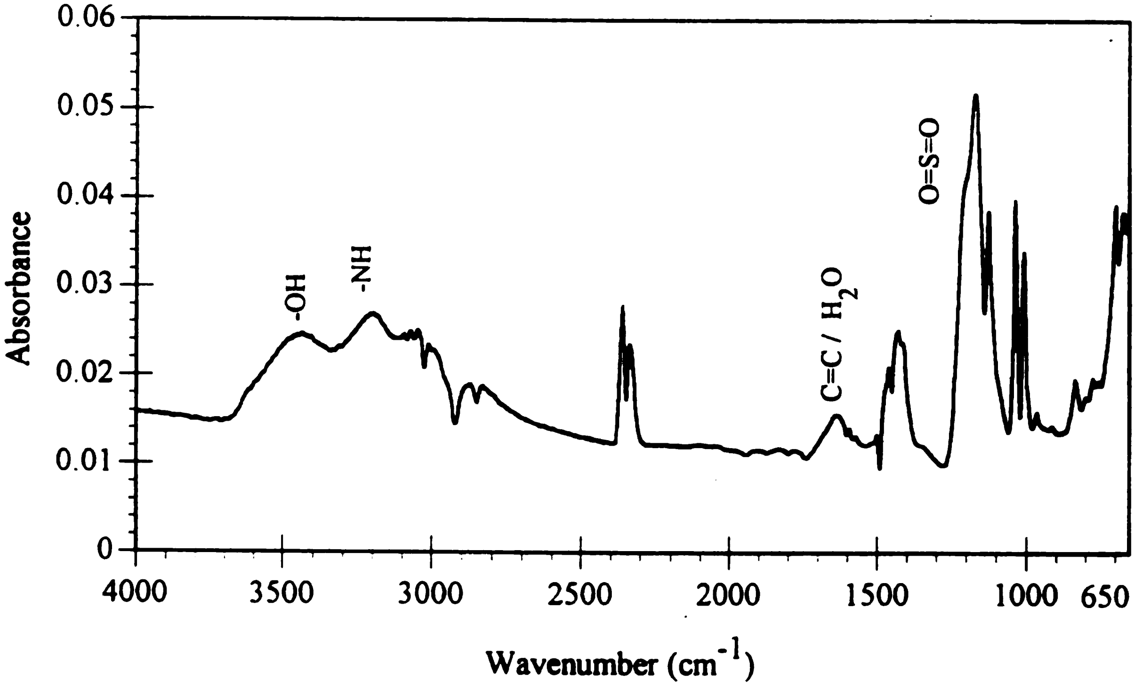


Figure 7.3a: **The difference spectra between 1 minute sulfonated polystyrene and unsulfonated polystyrene.**

