Grafting of Poly (2-Hydroxyethyl Methacrylate) onto Chitin Beads

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Submitted to the
Institute of Graduate Studies and Research
in partial fulfillment of the requirements for the Degree of

Master of Science
in
Chemistry

Eastern Mediterranean University
July 2014
Gazimağusa, North Cyprus

Approval of the Institute of Graduate Studies and Research

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ABSTRACT

Chitin was grafted with poly(2-hydroxyrthyl methacrylate) poly(HEMA) by using ceric ammonium nitrate (CAN) as the initiator. The effect of temperature, time, concentration of the monomer (HEMA), the amount of chitin beads and the initiator (CAN) concentration on the grafting yield has been studied under nitrogen atmosphere. The optimum conditions for the grafting process were established. The maximum grafting percentage of poly(HEMA) on to non porous chitin was found to be 65%, while for porous chitin beads it was 515%. The optimum conditions were 0.1 g of porous chitin beads, 8 mL (3.3 Mol/L) HEMA monomer, 0.5 g (4.6×10^{-2} mol/L) of CAN initiator for three hour reaction time at 35 °C.

The products were characterized by FT-IR, SEM, C13 NMR and XRD analysis. Swelling and dissolution behavior of the products were followed in different buffer solutions (pH = 1, 7 and 11).

Keywords: 2-hydroxyethyl methacrylate (HEMA), chitin, graft copolymerization, hydrogel, chitin bead.

ÖZ

Kitin redoks başlatıcısı serrik amonyum nitrat (CAN) ile poli (2-hydroksilmetilmethakrilat), poli (HEMA), ile aşılanmıştır. Sıcaklık, reaksiyon süresi, monomer konsantrasyonu, kitin ve başlatıcı madde, (CAN), konsantrasyonunun aşılama verimi üzerinde etkisi N_2 atmosferi altında incelenmiştir.Aşılama işlemi için en uygun şartlar 0.1 g gözenekli kitin boncuklar kullanılarak 35°C sıcaklıkta, üç saatlik bir reaksiyon süresi için, 8 ml (3.3 mol / L), HEMA monomer, 0.5 g (4.6 x 10-2 mol/L) CAN başlatıcı olarak bulundu. Aşılama yüzdesi gözenekli kitin boncuklarda en fazla 515% gözenekli olmayan kitin boncuklar içinse %65 olarak bulunmuştur. Ürünler FT-IR, SEM, C13 NMR ve XRD analizi ile karakterize edildi. Şişme ve çözelti içindeki davranışları farklı pH lardaki tampon çözeltilerde (pH = 1, 7 ve 11) takip edildi.

Anahtar kelimeler: 2-hidroksietil metakrilat (HEMA), kitin, aşı kopolimrizasyon, hidrojel, kitin kürecik.

ACKNOWLEDGEMENT

I would like to express the deepest appreciation to my supervisor Prof. Dr. Elvan Yilmaz. I have learned so much from her. She makes me think like a scientist.

I am grateful to Dr. Zulal Yalinca for her help and advice throughout my thesis. She was always ready to help me.

I would like to thank my family (my wife Rezan, my daughter Dlin and my son Dere) for their patience and their unwavering support and encouragement.

I owe my deepest gratitude to my parents, all of my brothers and sister. Thank you all.

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INTRODUCTION

Chitin is capable of gel formation via thermo reversible gelation and via coagulation of chitin/NMP/LiCl system form a non solvent (Hirano & Horiuchi 1989; Bianchi *et al*., 1997; Khor *et al*., 1997; Vachoud *et al*., 1997; Yusof & Khor 2001; Yilmaz & Bengisu 2003). Gels coagulated from a non solvent are more versatile for further use as they are stable at room temperature. One disadvantage of chitin gel beads is their poor swelling in aqueous solution which limits its potential as a bioadsorbent or in pharmaceutical applications. Swelling ratios of chitin gel beads were reported to be in the range 2.0 to 4.0 in aqueous solution under neutral, basic and acidic conditions (Yilmaz & Bengisu 2003). Poly (2-hydroxyethylmethacrylate), poly(HEMA), on the other hand, is a hydrophilic polymer which has found wide use in thermosetting paints, adhesion promoters for polymers, hydrophilic polymers, light-curing polymer systems, textile fiber grafting and component for lubricant additives to name but a few (Bayramoglu *et al*., 2013; Huang *et al*., 2013; Jaiswal *et al*., 2013; Krezovic *et al*., 2013; Yavuz, M. and Z. Baysal 2013). Hence, grafting of poly(HEMA) on to chitin gel beads would provide a new hybrid system with functionalized, hydrophilic bead surface which would impart improved physical and chemical properties to chitin. Especially porous chitin beads grafted with poly(HEMA) have a potential to act as scaffolds in tissue engineering as solid supports for enzyme drug and protein immobilization.

1.1 Chitin

Chitin is a polysaccharide which originates mostly from the external skeleton of shrimps and insects. Chitin is the second most abundant polysaccharide after cellulose. As a biopolymer, the annual production of chitin and cellulose together is estimated to be around 10^{11} tons per year (Kurita, 2001). In spite of its big annual production and ease of accessibility, chitin still becomes unusable biomass resource mainly because of its tenacious bulk structure (Khor, 2002). However it can be predicted that chitin will become an increasingly important natural organic material in the 21st century since chitin and its derivatives have a high potential for a broad range of applications like bio-related science (Li *et al.*, 2013; Pant *et al.*, 2013), technology (Kumar *et al.*, 2004; Mincea *et al.*, 2012), cosmetic (Ifuku, 2012), medical (Li *et al.*, 2013), pharmaceutical (Kumar *et al.*, 2013), agriculture (Ifuku, 2012), environmental safety (Antonio *et al.*, 2013; Yang *et al.*, 2013) and food industry (Dutta *et al*.,2012).

1.2 Chitin Structure and Properties

The main polysaccharide which had been found in cell walls of fungi and shells of crustaceous, is chitin [(1→4)-linked N-acetyl-β-D-glucosamine]. As shown in the Figure 1a. Chitin chemical structure and Figure 1b. Cellulose chemical structure chitin is comparable to cellulose; the only special characteristic between them is that in chitin instead of hydroxyl (-OH) group, there is acetamide group at C-2 location in the glucose unit (Jayakumar *et al.*, 2008).

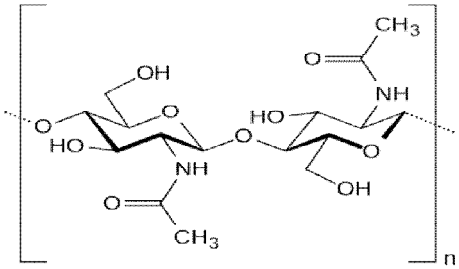


Figure 1a. chemical structure of chitin

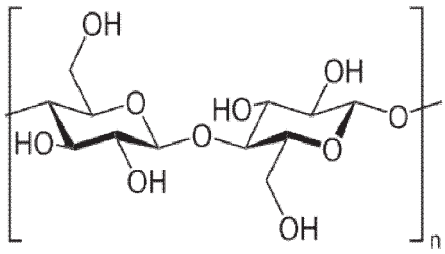


Figure 1b. chemical structure of cellulose

1.3 Alpha, Beta and Gamma Crystalline Structure of Chitin

The big problem of chitin which causes the main limiting factor in its application is poor solubility which is due to its crystalline structure. Researchers found three polymorphic crystalline structures for chitin: α, β and γ. α-chitins are found in arthropods, cyst of Entamoea and fungi, β-chitin is extracted from the Loligo squid pen. But γ-chitin can be extracted from cocoon fibers of the Ptinus beetle and Loligo stomach. Blackwell studied about physicochemical and structure of α-chitin and β-chitin, he reported that the parallel chains of chitin in bonded piles or sheets are arranged and connected together with (-N-H…O=C-) hydrogen bonds through the amide groups(Jang *et al.*, 2004; Aranaz *et al.*, 2009). According to the raw materials the crystalline structure of chitin are in a different way studied and presented. With respect to the derived material the structure of α-chitin and β-chitin are only different in that the chain piles are ordered alternately parallel in β-chitin while in α-chitin they are anti-parallel, in other hand the chemical structure for γ-chitin shows that two chains set in one track and the other chain sets in the reverse direction (Aranaz *et al.*, 2009).

X-ray diffraction (XRD) for α, β and γ. α-chitin structures which was suggested by Rudall and Blackwell, α-chitin has a physically powerful inter and inra sheet H-bonding but compare to α-chitin, β-chitin is describe as a weak intermolecular force, that's why display higher and more reactivity in different types of modification reactions and have more interest toward solvents than alpha chitin. In the past, studies observations was carried out by many scientists for each of α-chitin and β-chitin, but these properties for γ-chitin, first it was planned by Rudall et al. until now where not discovered because of the abnormal properties and the nature of the unprocessed material (Rinaudo, 2006).

1.4 Production of Chitin from Raw Materials

A schematic representation for chitin preparation process from raw materials, (Figure 2). Crustacean shells contain: 25-35% chitin, 35-45% protein and 30-50% $CaCO_3$, and also contain some lipids. The content ratio is variable with season and from one raw material to another (Bhattacharya & Misra, 2004; Aranaz *et al*., 2009).

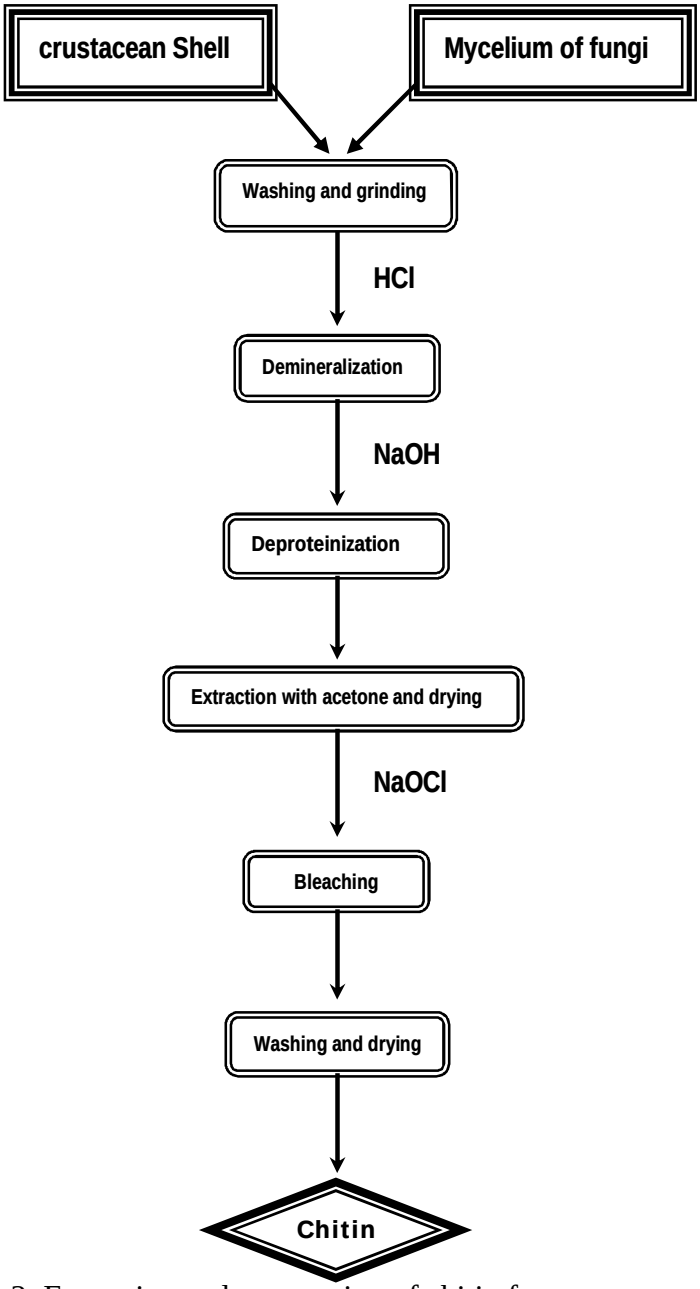


Figure 2. Extraction and preparation of chitin from raw materials.

1.5 Functional characterization of chitin

Not all chitin samples are useful for the same purpose and applications, because characteristics of chitin have a huge consequence on their properties and also their probable applications. Shortly; an absolute characterization of the samples is required. Rinaudo has reported that the origin of chitin may affect purity and crystallinity. It is also has been reported that the surface area of the chitin composition is directly associated to the origin of the sample (shrimp < lobster < crab) (Rinaudo, 2006).

Degree of deacetylation (DD), weight average molecular weight (Mw), crystallinity and polydispersity; they are those parameters which directly affect the polymer properties. On the other hand, for those applications related to the human utilization, such as medical applications, drug or food, moisture, endotoxin and protein content purity and heavy metal content should be considered. (Kassai, 2008; Aranuz *et al*., 2009).

1.6 Derivatives of Chitin

For chitin, there is a list of most useful derivatives which can be used for different applications in different fields such us biomedical, environmental, biological. Some of these derivatives are: Cyanoethylchitin, chitinxanthogenate, hydroxyalkylchitin, alkylchitin, carboxymethylchitin, alkalichitin, chitosan and all derivatives of chitosan (Figure 3).

