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Foreword

Chemistry has contributed significantly to the development of mankind. It has applications in all span of life. Department of Chemistry of MES Keveeyam College Valanchery has the declared objective of imparting scientific knowledge in the field of chemical science and to aid the development of student community and hence the society. Journal ChemY started publication in 2014 with the motto of promoting research publications of young scholars. We are thankful for the wide appreciation and support received for the previous issues. Of course, this obliges us to move ahead to our objective with a greater responsibility. We have great pleasure to place before you the fourth issue of the journal ChemY.

I sincerely thank all the authors who have contributed to this issue of ChemY. I also express my thanks to the reviewers of papers and also to the members of the editorial board. I am eagerly looking forward to more contributions to the forthcoming issue.

> Capt (Dr.) C Abdul Hameed (Chief Editor)

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Studies on the Swelling Behaviour of Polymeric Hydrogels Based on Gelatin

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ABSTRACT

Interpenetrating polymer network (IPN) hydrogels have been made from two hydrophilic polymers, namely, polyvinyl pyrrolidone (PVP) and gelatin (Gltn) using gluteraldehyde as crosslinking agent. Hydrogels have been prepared with varying amounts of crosslinking agent and the component polymers. The effect of the preparation conditions on the swelling behavior of these gels has been investigated in water. Dynamic swelling studies have been carried out and the kinetic parameters for the swelling process have been evaluated.

Key words : Hydrogels, Interpenetrating network systems, swelling, Diffusion

1. INTRODUCTION

Hydrogels are three dimensional networks of hydrophilic polymers obtained by physical or chemical crosslinking of the polymer chains. They possess the ability to absorb large amount of water while retaining the three dimensional structure and find extensive use in medical, pharmaceutical, agricultural and industrial fields (Peppas et. al. 1993). "Stimuli responsive hydrogels" refers to a special class of hydrogels which exhibit dramatic changes in their physical or chemical behaviour in response to slight variations in external conditions such as temperature, ionic strength or pH of the medium etc. Intensive studies are being carried out on the development of such hydrogel materials, especially for biomedical and pharmaceutical applications (Wu et. al, 2004).

Gelatin is a translucent, colourless solid substance. It has been commonly used as an emulsifier in food, pharmaceutical, cosmetic preparations and in photography (Bajpai et. al, 2005). Gelatin is an irreversibly hydrolyzed form of collagen and is a protein produced by partial hydrolysis of collagen extracted from the bones, connective tissues, organs, and intestines of some animals such as the domesticated cattle, and horses. It is a heterogeneous mixture of single or

multi-stranded polypeptides, each with extended left-handed proline helix conformations and containing between 300 - 4000 amino acids. It is a nontoxic, biocompatible and biodegradable material soluble at body temperature, which makes it an ideal material for pharmaceutical applications (Rokhade, et al, 2006).

PVP is an amorphous polymer with a glass transition temperature ranging from 126- 174°C for commercial grades. It has several very useful properties including very low toxicity, good film-forming and adhesive properties, and solubility in a broad range of solvents, including water, alcohols and a number of other organic solvents (Fried et. al, 2000). When dry it is a light flaky powder, which readily absorbs up to 18% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. In addition PVP is able to form complexes with a wide range of compounds through hydrogen bond formation between its carbonyl group and the hydroxyl groups of water, alcohols and hydroxyl containing polymers like PVA(Lu et. al, 2003).

The aim of the present investigation was to optimize the conditions for obtaining mechanically stable IPN gels of Gelatin and PVP using gluteraldehyde as the crosslinking agent. The gels have been characterized for their structure to study the influence of preparation method and film characteristics on the swelling and diffusion behavior of the films. The results have been analyzed to understand the mechanism of transport of water molecules through the films.

2. EXPERIMENTAL

Materials

Gelatin was obtained from Merck (Mumbai, India). Polyvinylpyrrolidone was obtained from S.D. Fine Chemicals (Mumbai, India). Doubly distilled water was used in the preparation of the films and in swelling studies.

Preparation of IPN Hydrogels

The following method was used in the preparation of the Gelatin/Polyvinylpyrrolidone hydrogels. 15% (w/v) aqueous solution of Gelatin and 1,5,10 & 15% aqueous solutions of PVP were made separately by stirring at a temperature of 45° C. The gelatin solution was mixed with solutions of PVP with varying amounts and the mixture obtained were stirred for 4 hours to make homogeneous. Then added 5% glutaraldehyde as the crosslinking agent. The experiment was repeated by varying the amount of glutaraldehyde and by keeping the amount of gelatin and PVP as

15 % and 10 % respectively. The crosslinking was carried out in beakers suspended in water bath at 60°C for a period of 4 hours. After that, the crosslinked gels were taken out and washed with distilled water to remove the adhering reactants. The gels thus obtained were dried at 40°C and stored. The details of the preparation conditions and the codes used for the designation of the gels are compiled in Table 1.

Gel Code	GLTN	PVP	GLA
	(%)	(%)	(%)
GP1	15	1	5
GP2	15	5	5
GP3	15	10	5
GP4	15	15	5
GP5	15	10	10
GP6	15	10	15
GP7	15	10	20

Table 1. Preparation of Gelatin/Polyvinylpyrrolidone hydrgels

FTIR Analysis

FTIR spectra of pure gelatin and IPN hydrogels of gelatin/PVP were recorded on Nicolet Avatar 330 FTIR spectrophotometer using silicon carbide disc.

Thermal Analysis

The DSC measurements were carried out with Mettler Toledo DSC 822 thermal analyzer. The samples were heated from -100 to 300°C and the heating rate was maintained at 10°C/min.

Scanning Electron Microscopic (SEM) Analysis

The SEM analysis of IPN hydrogels of gelatin/PVP hydrogels were carried out with a JEOL-JSM 5800LV scanning electron microscope. The micrographs were recorded with a magnification of 500 under a voltage of 20 kV.

Swelling Studies

The swelling behavior of the obtained gels was investigated by carrying out swelling measurements in water at room temperature. The data has been used for evaluating the swelling kinetic and diffusion parameters. The weight measurements were made with time using an electronic balance (Shimadzu AUX 120, Japan) with an accuracy of \pm 0.1 mg. Pre-weighed dry gels were immersed in excess of water maintained at constant temperature. After specific intervals of time, the gels were removed from the medium, the surface adhered liquid drops were wiped with

blotting paper and the increase in weights were measured. The measurements were continued till the weight of the swollen hydrogels attained a constant value. The swelling ratio (S) was calculated (M.Sen et. al 2002) using the following expression,

Swelling (S) % =
$$\left[\frac{(W_t - W_o)}{W_o}\right] \times 100$$
 (1)

Where Wo and Wt are the weights of the dry and swollen gels respectively. The maximum amount of water a swollen gel can hold at equilibrium was expressed as % equilibrium water content EWC(%), which was calculated (H.A.Essawy et al. 2005) using the following expression

$$EWC(\%) = \left[\frac{(W_e - W_o)}{W_e}\right] \times 100$$
⁽²⁾

3. RESULTS AND DISCUSSION

Characterization of gels

Structure and Morphology

The effect of presence of PVP on the surface structure and morphology of the Gelatin/PVP gels was investigated using SEM techniques. SEM photographs of pure Gelatin and Gelatin/PVP gels showed that, although the gelatin surface has a heterogeneous appearance, the Gelatin/PVP IPN surface has a homogenous appearance. The homogeneous texture is indicative of high miscibility between the two component polymers.



Figure 1. Scanning Electron Micrographs of (a) Gelatin & (b) Gelatin/PVP

FTIR Studies

The FTIR spectra of pure gelatin and a representative sample of gelatin/PVP are shown in Figure 2. The peaks due to the N_H stretching vibration of gelatin accounts for the appearance of

the broad band in the region 3100–3300cm⁻¹. The peak at 2935cm⁻¹ is attributed to aliphatic C_H stretching of gelatin. The amide I band of gelatin which appears at 1646cm⁻¹, overlapped with the 1686cm⁻¹ band of carbonyl stretching of PVP. The peak at 1302cm⁻¹ can be assigned to the C-N stretching of gelatin and that for PVP is observed at 1256 cm⁻¹. The FTIR spectra thus provides a conclusive evidence for the presence of gelatin and PVP in the IPN gels.



Figure 2. FTIR Spectra of (a) Gelatin & Gelatin/PVP

Thermal Characterisation

The DTG thermograms of pure gelatin and a representative sample of gelatin/PVP IPN gels were recorded in the temperature range 0 to 800°C at a heating rate of 10 °C /min., under N₂ atmosphere and are presented in Figure 3. The dehydration of Gltn was evidenced by an endothermic peak close to 100 °C. The peak corresponding to the T_g of Gltn appears around 225°C whereas the exotherm around 300°C is indicative of the beginning of decomposition. The peak at 115.08°C correspond to Tg of PVP. In the IPN system due to the presence of PVP the decomposition peak shifts and an additional peak appears 400°C.



Figure 3. DTG Spectra of (a) Gelatin & Gelatin/PVP

Swelling Studies

The effect of polymer composition and extent of crosslinking on the swelling behaviour of the gels was studied by maintaining the pH of the swelling medium at 7.0. The swelling behaviour exhibited by the hydrogels are shown in Figures 4a and 4b. Figure 4a shows that % swelling increases with increase in the amount PVP to a maximum and then decreases. Since PVC is hydrophilic in nature, as the amount of PVC increases in the matrix it can hold more amount of water. Once the saturation point is reached the compactness of the system increases and swelling decreases. As the amount of Gluteraldehyde increases from 5% to 20% swelling percentage decreases from 545 to 249. This indicates that with as the crosslink density increases the polymer matrix shrinks and thereby reduces the space available to hold more amount of water.



Figure 4. The swelling isotherm of gelatine/PVP gels as a function of (a) composition & (b) crosslink density

Kinetics of Swelling

The kinetic analysis of swelling process was made (S.Ekici et al. 2004) using the following equation,

$$\frac{\mathrm{dS}}{\mathrm{dt}} = k_{\mathrm{S}} \left(S_{\mathrm{eq.}} - S \right)^2 \tag{3}$$

where S_e and k_s denote the degree of swelling at equilibrium and the rate constant of swelling respectively. Eq. (3) on integration over the limits, S=0 at t = 0 and S = S at t=t, takes the form,

$$\frac{t}{S} = A + Bt$$

where B is the inverse of equilibrium swelling $(B=1/S_e)$ and $A=1/(k_s S_e^2)$ is the reciprocal of the initial swelling rate (R_i) and k_s is the swelling rate constant. The plot of 't/S' Vs. t for the representative gels are shown in Figure 5a.

The R_i and k_s were calculated from the intercept of the respective curves on the ordinate axis and theoretical equilibrium swelling (S_e) from the corresponding slopes. The values of these parameters obtained for the gels are presented in Table 2. The theoretical equilibrium swelling values calculated from the plots are in close agreement with the experimentally determined values. The R_i and k_s values are observed to depend on the composition of the gels and the compactness of the network chains governed by the extent of crosslinking.

To evaluate the diffusion phenomena of water into the gels (E.Karadag, et. al. 2004). the initial 60% of the swelling data were fit into the following equation

$$F = \left[\frac{\left(W_{t} - W_{o}\right)}{W_{o}}\right] = Kt^{n}$$
(4)

Where 'F' denotes the swelling power of the gel, defined as the amount of water contained in the gel/unit weight of the material; 'K' is the swelling constant characteristic of the polymer network and 'n', is the swelling exponent which characterizes the mechanism of diffusion of water into the network. The ln F Vs. ln t plots for the representative gels are shown in Figure 5b. The values of 'n' & 'K' calculated from the slopes and intercepts of the lines and are listed in Table 2. The n values for hydrogels were in the range of 0.18 - 0.58 indicating that the water transport mechanism in these gels was anomalous (relaxation controlled) diffusion.



Figure 5. (a) Swelling rate curves and (b) Swelling kinetic curves of gelatine/PVP gels

Formulation code	GP1	GP2	GP3	GP4	GP5	GP6	GP7
Swelling,	239	311	545	300	357	255	229
Equilibrium water content EWC %	70.56	75.67	84.51	75	78.11	71.84	69.63
The initial swelling rate $\mathbf{Ri} \times 10^{-2}$	10.4	5.4	6.5	4.4	2.1	4.2	2.7
Swelling rate constant ks ×10 ⁻³	17.4	5.22	1.97	4.44	1.36	5.98	4.70
Maximum equilibrium swelling S _{max} %	243	322	575	315	396	265	240
Swelling Exponent n	0.18	0.39	0.43	0.36	0.58	0.39	0.36
Swelling Constant K	0.7142	0.2390	0.3024	0.2483	0.0653	0.1931	0.1776

 Table 2. The swelling parameters for the gels

CONCLUSIONS

Interpenetrating polymer network (IPN) hydrogels were made from two hydrophilic polymers, namely, polyvinyl pyrrolidone (PVP) and gelatin (Gltn) using gluteraldehyde as crosslinking agent. Hydrogels have been prepared with varying amounts of crosslinking agent and the component polymers. The swelling nature of the network was found to depend on the concentration of component polymers and the extent of crosslinking. The equilibrium swelling of these hydrogels can be controlled by the network structure as well as the crooslink density. The diffusion of water into the gels was found to be governed by anomalous diffusion involving chain relaxation mechanism. From the present study, it can be concluded that these gels may find potential pharmaceutical and agricultural applications.

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Development and characterization of Hydrogels from Acrylic Monomers Megha Radhakrishnan¹ and Rajesh C¹

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ABSTRACT

Hydrogels have existed for more than half a century, and today they have many applications in various processes ranging from industrial to biological. Hydrogels are prepared from acrylic monomers by using N, N methylene bisacrylamide as crosslinker and potassium persulphate as initiator. Swelling of these gels in different medium and the mechanical properties are studied. The effects of concentration of monomer, initiator, cross linker, temperature and addition time of cross linker on the properties of hydrogel were studied. The biodegradability of the hydro gels was studied by soil burial test. FTIR and TGA analysis are also conducted.

Keywords: hydrogels; swelling; soil burial test

1. INTRODUCTION

Today, we are living in a polymer age. For the last 50 years the polymeric materials have experienced an explosive growth and brought revolutionary changes in the day-to-day life. They have penetrated extensively into every walks of human life to bring colorful changes. Truely speaking the plastics, rubbers and fibres have changed the common man's life style and standard of living to great extent. In fact, the polymers have become the symbol of modern life.

A polymer is a macromolecule with large number of repeating units and having molecular weight ranging from two thousand to one million. A polymer is formed by combination of large number of simple molecules. The individual simple unit from which the macromolecule is formed is called a monomer. Example: Polyethylene is formed from the simple monomer ethylene.

