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Microwave synthesis of starch-G-polymethylmethacrylate-G-polyvinyl alcohol for sustained urea release

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To address agro-environmental pollution concerns, a fully biodegradable formulation was developed by grafting potato starch with polymethylacrylate and polyvinyl alcohol (St-g-PMA-g-PVA). This eco-friendly formulation was synthesized using microwave irradiation. The successful grafting of polyvinyl alcohol onto the potato starch-poly(methylacrylate) backbone was verified using FTIR, confirming the desired chemical structure. TGA analysis provided evidence of the formulation's thermal stability under varying conditions. SEM images provided visual confirmation of the successful grafting process. The formulation's properties, including urea entrapment efficiency, equilibrium water absorption, and urea release kinetics from the copolymer, were investigated. The incorporation of hydrophilic PMA-PVA content significantly enhanced the swelling capacity of the starch matrix. Moreover, the control over the release rate of urea from the loaded copolymer could be achieved by adjusting the graft efficiency. This innovative approach demonstrates potential in mitigating environmental impact while offering controlled nutrient management in agriculture.

Keywords: Microwave synthesis, Characterization, Controlled release, Graft copolymers, Urea

INTRODUCTION

The realm of controlled drug delivery has emerged as a multidisciplinary field focused on enhancing drug administration. The purpose of drug delivery systems is to optimize drug release methods. Polymers have been instrumental in advancing drug delivery by enabling the controlled dispensation of therapeutic agents, ensuring consistent dosages over prolonged periods, cyclic administrations, and customizable release of both hydrophilic and hydrophobic medications [1]. The category of responsive polymers applicable to drug delivery encompasses hydrogels, micelles, polyplexes, and polymer-drug conjugates, which will be elaborated upon below.

Hydrogels represent hydrophilic networks formed by (co)polymers with the capacity to absorb substantial amounts of water or biological fluids [2]. Over time, biodegradable carbohydrate graft copolymers have been explored to address specific needs within the realm of polymer-based drug delivery. Carbohydrate-PVA based hydrogels, beads, and scaffolds have found extensive utility in sectors such as agriculture, biomedicine, environment, and food packaging [3-5]. Amidst the diverse polymer options for drug delivery, natural polymers stand out due to their remarkable biocompatibility, minimal toxicity, and efficient enzymatic degradation [6, 7]. Counteracting the limitations of raw starch in terms of mechanical strength and rapid release, chemical modifications have been conventionally undertaken to enhance its properties. Synthetic polymers offer favorable attributes, and the combination of natural and synthetic polymers yields both mechanical stability and biocompatibility, leveraging the synergies between the two materials for controlled drug delivery [8-14]. To achieve this, alterations have been applied through grafting, blending, or crosslinking [15-19]. Grafting of vinyl monomers onto natural polymers is a widely accepted strategy [20-24], having practical and academic significance in controlling drug molecule release. It presents a convenient avenue for modifications catering to the agrochemical field's needs, including sustained fertilizer release to reduce pollution and health hazards.

Recent strides have been made with hydrophilic starch graft copolymers exhibiting high swellability, prominent in crafting controlled release mechanisms for highly water-soluble agrochemicals and nutrients in agricultural applications [25-27]. These graft copolymers have outperformed individual conventional polymers in controlled release devices, thus expanding their scope and applications [28, 29]. Urea, among various fertilizers, stands out for its high nitrogen content and cost-effectiveness. However, its significant solubility results in economic losses and environmental pollution [30-33], issues that controlled release techniques effectively address. Utilizing controlled release formulations for agrochemical delivery offers economic advantages [34-36].

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Earlier studies have investigated controlled release of diverse herbicides like simazine, 2,4,5-trichlorophenoxy acetic acid, and triazine, employing polymeric matrices [37-39]. Starch-based hydrogels have been employed for carbendazim delivery [40]. St-g-polylactide and St-g-polyacrylic acid have facilitated urea release [8, 41]. Grafting synthetic monomers onto the starch backbone emerges as a potent strategy to enhance starch properties. In the present study, we explore grafting polyvinyl alcohol onto St-g-PMA matrix, aiming to enhance the mechanical strength of natural graft copolymers [42]. These composites are formulated into graft copolymers, subsequently loaded with agrochemicals.

