Characterization of Alkali Catalyzed Synthesis of Polyvinyl Alcohol

A

Dissertation submitted

In the partial fulfillment of the requirements for the degree of

M.Sc. (Chemistry)

Submitted by
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(301502036)

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Tanisha

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Date: 07/08/17

Certificate

This is to certify that the dissertation entitled **"Characterization of Alkali Catalyzed Synthesis of Polyvinyl Alcohol"** being submitted by Ms. Tanisha in the partial fulfillment of requirement for the award of degree of the Master of Science in Chemistry and being submitted to the School of Chemistry and Biochemistry, Thapar University, Patiala, is an original work carried by her under our supervision. The work has reached the standard necessary for submission. The contents of this dissertation have not been submitted for the award of any other degree or diploma.

For

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Candidate's Declaration

I hereby declare that the work being presented in the dissertation entitled "**Characterization of Alkali Catalyzed Synthesis of Polyvinyl Alcohol**" in partial fulfillment of the requirements for the award of degree of Masters of Science in Chemistry and being submitted to School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January to July 2017, under the supervision of **Dr. Sanjeev Kumar Ahuja** and **Dr. Raj Kumar Arya**. I have not submitted the contents embodied in this dissertation for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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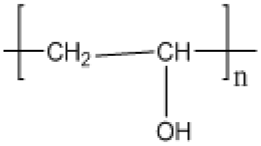
CHAPTER-1

INTRODUCTION

A monomer may be defined as the smallest unit of polymer. When these monomers are repeated over and over again by covalent or ionic bonds, they form a cluster called polymer. The number of monomers in polymer will decide the mass and size of the polymer. The physical properties, degree of polymerization, structures, thermal properties and viscoelasticity of polymers etc. are specified by number of monomers. Polymers on the basis of its monomer can be divided into two categories, i.e, copolymer and homopolymer. If in the polymeric chain, two different monomers are arranged in alternate manner, this polymer is known as a copolymer, for example rubbers made from styrene-butadiene. If, on the other hand, only a single unit of monomer is repeated one after another, this is called homopolymer. For example, polyvinyl alcohol.

1.1 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is a polymer synthesized from non-biodegradable precursor, but the obtained PVA is bio-degradable. It has the idealized formula $[CH_2CH(OH)]_n$. The chemical structure is given in Figure 1.1



$$\left[-CH_2-\underset{OH}{\underset{|}{CH}}-\right]_n$$

Figure 1.1 Structure of Polyvinyl Alcohol

1.1.1 Physical properties of PVA

Polyvinyl alcohol is in the form of solid granules, white or light yellow color flake. Its Boiling point is 228° C. It is crystalline in nature. It is a thermoplastic material having a glass transition temperature of 85°C. As, polyvinyl alcohol contains a large number of hydroxyl groups which causes intermolecular hydrogen bonding. Due to this H- bonding, polyvinyl alcohol has high melting point, 200°C. Also, it is hydrophilic in nature, it interact with water by H-bonding. It get solubilize in water at a temperature of 95°C when continuously dissolved by shaking. It hardly solubilize in organic solvents. It has a pH range 5.0-6.5 of 5% solution. Due to its film forming properties, it can be made to crosslink to form hydrogels. Polyvinyl alcohol grades depend upon molecular weight, particle crystal structure and dimensions of distribution.

1.1.2 Effect of molecular weight on physical properties

There is a significant effect of molecular weight on the physical properties of PVA [1]. On increasing the molecular weight the viscosity of the phase increases more quickly. Also, have high stability and aqueous solubility. Polyvinyl alcohol with high molecular weight has high tensile strength. But, in the case of low molecular weight, PVA has low viscosity, high solubility in organic solvents, high flexibility and high crystallinity.

1.1.3 Applications of PVA

- Although Polyvinyl alcohol is not natural polymer, it gets decomposed by organisms which mean it is biodegradable [2].
- It has various applications in industries, commercial, health, food sectors, etc. It is used in lacquers (Liquid substance used for coating of wood), surgical threads, food and paper coatings [3].
- PVA is a biodegradable and used in paper coating and textile sizing [4].
- Hydrophilic nature of PVA and its processing characteristics allow PVA blind with other polymers [5].
- It is preferred for nano-films and cross linked materials [6, 7].
- PVA is a polymer which decays naturally over aerobic and anaerobic conditions even after being petroleum based synthetic polymer [6].
- . PVA is non-toxic and harmless to living beings because it is noncarcinogenic.
- PVA supports for bone tissue engineering via selective laser sintering [8].
- Hydrogels are commonly the combination of biopolymers and PVA, which are used for wound dressing [9].

1.2 Chemistry behind the formation of polyvinyl alcohol

Preparation of PVA cannot obtain by direct polymerization of vinyl alcohol because polyvinyl alcohol cannot be found in stable form. As shown in Figure 1.2, vinyl alcohol exists in equilibrium with ketone which makes its polymerization impossible.

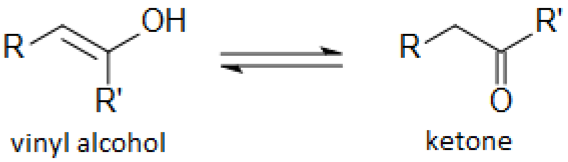


Figure 1.2. keto-enol tautomerism

The formation of polyvinyl acetate from vinyl acetate by radical polymerization is given by chemical reaction shown in Figure 1.3.

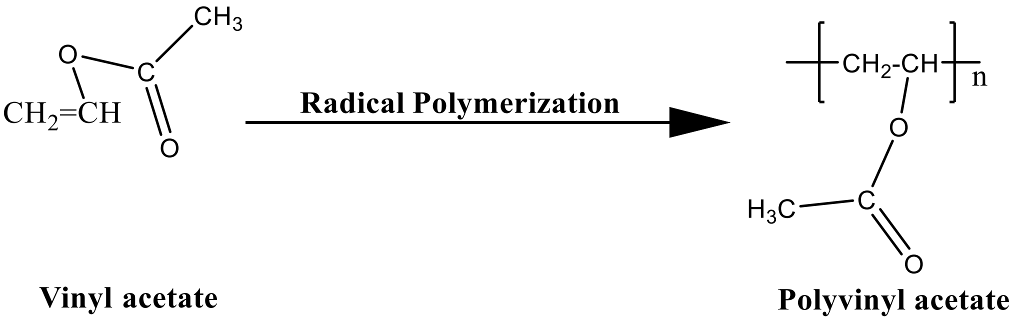


Figure 1.3. Free –radical polymerization

After radical polymerization of PVAc, next step is to convert it into PVA either by using acid or base catalyst. Alkaline hydrolysis in which sodium hydroxide and sodium methoxide are the important catalyst for alcoholysis, is carried out in the presence of alcohol such as methanol or ethanol. The conversion of PVAc into the polyvinyl alcohol (PVA) by alcoholysis using a base as catalyst is shown in Figure 1.4. In the reaction, polymeric structure formed is in atactic form. Polyvinyl alcohol was firstly prepared by Hermann and Haehnel in 1924 by alcoholysis of PVAc polymer in methanol with sodium hydroxide as catalyst [10].

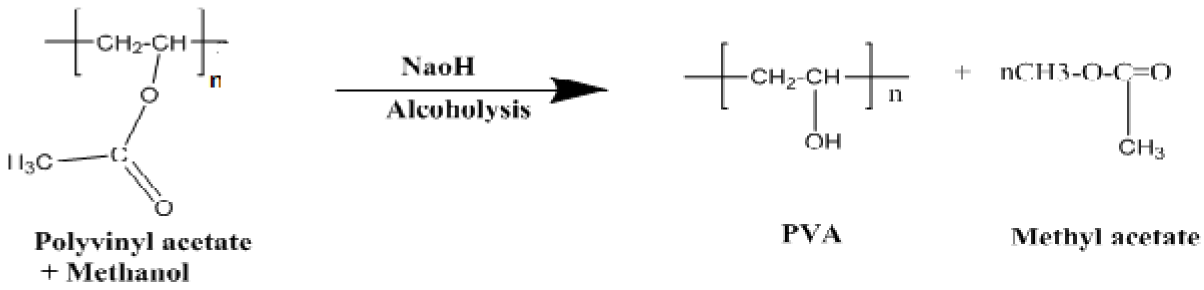


Figure 1.4. Conversion of polyvinyl acetate to polyvinyl alcohol using NaOH as a catalyst

PVA is also prepared by acidolysis [11]. In acidolysis, strong mineral acids like sulfuric or hydrochloric acid serve as catalyst. Using acid as catalyst to partially hydrolyze polyvinyl acetate to polyvinyl alcohol. The rate of hydrolysis by acid catalyst is much slower than using alkaline catalyst. The reaction of formation of PVA by using acid catalyst is shown in Figure 1.5. By using dry HCl which acts as catalyst with dry methanol for the alcoholysis of PVAc by maintaining temperature of -9°C.

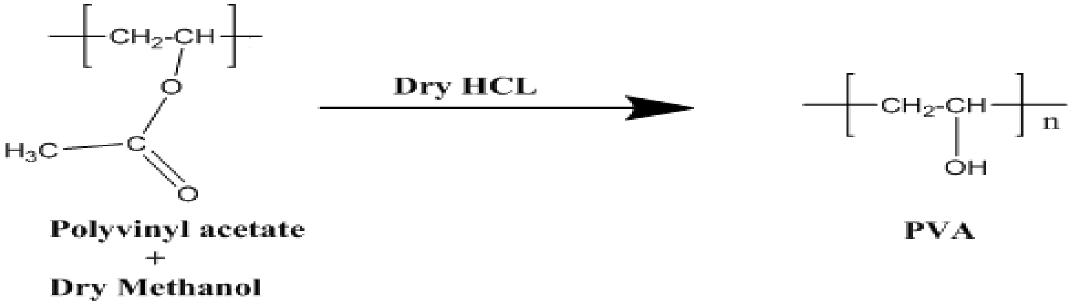


Figure 1.5. Conversion of polyvinyl acetate to polyvinyl alcohol using acid as a catalyst

1.3 Objective

The alkali catalyzed hydrolysis of PVAc is faster as compare to the acid catalyzed alcoholysis [11]. This would be helpful in the design of production units for PVA. The characterization of the prepared PVA for its porous nature is also important as has been reported for its possible applications in wound dressing and controlled drug delivery systems. The objective of the present work is to study characterization of alkali catalyzed synthesis of polyvinyl alcohol the kinetics of alkali catalyzed alcoholysis reaction of PVAc to form low cost PVA at different temperatures and catalyst loading and to characterize the polymer formed using NMR, SEM and TGA.

