TiO₂/starch-based biodegradable copolymer nanocomposite as a plant growth regulator

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This study describes the development of a nano-titanium dioxide (TiO₂)-based composite of starch-co-poly (acrylamide) (St-g-PAM) copolymer. The graft copolymer was characterised by Fourier transform infrared analysis, thermal gravimetric analysis (TGA), field emission scanning electron microscopy and X-ray diffraction. It was confirmed that acrylamide was grafted over starch successfully. Also, the effects of pH, initiator dosage, temperature and time on grafting percentage and efficiency were investigated. The synthesised titanium dioxide nanoparticle successfully enhancing the thermal and biological properties of a native copolymer was confirmed by TGA and biological assay. This titanium dioxide nanocomposite starch-co-poly(acrylamide) (titanium dioxide/St-g-PAM) showed some important properties, such as plant growth regulation, and acted as a superabsorbent polymer with excellent thermal properties and antibacterial activity. The synthesised titanium dioxide nanoparticle is biodegradable and environment-friendly and accomplished the concept of green chemistry.

Notation

GP	amount of acrylamide grafted onto the soluble starch
GE	ratio of insoluble acrylamide grafted onto the soluble starch to the total acrylamide
M_0	weight of the soluble starch
M_1	combined weight of the graft copolymer and the homopolymer
M_2	weight of the graft copolymer

1. Introduction

In material science, polymeric materials have unique importance because, in combination with suitable metal nanoscience, they give composites useful for developing advanced equipment.¹ Material chemists focus on natural polymers, such as starch, cellulose, chitosan and hemicelluloses, which are inherently biodegradable and capable candidates to meet different requirements.² Among these natural polymers, starch is regenerated from carbon dioxide and water by photosynthesis in plants.³ With this complete biodegradability, low cost and renewability, starch is considered a promising candidate for developing sustainable materials. Much effort has been exerted to create starch-based polymers for conserving petrochemical resources and reducing environmental impact.^{4–6} Also, the starch polymer exhibits hydrophilic properties and strong intermolecular association by way of hydrogen bonding formed by hydroxyl groups on the granule surface.⁷

Modification of starch using either a physical or chemical method is necessary to enhance the properties of starch-based materials.⁸ Also, the exponential growth of research activities has been seen in nanoscience and nanotechnology in the past decades. Starch-co-poly (acrylamide) (St-g-PAM) is an important superabsorbent polymer (SAP), and its wide applications in many technological and productive fields take advantage of the unique combination of

excellent agricultural properties, some good mechanical properties, thermal stability, weather resistance, model-ability and easy shaping. Starch can be chemically modified by reactions such as hydrolysis, etherification, grafting and dextrinisation. In the last few years, some reports on graft polymerisation of starch and acrylamide (AM) reported that polyacrylamide was bonded to the starch skeleton to form branched chains with low molecular weights in the presence of horseradish peroxidase (HRP)/hydrogen peroxide (H₂O₂).^{8,9} Also, titanium dioxide (TiO₂) has been widely used as a pigment in sunscreens, paints, ointments, toothpaste and so on. Nano-titanium dioxide photo semiconductors have many applications in various fields, including photocatalysis, agriculture, dye-sensitised solar cells and biomedical devices. Nanosize titanium dioxide protects both matrices and behind the matrix from degradation due to ultraviolet (UV) light.¹⁰ In recent years, starch grafting nano-titanium dioxide has attracted chemists because of increasing environmental concern and interest in eco-friendly products derived from cheaper, biodegradable and renewable natural polymers to replace petroleum-based synthetic polymers. Graft copolymerisation is one way to introduce biodegradability and improved properties to a polymer.¹¹ Graft copolymers are composed of natural and synthetic polymers in which the chains of a polymer made up of a monomer are grafted over a polymer chain of another monomer.

