

Study of Biodegradability by Graft Copolymerization of Starch Backbone with Acrylic Acid, Methacrylate, Acetonitrile with the Advancement of Ni-Doped Nanoparticles

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ABSTRACT

Grafting of starch backbone done with monomers such as acrylic acid, methacrylate and acetonitrile through a free-radical mechanism in the presence of Lutensol XL-100 using an initiator ammonium per-sulphate with constant stirring and heating at temperature of 80°C. Co-polymerization of acrylic acid, methacrylate and acetonitrile is the initial step followed by grafting. Nickel doped nanoparticles are attached on this grafted polymer to enhance the biodegradability property of starch. The property of this biodegradable mixture is studied by soil burial method. Study and analysis of these polymers is done with the help of FTIR, TGA and DSC and SEM. Results indicated that grafting is an efficient method to impart biodegradability to non-biodegradable polymers by the covalent attachment of monomers on starch backbone. Our research suggested that biodegradability of these grafted starch polymers enriched with nanoparticles increased and show resistance against Nano-composites with various strategies show resistance against microorganisms by oxidizing cell components or by making secondary products such heavy metal ions. These by-products ultimately led to the destruction of microbes so that can be used for packaging of food materials, in medical field to make clinical instruments for surgical purposes, for efficient delivery of drugs at targeted site and these biodegradable polymers is employed in agriculture field in the form of fibers and films due to their property of increased absorption of materials.

Keywords: Grafting, Starch, Acrylic acid, Methacrylate, Acetonitrile, Ammonium per-sulphate, Lutensol XL-100, Ni-doped nanoparticles

INTRODUCTION

Starch is a polysaccharide and present mainly in the form of hydrocolloids. It is the most abundant form of carbohydrate present in nature and has the highest rate of biodegradability [1,2]. Starch can be obtained from different sources such as grains, wheat, rice and green plants. Starch is soluble in water and present in two forms namely amylose and amylopectin. Amylose is the linear form while amylopectin is the branched form of starch (Figure 1). Both forms of the starch differ in the biodegradability, elongation and strength. Starch can be used for grafting because of its low cost, easily available, biodegradable and environment friendly [3] (Figure 2).

With emerging science and technology, it becomes the need of time to modify the polymers to obtain various beneficial properties for target applications. There are number of methods available for the polymerization of monomers onto starch, grafting is one of the best approach where monomers are covalently bonded onto a starch. Acrylic acid, methacrylate and acetonitrile (monomers) covalently attached on starch with the free-radical mechanism by ammonium per-sulphate used as initiator [4-6].

High viscosity, thermal stability, biodegradability, good film forming properties and water absorption capacity are some of the properties shown by the graft copolymers of starch. TGA analysis revealed that starch grafted polymers shows higher thermal stability as compared to native starch. Grafting of these polymers on starch has given the most biodegradable products so that can be used for medical, agriculture, and in packaging applications [7,8]. In this era of plastics, millions of plastics are buried in landfills and causes clogging of landfills ultimately cause environmental pollution. Currently, researchers employing natural polymers such as starch based co-polymers to enhance the biodegradability. In agriculture sphere, these biodegradable polymers are used for microbial and oxidative degradation [9-12].

Co-polymerization of acrylic acid, methacrylate and acetonitrile is one of the essential and first steps in grafting. Ammonium per-sulphate used as an initiator in this reaction and it generates free-radical by constant magnetic stirring at specific temperature [13,14]. Lutensol XL-100 acts as an emulsifier and aid monomers to attach on starch. Because, Lutensol XL-100 coagulates all the free radicals generated by ammonium per-sulphate and help in monomers to attack on free-radicals on starch [15-17] (Figure 3).

Ni-doped nanoparticles attach on this grafted polymer to enhance the biodegradability of starch and increased resistance against microbes so make it worthy to use in different medical and food packaging applications. Biodegradability of these polymers can be analyzed by soil burial method and analysis of grafted polymer and biodegradation interpreted by FTIR, TGA and DCA analysis. This study mainly focuses on the grafting of starch backbone by co-polymerization of acrylic acid, methacrylate and acetonitrile monomers followed by the addition of Ni-doped nanoparticles [18-21].