CHAPTER-2

REVIEW OF LITERATURE

PVA is derived from PVAc by partial or full hydroxyalation via acidolysis or alcoholysis. Polyvinyl alcohol is usually produced from polyvinyl acetate, through a continuous process. Polyvinyl alcohol has become very popular for various applications because of its –OH functional group which makes it water soluble in spite of having a high molecular weight. PVA has low protein adsorption characteristics, biocompatibility high water solubility, and chemical resistance and so, it is commonly used in medical devices. PVA is present with dyes in television tubes and other optical pigments. These days PVA of desired molecular weight is synthesized for specific applications.

2.1 Synthesis and characterization

Wang et al. [12] aimed to study the preparation of polyvinyl alcohol by the saponification of PVAc with degree of polymerization (DP) of 10,660 obtained at 10^{o}C. PVA with a DP of 8,270 was obtained. The initiator potassium per sulphate to monomer molar ratio was 1/2000. The agitation speed was maintained at 160 rpm. This reaction led to 90% conversion. In this, the rate of polymerization was affected by the initiator concentration, monomer concentration, reaction temperature and agitation speed. The order of reaction was 0.84 and 1.87 with respect to initiator concentration and monomer concentration, respectively. DP decreased on increasing initiator concentration and polymerization temperature, and DP increased as the monomer concentration was increased. By Fourier Transform Infrared Spectroscopy (FTIR), the structures of PVA and PVAc were studied. Absorption peaks were at 3330 cm^{-1} (OH), 1738 cm^{-1} ($C=O$), 1240 cm^{-1} ($C-O$), 2963 cm^{-1} (CH_3), and 2927 cm^{-1} (CH_2). The peak at 1738 cm^{-1} ($C=O$) got disappeared and was replaced with that of 3330 cm^{-1} (OH). Spectra of PVA and PVAc polymer after acetylation were identical. ^{1}H NMR of PVA was also analyzed.

Haweel and Ammar [10] studied the prepration of polyvinyl alcohol using polyvinyl acetate emulsion with sodium hydroxide as a catalyst. Polyvinyl acetate emulsion was coagulated by sodium sulphate solution. Then, the solid polyvinyl acetate was converted to polyvinyl alcohol using methanol while NaOH acted as a catalyst. Degree of hydrolysis was affected by varying the ratio of catalyst in the range of 0.01 – 0.06, reaction time from 20 to 90 min, and reaction temperature from 25-50^{o}C. The resulting polymer was analyzed and tested for volatile content and degree of hydrolysis using gravimetric, volumetric and viscometric methods. The degree of polymerization of PVA formed was increased with increase in degree of hydrolysis until 75% hydrolysis and decreased subsequently. Water solubility of PVA increased with increase in degree of hydrolysis until 87% hydrolysis and then decreased at constant temperature, after this value the solubility of PVA decreases. This study also indicated some degree of autocatalytic effect.

Park and Yoon [13] aimed to study, the conversion of polyvinyl acetate to polyvinyl alcohol through acidolysis. This literature studied two different solvent compositions. In the two sets of reactions, the quantity of PVAc, acetic acid and HCl were the same, but there was change only in the amount of water in the two different reactions. The formation of polyvinyl acetate copolymer polyvinyl alcohol was confirmed by NMR spectra. The mole fractions of vinyl acetate and vinyl alcohol were known by NMR. K_{eq}, the equilibrium constant of reaction was determined using the mole fractions of VAc and VA.

$$K_{eq} = [VA][HOAC] / [VAc][H_2O]$$

The calculated equilibrium constant at 35^{o}C was 0.76 in the first reaction and 0.69 in the second reaction. This reaction was a pseudo first order reaction with a rate constant of $1.2x10^{-12}$ hours^{-1} or $3.4x10^{-6}s^{-1}$.

Tamaki and Chujo [14] studied polyvinyl alcohol and silica gel hybrids. These were synthesized using PVAc dissolved in methanol, dimethyl sulfoxide and HCl, and stirring at a constant temperature for 5 hours, and heating at 60^{0}C for 1week. After this period, a hard glass like material was obtained. It was crushed into powder. It was reported that PVAc provided –OH with acid catalysts. Rate of hydrolysis of PVAc and the formation of silica gel could be controlled by varying catalyst and reaction temperature. Fourier transform infrared spectroscopy exhibited that the intensity of C=O stretching vibration (peak) decreased by increasing the amount of acid catalyst and almost disappeared at 1.6 ml of acid. The peak got shifted to lower wave number due to H-bonding between silanol group in silica gel and acid. The degree of hydrolysis was confirmed by ^{13}carbon NMR in which peaks of C=O was observed at 170 ppm for hybrid prepared using 0.02 ml of catalyst. When the acid catalyst was increased to 1.6 ml, the peak at 170 ppm disappeared. Homogeneity of polymer hybrid was determined by nitrogen sorption porosimetery of porous silica was obtained by partial burning at 600^0C. Pore size distribution had a peak near 0.39 nm. The surface area had the value 102 m^2g^{-1}. The pore size distribution and surface area confirmed the dispersion of PVA in the hybrid.

Pereira et al. [15] studied a new category of materials based on the combination of inorganic and organic species at a nanoscale level. The basic idea behind this work was to produce hybrid materials having controllable properties, which was applied to obtain foams and they provide basic support for tissue engineering. On reacting polyvinyl alcohol in acidic solution with tetraethylorthosilicate, hybrids were synthesized. The inorganic state was also getting changed by including a calcium compound. Hydrated calcium chloride was used as parent material, which was the starting point. When a surfactant was added, foam was produced as a result of vigorous stirring. The formation of foam occured just before gelation point. In order to catalyze the gelation, hydrofluroric acid solution was added. The foamed hybrids were kept for a specified length of time at 40^oC for vacuum drying. Scanning electron microscopy, mercury porosimetry, nitrogen adsorption, X-ray diffraction and infra-red spectroscopy were used to examine the hybrid foams. Compression tests were done to calculate the mechanical behavior. Hybrid PVA-bioactive glass foams were successfully obtained using the sol-gel method. The foams were obtained having high porosity varying from 60 to 90% and the pore size ranged from 30 to 500 µm in macropore diameter. The inorganic state composition and polymer content in the hybrid both varied with the modal macropore diameter. With the increase of polymer concentration in the hybrids, the surface area and mesopore volume got decreased. The endure crack in the hybrid foams was basically greater than pure gel-glass foams.

2.2 Applications

Hosseinzadeh [16] studied polyvinyl alcohol superabsorbent hydrogel synthesis using chemical cross linker gluteraldehyde. Acetal linkage was formed between aldehyde group of glutaraldehyde and hydroxyl (-OH) group of PVA. Scanning electron microscopy showed that the synthesized PVA based hydrogel in this work had a porous structure. Swelling capacity of hydrogel decreased with higher concentration of crosslinker. But increase in PVA weight percentage from 1.2 to 2.4 increased the swelling capacity of hydrogel, which decreased upon further increment. There was a continuous increase in swelling with temperature upto 80^0C, as the rate of diffusion of gultraldehyde increased in PVA back bones. Reaction time increased the swelling upto 1 hour and after 1 hour it appreciably decreased. Swelling measurement of hydrogels in different salt solutions showed less swelling in comparison with that in the distilled water.

Zhang et al. [17] studied improvement of hydraulic effect and the resistance of polyvinyl alcohol hydrogel as a micro-organism immobilization material. This study helped in long time aeration of sewage treatment. Preparation of these was done by chemical co-croslinking with glycerol through the boric acid (H_3BO_4) and toughed PVA hydrogel beads. It was found that glycerol have ability to improve the utilization of H_3BO_4 and slow the cross-linkinking reaction of PVA. On using glycerol, crosslinked structures of borate PVA monodiol complex and PVA-borate-PVA didiol complex were found and the quality of PVA-borate-PVA didiol complex got multiplied. Also, the size of the pores of the core and surface layer became indistinguishable and the structure of PVA/glycerol hydrogel was comparatively consistent. The shear storage modulus and the essential network density increasing the glycerol content first, but on further increasing the glycerol content these values start decreasing. And the maximum value was obtained at 1.5% glycerol, specifying the formation of a thick network structure of the gel. The result was improvement in the tensile and crushing strengths of the gel beads. Outstanding hydrogel stability was shown by PVA having 1.5% by weight glycerol immobilized with and without microorganism, during long-term wastewater treatment process. The reactive toughening mechanism of glycerol on the PVA hydrogel was eatablished. The values of the oxygen uptake rate and chemical oxygen demand removal rate of the PVA hydrogel immobilized with activate sludge no clear distinction with the addition of glycerol, and a high microbial activity could be maintained.

Yu et al. [18] aimed to study polyvinyl alcohol–polyvinyl pyrrolidone (PVA-PVP) hydrogels containing silver nanoparticles used for antibacterial effect. The composition of silver in hydrogels was 0.1-1.0 weight percentage. The size of silver particle was 20 to 100 nm. PVA to PVP had a weight ratio of 70:30. Nano particles of silver were prepared by the reduction of silver nitrate using sodium citrate as a reducing agent. The preparation of this hydrogels was by repetition of freezing thawing treatment. The obtained silver (Ag) sol was greenish yellow in colour. Then, the aqueous solution of PVA-PVP was added into obtained Ag solution. Using PVA-PVP film containing silver particles model, the effect of sliver nanoparticles on the PVA-PVP matrix was studied by differential scanning calorimeter, infrared spectroscopy and UV-visible spectroscopy. The morphology of PVA-PVP hydrogel and dispersion of silver nanoparticles in matrix was studied by SEM. Water absorbing property of hydrogel leads to the release of silver ions from hydrogel. The antibacterial effect of hydrogel towards Escherichia coli and Staphylococcus aureus were studied.

