



Research Article

GRAFTING STUDIES OF CHITIN

Nevin CANKAYA *¹¹Department of Chemistry, University of Usak, USAK; ORCID: 0000-0002-6079-4987

Received: 06.12.2018 Revised: 03.01.2019 Accepted: 04.02.2019

ABSTRACT

In this study, some new chitin materials by the grafting of chitin with the monomers such as 1-vinylimidazole (VIM), methacrylamide (MAM) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were synthesized. Firstly, chitin methacrylate was prepared by esterification of primary -OH group with methacryloyl chloride with a 29.24% yield by mole. Secondly, the monomer that VIM, MAM, and AMPS were grafted into a chitin methacrylate via free radical polymerization using 2, 2'-Azobisisobutyronitrile as an initiator in N, N-dimethylformamide. The graft copolymers were characterized by FT-IR spectra and elemental and thermal analysis. The substitution degree is compatible with the literature. Thus, semi-synthetic natural polymers were successfully synthesized.

Keywords: Chitin, chitin methacrylate, graft copolymer, characterization, thermal stability.

1. INTRODUCTION

The development and application of biopolymers has received increasing interest because of their good biocompatibility, biodegradability, availability. Chitin is one particular biopolymer that has a long-chain biopolymer of N-acetylglucosamine. It is available from a number of natural sources [1]. It is found in the cuticles of insects and shells of crustaceans and is the most abundant polysaccharide after cellulose [2]. It has a similar structure to cellulose except for acetyl group instead of hydroxyl group is bounded. Substantially, chitin composed of 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine) units linked by β -(1,4) linkage [1]. It accommodates strong inter- and intra-molecular hydrogen bonds between the polymer chains and its water-insolubility gives it a rigid crystalline structure [3]. The pKa value of the chitin N-acetyl side chain is 6.1 [4].

Medical industry widely utilizes chitin and chitosan thanks to their bio friendliness and availability. However medicine is not the only science that chitin and chitosan could be used. Materials science is also interested in them because of their above mentioned properties. Its strong inter/intra-molecular hydrogen bonding and high degree of crystallization as well as low solubility in common solvents limits the applications of chitin [5]. Chitin is soluble in strong acids and polar solvents [6,7]. A method has been developed to dissolve of chitin by freezing/thawing in NaCl/ urea aqueous solution [5,8].

* Corresponding Author: e-mail: nevin.cankaya@usak.edu.tr, tel: (276) 221 21 21 / 2533

In this study, without allowing the chitin to dissolve, crude chitin was modified with methacryloyl chloride. Changes in structure were observed by attaching different monomers onto chitin methacrylate that modified semi-synthetic polymer.

2. EXPERIMENTAL

2.1. Materials and Instruments

Raw chitin, potassium tert-butoxide ($(\text{CH}_3)_3\text{CO}^-\text{K}^+$), methacryloyl chloride, 2, 2'-azobisisobutyronitril (AIBN) as initiator, 1-vinylimidazole (VIM), methacrylamide (MAM) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) as commercial monomer were purchased from Sigma-Aldrich. N, N-dimethylformamide, acetonitrile, ethanol, diethyl ether were used as solvent. The IR spectra of all samples were performed with a PerkinElmer Spectrum Two (UATR) IR spectrometer in the range of $4000\text{-}450\text{ cm}^{-1}$. Leco CHNS-932 was used for elemental analysis. Thermal analysis was performed with a Hitachi 7000 thermo balance at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen flow of 10 ml min^{-1} .

2.2. Synthesis of Chitin Graft Copolymers

To obtain chitin graft copolymers, chitin methacrylate was synthesized, primarily. Chitin methacrylate and its graft copolymers were synthesized by a method adapted from the literature [9-13]. Raw chitin was swollen in acetonitrile at the room temperature overnight, followed by adding a potassium-tert-butoxide ($(\text{CH}_3)_3\text{CO}^-\text{K}^+$) solution in acetonitrile. The mixture was stirred at the room temperature, and then methacryloyl chloride in solvent was added dropwise while stirring continued at the same temperature. The reaction mixture was refluxed for 48 hours, followed by a cooling and filtering procedure. Chitin methacrylate was washed away to remove salt and impurities with acetonitrile, water, ethanol, and diethyl ether. The synthesis reaction of the chitin methacrylate is shown in Figure 1.

