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CHITOSAN-ACRYLIC ACID COMPOSITE MATERIAL: SYNTHESIS AND ANALYSIS OF GRAFTING PERCENTANGE BY VARYING PARAMETERS

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Abstract : The modification of natural polymers through graft copolymerization has emerged as a promising strategy to enhance their physicochemical properties for advanced applications. In this study, a composite material based on chitosan and acrylic acid was synthesized using a hot air oven method. The primary objective was to analyze the influence of various synthesis parameters including monomer concentration, amount of solvent, initiator dosage, crosslinker concentration, and reaction time on the grafting percentage. The grafting process aims to improve the structural stability, hydrophilicity, and functional group availability of the chitosan matrix by introducing carboxylic functionalities from acrylic acid. The grafting efficiency was determined for each set of conditions, allowing for the identification of optimal parameters that yield the highest grafting percentage which comes out to be 1776%. Results indicate that the grafting percentage is significantly affected by the variation of these synthesis conditions. The modified composite material demonstrated enhanced properties compared to native chitosan, indicating its potential for use in environmentally sustainable applications. This study provides valuable insights into the design and optimization of biopolymer-based composites for functional material development.

IndexTerms **– Chitosan, Acrylic Acid, Grafting Percentage, Biopolymer Composite, Optimization, Sustainable Applications.**

INTRODUCTION

In recent years, there is growing interest in natural polymers like chitosan as a result of the hunt for effective, biodegradable, and sustainable adsorbents [1]. One of the most significant byproducts of chitin, the second most prevalent natural biopolymer on Earth after cellulose (No and Meyers 1989), is chitosan. Chitin is a key component of the shells of crustaceans, including shrimp and crabs. Deacetylation of chitin yields chitosan, a co-polymer comprising glucosamine and N-acetylglucosamine units connected by one to four glucosidic linkages [2]. Because of its many uses in industrial and biomedical fields, including wastewater treatment fiber, cements, paper production, textile finishes, photographic products, and film formations, chitosan—a non-toxic, biodegradable, and biocompatible polysaccharide polymer—has drawn a lot of attention globally as one of the most promising renewable polymeric materials (Rathke and Hudson 1994). Additionally, it may be utilized in chemical plants for wastewater treatment, the biomedical industry for enzyme immobilization and purification, and the food industry for food formulations as a binding, gelling, thickening, and stabilizing agent (Knorr 1984) [3-4]. However, there are drawbacks to pure chitosan, including limited mechanical strength and, under certain circumstances, decreased adsorption capability. To overcome these limitations, chemical modification techniques have been widely explored. Among them, graft copolymerization has proven to be one of the most effective methods to enhance the performance of chitosan without compromising its biodegradability and eco-friendly nature [5]. Grafting involves the introduction of synthetic monomers onto the polymer backbone, which adds new functional groups that significantly enhance the material's chemical reactivity, mechanical stability, and interaction capabilities. One of the monomers extensively used for this purpose is acrylic acid [6]. It contains reactive carboxyl groups that, when grafted onto chitosan, increase the number of active binding sites and improve the material's hydrophilicity and compatibility with aqueous environments. This modification enables the composite to better interact with various substances, enhancing its overall functional performance [7]. The presence of additional carboxyl groups promotes electrostatic attractions and hydrogen bonding interactions, making the composite more effective in a wide range of applications [8]. A crucial aspect of grafting is the grafting percentage, which quantifies the extent of monomer incorporation onto the chitosan structure. The grafting efficiency is influenced by several parameters, including the concentration of the monomer, the amount of initiator used, the temperature, and the duration of the reaction [9]. Understanding the effect of these parameters is essential to optimizing the synthesis process, ensuring reproducibility, and tailoring the material for specific industrial and environmental uses [10]. This systematically investigates how variations in the reaction parameters affect the grafting percentage. By analyzing these effects, the research seeks to determine the optimal conditions for maximizing the modification efficiency [11].

MATERIALS

Analytical grade chitosan, obtained from Shrimp Shells 75%, and acetic acid and acrylic acid, sourced from SD Fine chemicals, were used without further purification. Methylene Blue solution was prepared by dissolving synthetic Methylene Blue in Distilled water. Distilled water was used for the preparation of all solutions, buffers, and during the polymerization process.