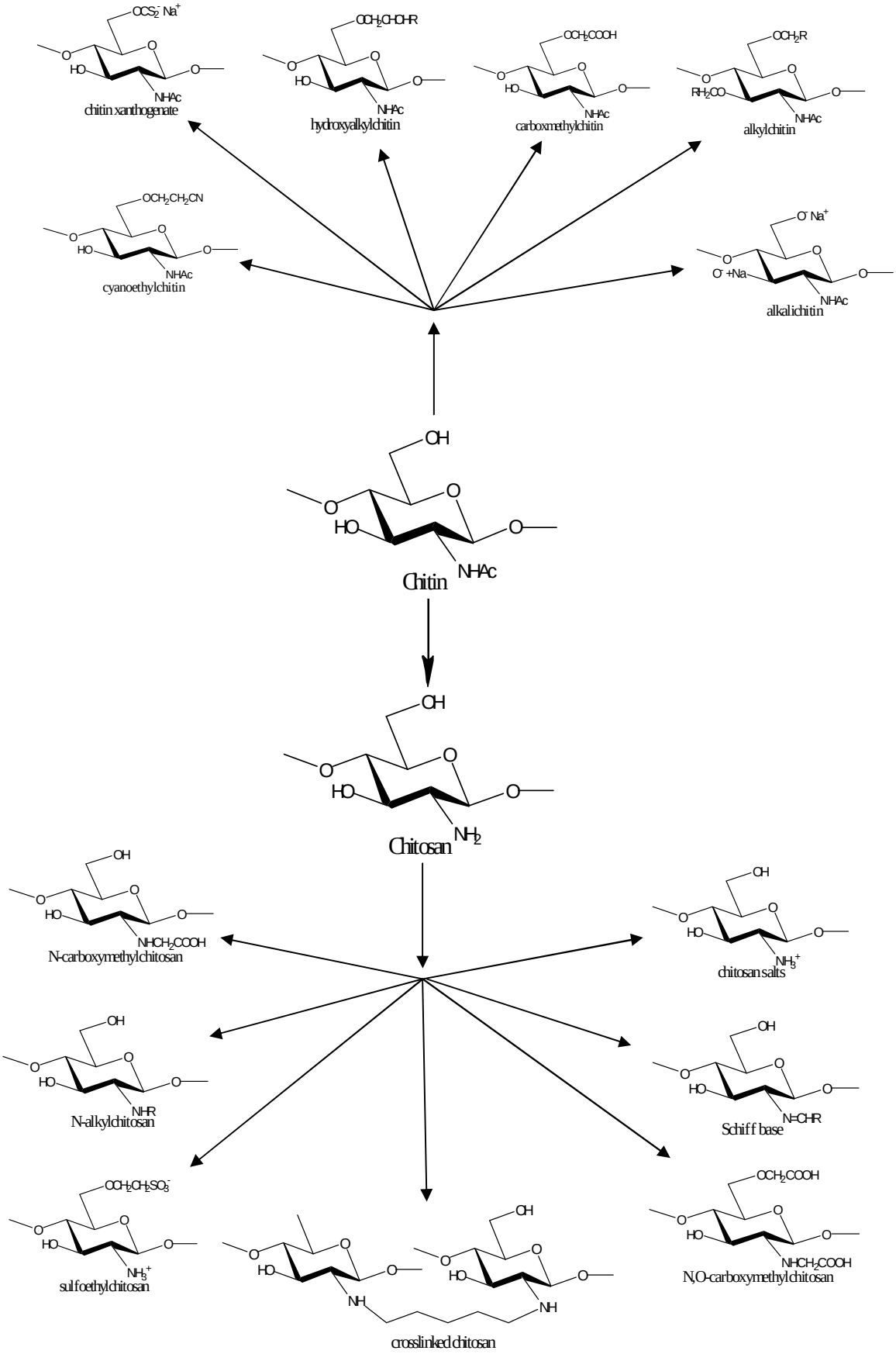


Figure 3. Chitin derivatives. (Uzun & Topal, 2013).

1.7 Applications of Chitin and Chitin Derivatives

Today, there is interest toward utilization of chitin and its derivatives in different fields due to their versatile physic chemical characteristics. The most important drawback of the polymer being its rigidity and limited solubility.

In this part, some applications of chitin and its derivatives in different fields summarized as below:

Due to resistant to corrosion, film forming capability and optical characteristics, chitin can be use in applications which related to photography (Kumar, 2000). Chitin and chitosan are also used in creams and lotions. It have been reported that some of chitin derivatives are useful in making nail polish (Kumar, 2000).

N-acetyl glucosamine (NAG), in the human milk, have role to encourage the growth of bifidobacteria. Bifidobacteria are used for many conditions affecting the intestines, including preventing diarrhea in infants and children; as well as traveler's diarrhea in adults (Hu and Zhu, 2012).

Chitosan is applicable for development of ocular bandage lenses because of the wound healing, antimicrobial properties and film capability. Having all the required characteristics for creating the best contact lens such us mechanical stability, optical correction and clarity, physical properties and gas permeability particularly to oxygen immunological compatibility and wettability, make it is useful in this field with a high quality polish (Kumar, 2000).

Nowadays, one of the most important global problems is environmental protection. Chitin and its derivatives have a significant role in this field of application. Like, Metal capture from waste water by using water soluble derivatives of chitin especially hydroxymethyl chitin (Bulbul Sonmez, 2002). Also chitosan have high affinity for Sorption most of the classes of dyes (Hu and Zhu, 2012).

In paper manufacturing, hydroxymethyl chitin and other water soluble derivatives of chitin are helpful. It has been reported chitosan has ability to import wet potency to paper (Allan *et al*., 1972). This polymer potentially accessible in great quantities. The industrialist can use this polymer for improved finish paper properties.

Chitin and chitosan are biodegradable polymers that are significantly practical for drug delivery purposes. Manufacturing of slow release (SR) drugs is more and more interesting in current time. The release of drugs encapsulated or absorbed by polymer materials, engaged their controllable and slow diffusion from or through polymeric matters.

Chitin has two –OH hydroxyl group and for chitosan in the repeating hexosamide part have two hydroxyl group and one amino group. Different biofunctional macromolecular products can be generated from the chemical modifications of this functional groups which they have new organization or same organization like before modification. These modified products can be use in cell-stimulating materials for plants and for animals, by treatment with chitin and chitin derivatives, the extracellular lysozyme activity can be improved in animals. Furthermore, chitin and its derivatives can be applicable in some more different biological fields, for

example; chitosan can act like antibacterial agent, which is inhibiting the growth of Escherichia coli. Also chitin and chitosan sulphates they have anti coagulant activities (Pant *et al*., 2013).

1.8 Chemically Grafted Chitin

Because of functional properties of chitin and its derivatives which can be used in biomedical, medical and environments protection fields, but as mentioned before, there is some limitation for utilizing chitin and chitin derivatives due to its rigid chemical structure. Hence it has been reported chemically there is some papers related to grafting on to chitin and chitin derivatives so as to make it be more flexible to use. Some grafted chitin and its characteristics published in recent articles are given in the following subsections:

1.8.1 Production of (Chitin-graft-Polystyrene) by the use of ATRP Initiated from a Chitin Macroinitiator

Yamamoto reported that (chitin-graft-polystyrene) has been produced by graft polymerization of styrene from a chitin macroinitiator by the use of atom transfer radical polymerization (ATRP). The chitin macroinitiators were created by using 2-bromopropionyl bromide in (AMIMBr) ionic liquid for acylation of chitin. Then, graft polymerization of styrene from the obtained chitin macroinitiator with DS - 1.86 was performed by ATRP using CuBr as the catalytic system and pentamethyldiethylene triamine. With increasing the feed ratios of styrene to chitin macroinitiator initiating site, the yield products increased. By the use of alkaline hydrolysis, Polystyrene chains were separated from the main chain of chitin. (Yamamoto *et al.*, 2013).

1.8.2 Homogeneous Synthesis of Chitin-based Acrylate Superabsorbents by using Sodium hydroxide and Urea for Dissolving Chitin

A transparent homogeneous solution was obtained by dissolving chitin in NaOH / urea solution with a modified freezing-thawing cyclic (FTC) process. It was operated directly for creating the superabsorbent polymers (SAPs) by grafting copolymerization under fixed conditions without N_2 gas. The acrylic acid was used easily without neutralization. Liu *et al.* reported that the product was a hydrogel without any excess reagent productions. He reported that optimum conditions for this grafting, the adsorption capacity was 2833 (g/g) and yield of the grafted product was 81.65%, it was reported that the product was very clean, transparent gel without remaining particles of chitin. The regenerated chitin and grafted one were characterized by XRD, FTIR, SEM and TG. The prepared samples, offered a more amorphous state and better thermal stability (Liu *et al., 2013*).

1.8.3 Grafting Chitin nano Crystals with Poly-HBV

Wang *et al*. showed that acetyl amino group will keep in the chemically grafting poly-HBV onto backbone of chitin through chlorination. The structure of (PHBV-g-chitin nanocrystals) was characterized by FTIR. The effects of chitin and chitin nanocrystals-g-PHBV on the crystallizing and melting behavior of PHBV were studied by (DSC) differential scanning calorimeter. The results showed that both unmodified and grafted chitin nanocrystals concealed crystallization of PHBV. PHBV melting point was increased after being mixed with nanofillers (Wang *et al*., 2012).

1.8.4 Chitin Grafting with Polystyrene using Ammonium Persulfate Initiator

Chitin was grafted with PS by free radical polymerization mechanism, by using ammonium persulfate (APS) as initiator and the reaction was performed in aqueous medium, the optimum condition for the grafting was 0.4 g APS, chitin to PS ratio was 1:3 at pH 7, reaction time and temperature were 2 hour and 60 °C respectively, FTIR, TGA, GPC and DCS characteristics for the grafted chitin showed that the grafting was achieved successfully (abu Naim et al., 2013).

1.8.5 Chitin-graft-Poly(4-vinylpyridine) Beads

Oylum *et al*. stated another method for grafting on to chitin; chitin was modified by grafting with (P4VP) to produce chitin-graft-P4VP. The grafting yield was up to 226%, by using potassium persulfate (KPS) as an initiator and reaction was carried out under homogeneous condition. Grafted chitin was then coagulated in non solvent ethanol to form grafted beads. Furthermore, the Chitin-graft-P4VP was characterized by XRD, FTIR, TGA and SEM analyses. And also they studied about swelling behavior of the beads in acid, distilled water, and phosphate buffers. XRD showed that the crystallinity for unmodified chitin is more than the grafted P4VP product. Also the grafted product was less stable toward thermal treatment than chitin when revealed by TGA analyses. Due to a microporous bead surface and chemical modification the beads found on chitin-graft-P4VP were reported to have higher adsorption capacities than chitin beads (Oylum *et al*., 2013).

1.9 2-Hydroxyethyl Methacrylate (HEMA)

HEMA is abbreviation of 2-hydroxyethylmethacrylate, it have an active surface, its hydrophilic and high purity dual functionality monomer. HEMA is a clear liquid with an ester-like odor at standard temperature and pressure. Its melting point is expected to be at -99°C and a boiling point at 213°C. It has a density of 1.071 which is slightly higher than that of water. High water soluble and a low vapor pressure. The substance is not classified as flammable, explosive or oxidizing.

Those hydrogels that are formed from 2-hydroxyethylmethacrylate (HEMA) are commonly studied for use in different applications as biomaterials. This biomaterial was first studied by Wechterle & Lim, 1960. It was shown that it can be used as soft contact lenses, but because of the low mechanical properties of polyHEMA hydrogels, till now still there are some tricky for using them as implant devices.

The solution polymerization of HEMA monomer let the formation of porous structure. On other hand, the polymer created by bulk polymerization from HEMA monomers was non porous and it was glassy and transparent. Both porous and non porous gels have some applications. Porous hydrogel can be used as sponge like biomaterials for tissue repair. While non porous or dense one (optically transparent), are used in soft contact lenses (Malmonge *et al.*, 1997). Furthermore, due to dual functionality of HEMA monomer, surface active and a hydrophilic property, it can be used broadly in dental adhesive systems and polyHEMA in several biomedical applications (Dragusin et al., 2012).

Table 1. Chemical identity of HEMA monomer

Name	2-Hydroxyethyl methacrylate (HEMA)
Chemical structure	
(IUPAC) Name	2-Hydroxyethyl 2-methylprop-2-enoate
Other names	HEMA; Hydroxyethyl methacrylate; Glycolmethacrylate; Glycol monomethacrylate; Ethylene glycol methacrylate; 2-(Methacryloyloxy) ethanol
Molecular formula	$C_6H_{10}O_3$

Table 2. Properties and values for HEMA monomer

Property	***Values***
Molecular weight	130 g/mole
Water solubility	100 g/l (20°C)
Density	1.071 g/cm3 (20°C)
Vapor pressure	0.008 KPa (20°C)
Melting / Boiling point	-99°C /213°C
Flashpoint	106°C

1.9.1 Copolymers Based on Poly(HEMA) and Their Applications as Hydrogels

Semi-interpenetrating network poly(HEMA)/poly(IA) and poly(VP) were prepared. With increasing the amount of poly(VP), mechanical properties were improved. The produced hydrogels demonstrated to have antibacterial activity (Krezovic *et al.*, 2013). Poly(HEMA)/poly(acrylic acid)/gelatin scaffolds (Jaiswal & Koul 2013) and electrospun poly(HEMA) were useful for tissue engineering purposes (Ramalingam *et al.*, 2013). Microspheres prepared from poly(HEMA)/poly(acrylic acid) cross

linked to N,N-Methylenebisacrylamide were successful in controlled drug release applications (Swamy *et al*., 2013).