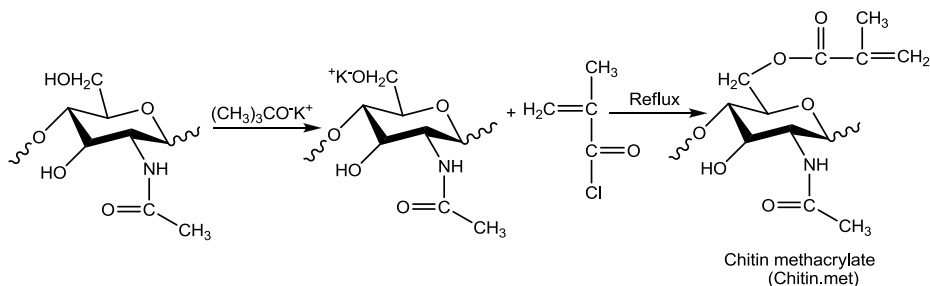


Figure 1. Synthesis of chitin methacrylate

1 g chitin methacrylate, 5 g monomer that VIM, MAM and AMPS in N,N-dimethylformamide and 0.05 g AIBN as a free radical initiator were added into a polymerization tube, and argon was passed through. The monomer was allowed to graft onto chitin at $\pm 72\text{ }^\circ\text{C}$ for 36 h, stirring. Grafted copolymers were filtered and thoroughly washed with N,N-dimethylformamide, acetonitrile, ethanol, and diethyl ether to eliminate oligomer and homopolymer formed in the reaction as products. Synthesized graft copolymers were dried, and analyzes were performed. The synthesis reaction of the grafting of chitin methacrylate with VIM, MAM and AMPS monomers is shown in Figure 2.