Mathews, et al. [19] studied SEM, uniaxial testing, and a biaxial tubular vessel inflation experiment to analyse the effect of freeze–thaw cycles and chitosan type (water-soluble or insoluble) on the morphological and mechanical characteristics of PVA/chitosan hydrogels. Without chitosan, multiple freeze–thaw cycles had no effect on pore size for PVA hydrogels. SEM images showed that, both types of PVA–chitosan hydrogel developed a more porous structure with a greater distribution of pore size. Uniaxial mechanical tests demonstrated that the elasticity for successive freeze–thaw cycles decreased with the increase of freeze-thaw cycles within a range comparable to porcine aortic tissue. The elastic response of the hydrogels after the first loading cycle was modified by conditioning effects. The PVA–chitosan (water-soluble) hydrogels coefficients for hyperelastic material models were determined. The internal pressurization and axial extension of a tubular vessel within the physiological range studied experimentally. To describe the behavior of each PVA–chitosan water-soluble membrane for one, two, three, and four freeze–thaw cycles, nonlinear hyperelastic constitutive Ogden models were used. Internal pressurization acknowledged well with the experimental measurements for the selected case of a three freeze–thaw cycle PVA–chitosan water soluble hydrogel vessel. The total number of freeze–thaw cycles was shown to have a important effect on the morphological properties of the PVA–chitosan water soluble and insoluble hydrogel membranes. PVA–chitosan hydrogels can be used to fabricate vessels with suitable mechanical and structural characteristics for *in vitro* vascular cell culture studies in a vascular bioreactor and credit further scrutinity for tissue engineering applications.

Nho and Park [9] prepared hydrogel for wound dressing which contained mixture of chitosan and PVA/PVP (polyvinyl alcohol–polyvinyl pyrrolidone) by freezing and thawing , X-ray irradiation, or combined freezing and thawing, or combined freezing and gamma rays. In order to calculate the utility of wound dressing, the physical properties were examined, such as gelation, water absorptivity and gel strength. The constitution of PVA-PVC was 60:40, PVA-PVP chitosan ratio was in the range of 9:1-7:3 and the concentration of PVA/PVP was 15% by weight. A mix of PVA/PVC-chitosan was exposed to gamma irradiation which was used in the amounts of 25, 35, 50, 60 and 70 kGy in order to see the effect on the physical properties of hydrogel. In these experiments, water-soluble chitosan was used. When a mixture of freezing and thawing and irradiation were used instead of just freezing and thawing, then the physical properties of hydrogel were higher. The amount of composition of PVA/PVC-chitosan and irradiation had a great effect on swelling rather than gel content. When the irradiation was greater than 25 kGy, then it did not have high effect on gel % of hydrogel. Swelling % increased on increasing chitosan in PVA/PVP-chitosan composition. This hydrogel was tested on wounded surface and resulted in stoping the bleeding and its curing effect was better than Vaseline gauze.

Biodegradable polymeric microspheres can be utilized to convey drugs through controlled rate and targeted processes. The drug is discharged from the particles by drug filtering or degradation of the polymeric matrix. Crystallinity can assume an imperative part in the degradation of polymeric matrixes; it can influence the drug discharge rate, particularly in chemoembolization therapy. The common embolic agents have a low level of crystallinity, and the connection between the drug transportation rate and the degree of crystallinity is not completey understood. Semenzim et al. [20] examined appropriate preparation conditions for the highly crystalline PVA and PVA/PVAc microspheres and physicochemical characterization by scanning electron microscopy, X-beam diffraction and differential scanning calorimetry. The synthesis of crystalline microspheres of PVA was successfully done by the saponification reaction. During the saponification reaction of PVAc, high concentration of NaOH solutions was used and the obtained crystallinity of PVA was superior. The reason behind the high crystallinity of the sample was the intermolecular hydrogen bonding present between -CH hydrogen of the polymer with the -OH group in the crosslinked region.

Qin et al. [21] studied the polyvinyl alcohol anion trade resin composite layer functionalized with CoOOH for use in coordinate borohydride fuel cell (DBFCs). The CoOOH functionalized layer had a higher ionic conductivity and a lower borohydride particle porousness than the film without CoOOH. The DBFCs with the CoOOH functionalized film resulted in better execution as the power thickness peaked at 144 mWcm^{-2} at 30^{o}C than those without CoOOH. The execution change was because of CoOOH functionalization as the Co species decreased the crossover of the borohydride ion but maintained high conductivity for hydroxyl species. With the addition of the Co species, the conductivity-porousness trade-off difficulty in the conventional anion trade films was avoided. The functionalization of the layer explained the improvement of anion trade film fuel cells. The addition of $CoSO_4$ in membrane resulted in good cell performances with a maximum power density of 144 mWcm^{-2} at 30 °C.

Qian and Zhu [22] studied the preparation of nanocomposite using PVA-Ag_2S, by using hydrothermal process in the situ reaction with CS_2 as sulphur resource. As CS_2 was used as sulphur source to avoid formation of the side products, instead of using Na_2S and K_2S which forms side products like NaCl and KCl. PVA absorbs strongly in 200-400 nm region. When $AgNO_3$ was added in PVA solution with stirring for several hours, a light brown color appeared. UV-VIS spectra bands of PVA-$AgNO_3$ solution were visible at a wavelength 340 nm. XRD indicated the pure phase of Ag_2S. It also indicated that the crystallinity of PVA highly decreased after the composition with nano sized sulfides. The shape of Ag_2S was spherical with diameter in the range of 80-120 nm as shown by scanning electron microscopy. The calculated results of XRD analysis show the size of the single crystal, SEM of the sample shows cluster of Ag_2S particles. These nanocomposite particles have applications in optics and electron microscopy.

Tripathi et al. [23] developed a novel antimicrobial coating based on chitosan and PVA to calculate its effect on minimally processed tomato by means of microbiological analyses. In this work, an antimicrobial film was prepared by blending chitosan and PVA with glutaraldehyde as the cross-linker. There was a molecular miscibility between PVA and chitosan which got pointed out in the FTIR results. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were use to investigate the miscibility and morphology of the film. The PVA-chitosan matrix was homogenous and not having cracks or pores. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used to examine the thermal property of the chitosan–PVA film. The antimicrobial activity of the film against food pathogenic bacteria viz. Escherichia coli, Staphylococcus aureus, and Bacillus subtilis signify by the microbiological screening. From this work, interesting results were obtained that specify the film may be a good material for food packaging applications.

CHAPTER- 3

MATERIALS AND METHODOLOGY

This chapter deals with the materials and methodology used during the research work. This includes chemicals, glasswares, sonicator, mechanical stirrer, digital water bath, oven, and the instruments like NMR, TGA, and SEM used to characterize the obtained polyvinyl alcohol.

3.1 Materials

3.1.1 Apparatus

Digital water bath (Lab tech), three necked round bottom flask , stirring rod, mechanical speed stirrer, thermometer, reflux condenser, sonicator (Branson), filtration flask, beakers (250 ml and 500 ml), measuring cylinders, glass rod, buchner funnel, filter paper and vacuum pump.

3.1.2 Chemicals used

Polyvinyl acetate emulsion (PVAc) was purchased from Shiva Polymers, Faridabad, India, Sodium Sulphate (Na_2SO_4), Methanol (CH_3OH), Sulphuric acid (H_2SO_4), Sodium hydroxide flakes (NaOH) and Hydrochloric acid (HCl) were purchased from Loba Chemie, India. All these chemicals were of analytical grade.

3.2 Instruments used

3.2.1 Digital water bath

Water bath was used to maintain the desired temperature for a particular chemical reaction. It contained temperature sensors that tell us about the digital value of water temperature in water bath. The temperature accuracy of water bath was ± 1^0C.

3.2.2 Sonicator

The process of disturbing particles in the solution with the help of sound waves is known as sonication. Such disturbance can be used to mix solutions, speed the dissolution of a solid into a liquid (like sugar into water), and eliminate the dissolved gas from liquids. In our work, it was used to well dissolve PVA present in the reaction mixture into water.

3.3 Methodology

The methodology followed is shown in the following Figure 3.1.

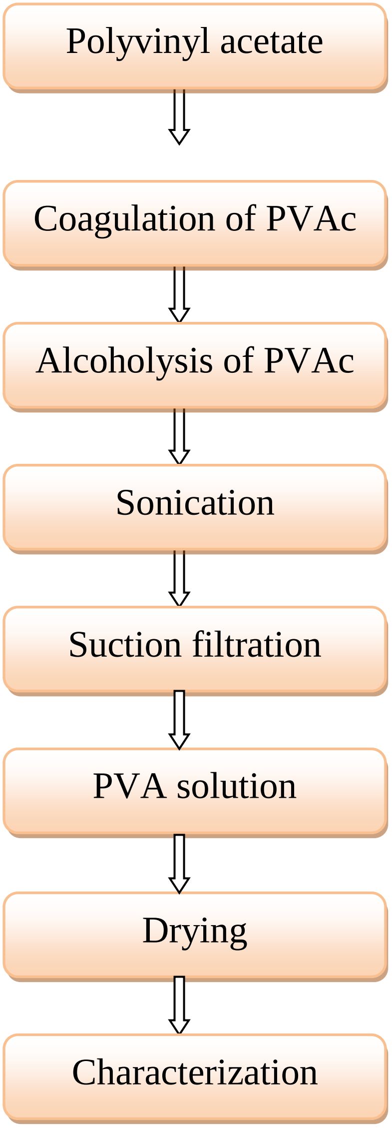


Figure 3.1 Steps involved for the synthesis of Polyvinyl Alcohol

3.3.1 Coagulation of polyvinyl acetate from emulsion

The list of chemicals used to coagulate PVAc emulsion is shown in Table 1. Each chemical is mentioned with its respective quantity.