1.9 Aim of the thesis

This thesis work aimes at finding out the optimum conditions for grafting of HEMA on to chitin beads. The effect of monomer concentration, initiator concentration, time and temperature as well as bead morphology on the grafting yield need to be investigated to optimize the grafting conditions.

Chapter 2

EXPERIMENTAL

2.1 Materials

The chemicals used are listed below. All materials were used are received.

Table 3. The chemicals and their manufacturers

No.	Chemicals	Manufacturers
1	Chitin	Aldrich-Germany
2	2-hydroxyethyl methacrylate (HEMA)	Aldrich-Germany
3	Acetic acid	Aldrich-Germany
4	Ethanol	Riedel-deHan-Germany
5	Toluene	AnalaR-UK
6	Dimethylformamide (DMF)	Merck-Germany
7	Dimethylacetamide (DMAc)	Aldrich-Germany
8	Dimethyl sulfoxide (DMSO)	Aldrich-Germany
9	n-Hexane	Emplura-Germany
10	Chloroform	Emplura-Germany
11	Acetone	Aldrich-Germany
12	N-methyl-2-pyrrolidinone 99% (NMP)	Aldrich-Chemi-GmbH
13	Lithium chloride	Aldrich-Chemi-GmbH
14	Nitric acid	AnalaR-BDH-England
15	Ceric ammonium nitrate (CAN)	Aldrich-Chemi-GmbH
16	Azobisisobutyronitrile (AIBN)	Aldrich-Chemi-GmbH
17	Potassium persulfate (KPS)	Aldrich-Chemi-GmbH
18	Sodium hydroxide	Aldrich-Germany

19	Potassium dihydrogen phosphate	Aldrich-Germany
20	Sodium bicarbonate	Aldrich-Germany
21	Potassium chloride	Aldrich-Germany
22	Hydrochloric acid	Aldrich-Germany

2.2 Methods

2.2.1 Dissolution Properties of HEMA

Solubility of HEMA monomer was determined in double distilled water, dimethyl formamide, acetic acid, DMAc/LiCl, ethanol, toluene, dimethyl sulfoxide, hexane, NMP/LiCl, chloroform and acetone. A sample 0.50 mL HEMA was mixed with 5.0 mL of the solvent at room temperature, and the behaviour was observed.

2.2.2 Preparation of the Solvent System

Molecular sieves (400 Å) which were activated at 280ºC for minimum 4 hours were used to remove any humidity from the NMP or DMAc solvent. LiCl salt was dried at 130ºC, and then dissolved in dry NMP with continuous stirring to prepare a 5% (w/w) solution.

2.2.3 Preparation of Chitin Solution

Two different concentrations of chitin solution 0.5% (w/v) and 1.0% (w/v) were prepared by dissolving a given amount of chitin in NMP/5%LiCl solution with continuous stirring at 25 ºC (48 hour) to get a clear and transparent solution.

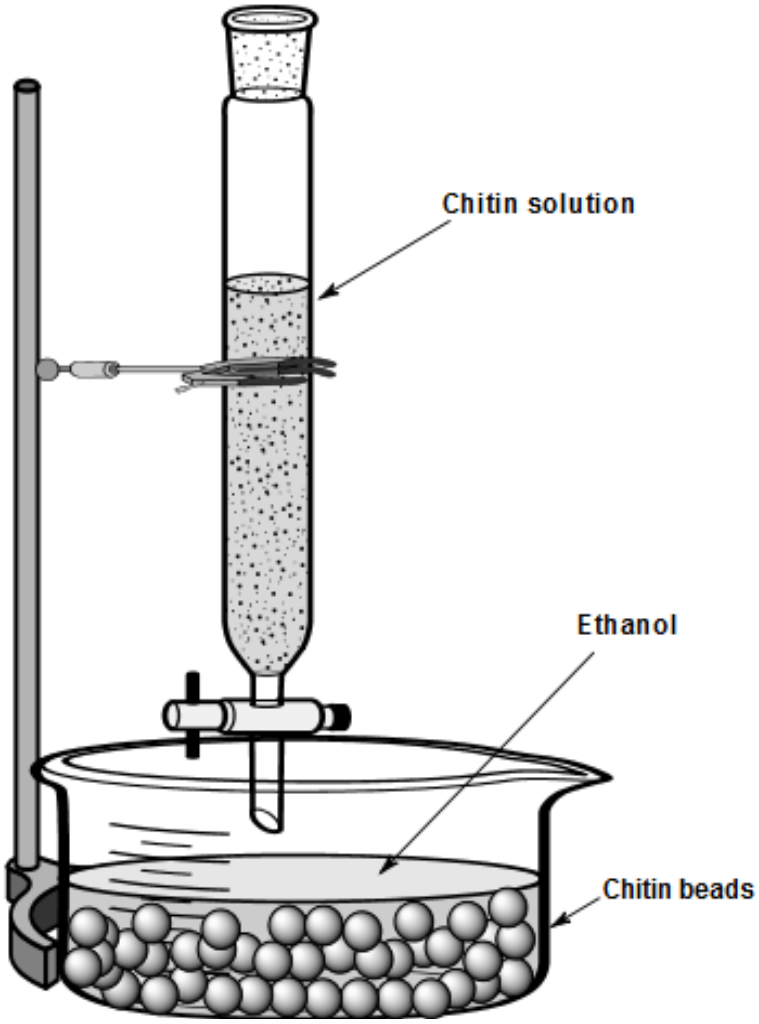
2.2.4 Preparation of Non-Porous Chitin Beads

The NMP/LiCl prepared solution was used to dissolve purified chitin to create the beads. Chitin solution was kept under stirring until a clear solution was obtained. Then the solution was sucked into a burette and dropped slowly into ethanol (Scheme 1). Beads produced were kept in nonsolvent ethanol to allow solvent exchange.

Ethanol was separated by filtration. This process was repeated 2-3 times to be sure that formed beads were cleaned from any impurities then dried at 50 ºC in the oven.

2.2.5 Preparation of Porous Chitin Beads

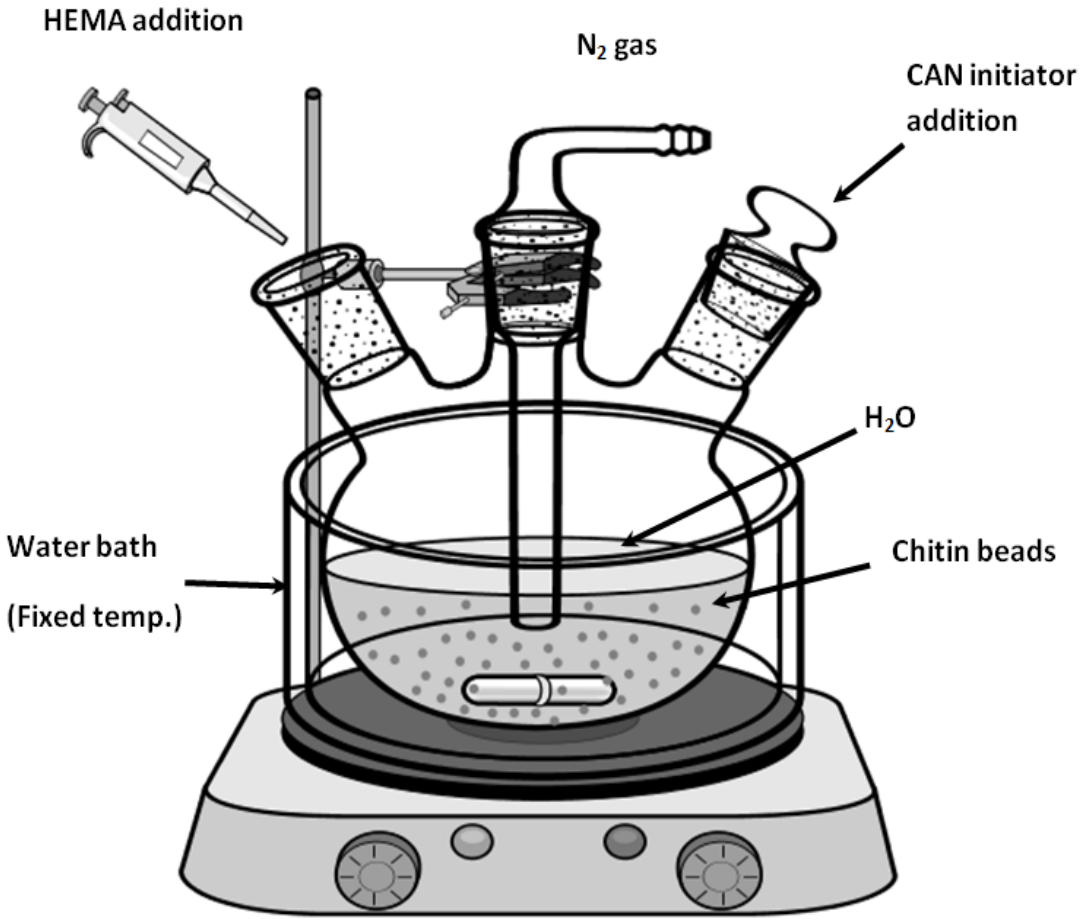
The porous chitin beads were prepared according to the method reported by Chow and Khor in 2000. $CaCO_3$ was added to 1% chitin solution to prepare a 5% solution with respect to $CaCO_3$. Complete dissolution of the salt in the chitin solution was achieved by stirring overnight. Then the solution was taken into a pipette and dropped slowly in to ethanol (Scheme 1). The beads were then left in the nonsolvent for 4 hours, to allow for solvent exchange. Then the prepared beads were placed in 3M HCl solution with constant stirring (200-250 rpm) for nearly 6 hours so as to dissolve away calcium carbonate inside the beads. Then the beads were washed by double distilled water with stirring for 2 hours. This step was repeated 2-3 times. Then water was filtered off and dried at 50 ºC in oven.



Scheme 1.Preparation of Chitin Gel Beads

2.2.6 Preparation of chitin-graft- poly(HEMA)

Given amounts of chitin gel beads (0.1g) and HEMA monomer were added to double distilled water in a round bottom flask which was placed in a water bath at fixed temperature. Nitrogen gas was bubbled for 30 min to remove any oxygen in the system. A given amount of CAN initiator was slowly added to the three_necked flask to initiate grafting. During reaction the nitrogen gas was kept flowing (Scheme 2). Reaction products were filtered washed with ethanol and double distilled water. Any homopolymers formed (PHEMA) was extracted with ethanol for 4 hours, and the samples were dried at 50°C for 24 h.



Scheme 2. Preparation of Chitin-graft-poly(HEMA) by free radical polymerization by using CAN as an initiator.

2.3 Optimization of Grafting Conditions

The grafting conditions were optimized by changing any of the initiator concentration, monomer concentration, reaction duration and temperature keeping other variables constant. A complete list of grafting conditions is given in Table 4.

2.3.1 Effect of Monomer Concentration on Grafting Yield

For studying the effect of monomer on grafting yield, different amounts of HEMA (1.0 mL, 2.0 mL, 4.0 mL, 8.0 mL, 12.0 mL) were used. The grafting yield was calculated for each sample.

2.3.2 Effect of Chitin Concentration on Grafting Yield

Chitin beads obtained using two different chitin concentrations, namely 0.5% w/v and 1% w/v were used and the effect on the grafting yield was determined.

2.3.3 Effect of the Type Initiator on Grafting Yield

Specific amount (0.5g) of three different initiators was used so as to find the best initiator for the grafting HEMA on chitin and also effect of them on grafting yield. The initiators were azobisisobutyronitrile (AIBN), ceric ammonium nitrate (CAN) and potassium persulfate (KPS).

2.3.4 Effect of the Initiator (CAN) Concentration on Grafting Yield

Different amount of CAN were used (0.251 g, 0.503 g, 1.005 g) for determining the effect of initiator on the grafting yield.

2.3.5 Effect of Reaction Time on Grafting Yield

The reaction was carried out for different periods of time (2 hours, 3 hours, 4 hours, and 6 hours) so as to determine the effect of time on grafting percentage.

2.3.6 Effect of Reaction Temperature on Grafting Yield

The reaction was carried out at (35 ºC, 70 ºC, 90 ºC), and the grafting yield was determined at each temperature.

2.3.7 Effect of Porosity on Grafting Yield

Porous beads were prepared using 1% w/v chitin solution as described in Section 2.2.6 was grafted with poly(HEMA). The effect of porosity on the grafting yield was observed.

Table 4. Different conditions for grafting poly(HEMA) on to chitin.