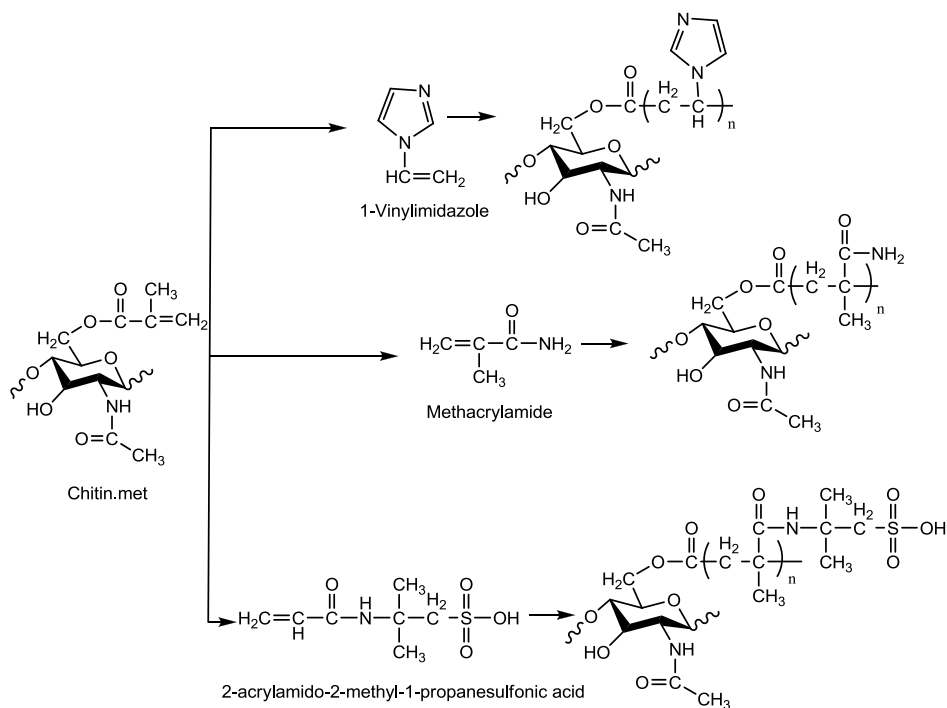


Figure 2. The grafting of chitin with some monomers

3. RESULTS AND DISCUSSIONS

3.1. Grafting of Chitin and its Characterization

The reaction of chitin with $(\text{CH}_3)_3\text{CO}^-\text{K}^+$ produces the alkoxide of chitin only on primary OH group even if an excess amount of $(\text{CH}_3)_3\text{CO}^-\text{K}^+$ was used. The treatment of the potassium chitin alkoxide with methacryloyl chloride results in the formation of chitin methacrylate (Chitin.met). As mentioned in the experimental section, a series of grafting studies on Chitin.met were carried out by using AIBN as a free radical initiator with VIM, MAM and AMPS (Fig 1 and 2). The FT-IR technique is the first spectroscopic method used to identify functional groups within a molecule. The spectrum of chitin shows the characteristic bands at 3440 cm^{-1} (O-H stretch), 3260 cm^{-1} (N-H stretch), 2880 cm^{-1} (N-H symmetric stretch), 1654 cm^{-1} (C=O amide stretch), 1615 cm^{-1} (N-H bending), 1552 cm^{-1} (N-C stretch), 1375 cm^{-1} (C-H bending vibration), 1015 and 1050 cm^{-1} (C-O symmetric and asymmetric vibration at C-O-C bonds) were observed [7,14]. The presence of a new band 1620 cm^{-1} (-C=O stretching), in which there is no band for chitin, indicates that the methacrylate group has attached to the chitin. Also, the most important evidence to demonstrate the grafting of methacrylate groups onto chitin is the increase in ester peak (-C=O) observed at 1720 cm^{-1} peaks (Figure 3).

The elemental analysis of the polymers is shown in Table 1. The substitution degree in the glucose units of chitin was calculated as 29.24% by mole (y) from and 35.61% by weight (Y) the percentage of carbon [9-13]. The substitution percentage of the glucose units in chitin was calculated from the expression

$$Y = \frac{A-B}{C-D} \times 100$$

where

A = % carbon found for modified chitin

B = % carbon found for starting chitin

C = % carbon calculated for 100% modification

D = % carbon calculated for starting chitin.

Table 1. Elemental analyses results of grafting on chitin with some monomers

Polymer	Elemental Analysis			
	C %	H %	N %	S %
Chitin	43.93	6.31	6.66	-
Chitin methacrylate	46.01	5.23	6.45	-
Chitin.met-g-VIM	45.69	6.70	8.86	-
Chitin.met -g-MAm	45.80	6.47	7.28	-
Chitin.met -g-AMPS	47.15	6.65	7.32	5.60

When the FT-IR spectra of the grafting studies on chitin methacrylate are examined, the following results are observed. FT-IR results of all chitin containing polymers show OH peaks at 3440 cm^{-1} , NH peaks at 3260 cm^{-1} and amide peaks at 1654 cm^{-1} region clearly. For Chitin.met-g-MAm and Chitin.met-g-AMPS, an increase in amide peaks due to polymerization of the monomer is observed. Furthermore, the weight increase in the synthesis of the graft copolymers as a result of the values calculated by gravimetric analysis is also evidence that graft copolymers are formed. FT-IR spectra of chitin, chitin methacrylate, the graft copolymers of chitin with poly(1-vinylimidazole) (Chitin.met-g-VIM), poly(methacrylamide) (Chitin.met-g-MAm), and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (Chitin.met-g-AMPS) are shown in Figure 3.