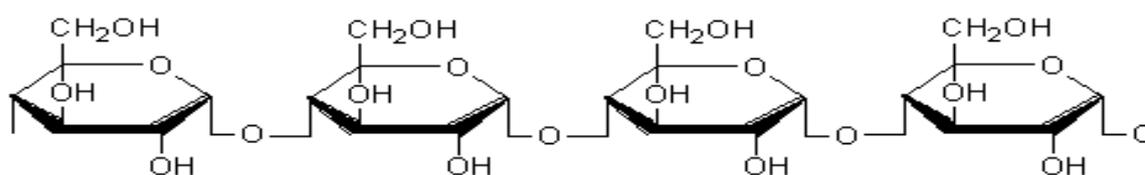


Figure 1: Structure of amylose a linear polymer in starch

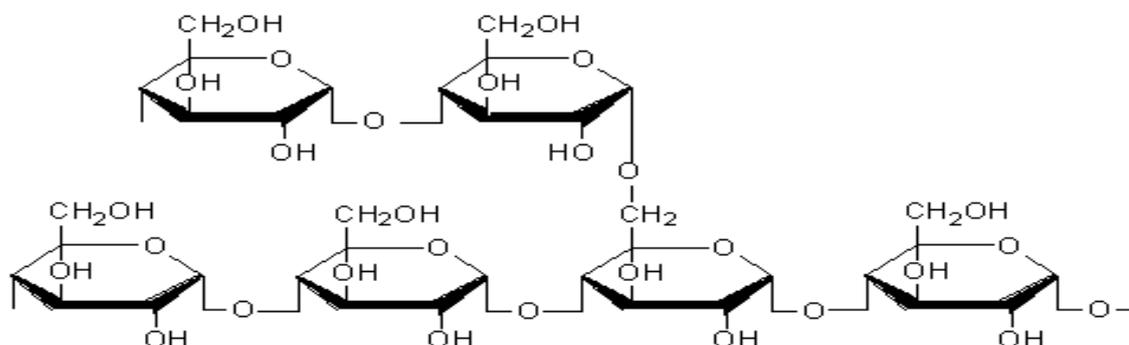


Figure 2: Structure of amylopectin a branched polymer in starch

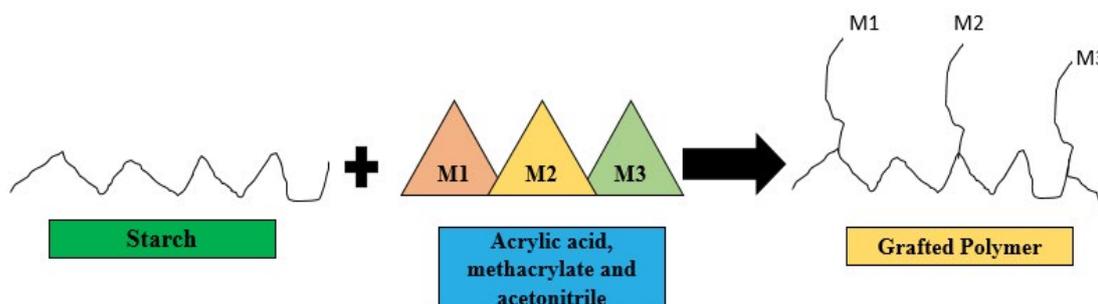


Figure 3: Co-polymerization and grafting;
M1: Acrylic acid, M2: Methacrylate and M3: Acetonitrile

EXPERIMENTAL

Materials

Starch (commercial grade), ammonium per-sulphate (Merck), Lutensol XL-100 (Merck), Acrylic acid, Methacrylate, Acetonitrile (Merck) and Nickel nanoparticles and distilled water. Three necked reaction flask 500 ml, beakers 100 ml and 250 ml, thermometer 360°C, petri dishes and glass rod and applicator is used.