Table 1. Lists of chemicals used to coagulate PVAc emulsion

S.No.	Materials	Quantity
1	PVAc Emulsion	50.026 g
2	Na_2So_4	50.351 g
3	Methanol	15.805 ml
4	H_2SO_4	0.271 ml
5	Distilled water	125 ml

The first step for the synthesis of PVA was to coagulate the polyvinyl acetate from emulsion. Initially, the solid content in the polyvinyl acetate emulsion was calculated. The emulsion was weighed in a petri dish. After that, the emulsion was dried in an oven for 24 hours. The weight of the dried emulsion was calculated by the difference of weight of petri dish and the weight of petri dish containing the dried emulsion. A centigram weighing balance was used to weigh 50.02 g of polyvinyl acetate emulsion (56.29% by weight solid content) in the flask. Then, 15.8 ml of methanol, aqueous solution of sodium sulfate salt (50 gm Na_2SO_4 and 125 ml of water) and 0.27 ml of H_2SO_4 were transferred in it. The mixture was stirred by using mechanical stirrer for 20 minutes at 35^0C. After stirring, the obtained mixture was allowed to settle for about 30 minutes at the room temperature for the coagulation of polyvinyl acetate. The mixture was filtered for the isolation of the polymer. The resulting solid consisted of 65-70% polymer and 30-35% of water. Figure 3.2 shows the coagulation of PVAc. Figure 3.3 shows the pretreated PVA.

Figure 3.2 Coagulation of PVAc

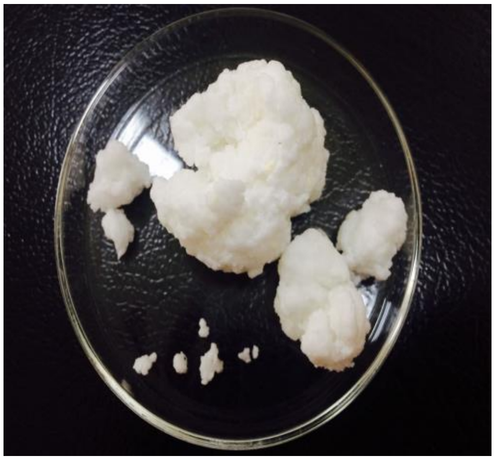


Figure 3.3 Pretreated PVAc

3.3.2 Preparation of polyvinyl alcohol by Alcoholysis Process.

The list of materials used for alcoholysis process is shown in Table 2. Each material is mentioned with its respective quantity.

Table 2. Chemicals required for the alcoholysis

S.No.	Materials	Quantity
1	Pretreated PVAc	43.918gram
2	NaOH (2%)	0.8783gram
3	Methanol	111.004ml
4	Methanol to dissolve NaOH	22.200ml
5	HCl	0.6735ml

The second step was to prepare the PVA from the obtained PVAc in the first step (section 3.3.1). For this, the reaction was carried out in a round bottom flask (1 litre) equipped with a speed stirrer (80-100 rpm), thermometer (0-100^{0}C) and reflux condenser, under isothermal conditions. The pretreated PVAc polymer in the first step (section 3.3.1) was charged in the round bottom flask. 111.0 ml of methanol was transferred under continuous stirring at required temperature. The required temperature was maintained by immersing the round bottom flask in a digital water bath. The water bath had an accuracy of ±1^0C. The NaOH solution (0.878g of NaOH in 22.2 ml methanol) was added simultaneously which acted as a catalyst. Within 7-10 minutes, the reaction mixture thickened and hence, the speed of the stirrer was increased. At the end of reaction, HCl was added for neutralization of NaOH to quench the reaction. The resultant mixture was poured in a beaker from the round bottom flask and then weighed. The weight of resultant mixture left in round bottom flask was calculated by the difference of weight of empty round bottom flask and the weight of flask containing resultant mixture. Also, the resultant mixture got stuck to the mixing rod. Finally, the weight of the resultant mixture came out to be the weight of the mixture in the beaker plus that left in the round bottom flask and that stuck to the rod. The beaker containing mixture was then treated for sonication (section 3.3.3).

Two sets of experiments were performed; the first set was at 40^0C and the second set at 60^0C. In each set, the effect of catalyst loading and reaction time were studied. The experimental runs corresponding to 40^0C were repeated at 2%, 4% and 6% catalyst loading (weight of catalyst /weight of pretreated polyvinyl acetate). Moreover, the reaction was carried for different time period i.e. at 10, 20, 40, 60 and 90 min. individually.

3.3.3 Sonication of resultant mixture

In this process, polyvinyl alcohol formed in the resultant mixture was separated from the unreacted solid polyvinyl acetate. 250 ml of water was added in the beaker containing resultant mixture (section 3.3.2) and sonicated for 1 hour 40 minutes with continuous heating at 40-45^0C. During the sonication process, the rate of dissolution of polyvinyl alcohol increased in water. Due to the tendency of polyvinyl alcohol to form hydrogen bonding in aqueous solutions, it can be solubilized in water because of its hydrophilic property. Hence, the PVA present in the reaction mixture was completely dissolved into water and the unreacted solid material was separated by suction filtration. The filtrate obtained was the solution of polyvinyl alcohol.

3.3.4 Drying

By using the water bath, the solvent and the reaction byproducts were evaporated from the obtained PVA solution (section 3.3.3) by heating. The temperature was maintained at 90-95^0C on the digital water bath. After the evaporation, PVA sample was dried in an oven for 12 hours at 40^0C. Finally, this sample was characterized using Thermo Gravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) and Nuclear Magnetic Resonance (NMR).

3.3.5 Characterization

a) Scanning electron microscopy

A scanning electron microscope is an electron microscope which accelerates the electron in the form of beam. It produces secondary electrons when this beam hits the surface of the sample. These secondary electrons are detected by the positively charged electron detector producing various signals that contain information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample’s surface topography and composition.

b) Thermo gravimetric analysis

Thermo gravimetric analysis is a useful analytical technique to access thermal stability of materials including polymers by recording weight loss of a sample as a function of temperature. It is a beneficial technique for the research of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints. It gives important information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption and desorption. Also, it tells about the chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (like oxidation or reduction).

c) Nuclear magnetic resonance

Nuclear magnetic resonance is a phenomena that occurs when the spins of atomic nuclei is lined up with an applied magnetic field to absorb energy and change the spin opposite to the applied field. The nuclear magnetic resonance deals with the magnetic effect generated by the spin of protons and neutrons whereas magnetic measurements rely on the spin of unpaired electron. NMR is a quantitative analysis because the area under a peak depends upon the number of nuclei responsible for that peak. The presence of particular functional group can be detected by these phenomena. The relative position of functional groups in a particular structure can also be determined.

3.4 Calculations

The sample calculations are shown below.

3.4.1. For calculating weight percentage of solid content in polyvinyl acetate emulsion

Weight of Emulsion = 25.991 g

Weight of petri dish = 41.185 g

Weight of dried emulsion + weight of petri dish = 56.486 g

Weight of dried emulsion = 56.486 g – 41.185 g = 14.632 g

Weight of solvent evaporated = 25.991 g – 14.663 g =11.358 g

Weight % of solid content = $\frac{14.6321}{25.99060}\times 100 = 56.297$ %

Weight % of solvent evaporated = 100 – 56.297 = 43.702339 %

3.4.2. For calculating weight percentage of solid content in polyvinyl acetate pretreated

Weight of pretreated polyvinyl acetate =36.860 g

Weight of petri dish = 43.203 g

Weight of dried pretreated PVAc + wt. of petri dish = 68.182 g

Weight of dried pretreated PVAc = 68.182 – 43.203 g =24.978 g

Weight of solvent content = 36.860 g – 24.978 g = 11.882 g

Weight % of solid content = $\frac{24.978}{36.860}\times 100 = 67.764$ %

Weight % of solvent present = 32.235 %

3.4.3. For calculating percentage yield for 2% catalyst

Pretreated PVAc (containing 32.23% of H_2O) = 43.92 g

Solid content in pretreated PVAc = $\frac{43.92\times 67.76}{100}$ =29.76 g

Weight of reaction mixture in beaker = 103.39 g

Weight of round bottom flask = 408.19 g

Weight of round bottom flask with reaction mixture left in it = 420.52 g

Weight of reaction mixture left in round bottom flask = 420.52 g – 408.19 = 12.33 g

Weight of mixing rod = 52.34 g

Weight of rod with the resultant mixture = 53.03 g

Weight of reaction mixture stuck on rod = 53.03 g – 52.34 g = 0.69 g

Weight of reaction mixture in (beaker + round bottom flask + on rod) =116.41 g

Weight of reaction mixture only in beaker =103.3871 g

After filtration, weight of PVA solvent + 250 ml of water = 284.75g

After drying, weight of dried PVA sample for 2 % catalyst = 11.78g

Percentage yield = $\frac{\text{wt.of PVA}}{\text{wt.of PVAc}}\times 100 = \frac{11.78}{29.76}\times 100$ = 39.58%

Similarly, for other catalyst i.e. 4% and 6% catalyst loading reactions, calculations were done in the same manner.

CHAPTER- 4

RESULTS AND DISCUSSIONS

4.1 Effect of temperature and reaction time

Figure 4.1 shows the smoothed plots of percentage yield of PVA versus time at two different temperatures. In this Figure, PVA samples at temperatures of 40^0C and 60^0C show similar behavior. The percentage yield of PVA increases with reaction time. With increase in reaction time, the number of replaced groups (-OH) increases on the polymer chain. On further increasing reaction time, yield remains constant. The curve for 60^0C temperature lies above 40^0C. The actual data is given in Table 3. According to Arrhenius dependency, the rate of reaction increases on increasing temperature. The points shown in Figure 4.1 are only to distinguish different runs. These are not actual data points. Table 3 shows the calculated data of the percentage yield with respect to temperature and reaction time.