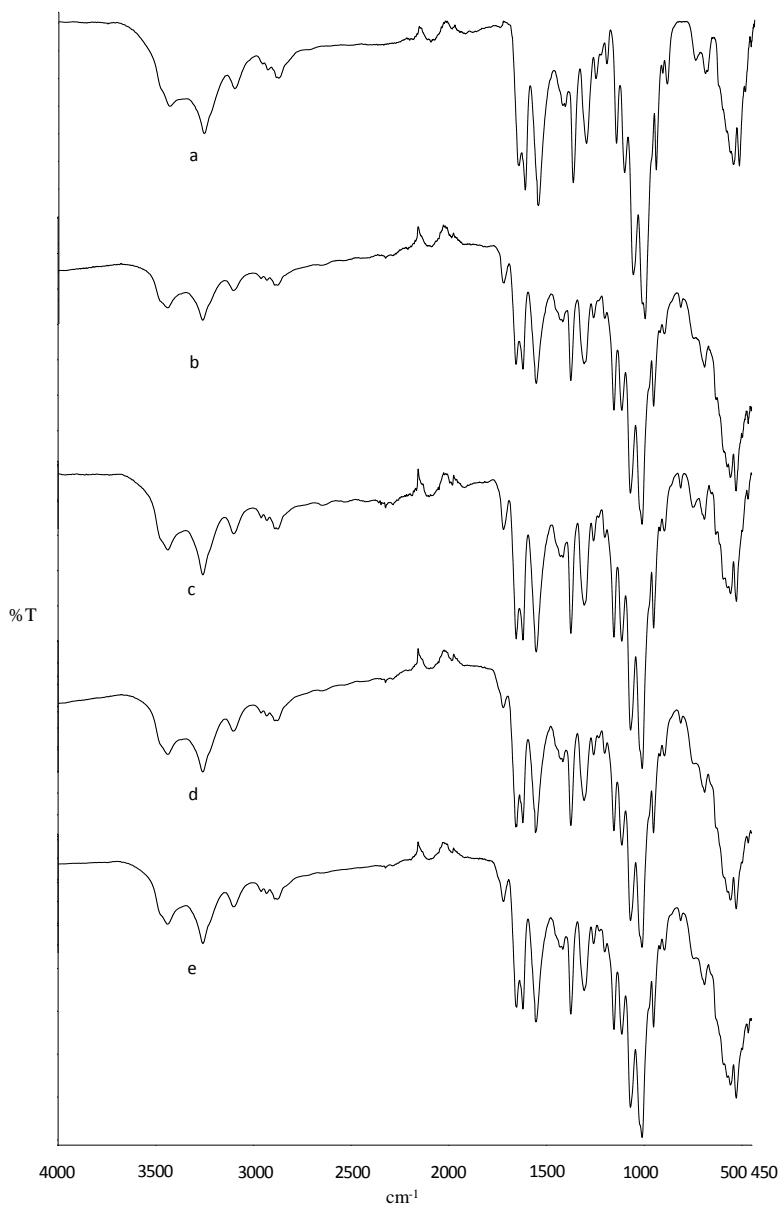


Figure 3. FT-IR spectra of the a) Chitin b) Chitin.met c) Chitin.met-g-VIM d) Chitin.met-g-MAM e) Chitin.met-g-AMPS

Thermal analysis measurements were made at a heating rate of 10 °C/min at a N₂ gas flow of 10 ml/min. Referring to Figure 4, the thermal stability of the chitin is higher than that of graft copolymers. Initial decomposition temperature and temperature of a weight loss of 50%, decreased by grafting. All the polymers show that thermal degradation was completed in one

steps. It is observed that the synthetic polymers attached to chitin methacrylate decreased the thermal stability. Thermograms obtained for chitin, chitin methacrylate, and its graft copolymers are presented in Figure 4, while some thermal data are given in Table 2.

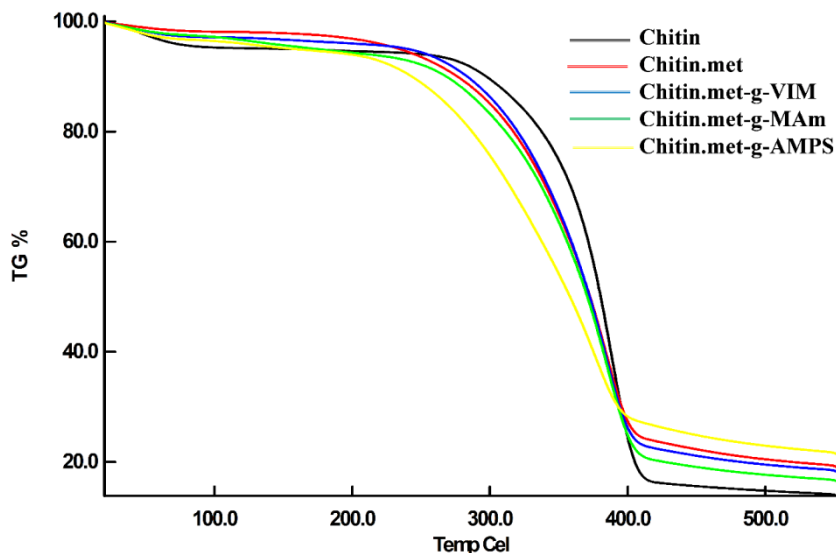


Figure 4. TGA curves of chitin, chitin methacrylate and its graft copolymers

Table 2. Thermal analyses results of grafting on chitin with some monomers

Polymer	Max. Decomposition Temperature (°C)	Temperature of 50% weight loss (°C)	%Weight loss (300 °C)	%Weight loss (400 °C)	%Residue (550 °C)
Chitin	390	380	11	76	14
Chitin methacrylate	386	372	15	73	19
Chitin.met-g-VIM	385	372	14	74	18
Chitin.met -g-MAm	387	371	16	75	17
Chitin.met -g-AMPS	377	358	24	72	21