No.	Chitin bead % w/v	Chitin (g)	HEMA (mL)	HEMA (Mol/L)	CAN (g)	CAN (Mol/L)	D.W (mL)	Temp. (°C)	Time (h)
1	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	35	2
2	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	50	2
3	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	70	2
4	1 (nonporous)	0.20	4.00	0.82	1.00	4.6×10^{-2}	40	35	2
5	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	2
6	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	3
7	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	4
8	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	6
9	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	2
10	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	3
11	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	4
12	1 (porous)	0.10	1.00	0.41	0.50	4.6×10^{-2}	20	35	3
13	1 (porous)	0.10	2.00	0.82	0.50	4.6×10^{-2}	20	35	3
14	1 (porous)	0.10	8.00	3.3	0.50	4.6×10^{-2}	20	35	3
15	1 (porous)	0.10	8.00	3.3	1.00	9.1×10^{-2}	20	35	3
16	1 (porous)	0.10	8.00	3.3	0.25	2.3×10^{-2}	20	35	3
17	1 (porous)	0.10	12.0	4.95	0.50	4.6×10^{-2}	20	35	3

2.4 Characterization

2.4.1 Gravimetric Analysis

The grafting yield was calculated by the following equation.

$$\boldsymbol{Grafting}\ (\%) = \frac{\mathbf{m2-m1}}{\mathbf{m1}} \times \mathbf{100} \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(1)}$$

m1 = weight of chitin beads before grafting.

m2 = weight of grafted chitin beads.

2.4.2 Dissolution Properties

The swelling kinetics for the beads was studied in aqueous buffer solutions at different pH values 1, 7 and 11. The three sets of buffer solution were prepared for swelling behavior with different chemical components as shown in Table 5. Swelling properties of the prepared beads were qualitatively measured in different pH buffer solutions at room temperature. The swelling capacity was calculated according to the equation (2) given below.

$$\boldsymbol{swelling}\ (\%) = \frac{\mathbf{m\ swollen-m\ dry}}{\mathbf{m\ dry}} \times \mathbf{100} \ldots\ldots\ldots\ldots\ldots\mathbf{(2)}$$

Table 5.Buffer solution preparation

pH	Components were used	Total volume
1	25 mL of 0.2M KCl + 67.0 mL of 0.2M HCl	100 mL
7	0.681g potassium dihydrogen phosphate in 29.1mL of 0.10M NaOH	100 mL
11	0.21g sodium bicarbonate in 22.7mL of 0.10M NaOH	100 mL

2.4.3 FTIR Analysis

The FTIR spectra of the products were recorded on a Perkin Elmer spectrum-65 FTIR spectrometer.

2.4.4 C-13 NMR Analysis

The produced samples were analyzed by solid state 13CP MAS analysis using a Bruker Super Conducting FT NMR Spectrometer Avance TM 300 MHz WB at ODTÜ MERKEZ LABORATUVARI (METU).

2.4.5 XRD Analysis

The produced samples were analyzed using Rigaka Ultimate-IV X-Ray Diffractometer at (METU) ODTÜ MERKEZ LABORATUVARI.

2.4.6 SEM Analysis

The bead surface was investigated using SEM. The analysis was carried out at TUBITAK-MAM.

Chapter 3

RESULTS AND DISCUSSION

Chitin-graft-poly(HEMA) was prepared under homogeneous conditions using ceric ammonium nitrate (CAN) as redox initiator. The grafting reaction was carried out on chitin beads. The product was separated from the solution by filtering, washed with double distilled water and ethanol so as to remove any homopolymers formed. The cleaned product was dried in the oven at 50 °C. Gravimetry was used to follow the effect of the amount of chitin, monomer concentration, time, temperature, porosity, types and amount of initiator on the grafting yield (%G). The grafted beads were characterized by SEM, FTIR, C13 NMR and XRD analysis, The swelling test was studied in buffer solutions of pH=1, pH=7.0 and pH=11.0.

3.1 Dissolution Properties of HEMA

The dissolution properties of HEMA were tested in different solvents (Table 6). It was found that HEMA was soluble in most of the solvents. Distilled water was chosen as the solvent to be used since it is cheap, available and non toxic.

Table 6. Testing different solvents for choosing best solvent for HEMA monomer.

Double D.W	Soluble
Acetic acid	Soluble
Ethanol	Soluble
Toluene	Soluble
Dimethyl formamide	Soluble
Dimethyl acetamide (DMAC)	Soluble
N-methyl-2-pyrrolidinon (NMP)	Soluble
Dimethyl sulfoxide	Soluble
Hexane	Insoluble
Acetone	Soluble

3.2 Preparation of non Porous and Porous Chitin Beads

The non porous and porous chitin beads were prepared as mentioned in section (2.2.4) and (2.2.5). It was observed that the beads produced from 0.5% chitin solution were not stable. The beads were destroyed after drying. The beads had irregular shapes and stuck to the Petri dish. On another hand, beads obtained from 1% chitin solution were very stable, had a regular shape and good physical integrity. The optical pictures of the beads obtained from 0.5% (w/v) chitin solution and 1% (w/v) chitin solution are shown in Figure 4 and Figure 5 respectively.

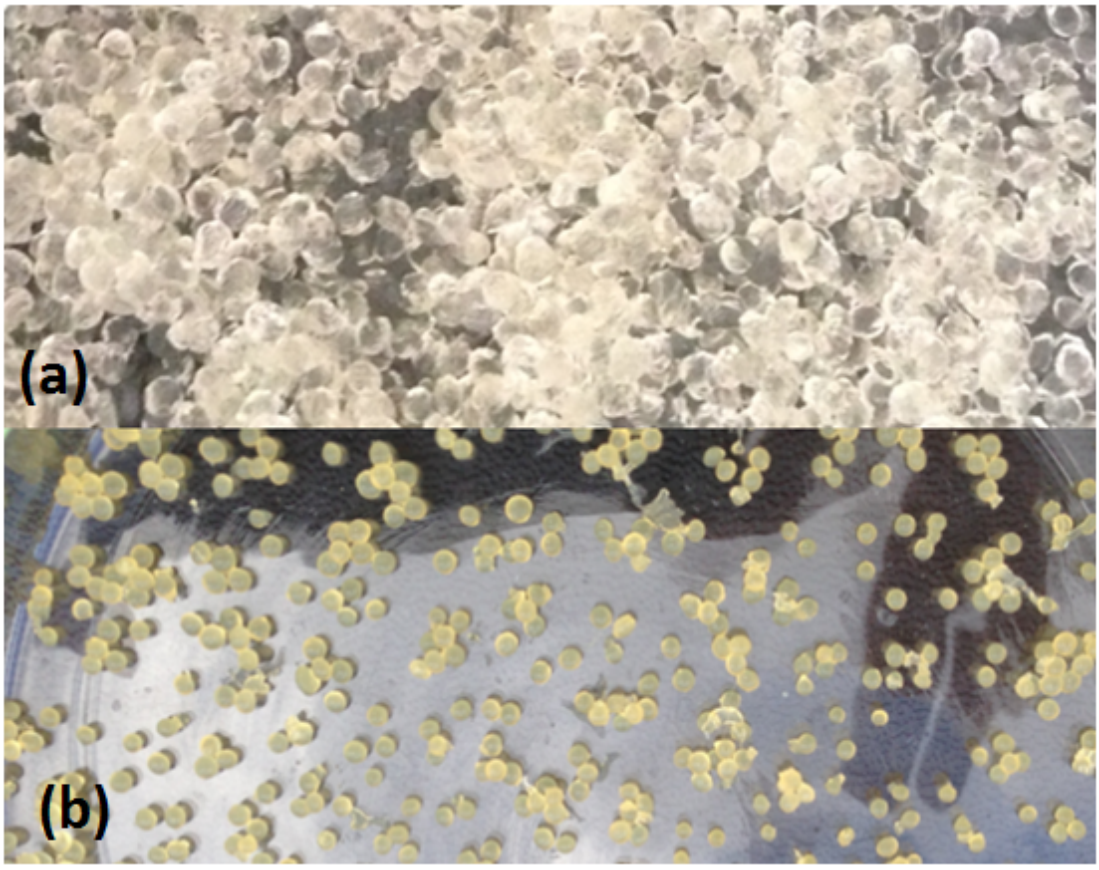


Figure 4. Non porous chitin beads obtained from 0.5% (w/v) chitin solution (a) before drying and (b) after drying.

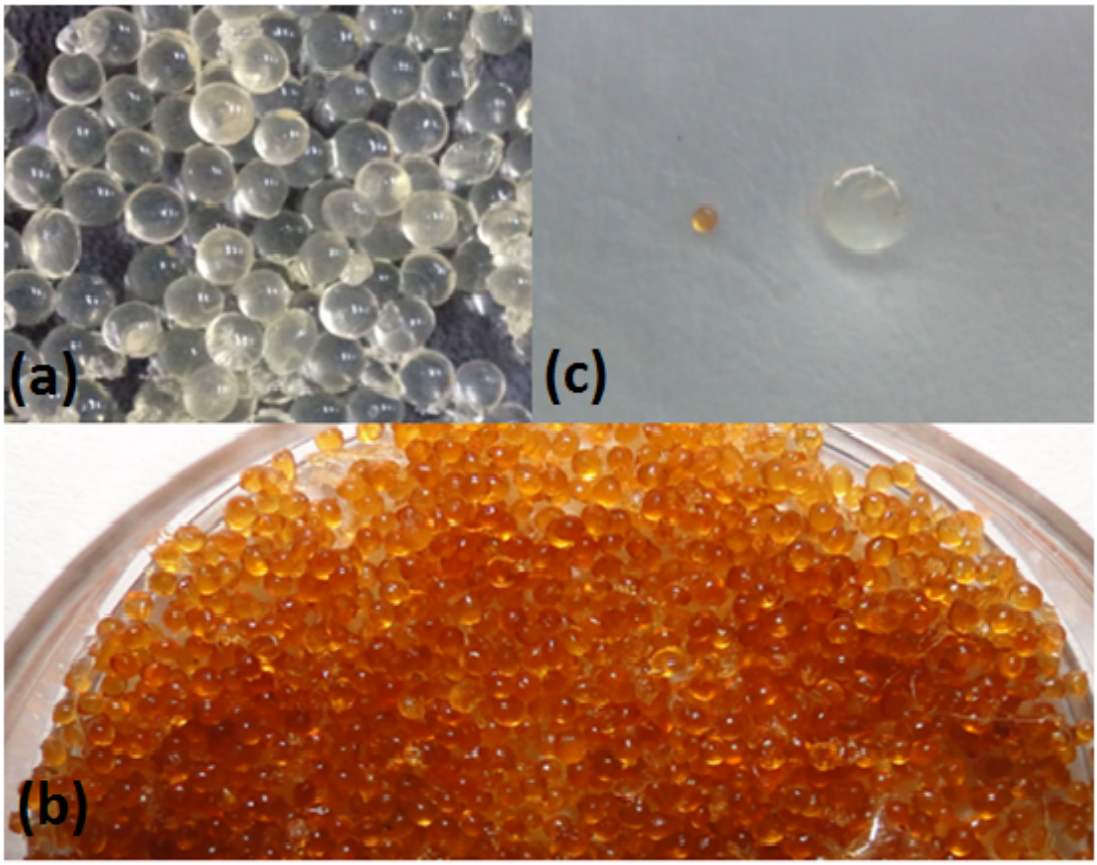


Figure 5. Non porous chitin beads obtained from 1% (w/v) chitin solution (a) before drying, (b) after drying and (c) illustrates size reduction after drying.

3.3 Preparation of non Porous and Porous Chitin-graft-poly(HEMA)

The grafting process has been illustrated in Scheme 2 page 20. The bead diameters are approximately around 450 μm for non porous beads and 550 μm for porous chitin beads.

Porous and non porous chitin beads were grafted with HEMA monomer using CAN as redox initiator at given time, temperature intervals and concentration ranges as shown in Table 7. The grafting conditions were established and the products were analysed by FTIR, C13 NMR, SEM and XRD analysis.