In the past few years, research worldwide, particularly in Iran, China, Europe and the United States, has led to the development of a class of SAP that can increase water use efficiency and enhance crop yield. Soil conditioning with SAP is an attractive and exciting fact in modern agriculture. It is shown that SAP materials are hydrophilic and easily absorb and retain large amounts of water. A few SAPs are used in the agricultural field, such as cross-linked polyacrylates, starch-graft copolymers, AM-acrylate copolymers and cross-linked polyacrylamides. Out of these, St-g-PAM graft polymer is one of the

best because of its important properties, such as its ability to increase water holding capacity, gradual biodegradability without the formation of toxic species and enhancement of soil permeability and infiltration rate.¹²

In this work, AM monomer was grafted on a polymeric starch to form St-g-PAM graft copolymer, and synthesised titanium dioxide nanoparticles were composited to build titanium dioxide/St-g-PAM to enhance the thermal and biological properties of the native copolymer, which was characterised by thermal gravimetric analysis (TGA), Fourier transform infrared (FT-IR) analysis, X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) techniques. The effects of pH, initiator dosage, temperature and time on grafting percentage (GP) and grafting efficiency (GE) were also investigated. Also, this synthesised material was employed in the agricultural field as an SAP for plant growth regulation (PGR) applications.

2. Material and experimental details

2.1 Materials

AM and starch were obtained from Spectrochem Pvt. Ltd., Mumbai, India. Nitric acid and potassium persulfate (KPS) were purchased from S.D. Fine-Chem. Ltd, Mumbai, India. Titanium tetraisopropoxide [Ti(OCH(CH₃)₂)₄] and isopropanol were used as received without any further purification from Sigma Aldrich, Mumbai, India.

2.2 Synthesis of titanium dioxide nanoparticles¹³

In a 20 ml round-bottomed flask, the solution of titanium tetraisopropoxide was added drop by drop into 22 ml of a solution containing 10 ml isopropanol and 12 ml deionised water under constant stirring at 80°C. After 1 h, the mixture of 8 ml of concentrated nitric acid (HNO₃) and deionised water was added into the titanium tetraisopropoxide solution and kept under constant stirring at 60°C for 6 h; after 6 h a highly viscous sol-gel was obtained. The prepared sol-gel was heated at 300°C for 2 h in the open atmosphere. After annealing, the titanium dioxide nanocrystalline powder was obtained.

2.3 Synthesis of titanium dioxide/St-g-PAM

Soluble starch (2.5 g, dry weight) and 90 ml water were placed in a three-necked, round-bottomed flask and gelatinised by stirring for 10 min at 100°C, then cooled at room temperature. After cooling, 3 g of AM was added to the three-necked flask under a nitrogen atmosphere and stirred for 30 min. Then, titanium dioxide nanoparticles (1%) were added and stirred at room temperature for 10 min. Then, 0.5 g of potassium persulfate was added as a radical initiator with constant stirring at 80°C. The resulting copolymer of the nanocomposite was cooled to room temperature as shown in Figure 1.

2.3.1 Plant growth assay

Five hundred grammes of soil was dried in sunlight for 2 days. After drying, 250 g of soil was added to each of two separate beakers. The mung bean (*Vigna radiata*) was selected for this

study because of its ready availability, fast germination time and edibility. Two seeds were added to each beaker containing the same amount of soil. Then, 10 g of titanium dioxide/St-g-PAM was added to a test beaker (T), but not to a control beaker (C, without polymer). The same amounts of water were added to both beakers, and changes were observed after each day.

2.3.2 Antibacterial assay

Antibacterial activity screen studies of St-g-PAM and titanium dioxide/St-g-PAM were performed through the gel trapping method, and reduction percentage was calculated (Table 1). Three flasks were labelled as (a) treated, (b) untreated and (c) inoculum, respectively. Then, 10 ml of working dilution of bacterial inoculum was prepared in each flask. After capping, the flask was put on a rotary shaker (100 revolutions/min) for 1 min. Each flask is considered as a '0 contact time'. The bacterial concentration was determined by performing serial dilutions and standard plate count techniques. All the Petri dishes were incubated for 24 h. Then colonies in a Petri dish were counted as colony forming units (CFU).