METHODOLOGY

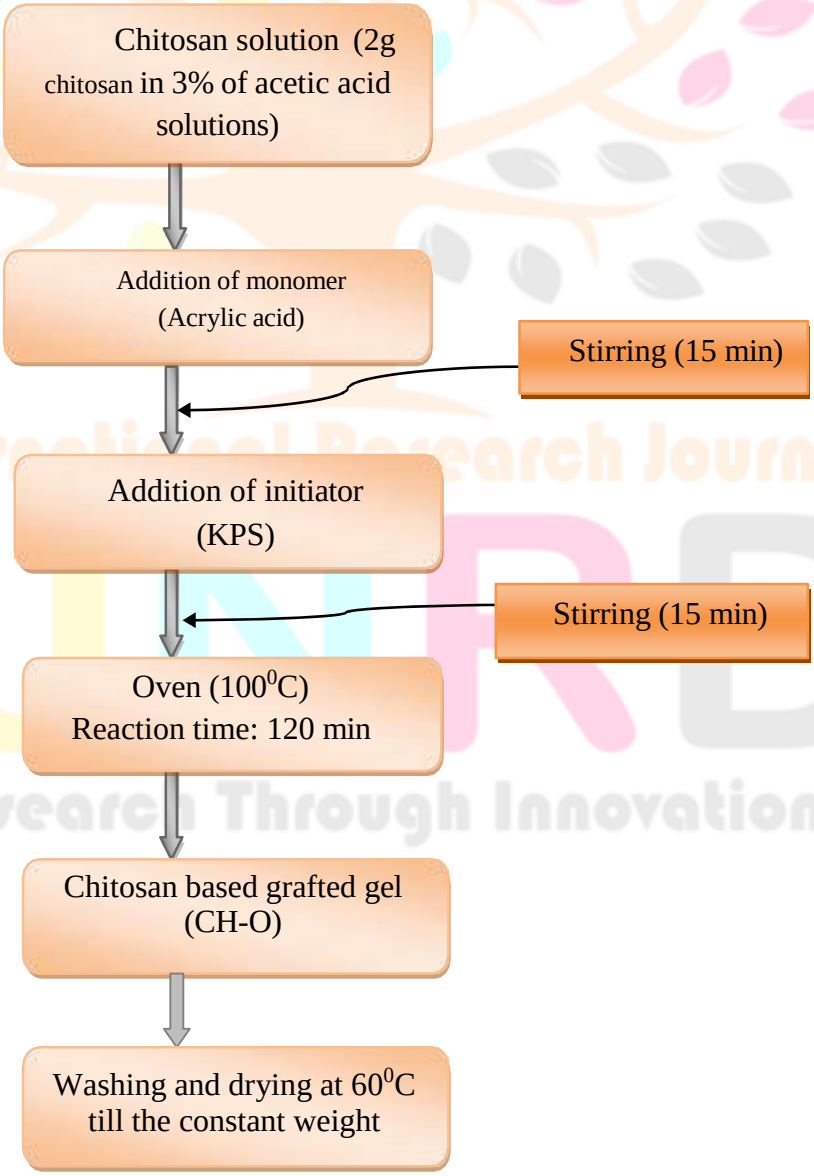
The methodology section outlines how the preparation of chitosan-based materials was carried out using Hot Air Oven synthesis technique.

3.1. Hot Air Oven Synthesis of Chitosan based hydrogel (CH-O)

CH-O was prepared by dissolving 0.5g of chitosan in 3% acetic acid solution in 250 ml reaction vessel. Reaction vessel was equipped with magnetic stirrer. Requisite amount of acrylic acid was added drop wise in homogenized viscous chitosan solution under continuous stirring [12]. The mixture was further stirred for 10 min for proper distribution of monomer, followed by the addition of appropriate amount of potassium per sulphate (KPS) initiator and glutaraldehyde crosslinker. The mixture was poured into the reaction flask and was kept in oven at 100°C temperature for 120 minutes. The synthesized gel obtained was washed properly with warm distilled water to remove the unreacted monomer and dried in the oven at 60°C till a constant weight was obtained [13]. The reaction parameters such as effect of solvent, reaction time, initiator, monomer and crosslinker concentrations were optimized on the basis of percentage grafting calculated using equation:

$$Pg = \left(\frac{W2 - W1}{W1}\right) \times 100$$

where W_1 and W_2 are the weights of chitosan and chitosan based grafted gel CH-O, respectively [14].



