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ULTRASONIC ASSISTED SYNTHESIS AND CHARACTERIZATION OF CHITOSAN GRAF WITH 2-(DIMETHYLAMINOETHYLMETHACRYLATE) (DMAEMA) Cs-g-PDMAEMA

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Abstract

Purpose: Many researchers reported the use of chitosan in various applications due to its desirable properties, but then its application in a certain condition is limited due to its lower mechanical stability, lower solubility in certain solvents, and crystallinity of the polymer. Numerous report has been published by many researchers across the world modifying chitosan to enhanced its properties thereby improving its application in various field

Methodology: Poly (2-dimethylaminoethyl methacrylate) (Cs-g-PDMAEMA) were successfully synthesized by Ultrasonic methods for the first time. The synthetic method was optimized by varying various reaction parameters and reaction conditions. The grafting was confirmed by characterizing the copolymer with FTIR, XRD, XPS, SEM, TGA, DTG, and DTA.

Findings: The results show a good percent grafting and percent yield up to 132%G and 94.7%Y at optimum condition, and also shows a decrease of thermal stability and crystallinity of chitosan, there was improved in porosity of the surface, and complexity of the surface functional group making it a good candidate for metal chelating. Observing various changes in the spectrum of these derivatives and that of pure chitosan in addition to the change in properties of these polymers such as surface morphology, thermal stability, and crystallinity.

Uniqe contribution to the theory, practice and policy: It was suggested that this modification may improve the application of these polymers.

Key Words: *Chitosan, Cs-g-PDMAEMA, Ultrasonication, Grafting*

1.1 INTRODUCTION

Chitosan is an N-deactivated derivative of chitin, which is one of the most abundant organic materials found in the crustacean, mollusks, and insects where it is an important constituent of the exoskeleton. Chitosan, as the largest number of natural organic containing nitrogen carbohydrates and the second abundant organic natural resources, is nontoxic, cheap, biodegraded, and thus belonging to a typical "environment-friendly" material. The desirable properties of chitosan have attracted the attention of the scientific community making it fitted in various applications such as drug delivery, adsorption technology, corrosion inhibition, biomedical research, and many more. (Wang et al, 2020) Properties such as poor mechanical stability, pH sensitivity, poor solubility in some solvents, water resistance limit its utility in some applications (El-Arnaouty et al, 2020).

Polymer modification is a vast research area in which different properties can be added to the polymer to enhance its performance and expand its application. Therefore the modification of chitosan by the addition of different functional monomers became a common method to improve the properties of chitosan. Polymer grafting has been proved to be one of the best methods of polymer modification. Poly (2-dimethylaminoethylmethacrylate) is a polyelectrolyte characterized to be both temperatures- and pH-sensitive polymer, due to the presence of hydrophilic amino groups, and the hydrophobic segments at the end of the side chains. In a highly acidic environment (pH<5) PDMAEMA is hydrophilic and fully ionized by protonation of the tertiary amine, and it interacts strongly with surrounding water molecules. Ion-dipole interactions between ammonium ions and polar water molecules create strong solvation or hydration shells. However, as the pH increases, this interaction is weakened due to decreasing protonation of amine groups, and the hydrophobic properties of the methylated amines become more pronounced, resulting in amphiphilic behavior (Islas, Burillo and Ortega, 2018).

The application of high-intensity ultrasound in the field of chemistry has been shown to provide great promises in promoting a wide range of chemical processes. One of the advantages of this process over the conventional grafting technology is that ultrasonic consume less energy as the reaction can proceed at low temperature, most of the reactions require no initiator to proceed and are low cost. The wide applications of ultrasound in chemical processes have attracted intense attention in various fields of chemistry, materials science, and chemical engineering. bubbles present in the solution grow and collapse when sound waves pass through a liquid. This results in the generation of radicals, excited-state species, enhancement of reaction rates, and excellent mixing of multiphase systems. (Thankamony et al, 2018) this research aims to synthesize Chitosan grafted Poly (2-dimethylaminoethyl methacrylate) (Cs-g-PDMAEMA) copolymer by Ultrasonic methods.

2.0 MATERIAL AND METHODS

2.1 Materials

Chitosan (Cs), 2-dimethylamino-ethyl methacrylate (DMAEMA), and alumina were purchased from Sigma Aldrich, Conical flask, volumetric flasks, measuring cylinder, pipet, Soxhlet extractor setup, oven, Thermometer, Filter Paper, Beaker, Digital weighing balance, spatula, refrigerator,

desiccator, and alumina column. X-ray diffraction spectroscopy (XRD), X-ray Photon Spectroscopy (XPS), Fourier transformed infrared spectroscopy (FTIR), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Thermostat Ultrasonic Machine.