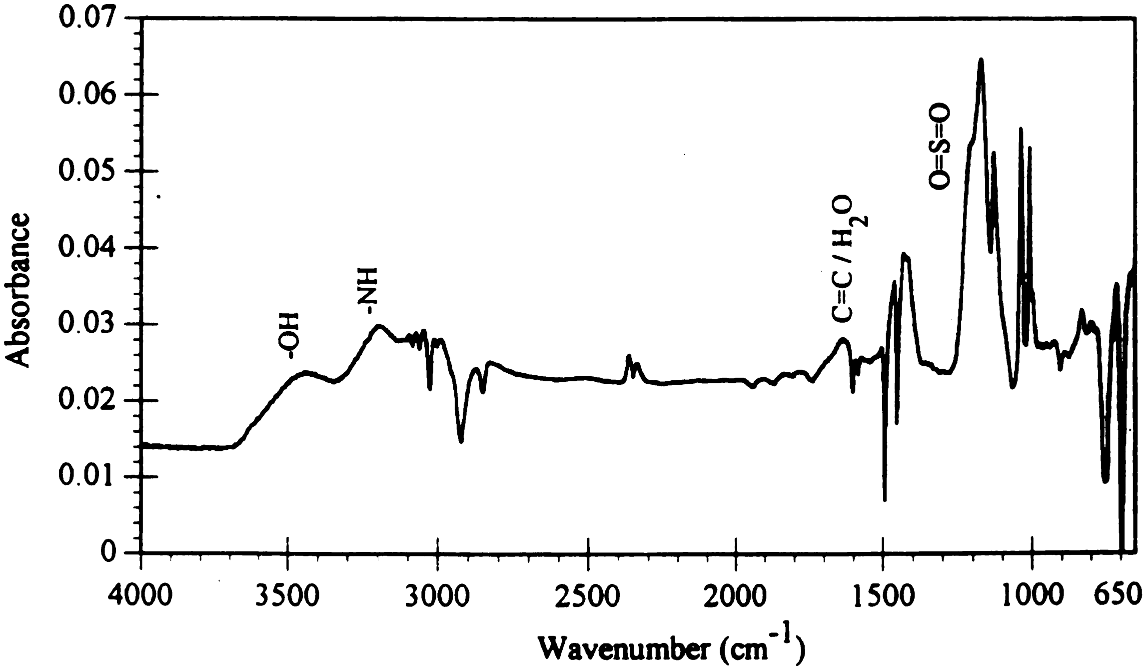


Figure 7.3b: **The difference spectra between 2 minute sulfonated polystyrene and unsulfonated polystyrene.**

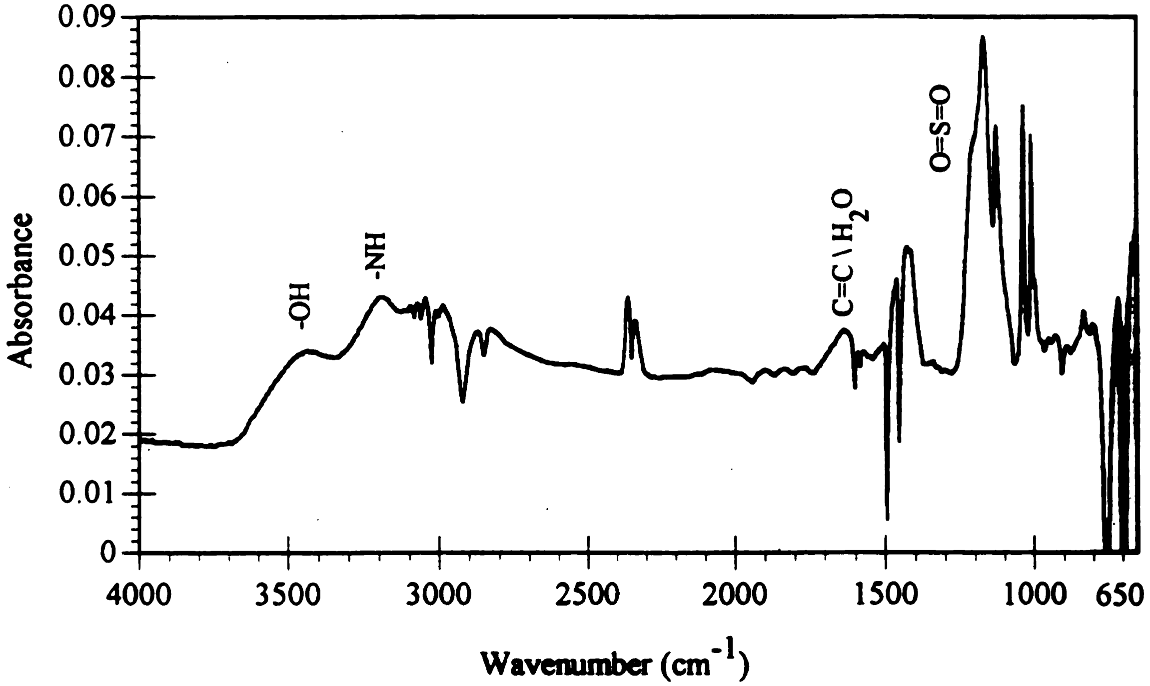


Figure 7.3c: The difference spectra between 3 minute sulfonated polystyrene and unsulfonated polystyrene.