Methodology

Take weighted amount 0.50 g of starch and dissolve in 25 ml distilled water and digest the starch with the help of Bunsen burner. In the next step, transfer this dissolved starch in the three-necked reaction kettle attached with magnetic stirrer then into the thermo-stat water bath. Magnetic stirrer is responsible for continuous stirring of the starch in distilled water. Water bath is required to maintain a temperature of 80°C. When a clear solution is obtained add 10-12 drops of Lutensol XL-100. Lutensol XL-100 acts as an emulsifier in this reaction. Lutensol XL-100 assists monomers to attach efficiently on a starch by coagulation of free-radicals around starch. After 10 min add 0.150 g of ammonium per-sulphate used as an initiator responsible to produce free radicals. Allow this mixture up to 10 min to mix gently with stirrer. In a separate beaker mixture of monomers acrylic acid, methacrylate and acetonitrile is prepared in distilled water and as a result co-polymerization of three monomers would result then add this mixture into the three-necked flask with the rate of 1ml per minute and mix gently so that co-polymerized monomers can attach on starch by free radical mechanism then remain this reaction mixture under water bath for about 90 min at 80°C. Transfer this liquid mixture onto a petri dish and allow this mixture to cool for 30 min. After cooling, apply this mixture onto a glass sheet with the help of applicator for FTIR, TGA-DSC analysis [22].

Addition of copolymer nano-composites is the last step in this reaction. Prepare 0.02 g nickel doped nanoparticles and add into the three-necked reaction flask, allowed this reaction to proceed for further 15 min. Nickel doped nanoparticles are attached on grafted starch backbone and then a thin film is prepared with the help of applicator on plastic sheet for FTIR, TGA-DSC analysis. Summary of the reaction is depicted in Figure 4.

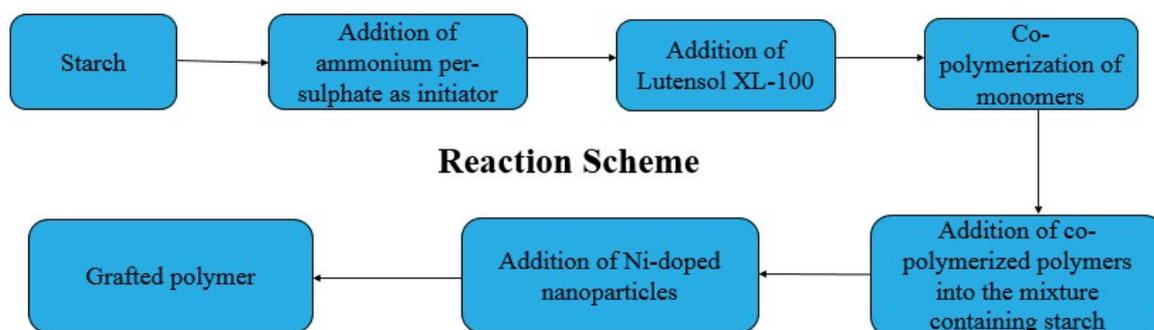


Figure 4: Generalized scheme of the reaction depicting basic steps of the experimental work

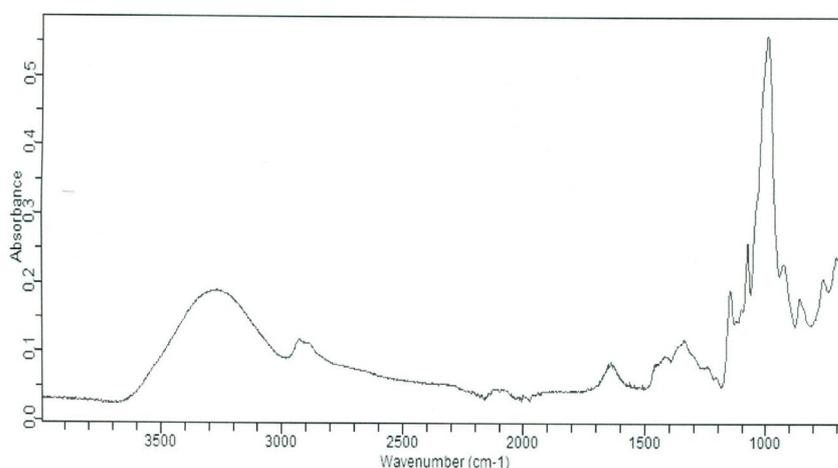


Figure 5: FTIR spectrum of starch

RESULTS AND DISCUSSION

For the analysis of grafted polymers as FTIR, SEM, DSC and TGA are applied. The FTIR technique is mostly used to confirm the grafting process.

FTIR spectrum of starch

Analysis of starch with the help of Fourier-transform Infra-red spectroscopy shows that a hump is present in between 3000-3500 cm^{-1} represents the stretching of O-H bond. Peak obtained at 2950 cm^{-1} represent the stretching of C-H bond. Peak at 1070 cm^{-1} indicate the presence of glycosidic bond and a ring structure of glucose in the starch [23] (Figure 5).