Table 3. Results for variation of % yield PVA on changing time and temperature

S.No.	**Temperature (^{0}C)**	**Time (min.)**	**% Yield (gm/gm)**
1.	40	0	0
		10	15.10
		20	29.07
		40	42.07
		60	47.857
		90	48.6
2.	60	0	0
		10	18.2
		20	33.35
		40	46.5
		60	51.72
		90	52.87

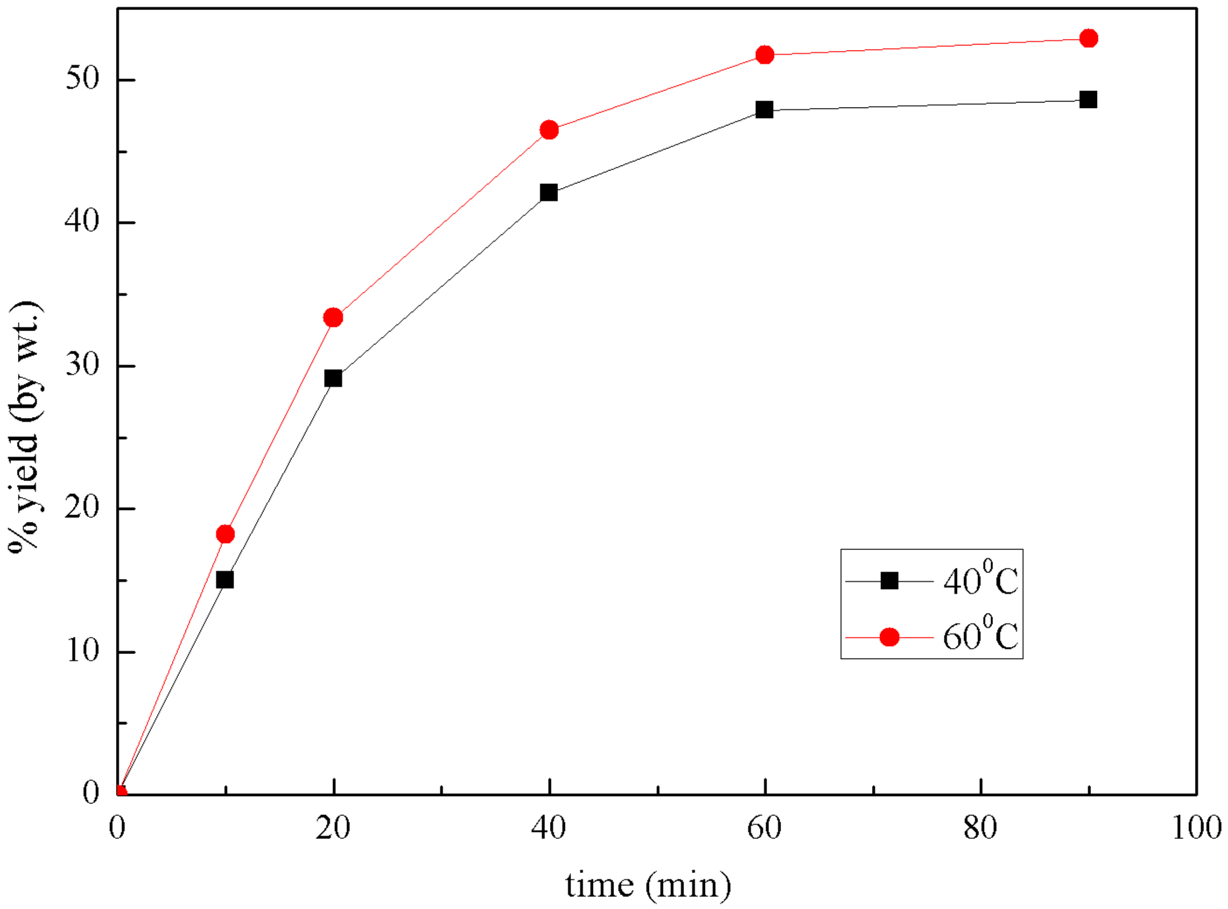


Figure 4.1 Effect of reaction time and temperature on the percentage yield

4.2 Effect of catalyst loading

In Figure 4.2, the graph is in between percentage yield and catalyst percentage. The effect of catalyst loading on the yield of PVA at 40^0C for the 90 min reaction time is shown. When the catalyst percentage is varying from 2% to 4% then the yield increases. But, from 4% to 6% increase of catalyst loading, the percentage yield is relatively less. Hence, the catalyst increases the rate of alcoholysis. With addition of catalyst, the activation energy required is less for the anion (–OH) to replace carbonyl group of the reactant. Thus the rate of collisions increases with catalyst and as a result the rate of reaction increases.

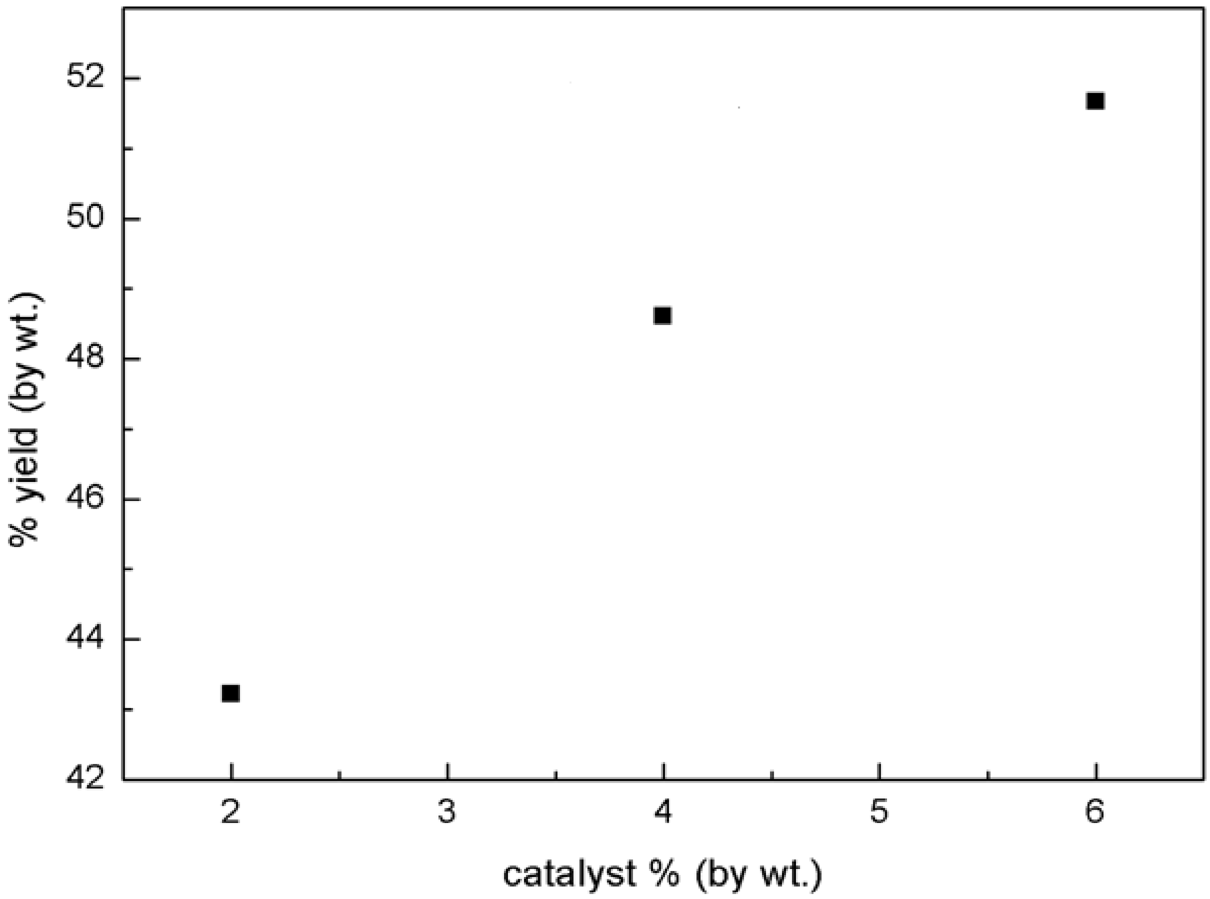


Figure 4.2 Effect of catalyst loading on percentage yield.

4.3 Thermo gravimetric analysis

Thermo gravimetric analysis is a useful analytical technique to asses the thermal stability of materials including polymers by recording weight loss of a sample as a function of temperature. As shown in Figures 4.3 and 4.4, the TGA behaviors of the 2% catalyst sample synthesized at 40^0C and of the 4% catalyst sample synthesized at 40^0C show similar trends. This indicates the consistency of obtained PVA at different conditions of catalyst loading. Also, both the figures show a sharp weight loss in between the temperatures of 220 to 300^0C. This shows a phase transition behavior of PVA in this temperature range, consistently for both the synthesized samples.

The thermal decomposition of PVA is a two-stage phenomenon. In the Figure 4.3, the TGA graph for the 2% catalyst in the 220^0C -270^0C temperature range, the loss of weight is from 5.5 mg down to 4.8 mg. In the 310^0C - 570^0C temperature range, the loss of weight is from 4.8 mg to 4.3 mg. On further increase of temperature, i.e., 600^0C weight loss of PVA is minor. Similarly, in Figure 4.4 of TGA at catalyst 4% in the 240^0C -300^0C temperature range, the loss of weight is from 5.3 mg to 2.5 mg. In the 310^0C - 520^0C temperature range, the loss of weight is from 2.4 mg to 1.5 mg .On further increase of temperature i.e. at 600^0C, the weight loss of PVA is minor. The above TGA behavior conforms to the behavior of pure PVA samples reported in the literature as the graphs are comparable [24-26].

