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SYNTHESIS AND CHARACTERIZATION OF BARLEY STARCH-G-POLYACRYLAMIDE/ZINC SULFATE COMPOSITE

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Abstract

The present study describes the synthesis and detailed characterization of a barley starch-g-polyacrylamide/$ZnSO_4$ composite developed to improve material performance. The composite was synthesized through free-radical graft polymerization of acrylamide onto a barley starch backbone, followed by the incorporation of zinc sulfate into the resulting polymeric network.
Comprehensive structural and physicochemical characterization was carried out using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and thermal analysis techniques. The findings confirmed the successful grafting of polyacrylamide chains onto the starch backbone, along with the homogeneous distribution of $ZnSO_4$ throughout the composite matrix.
Compared with native starch, the prepared composite exhibited enhanced thermal stability, improved structural integrity, and a modified surface morphology. Swelling studies and functional performance evaluations further demonstrated superior properties, highlighting the material's potential for applications in agriculture, environmental remediation, and controlled-release systems.
Overall, this work demonstrates the effectiveness of starch-based grafted composites as sustainable, high-performance functional materials with promising practical applications.

1. INTRODUCTION

Starch, a carbohydrate, in flora it also known as amylum, consists of amylose and amylopectin.[1] Starch is a biopolymer composed of linked 1, 4-linked D-glucose units joined by α-glycosidic bonds. Film forming capacity of starch is due to amylose content. Crystalline structure of starch particle is 30 % while 70 % is amorphous. Starch is not soluble in cold water but soluble when it is heated to form a gelatinized starch.[2] Starch can be recycled by microorganism.

In medical industry starch based biodegradable biopolymer is used as an efficient bone cement. Sutures a nontoxic biodegradable polymer also being used by surgeons in operations. It is sterilized dissolve in the body until the surrounding tissue have healed.[3] Many starch derivatives are used as fat substitute. These derivatives contribute zero calories to the food on ingesting. Crosslinking treatment lower the viscosity and hardening of paste in cooking due to which potato starch is suitable for canned food and other food application. Crosslinked starch is a source of dietary fibre and have a nutritional benefit.[4] Film blend with nano-SiO_2 /potato starch exhibited better packing and conservation properties and therefore increase the storage period of food without alter the quality of food. Absorbance of higher light by the edible film increase the quality of packed food because it protects the content of food from light.[5]

Starch form viscous solution during film formation. Water attacks the amorphous phase of starch and form the strong interaction with starch. Greater amylose content induces greater moisture sensitivity that improves the properties (mechanical strength, elongation etc.) of starch-based film. Greater amount of amylopectin reduces the solubility of film in water and lower the mechanical properties of starch-based films. At 60-70 °C starch's granules swell and loss of birefringence and above 90°C a complete loss of mechanical integrity occurs.[6]

Polyacrylamide, a synthetic polymer, has linear chain structure produced by free radical polymerization of acrylamide.[7] Amount of amide group conversion into carboxylate group known as degree of hydrolysis (DH).[8] Partially hydrolysed polyacrylamide (HPAM) having DH from 0-60 %. It is neutral in pure state. But at high temperature and higher saline condition make it unstable.[9] High temperature lowers the activation energy by acting as an initiator. It is thermally stable polymer but high temperature effects the rheological properties of polyacrylamide solution and reduced the viscosity of solution due to formation of brine or water at high temperature.[10] Polyacrylamide is modified for the biodegradation of material. Incorporation of N-benzyl-4-vinylpyridium chloride to main polymer chain increment its biodegradability. Resultant biodegradable polymer can be used for water disinfectant by coagulating and sedimenting bacteria. Synthesized co-polymer consist of N-benzvl-4- vinylpyridinium chloride, acrylamide and a little concentration of acrylic acid. Poly acrylamide has low curing temperature excellent impact strength, and abrasion resistance characteristics.

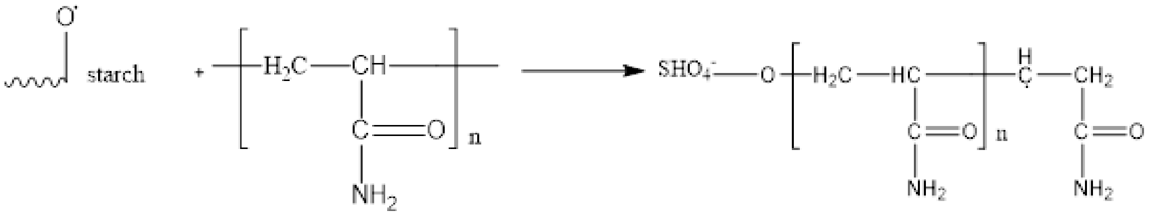
Polyacrylamide application for treatment of industrial effluents and treating municipal sewage waste is of crucial importance. Cationic, anionic and non-ionic polyacrylamide are used for wastewater treatment of food, beverage, and chemical industries.[11] Retention of fillers and fine particles of paper enhanced by cationic and anionic polyacrylamide and derivatives of polyacrylamide. Enhanced oil recovery (EOR) treatment used water soluble polyacrylamide or partially hydrolysed polyacrylamide and its derivatives. In the process of mining, high molecular weight ionic and non-ionic polyacrylamide are used which remove water for metal concentrate and to treat the aqueous waste.[12] For composite formation free radicle on the starch first generate which act as a macro-initiator for vinyl monomers acrylamide. In the presence of a redox initiator such as cerium ion grafting acrylamide side chains onto a starch backbone is feasible Ceric ions generally act as an oxidizing agent, resulting in the formation of radicals on polymer chain. Ce^{+4} is common initiator for this type of polymerization.[13]