2.3.3 Calculation

The per cent reduction of the organisms resulting from contact with the specimen was calculated using the following formula. Results can be presented in either per cent reduction when measuring CFU/ml or as a death rate constant when calculating the mean log₁₀ density of bacteria.

$$1. \text{Reduction \% (CFU/ml)} = \frac{B - A}{B} \times 100$$

A is the CFU per millilitre (or mean log₁₀ density of bacteria) for the flask containing the treated substrate after 1 h contact time, and *B* is '0' contact time CFU per millilitre (or mean log₁₀ density of bacteria) for the flask used to determine *A* before the addition of the treated substrate.

2.4 Methods

2.4.1 FT-IR analysis

The infrared spectra of the samples were recorded on a Shimadzu FT-IR-8400 with the frequency ranging from 400 to 4000 cm⁻¹ using KBr flakes. The samples were scanned 28 times before the final recording of the spectra at the Institute of Chemical Technology, North Maharashtra University, Jalgaon, India.

2.4.2 TGA

The thermal behaviour of the prepared samples was examined using the Thermogravimetric Analyzer model Perkin Elmer TGA 4000 at SAIF Department, IIT Bombay, India, from ambient temperature to 850°C. A heating rate of 10°C/min was used under a nitrogen atmosphere and at a flow rate of 30 ml/min. A dry sample weighing about 6.9012 mg was used. The standard uncertainty of the sample mass measurement was ±1%. The instrument was calibrated using calcium oxalate, which was supplied along with the instrument.

Figure 1. Schematic representation of titanium dioxide/St-g-PAM preparation

2.4.3 XRD

XRD measurements of the prepared samples were recorded with a Bruker Advance 8 CuK α radiation X-Ray Diffractometer at the Institute of Chemical Technology, North Maharashtra University, Jalgaon, India, equipped with CuK α radiation and operated at

40 kV and 100 mA. The diffractograms were recorded in the range of 2θ from 5° to 60° at a speed rate of 2°/min.

2.4.4 Morphological analysis (FE-SEM)

The morphology of the dried sample was examined using a scanning electron microscope (SEM), S-4800, JEOL, JSM 6360 and JSM 5400 with the voltage range of 0.5 to 30 kV after coating the sample with gold film at the Institute of Chemical Technology, North Maharashtra University, Jalgaon, India.

2.4.5 Biological activity

The antibacterial activity of native copolymer and the titanium dioxide/St-g-PAM was studied at the Microbiology Department, RCP ASC College, Shirpur, India.

Table 1. Reduction rate of St-g-PAM and titanium dioxide/St-g-PAM

Bacteria	Reduction percentage: %		
	St-g-PAM	Titanium dioxide/St-g-PAM	Chloramphenicol (standard)
Gram-positive bacteria			
<i>Staphylococcus aureus</i>	13	17	24.47
<i>Bacillus subtilis</i>	8	16	29.68
Gram-negative bacteria			
<i>Escherichia coli</i>	11	8	26.52
<i>Pseudomonas aeruginosa</i>	6	3	14.18

3. Results and discussion

3.1 Nanocomposite formation studied by infrared spectroscopy

The infrared spectra of St-g-PAM are given in Figure 2. The merged bands in a range 3600–3500 cm⁻¹ may be due to the presence of –NH₂ from AM, water in the hydrogel, and –OH

Figure 2. Infrared spectra of St-g-PAM and titanium dioxide/St-g-PAM

stretching of a starch polymer. The band at 2950 cm^{-1} was attributed to asymmetric stretching vibrations of $-\text{CH}_2$ groups in the polymer. Amide carbonyl was seen at 1700 cm^{-1} , whereas the bands found between 800 and 400 cm^{-1} were attributed to bending between NH and OH groups. The band at $1000\text{--}1300\text{ cm}^{-1}$ was associated with the strong stretching of C–O–C ether linkage in starch from the copolymer.