EXPERIMENTAL

Materials

The graft copolymer synthesis was conducted utilizing a household microwave oven, specifically the LG Intellocook TM-MS-1947 C model, operating at a frequency of 2450 MHz and capable of delivering up to 800W of power. The polyvinyl alcohol (PVA) used, with a molecular weight of 125,000, was sourced from Sd Fine Chemical limited in Mumbai, India, and was employed without additional purification. The procurement of potassium persulfate ($K_2S_2O_8$) was from Merck, India. The entirety of the study relied on distilled water. The St-g-PMA copolymers, integral to this synthesis, were prepared as detailed in the subsequent sections.

Synthesis of starch-g-PMA

In a 250 ml flask, the starch solution (0.1 g dissolved in 30 ml of hot distilled water) served as the base. To this solution, thiourea (TU) (0.01M) and $K_2S_2O_8$ (0.02M) were introduced. Following thorough stirring, methylmethacrylate (MA) (0.11 M) was incorporated into the reaction mixture. Subsequently, the flask was placed within a microwave oven and exposed to irradiation. The irradiation process occurred under microwave power (MW) of 320 W for a duration of three minutes. After the reaction reached completion, the initial product was obtained, which was then precipitated using a methanol:water mixture (3:1 ratio), where the homopolymer dissolves. The resultant graft copolymer solid was subsequently cleansed with a methanol:water mixture to eliminate any unreacted monomers and reagents. Finally, the graft copolymer solid was dried in a vacuum oven at 40°C until a consistent weight was achieved.

Synthesis of St-g-PMA-g-PVA

The PVA solution (5% w/v) was formulated by dissolving the requisite PVA amount in hot distilled water (100 ml). The dispersion of starch graft PMA in water was achieved through heating at 100°C under continuous stirring, ensuring a uniform blend. Into this mixture, 0.02 M $K_2S_2O_8$ was introduced while maintaining constant stirring. Following this, the flask underwent exposure to microwave irradiation for three minutes at 640 W. Upon completion of the reaction, the mixture underwent cooling, and the resultant product was precipitated using a methanol:water mixture (3:1 ratio). The preliminary product was filtered, washed twice with water, and dried at room temperature until reaching a consistent weight.

Urea encapsulation

The encapsulation process for urea involved immersing a precisely weighed quantity of the prepared matrix (on a dry basis) into a saturated urea solution at room temperature, allowing it to achieve swelling equilibrium. Once equilibrium was reached, the swollen graft copolymers were removed, and excess liquid on their surface was absorbed using filter paper. The subsequent step involved gradual evaporation of the water at 40°C. Before initiating the release experiments, the samples underwent two rounds of thorough washing with water to eliminate surface-exposed urea from the graft copolymers.

CHARACTERIZATION

FTIR spectrum

Fourier-transform infrared (FTIR) spectra measurements were conducted using a Perkin-Elmer FTIR spectrophotometer from the USA, utilizing KBr pellet technique. The FTIR spectrum analysis of pure PVA (depicted in Figure 1c) exhibited a broad peak approximately at 3426.1 cm^{-1}, indicating the presence of intramolecularly hydrogen-bonded hydroxyl groups within singular bridge compounds. Notably, peaks observed at 3022.1 and 1217.1 cm^{-1} were attributed to C-H stretching, denoting the presence of a hydrocarbon chromophore in the PVA structure. Regarding the St-g-PMA spectrum (illustrated in Figure 1a), distinctive peaks emerged at 3450.6 and 1047.8 cm^{-1}, likely attributed to –OH stretching and skeletal (C-O-C) vibrational stretching arising from the starch component. Furthermore, a discernible band at 1746.1 cm^{-1} was observed, indicative of the presence of a carboxylic group (>C=O) in the structure.

The FTIR spectrum of the St-g-PMA-g-PVA matrix (depicted in Figure 1c) demonstrated a distinct peak at 3434.3 cm^{-1}, suggestive of intermolecular hydrogen-bonded hydroxyl groups that contribute to polymeric association. Alongside these observations, the graft copolymer matrix also exhibited peaks at 3025.1 and 1217.8 cm^{-1}, which are indicative of the presence of a hydrocarbon chromophore. Notably, the characteristic peak associated with the carboxylic group at 1746.1 cm^{-1} was absent, indicating the absence of >C=O groups in this structure [42]. This absence strongly suggests that all the carboxylic groups of St-g-PMA have been engaged in the grafting process, signifying the successful grafting of PVA onto the St-g-PMA backbone.