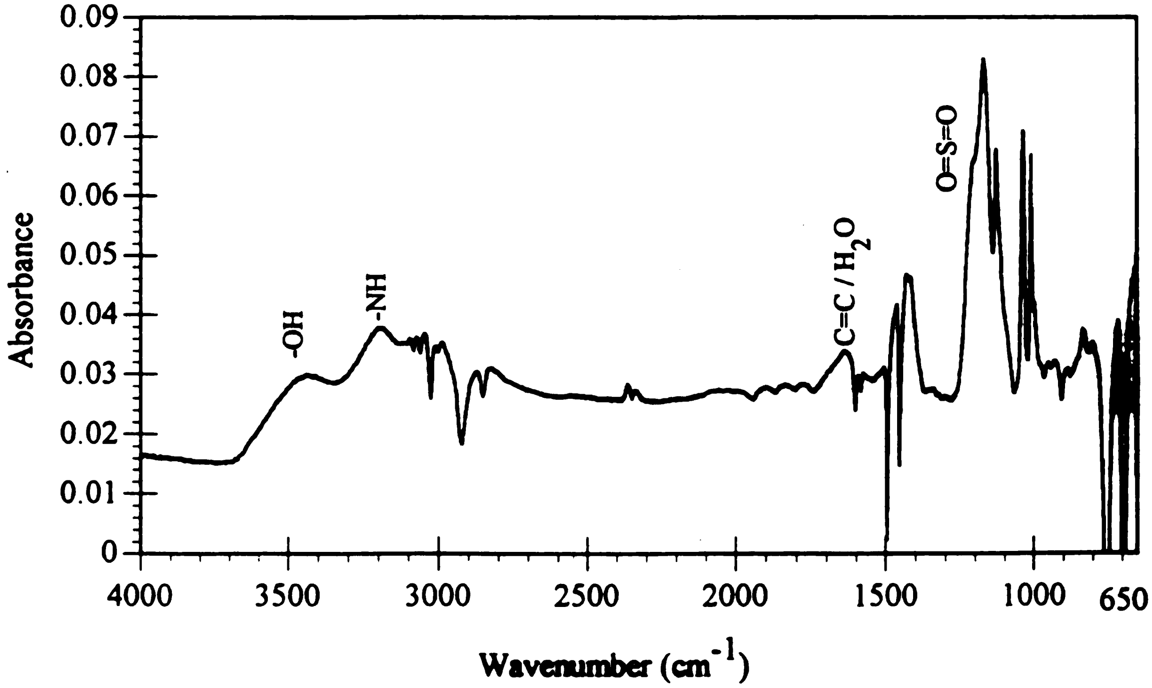


Figure 7.3d: The difference spectra between 4 minute sulfonated polystyrene and unsulfonated polystyrene.