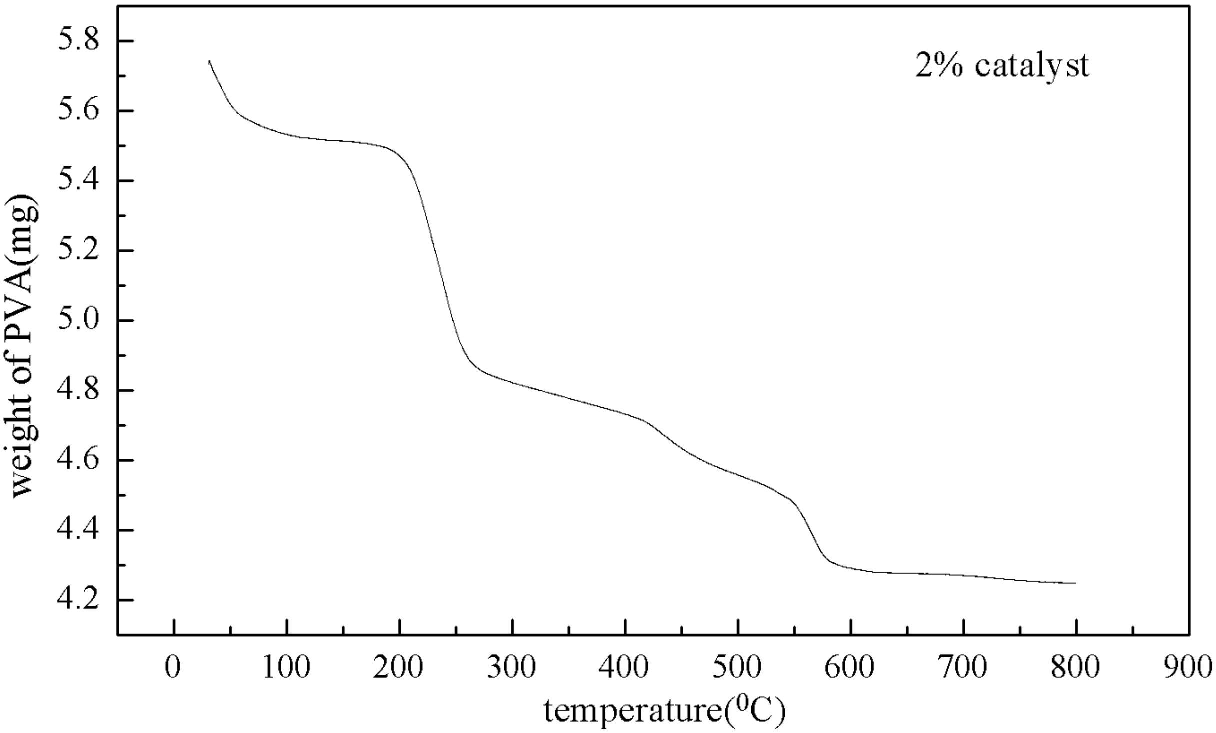


Figure 4.3 Thermo gravimetric analysis of PVA for 2% catalyst

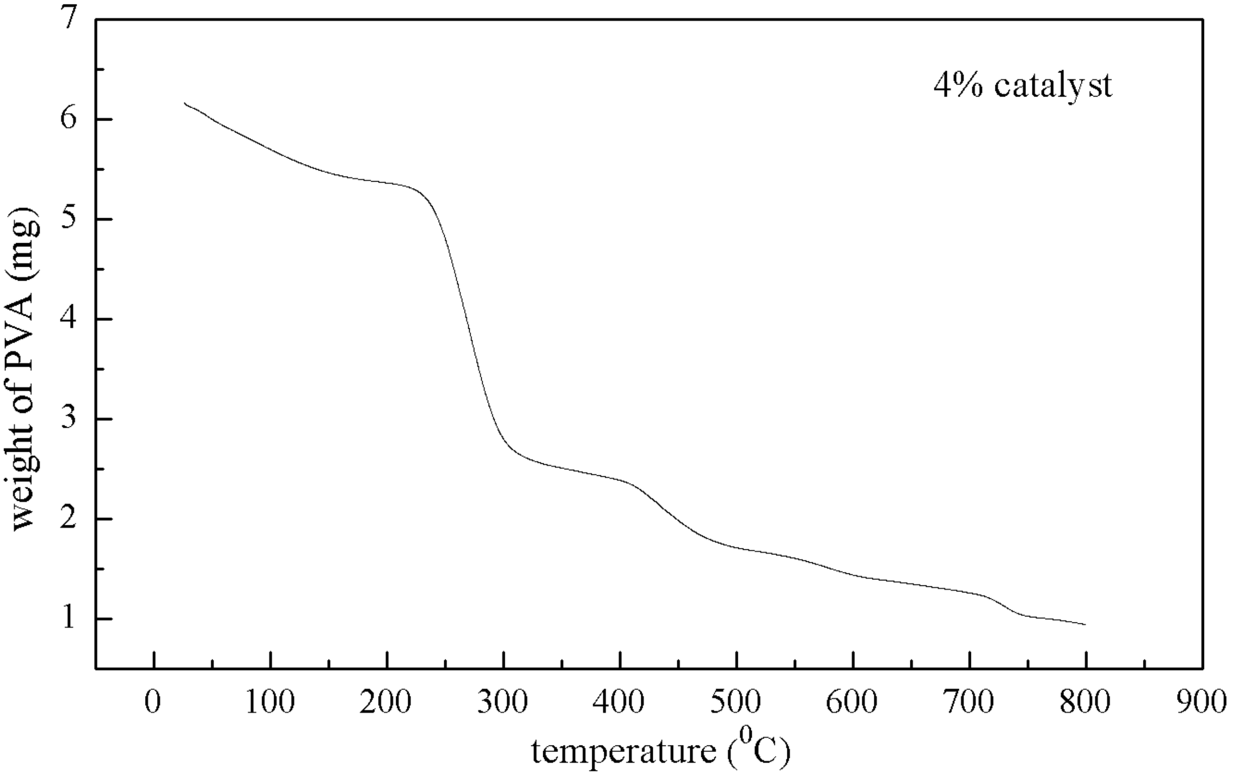


Figure 4.4 Thermo gravimetric analysis of PVA for 4% catalyst

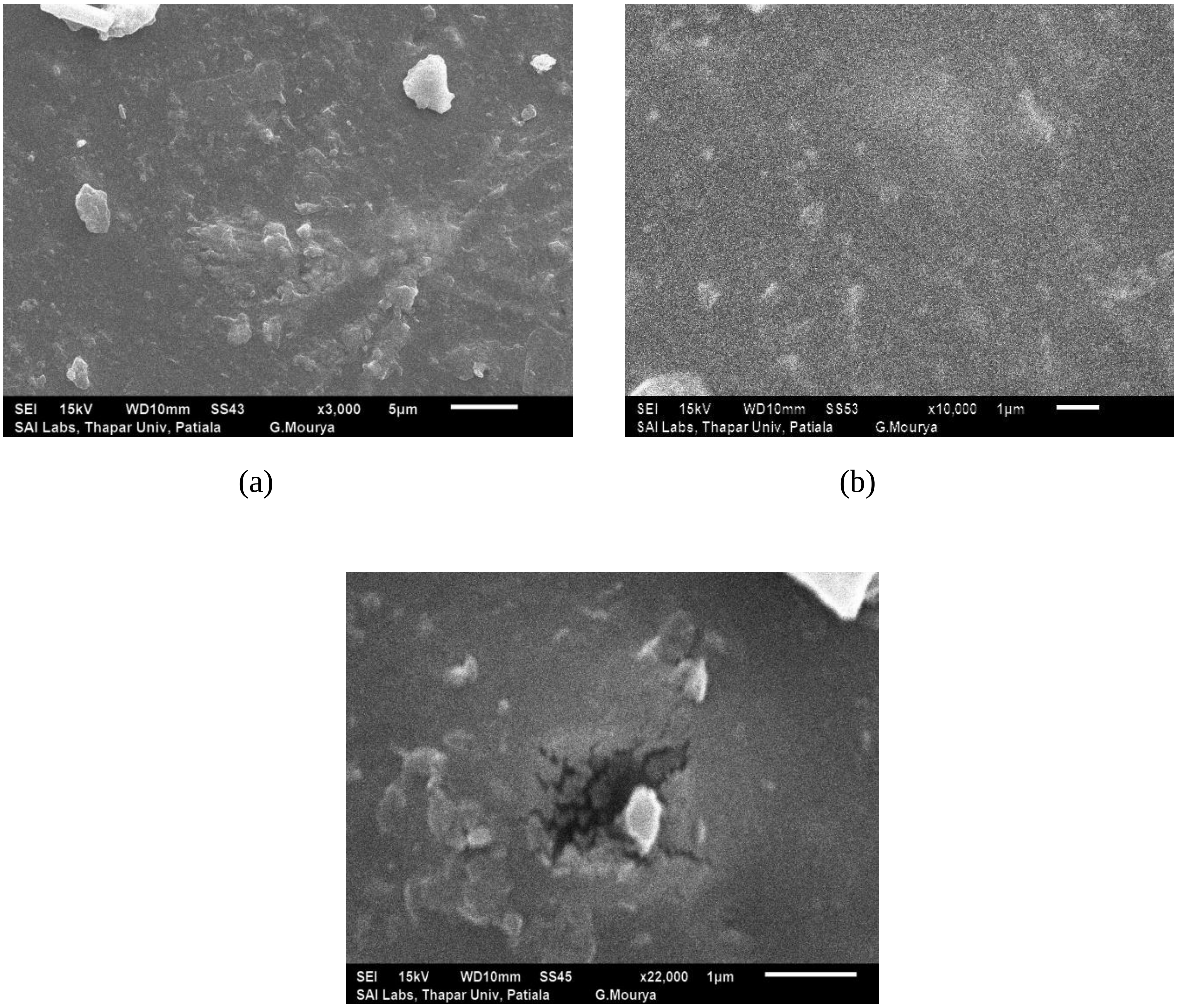
4.4 Scanning electron microscopy

SEM analysis allows investigating the porous structure of PVA. As noted in the literature review, polyvinyl alcohol has the characteristic that makes it suitable for several applications based on its porous structure. Hydrogels of polyvinyl alcohol with water soluble chitosan and polyvinyl alcohol with water insoluble chitosan were prepared having the pore sizes proper to get membranes for cell growth. These hydrogels supported vascular cell culture [19].

The structure morphology of EAB-SAI was studied using JSM541-V, JOEL scanning electron microscopy. Figure 4.5 (a) shows that the magnification of the sample at (x3,000). In this figure, PVA is dispersed uniformly. However, the cluster of PVA molecules is detectable in between. The porous structure of PVA is not visible. The magnified image of PVA sample at (x10,000) in

Figure 4.5 (b) shows that it has a porous nature. As it was magnified further to (x 22000), a pore is clearly visible in Figure 4.5(c).

In Table 4, the pore sizes at two different magnifications are depicted. The sample with magnification at (x10,000) has a pore size of 150.966 µm and the same sample with magnification at (x22,000) has a pore size of 212.566 µm.



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(a) (b)

(c)

Figure 4.5 Scanning electron micrographs of PVA at different magnification (a) x3,000 (b) x10,000 (c) x22,000

Table 4. Pore sizes of PVA sample magnified at x10,000 and x22,000

S.No	Sample	Maximum(μm)	Minimum (μm)	Average (μm)
1	PVA(x10,000)	209.020	106.335	150.966
2	PVA(x22,000)	255.000	166.831	212.566

4.5 Nuclear magnetic resonance

The PVA sample was completely dissolved in DMSO D6 solvent and was analyzed using ^{1}H NMR spectroscopy, ^{13}C spectrum and ^{13}C DEPT spectroscopy.