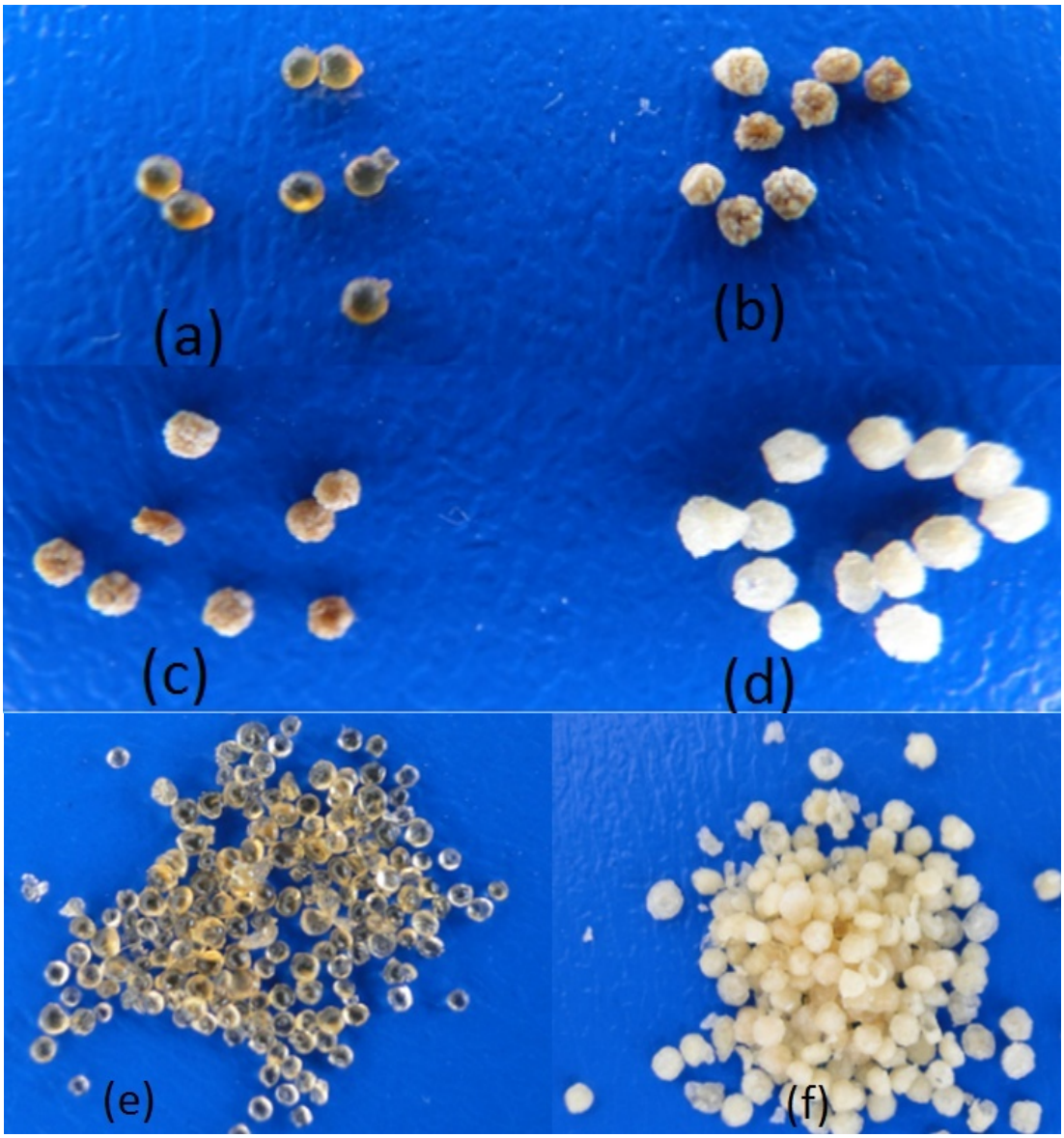


Figure 6. Optical picture for the comparison between (a) non porous not grafted chitin beads with (b) porous not grafted chitin beads, (c) porous not grafted chitin beads with (d) porous chitin-graft-poly(HEMA), and (e) non porous chitin-graft-poly(HEMA) with (f) porous chitin-graft-poly(HEMA).

3.4 Gravimetric Analysis for Chitin-graft-Poly(HEMA)

The effect of monomer concentration, temperature, initiator amount, reaction time on the grafting yield (%G) was tested by the gravimetry to find out the optimum grafting conditions. Table 7 shows the % grafting values obtained at 35°C, 50°C and 70°C. It was observed that 3 hours reaction time was sufficient to obtain the maximum grafting yield. For porous chitin beads, at 35 °C, the maximum grafting yield (%G) was obtained as 515% using 8 mL of HEMA monomer. Shortly, the optimum condition is 3 hour time, 35 °C, 0.5 g CAN initiator and 20 mL distilled water for grafting 8 mL of HEMA monomer on to 0.1 g porous chitin beads prepared from 1% (w/v) chitin solution.

3.4.1 The Effect of Monomer Concentration on Grafting Yield

The monomer concentration effect is shown as in Figure 7, maximum yield was obtained where 8 mL HEMA monomer used at 3 hour time, 35°C, 0.5 g CAN initiator and 0.1 g porous chitin beads prepared from 1% (w/v) chitin solution. By increasing the amount of monomer, the %G will increase till 8 mL, but after that it will decrease, it was observed when the amount of the monomer added, HEMA monomers homopolymerized to form PHEMA, it shows that the optimum amount of HEMA for this grafting at the optimum condition is 8 mL of HEMA monomer.

Table 7. The effect of reaction duration, temperature, CAN concentration, chitin concentration, and HEMA concentration On grafting % of chitn-graft-poly(HEMA).

No.	Chitin bead % w/v	Chitin (g)	HEMA (mL)	HEMA (Mol/L)	CAN (g)	CAN (Mol/L)	D.W (mL)	Temp. (°C)	Time (h)	%G
1	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	35	2	4
2	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	50	2	4
3	1 (nonporous)	0.25	4.00	0.33	0.25	4.6×10^{-3}	100	70	2	8
4	1 (nonporous)	0.20	4.00	0.82	1.00	4.6×10^{-2}	40	35	2	65
5	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	2	60
6	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	3	30
7	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	4	zero
8	1 (nonporous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	6	10
9	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	2	80
10	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	3	140
11	1 (porous)	0.10	4.00	1.65	0.50	4.6×10^{-2}	20	35	4	130
12	1 (porous)	0.10	1.00	0.41	0.50	4.6×10^{-2}	20	35	3	25
13	1 (porous)	0.10	2.00	0.82	0.50	4.6×10^{-2}	20	35	3	75
14	1 (porous)	0.10	8.00	3.30	0.50	4.6×10^{-2}	20	35	3	515
15	1 (porous)	0.10	8.00	3.30	1.00	9.1×10^{-2}	20	35	3	351
16	1 (porous)	0.10	8.00	3.30	0.25	2.3×10^{-2}	20	35	3	254
17	1 (porous)	0.10	12.0	4.95	0.50	4.6×10^{-2}	20	35	3	250

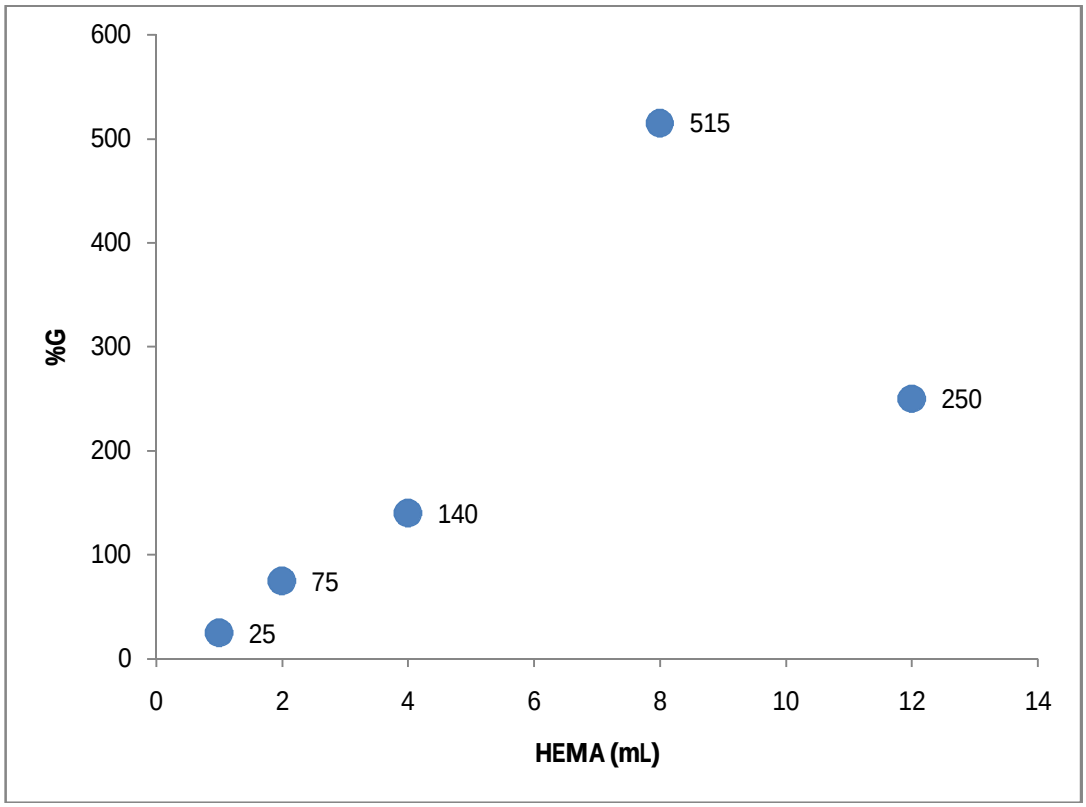


Figure 7. Effect of monomer concentration on the grafting yield

3.4.2 The Effect of Reaction Temperature

It was observed that upon increasing temperature from 35 °C to 70 °C the beads dissolved. Above 40 °C it was observed that there were no beads inside the reaction flask, one reason is stirring effect during the grafting process and and one another reason is that the porous beads is easy to decompose. It shows that the best temperature for this system is 35 °C.

3.4.3 The Effect of Different Types of Initiator

Three different types of initiator namely (CAN, AIBN and KPS) were tested at 35 °C, 3 hours reaction time with 0.1 g porous chitin beads and 8 mL HEMA. In the presence of AIBN or KPS initiators the beads either disappeared or the %G was approximately zero and the monomer homopolymerized instead of copolymerization, while CAN gave a grafting yield of 515% under the same condition. It means the best initiator for this grafting system is CAN initiator.

3.4.4 The Effect of Amount of Initiator

The grafting reaction was carried out using different amounts of initiator while the other parameters were kept fixed at optimum conditions (3 hour reaction time, 35 °C, 8 mL monomer and 0.1 g porous chitin beads prepared from 1% (w/v) chitin solution). Three samples of CAN (0.25 g, 0.5 g and 1 g) were used. It was found that 0.5 g of the initiator gave the maximum grafting Yield, the point is that when the amount of initiator is much, it will accelerate homopolymerization instead of copolymerization as shown in Figure 8.

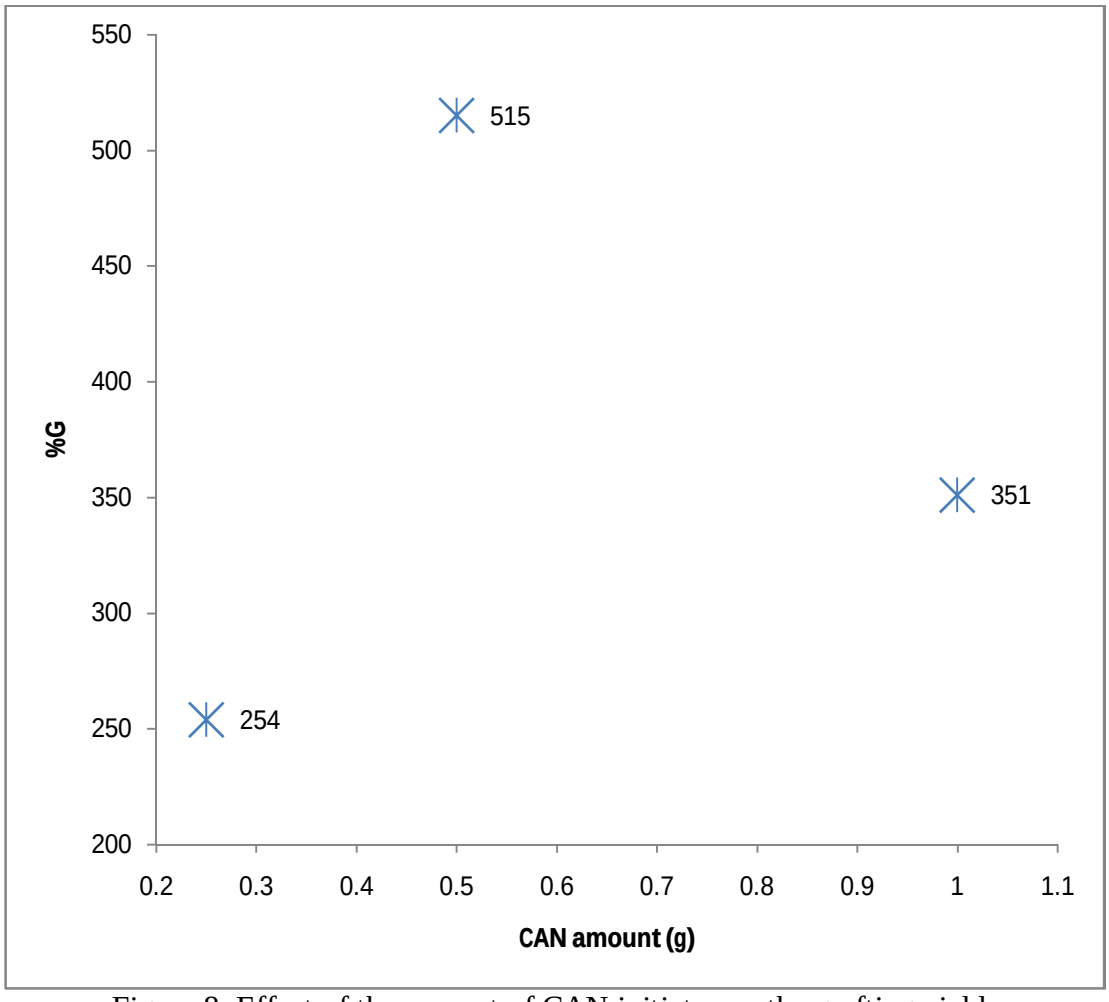


Figure 8. Effect of the amount of CAN initiator on the grafting yield

3.4.5 The Effect of Reaction Duration on Grafting Yield

The grafting reaction was carried out at different duration of time and the observations was recorded and found that for this grafting system. The best reaction duration was 3 hour, as shown in Table 7 and Figure 9. Over 3 hour some of the beads were decomposed because of stirring.