The infrared spectra of titanium dioxide/St-g-PAM are given in Figure 2. Bands at $1400\text{--}1500\text{ cm}^{-1}$ show stretching vibrations of Ti–O–Ti nanoparticles that disappear in the pure copolymer.¹² The bands at $3000\text{--}2900\text{ cm}^{-1}$ became somewhat sharp compared with the pure copolymer because of interactions between nanoparticles with the copolymer.¹³ The remaining peaks are the same as in the pure copolymer of the St-g-PAM polymer.

3.2 Morphological study of titanium dioxide nanoparticles

Figures 3(a) and 3(b) show the FE-SEM images of the synthesised titanium dioxide nanoparticles. The FE-SEM images

show the high degree of crystallinity of the titanium dioxide nanoparticles. In the FE-SEM image, as shown in Figure 3(a), the particle was found as spherical, and surface morphology was found homogenous in specific regions. From the FE-SEM images in Figure 3(b), an aggregated spherical shape was obtained with particle size $\sim 60\text{ nm}$. The agglomeration of the particles was seen in the FE-SEM images.

3.3 Morphological study of pure St-g-PAM polymer

The porous structure of the St-g-PAM polymer is presented in Figures 4(a) and 4(b). It was observed that the hydrogels exhibited a homogeneous porous structure, resulting in greater swelling behaviour. The average pore diameters of hydrogels were found to increase from 100 to 200 nm . It is supposed that these pores are the regions of water permeation and interaction sites between external stimuli and the hydrophilic groups of the gel. These pores were produced from water evaporation.¹⁴

3.4 Morphological study of titanium dioxide/St-g-PAM polymer

The titanium dioxide/St-g-PAM nanocomposite structure is presented in Figure 5(a). It was observed that the hydrogels exhibited a homogeneous dispersion of nanoparticles into the polymer matrix. This resulted in a decrease in the porous structure because nano-titanium dioxide is incorporated in the pores of the native copolymer with an average size of 70 nm and with a smooth surface structure, as shown in Figure 5(b). This nano-titanium dioxide was effective for enhancing the thermal and biological activity of the native polymer. Hence, from the FE-SEM micrographs, it was concluded that with the addition of nano-titanium dioxide, the structure of the native polymer became dense, smooth and non-porous, as successfully confirmed.

3.5 GP and GE

The degree of grafting was reflected by the GP and GE. GP indicates the amount of AM grafted onto the soluble starch. GE expresses the ratio of insoluble AM grafted onto the soluble starch to the total AM. The GP and GE were calculated using the following equations:

Figure 3. FE-SEM analysis of synthesised titanium dioxide nanoparticles: (a) spiral shape at 300 nm and (b) size of titanium dioxide nanoparticles

Figure 4. FE-SEM analysis of St-g-PAM polymer: (a) porous nature and (b) average size of pores in the St-g-PAM polymer

Figure 5. FE-SEM analysis of prepared titanium dioxide/St-g-PAM: (a) surface morphology and (b) average size of titanium dioxide in St-g-PAM polymer

$$2. \quad GP = \frac{M_2 - M_0}{M_2} \times 100$$

$$3. \quad GE(\%) = \frac{M_2 - M_0}{M_1 - M_0} \times 100$$

where M_0 is the weight of the soluble starch taken, M_1 is the combined weight of the graft copolymer and the homopolymer formed and M_2 is the weight of the graft copolymer.