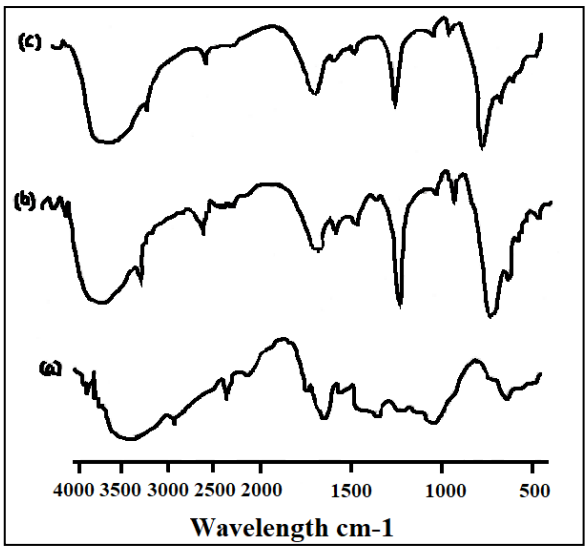

Fig. 1. FTIR spectra (a) St-g-PMA (b) St-g-PMA-g-PVA (c) PVA

Thermogravimetric analysis

The thermal stability and degradation patterns of the St-g-PMA and St-g-PMA-g-PVA matrices were assessed using an EXSTAR TG/DTA 6300 instrument under atmospheric conditions. Melting studies were conducted over a temperature range of 25°C to 800°C, employing a heating rate of 20°C/minute in an oxygen environment. The TGA results are graphically presented in Figure 2. The thermogram of St-g-PMA (Figure 2b) exhibits a three-stage weight loss profile. Initially, up to 100°C, a weight loss of 3.7% occurred, likely attributed to moisture loss. Subsequent weight losses were observed at 9.4%, 41.8%, and 86.2%. These losses occurred at temperatures of 200°C, 300°C, and 500°C. Previous reports have indicated that pure PVA undergoes decomposition in two stages and remains thermally stable up to around 265°C, with a weight loss of approximately 15% [42, 43]. Decomposition products of pure PVA have also been documented [44]. Turning to the TG curve of the St-g-PMA-g-PVA matrix (Figure 2a), the graft copolymer demonstrated a gradual weight loss until 290°C, primarily due to 1.3% residual surface water loss. Beyond this point, a rapid weight decrease was evident. The matrix exhibited decomposition temperatures at 200°C, 300°C, 400°C, 500°C, and 600°C, resulting in weight losses of roughly 7.3%, 33.3%, 48.2%, 69.6%, and 89.0%, respectively. A comparative thermal analysis underscores the enhanced thermal resistance of the prepared graft copolymer, St-g-PMA-g-PVA, up to 600°C.

Swelling equilibrium

A precisely weighed composite matrix sample was immersed in distilled water at room temperature until equilibrium was reached. Subsequently, the swelled samples were extracted from the water and gently dried using filter paper to remove excess water. The equilibrium water absorbancy (Qev) of the matrix was calculated by weighing the swollen samples and employing the following equation [45]:

$$\text{Qev (g/g)} = \frac{M2-M1}{M1}$$

where M_2 is the weight of the swelled sample and M_1 is the weight of the dried sample. Qev is expressed in gram/g.

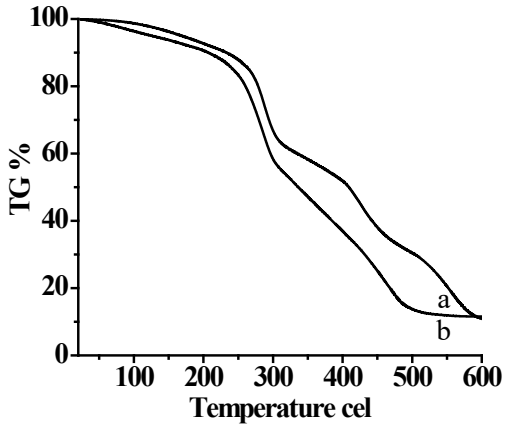

Fig. 1. Comparative TGA graph of St-g-PMA (b) St-g-PMA-g-PVA (a).

Encapsulation efficiency

The encapsulation efficiency of the matrix is indicated by the total weight percentage of the substance enclosed within it. To accurately quantify the amount of encapsulated urea, the samples were weighed and subjected to washing with 20 ml of water to eliminate excess surface-bound urea. The urea content in the water was subsequently determined spectrophotometrically at 420 nm [46].

The encapsulation efficiency was computed using the following formula:

$$\text{EE}\ (\%)\ = \frac{[1 - \text{W2}\ ]\ \text{X100\%}}{[\text{WoxC}]}$$

where W_0 is weight of loaded urea sample, W_2 is the urea exposed on surface of the grafted matrix and C is the urea content of the matrix calculated from the feed composition.