Polymerization is a process which allows simple low molecular weight compounds to combine and form a complex high molecular weight compound. For this each molecule of the compound should have the capillary to react at least with two other molecules of the same or some other compound. In other words, they should have a functionality of at least two. Functionality of a compound depends on the number of reactive sites it has. Example: -COOH, -OH, -NH₂. Some compounds do not contain any reactive functional groups but the presence of double bond or triple bonds in the molecule bestows polyfunctionality on them [1].

A hydrogel is a three dimensional network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure due to chemical or physical cross linking of individual polymer chains. Hydrogels were first reported by Wichterle andLim (1960) [3]. By definition, water must constitute at least 10% of the total weight or volume for a material to be a hydrogel. Hydrogels also possess a degree of flexibility very similar to natural tissue due to their significant water content. The hydrophilicity of the network is due to the presence of hydrophilic groups such as –NH₂, COOH, -OH,-CONH₂,-SO₃H. Hydrophilic gels that are usually referred to as hydrogels are networks of polymer chains that are sometimes found as colloidal gels in which water is the dispersion medium [4].

Researchers, over the years, have defined hydrogels in many different ways. The most common of these is that it is a polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water. Hydrogels have received considerable attraction in the past 50 years, due to their exceptional promise in wide range of applications [5-7].

Many materials both naturally occurring and synthetic, fit the definition of hydrogels. During last two decades natural hydrogels were gradually replaced by synthetic hydrogels which has long service life, high capacity of water absorption and high gel strength. Fortunately, synthetic polymers usually have well-defined structures that can be modified to yield tailorable degradability and functionality. Hydrogels can be synthesized from purely synthetic components. Also it is stable in the condition of sharp and strong functions of temperature [8].

Recently hydrogels have been defined as two or multi component systems consisting of a three dimensional network of polymer chains and water that fills the space between macromolecules. Depending on the properties of the polymer (polymers) used, as well as on the nature and density of the network joints, such structures in an equilibrium can contain various amounts of water: typically in the swollen state, the mass fraction of water in a hydrogel is much higher than the mass fraction of polymer. In practice, to achieve high degrees of swelling if is common to use synthetic polymers that are water soluble when in non cross linked form.

The method of preparation leads to some important classes of hydrogels. It includes homopolymeric, copolymeric, and interpenetrating. Homopolymeric hydrogels are referred to as polymer network divided from a single species of monomer which is basic structural unit comprising of any polymer network. Copolymeric hydrogels are comprised of two or more different monomer species with at least one hydrophilic component, arranged in a random, block or alternating configuration along the chain of the polymeric network. Multipolymer interpenetrating polymeric hydrogel (IPN) an important class of hydrogel, is made of two independent crosslinked synthetic or natural polymer component contained in a component is a crosslinked polymer and other component is a non crosslinked polymer[9,10].

According to the source, hydrogels can be divided into those formed from natural polymers and those formed from synthetic polymers [11]. Hydrogels can be prepared from polymers derived from nature or synthesis. Examples of natural polymers such as collagen,gelatin,fibrin,silk,chitosan,dextran have been employed for hydrogel preparations. It usually possess innate biocompatibility and biodegradability. Hydrogels based on synthetic polymers such as poly(ethylene glycol), poly(lactic acid), PVA offer great versatility in controlling polymer chemical structure and architecture, which is essential to prepare hydrogels with tailorable network and mechanical strength. It is also possible to divide hydrogels into two categories based on the chemical and physical nature of the crosslinking junctions. Chemically, crosslinked networks have permanent junctions. Physical networks have transient junctions that arise from either polymer chain entanglements or physical interactions such as ionic interactions, hydrogen bonds or hydrophobic interactions.

There another type of classification based on the response of the hydrogel. Chemical gels use covalent bonding that introduces mechanical integrity and degradation resistance compared to other weak materials. In biochemical hydrogels, biological agents like enzymes or amino acids participate in the gelation process. Several enzymes and ligands are also participated. Physical hydrogels can undergo a transition from liquid to a gel in response to change in environmental conditions such as temperature, pressure and light.

Any pH-sensitive polymer structurally contains hanging acidic (e.g. carboxylic and sulfonic acids) or basic (e.g. ammonium salts) groups that respond to the pH changes in their environment by gain or loss of protons. Poly-electrolytes are polymers that have a large number of such ionizable groups. Anionic poly-electrolytes such as poly (acrylic acid) (PAA) are deprotonated in basic environmental conditions and then electrostatic repulsions between the chains strongly increase, which allow water molecules to penetrate causing drastic swelling of the hydrogel. However, in an acidic media, the acidic polymer protonates resulting in a decrease of charge density and polymer volume collapse.

If the ionization of the ionizable component is complete, the swelling process stops and further pH increase only increases the ionic strength [12,13]. The phase transition pH range can be modulated by selecting the ionizable moiety with a pKa matching the desired pH range or by incorporating hydrophobic moieties into the polymer backbone [14]. Different pH-sensitive behaviors and degrees of swelling can be achieved by using different monomers. The most commonly studied ionic polymers for pH-responsive behavior includePoly (acrylamide) (PAAm), PAA, poly (methacrylic acid) (PMAA), poly (diethylaminoethyl methacrylate) (PDEAEMA), and

poly (dimethylaminoethyl methacrylate) (PDMAEMA).Polymers containing phosphoric acid derivatives have also been reported.

Temperature-sensitive hydrogels (thermogels) are aqueous monomer/polymer solutions, which have the ability to form a gel upon temperature change and have a slightly hydrophobic characteristic due to the presence of groups such as methyl, ethyl, and propyl, which preferably interact with water molecules by hydrogen bonds that cause the hydrogel to swell. These hydrogen bonds are correlated to the temperature.

The common characteristic of temperature-sensitive polymers is the presence of hydrophobic groups. Most polymers increase their water solubility as the temperature increases. However, in some cases water solubility decreases with an increase in temperature (inverse or negative temperature dependence) [15]. This unusual behavior produces a phenomenon of polymer phase transition as the temperature is raised to a critical value called the "lower critical solution temperature" or LCST, which is an entropy-driven process. In the case of hydrogels with negative thermosensitivity, right below the LCST, water is a good solvent for the polymer, and hydrogen bonding interactions between the polymer and water molecules lead to enhanced dissolution in water. However, when the temperature exceeds the LCST, these interactions are broken, and the polymer chains collapse and then precipitate in the media [14,16].Poly (N-isopropylacrylamide) (PNIPAM) is the most studied thermo-sensitive hydrogel in tissue engineering investigations. This is due to the ability of PNIPAM to squeeze out the absorbed drug when temperature is near that of the human body [17]. Other examples of thermo-sensitive hydrogels are collagen, agarose, hyaluronic acid, poly-(organophosphazenes), and chitosan [18,19]

Electro-sensitive hydrogels, as the name indicates, undergo shrinking or swelling in the presence of an applied electric field. Like pH-sensitive hydrogels, they are usually composed of poly-electrolytes. Under the influence of an electric field, a force on counter ions and immobile charged groups is produced in the network, which attracts mobile ions to the electrodes. As a result, the hydrogel can swell and shrink regionally at the cathode and anode, respectively. Electrosensitive hydrogels can selectively be permeable for a specific molecular size and adjust the water permeability by expanding and contracting in micropore size under electrical stimulation [20]. Because electro-responsive hydrogels can transform electrical energy into mechanical energy and have promising applications in biomechanics, sensing, energy transduction, sound dampening, chemical separations, controlled drug delivery [21], and tissue engineering, these polymers are an increasingly important class of smart materials.

Photo-responsive hydrogels undergo a change in their properties when irradiated with light of the appropriate waveleng th. Typically, these changes are the result of light-induced structural transformations of specific functional groups along the polymer backbone or side chains. Lightsensitive hydrogels can expand and contract upon exposure to ultraviolet (UV) or visible light. The mechanism of visible light-induced volume change of hydrogels is based on the induction of temperature changes by incorporating a photo-responsive functional group (chromophore) into the polymer network. Under exposure to a specific wavelength, the chromophore absorbs light which is then dissipated locally as heat, increasing the "local" temperature of the hydrogel. The resulting temperature change alters the swelling behavior of the thermo- sensitive hydrogel [15]. At a fixed temperature, the hydrogels discontinuously swelled in response to UV irradiation but shrank when the UV light was removed [22]. The potential applications of light-responsive hydrogels in the development of artificial muscles, reversible valves in microfluidic devices [23], and temporal drug delivery were proposed.

The production of polymeric hydrogels is typically accomplished by one of two wellestablished schemes: (a) polymerization of hydrophilic monomers and (b) modification of functionalization of existing polymers (natural or artificial).

The technology of hydrogel production will be discussed in the following sections with an emphasis on recent methods and techniques. The original sources of hydrogels are often divided into two main classes; i.e., artificial (petrochemical-based) and natural.

The latter can be divided into two main groups, i.e., the hydrogels based on polysaccharides and others based on polypeptides (proteins). The natural-based hydrogels are usually prepared through addition of some synthetic parts onto the natural substrates, e.g., graft copolymerization of vinyl monomerson polysaccharides. It should be pointed out when the term "hydrogel" is used without specifying its type; it actually implies the most conventionaltype of hydrogels, i.e., the anionic acrylic that comprises a co-polymeric network based on the partially neutralized acrylic acid or acrylamide[33]. The greatest volume of hydrogels comprises full artificial orof petrochemical origin. They are produced from the acrylicmonomers. Acrylic acid and its sodium or potassiumsalts, and acrylamide are most frequently used in thehydrogel industrial production. The two general pathways toprepare acrylic hydrogel networks are simultaneous polymerization and cross-linking by a polyvinyl cross-linker and cross-linking of a water-soluble pre-polymer by a poly-functional cross-linker.

Swelling properties of hydrogels are due to the high thermodynamical affinity that this class of materials has the solvent for itself. In the past years, this characteristic, coupled with a high versatility and a high tenability of materials properties, leads to deep researchers and exploitation of hydrogels. These networks establish equilibrium with the liquid and temperature of this surrounding for shape and mechanical strength. Variations in the concentration, structure and for functionality of the monomer and cross-linker used in such gels can change the strength. Indeed, many new gel form materials, with a plethora of aims were developed and tested in different fields and engineering, biotechnology and other disciplines[37].

The first cross-linked network material that appeared in literature and has been described by its typical hydrogel properties, one for all the high water affinity was a poly hydroxyethyl methacrylate(pHEMA) hydrogel developed much later in 1960. With the ambitious goal of using them in permanent contact applications with human tissues, hydrogels are the first materials developed for uses inside the patient[38,39].

An interesting way to solve the problem of pollutants is to modify the hydrogels to let them seize and keep the pollutants inside the networks. Many authors have tried this way to seize metal ions: the group of Irani discussed a new composite hydrogel for Pb(II) removal. Briefly, they created a poly-ethylene-g-poly-(acrylic acid)-co-starch/OMMT(LLDPE-g-PAA-co-starch/OMMT) by hydrogel composite, using it like an absorbent pollutant[Pb(II)] remover. They put the hydrogel in a solution containing lead acetate and then measured the absorption with an atomic absorption spectrometer. They reported that the equilibrium absorption data of the hydrogel was consistent with Langmuir isotherm and the 430 mg/g absorption capacity was in line with other common absorbents [40].

Another feasible way to achieve an interesting water filling is explained by Yan-et-al, where the group performed etherification and consequent functionalization of chitosan beads in order to obtain carboxymethylated chitosan with an enhanced adsorption of metal ions. This has been proven to improve selective adsorption of specific ions like Cu(II), Pu(II), and Mg(II)[41].

Hydrogel electrolytes can be composed by organic polymers. According to Choudhuri-et-al, poly-(ethylene oxide), Potassium poly-(acrylate),PVA and gelation are among the most promising materials for the purpose of high tunability and precision of capacities with hydrogel dielectrics.Organic hydrogels seem to show lower properties than inorganic ones.

Over the past decades, significant progress has been made in the field of hydrogels as functional biomaterials. Biomedical application of hydrogels was initially hindered by the toxicity of cross-linking agents and limitations of hydrogel formation under physiological conditions. Hydrogel matrices comprise a wide range of natural and synthetic polymers held together by a variety of physical and chemical cross-links[42].

Shi et al. have recently synthesized a 3D nanostructured conductive polypyrrole hydrogel via an interfacial polymerization method. The high-performance flexible solid-state super capacitor demonstrated promising capacitive properties and good electrochemical stability during long-term cycling [43]. So far, many aspects such as conductivity and morphology of conductive polymer

hydrogels have been extensively studied. Chen [44] produced acrylic acid-sodium acrylate super absorbent through concentrated (43.6 wt%) solution polymerization using potassium persulphate as a thermal initiator.

The pioneering work of Wichterle and Lim on crosslinked hydrogels[45], and because of their hydrophilic character and potential to be biocompatible, hydrogels have been of great interest to biomaterial scientists for many years[46-49]. The important and influential work of Lim and Sun in 1980[50] demonstrated the successful application of calcium alignate microcapsules for cell encapsulation. Later in the 1980's, Yannas and coworkers [51] incorporated natural polymers such as collagen and shark cartilage into hydrogels for use as artificial burn dressing.

Melero-Martins et al [52] demonstrated that bioengineering human vascular networks inside methacrylated gelatin constructed in a liquid form could be injected into immunodeficient mice, followed by instantaneous crosslinking when exposed to UV light.

A three dimensional scaffold containing self assembled polycaprolactone sandwiched in a gelatin chitosan was developed for application as a biodegradable patch for surgical reconstruction of congential heart defects [53]. Thomas et al., synthesized a copolymeric hydrogel by free radical copolymerization of two monomers namely acrylamide and acrylic acid using N,N methylene bisacrylamide and potassium persulphate as crosslinker and initiator respectively. Silver nanoparticles where embedded into it. The silver nanocomposites exhibit excellent antimicrobial activity [54].

2. EXPERIMENTAL Synthesis of hydrogel

To a 100 ml beaker were added, 4g acrylamide, 1g potassium persulphate, .04g N, N methylene bisacrylamide and 50 ml distilled water. The solution is kept in a water bath with continous stirring. The temperature is maintained as 60°C, for a definite time period. So the whole mass got solidified and converted to a transparent gel. Then the gel is transferred to a petridish and was placed in an oven at 100°C for 24 hour, so that the gel changed into a rubbery but smitransparent form of smooth surface. Weighing continued till its weight become constant. The hydrogel was cut into several pieces of equal weights and stored in polyethylene packing. Figure 3.1 shows the synthesis of acrylamide hydrogel.



To investigate the role of monomer, initiator, cross-linker on hydrogel, these are added in different ranges to the reactant mixture. Effect of addition time of cross-linker also studied. Temperature of the external medium is another important parameter. Monomers are taken in the amounts of 4g, 6g, 8g & 12g. Initiators are in 0.4g, 0.8g, 1g and 1.2g and cross-linker .04g, .08g, 0.12g, 0.16g. Addition time of cross-linker also varied as 2 minutes, 5 minutes and 8 minutes. Hydrogels prepared at different temperatures of 50°C, 60°C, 70°C, 80°C and rests are maintained constant.