2.2 Methods

Synthesis of Chitosan Grafted 2-dimethylaminoethylmethacrylate (Cs-gPDMAEMA) PDMAEMA monomer was first clean according to the method of (Ne´dez, and Ray 1999). Poly 2-dimethylamino-ethyl methacrylate (DMAEMA) was grafted on chitosan by mixing 1ml of DMAEMA monomer with 2 grams of chitosan dissolved in 100 ml of 0.01M acetic acid solution and 1ml of TBH in a beaker. This mixture was then taken to an Ultrasonic machine and sonicated for 90 minutes at 30 0C. A white solid (Cs-g-PDMAEMA) formed at the bottom of the container with a clear colorless liquid. The solution was filtered through 11µ filter paper. The filtrated Cs-g-PDMAEMA was then extracted with deionizing water using soxhlet extraction at 600C for six (6) hours. The extracted copolymer was then dried in an oven at 600C for 6 hours and stored in a desiccator. The grafting percentage (GP) and the grafting efficiency (GE) of Pdmaem on CS were determined according to the following equations.

$$(1)\ \mathrm{GP}(\%) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

$$\mathrm{GE}(\%) = \frac{W_2 - W_1}{W_3} \times 100 \qquad (2)$$

Where *W*1, *W*2, and *W*3 are the weights of CS, CS-*g*-PDMAEMA, and DMAEMA monomer, respectively.

3.0 RESULTS AND DISCUSSION

3.1 Reaction condition

Monitoring the Effect of parameters (such as Sonucating time, Reaction temperature, and monomer concentration,) on the grafting % and grafting yield of Cs- g-Pdmaema is very important this allowed you to carried out the synthesis within the shortest possible time and a limited amount of energy and substrates.

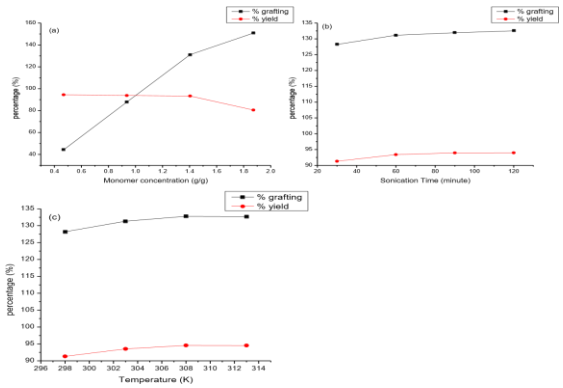

Figure 1.0 effect of (a) Monomer Concentration (b) Sonication Time and (c) Reaction Temperature on grafting efficiency and grafting yield

To minimize the use of excess monomer for the synthesis, the effect of monomer concentration on the grafting % and grafting yield of Cs-g-Pdmaema was monitor so that the exact amount of monomer that will give a good yield with good efficiency would be used, this shown in Figure 1(a) Increases of monomer loading lead to increases in % yield and slightly decrease to some extent after then as monomer loading exceeded 1.4g/g then the % yield will be decreasing.% grafting efficiency increases linearly with monomer concentration up to a certain level then it remains constant. This shows that a certain amount of monomer can be grafted on a certain amount of chitosan and when this amount is exceeded the grafting process .will be very low as most of the monomer will be ungrafted and could be removed by the purification process. This is because at that condition most of the active site on the chitosan has been covered by the grafted polymer even though some of this monomer may be polymerized on the already grafted polymer but some may remain as homopolymers. Monitoring sonication time allowed you to carry out the synthesis within the shortest possible time figure 1(b) shows the effect of sonication time on the grafting % and grafting yield of Cs-g-Pdmaema. The figure shows that the grafting yield and grafting efficiency increases linearly with time and at the optimum time it becomes almost constant it means the reaction is completed. This shows that almost all the grafting process using this method was completed between 60-90 minutes. To save the energy variation of temperature on grafting yield and grafting efficiency was studied. Figure 1(c) shows this variation and percent yield increases linearly with temperature up to 303K then it became independent of temperature the highest percentage (132.7% and 94.5%) at 313K even though it shows a promising % at 250C of up to 128.3 % and 91% grafting efficiency % and grafting yield of Cs-gPdmaema respectively.