Urea release study

The investigation into the *in vitro* release of urea from the St-g-PMA-g-PVA matrix involved placing 200 mg of dried and loaded samples in 500 ml of distilled water at 25°C. At set intervals, a 2 ml portion of the solution was extracted, and an equivalent volume of water was introduced to maintain a constant volume. The measurement of the released urea amount was conducted using a UV-spectrophotometer at 420 nm [46].

Surface morphology

The surface morphology assessment of both the St-g-PMA matrix and the prepared St-g-PMA-g-PVA matrix was carried out using an LEO 430 SEM model. Before examination, the specimen surfaces were coated with a layer of gold through sputter coating. In the SEM micrographs of the grafted starch matrix, a relatively coarse surface was observed, indicating that the amorphous starch had undergone partial miscibility with poly(methylacrylate) (as depicted in Figure 3). Figure 4 showcases the polyvinyl alcohol dispersion within the St-g-PMA matrix, revealing a relatively smooth surface with voids. This is in contrast to the agglomerated surface of St-g-PMA. Furthermore, Figure 5 displays the SEM images of the graft copolymer matrix loaded with urea. Evidently, the grafting of polyvinyl alcohol occurred uniformly onto the grafted starch backbone. The SEM analysis of the St-g-PMA-g-PVA matrix unveiled that the grafting of PVA and PMA resulted in physical and chemical crosslinking, as discernible pores are evident in the micrographs. It's hypothesized that these pores correspond to regions of water permeation and interaction sites for external stimuli with the hydrophilic groups of the graft copolymers.

RESULTS AND DISCUSSION

In the St-g-PMA matrix, the unbound carboxylic groups (>C=O) of PMA engage with OH groups of PVA through microwave irradiation, resulting in the formation of the graft copolymer. During this grafting process, only a minimal quantity of homopolymer is produced. The grafted product and PVA can be conveniently separated through cold water treatment, as PVA exhibits solubility in this condition. This solubility tends to increase with the augmentation of poly(methylacrylate) content. The graft copolymerization involving synthetic hydrophobic monomers like poly(methylacrylate) distinctly reduces the swellability of the St-g-PMA matrix. Conversely, water absorbancy shows an increase with elevated PVA content. This is attributed to the abundance of free hydroxyl groups, leading to a greater presence of hydrophilic groups and subsequently enhancing water absorbancy. A comparative assessment of the swelling equilibrium for both St-g-PMA and St-g-PMA-g-PVA copolymers is presented in Table 1. The optimal swelling equilibrium is achieved when the contents of St-g-PMA and PVA are in equal proportions. Similarly, maximum urea loading is attained under these balanced conditions. The resulting graft copolymer matrix exhibits an equilibrium swelling of 364% after eight hours, and this value remains relatively constant for up to 250 hours. This equilibrium swelling is anticipated to diminish after this duration.

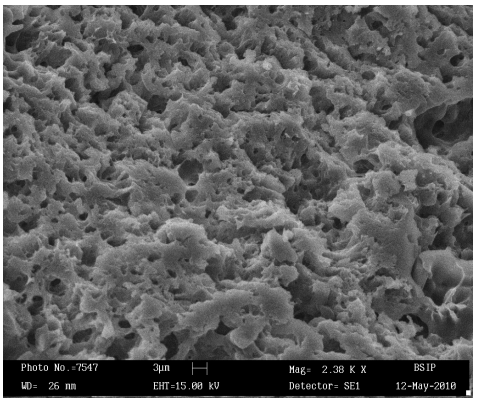

Fig. 3. SEM of St-g-PMA copolymer

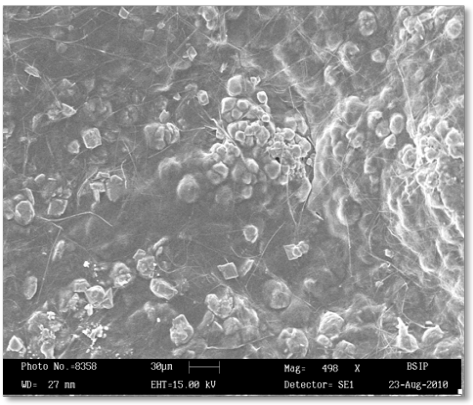

Fig. 4. SEM of St-g-PMA-PVA copolymer

Table 1. Swelling equilibrium of St-g-PMA and St-g-PMA-g-PVA copolymer

GSC	WH %	UH %	SW Qeq
St-g-PMA: PVA (25:75)	6.1	43.70	286
St-g-PMA: PVA (50:50)	4.2	69.98	364
St-g- PMA:PVA (75:25)	2.5	32.1	186
St-g-PMA (100)	1.5	14	150