FTIR spectra of nano-composites

Peaks which are obtained at 1430 cm^{-1} indicating the stretching of carbon-carbon double bond C=C in the nano-composites. The peaks which are obtained at 1700 cm^{-1} represent the presence of Carbonyl group in the sample. There is slight peak at 1070 cm^{-1} representing the glycosidic linkage and the peak at 1150-1180 cm^{-1} represents the presence of ester group in the sample [24,25] (Figure 6).

FTIR spectra of sample without nano-composites

FTIR spectrum without nano-composites shows different peaks. The peaks at 1430 cm^{-1} indicating the carbon-carbon double bond stretching. The peak obtained at 1080 cm^{-1} representing the glycosidic linkage and the peak observed between 1150-1170 cm^{-1} representing the ester group [26] (Figure 7).

TGA-DSC analysis of starch-g-polymer

Thermogravimetric analysis and differential scanning calorimetry are two significant techniques for the analysis of biodegradability of polymers. The TGA line indicates the decomposition of polymers. At 250°C, 5% polymer is decomposed while increasing the temperature led to the more decomposition of polymers and the weight of polymers rapidly decreasing [27]. A steady steep has been observed between 425-500°C. 86% was decomposed at 500°C. On the other hand, DSC analysis indicated that sample has 10% impurity due to moisture and some unreacted monomers present in the sample. The heat flow of the polymer examined three humps. The complete melting point of the polymer was observed at 330°C. After it recrystallize again and show a slight behavior of melting at 400°C (Figure 8).

TGA-DSC analysis of starch copolymer nano-composites

Its 5% weight was exhausted at the 275°C which was more than sample first. The 50% weight was exhausted at 360°C and 85% exhausted at the 500°C. 15% was not exhausted up to the 500°C. DSC line has been shown the three humps;

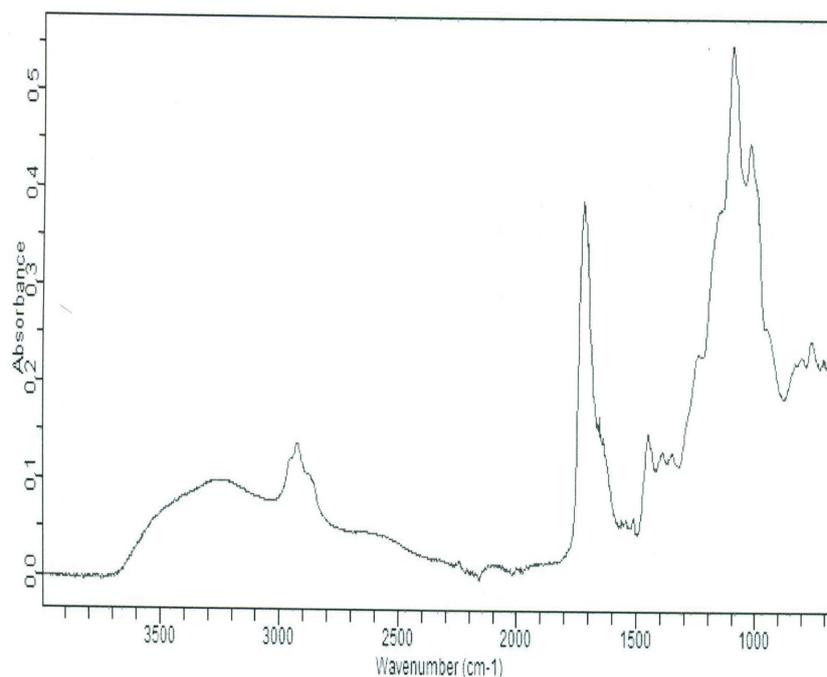


Figure 6: FTIR spectrum of nano composites

it melts on 350°C and then recrystallizes. And its second melting point was 450°C which described the presence of nanoparticles (Figure 9).