3.6 Optimisation of the graft copolymerisation

The pH was optimised by testing at pH values of 5.0, 6.0, 7.0, 8.0 and 9.0 using potassium persulfate (0.5%) in phosphate buffer at 70°C for 90 min. For optimisation of the initiator concentration, the potassium persulfate concentrations tested were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8% at optimum conditions of pH. For optimising the temperature, the temperatures tested were from 20°C to 100°C using an optimum initiator concentration.¹⁴ The procedure was the same as described for the optimisation of the

initiator concentration. The reaction times chosen were 20 to 160 min, the other reaction conditions being optimum, based on the above experiments.

3.7 Optimisation of conditions for graft copolymerisation

The optimised conditions for the St-g-PAM copolymer grafting, including the pH of the phosphate buffer, reaction temperature, concentrations of initiator and the reaction time, are shown in Figure 6. Referring to the graph (Figure 6(a)), the titanium dioxide/St-g-PAM and GP values at a pH value of 7 are evident. At a temperature of 70°C, the maximum values of GP and GE were obtained, which can be seen from the curves for temperature (Figure 6(b)). This can be attributed to the inactivation of the copolymer at higher temperatures.¹⁵ Therefore, the optimum temperature for the copolymer formation was found to be 70°C. From the curves of effects of the initiator concentration (Figure 6(c)), the results showed that the GP increased greatly with the addition of the initiator until it reached its maximum value, with an initiator concentration of 0.5 g, and then decreased. This showed that an increase in the concentrations of the initiator accelerates the graft copolymerisation after the peak, consequently decreasing the GP and GE. Finally, from the graph of

Figure 6. Optimisation of GP and GE: (a) at pH 5–9, (b) incubation temperature, (c) initial dosage and (d) reaction time of titanium dioxide/St-g-PAM

the reaction times (Figure 6(d)), the optimum time was found to be 90 min. Prolonging the reaction further resulted in the decrease in GP and GE, resulting from the depolymerisation of parts of the copolymer. In conclusion, the optimum conditions for grafting copolymerisation of AM onto starch are 0.5 g initiator, the temperature of 70°C, pH 7.0, and time of 90 min.^{16–18}

3.8 XRD analysis

The powder X-ray patterns for individual St-g-PAM and titanium dioxide/St-g-PAM copolymer are shown in Figure 7. As per the literature, the X-ray spectrum of the titanium dioxide nanoparticle powder shows characteristic intense peaks at 25, 36, 47, and 52 2θ due to its crystalline nature.¹³ Comparing the pattern for titanium dioxide/St-g-PAM with that of St-g-PAM reveals a marked difference. It is significant to remark that the peak intensity in nanocomposite is increased concerning the XRD of titanium dioxide/St-g-PAM, indicating the higher degree of crystallinity (52%) for the nanocomposite as compared with the St-g-PAM (15%), which was due to incorporation of titanium dioxide nanoparticles into the matrix.

Figure 7. XRD of St-g-PAM and titanium dioxide/St-g-PAM

of the St-g-PAM copolymer.¹⁹ Further, titanium dioxide acted as filler, which improved the crystalline nature of the copolymer.

3.9 TGA

The thermal stability of pure St-g-PAM and titanium dioxide/St-g-PAM was studied using TGA, and thermograms are depicted in Figure 8. St-g-PAM shows that two degradation steps occurred for the grafted starch. The thermal curve from room temperature to 320°C represents the weight loss of the starch backbone, 43.660% of the total weight of the polymer. As per the literature survey, it should be noted that the decomposition temperature of the grafted starch was higher than those for the native starch (290°C). The second degradation from 320 to 490°C is the thermogram of the AM in the St-g-PAM. The weight loss of 36.768% represents the decomposition of the AM grafted onto the starch.