Another set of hydrogels are prepared with monomer acrylic acid and the initiator and cross-linker are kept same as above. A comparative study of hydrogels of acrylic acidwith that of acrylamide is made.

3. RESULTS AND DISCUSSSION

Swelling analysis of acrylamide hydrogel

(a) Effect of acrylamide composition on swelling

Acrylamide is an ionic monomer and has a major impact on the swelling characteristics of the hydrogel. To investigate the effect of acrylamide composition on the swelling behavior, hydrogels with varying amount of the monomer were prepared and their swelling ratio compared.

Figure 1 shows the variation of swelling ratio with amount of monomer. Initially, swelling ratio (SR) increases upto 6g of monomer and thereafter it decreases. It is explained by the fact that on increase in the concentration of the monomer in the gel, the network density becomes so large that penetration of water molecules becomes relatively difficult and consequently, the swelling decreases.



Concentration of monomer $(g) \rightarrow$

Figure 1 Swelling ratio of hydrogel with different monomer concentration

(b). Effect of Potassium peroxodisulfate (initiator)

Onvarying the amount of initiator as 0.8g, 1g, 1.2g to the reaction mixture, swelling ratio increases. Potassium peroxodisulfate helps to initiate the polymerization of acrylamide. The polymerization rate of acrylamide solution increases with increasing the amount of potassium peroxodisulfate initiator. Obviously its increasing proportion in the gel composition will result in a greater swelling of the hydrogel. The result of this experiment is shown simply by a graph (Figure 2).



Concentration of initiator $(g) \rightarrow$

Figure 2 Swelling ratio of hydrogel with different initiator concentration

(c) Effect of N, N methyl bisacrylamide (crosslinker)

The influence of crosslinking on the swelling behavior of the hydrogel was investigated using different amount of crosslinking agent on the gel preparation. When N, N methylebisacrylamide was used in the concentration of 0.04g and0.08g, the swelling ratio increased while after this range, a drastic fall in the swelling was observed. Higher the concentration of crosslinker N, N methyl bisacrylamide , higher will be the density and lower will be the porosity.



Concentration of crosslinker (g) \rightarrow

Figure 3 swelling ratio of hydrogel with different concentrations of crossslinker

(d) Effect of temperature



Temperature (°c)

Figure 4 swelling ratio of hydrogel preparing at different temperatures

The temperature of the external medium is another important parameter that largely influences the swelling pattern. In the present study, the effect of temperature on swelling has been investigated by changing the temperature of the bathing medium from 50°C to 80°C. The results are depicted in figure 4. These clearly revealed that the swelling ratio increased when the temperature was changed from 50°C to 80°C. The results can be simply explained by the fact that on increasing the temperature of the bathing medium, the segmental mobility of the hydrogel network macromolecular chains also increases and this obviously provides increasing free volumes to the penetrant water molecules and, therefore the swelling increases. On increasing temperature, the diffusion of water molecules become faster and this enhances the swelling rate.

(e) Effect of addition time of crosslinker

Figure 5 shows the swelling ratios of acrylamide hydrogel by varying the adding time of the crosslinker as 2 minutes, 5 minutes and 8 minutes after polymerization of acrylamide. Swelling capacity of a hydrogel increases with increasing the time of addition of crosslinker.



Addition time of crosslinker

Figure 5 Swelling ratio of hydrogel with variation of addition time of crosslinker. Analysis of swelling of acrylamide hydrogel in buffer solution (pH 4)

Amongst the stimuli responsive hydrogels, pH sensitive hydrogels are the most studied hydrogels. Swelling of hydrogel having acidic or basic groups on the polymer chains depends upon the pH of the surrounding medium relative to the respective pKa and pKb values of the functional groups. Cationic networks, (here the monomer having amino, -NH₂ group), if the pH of the surrounding medium is less than the pKb value of the basic groups, protonation (ionization) of the functional group takes place which results in an increased number of fixed positive charges on the polymer chains and mobile negative charges in the solution. Consequently, this causes swelling due to an increase in

- (1) the hydrophilic nature of the polymer chains.
- (2) number of fixed positive charges.
- (3) electrostatic repulsion between chain.

Swelling experiments are repeated by using same hydrogel combinations in the buffer solution of pH4 and the results are given in the tables 1 to 5. Effect of monomer concentration, initiator concentration, crosslinker concentration, temoerature and addition time of crosslinker were the same as the water (pH=4). All these studies revealed that at higher concentration, swelling capacity decreases.

Monomer	Swellig
concentration(g)	ratio
4	8.942
6	9.39
8	10.75
12	7.44

Initiator	Swelling
concentration(g)	ratio(SR)
0.4	7.89
0.8	8.033
1	8.94
1.2	7.28

Table 3

Table 4

Crosslinker	Swelling
concentration(g)	ratio
0.04	5.88
0.08	6.55
0.12	5.98
0.16	6.11

Temperature(°C)	Swelling
	ratio
50°C	9.98
60°C	8.94
70°C	9.57
80°C	7.33

Table 5

Addition time of	Swelling
crosslinker (min)	ratio
2	5.33
5	8.25
8	10.90

Comparison of swelling of acrylamide hydrogel in different medium

At a particular concentration of monomer, initiator and crosslinker, the swelling ratio's of acrylamide hydrogel with different pH were compared. Swelling capacity of a hydrogel increases with increase in pH. Here, swelling of hydrogel in water (pH 7), is higher than that in buffer solution of pH=4. The results are shown in figure 1.

The findings are discussed on the basis of the influence of pH on the ionization of carboxyl groups, hydrogen bonding chelation and hydrophobic interactions. With increasing pH, hydrogel become ionized by deprotonation. Electrostatic repulsion between these adjacent ionized groups and the

osmotic pressure generated by mobile concentration produce an increase in the hydrodynamic volume of the network. So the swelling capacity increases.



Figure 6 S.R of hydrogel with different pH at a particular monomer concentration



Figure 7 S.R of hydrogel with different pH at a particular initiator concentration of 1g.



Figure 8 S.R of hydrogel with different pH at a particular crosslinker concentration of .04g.



Figure 9 S.R of hydrogl with different pH at a particular temperature of 60°C.



Figure 10 S.R of hydrogel with different pH at a particular addition time of crosslinker (5 min).

Swelling analysis of acrylic acid hydrogel

Acrylic acid hydrogels swell rapidly when placed in an aqueous environment due to the ionization of carboxyl groups. These carboxyl groups are strongly associated with water molecules which results in a large osmotic swelling force.

The swelling studies were carried out with hydrogels of acrylic acid. The effect of monomer, initiator, crosslinker, temperature and addiction time of crosslinker etc on the swelling behavior studied and the results are given in the figure 4.11 to 4.15. It can be seen that same gradation in swelling behavior was observed as with acrylamide hydrogel.



Concentration of monomer \rightarrow

Figure 11 swelling ratio of hydrogel with different amounts monomer



Figure 12 swelling ratio of hydrogel with different amounts of initiator



Figure 13 Swelling ratio of hydrogel with different amounts of crosslinker



Figure 14 Swelling ratio of hydrogel prepared at different temperatures.



Addition time of crosslinker \rightarrow

Figure 15 swelling ratio of hydrogel with differrent addition time of crosslinker Comparison of swelling of acrylamide hydrogel and acrylic acid hydrogels

At a particular amount of monomer, initiator and crosslinker the swelling of hydrogels of acrylamide (Am) and that of acrylic acid (AA) were compared and the results are given below:



Figure 16 (a) S.R of the different hydrogels at a monomer concentration of 4g.



Figure 16 (b) S.R of the different hydrogels at an initiator concentration of 0.4g.





From all of these studies, swelling of acrylamide hydrogel is higher than that of acrylic acid. The former have a more effective role in swelling than latter. Here, more hydrogen bonds can be formed between water and amide groups than carbocyclic groups: oxygen is more electronegative than nitrogen. Therefore, swelling ratio increased in acrylamide gel.

Mechanical properties of acrylic acid hydrogel

The tensile strength of the hydrogels are determined by stretching test pieces having 3 cm of guage length and 1 cm width at a constant rate using on a universal testing machine. Tensile strength is the maximum stress that a material can withstand while being stretched or pulled before failing or breaking. It is the load required to rupture a test piece by stretching at a constant rate. Figure showing the variation of tensile strength of the hydrogel with different compositions.







Figure 17(b)



Figure 17(c)



Figure 17 (d)

Here, tensile strength increases with increasing monomer and crosslinker. However, further addition of this component makes the gel thicker. Then the value of tensile strength decreases. With increase in addition time of crosslinker, tensile strength increases.

Soil Burial Test

All combinations of acrylamide and acrylic acid hydrogel are dug in to the soil for 15 days and swelling experiments are repeated. The hydrogels can swell with water during rains and release the moisture into the soil during dry times, both watering plants and helping to control erosion. After soil burial test, there is a loss in swelling capacity of acrylamide hydrogel, but not significant. At a particular concentration of monomer, initiator and crosslinker, swelling of the hydrogel before and after biodegradation are determined and the results are given in the graphs.



Figure 18 Effect of soil burial on S.R of acrylamide hydrogel at a fixed monomer concentration of 4g



Figure 19 Effect of soil burial on S.R of acrylamide hydrogel at a particular initiator concentration of 0.4g.



Figure 20 Effect of soil burial on S.R of acrylamide hydrogel at a particular cosslinker concentration of 0.08g.

From the 15 days of experiment, it is observed that the hydrogel degraded around nearly 50 % weight loss. Degradation of samples was enzymatic and chemical process occurring under microberich compost. Biodegradation may be led to cleavage of bonds and loss of functional groups, which was evident from swelling studies of these gels after soil burial test.

Thermogravimetric Analysis (TGA)

Out of these prepared hydrogels, those with highest swelling weresubjected to thermogravimetric analysis and the results are given below. TGA of the hydrogels was run in an atmosphere of nitrogen gas.

In the case of acrylamide hydrogel with monomer concentration 6g, the TGA curve is shown in figure 4.4.1. Here, the decomposition of hydrogel starts from 40.54°C to 734.2°C under nitrogen gas. The first stage of decomposition takes place between 40.54°C to 160°C. This attributes to a dehydration process (loss of water). The weight loss at this stage is 11%. The second stage occurs in the temperature range of 160° C – 240° C. This is attributed to the loss of NH₂ group in the form of ammonia along with the formation of imide group via cyclization. Polyacrylamide hydrogel

undergoes a very fast and steep degradation in the temperature range. The weight loss at this stage is 9%. Third stage is most probably due to decrosslinking of two network structure with weight loss of 15% and the temperature range is 240°C-300°C. This is because of the decomposition of functional group of polyacrylamide and N,N dimethylene bisacrylamide.

Fourth stage in the temperature range 300°C-460°C with weight loss 36%. The main degradative part is found at the fourth stage. In this range, breakage of the C-C bonds in hydrogel. Fifth stage in the temperature range460°C-610° with weight loss of 17%, indicates the extra energy needed to break the crosslinked structures. On the sixth stage degradation is observed with a weight loss of about 8%. It undergoes complete thermal degradation at 610°C-734.2°C due to a depolymerization process in the fifth stage followed by decomposition in the sixth stage.



Figure 21 TGA of acrylamide hydrogel with monomer concentration of 6g.


Figure 22 TGA of acrylamide hydrogel with initiator concentration of 0.4g.



Figure 23 TGA of acrylamide hydrogel with crosslinker concentration of 0.08g.



Figure 24 TGA of acrylic acid hydrogel with monomer concentration of 8g.



Figure 25 TGA of acrylic acid hydrogel with initiator concentration of 1g.



Figure 26 TGA of acrylic acid hydrogel with crosslinker concentration of 0.08g.

Hydrogels of acrylamide and acrylic acid are degraded thermally nearly at the same range. The TGA curves presented in the above figures suggest that under heating, the thermal decomposition of polyacrylamide and polyacrylic acid hydrogels give 6 distnictive stages of decomposition.

FTIR Analysis

FTIR Spectra of acrylamide hydrogel

IR spectra of the polyacrylamide based hydrogel show the presence of absorption bands characteristic to crosslinking bridges. In an acrylamide hydrogel with monomer concentration of 6g,(Figure 4.5.1) there is a peak at 3182.55 cm⁻¹ is attributed to the valance vibration corresponding to the N-H group or acrylamide unit from the crosslinking bridges while the assigning valance vibration from 2931.80 cm⁻¹ is assigned to the CH₂ groups included in the macromolecular chains and crosslinking bridges. The band corresponding to the C=O and N-H links from the amidic group appears at 1662.64 cm⁻¹ and 1535.34cm⁻¹. The peaks in acrylamide monomer and that in acrylamide hydrogel are not very different.



Figure 27 FTIR spectra of acrylamide hydrogel with monomer concentration of 6g.



Figure 28 FTIR spectra of acrylamide hydrogel with initiator concentration of 0.4g.



Figure 29 FTIR spectra of acrylamide hydrogel with crosslinker concentration of 0.08g. In figure 4.5.2, the value 1718.58 represents the amide group and in figure 4.5.3, that shows at 1651.07cm⁻¹. The peaks at 3190.26 cm⁻¹ and 3317.56 cm⁻¹ show the symmetrical and asymmetrical stretching of N-H groups. Alkene stretching represented by the peak, at 2931.80 cm⁻¹.

FTIR spectra of acrylic acid hydrogel

The IR spectra of polyacrylic acid gel contain large bands, determined by the multitude of possible local conformation of the polymeric chains.

Figure 4.5.4 shows the FTIR spectra of acrylic acid with monomer, acrylic acid with 8g in amount. At 1703.14 cm⁻¹, the band is assigned to the vibrations of the carboxyl group of the monomer. The bands between 1130 cm⁻¹-1300 cm⁻¹ shows C=O stretching and –OH bending vibrations. The peak between 3400 cm⁻¹-2400 cm⁻¹ indicates the presence of COOH groups. The peaks of acrylic acid monomer and that of acrylic acid hydrogel are not significantly different.



Figure 30 FTIR spectra of acrylic acid hydrogel with monomer concentration of 8g.



Figure 31 FTIR spectra of acrylic acid hydrogel with initiator concentration of 1g.



Figure 32 FTIR spectra of acrylic acid with crosslinker concentration of 0.08g.

4. CONCLUSIONS

A hydrogel is a three dimensional network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure due to chemical and physical crosslinking of individual polymer chains.

In our work, hydrogels are prepared from monomers of both acrylamide and acrylic acid by using N,N methylene bisacrylamide as crosslinker and potassium persulphate as initiator and the effect of composition of these components on swelling are studied. The studies show that swelling is increased initially with increase in the concentration of monomer, initiator and crosslinker. But at higher concentration, there is a drastic fall in swelling. With increase in temperature and addition time of crosslinker, swelling of both hydrogels increased. Swelling capacity of hydrogel decreased after soil burial test for 15 days of experiment due to the biodegradation of gels.