Initiation

$$S_2O_8^{2-} \longrightarrow 2\dot{S}O_4^-$$

$$\text{Starch—OH} + S_2O_8^{2-} \longrightarrow \text{Starch—O}^{\cdot} + H_2SO_4 + \dot{S}O_4^-$$

Propagation



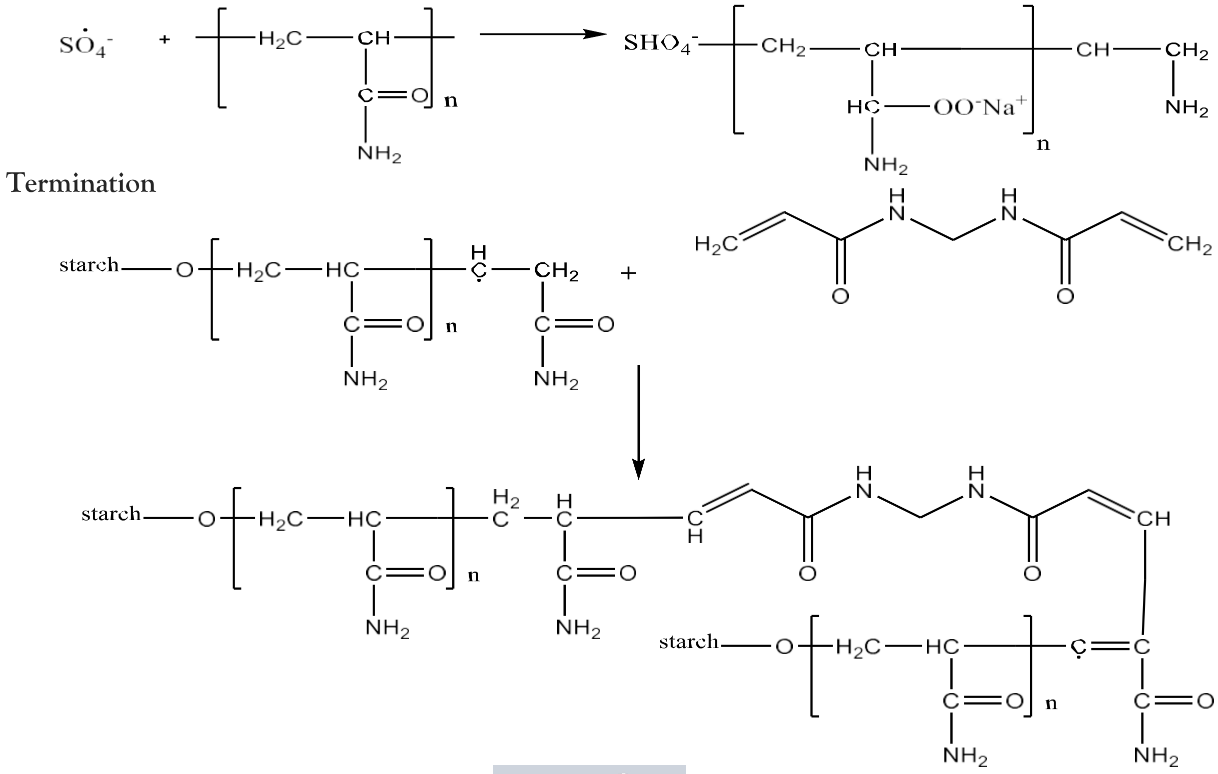


Figure 1. Mechanism for synthesis of starch-g-polyacrylamide composite.

Mechanism consists of three main steps

i. **Initiation:** First of all, free radical (hydroxyl) produced on starch chain.

ii. **Propagation:** A polymer chain is produced by polyacrylamide monomer with hydroxyl free radical.

iii. **Termination:** Termination occur when two polymer chain are crosslinked.