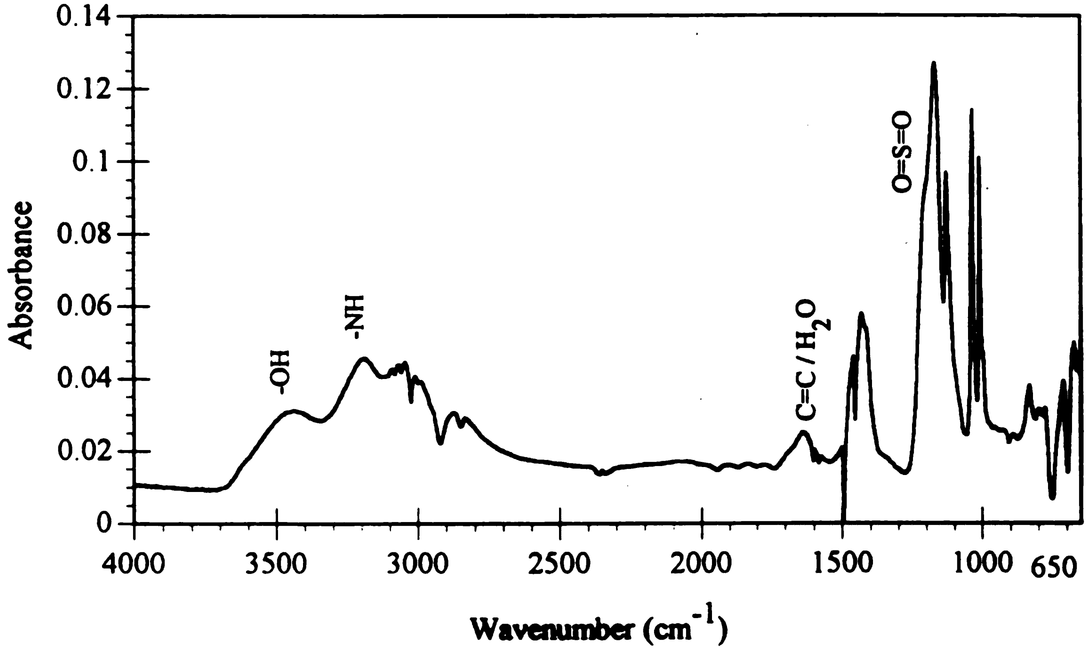


Figure 7.3e: The difference spectra between 5 minute sulfonated polystyrene and unsulfonated polystyrene.

7.3.1 Proposed Reaction Scheme

Unlike polypropylene, there is no documented evidence of degradation of polystyrene under the influence of SO_3 /H_2SO_4 or other strong oxidants. In the present work also no degradation was observed. There was no degraded/ low molecular weight material which sloughed off on neutralising. This inertness against strong oxidants has been attributed to the stability imparted to the structure due to the delocalised electrons of the phenyl ring. Desulfonation of sulfonated species is a low probability event in polystyrene because the probability of formation of H_2SO_3 by the extraction of hydrogen from the neighbouring carbon is extremely low because of the aromatic nature of the ring. In the case of polypropylene, all the carbons were aliphatic which makes the extraction of hydrogen easier and thus formation of H_2SO_3 easier.

The largest fraction of carbons in the polystyrene polymer are contained in its phenyl rings. As the data shows, the ortho and para positons are the main sites for attack by SO_3 due to its high electron density and steric availability resulting in formation of o,p-sulfonic acids. However, there is a probability of the aliphatic carbons also being sulfonated albeit very less. However based on these IR results it can be concluded that sulfonic acids are the most probable species in the system linked to the phenyl ring primarily at the para position and less at the ortho position. The proposed scheme of reaction has been shown in Figure 7.4 and 7.5. Para substituted sulfonic acids are the main product along with ortho substituted sulfonic acid. However, as was indicated earlier due to steric hinderance the probability of formation of ortho sulfonic acids is less. This is in consonance with the past literature available on sulfonation of polystyrene [35].