Scheme 3.1. Synthesis of Chitosan based Grafted Gel without crosslinker (CH-O)

IV. RESULTS AND DISCUSSION

4.1 Effect of Amount of Solvent on Percentage Grafting (Pg) CH-O

The effect of solvent (acetic acid) on the percentage grafting (Pg) was studied by varying the solvent volume from 10mL to 35mL of 3% acetic acid keeping other reaction conditions constant. Maximum percent grafting (604%) was observed with 25mL of solvent. Afterwards, a reduction in percentage grafting was obtained due to the diffusion-controlled nature of these reactions [15]. Figure 4.1 shows maximum % age grafting with 25mL of solvent and further increase in solvent resulted in decreased Pg.

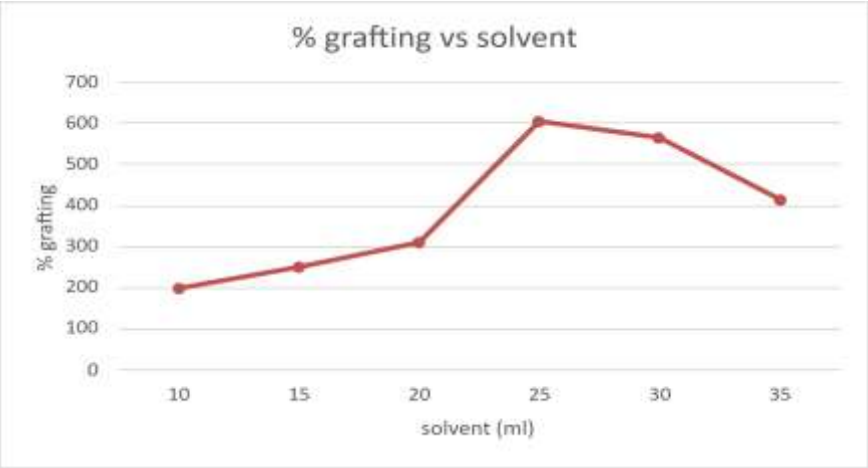


Figure 4.1. Effect of Amount of Solvent on Percentage Grafting (Pg) CH-O

4.2 Effect of Concentration of Initiator on Percentage Grafting (Pg) CH-O

The effect of potassium per sulphate concentration on the extent of grafting, while keeping the other reaction conditions fixed, is shown in Figure 4.2. The percentage grafting get increased with increase of initiator concentration and reached a maximum (1004%) at 0.0025(mol/L). This happens due to the direct attack of free radicals on the characteristic group (NH_2) of the chitosan backbone and initiates the graft co-polymerization process [16].

Figure 4.2. Effect of Concentration of Initiator on Percentage Grafting (Pg) of CH-O

4.3 Effect of Dose of Crosslinker on Percentage Grafting (Pg) of CH-O

The dose of crosslinker(glutaraldehyde) varies from 0.5 to 2.5 mL. Figure 4.3 shows that Pg increases with a dose of glutaraldehyde up to 1mL and after that Pg decreases because of dense polymer structure formed at higher doses [17].