Biodegradability testing by soil burial method

This test is performed in soil exposure. For this purpose, we prepare soil beds in the lab by mixing commercial soil with standard sieved soil. The test sample are buried into the soil beds and placed for 4 weeks and supplied with organic fertilizer to increases the growth of microorganism. The best criteria for the study of microbial activity are on cotton textile strip. When this strip placed more than ten days in the soil then it loses more than 90% of its tensile strength [28,29]. Besides for this, none of any one type of materials are prepared and acts as standard for all polymeric materials. The soil containing the test samples are placed in an incubator with fix temperature for between 15 days to 30 days. The moisture content is normally set at 25-35%, when the moisture percentage increases then degradation increases. The soil contains 35-45% of the moisture and has high ability to hold water. Different soil structure shows different variation in microbial activity. After a certain time, sample is removed and examined with SEM and light microscope to indicate the damage surfaces which represent the presence of microorganism and their growth. Fragmentation is also measured from this test [30,31].

Preparation of samples for biodegradability

First, we prepared various sample then we select the sample in which films are formed. These sample cut into specific strips with definite size. These strips are 1.5 cm in width, 8 cm long and the thickness is 0.1 cm and the weight of each strip is approximately 1 g. Equal quantity of soil was taken in two pots. Then we calculate the weight of these two pots and then placed the sample in the pots. Before placing the pots in room temperature, they covered with aluminum foil, and calculate the weight loss after 30 days [30]. The weight loss percentage can be calculated by using following formula.

Wt. loss percentage= $\frac{\text{Initial Wt. of sample} - \text{Wt. after passing days}}{\text{Wt. of Sample taken at initial stage}}$

Biodegradation of both samples with and without nano-composites %weight loss

The biodegradation results were explained that percentage weight loss of nano-composites polymer was very low than simple grafted polymer. These results were proved that nanoparticles resist against the microbes that's why their polymer was shown the low percentage weight loss. Nano-composites polymer was not moisture absorber and its degradation rate was slow, so these are best for the packing purposes and in medical fields (Figure 10 and Table 1).

Analysis by scanning electron microscopy

SEM photographs cannot depict the quantitative analysis; through this approach morphology of the products of grafted polymers can be determined. The SEM graphs of pure starch depict granular structures (Figure 11a) which are disordered during gel formation (Figure 11b). The grafted polymer showed different morphology, dependent upon the degree of grafting with backbone of starch. At low concentration of monomer there are little changes in the morphology but the structure does not give a clear idea (Figure 11c). The SEM pictures at higher concentration of monomers show a porous structure and show a more grafting in this area which can be seen in following figure (Figure 11d). These hollow structures also represent the formation of the agglomeration of the minute particles [31] (Figure 11).