3.4.1 Characterization

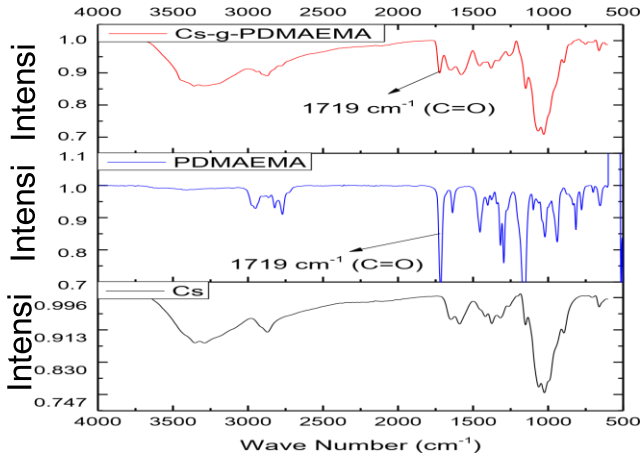

Figure 2.0 Attenuated furrier transform infrared spectroscopy (AFTIR) spectra.

Figure 2.0 confirms the formation Cs-g-Pdmaema, this can be proved by the formation of a new peak around 1700 cm-1 corresponding to C=O stretch which is one of the characteristic peaks in the pure DMAEMA FTIR spectrum. The formation of this new peak and increase of intensities of other peaks together with the shift of wavenumbers is an indication that chitosan was modified with poly DMAEMA. The absorption band at 1190 cm−1 of copolymer corresponded to the symmetric stretching vibration of the C-N band associated with the DMAEMA unit (Yin et al, 2017).

3.4.2 X-ray Diffraction Spectroscopy

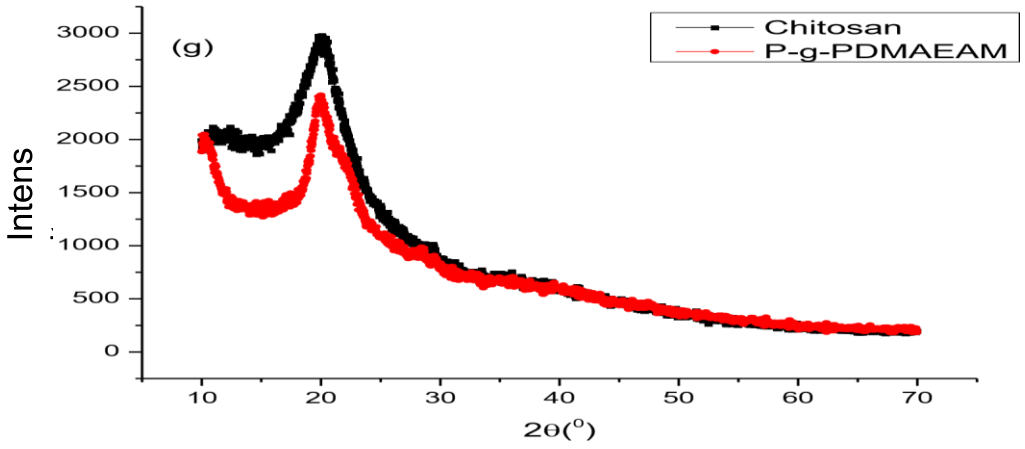

Figure 3.0 X-ray Diffraction Spectrum

The crystalline structure of pure chitosan was confirmed by the observed intense and strong peaks around $2\theta = 20^0$. Similarly, Cs-g-Pdmaema spectra show crystalline peaks around $2\theta = 20^0$, but the intensity of the peak is lower as compared to that of pure chitosan this indicates that grafting of chitosan with these polymers affected the crystallinity of the chitosan by breaking the crystal zone in the chitosan system, making it less crystal. This is in good agreement with the report by (Kong et al, 2019).