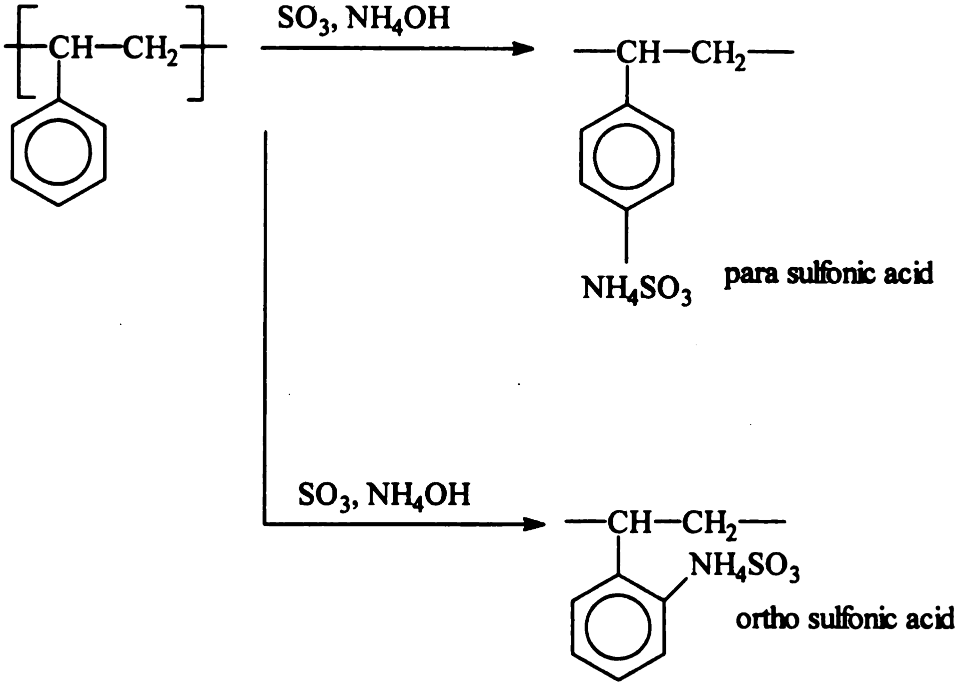


Figure 7.4: **The figure illustrates the formation of aromatic sulfonic acids on reaction with SO_3. The para position is the most probable site of attack due to ease of steric reasons.**

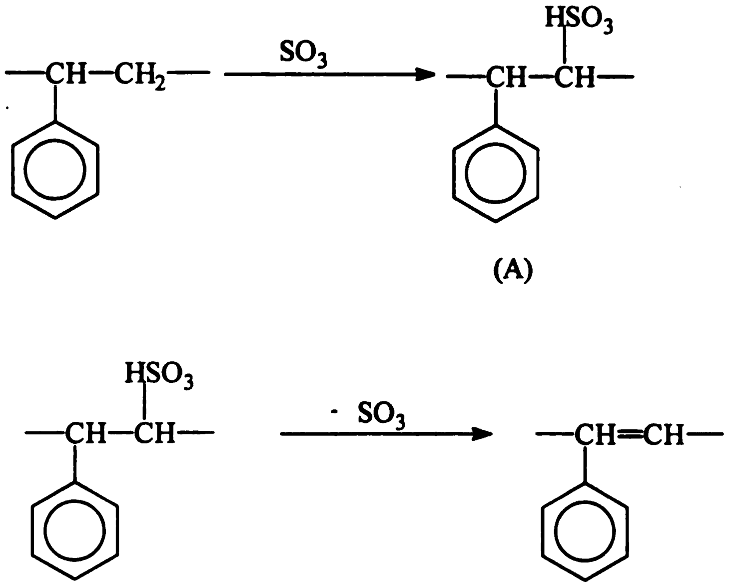


Figure 7.5: The figure illustrates the formation of alkene species during sulfonation of polystyrene.

7.4 XPS OBSERVATIONS AND RESULTS

As was pointed out in the previous chapter, X-ray Photoelectron Spectroscopy (XPS) is an surface sensitive technique analysing the top 2-5 nm of the surface. Similar analysis was carried out for polypropylene. In this section XPS results for polystyrene have been discussed.

7.4.1 Quantitative Analysis of XPS Results.

The following table gives the atomic concentrations of the different elements in percentage terms.

Table 7.2: The table shows the data for atomic concentration for polystyrene sulfonated for 1 thru 5 minutes as obtained from XPS.

Sample	Carbon	Oxygen	Sulfur	Nitrogen
0 minute	96.7 ±1.97	3.2 ±1.84	-	-
1 minute	61.4 ± 0.20	24.5 ± 0.32	6.9 ± 0.03	6.84 ± 0.60
2 minute	61.1 ± 0.70	24.6 ± 0.42	6.9 ± 0.08	7.3 ± 0.2
3 minute	60.8 ± 0.66	24.4 ± 0.55	7.0 ± 0.05	7.5 ± 0.45
4 minute	61.7 ± 1.35	23.7 ± 1.81	7.1 ± 0.16	7.1 ± 0.07
5 minute	61.2 ± 2.44	24.1 ± 2.18	7.1 ± 0.14	7.5 ± 0.11

The following observations can be made from data in the above table.

(i) The percentage composition of the untreated sample is changed in the very first minute of treatment and stays constant with additional treatment.

(ii) The percentage concentration of the various elements are a constant within the experimental errors. Unlike polypropylene where there were marked changes with treatment time in polystyrene there is no detectable change. The surface saturates in the first minute.

(iii) No visible signs of degradation (e.g. darkening) were seen on the surface.