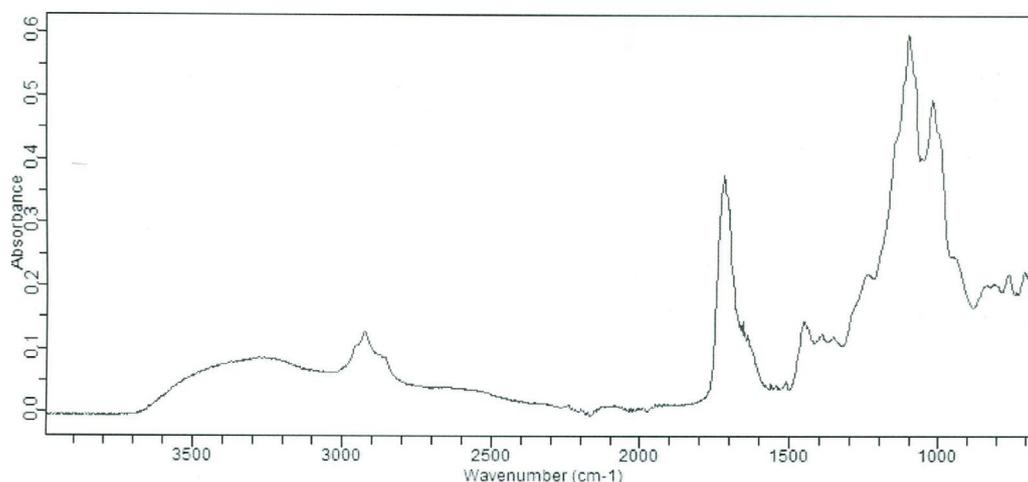


Figure 7: FTIR spectrum of sample without nano composite

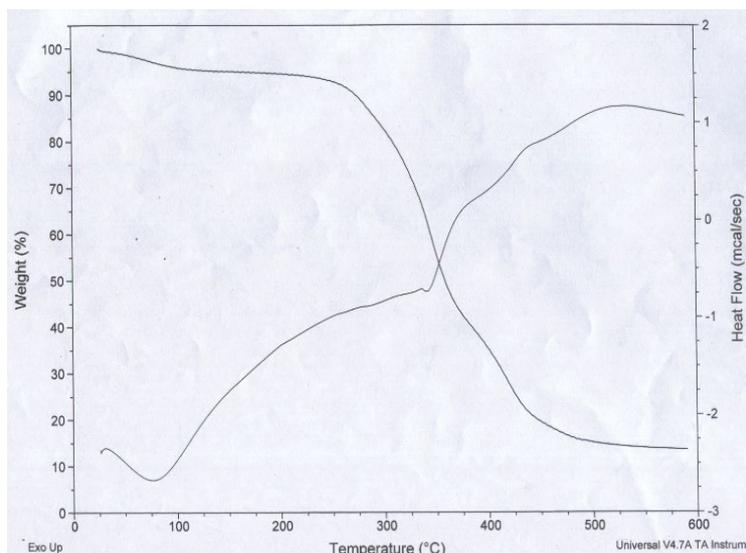


Figure 8: TGA-DSC curves starch-g-monomer polymers

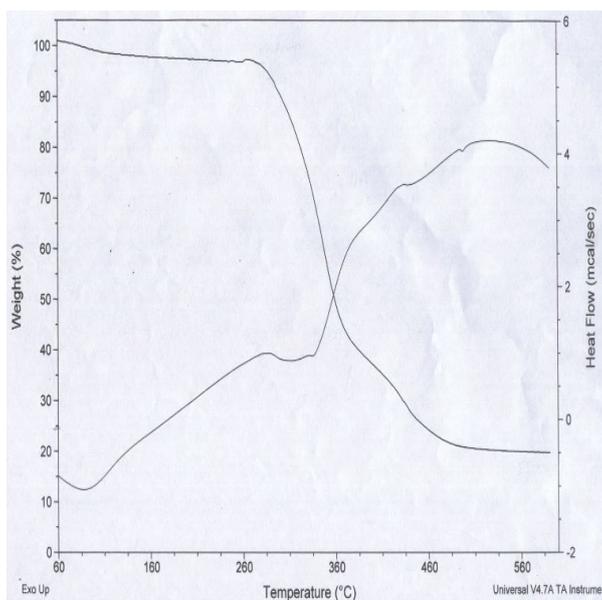


Figure 9: TGA-DSC curves of sample starch-g-monomer polymers

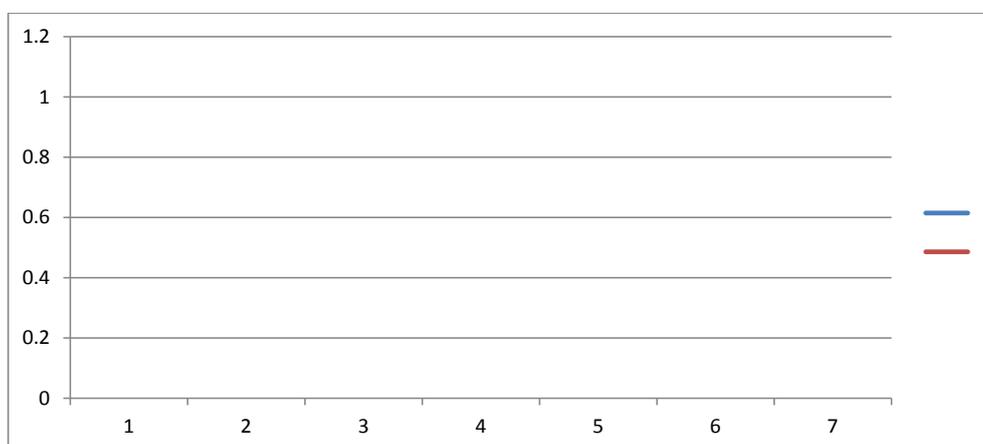


Figure 10: %weight loss of samples with and without nanocomposites

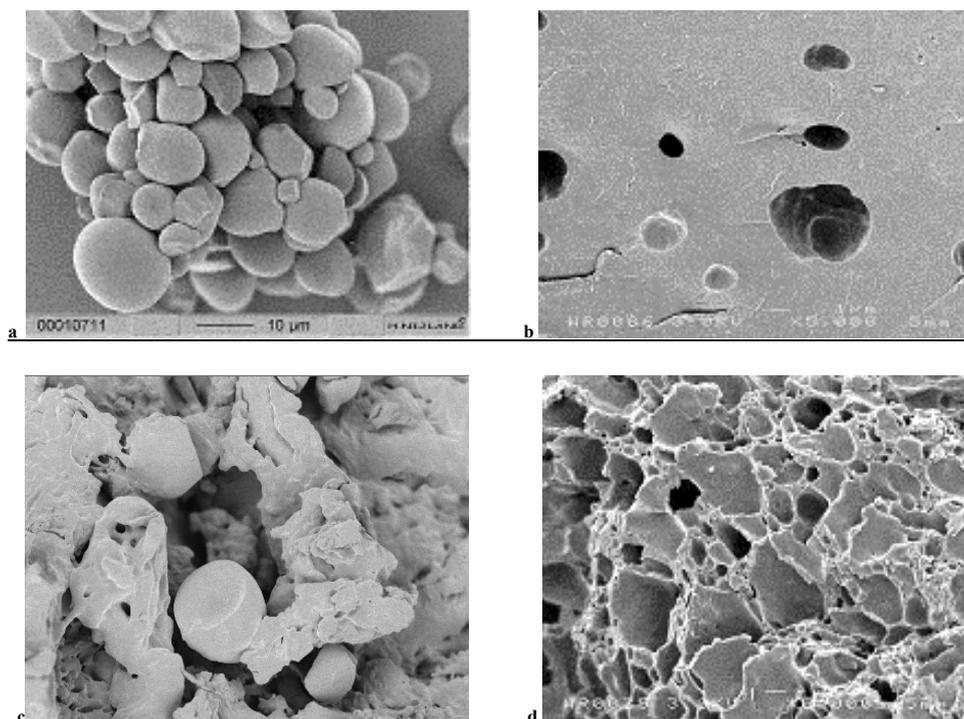


Figure 11: SEM photographs (a) magnification of pure starch at 1500, (b) Gel formed starch at magnification 5000 (c) magnification at 5000 of starch grafted polymers when low add-on (d) magnification at 5000 of grafted starch polymers when high add-on.

Table 1: Biodegradability of both samples with and without nano-composites in % weight loss

Sample	Initial weight of Sample (grams)	%Weight loss after 10 days	%Weight loss after 20 days	%Weight loss after 30 days	%Weight loss after 40 days	%Weight loss after 50 days	%Weight loss after 60 days
Sample H-1 with nanocomposites	1.12	-1.78	2.67	5.35	8.92	12.5	23.21
Sample H-2 without nanocomposites	1.05	-1.90	3.80	2.85	9.52	10.47	16.19

CONCLUSION

The graft copolymerization of starch with different monomer (acrylic acid, methyl methacrylate, and acrylonitrile) was investigated using a free radical initiator system ammonium per-sulphate with constant stirring and heating at certain temperature. Number of characterization techniques is available to determine the grafting reaction taking place on the backbone of starch. These techniques are FTIR, TGA-DSC and SEM. The peaks which are obtained at 1700, 1430 and 1100-1150 cm^{-1} shows the valid proof of grafting of the starch backbone. The SEM image revealed the hollow structures when the monomers are at high add on in starch backbone and show the grafting process. TGA and DSC were estimated the degradation and melting points of the copolymer and nano-composite polymer. The TGA analysis proved the degradation rate of nano-composite polymer is low than the simple grafted polymer. DSC proved that its melting point is also more than the simple copolymer. Soil burial method was used for the estimation of biodegradation of these polymers. The biodegradation study of these prepared samples has shown that % weight loss of nano-composite is very low than the copolymers. Results suggested that nano-composite polymer was the moisture resistant and low biodegradation rate. The degradation of Nano composite depends upon the following factors but most prominent is moisture loving. After that a decrease in weight was also calculated by using formula. Results explained that the grafting was a unique property which induced the microbial degradation that was not in the synthetic polymers. The nano-composite polymers imparted resistance against the fungi and bacteria, therefore these nano-composite polymers are best for packing and in medical fields.

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