2. MATERIALS AND METHODS

2.1. Materials

Materials used in procedure are Beakers, Pipette, Glass rods, Magnet bar, Spatula, Measuring cylinder, Conical flask, Funnel, Teflon plate, Filter paper, Aluminium foil, Magnetic stirrer, Furnace and Weight balance. Chemical utilized in the preparation of starch-grafted- polyacrylamide composites were laboratory grade and were used without any purification such as Polyacrylamide, (Pam), Barley Starch, (St), Zinc Sulphate, ($ZnSO_4$), Distilled Water, (H_2O)

2.2 Synthesis of barley starch-g-polyacrylamide composite

1.35 g polyacrylamide dissolve in 15 mL distilled water and stirred at 600 rpm for 1 h to form a homogenous mixture. In other conical flask 5 mL distilled water heat for 2-3 minutes and stirred at 700 rpm. During stirring 0.5 g barley starch was added to form a gelatinized starch. Homogenous mixture of barley starch formed in 30 minutes. Polyacrylamide solutions poured into barley starch solution. Resulting barley starch and polyacrylamide solution was stirred at 600 rpm continuously for 24 h to form a homogenous solution. Solution was poured into Teflon plate for casting. Teflon plate containing the solution dried at room temperature (25 °C) for 36 h. A smooth film was obtained of starch-polyacrylamide composite at the end of whole process. The composite formed in this way containing 80 % and 20 % ratio of both polyacrylamide and starch respectively.

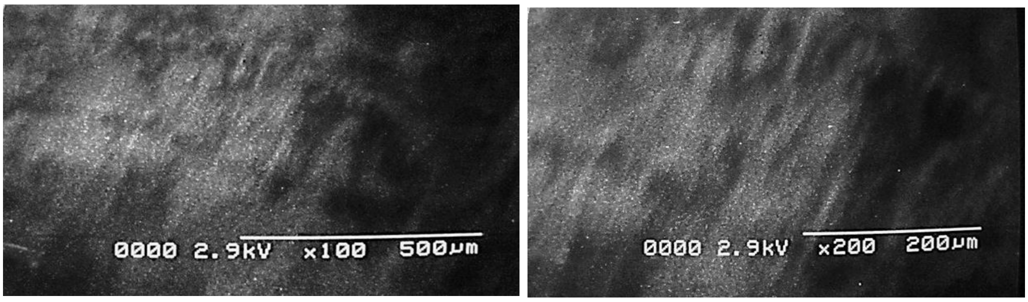
2.3 Synthesis of barley Starch-g-Polyacrylamide composite containing ZnSO4

1.35 g polyacrylamide dissolve in 15 mL distilled water, total volume of solution become 16 mL and stirred at 600 rpm for 1 h to form a homogenous mixture. Different concentration containing 1 % and 10 % of ZnSO4 was taken in 5 mL distilled water and solution was filtered. Filtered solution was added into homogenous polyacrylamide solution which makes the total volume of solution 21 mL and stirred for overnight to form clear solution. Another conical flask was taken having 5 mL distilled water heat for 2-3 minutes and stirred at 700 rpm. During vigorous stirring 0.5 g barley starch was added to form a gelatinized starch. Homogenous mixture of barley starch formed in 30 minutes. Polyacrylamide metal solution was added into starch solution during vigorous stirring about 750 rpm. Resulting solution was stirred for 36 h to form a homogenous solution. All the procedure was carried out at room temperature (25 °C). This solution was casted into Teflon plate and dried at room temperature. Smooth film containing 1 % and 10 % of ZnSO4 were obtained at the end of whole process. The composite formed in this way containing 80 % and 20 % ratio of both polyacrylamide and starch respectively.

3. RESULTS AND DISCUSSION

3.1. Scanning Electron Microscope

Scanning electron microscopy (SEM) is an important electron microscopy technique which produce highly resolved visual image of a particle with spatial resolution of 1 nm. X-rays provide information about a material's topography, composition and crystallography of particle.[14] Magnifications of up to 290,000 times are possible with SEM. SEM does not provide any interior information and is only used to see surface images of a substance. SEM can provide information on the type of elements and compounds in the sample and arrangement of atoms in single crystal particles, as well as the degree of order. SEM.[15] There are specimens that are too thick to be examined by direct transmission but do not lend themselves well to replica production, either because they are too delicate, because their surfaces are undercut so that the replica can be keyed to them, or because high-temperature observation is needed. The irradiation of the specimen with the scanning microscope is proven to be substantially less severe than with other electron microscopes.[16] A typical SEM photographic image of starch-g-polyacrylamide is translucent, and smooth with a slippery surface.[17] A larger mole ratio of polyacrylamide to starch gives lower end product's strength. Amount of starch used influenced surface morphology of coating ratios in starch/polyacrylamide composite. The scanning electron microscopic image (as shown in figure 2) of starch/polyacrylamide composite without any addition of inorganic metal salt are shown here. There is some extent of roughness in film rather the film is smooth and give the most translucent and uniform surface. Uniform structure of blank composite can be clearly observable in image. Smoothness in composite shows that effective crosslinking in starch/polyacrylamide composite has been developed. The SEM scans show a non-porous network structure with a maximum thickness of 10 µm.