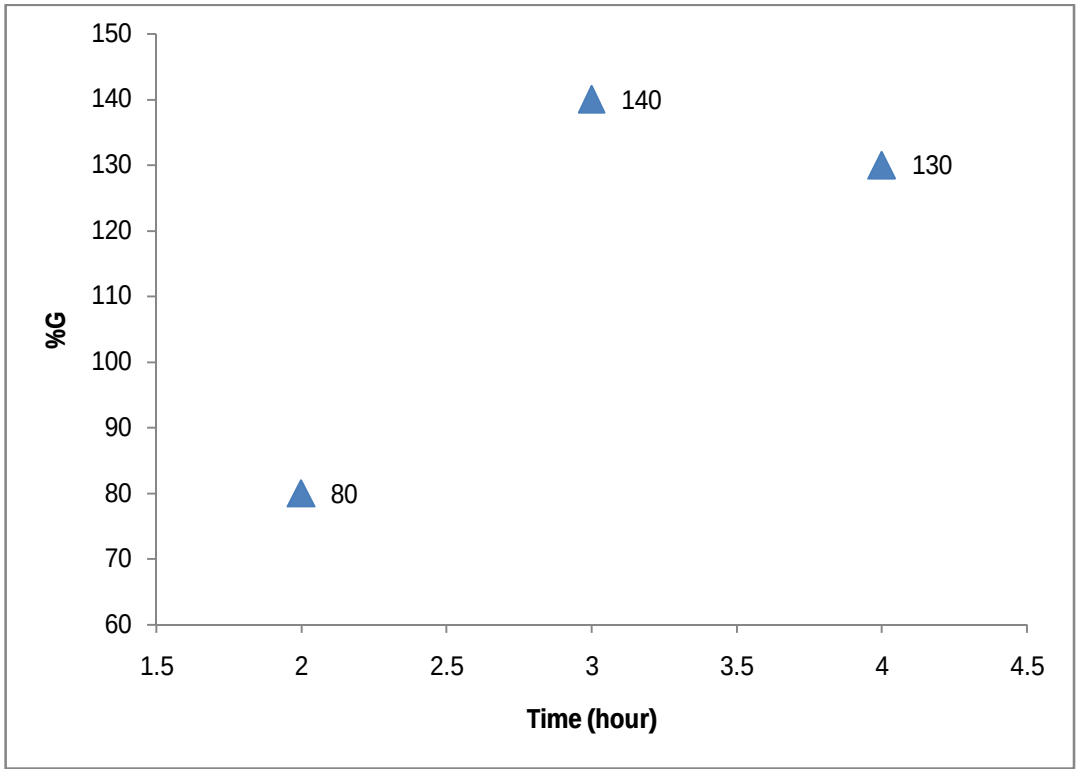


Figure 9. The effect of reaction duration on grafting % for chitin-graft-PHEMA

3.4.6 Effect of Porosity on the Grafting Yield

Porosity has a great effect on % grafting as shown in the Table 7 for sample number 6 (non porous chitin bead) and sample 10 (porous chitin bead) which were obtained under the same conditions exactly, except that one sample was porous while the other was not. The %G was 30% and 140% for non porous and porous chitin respectively because in the case of porous beads the surface area increased that have a great affect on grafting yield by filling effect with the monomer.

3.5 FT-IR Analysis for Chitin-graft-Poly(HEMA)

The FTIR spectrum of chitin, HEMA and chitin-graft-poly(HEMA) is shown in Figure 10 (a), (b) and (c) respectively. In spectrum of chitin, a broad O-H stretching band at 3402 cm^{-1} and asymmetric and symmetric N-H stretchings at 3257 cm^{-1} and 3102 cm^{-1} respectively can be observed. The three absorption bands at 2961 cm^{-1}, 2932 cm^{-1} and 2878 cm^{-1} region can be attributed to $-CH_3$ and $-CH_2$ stretchings. The amide I bands appear at 1648 cm^{-1} and 1620 cm^{-1}. The amide II band C-N-H stretching is observed at 1554 cm^{-1}. Methylene carbons ($-CH_2$) stretching and C-CH_3 stretching appear at 1411 cm^{-1} and 1376 cm^{-1}. Amide III appears at 1307 cm^{-1} and the pyranose ring (C-O) stretching at 1154 cm^{-1} and C-O stretchings of alcohol groups at 1000-1120 cm^{-1} region (Figure 10 a).

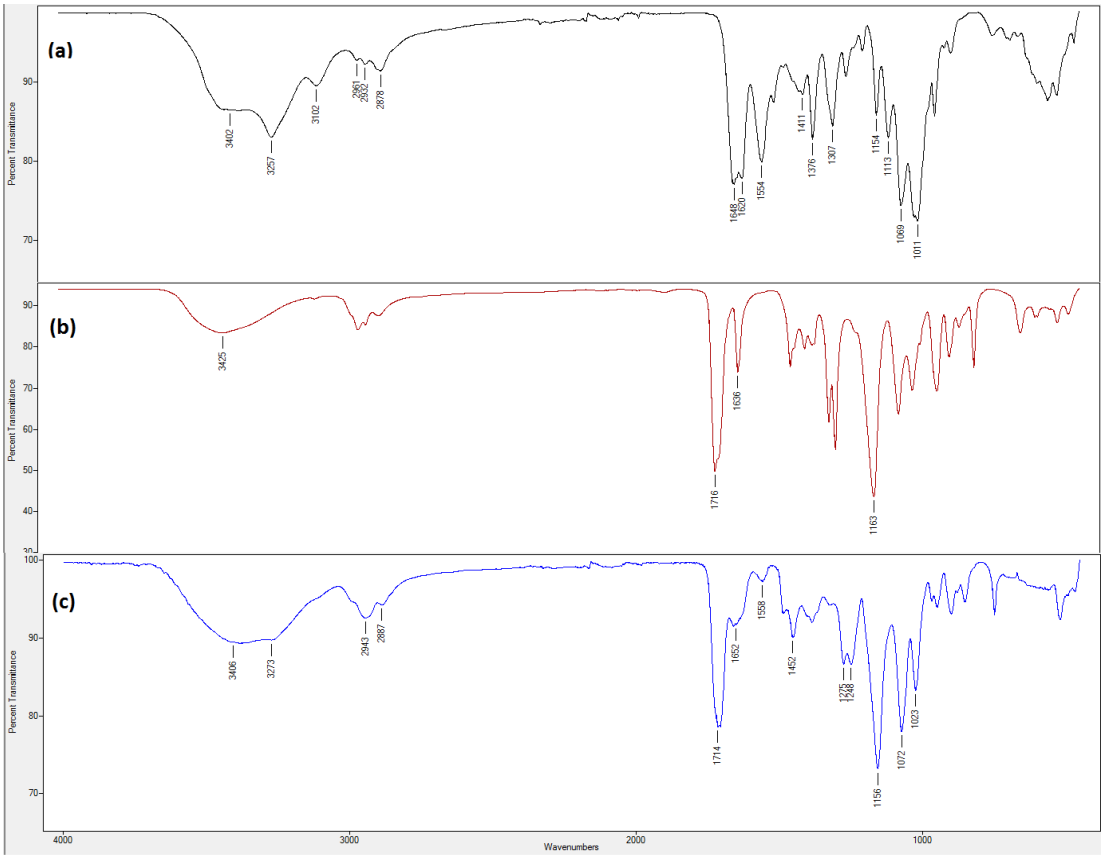


Figure 10. FTIR spectrum of (a) porous chitin, (b) HEMA and (c) porous chitin-graft-poly(HEMA) respectively.

An examination of the spectrum of the monomer (HEMA), reveals characteristic peaks at 3425 cm^{-1} band (OH) stretching, 1716 cm^{-1} the ester carbonyl, 1636 cm^{-1} (C=C) double bonds and (C=O) stretching at 1163 cm^{-1} (Figure 10 b).

The spectrum of the grafted product (Figure 10 c) contains a broad O-H stretching at 3406 cm^{-1}. The intensity of (N-H) stretching of chitin (3257 cm^{-1}) has decreased compared to the N-H stretching band at (3273 cm^{-1}) for grafted sample. A more intense $-CH_2$ stretching band is observed at 2943 cm^{-1} compared to the chitin spectrum indicating the contribution of methylene groups of HEMA. The ester carbonyl of HEMA appears at 1714cm^{-1}. Furthermore, the amide I and amide II bands at 1652 cm^{-1} and 1558 cm^{-1} respectively of both chitin and C-O stretching of both chitin and HEMA in the 1200 -1000 cm^{-1} region are observable indicating successful grafting of poly(HEMA) on to chitin.

3.6 C-13 NMR Analysis

In the previous studies reported in the literature, it is possible to find out information about C-13 NMR analysis of copolymers based on polyHEMA. The proton decoupled 13C-NMR spectrum of the copolymer poly(BrPMMAm-co-HEMA). The amide carbonyl of BrPMAAm appeared at 166.1 ppm while the ester carbonyl of HEMA appeared at 168.6 ppm. The hydroxyethyl carbon atoms of HEMA unit appeared at 64.4, 66.4 ppm, respectively (Soykan, 2007).

C-13 CP/MAS NMR spectrum of chitin and chitin-graft-poly(HEMA) shown in Figure 11 and Figure 12 respectively. In spectrum of chitin, the amide carbonyl appears at 169 ppm while C-1 and C-4can be observed at 100-90 ppm. The other carbons, C-3 and C-5 appear at 70-60 ppm, C-2and C-6 at 60-50 ppm. The methyl

group can be identified at 20 ppm. In the spectrum of the chitin-graft-poly(HEMA) sample (%G= 515) it can be observed that in addition to chitin peaks interpreted as above additional peaks are available to confirm the presence of poly(HEMA) in the structure. The methyl group of HEMA appears 8-9 ppm accompanied with a chemical shift at 20 ppm which can be attributed to the methyl group of chitin. The peak at a chemical shift 40 ppm belongs to the tertiary carbon of HEMA followed by backbone methylene in poly(HEMA) and C-2 and C-6 peaks of chitin in the 50-60 ppm region. The peaks at chemical shifts 69-65 ppm region belongs to C-3 and C-5 of chitin and the hydroxy ethyl carbons of HEMA appear at 70 ppm. C-4 and C-1 of chitin are observed at 90 and 100 ppm respectively. The 100 and 150 ppm region is blank indicating the absence of (C=C) double bonds. Hence, confirming the absence of any unreacted monomer. The amide carbonyl of chitin appears as a shoulder at 170 ppm and the ester carbonyl of HEMA at 175 ppm. Since chitin beads have been surface modified by grafted poly(HEMA) chains, the C-13 spectrum of the grafted product contains poly(HEMA) peaks with higher intensity compared to chitin peaks.