By studying mechanical properties, tensile strength increases initially with increase in monomer and crosslinker. Further addition of these components makes the hydrogel thicker. Then the value of tensile strength decreases.

The conformation of structure of polyacrylic hydrogels was received by FTIR spectra. Thermal degradation of the gels was studied by TGA analysis.

By comparing the properties of acrylamide hydrogel with acrylic acid hydrogel, we concluded that former have better swelling property than the latter.

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Studies on Mechanical Properties and Oil Resistance of Biocomposites of Starch from Amorphophallus Sylvaticus and NR-NBR blend Husna V¹ and Suraja PV²

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ABSTRACT

Starch from Amorphophallus sylvaticus is used as reinforcing agent in acrylonitrile butadiene rubber (NBR)/Natural rubber (NR) blend and composite materials were prepared. Starch was mixed in to NBR/NR blend using a Two roll mixing mill. The cure characteristics, mechanical properties and oil resistance of both NR-NBR blend and composites were studied. The structural analysis of blend and composites were conducted using FTIR.

Keywords: Two roll mixing mill; Amorphophallus sylvaticus; structural analysis;

1. INTRODUCTION

Mixing of two or more different polymers together makes possible to achieve various property combinations of the final material, mostly in a more cost-effective way than in the case of synthesis of new polymers. Therefore, great attention has been paid to the investigation of these systems as well as to the development of specific materials. [3]

Mixing of two amorphous polymers can produce either a homogeneous mixture at the molecular level or a heterogeneous phase-separated blend. Demixing of polymer chains produces two totally separated phases, and hence, leads to macrophase separation in polymer blends. Generally miscible polymer blend and immiscible polymer blends are found. A miscible polymer blend means a blend of two or more amorphous polymers homogeneous down to the molecular level and fulfilling the thermodynamic conditions for a miscible multicomponent system. An immiscible polymer blend is a blend that does not comply with the thermodynamic conditions of phase stability. The term compatible polymer blend indicates a commercially attractive polymer mixture, which is visibly homogeneous, frequently with improved physical properties compared with the constituent polymers. Composite material is a multi-phase combination material of two or more component materials with different properties and different forms through compounding processes, it not only maintains the main characteristics of the original component, but also shows new character which are not possessed by any of the original components. Composite materials should have the following characteristics: microscopically it is non-homogeneous material and has a distinct interface; there are big differences in the performance of component materials; the formed composite materials should have a great improvement in performance. From analysis of the composition and the internal structure of composite materials we found that it includes three basic physical phases. One is called matrix phase which is continuous, another is called reinforcement which is scattered and surrounded by the matrix. The other is called composites' interface which is an interphace between reinforcement phase and matrix phase. For further study on micro-structure level, we found that, owing to the complex physical and chemical reasons in compounding process, the reinforcement phase and the matrix phase near the interface become a complex structure which is different from both of the matrix phase and the reinforcement phase of their own. And at the same time, we found that the structure and morphology have an impact on macroscopic performance of composites, so the microscopic area near the interface changes in structure and properties. Thus it becomes the third phase of composites, which is called interphase. Therefore, composite material is composed of matrix phase, reinforcement phase and interphase. The structure and the nature of these three phases, their configuration and interaction, as well as the relative content determine the performance of composite materials [5]

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibres such as cotton, flax, hemp and the like, or fibres from recycled wood or waste paper, or even by-products from food crops. Regenerated cellulose fibres (viscose/rayon) are also included in this definition, since ultimately they too come from a renewable resource, as are natural 'nano fibrils' of cellulose and chitin. Matrices may be polymers, ideally derived from renewable resources such as vegetable oils or starches. Alternatively, and more commonly at the present time, synthetic, fossil-derived polymers preponderate and may be either 'virgin' or recycled thermoplastics such as polyethylene, polypropylene, polystyrene and polyvinyl chloride, or virgin thermosets such as unsaturated polyesters, phenol formaldehyde, isocyanates and epoxide[6]

In recent years, interest in natural fiber composites for industrial applications has increased significantly. This is partly due to the environmental concern about manmade composites. Natural fibers are biodegradable and are from a renewable resource. Secondly, natural fibers have a potential in cost and weight reduction. They have a high specific stiffness and natural fiber composites have a non-brittle fracture behavior which is an advantage in automotive interior. From the view of occupational (during assembly and handling) health and safety, natural fibers are preferred to glass fibers. Natural fibers are less abrasive for tooling while glass in the form of airborne particles can cause respiratory problems.

N.M. Barkoulaa et al showed the addition of flax fibres along with controlled processing conditions seems to be a convenient way of toughening of the PHB matrix. Composites manufactured through injection moulding exhibited lower impact strength than those manufactured through compression moulding. Based on the biodegradation study of PHB/HV composites the tensile properties drop significantly in the initial stage of degradation. The drop in tensile properties is more gradual in the later stages of biodegradation [9].

Shukanta Bhowmik et al extracted crystalline cellulose from cotton and reinforcing gelatin film for biomedical applications, especially as a wound dressing material for its exceptional biocompatibility and bio-activity[10]. Hesham Moustafa et al studied utilization of date stones (DS) as reinforcing and flame retardant biofiller in polyamide-6 (PA6) with and without maleic anhydride-grafted polypropylene (PP-g-MAH) compatibilizer. The flame retardant properties significantly improved with increasing DS filler content [11].

Sheeja R.G et al synthesised low density polyethylene-g-maleic anhydride-g-starch nanoparticle (LMNS) biocomposites in water medium. LMNS biocomposites were fabricated with different starch nanoparticle (NS) loadings (2, 4, 6, 8, and 10 wt %) by compression molding technique. The morphology analysis of samples revealed homogenous distribution and good interfacial adhesion. The biodegradation enhancement of samples has been revealed by fungal and soil burial tests [12]. J. Rout et al prepared biocomposites from a cheap, renewable natural fiber, coir (coconut fiber) as reinforcement with a biodegradable polyester amide (BAK 1095) matrix. s. More than 70% decrease in flexural strength is observed for alkali treated coir-BAK composites after 35 days of soil burial. The loss of weight and the decrease of flexural strength of degraded composites are more or less directly related.[13]

Vladimr Se et al prepared Environmentally friendly polymeric biocomposites based on whey powder, a waste material of the dairy industry, and fully or partially hydrolyzed poly (vinyl alcohol) were prepared and characterized with optical microscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry, and stress–strain analysis, and their biodegradation was evaluated with the modified Zahn–Wellens method and the spectrophotometric determination of poly(vinyl alcohol). Whey powder is suitable for the modification of polymers, and this is important for the production of biodegradable polymer materials and the consequent reduction of the environmental load. [14]

Vatsala S et al examined potato peel powder (POPL), which is biodegradable, as filler material in polypropylene (PP) matrix in varying concentration from 10 to 40% by weight to prepare biocomposites and investigated water absorption, physicomechanical and thermal properties[15]. Kestur G.S et al prepared nanocomposites based on starches and biofillers highlighting some details about biopolymers and nanosized natural fibers, as well as processing methods of bionanocomposites using these. Some results on structure, properties applications and potentials of bionanocomposites are also presented, which lead to the opportunities they provide with offering new technology and business opportunities for all sectors of industry in addition to being environmentally friendly[16].

Akil and Zamri [17] studied the dynamic mechanical properties of natural fiber reinforced composites. Special emphasis has been given to kenaf and jute fiber reinforced unsaturated polyester composites produced using the pultrusion method. Benjamine et al. [18] made tensile tests on wet and dry flax yarn and the results showed that moisture content has large effect on the modulus of elasticity of flax fiber. Yan et al. [19] examined light-weight honeycomb core sandwich panels containing biofiber-reinforced thermoset polymer composite skins. The effects of honeycomb core height and cell size on the flexural properties of the lab made sandwich panels were evaluated. The lab made paper reinforced polymer composite honeycomb core sandwich panels had comparable bending rigidity and flexural load bearing capability but lower area weights when compared to the commercial products suggesting that paper reinforced polymer composites as skin materials in sandwich panel fabrication.

Sonia et al. [20] examined celluloses microfibers reinforced poly (ethylene-co-vinylacetate) composites. Dynamic mechanical analysis of composites showed increased storage modulus and decreased stiffness and damping properties with cellulose microfibers (CMF) loading. Composites

were exposed to gamma radiation at different radiation dosages. Tensile strength of composites decreased after gamma exposure. The effect of thermal ageing on polymer composites was studied by investigating their weight loss at different intervals of time. Ahmed et al. [21] examined the characterization of treated date palm tree fiber as composite reinforcement. Chemical and mechanical characterization study on date palm tree fibers is essential to be able to evaluate the behavior of these fibers as mutual reinforcement for polymer based composites. Miki et al. [22] examined development of green composite consists of woodchips, bamboo fibers and biodegradable adhesive. The woodchips matrix composite with a biodegradable resin and bamboo fibers was developed. The composite has the high bending strength, high impact strength and good water resistance.

Nitinat and Kasama [23] examined mechanical properties and flammability of sisal polypropylene composites. The flame retardancy of sisal polypropylene composites can be enhanced by the addition of magnesium hydroxide and zinc borate without sacrificing their mechanical properties. Threepopnatkul et al. [24] conducted experiments on effect of surface treatment on performance of pineapple leaf fiber- polycarbonate composites. The modified pineapple leaf fibers composite was used to enhance mechanical properties of the composite. The Young's modulus is the highest in the case of pineapple leaf fibers treated with sodium hydroxide whereas the pineapple leaf fibers treated with aminopropyotrimethoxysilane showed the highest tensile strength and impact strength. Sisal and short pineapple fibers have been used for the reinforcement of natural rubber [25-29] and low-density polyethylene [30-32].

Adhesion between the fiber and rubber can be improved by subjecting the fiber to suitable chemical treatment. Acetylation of cellulose and lignin in jute hasbeen made by Callow [33]. Bleaching of jute with per acetic acid has also been done [34]. Surface modification of natural fibers and performance of the resulting bio-composites have been reviewed by Misra et al [35]. Ibrahim et al. studied the effect of graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch fiber [36]. Action of weak alkali on jute has been studied by Siktar et al. [37]. Mercerization was performed using different types of alkali by Chen and Chen [38]. They reported that the effectiveness was the highest with lithium hydroxide followed by NaOH. The structural and mechanical properties of untreated and chemically modified sisal fibers were investigated by Barkakaty and found that alkali treatment in 18% NaOH for 24 hour showed considerable enhancement in properties of the composites [39].It was noted that the strength of these composites almost doubled when fibers were treated with NaOH for 80-90 hours, but decreased for longer periods. Effects of mercerization and acetylation on rubber reinforcement were studied by Martins

and Joekes [40]. Aspects of alkali treatment of sponge fibers on the flexural properties of polyester matrix composites were studied by Boynard et al. [41].

Srabayeeta et al. studied about biodegradability of biocomposites of polypropylene reinforced with potato starch [42]. You-Ping Wu et al. developed a strategy to prepare high performance starch-rubber composites [43].

Plants of the genus Amorphophallus belongs to the family Araceae. About 200 species of Amorphophallus are distributed throughout the world and 20 species are reported from India.Different varieties of amorphophallus are available. Amorphophallus sylvaticus is a non edible tuber which is used for tooth ache in certain areas[7]. Starch is composed of a large number of glucose units . These units are joined together by glycosidic bonds. Its molecular formula is $(C_6H_{10}O_5)$ n All green plants produce it as store of energy. Starch molecules arrange themselves in the plant in semi-crystalline granules. Each plant species has a unique starch granular size[8]. Starch is composed of two different kinds of molecules viz. linear and helical amylase structure, and branched amylopectin structure. These molecules vary plant to plant. Generally 20 to 25% amylase and 75 to 80% amylopectin is found in starch.

2. EXPERIMENTAL

Starch filler from Amorphophallus sylvaticus

Starch is an important polysaccharide. Plants synthesize and store starch in their structure as an energy reserve. It is generally deposited in the form of small granules or cells with diametersbetween 1-100 pm. Starch found in tuber of amorphophallus sylvaticus is used as filler in this work.

Starch polymers consists of two types of anhydroglucose (AHG). amylose and amylopectin. Amylose is essentially a linear polymer in which AHG units are predominantly connected through oc-D-(1,4) glucosidicbonds. Amylopectin is a branched polymer, containing periodic brancheslinked with the backbones through oc-D-(1,6) glucosidic bonds. Starch in pure form is a powder of white appearance. It is odorless and tasteless, and is insoluble in alcohol and cold water. It is heavier than water having the density of 1500kg/m3. It does not possess a sharp melting point, rather decomposes over a temperature range. It auto-ignites at 410 °C. Starch is composed of two different kinds of molecules viz. linear and helical amylase structure, and branched amylopectin structure. These molecules vary plant to plant. Generally 20 to 25% amylase and 75 to 80% amylopectin is found in starch. [3]

Starch extraction

The sample plant tubers were collected in large quantity. The tubers were washed and peeled, exposing the whitish body. The tuber cut into small pieces and washed again and steeped in water for 2-3 minutes. The pieces were grinded using a mixer for 1 minute at the low speed in presence of water to cover the pieces. The slurry was sieved with a lot of water using a clean cloth. The filtrate is allowed to settle for 8-10 hours. The liquid portion is decanted carefully and starch remains as a cake. It is then collected and dried in an air oven. Powdered and dried again using vacuum oven. The starch after drying was collected and stored in a polythene bag.

Rubber chemical

Ethylene vinyl acetate (EVA) is used as the compatibilizer. It offers excellent heat, ozone, and weather resistance; whereas the vinyl acetate groups provide oil resistance to the blend.40% activated Dicumyl Peroxide (DCP) was used as a vulcanizing agent. It acts as a free radical initiator.

Blend Preparation

Formulations of NR NBR blends used in the present study is given in the Table 1. The blends were prepared using two roller mixing mill. Initially NR and NBR are masticated separately for 3 minutes followed by mixing two rubbers and blends of different formulations are prepared by the addition of compatibilizer and curing agents. The nip gap, mill roll speed ratio and the number of passes were kept the same for all the mixes [4].

Compounding							
incredients	A ₀	B_0	C_0	D ₀	E_0	F ₀	G_0
NR	0	20	40	50	60	80	100
NBR	100	80	60	50	40	20	0
EVA	2.5	2.5	2.5	2.5	2.5	2.5	2.5
DCP	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Table 1- Formulation of NR NBR blend (*phr)

*NR-Natural rubber. *NBR-Nirile butadiene rubber. *EVA-Ethylene vinyl acetate. *DCP-Dicumyl peroxide. *phr-parts per hundred rubber.

Composite preparation

Formulations of biocomposites of NR NBR blend with starch as filler is given in the table 2[8]. NR 60 NBR 40 composites are prepared by the addition of 10 phr,20 phr,30phr of starch forming composites A_1,B_1,C_1 respectively.Similarly,NBR 60 NR 40 composites D_1,E_1,F_1 were prepared .Each sample contains 2.5 phr DCP and EVA.