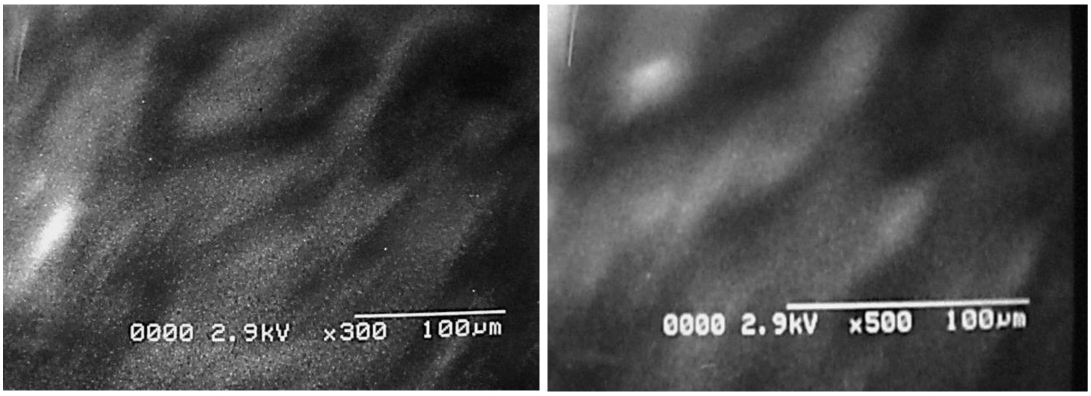
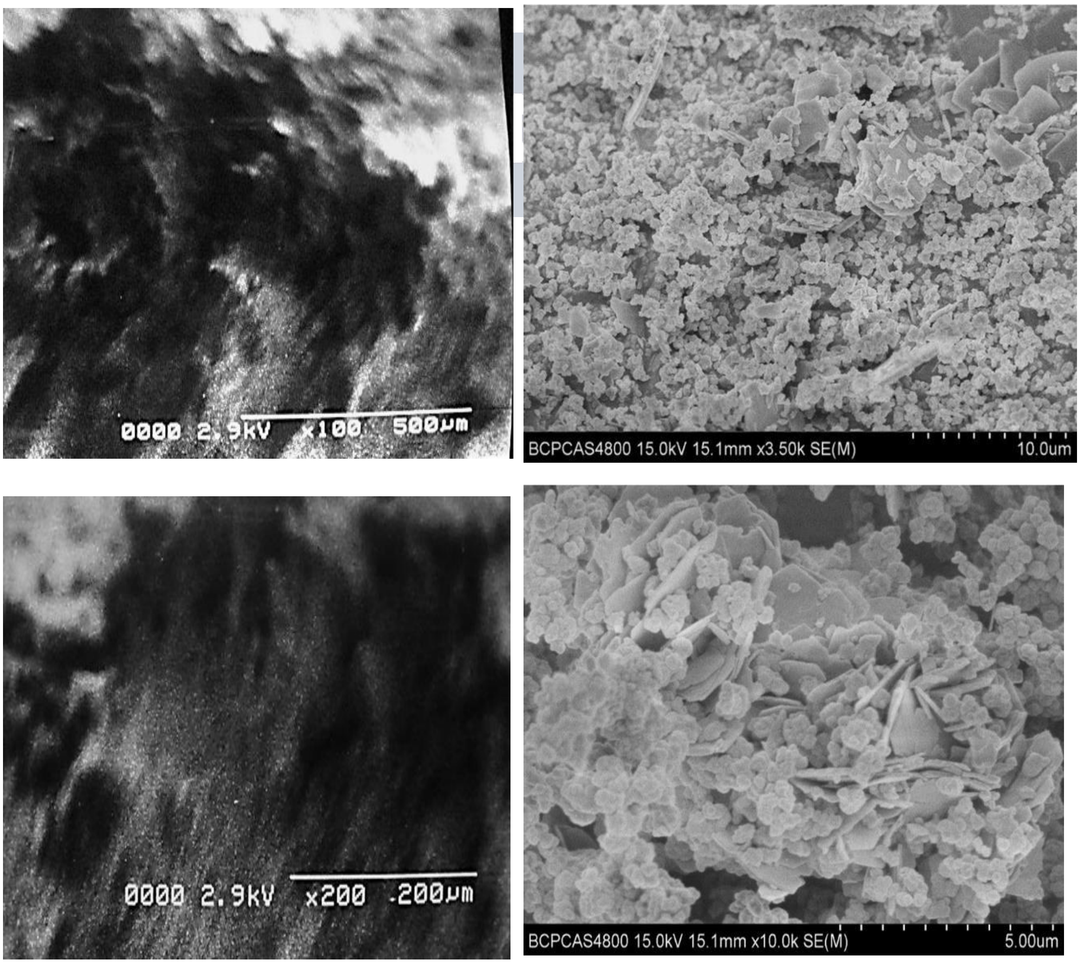


Figure 2. SEM images of starch/polyacrylamide (St-g-Pam) composite having uniform structure.