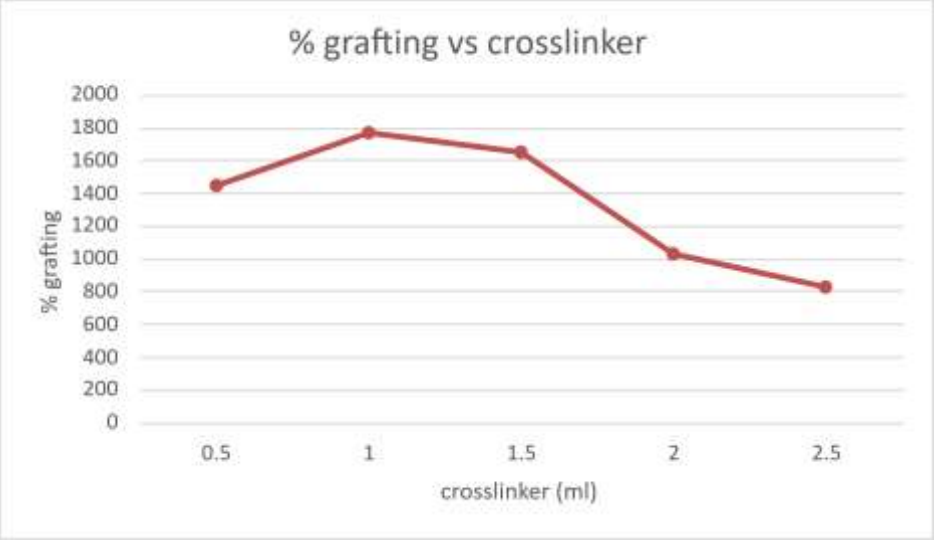


Figure 4.3. Effect of Crosslinker Concentration on percentage Grafting

4.4 Effect of Concentration of Monomer on Percentage Grafting (Pg) of CH-O

The effect of monomer concentration on the grafting of acrylic acid onto the chitosan is shown in the Figure 4.4.4. The volume of acrylic acid monomers varied from 10mL to 55mL. The maximum optimum Pg (1776%) was recorded at 0.225mol/L of monomer concentration. But with further increase in monomer concentration, decrease in Pg was observed [18]. This trend was expected at higher concentration of monomer as chances of the termination of growing polymerization radicals to form homopolymer increases, thus resulted in decrease in Pg.

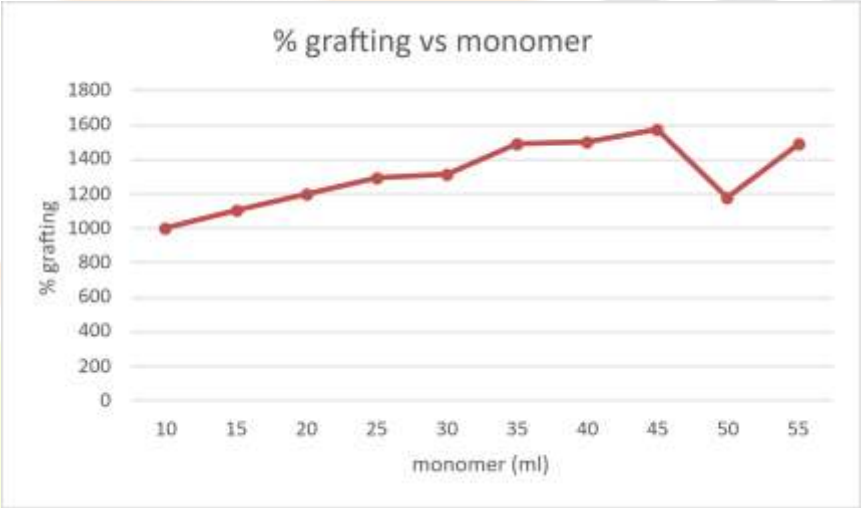


Figure 4.4. Effect of Concentration of Monomer on Percentage Grafting (Pg) of CH-O

4.5 Effect of Reaction Time on Percentage Grafting (Pg) of CH-O

Reaction time varied from 120 to 360 min at 80ºC oven temperature and maximum Pg was found to be (2928%) at 180 min. Further increase in time, resulted in a decrease of Pg. The active sites on the backbone and monomer increases with increase in reaction time which resulted in enhanced grafting of monomer onto chitosan up to certain limit [19]. Beyond the optimum reaction time, the concentration of the free radicals limits the length of the polymeric chains by initiating numerous chains simultaneously, which results in decreased percentage grafting (Figure 4.5). Optimized reaction parameters were given in Table 4.8.