Table 2 Formulations of NR NBR blend composites.

SAMPLE	NR	NBR	EVA	STARCH	DCP
A ₁	60	40	2.5	10	2.5
B ₁	60	40	2.5	20	2.5
C ₁	60	40	2.5	30	2.5
D ₁	40	60	2.5	10	2.5
E ₁	40	60	2.5	20	2.5
F ₁	40	60	2.5	30	2.5

Swelling Experiments

For swelling studies, circular specimen was punched out from the vulcanized composite sheets by using a sharp steel die having a diameter of 1.5 cm. The weighed dry specimens were immersed in distilled aromatic non polar solvents like xylene, toluene and in polar solvents like DMF and acetonitrile and placed in diffusion bottles and were kept in an air oven at constant temperature. After a particular time interval, they were removed from solvent and wiped using tissue papers. The weights of these specimens after swelling in the solvents were determined by using a highly sensitive electronic balance at regular interval until no further increase in solvent uptake was detected i.e., weighing was done until equilibrium sorption was reached. The thickness and diameter of the sample before and after swelling were determined using a thickness gauge micrometer and Vernier calipers, respectively [17].

Swelling data analysis

Swelling coefficient: The swelling coefficient is the index showing the extent to which the samples swell. The gum and the fibre filled vulcanisates were swollen in a suitable solvent at room temperature and the swelling coefficient was evaluated by the equation;

Swelling coefficient (α) = $\frac{W2-W1}{W1} \times \rho_s^{-1}$

Where W_1 , the initial weight of the sample, W_2 the final or swollen weight of the sample and ρ_s is the density of solvent used [18]

Characterization

The cure characteristics of the mixes were measured by using a rheometer. Two roll mixing mill is used to mix or homogenize polymer materials. Vulcanization of mixes was done at 150°Cusing a hydraulic press having electrically heated plates to their respective cure times obtained from the rheographs. The sheets were kept for 24 hours. Tensile properties of different mixes were examined using a Shimadzu Universal Testing Machine at crosshead speed of 500mm/min. A universal testing machine (UTM) is used to test the tensile stress and compressive

strength of materials. FTIR analysis of various blend and composites were carried out using Shimadzu FTIR spectrophotometer.

3. **RESULTS AND DISCUSSION** Cure characteristics of NR NBR blend

NO	SAMPLE	MINIMUM	MAXIMUMTORQUE(NM)	T 90
	NAME	TORQUE		(MIN)
		(NM)		
1	NBR 100(A ₀)	0.09	1.37	19.33
2	NBR 80 NR	0.07	1.03	20.68
	20(B ₀)			
3	NBR 60 NR	0.06	0.96	21.74
	40(C ₀)			
4	NBR 50 NR	0.05	1.01	20.16
	50(D ₀)			
5	NBR 40 NR	0.06	0.95	20.64
	60(E ₀)			
6	NBR 20 NR	0.06	0.83	17.60
	80(F ₀)			
7	NR 100 (G ₀)	0.04	0.69	18.22

Table 3 Cure characteristics of NR NBR blend.

Table 3 shows that as proportion of NBR decreases from 100 to 60 maximum torque decreases and cure time increases.



Figure 1Rheographs of blends

From figure 1 It can be seen that as NBR decreases, torque decreases.100 NBR has maximum torque value and 100 NR shows minimum torque value. The maximum torque is a measure of crosslink density and stiffness in the rubber. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix, whereas increase in torque is due to the cross linking of rubber. The levelling off is an indication of the completion of curing. The increase in torque values with increasing filler loading indicates that as more and more filler gets introduced into the matrix, the mobility of macromolecular chains of NR is reduced resulting in more rigid vulcanisates. Maximum torque value indicates that there is no further crosslinking possible.

Cure characteristics of composites of NR NBR blend



Figure 2 Effect of filler loading on composites

Figure 2shows higher torque value for 60NBR 40 NR composites with 10 phr filler than curresponding blend. This shows that presence of starch increases torque value.

Mechanical properties of blend

The mechanical properties are determined by stretching standard test pieces at a constant rate using a tensile testing machine. Tensile strength is the maximum stress that a material can withstand while being stretched or pulled before falling or breaking. It is the load required to rupture a test piece by stretching at a constant rate. Table 4.2 shows mechanical properties of NR - NBR blend.

Sample	Tensile strength (N/mm ²)
A ₀ (100NBR)	2.99133
B ₀ (80NBR20NR)	3.50036
$C_0(60NBR40NR)$	4.26523
E ₀ (40NBR60NR)	4.67444
G ₀ (100 NR)	4.68112

Table 4 Mechanical properties of NR - NBR blend.

Where A_0, B_0, C_0, D_0, G_0 are the samples of NR - NBR blend. In A0 there is 100% NBR and 0% NR. In B0 there is 80% NBR and 20 % NR. In C_0 it has 60% NBR and 40 % NR. In E_0 there is 40% NBR 60% NR. G_0 conatins 100% NR.

Figure 3 shows that tensile strength of composites increases with increase in % of NR.100 NR shows highest tensile strength. NR has unique properties due to the presence of 99.9% highly stereoregular cis-1.4 structural units, which provide high crystallizing capability to NR. The crystallization enhances the intermolecular attractive forces, and this reinforces the strength of the polymer. Thus, higher tensile strength is observed along the axis of deformation.



Figure 3 Tensile strength of NR-NBR blend

Effect of biodegradation on mechanical properties of NR-NBR blend

Table 5. Tensile strength of NR - NBR blend after biodegradat

Sample	Tensile strength (N/mm)
A ₀ (100NBR)	1.44067
B ₀ (80NBR20NR)	3.45120
C ₀ (60NBR40NR)	2.8299
$E_0(40NBR60NR)$	3.97894

G ₀ (100 NR)	4.11334

The tensile strength after burial in the soil is less compared to the tensile strength before it is buried in the soil. This result shows biodegradation.

Mechanical properties of composites

Table 6 gives tensile strength of composites.

Sample	Tensile strength(N/mm ²)
NR 60 NBR 40 STARCH20 (B ₁)	5.58455
NR 60 NBR 40 STARCH 30 (C ₁)	5.11989
NBR60 NR 40 STARCH 10(D ₁)	5.45357
NBR 60 NR 40 STARCH 20(E ₁)	4.16563
NBR 60 NR 40 STARCH 30 (F ₁)	3.86911

Two different blends are used for composite preparation that is NR60NBR40 and NR40NBR60. Starch was added to it in different quantities to form composite. It can be seenthat the tensile strength decreases as the level of the starch increases. Table shows that NR 60 NBR 40 composites shows higher tensile strength than NR 40 NBR 60 composites. NR 60 NBR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 20 phr load and NBR 60 NR 40 composites shows higher tensile strength at 10 phr of starch.



Figure 4 Effect of starch loading in NR 60 NBR 40 composites.

Figure 4 shows that the tensile strength increases with starch loadingin NR 60 NBR 40 blends. blend.Also,Composite shows higher value at 20 phr loading.Initially fillers improves mechanical properties.After a particular loading, fillers leads to agglomeration.Figure shows that after 20 phr loading tensile strength goes on decreasing.



Figure 5 Effect of starch loading in NBR 60 NR 40 composites.

Figure 5 shows that tensile strength increases with starch loading in NBR 60 NR 40 blend.Composites shows higher value at laoding 10 phr.

Effect of biodegradation on tensile strength of composites of NR NBR blend

Table7 Effect of biodegradation on mechanical properties of composites of NR NBR blend.

Sample	Tensile
	strength(N\mm)
60NR40NBR STARCH 20	5.36435
60NR40NBR STARCH 30	4.75616
40NR60NBR STARCH 10	5.29149

40NR60NBR STARCH 20	4.15760
40NR60NBR STARCH 30	3.20844

As the amount of starch increases, the tensile strength decreases. It shows biodegradation. Since starch is biodegradable therefore the biodegradability of composite will be increased.

Percentage decrease in tensile strength of composite

Table 8 shows percentage decrease in tensile strength of composite

Sample	Percentage decrease in tensile strength
60NR40NBR STARCH20	3.94
60NR40NBR STARCH30	7.10
40NR60NBR STARCH10	2.97
40NR60NBR STARCH30	17.07



Figure 6 comparison of percentage decrease in tensile strength of composites of 60NR40NBR Figure 6 shows that percentage decrease in tensile strength increases with starch loading. This shows that biodegradability increases with increasing starch load.



Figure 7 comparison of percentage decrease in tensile strength of composites of 40NR60NBR Figure 7 shows that percentage decrease in tensile strength increases with starch loading. This shows that biodegradability increases with increasing starch load.

Swelling coefficients of blend

Swelling coefficient is index showing the extend to which the sample swells. The samples were swollen in the suitable solvents at room temperature. Table 9 shows the swelling coefficient in Toluene, Xylene, acetonitrile and DMF.

	Swelling coefficients in different solvents				
Samples	Toluene	Xylene	Acetonitrile	DMF	
A ₀ (NBR100)	2.9939	2.4756	0.8640	0.8790	
B ₀ (NBR80NR20)	4.2902	3.3898	0.7882	0.8799	
$C_0(NBR60NR40)$	6.3152	4.9395	0.5301	0.3983	
D ₀ (NBR50NR50)	5.3168	4.5844	0.4994	0.5060	
E ₀ (NBR40NR60)	4.9222	3.9802	0.5625	0.5111	
F ₀ (NBR20NR80)	7.2544	6.4277	0.2010	0.1961	
G ₀ (NR100)	6.8558	6.9226	0.007	0.0395	

Table 9 Swelling coefficient in Toluene, Xylene, acetonitrile and DMF.

Figure 8 shows the comparison of swelling coefficients of various blends in polar solvents like acetonitrile and DMF.It can be seen that swelling coefficients of blend is lower than that of pure NBR.Addition of NR to NBR decreases the intake of polar solvents and hence swelling coefficient decreases.



Figure 8 Comparison of swelling coefficient of blend in polar solvents

Figure 9 Comparison of swelling coefficients of blend in non polar solvents

Figure 9 shows comparison of swelling coefficients of blends in non polar solvents. In toluene and xylene, which are non polar solvents, the swelling coefficient value of blend is lower. Addition of NBR to NR decreases the swelling in non polar solvents.

Swelling coefficients of NR-NBR blend starch composites

Swelling coefficients of various composites are given in the table 10

	Swelling coefficients in different solvents			
Samples	Toluene	Xylene	Acetonitrile	DMF
A1(NR60NBR40 STARCH 10)	3.8623	3.8744	0.2810	0.456
B ₁ (NR60NBR 40 STARCH 20)	3.8530	3.5634	0.2532	0.3844
C ₁ (NR60NBR40 STARCH 30)	3.550	3.2106	0.2322	0.3609
D ₁ (NBR 60 NR 40 STARCH 10)	3.1600	3.0016	0.4296	0.3536
E ₁ (NBR 60 NR 40 STARCH 20)	3.1413	2.8100	0.4073	0.3324
F ₁ (NBR 60 NR 40 STARCH 30)	2.5025	2.516	0.3559	0.2916

Table 10 Swelling coefficients of various NR-NBR blend starch composites

Figure 10Effect of starch loading in polar solvents

Figure 10 shows effect of filler loading in swelling coefficients of NBR 60 NR 40 composites in non polar solvents like acetonitrile and DMF. It shows that as starch loading increases swelling coefficient decreases.

Figure 11Effect of starch loading in non polar solvents

Figure 11 shows that increase in starch loading decreases the swelling coefficient in non polar solvents.

Structural Properties

FTIR spectra of NBR,NR,NR-NBR blend, composites are given.

Figure 12 FTIR spectra of NBR

Figure 13 FTIR spectra of NR

Figure 12 and figure 13 shows the FTIR spectrum of NBR and NR.There are peaks at 2922.16 and 2848.86 cm⁻¹which are in between 3000-2840 cm⁻¹.This corresponds to C-H stretching in alkanes. There are two peaks at 1444.68 and 1375.25 cm⁻¹ which are in between 1450 and 1375 cm⁻¹.This corresponds to CH₃ bend. It is the characteristic peak in NR.

Figure 4.14 FTIR spectra of NBR 60 NR 40 blend

Figure 4.14 shows the FTIR spectra of NBR60 NR40 blend. There are peaks at 2922.16 and 2854.65 cm⁻¹which are in between 3000-2840 cm⁻¹. This values shows a slight difference from pure NBR values. This corresponds to C-H stretching in alkanes. When comparing the transmittance of pure NBR and blend, blend shows an increase in transmittance. It is due to some of the interactionsduring blending. This peak is characteristic peak in the acrylonitrile butadiene rubber. A peak shows at 1735.93 cm⁻¹ which is in between 1750-1730 cm⁻¹. This corresponds to ester group in EVA. There are two peaks shows at 1373.32 and 1442.75 cm⁻¹ which are in between 1450-1375 cm⁻¹. It is the characteristic peak in NR. This corresponds to CH₃ bend. This values shows a slight difference from pure NR values. When comparing the transmittance of pure NR and blend, blend shows an increase in transmittance of pure NR and blend, blend shows an increase in transmittance of pure NR and blend, blend shows at 682.80 and 970.19 cm⁻¹ which are in between 1000-650 cm⁻¹. This corresponds to out of plane bend of alkenes.

Figure 15 FTIR spectra of NBR 60 NR 40 starch 30 composites.

Figure 15shows FTIR spectra of NBR60 NR40 starch 30 composite. There are peaks at 2922.16 and 2852.72 cm⁻¹which are in between 3000-2840 cm⁻¹. This corresponds to CH stretching in alkanes. This values shows a slight difference from pure NBR values. When comparing the transmittance of pure NBR and composite, composite shows an increase in transmittance. It is due to some of the interactions during filler addition. This peak is characteristic peak in the

acrylonitrile butadiene rubber. A peak present at 1645.28 cm⁻¹ which is in between 1680-1600 cm⁻¹. This corresponds to C=C alkenes. There are two peaks at 1377.17 and 1438.90 cm⁻¹ which are in between 1450-1375 cm⁻¹. This values shows a slight difference from pure NR values. When comparing the transmittance of pure NR and composite, composite shows an increase in transmittance. It is due to some of the interactions during filler addition. This peak is characteristic peak in the NR. This corresponds to CH₃ bend and also two peaks are present at 678.94 and 806.25 cm⁻¹ which are in between 1000-650 cm⁻¹. This corresponds to out of plane bend in alkenes. A peak shown at 1022 cm⁻¹ which is in between 1300-1000 cm⁻¹. This corresponds to C-O bond of ester group in EVA.

4.CONCLUSIONS

NBR is one of the most commonly used synthetic rubber due to its high oil resistance. It has wide applications in automotive and aeronautical industries to make fuel and oil handling hoses, seals and gaskets. Natural rubber has excellent tensile strength. Due to its structural regularity natural rubber tends to crystallize spontaneously at low temperature or when it is stretched.