4. CONCLUSION

In this study, chitin methacrylate was prepared by esterification of primary –OH group with methacryloyl chloride with a 29.24% yield by mole. The monomers such as 1-vinylimidazole (VIM), methacrylamide (MAm) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were grafted into the chitin methacrylate via free radical polymerization using 2, 2'-Azobisisobutyronitrile (AIBN) as an initiator in N,N-dimethylformamide. The graft copolymers were characterized by FT-IR spectra and elemental analysis. Thermal stability of the chitin graft copolymers was determined by the thermal methods and compared to each other. Since chitin is low cost, biodegradable, and easily obtainable, the synthesized chitin-containing polymers will also have the same properties. The newly synthesized biopolymer-containing graft polymers is supposed to increase the application area.

Acknowledgement

The authors would like to thank the Usak University Research Fund for financial support of this work (2012/MF006).

REFERENCES

- [1] Akkaya G., Uzun İ., Güzel F. (2009) Adsorption of some highly toxic dyestuffs from aqueous solution by chitin and its synthesized derivatives. *Desalination*. 249, 1115–1123.
- [2] Kittur F. S., Harish Prashanth K. V., Udaya Sankar K., Tharanathan R.N. (2002) Characterization of chitin, chitosan and their carboxymethyl derivatives by differential scanning calorimetry. *Carbohydr. Polym.* 49, 185–193.
- [3] Murray S. B., Neville A. C. (1997) The role of the electrostatic coat in the formation of cholesteric liquid crystal spherulites from α -chitin. *Int. J. Biol. Macromol.*, 20, 123–130.
- [4] Sugimoto M., Morimoto M., Sashiwa H., Saimoto H., Shigemasa Y. (1998) Preparation and characterization of water-soluble chitin and chitosan derivatives. *Carbohydr. Polym.* 36, 49–59.
- [5] Liua M., Zhanga Y., Li J., Zhoua C. (2013) Chitin-natural clay nanotubes hybrid hydrogel. *International Journal of Biological Macromolecules*. 58, 23–30.
- [6] Saravana D., Gomathi T., Sudha P. N. (2011) Synthesis, Characterization and Thermal Behavior of Natural Polymer Blend. *International Journal of Chemical and Analytical Science*. 2 (12), 1265-1269.
- [7] Saravanan D., Sudha P. N. (2012) Enhancement of thermal stability in the presence of crosslinking using natural biopolymer. *Elixir Appl. Chem.* 44, 7374-7377.
- [8] Chang C., Chen S., Zhang L. (2011) Novel hydrogels prepared via direct dissolution of chitin at low temperature: structure and biocompatibility. *Journal of Materials Chemistry*. 21, 3865–3871.
- [9] Çankaya N., Temüz M. M. (2015) Grafting of Some Monomers onto Cellulose and Determination of Metal and Water Uptake Properties. *Cellulose Chemistry and Technology*. 49 (2), 135-141.
- [10] Çankaya N. (2016) Synthesis of Graft Copolymers onto Starch and its Semiconducting Properties. *Results in Physics*. 6, 538–542.
- [11] Çankaya N., Temüz M. M. (2012) Characterization and Monomer Ratios of Grafted Cellulose with N-(4-nitrophenyl)acrylamide and Methyl Methacrylate by Atom Transfer Radical Polymerization. *Cellulose Chemistry and Technology*. 46 (9-10), 551-558.
- [12] Çankaya N., Temüz M. M. (2014) Monomer Reactivity Ratios of Grafted Cellulose with N-cyclohexylacrylamide and Methyl Methacrylate by Atom Transfer Radical Polymerization. *Cellulose Chemistry and Technology*. 48 (3-4), 209-215.
- [13] Çankaya N., Temüz M. M., Yakuphanoglu F. (2018) Grafting of some monomers onto cellulose by atom transfer radical polymerization. Electrical conductivity and thermal properties of resulting copolymers. *Cellulose Chemistry and Technology*. 52 (1-2), 19-26.
- [14] Ifuku S., Nomura R., Morimoto M., Saimoto H. (2011) Preparation of Chitin Nanofibers from Mushrooms. *Materials*. 4, 1417-1425.