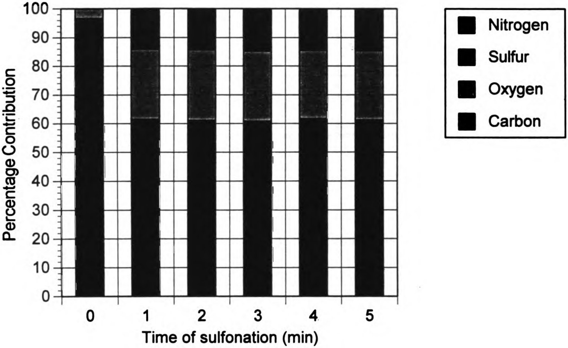


Figure 7.6: The figure illustrates the atomic concentrations of various elements present in polystyrene as a result of sulfonation. Notice the constancy achieved in all the samples.

The changes in terms of atomic ratios has been shown below.

Table 7.3: The data presented in the table shows the respective atomic ratios using the data from Table 7.2. Notice the constant saturation levels reached in the first minute of treatment itself. The ratios stay constant throughout.

Sample	O/C	S/C	O/S	N/S
0 minute	0.03 ± 0.02	-	-	-
1 minute	0.39 ± 0.007	0.112 0.000	3.54 ± 0.063	0.919 ± 0.084
2 minute	0.40 ± 0.011	0.113 ± 0.002	3.54 ± 0.013	1.053 ± 0.016
3 minute	0.40 ± 0.013	0.115 ± 0.002	3.48 ± 0.054	1.063 ± 0.056
4 minute	0.38 ± 0.038	0.115 ± 0.000	3.32 ± 0.336	0.997 ± 0.032
5 minute	0.39 ± 0.052	0.116 ± 0.007	3.39 ± 0.239	1.051 ± 0.006

It is clear from the above table that a state of saturation is eached on the surface of polystyrene in the first minute of treatment itself. Observation of the above data shows that the O/S ratio rests around 3.3 while ideally it should be almost 3.0. This descrepancy can be attributed to the presence of moisture due to the hygroscopic nature of sulfonic acids. This is supported by the IR spectra also where peak region 1600-1700 cm^{-1} is a contribution from moisture. However, an interesting result is that N/S ratio is almost unity throughout. This indicates that there has been almost complete neutralisation of the sulfonated species. In other words, all the sulfur containing species have the hydrogen which can be replaced by NH_4^+ from ammonium hydroxide. This further supports the conclusion that the formation of sultones species is almost negligible in sulfonation of polystyrene when the hydrogen for replacement with NH_4^+ is not available.

7.4.2 Qualitative Analysis of XPS Results

The process of analysis of XPS data for polystyrene was similar to that followed for polypropylene. Since the main linkages are of C-C/C-H type, the C1s peak was chosen as the reference peak and all the C1s peaks obtained were shifted to 284.6 eV. Correspondingly, the O1s, S2p and N1s peaks were also shifted by the same amount respectively. The final peak positions assumed by the respective elements with C1s at 284.6 eV are 531.8 ± 0.08 eV for O1s, 167.9 ± 0.1 for S2p, 401.8 ± 0.1 for N1s. These values are in good agreement with the values obtained for Polypropylene (531.8 ± 0.16 for O1s, 167.6 ± 1.63 for S2p and 401.8 ± 0.2 for N1s). Thus, it can be concluded that essentially the nature of species being formed in both polymers is the same.

Since carbon is the main constituent of the system and undergoes maximum chemical changes, C1s peak was deconvoluted to determine the nature of chemical changes occuring on it. The data shows that only one peak can be fitted in the main peak located at 284.6 eV. Now, from IR data and previous literature it is known that formation of sulfonic acid at ortho and para position is the main chemical change occuring in the system. Thus, it implies that C-S linkage is located very near the main C-C/C-H/C=C peak. This is in agreement with the work done by Clark et. al.[38]. They proposed that the substituent effect of sulfur on C1s is very small (~0.4 eV). The other interesting point which emerges from the deconvolution of C1s peak is the absence of peaks related to C-O/C=O/-COOH. This supports the propositions that almost all the oxygen present in the system is bonded to sulfur (-HSO_3) as illustrated in the reaction scheme presented in Figures 7.4 and 7.5.