3.4.3 Thermo Gravimetric Analysis (TGA)

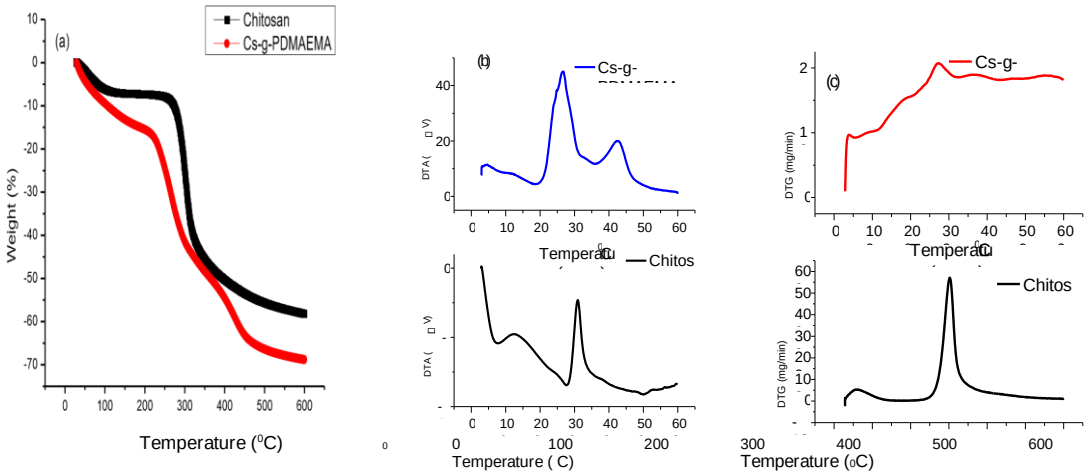

Figure 4.0 Thermogram of Chitosan and Cs-g-Pdmaema (a) TGA (b) DTA and (c) DTG

The TGA shows a three-step thermal degradation The first step weight loss (13.93%) at around 100^0C correspond to the Evaporation as a water molecule, the second stage is around 260^0C to 400^0C (31.17%) due to depolymerization of chitosan and the decomposition of the amine group of the chitosan, The third stage 425^0C to 500^0C (23.31%) which associated decomposition of PDMAEMA. DTA of pure Cs show sharp exothermic peaks around 300^0C which are accompanying thermal pyrolysis of the chitosan thermal decomposition of amino and N-acetyl residues (Ziegler-Borowska, Chełminiak & Kaczmarek, 2015). DTG of Chitosan exhibited maximum thermal decomposition temperature (Tmax) at 300^0C. However, that of Cs-gPdmaema has two Tmax around 266^0C (249.7µg/min) and 425^0C(199.3 µg/min). Cs-g-Pdmaema shows lower thermal stability than pure chitosan as the decomposition of the copolymer started earlier than that of pure chitosan because in pure chitosan there are extensive inter and intramolecular hydrogen bonding, and this contributed to the higher thermal stability of the polymer, thus grafting with another polymer, the grafted polymer will tend to break these bond, in turn, reduced the thermal stability of the polymer.