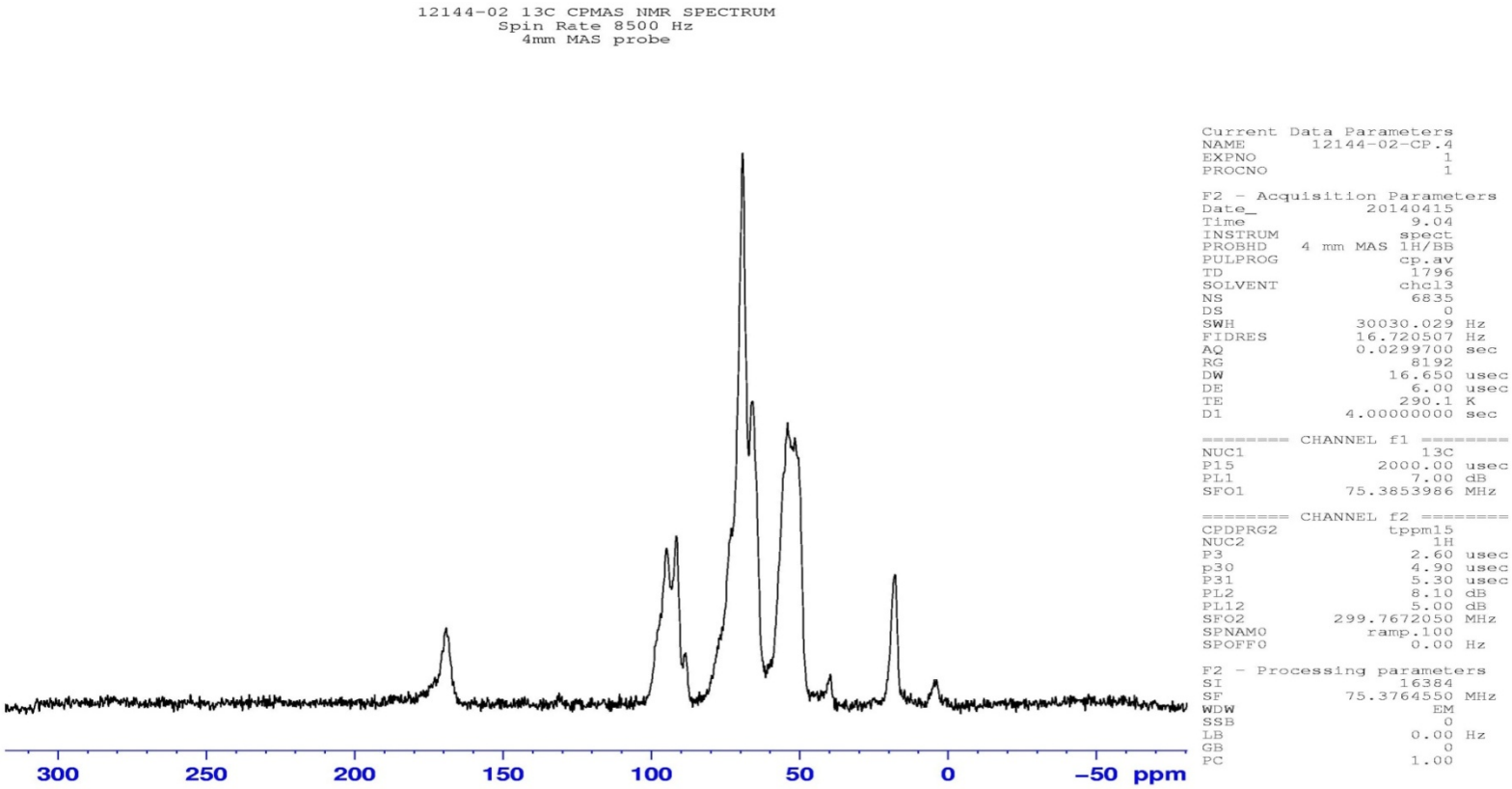


Figure 11. C13 NMR for porous chitin sample

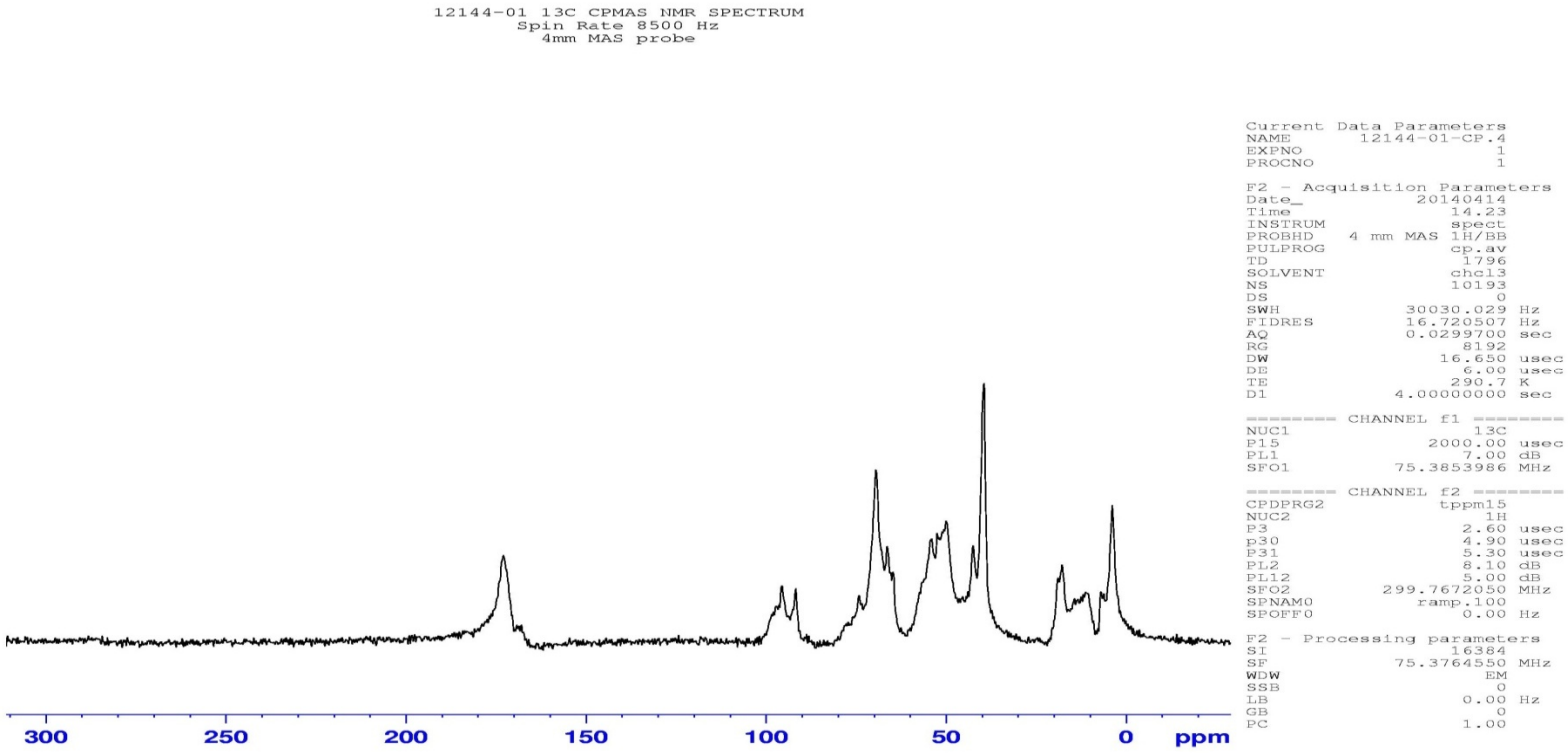


Figure 12. C13 NMR for porous chitin-graft-poly(HEMA

An exact structure for chitin-graft-poly(HEMA) cannot be proposed without any further elaborate spectroscopic and chemical analysis. The structure proposed is one example based on the FTIR and C-13 NMR data obtained in this work (Figure 13).

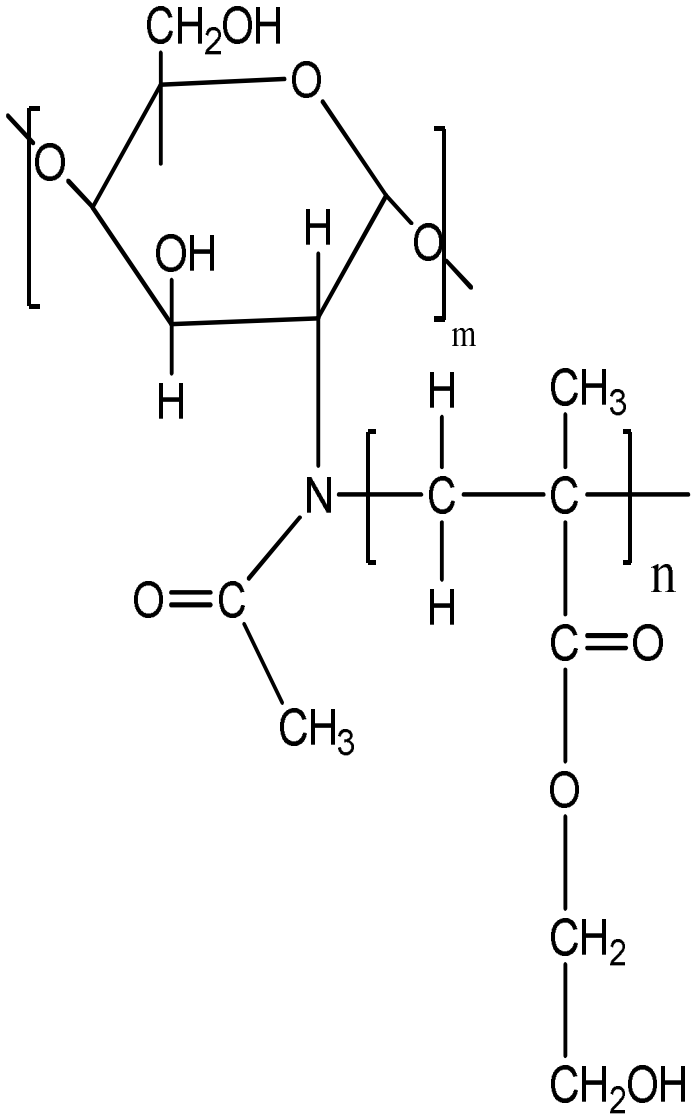


Figure 13. The Proposed Structure for Chitin-graft-Poly(HEMA)

3.7 XRD analysis

XRD patterns of porous chitin and poly(HEMA) grafted porous chitin beads are shown in Figure 14 and 15 respectively. Chitin beads exhibit two main crystalline peaks at 2θ = 19° and 2θ = 26° in the 2θ range 10° - 70°. An amorphous hump is observed at 2θ = 12°. The % crystallinity of the samples have been calculated according to the method for cellulose and applied to chitin (Cardenas *et al.*, 2004). Crystallinity index is calculated according to the equation given bellow:

$$\boldsymbol{Cr\ I}\ (\%) = \frac{\boldsymbol{I\ cryst.} - \boldsymbol{I\ am.}}{\boldsymbol{I\ cryst.}} \times \mathbf{100}$$

When (I cryst.) corresponds to the intensity (cps) of the crystalline peak and (I am.) is the intensity of the amorphous 'halo'. The peak at 2θ = 19° has been taken as reference for % crystallinity calculation. Following previous researchers (Cardenas, 2004; Yilmaz, 2003), % crystallinity of the porous chitin beads has been calculated as 72% whereas this value falls to 60% for the poly(HEMA) grafted porous chitin beads. Hence, crystallinity decreases after grafting. Increased amorphous character of chitin-graft-poly(HEMA) can be followed from the broader nature and decreased intensity of the crystalline peaks in Figure 13. The results illustrated in Table 8.

Table 8. XRD data for calculating the crystallinity index

Sample	$I_{19.18}$	$I_{12.90}$	% CI
chitin	416.7	118.3	72
Chitin-graft-poly(HEMA)	395.0	156.7	60

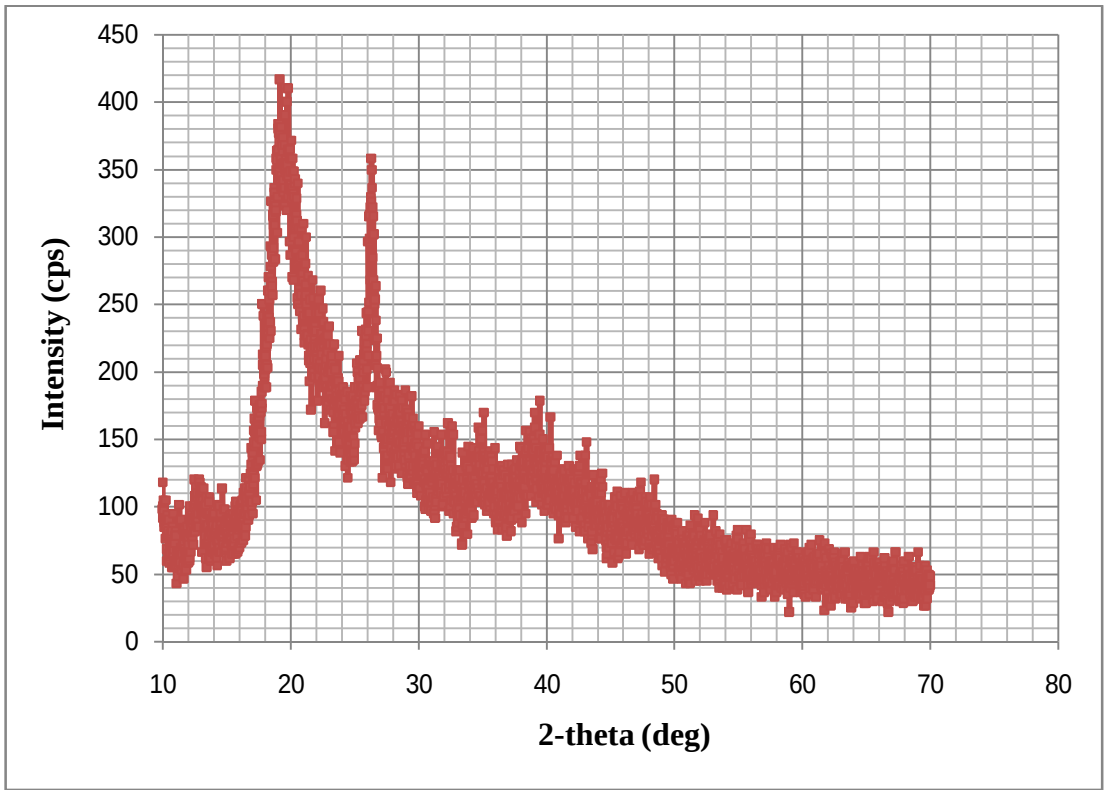


Figure 14. XRD patterns of porous chitin sample.