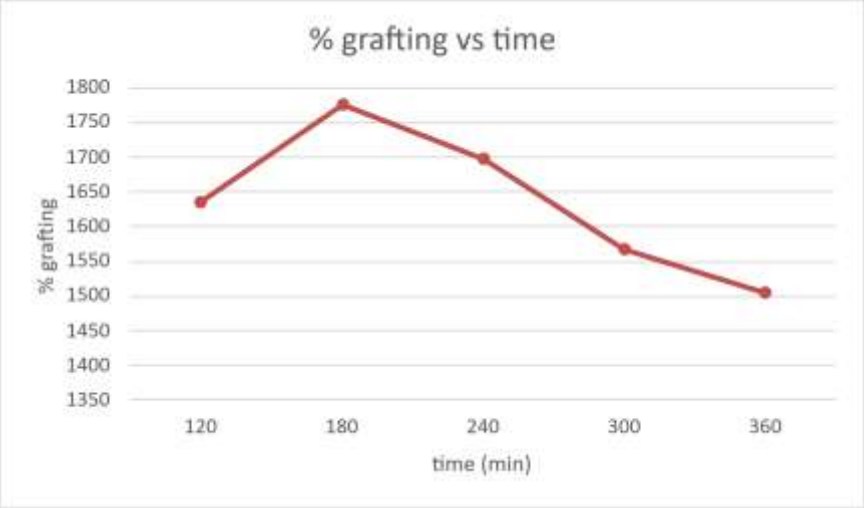


Figure 4.5. Effect of Reaction Time on Percentage Grafting (Pg) of CH-O

Table: 4.1: Effect of Reaction Parameters on Percentage Grafting by Hot Air Oven Synthesis of CH-O

Solvent (mL)	Monomer (mL)	Initiator (mL)	Crosslinker (mL)	Time (min)	% grafting
Effect of Variation in Solvent					
0.5g in 10mL	10	10	1	120	200
0.5g in 15mL	10	10	1	120	250
0.5g in 20mL	10	10	1	120	310
0.5g in 25mL	10	10	1	120	604
0.5g in 30mL	10	10	1	120	564
0.5g in 35mL	10	10	1	120	416
Effect of Variation in Initiator Concentration					
0.5g in 25mL	10	10	1	120	604
0.5g in 25mL	10	12	1	120	634
0.5g in 25mL	10	14	1	120	684
0.5g in 25mL	10	16	1	120	830
0.5g in 25mL	10	18	1	120	870
0.5g in 25mL	10	20	1	120	904
0.5g in 25mL	10	22	1	120	1004
0.5g in 25mL	10	24	1	120	890
Effect of Variation in Monomer Concentration					
0.5g in 25mL	10	22	1	120	1004
0.5g in 25mL	15	22	1	120	1106
0.5g in 25mL	20	22	1	120	1196
0.5g in 25mL	25	22	1	120	1292
0.5g in 25mL	30	22	1	120	1316
0.5g in 25mL	35	22	1	120	1492
0.5g in 25mL	40	22	1	120	1500
0.5g in 25mL	45	22	1	120	1570
0.5g in 25mL	50	22	1	120	1776
0.5g in 25mL	55	22	1	120	1496
Effect of Variation in Reaction Time					
0.5gin25mL	50	22	1	120	1634
0.5gin25mL	50	22	1	180	1776
0.5gin25mL	50	22	1	240	1698
0.5gin25mL	50	22	1	300	1568
0.5gin25mL	50	22	1	360	1504
Effect of Variation in Crosslinker Concentration					
0.5g in 25mL	10	10	0.5	180	1450
0.5g in 25mL	10	10	1	180	1776

0.5g in 25mL	10	10	1.5	180	1648
0.5g in 25mL	10	10	2	180	1029
0.5g in 25mL	10	10	2.5	180	824

Table 4.2: Optimized Reaction Conditions for Synthesis of CH-O Hydrogel

Chitosan	0.5g (fixed)
Acetic acid	25mL
Acrylic acid concentration	0.225mol/L
KPS concentration	0.0025mol/L
Glutaraldehyde	1mL
Reaction time	180 min
Maximum percentage grafting	1776%

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