Figure 3 is the SEM result of starch/polyacrylamide composite containing 10% $ZnSO4$ salt. SEM image shows the discrete surfaces inside composite and decrease in smoothness of composite film than composite without $ZnSO4$ salt. This roughness is the indication of weak interaction of Zn^{+2} ions with amide and hydroxyl group of composites. The Zn^{+2} ions are present in slight discrete form inside the composite.



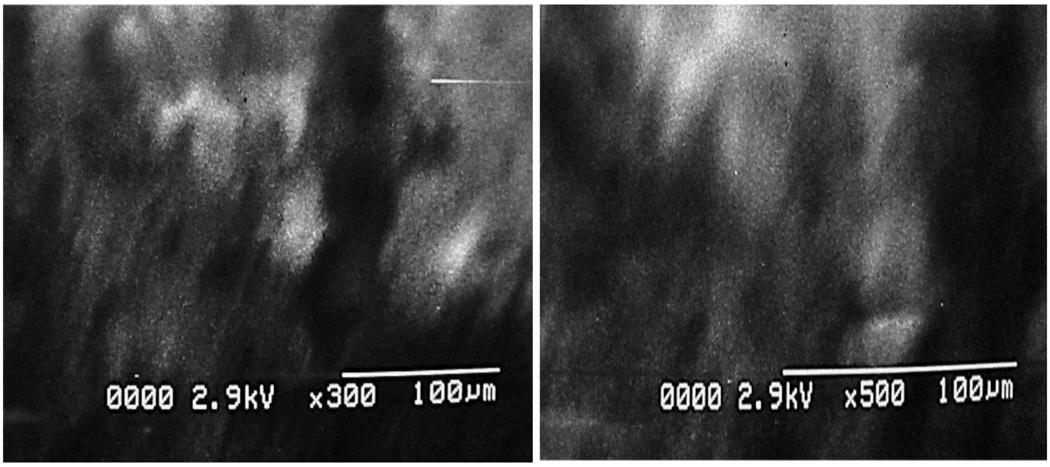


Figure 3. SEM images of starch/polyacrylamide composite containing 10% ZnSO4.

Figure 4 indicates the SEM image of composite containing 1 % ZnSO4 reveal the highly discrete structure of this composite and roughness is observed in this composite than composite containing 10 % ZnSO4. A random crosslinking structure, and the surface of the granules is rough with holes, cracks or layered structure. The difference in morphology indicates that the polyacrylamide has been grafted onto the starch