Preparation of NR NBR blend improves properties of both rubbers.Starch from non edible tuber Amorphophallus sylvaticus was used as filler in preparation of biocomposites from NR-NBR blend.The cure characterestics ,mechanical properties,swelling characteristics of composites were studied.The investigation shows that mechanical properties were improved on blending.Swelling study reveals that oil resistance property of NBR has also been improved.

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Studies on biocomposites of acrylonitrile butadiene rubber with starch from colocasia esculenta

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ABSTRACT

Colocasia esculenta starch was used as reinforcing agent in acrylonitrile butadiene rubber (NBR) and composite materials were prepared. Starch was mixed in to NBR using a two roll mixing mill. The mechanical properties like tensile strength, tear strength, modulus and elongation at break of the composites were studied. The effect of starch on the oil resistance behavior of NBR was studied by equilibrium swelling technique. The structural change that takes place to NBR upon the incorporation of starch was analyzed by FTIR. The results showed that addition of starch improved the solvent resistance of NBR without compromising its mechanical properties.

Keywords: Colocasia esculenta; NBR; swelling; solvent resistance

1. INTRODUCTION

Recently short fibres have found a variety of applications in rubbers due to the ease of mixing and the consequent processing advantages in fabricating products of complicated design coupled with greater reinforcement. Considerable work has been reported on short fibre reinforced rubber composites.Many researchers have used short glass fibres and synthetic fibres such as nylon, rayon aranid, carbon and polyester for reinforcing rubbers because of their high modules, high strength and low creep [1-4]. Scanning electron microscopic studies of failure surfaces of short glass fibre reinforced rubber composites have been done [5]. Studies were conducted on the cure characteristics and mechanical properties of natural rubber short nylon fibre composites [6]. A study has been conducted on the effect of diazide as adhesive agent in short polyamide fibre reinforced elastomeric composites [7]. But these materials are expensive and are based on nonrenewable resources.

Owing to the uncertainties prevailing in the supply and price of petroleum based products, it is highly important to use the naturally occurring alternatives. Proper utilization of indigenously available raw materials will open up new markets for these natural resources. Hence studies on composites containing natural fibres such as jute, sisal, coir, pineapple fibre, banana fibre, flan and oil palm fibre are important. The possibility of using these natural fibres as reinforcement in polymer based composites has been examined [8-13]. Studies on risalfibre and its composites were reviewed by Li et al. [14]. Coran et al. studied the morphologicaland mechanical properties of oriented cellulose fibre-reinforced elastomeric composites [15]. Murty and De reported on the effect of bonding agents in short silk fibre-reinforced natural rubber based composites [16]. Sisal and short pineapple fibres have been used for the reinforced carboxylated nitrile rubber composites have been done [19]. Bledzki and Gassan reviewed the studies on composites reinforced withcellulosic fibres [20]. Studies on composites containing short banana fibres andpolyester resin have been conducted [21].

Adhesion between the fibre and rubber can be improved by subjecting the fibreto suitable chemical treatment. Acetylation of cellulose and lignin in jute hasbeen made by Callow [22]. Bleaching of jute with per acetic acid has also been done [23]. Surface modification of natural fibres and performance of the resulting bio-composites have been reviewed by Misra et al [24]. Ibrahim et al. studied theeffect of graft copolymerization of methyl methacrylate onto oil palm empty fruit bunch fibre [25]. Action of weak alkali on jute has been studied by Siktar et al. [26]. Mercerizationwas performed using different types of alkali by Chen and Chen [27]. They reported that the effectiveness was the highest with lithium hydroxide followed by NaOH. The structural and mechanical properties of untreated and chemically modified sisal fibres were investigated by

Barkakaty and found that alkali treatment in 18% NaOH for 24 hour showed considerable enhancementin properties of the composites [28]. It was noted that the strength of these composites almost doubled when fibres were treated with NaOH for 80-90 hours, but decreased for longer periods.Effects of mercerization and acetylation on rubber reinforcement was studied by Martins and Joekes [29].
2. EXPERIMENTAL Isolation of Starch

Starch extraction is carried out by using tap water. Freshly harvested tubers were washed and peeled. The tuber was cut into small pieces and washed again. Approximately 1 kg sample of the pieces were washed and steeped in water for 2-3 min. The pieces were disintegrated in a Remi mixer for 1 min at low speed in the presence of water cover the pieces. The pulp is allowed to remain in the solution for approximately 2 hour before filtration is carried out successively through a clean cloth. The filtrate is allowed to settle for 48 hours. The liquid proportion is decanted to leave the starch as a cake. It is then collected, powdered and dried in an oven at 100° C. The starch, after drying was collected and stored in polythene bag [9-11].

Composite Preparation

Compounding

Table 1 show the formulations of mixes used in the present work. A, B, C, D and E represents mixes containing NBR and taro tuber starch with dicumyl peroxide as vulcanizing agent. Mix A is the gum sample. B, C, D and E represent mixes containing 5phr, 10phr, 15phr and 20phr of taro tuber starch respectively. The composites were prepared by using a laboratory two roll mixing mill. Initially NBR was masticated on the mill for 3minutes followed by the addition of the ingredients. The nip gap, mill roll speed ratio and the number of passes were kept the same for all the mixes. The samples were milled for constant time to disperse the in the matrix [12-14].

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В С F Е Α D Nitrile 100 100 100 100 100 100 Rubber[NBR] DCP* 1.5 1.5 1.5 1.5 1.5 1.5 Starch 0 5 10 15 20 25

Table 1. Formulation of NBR composites [phr*]

*phr:parts per hundred rubber

Swelling Coefficient

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Swelling coefficient is index showing the extent to which the sample swells. The reinforced composites were swollen in the suitable solvent at room temperature and the swelling coefficient was evaluated by the equation [28].

 $\alpha = \frac{(w2 - w1)}{w1} * 1/\rho s$

where w2 is the swollen weight of the sample.

w 1 is the intial weight of the sample.

 $\rho_{\rm e}$ is the density of the solvent

Characterization

The changes in the structural properties that takes place to NBR up on the incorporation of starch was analysed by Fourier Transform Infrared Spectroscopy. ASTM D624 Type C specimens are used for measurement of tear strength. A universal testing machine (UTM) is used to test the tensile stress and compressive strength of materials. Tensile properties of different mixes were examined using Shimadzu Universal Testing Machine at crosshead speed of 50mm/min. Vulcanization of the mixes was done at 150°C using a hydraulic press having electrically heated plate to their respective cure times as obtained from the rheographs. The cure characteristics of

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the mixes were measured by using a Gottfert lastograph rheometer. Two roll mill is used to homogenize polymer materials.

3. RESULTS AND DISCUSSION Mechanical properties NBR- Starch Composites

The mechanical properties are determined by stretching standard test pieces at a constant rate using a tensile machine. Mechanical properties of NBR starch composite is shown in table 2.

Properties	Starch loading (phr)					
	0	5	15	20	25	
Tensile Strength N/mm2	1.1486	1.3851	1.4474	1.6024	1.5184	
Tear strength KN/m	6.7885	8.1443	8.6847	9.8069	9.9041	
Modulus at 10% elongation	0.6274	0.7086	0.8567	0.8844	1.0314	
Elongation at break %	536.849	478.516	387.960	305.182	254.627	

Table 2 Mechanical properties of NBR- starch composite at various starch loading

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Tensile strength

Tensile strength is the maximum stress that a material can withstand while being stretched or pulled before failing or breaking. It is the load required to rupture a standard test piece by stretching at a constant rate. The variation of tensile values with the loading of seed starch is shown in Figure 1. It can be seen that as the amount of wild taro starch increased in the composite, the tensile strength also increases and attains a highest value at starch loading of 20 phr. Tensile strength decreases on further increase of starch loading due to agglomeration. The reinforcing effect of starch is reflected.



Figure 1 Variation of Tensile strength with starch loading

Tear Strength

Tear resistance or tear strength is a measure of how well a material resists the growth of any cuts when under tension. Variation of tear strength with loading of starch is

ChemY Journal for Young Researchers in Chemistry shown in Figure 2. Tear strength of gum sample is 6.7885. When starch loading increases tear strength also increases. It increases up to 9.9041 at starch loading of 25 phr. It shows that there is a good action between starch and NBR matrix.



Figure 2 Variation of Tear Strength with starch loading

Modulus at 100% elongation break

Modulus is also known as elastic modulus, which is a mechanical property of linear elastic solid materials. It defines the relationship between stress (force per unit area) and strain (proportional deformation) in a mate.Modulus is measured as the force per unit area





Figure 3 Variation of modulus at 100% elongation with starch loading

Elongation at break

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Elongation is defined as the extension produced by force applied to standard specimen. Ultimate elongation is the elongation at the time of rupture and is determined simultaneously with the tensile strength test. Variation of elongation at break with loading of starch is shown in Figure 4. From the data we can understand that, addition of starch increases elongation at break decreases







Swelling Coefficient

Swelling coefficient is index showing the extent to which the sample swells. The reinforced composites were swollen in the suitable solvent at room temperature. In the case of DMF, Acetonitrile and Petrol swelling coefficient decreases with increase in the starch loading. Table 3 shows the swelling coefficient in DMF, acetonitrile and petrol. Figure 5 shows the variation of swelling coefficient with starch loading in these solvents.

	Samples In				
	DMF	ACETO	PETROL		
Filler loading [phr]		NITRILE			
0	1.900	1.0978	0.6687		
5	1.558	0.9790	0.6313		
15	1.4583	0.9400	0.6092		
20	1.3548	0.9047	0.5828		
25	1.349	0.7940	0.5626		

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Figure 5 Variation of swelling coefficient with starch loading

Structural Properties

FTIR spectroscopy revealed the structural changes in the composite from the constituents of the composite. Figure 6, 7 and 8 shows FTIR spectrum of Gum sample, starch and composite ontaining 25 phr starch respectively.



Figure 7 FTIR spectrum of Starch

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Figure 8 FTIR spectrum of sample T₂₅.

On comparing the IR spectrum of composite (figure 8) with that of Gum sample (figure 6), We can see that some of the peaks present in NBR are present in the composite. There are peaks at 2918.30 and 2848.86 cm⁻¹which are in between 3000-2840 cm.⁻¹This corresponds to C-H stretching in alkanes. This peak is characteristic peak in the acrylonitrile butadiene rubber. A peak in between 2260-2240 cm⁻¹is presents which corresponding to C-N stretching due to presence of -C=N which is also a characteristic peak present in NBR. In FTIR spectrum of starch (figure 7) there are peaks between 1000-1300 cm⁻¹which corresponds to C-O stretching in ether groups. A peak at 1105 cm⁻¹ is indicating presence of dialkyl ether group. A broad absorption peak between 3500-3000 cm⁻¹ reveals the presence of OH group (stretching vibrations). A peak at 3647.39 cm⁻¹ is characteristic of free OH group. peaks corresponding to alcoholic CO stretching is present between 1260-1000 cm⁻¹.

On analyzing the FTIR spectrum of composite (figure 8) we can see some of the characteristic peaks of starch are present. Peaks between 1000 and 1300 cm⁻¹ is present which is a structural feature of starch. Peaks around 1000 cm⁻¹ are visible both in the

ChemY Journal for Young Researchers in Chemistry spectrum of composite and starch which is due to the presence of C-OH group (bending vibrations). From the FTIR study we can see that the composite contains both the structural features of starch and NBR. Hence we can conclude that a heterogeneous system has formed between starch and NBR.

4. CONCLUSIONS

NBR is the most commonly used synthetic rubber due to its high oil resistivity. It is used in the automotive and aeronautical industries to make fuel and oil handling hoses, seals and gaskets. The oil resistant power of NBR withstands a range of applications. In the present work, we have made composites of NBR filled with varying amount of Colocasiaesculenta tuber starch and studied the mechanical properties and swelling characteristics of composites. The properties like tensile strength, elongation at break, modulus etc. were studied using universal testing machine.

The studies show that with increase in the loading of Colocasiaesculenta tuber starch in NBR, the tensile strength increases progressively up to 20 phr loading. Tensile strength increased due to the increase in interaction between NBR matrix and the filler. The swelling characteristics of NBR starch composites have been studied using DMF, acetonitrile and petrol as the solvents. With these solvents swelling coefficient is decreased with the filler loading. That is the solvent resistivity increased with the filler loading.

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Preparation and characterization of graphene–manganese oxide Nanocomposites Asa P S¹*and Reshma R¹

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ABSTRACT

Graphene is an amazing material, made of a single layer of carbon atoms that are bonded together in a repeating pattern of hexagons. Graphene exhibits many unusual and useful property such as a large theoretical surface area, flexibility, high values of young's modulus, excellent thermal conductivity and intrinsic mobility. It has attracted tremendous interest in different areas in recent year including biomedicine, catalysis, photochemistry etc. A composite is a material having two or more distinct constituent or phases. Graphene nanocomposites at very low loading show substantial enhancements in their multifunctional aspects, compared to conventional composites and their materials. High quality grapene material, composite with several structures material organic frameworks, polymer, biomaterials, organic crystals and inorganic crystals and inorganic nanostructures are used in various emerging fields. In this work graphene oxide was prepared by modified Hummer's method. Using that graphene oxide, graphene manganese oxide nanocomposite was prepared through sonication method. The nanocomposite was characterized using XRD and SEM.

Keywords: graphene oxide; manganese oxide; nanocomposites

2. INTRODUCTION

A composite is a material having two or more distinct constituent or phases. The consitutent phase has different properties and hence the composite properties are noticably different from the properties of the constituent. Composite contain two or more nanosized fillers.

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Journal for Young Researchers in Chemistry Graphene nanocomposites at very low loading show substantial enhancements in their multifunctional aspects, compared to conventional composites and their materials. This not only makes the material lighter with simple processing, but also makes it stronger for various multifunctional applications. The remarkable properties of graphene are able to improve the physicochemical qualities of the host matrix upon distribution. This helps in strengthening and increasing the interfacial bonds between the layers of graphene and the host matrix. Epoxy-based few-layer graphene nanocomposites show fascinating properties for the electronics industry, ideal for development of thermal-interface-based materials.