^{1}H NMR spectroscopy

^{1}Hydrogen NMR spectroscopy of the synthesized PVA sample was conducted at 399.8 MHz frequency. ^{1}H NMR spectrum of aliphatic protons was observed resonating at δ 4.723-4.399 (t, 1H). A broad singlet corresponding to proton of hydroxyl was found at δ 3.383 (brs, 1H). A doublet corresponding to two protons of $–CH_2$ was observed at δ 1.418-1.306. Figure 4.6 shows the ^{1}H NMR spectra.

^{13}C NMR spectrum

^{13}Carbon NMR spectrum of PVA was conducted at 100.52 MHz frequency. ^{13}Carbon NMR, aliphatic carbon adjacent to hydroxyl group was observed resonating at δ 66.200. Carbon of $–CH_2$ group was found resonating at δ 46.320. In Figure 4.7 shows the ^{13}Carbon NMR spectrum.

^{13}C DEPT spectroscopy

^{13}Carbon DEPT spectroscopy, peak of carbon atom was pointing down which signify carbon of $–CH_2$ group. It was found resonating at δ 46.320. ^{13}C DEPT spectrum was shown in Figure 4.8. So, here by we can say that the structure obtained by the analysis of peaks is of polyvinyl alcohol [27, 28].

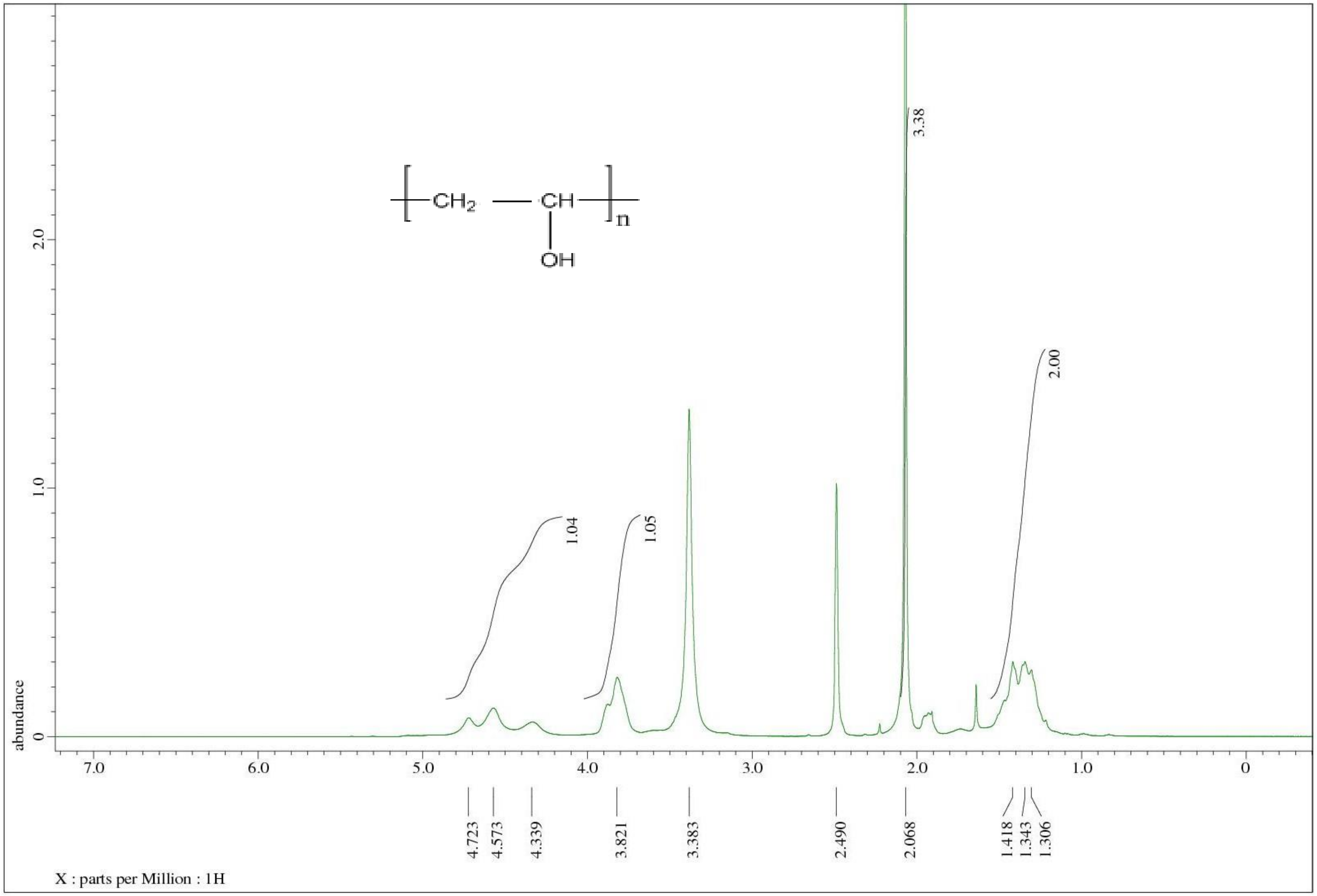

Figure 4.6 ^{1}H-NMR spectrum of polyvinyl alcohol

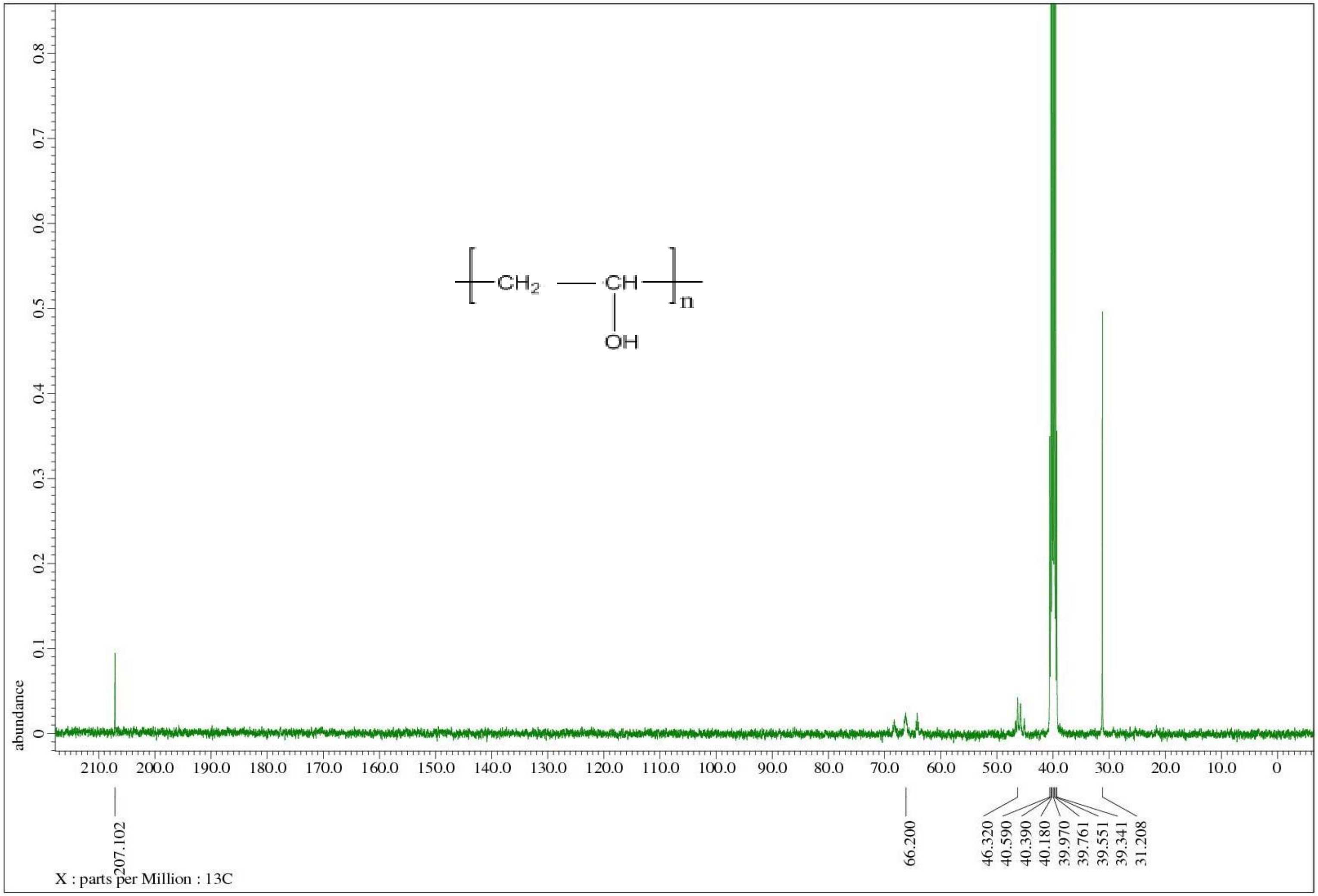

Figure 4.7 ^{13}C-NMR spectrum of polyvinyl alcohol

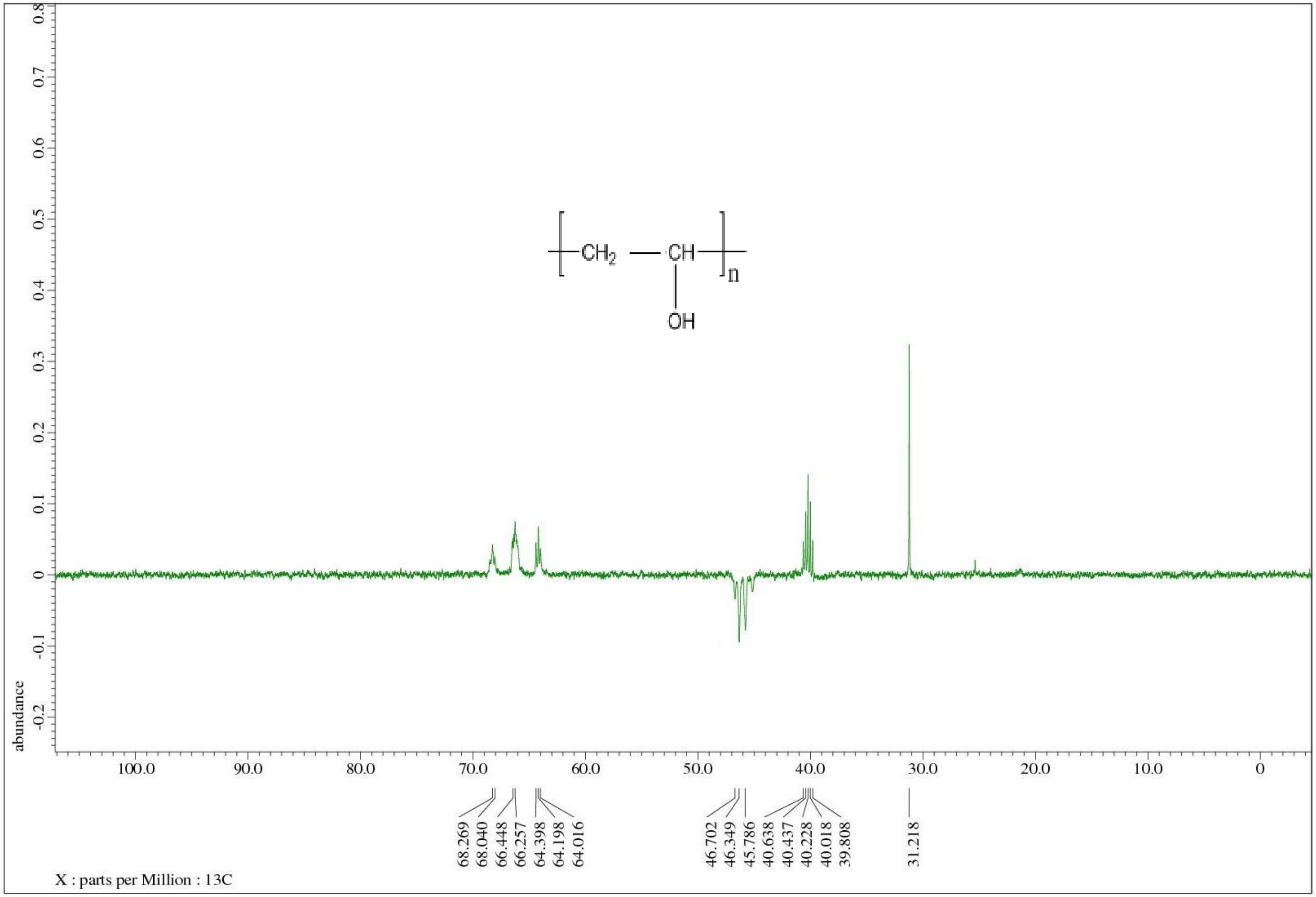

Figure 4.8 ^{13}C DEPT spectroscopy of polyvinyl alcohol

CHAPTER-5

5.1 CONCLUSION

This work carries out the Characterization of alkali catalyzed synthesis of polyvinyl alcohol from the polyvinyl acetate emulsion. In this process, polyvinyl acetate polymer is first solidified from emulsion using sodium sulphate solution. Then, polyvinyl acetate is alcoholyised by methanol and sodium hydroxide which acts as a catalyst. The percentage yield of polyvinyl alcohol increases with increase in temperature and catalyst loading. The percentage yield with time shows an increase that becomes asymptotic after nearly 80 min of reaction time. The rate of reaction decreases with time. However, this behavior does not indicate any autocatalytic effect suggested in the literature. TGA shows a phase transition between 220 to 320^{o}C. SEM shows porous nature of the formed polyvinyl alcohol. NMR and TGA studies confirm that the obtained product is polyvinyl alcohol.

5.2 FUTURE PROSPECTS

- To obtain a mathematical model using the kinetic data generated in this study.
- To study the Arrhenius dependency of the rate constant.

REFERENCES

[1] J.I. Jones, Polyvinyl alcohol. Properties and applications. Edited by CA Finch. John Wiley, Chichester. 1973. Pp. xviii+ 622., in, Wiley Online Library, 1973.

[2] P. Scholes, A. Coombes, L. Illum, S. Davis, J. Watts, C. Ustariz, M. Vert, M. Davies, Detection and determination of surface levels of poloxamer and PVA surfactant on biodegradable nanospheres using SSIMS and XPS, Journal of Controlled Release, 59 (1999) 261-278.

[3] C. DeMerlis, D. Schoneker, Review of the oral toxicity of polyvinyl alcohol (PVA), Food and Chemical Toxicology, 41 (2003) 319-326.

[4] M. Liu, B. Guo, M. Du, D. Jia, Drying induced aggregation of halloysite nanotubes in polyvinyl alcohol/halloysite nanotubes solution and its effect on properties of composite film, Applied Physics A, 88 (2007) 391-395.

[5] S.-H. Hyon, W.-I. Cha, Y. Ikada, M. Kita, Y. Ogura, Y. Honda, Poly (vinyl alcohol) hydrogels as soft contact lens material, Journal of Biomaterials Science, Polymer Edition, 5 (1994) 397-406.

[6] K. Qiu, A.N. Netravali, A Composting study of membrane-like polyvinyl alcohol based resins and nanocomposites, Journal of Polymers and the Environment, 21 (2013) 658-674.

[7] Y. Tang, D. Zhou, J. Zhang, Novel polyvinyl alcohol/styrene butadiene rubber latex/carboxymethyl cellulose nanocomposites reinforced with modified halloysite nanotubes, Journal of Nanomaterials, 2013 (2013) 128.