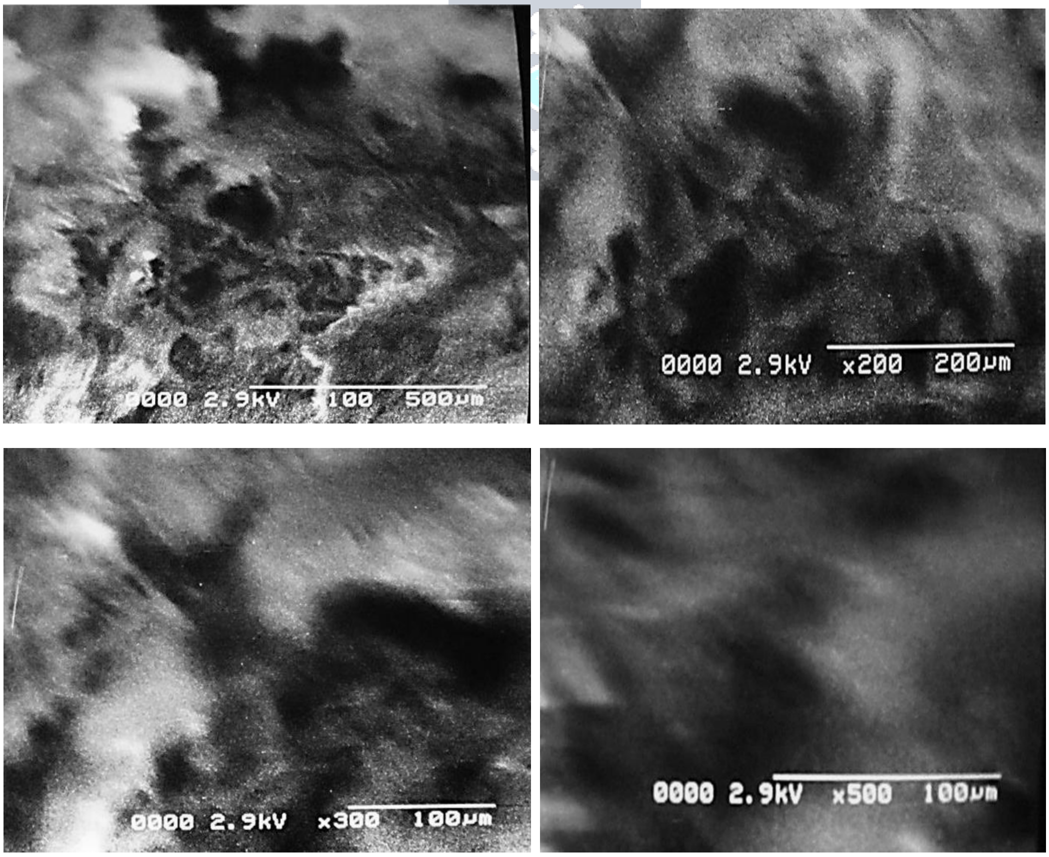


Figure 4. SEM images starch/polyacrylamide composite containing 1% ZnSO4 having high extent of roughness than 10 % ZnSO4 salt.

It can be concluded that starch/polyacrylamide composite has more uniform structure than composite containing 10 % ZnSO4 salt which is further smoother and has uniform structure than composite containing 1% ZnSO4. So, composite containing ZnSO4 salt has rough surface with porous structure than blank composite film.

3.2. Powder X-ray Diffraction

The technique of Today, atomic spacing and crystal structures are frequently studied using X-ray diffraction[18]. The theory behind X-ray diffraction is that monochromatic X-rays collide effectively with a crystalline material. When high-velocity electrons strike a metal target (anode) within an evacuated x-ray tube, they produce X-rays with wavelengths on the order of 10^{-3} to 10^{1} nm.[19]The most frequent use of X-ray powder diffraction is to identify unknown crystalline substance.[20] Geological, environmental, material, engineering, and biological research all depend on the determination of unknown solids.[21] Other application involves crystalline material characterization, identification of optically difficult-to-identify fined minerals.[22]

At 13.5° and 20.8°, starch has 2θ sharp distinctive diffraction peaks with low intensity and broad amorphous peaks. As a result of the retrograded starch chains, the starch crystals produced a strong diffraction peak at around 17.5 2θ three weak peaks at approximately 2θ of 20°, 22°, and 25°, and an extra peak at 15° 2θ. Polyacrylamide 's strongest peak is around 19.7, 27.7, 34.5 and 42.2 at 2θ with crystallinity of 36 %. [22] Xray diffraction pattern composite containing both barley starch and polyacrylamide is shown in Figure 5. The data for composite of barley starch and polyacrylamide give only one hollow peak at θ is 30 with intensity of peak is 60. The change in diffraction peak position than pure polymer indicates that the intramolecular interaction between the amide and hydroxyl group of polyacrylamide and starch respectively limit the molecular movement of starch chain. The composite containing barley starch-g-polyacrylamide show a more crystalline structure with high intensity than pure starch and polyacrylamide having less crystalline structure.

Figure 6 show the X-ray spectrum of starch/polyacrylamide composite containing 1 % Zinc Sulphate (ZnSO4) salt. There is change in peak position and peak intensity. Xray spectrum show a main peak at θ = 32, 45, 57, 66 and at 75 with intensity 190, 150, 70, 50, and 60 respectively. As intensity of peak is sharp higher will be crystallinity of composite. So, addition of metal salt increases the ordered arrangement of composite. Figure 7 show the X-ray spectrum of starch/polyacrylamide composite containing 10 % Zinc Sulphate (ZnSO4) salt. There is no change in peak position but there is decrease in intensity (θ = 32, 45, 57, 66 and 75 with intensity is 120, 115, 60, 40 and 60 respectively) of composite and show an amorphous state of composite with 10 % ZnCl2 metal salt. Lower crystallinity is observed incomposite containing 10 % Zinc Sulphate (ZnSO4) salt than composite containing 1% Zinc Sulphate (ZnSO4) salt. It can be concluded that starch/polyacrylamide composite containing 1 % Zinc Sulphate (ZnSO4) metal salt increased the crystallinity of composite due to lower angle of diffraction than Composite containing 10 % Zinc Sulphate (ZnSO4).

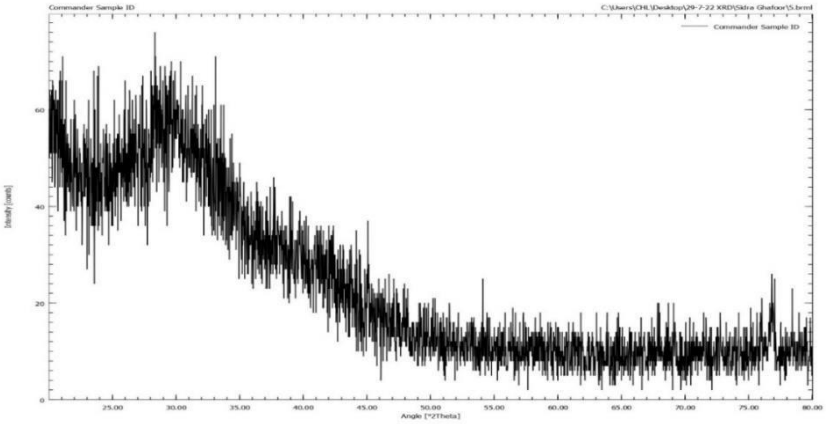


Figure 5. XRD of Barley starch-g-Polyacrylamide composite with one hollow peak at θ is 30 with intensity of peak is 60 represent the interaction between pure polymers.