Titanium dioxide/St-g-PAM shows two degradation steps that occurred for the titanium dioxide nanocomposite polymer. The thermal curve from room temperature to 340°C represents the weight loss of the starch backbone, 36.37% the total weight of the polymer. Note that the decomposition temperature 340°C for the titanium dioxide/St-g-PAM is higher than those for the pure St-g-PAM (320°C); that is, thermal stability increases due to the titanium dioxide nanoparticles. The second degradation from 340 to 500°C is the degradation of the AM in the St-g-PAM. The weight loss of 36.000% represents the decomposition of the AM grafted onto the starch.²⁰

It is worth noting the percent weight loss for residual degradation of 30% for the titanium dioxide/St-g-PAM polymer, which is higher than that of pure St-g-PAM (20%). This confirmed that the titanium dioxide nanoparticles succeeded in increasing the thermal stability of the St-g-PAM polymer.

Figure 8. Thermal curves of St-g-PAM and titanium dioxide/St-g-PAM

3.10 Plant growth study

Figure 9 shows the plant growth study of the mung bean plant with the titanium dioxide/St-g-PAM polymer (one tested (T) and one control (C)). Plant growth is better in the case of (T) than in (C), as seen by human eyes. Nano-titanium dioxide was selected for the composite because it is a photoconductor with many application possibilities in agriculture, including degradation of pesticides, plant protection and residue detection.²¹ This is because the titanium dioxide nanocomposite in the St-g-PAM polymer increases the water-holding capacity and enhances soil permeability, and the infiltration rate decreases evaporation of water.²² This nanocomposite system works as water reservoirs around the root of the plant. It can expand to around 200–800 times the original volume in the presence of water. SAP mixed with soil not only increases soil permeability and improves germination rates, but also reduces drought impact on plants, leading to overcoming stress and oxygen radical formation. This, in turn, provides scope for better growth and yield even in unfavourable climatic conditions. Titanium dioxide nanoparticles that are present in the polymer enhanced the water-holding capacity as compared with the native polymer with increased thermal stability, as discussed in the TGA method. Also, titanium dioxide nanoparticles show antimicrobial activity, which inhibits the growth of bacteria present in the soil. Hence, the synthesised titanium dioxide nanoparticles in the St-g-PAM polymer matrix succeeded in enhancing the thermal, biological and water-holding capacity of the natural polymer, easily visible to human eyes as in Figure 9. Moreover, this titanium dioxide/St-g-PAM polymer is safe and non-toxic and thus prevents pollution of agroecosystems.²³

Figure 9. Photograph of plant growth of the mung bean in the control condition (C) and with titanium dioxide/St-g-PAM in the tested condition (T)

Figure 10. Antibacterial activity of titanium dioxide/St-g-PAM against Gram-positive and Gram-negative bacteria

3.11 Antibacterial activity studies

The in vitro antibacterial screening of St-g-PAM and its nano-titanium dioxide analogues has been performed against two Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and two Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteriocides. The results suggest that the titanium dioxide/St-g-PAM showed more antibacterial effect than pure copolymeric hydrogel under similar conditions (Table 1). The increased antibacterial impact of titanium dioxide/St-g-PAM may be due to titanium dioxide nanoparticles coming out quickly and interacting with the lipid layer of a cell membrane. As shown in Figure 10, the authors revealed that titanium dioxide/St-g-PAM showed better activity against Gram-positive bacteria than Gram-negative bacteria.

4. Conclusion

St-g-PAM was prepared by graft copolymerisation of monomers at reactive sites on the molecular backbone of starch for improvising the existing properties or for obtaining specific features. The new type of biopolymer-based composite hydrogel with improved thermal and biological properties is synthesised by the incorporation of titanium dioxide nanoparticles. FT-IR, TGA, FE-SEM and XRD techniques revealed that the AM monomers had been grafted onto the starch backbone to form titanium dioxide/St-g-PAM. The present work showed that the graft copolymers of starch with AM were synthesised successfully by copolymerisation of soluble starch with optimisation conditions of 0.5 g initiator, 70°C temperature and pH 7.0 for 90 min. This environmentally friendly process provides an attractive alternative for modification of starch, thereby extending its application in the field of agriculture as a plant growth regulator.

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