7.5 CONTACT ANGLE RESULTS

In order to characterise the topmost layer of the surface contact angle analysis was carried out with water as the probe liquid. A Rame-Hart Goniometer Model 100-00 was used. 5 μl drops were placed manually on the surface with a pipette and the contact angle measured through a calibrated eye-piece. Almost 10-15 drops were measured for each sample. The results are presented in Table 7.4 below.

Table 7.4: The table shows the contact angles obtained on sulfonated polystyrene using water as a probe liquid. Note the saturation achieved in the first minute of treatment itself.

Sample	Contact Angle (θ) (degrees)	cosine θ
0 minute	94.5 ± 1.8	-0.078
1 minute	4.7 ± 1.4	0.997
2 minute	4.1 ± 1.1	0.997
3 minute	3.1 ± 1.1	0.998
4 minute	3.6 ± 1.1	0.998
5 minute	3.5 ± 1.4	0.998

As in the case of polypropylene, the drops tended to spread unevenly on the surface in this case also. The drops would collapse when placed on the surface and had to be placed sufficiently far apart so that they do no merge into each other. The data however, clearly supports the proposition that the surface is chemically altered in the first minute of treatment.

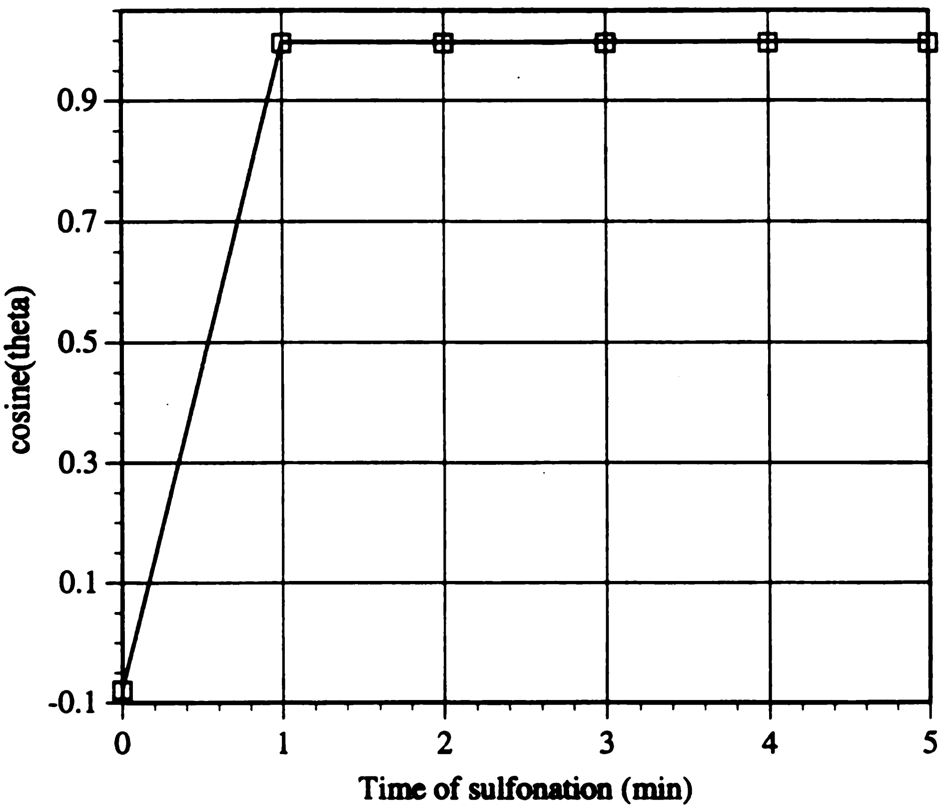


Figure 7.7: The plot illustrates the variation of contact angle of water on sulfonated polystyrene as time of sulfonation is varied.