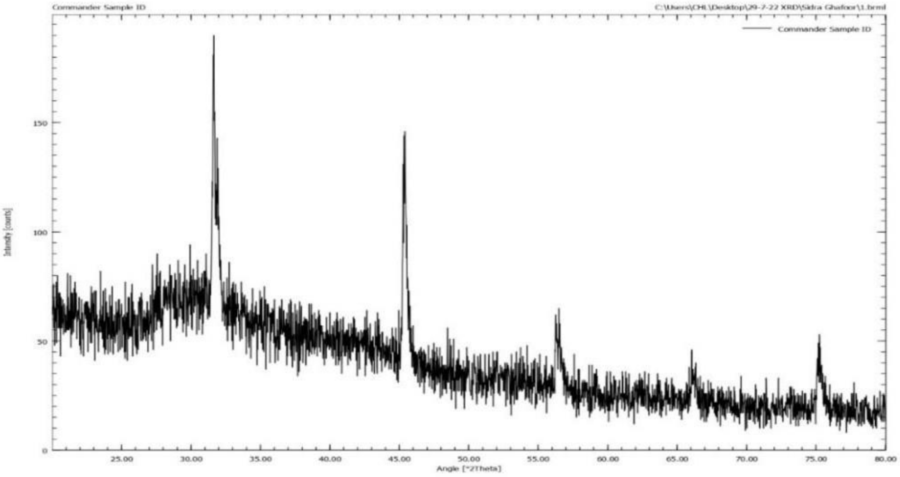


Figure 6. XRD of Starch-g-Polyacrylamide composite containing 1% $ZnSO_4$ salt. Five sharp peaks with high intensity show the strong interaction between composite and metal salt

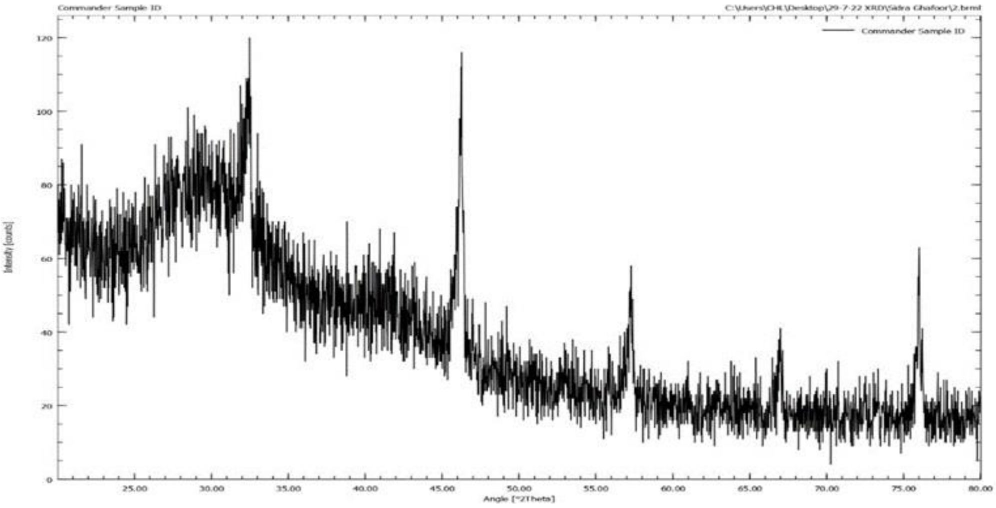


Figure 7. XRD of Starch-g-Polyacrylamide composite containing 10 % $ZnSO_4$. Five sharp peaks than pure composite shows the interaction between composite and metal salt.

3.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopic analysis includes the determination of molecular species and the identification of their concentration in the substance. FTIR used for qualitative (structural interpretation and compound determination) and quantitative analysis. An interferometer, radiation source and a detector are the three basic spectrometer components in an FTR. Michelson interferometer is the most often used interferometer. Scanning speed and sensitivity of FTIR is high with relatively low probability of mechanical breakdown. FT-IR used for the analysis of low molecular weight compound, chemical complexes, analysis of cell or tissue and for tissue imaging, for the study of protein, carbohydrates and lipids.[23] It is employed for the analysis of semiconductor, archaeology, pharmaceuticals and textiles.