Graphene has a great number of applications encompassing engineering, electronics, medicine, energy, industrial, household design, and many more. In recent years dealt with electronic/sensor-oriented applications, to generalize the broad applications of graphene and graphene-based nanocomposite into their respective disciplines. Extensively reviewed the biomedical applications of graphene including drug delivery, gene delivery, cancer therapy, biosensing and bioimaging, GO-based antibacterial materials, and scaffolds for tissue/cell culturing. Graphene and graphene-based materials and their applications in the field of memory devices for electronics, ranging from electrochemical sensors to instrumentation, energy storage and conversion, catalysis etc

V .Anitha Kumary and T.E. Marry Nancy worked on synergic catalytic effectof grapheme/nickel hydroxide composite for the simultaneous electrochemical determination of ascorbic acid, dopamine and uric acid. Here novel solargraphene –nickel hydroxide modified glassy carbon electrode wasdeveloped and used for the simultaneous detection of ascorbic acid (AA), dopamine (DA) and uric acid(UA). The sensor exhibited appreciable electrocatalytic effect for the simultaneous detection of lower concentration of the analytes compared to solar graphene modified glassy carbon electrode. Guohai Yang et al. reported Pt-Au / nitrogen doped graphene nano composite for enhanced electrochemical activities. The Pt-Au /N-G nanocomposites exhibited excellent electrocatalytic activity and stability

towards the methanol oxidation reaction with the highest capability observed for a Pt/Au atomic ratio of 3/1.[18] T.E.Marry Nancy et.al.prepared graphene Nickel nickel oxide composites were via solar exfoliation of GO Ni –acetate precursor and used as non enzymatic Glucose sensor using glassy carbon electrode modified with the composite. A glassy carbon electrode (GCE) modified with solar graphene (sG), was used for resolving the voltametric signals of ascorbic acid (AA), dopamine (DA) and uric acid (UA) by V Anitha Kumary et.al.

Zaixing jiang et.al. worked on the topic High efficiency H_2S gas sensor material; paper like Fe_2O_3 / nano sheets and structural alignment dependency of device efficiency. In the present work Fe_2O_3 /graphene was synthesized successfully by a super critical CO_2 assisted thermal method and further made into paper-like nano sheets by directed flow , vertical assembly of individual Fe_2O_3 / graphene nano sheets under a controlled magnetic field. Lin-Fei Zhang et.al. studied on multi functional $Co_{0.85}$ Se/ graphene hybrid nanosheet . Xiyiuan Fan et al. studied on magnetic Fe_3O_4 - graphene composite as targeted drug nano carriers for p H activated release. Here nano carrier was synthesized by covalently attaching modified Fe_2O_4 nano particles onto water soluble graphene sheets via the formation of an amide bond with the aid of 1-ethyl -3-(3-dimethyl aminopropyl0 carbodimide.

Robert.J.Young et .al studied on the topic of mechanics of graphene nano composite . Gil concalves , Paula A. A.P.Marques et.al . studied on the topic Surface Modification of graphene nano sheets with Gold nano particles ; The role of oxygen moieties at graphene surface on Gold nucleation and Growth . Gold nano particles are effectively grown at functionalized graphene surfaces using a simple chemical method in aqueous medium . There studies indicate that the graphene / gold nanocomposites are potential substrates for SERS (Surface Enhanced Raman Scattering) in particular for single gold particles SERS studies . Mohammad A. Rafiee, Javad Rafiee et.al. worked on

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the topic Enhanced Mechanical Properties of Nancomposites at Low Graphene content the results indicate that graphene plates significantly out-perform carbon nanotube additives.

Super capacitors (also known as electrochemical capacitors or Ultra capacitors) have drawn tremendous attention as an energy storage device for their high power density, good rate performance and long cycling life. They are playing an increasingly important role in various applications ranging from portable electronics to hybrid electric vehicle. They are usually defined into electrochemical double layer capacitors (EDLCs) and pseudo-capacitors based on their different energy storage mechanisms. Generally, the carbon based porous materials, including graphene, activated carbon and carbon nanotubes (CNTs) that offer high surface areas and readily accessible mesopores are widely used for EDLCs, where the charge storage process is non-Faradic and energy storage is electrostatic. At the same time, the capacitance of the pseudo capacitors is mainly from Faradic redox reaction. Their electrode materials generally involve various metal oxides and conductive polymers. In recent years, transition metal oxides have been drawn extensive research attentions for pseudo-capacitors since they could provide higher capacitance than carbon materials and longer cycle life than conductive polymers. Among transition metal oxides, Mn₃O₄ is one of the mostpromising electrode materials for commercial supercapacitors due to their good efficiency, better stability, high abundance, low cost, for supercapacitors, and they turned out to be a great break through for enhancing electronic performance of pure metal oxides. Wang et al. synthesized GM composites with MnO2 organosol and graphene, of which the capacitance was 175 F g-1 in 1 M Na2SO4 and 256 F g-1 in 6 M KOH. But the complicated synthesis processes greatly limited its commercial application. GM composites via one-step solvothermal process exhibited a specific capacitance of 147 F g-1. Noting that the utilization of toxic and oxidative dimethyl sulfoxide (DMSO) as solvent made it not environment friendly and probably could result in incomplete reduction of graphite oxide to

graphene. In a latest report, Mn3O4 nanorods were effectively deposited on graphene sheets. However, the composite only delivered a low capacitance of 121 F g⁻¹ at 0.5 A g-1. Which can be explained by the fact that those nanorods are just an intermediate product of Mn3O4 and unstable, then the composite presented an inferior electrochemical performance [20].Consequently, it is still a big challenge to develop a simple and rapid approach to synthesize better performance Mn3O4/grapheme (GM) composites. It is known that the electrochemical propertie of the composites are greatly depended on the conditions of formed graphene, such as the low defects, well distribution and so on. Here in, Mn₃O₄ nanoparticles are homogeneously embedded into the graphene nanosheets via a simple solvothermal process which need not to reduce graphite oxide to graphene at first and no and toxic organic solvent is used. However, the GM composites exhibit much better electrochemical properties in 1 mol L–1 Na2SO4 solution in comparison with those reported, which is probably due to the as-formed graphene sheets in the composites have lower defects, better distribution and highly reduction, and the detail reasons will be discussed in follow presentation.

2.EXPERIMENTAL

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Preparation of Graphene Oxide

Graphene Oxide (GO) was synthesized by the modified Hummer's method . 1g of graphite powder was mixed with 25 mL of 98% H₂SO4, and 1 g sodium nitrate in an ice bath for 3 hours followed by addition of 5 g potassium permanganate, the reaction was kept at 30 °C under vigorous stirring for 3 hours followed by slow addition of 100 ml of water; the resulting solution was placed at 80-90 °C for 2 hours, then the reaction treated with H₂O₂ (35%, 10 mL), finally filtered and washed thoroughly with several times with hot water. Graphene oxide is reduced by solar exfoliation method.

Manganese oxide/GO nano composite

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All reagents used in this experiment were of analytical gradewithout further purification. In the first step, graphite oxide (GO) was obtained from natural graphite (Sigma–Aldrich) by a modified Hummers method, and a 0.5 ml–1 homogeneous GO suspension was prepared by ultrasonication of 13.5 mg GO in 27 ml 9:1 ethanol/H2O mixed solvent for 3 h. Then 0.0027 mol of Mn(AC)2·4H2O was dissolved in the GO suspension by stirring. Finally, the resulting solution was transferred into a 30 ml Teflon lined stainless steel autoclave, and treated at 180 °C for 11 h. After the reaction, the autoclave was allowed to cool to room temperature. The precipitate was washed with deionized water and alcohol several times, then freeze dried for 24 h, and the final product was denoted as sample-0.5 mg/ml GO. In other two experiments, samples were synthesized by 1.0 mg/ml and 2.0 mg/ml GO suspension with same conditions of sample-0.5 mg/ml GO. For comparison, pure Mn3O4 and reduced graphite oxide (RGO) were prepared by the similar method

3. RESULTS AND DISCUSSSION

GO is prepared from graphite powder by modified Hummer's method./Graphene were prapared by sonicating $Mn(Ac)_24H_2O$ with prepared GO. Solvo thermal process ensure the formation of nano composites. Mn_3O_4 nano particles are homogenously embedded in to the graphene nano sheets. The prapared sample was characterised by XRD and SEM.

As seen in XRD, the peak at 11.7^{0} (2 θ) is indexed to the graphitic plane (001) of graphene nano sheets, all other peaks of GMn composite can be indexed to Mn₃O₄ for based on their good agreement with JCPDS card (No.24-0734). The pattern of reduced RGO contains a chracteristic peak (001) at 11.7 indicating GO resembled to form graphite like material after solvothermal treatment.

As for the graphene sheets formed in GMn composite, 2 reasons are suggested as follows: firstly high temperature during the solvo thermal treatment leads to reduction of

various oxygen containing functonal groups on GO, secondly the oxidation process of Mn^{2+} to Mn_3O_4 is beneficial to the reduction of GO to some extend. In addition, ethanol/H₂O mixed solvent with volume ratio of 9:1 reduces a homogeneous suspension of graphene oxide sheet. Thus resulting in well disstribution of graphene sheets in composites. As an application it can be further used as an ideal conductive matrix for enhancing the electrochemical performance of Mn_3O_4 , and GMn composite is a promising electrode material for super capacitors.



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XRD of pure Mn₃O₄



XRD of 0.2 GMn

The typical SEM image of sample 0.1 mg/Mn GO, Sample – 0.2mg/Mn GO as observed, Mn_3O_4 nano particles are densely dispersed on the graphene nano sheets. The multi layer structure and smooth surface of graphene nano sheets is more clearly seen.



SEM images of 0.1 GMn



SEM images of 0.2 GMn

From SEM EDAX of prepared Mn_3O_4/RGO composite, it is found to be composed of less impurities, and the amount of Mn is found to be comparitively high in the composite.



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Journal for Young Researchers in Chemistry SEM EDAX of 0.1 GMn

4. CONCLUSIONS

It is still a big challenge to develop a simple and rapid approach to synthesise better performance Mn_3O_4 /graphene (GO) c omposites,here GO is prepared from graphite powder by modified Hummer's method./Graphene were prapared by sonicating $Mn(Ac)_24H_2O$ with prepared GO.Solvo thermal process ensure the formation of nano composites. Mn_3O_4 nano particles are homogenously embedded in to the graphene nano sheets.The prapared sample was characterised by XRD and SEM. It can be used as an ideal conductive matrix for enhancing the electro chemical performance of Mn_3O_4 , and GMn composite is a promising electrod material for super capacitors.

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Synthesis of Iron Oxide Nano Structures and their Characterisation Ajitha S^{1*} and Vyshna V²

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ABSTRACT

Synthesis of iron oxides magnetite in the nano range and nano composites of iron oxide magnetite for various applications has been an active and challenging area of research during the last two decades. Several researchers have prepared magnetite with different properties and particle size.Still synthesis conditions need to be optimized for specific properties of pure magnetite with nanosize. The processes include careful choice of pH, concentration of the reactants, temperature, method of mixing, and rate of oxidation. The size and shape of the nanoparticles can be tailored with relative success by adjusting pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates, and nitrates), or the Fe(II/Fe(III) concentration ratio. In this paper we aim to synthesize magnetite from a mixture of Ferrous and ferric salts using poly saccharides like pectin, starch and cellulose as templates. The properties of magnetite before and after calcination are to be compared using several characterization techniques. The material so synthesized can be tested for its optical, magnetic, sorption and catalytic properties.

Keywords: iron oxides magnetite; poly saccharides; magnetic properties

1. INTRODUCTION

Nano materials of transition metal oxides have great attention from researchers in various fields due to their various technological applications. Among them

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nano crystalline iron oxide have an excellent attention due to its fascinating properties and its application such as catalysts, dye, sorbents, pigments, coatings, flocculants, gas sensors, ion exchangers and for lubrication , magnetic recording , magnetic data storage devices, and inks for xerography, magnetic resonance imaging , waste water treatment, bio separation and medicine. Cancer diagnosis, contrasting agent. These medical applications require superparamagnetic magnetite with particles size smaller than 20nm. Below a critical size, Fe₂0₃ nano particles can be used for applications like transparent iron oxide pigments, due to their durality, shade, UV adsorption control of the preparation process of these types of iron oxide pigments results in the formation of particles with very small size.

Iron oxide is a heterogeneous catalyst. The catalyst may be homogeneous or heterogeneous. Heterogeneous catalysis refers to the form of catalysis where phase of the catalyst differs from that of the reactants. Phases not only to solids, liquid, gas, but also immiscible liquids. Eg: oil and water. Magnetic nanoparticles now become most important in in vitro diagnostics, drug delivery system etc. Magnetic nanoparticles include the Fe₂0₃ magnetite Fe₂0₄, ferromagnetic, superparamagnetic when the size is less than 15nm. α - Fe₂0₃, a hematite, weakly ferromagnetic or anti ferromagnetic, γ - Fe₂0₃, maghemite, and it is a ferromagnetic substance. Fe0, wustite, antiferromagnetic one. Magnetite and maghemite is generally known and promising because of their biocompatibility [1].

Iron oxides are one of the most important transition metal oxides because of its technological importance. Sixteen pure phases of iron oxides, they include oxides, hydroxides and oxy- hydroxides. Oxides of iron are in 3 types, they are 1) iron (II) oxide, Fe0 (wustite). 2) Iron (II,III) oxide, Fe₃0₄ (magnetite). 3) Iron (III) 0xide (Fe₂0₃), it again sub divided into four type; they are α -phase, hematite(α -Fe₂0₃), β phase,(β - Fe₂0₃), γ -

phase,maghemite (γ -Fe₂O₃), epsilon phase (ϵ - Fe₂O₃). Hydroxides of iron are two types. 1) Iron(II) hydroxide (Fe (0H)₂). 2) Iron (III) hydroxide (Fe(0H)₃). Oxy-hydroxides include goethite (α -FeOOH), akaganeitr (β -FeOOH), lepidocrocite (γ -FeOOH), feroxyhyte (δ -FeOOH), ferrihydrite (Fe₃HO₈.4H₂O), High pressure FeOOH, green rust (FexFey (OH)3x+2y-z(A-)z; where A is Cl- or 0.5 SO₄ (2-), Schwertmannite (ideally Fe₈O₈(OH)₆(SO).nH₂O). Characteristics of these oxide compounds include mostly the trivalent state of iron, low solubility and brilliant colures. All the iron oxides are crystalline in nature except schwertmannite and ferrihydrite which are poorly crystalline.

Some crystalline phases of iron oxides are not very stable and can convert into others. Much work applied to convert akaganeite to hematite and magnetite phase give application in catalysis and gas sensing applications. Magnetite nanorods can be produced by the conversion of iron oxy hydroxides into hematite by heating above 400°c in air, or magnetite in a mixture of Ar gas and H₂. The iron oxy hydroxides can directly convert into magnetite by using hydrazine as a reducing agent. Here directly convert akaganeite into magnetite rather than using hematite as an intermediate. By using hydrazine, iron(III) ions can be reduced to iron (II). The change in coordination number to the iron atom will therefore transfer from Fe-OH to Fe-O by dehydration. The structure change is due to the loss of water molecule, it will create pores and holes within the framework. Continuous reaction with hydrazine will cause damage in the one dimensional nano structure. However this damaging is not seen in hematite because of its thermally stable structure under considered conditions. This method could be used for a controlled conversion of akaganeite to magnetite nano structures without high temperature treatment. These porous materials give applications in electronic and magnetic areas.[2]

The synthesis of stable magnetic nanoparticles using stabilizing agents like pectin, sucrose, starch, which may be simple molecules or polymeric. Among these

ChemY Journal for Young Researchers in Chemistry agents, biopolymers are the of great interest due to their biocompatibility and biodegradability. In past, templates like aluminium oxide, carbon nano tubes, surfactants, polymer fibers and egg shell membranes have been used. In presence of these types of templates, a careful removal of templates from particles should apply through selective conditions.