[8] C. Shuai, Z. Mao, H. Lu, Y. Nie, H. Hu, S. Peng, Fabrication of porous polyvinyl alcohol scaffold for bone tissue engineering via selective laser sintering, Biofabrication, 5 (2013) 015014.

[9] Y. Nho, K. Park, Preparation and properties of PVA/PVP hydrogels containing chitosan by radiation, Journal of Applied Polymer Science, 85 (2002) 1787-1794.

[10] C. Haweel, S.H. Ammar, Preparation of polyvinyl alcohol from local raw material, Iraqi J. Chem. Petrol. Eng, 9 (2008) 15-21.

[11] L. Minsk, W. Priest, W. Kenyon, The alcoholysis of polyvinyl acetate, Journal of the American Chemical Society, 63 (1941) 2715-2721.

[12] B. Wang, X. Bao, M. Jiang, G. Ye, J. Xu, Synthesis of high-molecular weight poly (vinyl alcohol) by low-temperature emulsifier-free emulsion polymerization of vinyl acetate and saponification, Journal of Applied Polymer Science, 125 (2012) 2771-2778.

[13] S.-S. Park, H.-S. Yoon, Acid-catalyzed hydrolysis reaction of poly (vinyl acetate), Polymer Korea, 29 (2005) 304-307.

[14] R. Tamaki, Y. Chujo, Synthesis of poly (vinyl alcohol)/silica gel polymer hybrids by in-situ hydrolysis method, (1998).

[15] M.M. Pereira, J.R. Jones, R.L. Orefice, L.L. Hench, Preparation of bioactive glass-polyvinyl alcohol hybrid foams by the sol-gel method, Journal of Materials Science: Materials in Medicine, 16 (2005) 1045-1050.

[16] H. Hosseinzadeh, Synthesis and swelling properties of a poly (vinyl alcohol)-based superabsorbing hydrogel, Current Chemistry Letters, 2 (2013) 153-158.

[17] Y. Zhang, B. Hui, L. Ye, Reactive toughening of polyvinyl alcohol hydrogel and its wastewater treatment performance by immobilization of microorganisms, RSC Advances, 5 (2015) 91414-91422.

[18] H. Yu, X. Xu, X. Chen, T. Lu, P. Zhang, X. Jing, Preparation and antibacterial effects of PVA-PVP hydrogels containing silver nanoparticles, Journal of Applied Polymer Science, 103 (2007) 125-133.

[19] D. Mathews, Y. Birney, P. Cahill, G. McGuinness, Mechanical and morphological characteristics of poly (vinyl alcohol)/chitosan hydrogels, Journal of applied polymer science, 109 (2008) 1129-1137.

[20] V.L. Semenzim, G.G. Basso, D.A. da Silva, A. de Vasconcellos, G. Agreli, A.P.M. Lima-Oliveira, R.S. Kawasaki-Oyama, D.M. Braile, J.G. Nery, Synthesis and characterization of novel, highly crystalline poly (vinyl alcohol) microspheres for chemoembolization therapy, Journal of Applied Polymer Science, 121 (2011) 1417-1423.

[21] H. Qin, Y. Hu, C. Zhu, W. Chu, H. Sheng, Z. Dong, Y. He, J. Wang, A. Li, H. Chi, Functionalization of polyvinyl alcohol composite membrane by CoOOH for direct borohydride fuel cells, Electrochemistry Communications, 77 (2017) 1-4.

[22] X.-F. Qian, J. Yin, J.-C. Huang, Y.-F. Yang, X.-X. Guo, Z.-K. Zhu, The preparation and characterization of PVA/Ag 2 S nanocomposite, Materials chemistry and physics, 68 (2001) 95-97.

[23] S. Tripathi, G. Mehrotra, P. Dutta, Physicochemical and bioactivity of cross-linked chitosan–PVA film for food packaging applications, International Journal of Biological Macromolecules, 45 (2009) 372-376.

[24] K. Strawhecker, E. Manias, Structure and properties of poly (vinyl alcohol)/Na+ montmorillonite nanocomposites, Chemistry of materials, 12 (2000) 2943-2949.

[25] A. Coats, J. Redfern, Thermogravimetric analysis. A review, Analyst, 88 (1963) 906-924.

[26] M.T. Taghizadeh, N. Sabouri, Thermal degradation behavior of polyvinyl alcohol/starch/carboxymethyl cellulose/clay nanocomposites, Universal Journal of Chemistry, 1 (2013) 21-29.

[27] J.-M. Petit, X. Zhu, 1 H and 13C NMR Study on Local Dynamics of Poly (vinyl alcohol) in Aqueous Solutions, Macromolecules, 29 (1996) 2075-2081.

[28] F. Horii, K. Masuda, H. Kaji, CP/MAS 13C NMR spectra of frozen solutions of poly (vinyl alcohol) with different tacticities, Macromolecules, 30 (1997) 2519-2520.

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