A moving mirror, a fixed mirror, and a beam splitter are its three functional parts. An interferometer, a relatively simple optical apparatus formed a unique signal with all of the infrared frequencies "encoded" in. The beam splitter in most interferometers collect the incoming IR beam and separates it into two rays of beams. A flat mirror that is set in situ reflects one beam. The other beam permits it to move a small distance away from the beam splitter. This is where the sample's specific frequencies are absorbed. These two beams "interfere" with each other, resulting in the signal that exits the interferometer is interferogram. The interferogram signal that was measured cannot be readily analysed for frequency spectrum. Fourier transformation "decode" various frequencies (FT). Finally, measurement done when beam reach to the detector. The detectors employed measured interferogram signal. [24]

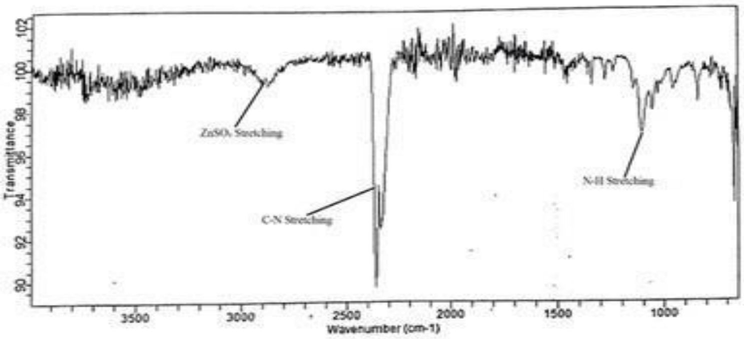


Figure 8 shows the spectrum of starch-g-polyacrylamide composite containing 2.5 % ZnSO4 metal salt. A broad peak appeared at 2900 cm^{-1} due to ZnSO4 stretching, at 2350 cm^{-1} due to C-N stretching and at 1100 cm^{-1} due to N-H stretching. In Figure 9 the composite with 5 % ZnSO4 shows the broad peak at 2850 cm^{-1} due to ZnSO4. A sharp peak at 2350 cm^{-1} due to C- N stretching and at 1100 cm^{-1} due to N-H stretching. Figure 10 shows spectrum of starch-g- polyacrylamide composite containing 10% ZnSO4. A broad peak at 2850 cm^{-1} due to ZnSO4 stretching. A sharp peak at 2350 cm^{-1} due to C-N stretching and at 1100 cm^{-1} due to N-H stretching. From these figures we concluded that ZnSO4 metal salts does not have strong interaction with composite as peak slightly become sharp by increasing concentration of metal salt, but peak position almost remains same.

Figure 8. FTIR spectrum of composite containing 2.5 % ZnSO4.

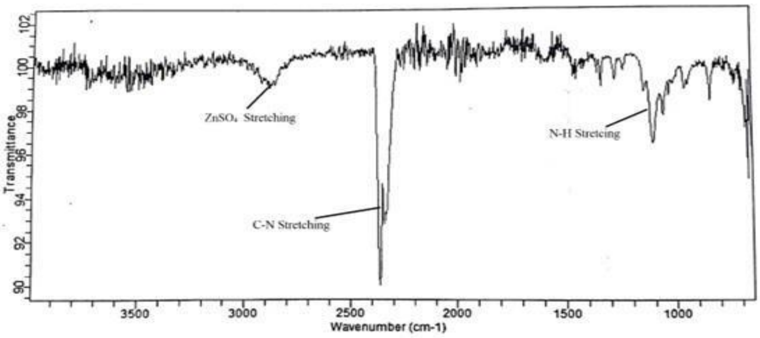


Figure 9. FTIR spectrum of composite containing 5 % ZnSO4.

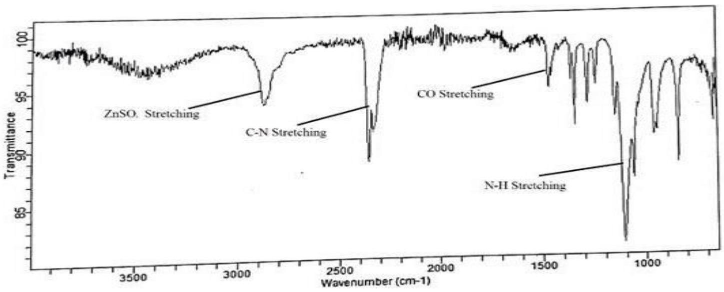


Figure 10. FTIR spectrum of composite containing 10 % ZnSO4.

4. CONCLUSION

In a nutshell, the addition of different concentration of inorganic Zinc Sulfate (ZnSO4) salt in starch-g-polyacrylamide composite clearly changed the morphological and physical properties of composite. The prepared composite was characterized by different techniques. It shows that increase in crystallinity of composite by the addition of inorganic Zinc Sulfate (ZnSO4) salt. Salt overlap with composite to form a coordinate covalent bond and increase the crystallinity of composite. Results shows that composite containing 1 % Zinc Sulfate (ZnSO4) salt is smoother and has uniform structure than starch-g-polyacrylamide composite containing 10 % Zinc Sulfate (ZnSO4) salt.

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