Stabilization of magnetite nanoparticles with a polymer is achieved in two ways; either by synthesis of magnetite nanoparticles in presence of the polymer or the magnetite nanoparticle are synthesized in one reaction and then coated with polymer in another different reaction. Synthetic polymers, such as polyethylene glycol, have been used to stabilize magnetite nanoparticles. Stabilization of magnetite nanoparticles by coating them with non-toxic polymers helps to reduce the toxicity of magnetite in living systems. Natural polymers are generally used to coat magnetite nanoparticles, because they are non-toxic and it is a good green chemistry approach.

Pectin is a complex polysaccharide that contains 1, 4-linked α –Dgalacturonic acid [3]. The complex structure of pectin depends on its source and the extraction process and its properties depend on its degree of esterification. Pectin used in food, cosmetics, pharmaceutical and biomedical industries because of their gel forming nature. Pectin is bioactive, biocompatible and biodegradable. It contains the hydroxyl (-0H) functional group which increases its chemical properties and COOH group which permit direct bonding to Fe₃0₄.

Templating is commonly employed for the controlled production of materials with ordered structure having desired properties. Starch and sucrose also used for templating process. Starch is a complex carbohydrate which is insoluble in water. It is used by plants as a way to store excess glucose [4]. It is used composed of glucose of polymers of amylase and amylopectin. The ratio of these is 30:70 or 20:80. Usually the amylopectin was found to be greater in amounts than amylase.

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Sucrose, or table sugar, is a common type of sugar made of glucose and fructose. It is a disaccharide and a simple carbohydrate. Sucrose is a crystal at room temperature that can be caramelized by heating. Sucrose is found naturally in foods, but it also added to processed food for preservation and flavor. To make sucrose, manufacturers extract it from sugarcane or sugar beets. Sucrose provides energy, but when eaten regularly and frequently it can put you at risk for diabetes heart disease, and cancer. Polymer encapsulated iron oxide nanoparticles are highly efficient for Fenton catalysis

Magnetite nanoparticles (Fe₃0₄) represent the most promising material in medical applications. To this magnetite nanoparticles have been synthesized using co precipitation in the presence of different bases such as Na0H, NH₄0H. Magnetite shows characteristics of superparamagnetism at room temperature and a saturation magnetization value depending on both the crystal size and the degree of agglomeration of individual nanoparticles. Such agglomeration appears to be responsible for the formation of mesoporous structures, which are affected by the pH, the nature of alkali, the slow or fast addition of alkaline solution and drying nature of synthesized powders.

Magnetite absorbs oxygen to form maghemite, which in turn, loses its susceptibility with time. The nano sized particles form less stable system. In the case of magnetic fields, to prevent agglomeration, the surface coating of particles is essential. They have stable colloidal dispersion in wide range of pH. [5]. The absorption layer can also enhance the resistance against oxidation of magnetite into maghmite (γ - Fe₂0₃).

The application of magnetite nanoparticles depend on the preparation method, which in turn influence particle size,shape,size distribution,agglomeration and the surface chemistry of the material.

The magnetite can be synthesized by various methods, including ultrasound irradiation, sol-gel, thermal decomposition and co-precipitation. Thermal decomposition and co-precipitation is most commonly used synthesis. Co-precipitation based on the

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hydrolysis of a mixture of Fe (2+) and Fe (3+) ions are used to fix the A to B molar ratio in the inverse spinel structure. Generally, the reaction is performed under an inert atmosphere using degassed solution to avoid uncontrollable oxidation of Fe(2+) into Fe(3+). In these type of preparations, Fe(2+) and Fe(3+) ions are generally precipitated in alkaline solutions, such as NaOH,KoH,NH40H etc. In most cases, the syntheses are performed at 70-80 °C or higher temperature. The effects of mixing methods, stirring rate, digest time, initial pH and presence or absence of magnetic field. On particles size, morphology and resulting magnetic properties were also discussed. Co-precipitation methods performed under various precipitation conditions were also conducted. Eg: when only Fe (2+) was used for precipitation, then H₂O₂ or NaNO₂ were adopted to partially oxidize Fe (2+) into Fe (3+) in the precipitation product. When only Fe (3+) was used for precipitation, then Na₂SO₃ partially reduces ferric to ferrous ion in the precipitation product. Some precipitation methods are employed in the presence of polymers, including PVA (poly vinyl alcohol), and dextran to prevent both agglomeration and oxidation of the nanoparticles. Sucrose, pectin, starch are also used as polymers. All these Co precipitation methods are comparatively complex and require strict control of precipitation conditions. The incomplete crystallization of magnetite, irregular morphologies of magnetite particles and the magneto static interactions are responsible for the agglomerisation of magnetite particles. Many of the Co precipitation methods are performed at elevated temperature. To evaluate the effect of temperature on the synthesis of magnetite, computer software developed by OLI systems, Inc (Morris Plans, NI, USA) was also used.

2. EXPERIMENTAL

Synthesis of Iron Oxide –Pectin Coated Nanoparticles

Iron oxide –pectin nanoparticles can be prepared by co precipitation method. Dissolve 1.25g of pectin in 250ml distilled water. Different concentration (%w/v) of pectin solution can be prepared. A continuous agitation is required to the pectin solution. The

reaction flask was deoxygenated for 30 minutes and then adds 50ml solution of 2:1 molar ratio of ferric and ferrous ions drop wisely. The reaction generated on the additional of iron salts. Then base was added drop wise till the solution become black. The black colour indicates the formation of magnetite. The black residue obtained is dried and characterized (FOPB). The dry sample calcinated at 500°c. The calcinated sample also characterized (FOPA).

Synthesis of Cellulose Coated Iron Oxide Nanoparticle

Cellulose was treated with 2:1 molar ratio of ferric and ferric mixture of solution, a suspension was produced. The reconstituted material was left for 30 minutes to absorb ferrite solution. After 30 minutes this suspension was treated with30 w % NH₃ solution and was vigorously stirred for 20 min. the reconstituted material was filtrated and wash with distillated water. Finished product should have a reconstituted material was filtrated and washed with distillate water. The finished product should have a neutral Ph. Such modified cellulose was dried for 3 hours at 105° c. Fe₃O₄ was produced by the following reaction.

$FeCl_+2FeCl_3+8NH_4OH \rightarrow Fe_3O_4 \downarrow + NH_4Cl + 4H_2O$

The result was a black suspension of a mixture of cellulose and magnetite. The black residue obtained is dried and characterized (FOCB). The dry sample calcinated at 500°c. The calcinated sample also characterized (FOCA).

Synthesis of Starch Coated Iron Oxide Nanoparticles

This method is similar to the preparation of pectin coated iron oxide nanoparticles. ie, co precipitation is the technique used here. Dissolve 1.25g of starch in 250ml of water. Continuous agitation is required for the starch solution. The reaction medium deoxygenated for 30 minutes. 50ml solution of a 2:1 molar ratio of ferric and ferrous ions added drop wise into the starch solution under stirring. The reaction medium further deoxygenated for an additional 20 minutes. Brown colour is formed on the addition of

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ChemY Journal for Young Researchers in Chemistry iron salts. Base was also added drop wise until a black residue is formed. It dried and characterized (FOSTB). The dry sample calcinated at 500°c in a furnace and then characterized (FOSTA).

Characterization

Characterization is of great important part of all research studies, since it deals with different type of materials. The important aspect of characterization is chemical composition, compositional homogeneity; structure identification and analysis of defects and impurities influence the properties of materials. X-ray diffusion (XRD), FTIR (Fourier transformed infra red), SEM (scanning electron microscopy), TEM (tunneling electron microscopy), UV-Visible spectroscopy are some of the characterization techniques used.

3. RESULTS AND DISCUSSION

XRD of all the samples exhibited peaks characteristic of magnetite phase. But the sample contains large amount of alpha-Fe₂O₃ as impurity phase, along with Fe₃O₄.



Fig.1 a) X-ray diffraction pattern of the prepared pectin templated Fe₃O₄ particles



Fig.1 b) X-ray diffraction pattern of the prepared starch templated Fe_3O_4 particles after calcination(FOSTA)

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after calcination(FOPA)





Fig.1d



5	1 1 1		
Sample	Interplannar spacing	Lattice parameter(a)	Crystallite size Dhkl
	dhkl		from xrd
FOPA	2.52855	8.38	23.05
FOSTA	2.52044	8.3593	11.2
FOPB	2.52044	8.3593	11.45
FOSTB	2.523356	8.369	18.044

Table 1.Crystallite size of prepared samples

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From **Fig.1 b**), it has been seen that the intensity of the diffraction pattern is slightly different from standard. Here the particle size is 11.2The lattice parameter 'a' and interplannar spacing *dhkl* are 8.964 and 2.70298 respectively. They are higher than the standard values reported for bulk magnetite.

From **Fig.1 c**), the reflections at $2\theta = 22.4^{\circ}$ corresponding to the crystalline part of cellulose. Then reflection at $2\theta = 32^{\circ}$ belongs to the hematite structure and $2\theta = 30$, 35.8 are typical for the magnetite and have an inverse cubic spinel structure. From the Scheerer equation, assuming ideal spherical shape the crystallite size was estimated to be 70 nm for magnetite phase.

In the FTIR spectrum (Figure 2) of the FOPA, the peaks at 3401cm-1 and 2923cm-1 represents secondary hydroxyl group and carboxylic hydroxyl groups. The peak at 1627cm-1 is a characteristic peak of pectin. The peak at 1096 cm-1 arises from the glycosidic bonds between two galacturonic sugars. From figure 8, the peaks are observed at 3356cm-1 and 2942 cm-1, represents secondary and carboxylic hydroxyl group. The peaks also observed at 1117 cm-1 is due the glycosidic bond.

From spectrum of FOSTA the peaks on 2922 cm-1 is due the carboxylic hydroxyl group and peaks on 1741 cm-1 is due the de-esterification of the polymeric chain. Peaks

Journal for Young Researchers in Chemistry also observed at 1386 and 1645 cm-1, they are due the stretching of COO-Fe linkage. In the spectrum of FOSTB(figure 10), the peaks observed at 2854 cm-1 maybe due the carboxylic hydroxyl group. The peaks at 1513 and 1386 cm-1 is due symmetric and asymmetric stretching of carboxylate -metal (COO-Fe) linkage.Peak at 1743 cm-1 is due the de-esterification of the polymeric chain.

In the spectrum of FOCB, the peaks observed at 3410cm-1 and 2990 cm-1 are due secondary and carboxylic hydroxyl groups and peak at 1448 cm-1 is due stretching of COO-Fe. From figure 12, the peaks are 1587 and 2359 cm-1. The former is due the stretching.



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Figure 2 FTIR spectrum of prepared samples

The morphology of the magnetite particles formed is examined by direct observation via high resolution transmission electron microscopy (Figure 3) for all the collected particles. The micrograph of Fe_3O_4 is given above. It is cleared that the tested

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particles are uniform in shape with a narrow size distribution and their particle sizes are 10.37 nm.



Figure 3 TEM images of the samples

The surface morphology of the selected samples analyzed using JSM -6390 electron microscope, they are presented below (Figure 3).



Figure 3a SEM images

Figure 3a shows the SEM images of pectin assisted synthesized magnetite after calcintion. All the pictures indicate that the particles have rod like morphology of almost uniform size. The picture also indicates the incomplete removal of pectin templates. Here SEM shows a uniform particles size.

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Figure 3b SEM images

SEM images of FOSTA (Figure 3b) shows a foam like structure indicating the retention of the polymeric coating around the oxide particle when NH₄OH is used as the precipitating agent in presence of starch.

Vibrating Sample Manetometer (Vsm)- Manetic Properties

When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed. It must be driven back to zero by a field in the opposite direction. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a hysteresis loop (see Figure 4). The lack of retraceability of the magnetization curve is the property called hysteresis and it is related to the existence of magnetic domains in the material. It is customary to plot the magnetization (M) of the sample as a function of magnetic field strength(H). Since H is the measure of the externally applied field which drives the magnetization. Remenence can be explained as when driving magnetic field drops to zero, the ferromagneticmaterial retains a considerable degree of magnetization. This is useful as magnetic memory device.

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Figure 4. (FOP2 = FOPA) Generic ferrimagnetic hysteresis loop

Coercivity is the intensity of the applied magnetic field required to reduce the magnetization of a given material to zero. in other words to coerce the material to surrender its magnetism. Retentivity is the capacity of an object to retain magnetism after the action of the action of the magnetizing force has ceased. The magnetic flux density increases from zero and reaches a maximum value. At this stage the material is said to be magnetically saturated.

Area of loop is a measure of the energy needed to magnetize and demagnetize each cycle. This is the enery required to do work against internal friction of the domains, this work done against friction, is dissipated as heat, it is called Hysteresis loss. Hard magnetic material like steel, cannot be easily magnetized or demagnetized, it have lare loop area as compared to soft magnetic material such as iron which can easily be

magnetized, so it have narrow hysteresis curves of small area to minimize the waste of energy



Figure 5 (FOPW=FOPB)

In the absence of hysteresis loop, it implies superparamagnetism. Here describes the magnetization of bulk magnetite as ferrimagnetic, generated by parallel alignment of magnetic moments on tetrahedral sites and anti-parallel alignment of ferrous and ferric spins on octahedral sites. Typical ferrimagnetic behavior exerts coercivity and remanence (retentivity) as displayed in Figure 4. As particle size is decreased, the amount of exchange-coupled spins resisting spontaneous magnetic reorientation is decreased, tending towards paramagnetic or superparamagnetic magnetization. Consequentially, decreasing magnetite particle size should demonstrate reduced ferrimagnetic and enhanced superparamagnetic behavior. Similarly, increasing temperatures enhance thermal energy particles and thus facilitate magnetic reorientation, or superparamagnetic magnetization. Coercivity slowly builds as magnetite particle diameter increases. Reduction in particle size also affects the Curie temperature, which defines the critical temperature where magnetization changes from ferrimagnetic to superparamagnetic.

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4. CONCLUSIONS

 Fe_3O_4 nano composites of magnetite are prepared by chemical coprecipitation in the presence of template pectin. The XRD pattern of pectin coated magnetite, the crystallite size and lattice parameters agreed with the standard values reported for magnetite. FTIR evidence of polysaccharide coatings on the metal oxide frame work. TEM of pectin template magnetite nano composite exhibited considerable reduction in the particle size. The SEM of pectin template magnetite indicated that the morphology of the sample could be controlled as rod shape. The results indicate that the pectin is a better template and under the given parameters chosen for synthesis.

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