3.4.4 Scarning Electron Microscope Image (SEM)

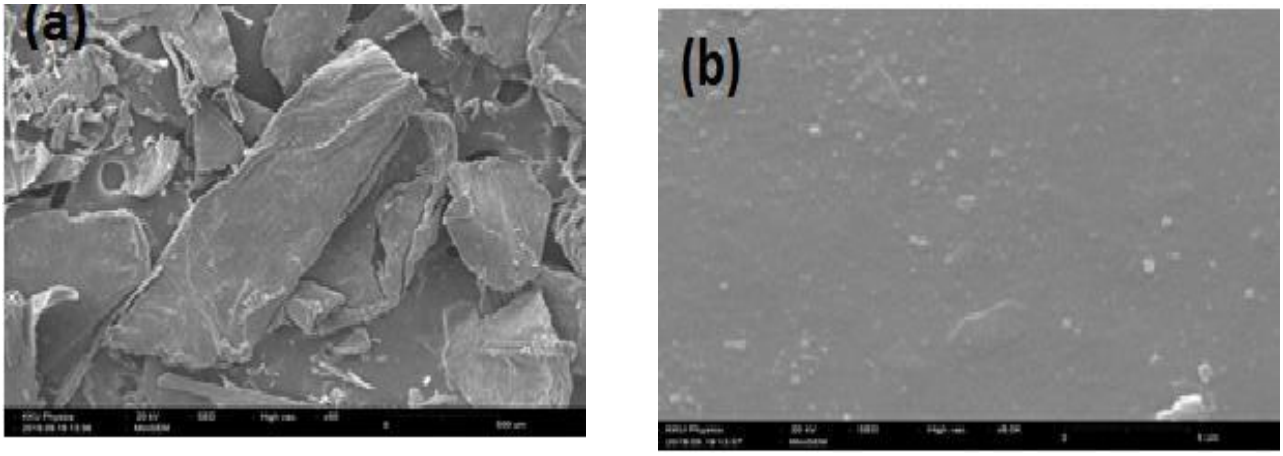

Figure SEM image of (a) Cs-g-PDMAEMA and (b) Chitosan

Figures 5a and 5b show SEM images of Cs-g-PDMAEMA and Cs respectively, the very high porous surface was observed in the SEM image of the grafted copolymer while that of pure chitosan shows a non-porous surface. SEM image reveals a semi-crystalline morphology was for pure chitosan while SEM image of Cs-g-PDMAEMA reveals amorphous form, this is in agreement with (Torabi et al, 2017).

3.4.5 X-ray Photon Spectroscopy (XPS)

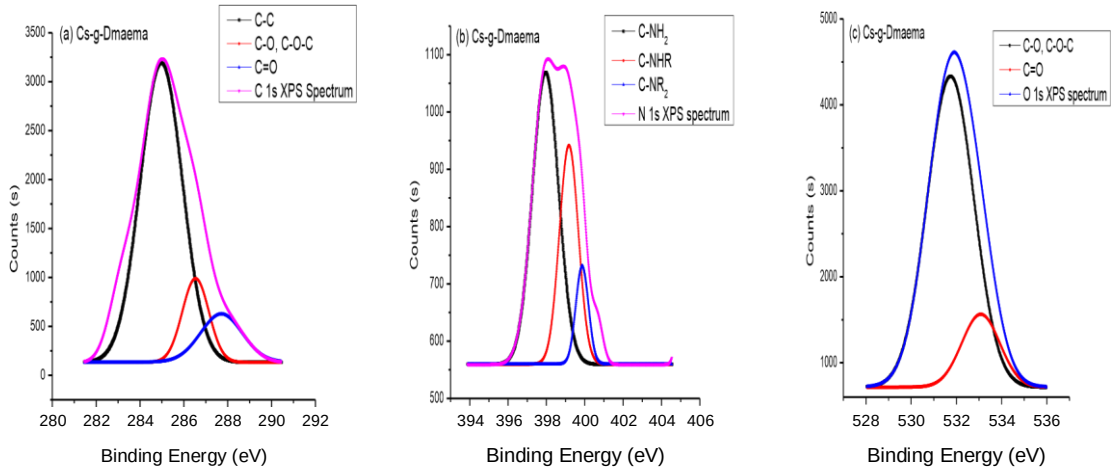

Figure 6.0 XPS Spectra of Cs-g-Pdmaema for (a) C1s (b) N1s and (c) O1s

Xps spectra of Cs-g-Pdmaema was presented in the figure 6.0, The deconvolution of each peak from the XPS spectrum of Cs-g-Pdmaema for each element associated with a peak was carried out to identified sub-peak component using the Gaussian–Lorentzian function based on previously

reported works (Mohd et al, 2021) using the origin lab software. Figure 6(a) shows C1s peak for which resolved into C–C bonds, C–O–C or C–O bonds and C=O with respective binding energy as 284.99 eV, 286.58 eV, and 287.6 eV. The presence of C=O indicates that Csg-Pdmaema was successfully grafted synthesized. The N1s XPS peak figure6.(b) deconvoluted into three sub-peaks at 397.9 eV correspond to C-NH2 and 399.16 eV which represent C-NH, and peak at 399.83 eV represent C-NR2. This shows that the anime group of chitosan participate in the grafting process (Mohd et al, 2021).The O1s spectra figure 6.(c) was deconvoluted into two peaks at 531.82 eV and 533.1 eV Representing C–O or C–O–C and C=O bonds, respectively.

4.0 CONCLUSION

Poly (2-dimethylaminoethyl methacrylate) (Cs-g-PDMAEMA) were successfully synthesized by Ultrasonic methods. The synthetic method was optimized by varying various reaction parameters and reaction conditions. The grafting was confirmed by characterizing the copolymer with FTIR, XRD, XPS, SEM, TGA, DTG, and DTA. The results show *a good percent grafting and percent yield up to 132%G and 94.7%Y at optimum condition, and also show* a decrease of thermal stability and crystallinity of chitosan, there was improved in porosity of the surface, and complexity of the surface functional group confirmed by XPS. The optimum condition was achieved at 308K, 60minute sonication time, and 1.4g/g monomer concentration. The synthesized co-polymer can be recommended for application such as adsorption technology and catalysis.

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