7.6 DISCUSSION

The data presented in the preceding sections shows that the surface of polystyrene is saturated with sulfonic acid species in the first minute of treatment itself. The high rate of reaction is attributable to the highly electrophilic nature of the sulfonation reaction. The high density of electrons on the phenyl ring drives the reactive SO_3 towards the ring. This is also aided by the greater concentration of phenyl ring carbons as compared to the aliphatic carbons. In polypropylene, desulfonation occurs by extraction of a hydrogen from a neighbouring carbon. This is not the case in polystyrene because extraction of hydrogen from the phenyl ring is extremely difficult because of the resonance stabilisation of the phenyl ring. The XPS data along with the IR data shows the absence of any kind of oxygen carbon linkage. This indicates that the formation of B-sultone, pyrosultone etc. species is a highly unlikely process in polystyrene. Also, as pointed out earlier the carbons in the phenyl ring are in a greater concentratin than aliphatic carbons in this polymer which increases the probability of SO_3 reacting with the ring.

7.7 CONCLUSIONS

The sulfonation of polystyrene results in an extremely high energy surface in the first minute of treatment itself. The IR data alongwith XPS data shows that sulfonic acid species at ortho and para positions is the most dominant chemical species which results due to sulfonation. Also, the surface is saturated within the first minute of treatment itself. There are no signs of degradation or desulfonation in polystyrene as was seen in polypropylene.

Conclusions

Chapter 8

The following conclusions can be drawn from the presented work.

1. The sulfonation of polymer surfaces is a highly electrophilic reaction as has been shown by the results on sulfonation of polypropylene and polystyrene. SO_3 tends to react at centers of high electron density. In polypropylene this center is at tertiary carbon and in polystyrene it is the aromatic ring .

2. Under the given conditions of reaction it is observed that desulfonation (which results in formation of H_2SO_3) occurs easily in case of polymers containing only aliphatic carbons as compared to a polymer containing aromatic carbons. This can be explained on the basis of ease of hydrogen extraction from the neighbouring carbons which is required to form H_2SO_3. Hydrogen extraction is easier in aliphatic systems because it results in the formation of a stable system of doubly bonded carbons while an aromatic ring is already stable due to the resonance structure.

3. The surface of polymers cannot be sulfonated beyond a limit. The main reason for this behaviour can be attributed to the large volume occupied by the -NH_4SO_3 group. As this gets incorporated in the system, there is chain movement in the polymer to accomodate it. After a limit spatial restrictions do not permit additional -NH_4SO_3 groups which leads to degradation.

In polypropylene the limit is reached in about 3 minutes of treatment time while in polystyrene the surface is saturated in the first minute itself. Also, it was observed that in polypropylene during the first minute the main chemical effect is oxidation of the surface rather than incorporation of sulfonic acids.

4. Degradation of the surface due to desulfonation occurs conspicously in polypropylene while in polystyrene it is not visible. Although, there may be chain scission at higher times of sulfonation in polystyrene too. An important reason for this besides differences in chemical nature of the polymers is crystallinity. Polypropylene is an ordered crystalline polymer while polystyrene is amorphous in nature. When sulfonation occurs the most important chemical species being formed (after neutralisation) is $-NH_4^+ SO_3^-$. Being a large molecule it would occupy substantial volume. The free volume is larger in polystyrene due to its amorphous nature as compared to polypropylene. This results in $-NH_4^+ SO_3^-$ being transported easily in polystyrene. On the other hand in polypropylene the chain movement is restricted due to crystallinity. As sulfonation proceeds there is extensive chain movement due to incorporation of $-NH_4^+ SO_3^-$ which leads to chain scission and ultimately degradation.

5. The sulfonation of polypropylene leads to formation of several kinds of chemical species. The final product not only contains a conjugated system of doubly bonded carbons but it has several chemical species which include alkene sulfonic acids, hydroxy sulfonic acids, ketones and aldehydes. On the other hand in polystyrene it is seen that the product is mainly para substituted sulfonic acid and lesser amounts of ortho sulfonic

acid. The formation of ortho sulfonic acid is less as compared to para because of steric reasons.

6. Adhesion results show that sulfonation is a viable technique and competitive with other techniques currently available. The polypropylene results show that for a 1 minute treated sample the failure is interfacial and as treatment time increases the failure tends to be cohesive in the polymer. For polystyrene the failure is cohesive for all the treatment times [25].

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