GSC* starch graft copolymers, WH* water holding %, UH* urea holding%, SWQeq* swelling equilibrium

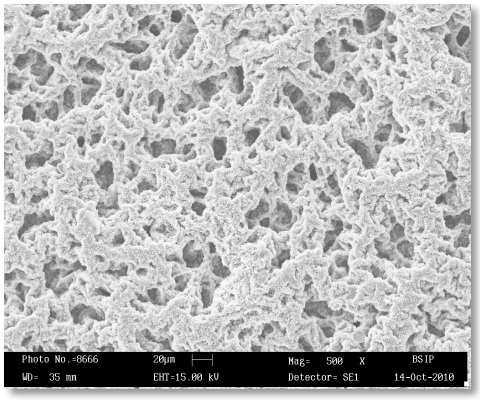

Fig. 5. Urea loaded St-g-PMA-g-PVA copolymer

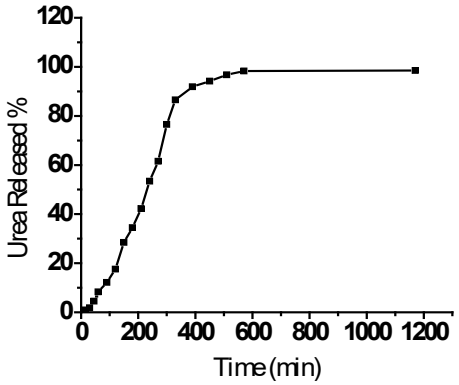

Fig. 6. Urea released percentage with time

The graft copolymer matrix exhibits enhanced urea encapsulation, primarily attributed to the presence of voids within the graft copolymer structure. In Figure 5, SEM micrographs of urea-loaded graft copolymers clearly illustrate the presence of these voids. The loading capacity for urea displays an upward trend with increasing PVA content, reaching its maximum capacity at 50% PVA content, corresponding to a grafting efficiency of 50% for PVA. The impact of graft modification and grafting ratio on the urea release rate from the grafted matrix is outlined in Table 1. Generally, the release rate of urea from the grafted matrix is diminished compared to the St-g-PMA matrix. The diffusion nature of urea into the graft copolymer matrix was predicted using the following equation.

$$F = M_T/M_0 = Kt^n$$

The fractional release of urea at time "t" denoted by M_T/M_∞, where "k" stands for the constant linked to the network structure, and the exponent "n" signifies the diffusion exponent indicative of the release mechanism. In instances of regular Fickian diffusion, the value of "n" equals 0.5. For Case II diffusion, "n" equals 1.0, and for non-Fickian diffusion, "n" ranges between 0.5 and 1.0. The release mechanism for urea from the grafted matrix is assumed to exhibit a non-Fickian diffusion behavior.

The maximum urea release from the St-g-PMA-g-PVA matrix reached approximately 98.38% within 26 hours (as demonstrated in Figure 6). During the initial stage, the release rate exhibited rapid progress, nearly reaching its maximum value within 6-7 hours. The pattern observed in the plot indicates a linear release rate behavior during the initial six-hour period, followed by a slower release rate that ultimately leads to almost complete release within ten hours. The graft copolymer matrix effectively releases the encapsulated urea in a controlled and prolonged manner, which is a critical requirement for the controlled use of agrochemicals to mitigate environmental and health concerns.

CONCLUSIONS

A St-g-PMA-g-PVA matrix was successfully synthesized through microwave irradiation, yielding a high product yield. The hydrophobic nature of poly(methylacrylate) contributed to a reduction in the swelling capacity of the grafted matrix, resulting in enhanced water resistance. The incorporation of PMA was effective in bolstering the mechanical properties of the compatible composite, along with fostering biodegradation. The grafting of PVA onto the St-g-PMA backbone led to improved swelling efficiency and enhanced thermal behaviors. Comparatively, the urea release rate from the St-g-PMA-g-PVA matrix exhibited a decrease compared to ungrafted starch. The release mechanism was

characterized as non-Fickian diffusion. The prepared graft copolymer matrix exhibits potential for application as a controlled-release carrier in environments involving heavy water.

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