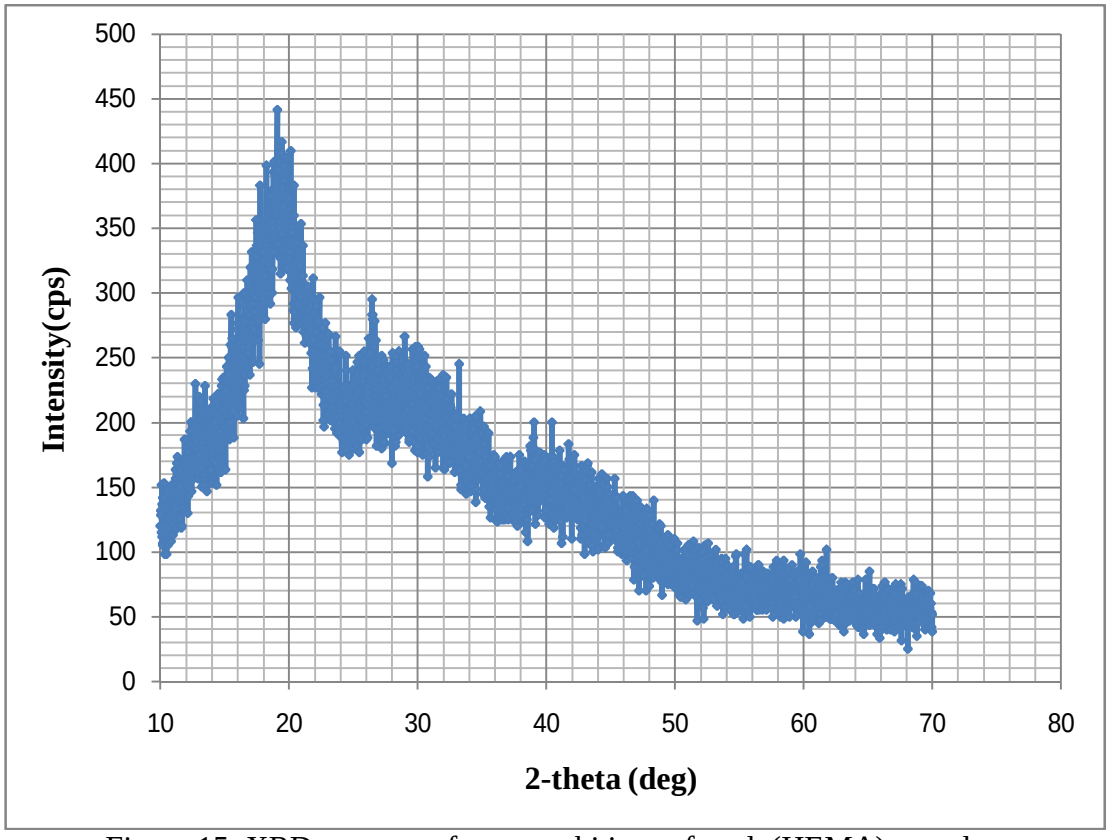


Figure 15. XRD patterns of porous chitin-graft-poly(HEMA) sample.

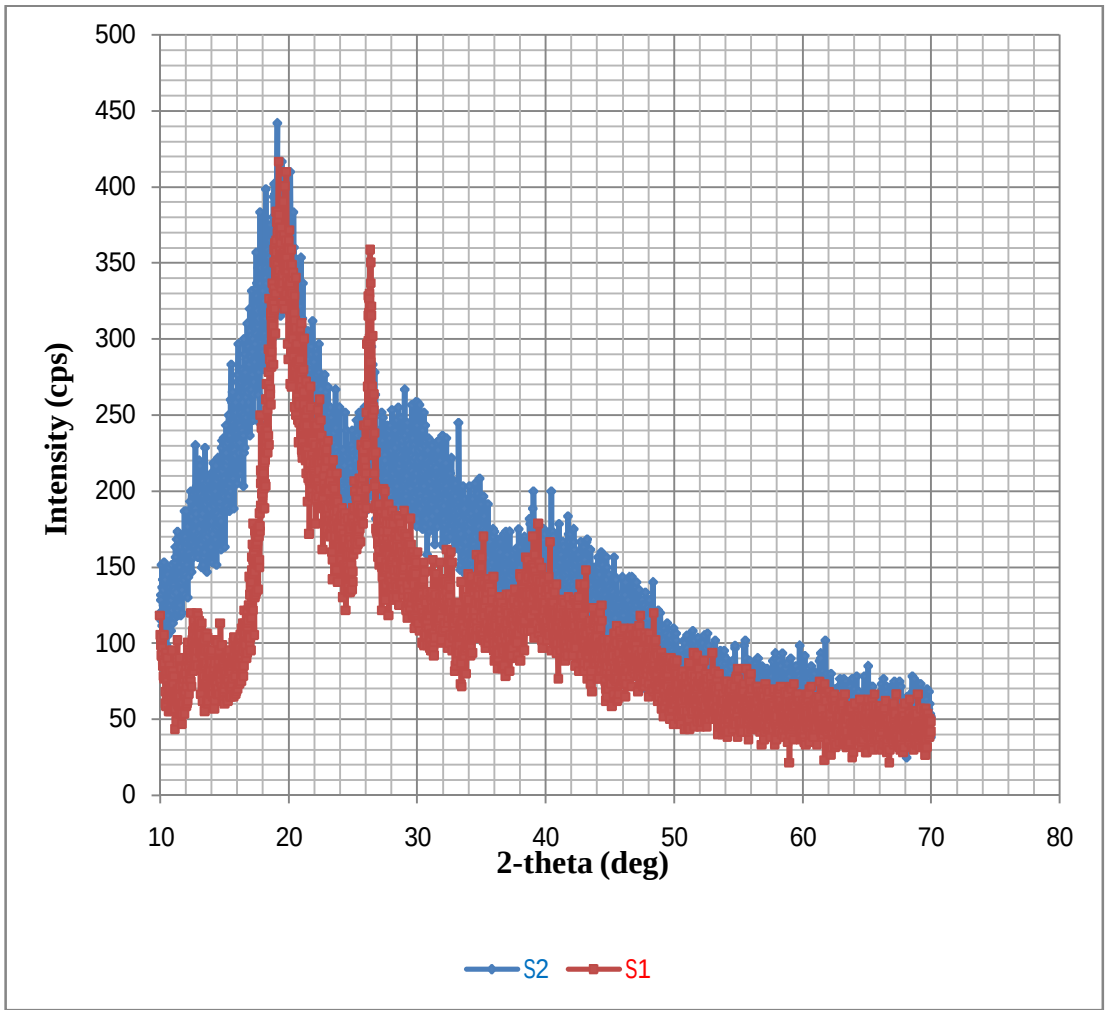


Figure 16. XRD patterns of porous chitin (S1) and porous chitin-graft-poly(HEMA) (S2) sample.

3.8 SEM Analysis

SEM micrographs of the chitin, grafted chitin, porous chitin and grafted porous chitin beads are given in Figure 17, 18, 19, 20 respectively.

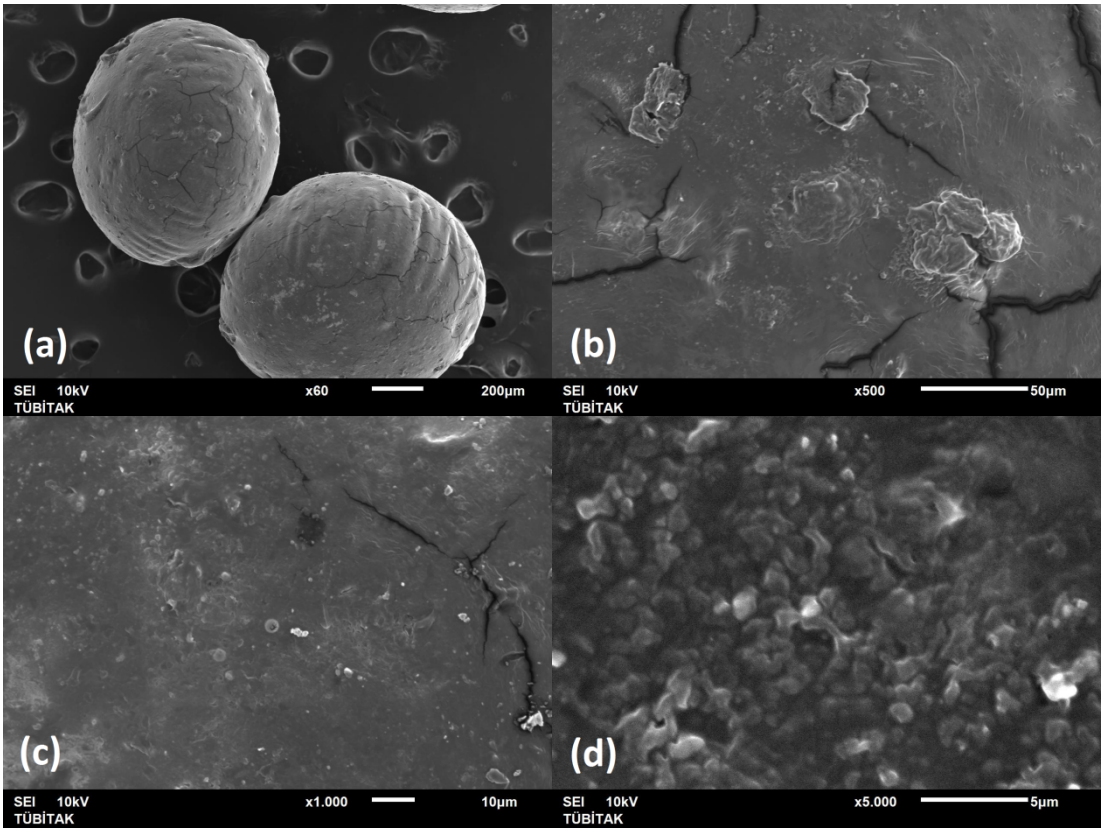


Figure 17. SEM micrograph of non porous not grafted chitin beads magnified by (a) x 60, (b) x500, (c) x1000 and (d) x5000.

In Figure 17, some cracks are available on the surface which can be caused by the drying process. Figure 18 shows the SEM pictures of poly(HEMA) grafted on to non porous chitin beads. It can be observed that the surface of the grafted beads is more homogeneous compared to that of the non grafted one.

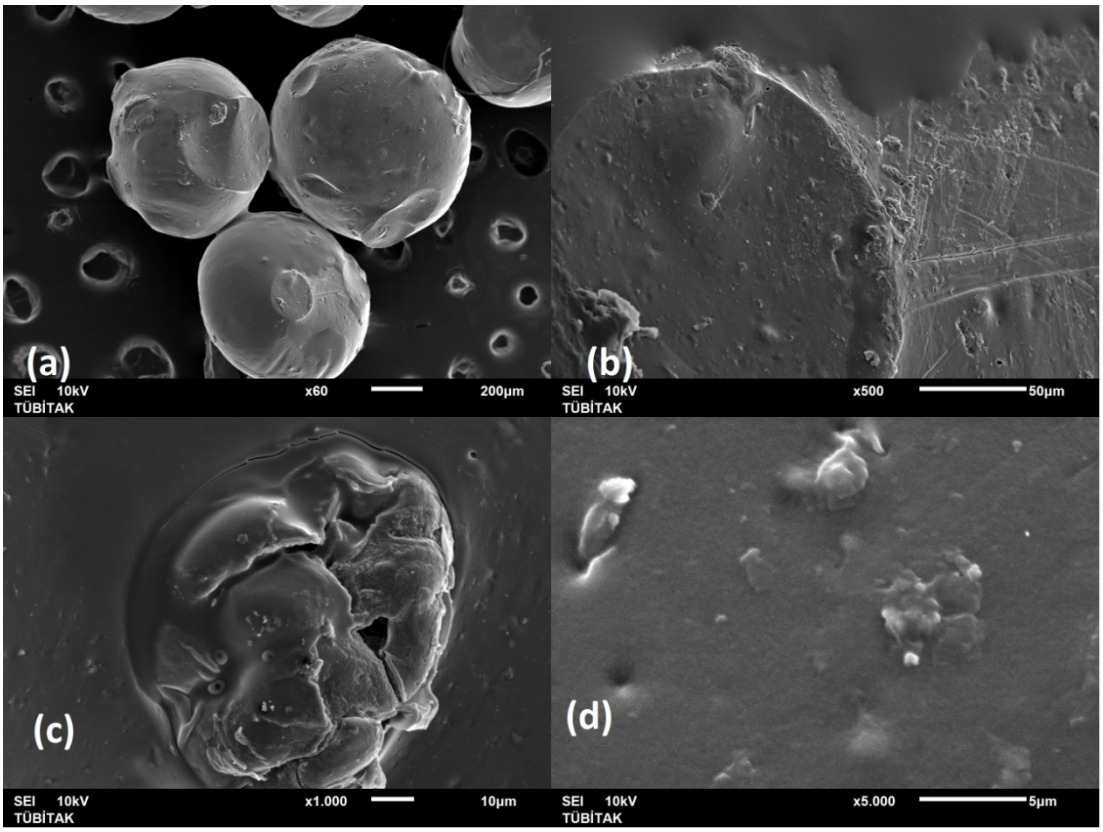


Figure 18. SEM micrograph of non porous grafted chitin beads magnified by (a) x60, (b) x500, (c) x1000 and (d) x5000.

In Figure 19, it can be observed that some pores and some channels which are heterogeneously distributed are available on the surface of the bead. However, a homogeneous and in-depth porosity could not be achieved because of stirring process during $CaCO_3$ extraction inside the beads for the purpose of porosity and also may caused by the treatment of the beads with strong hydrochloric acid (HCl 3M).

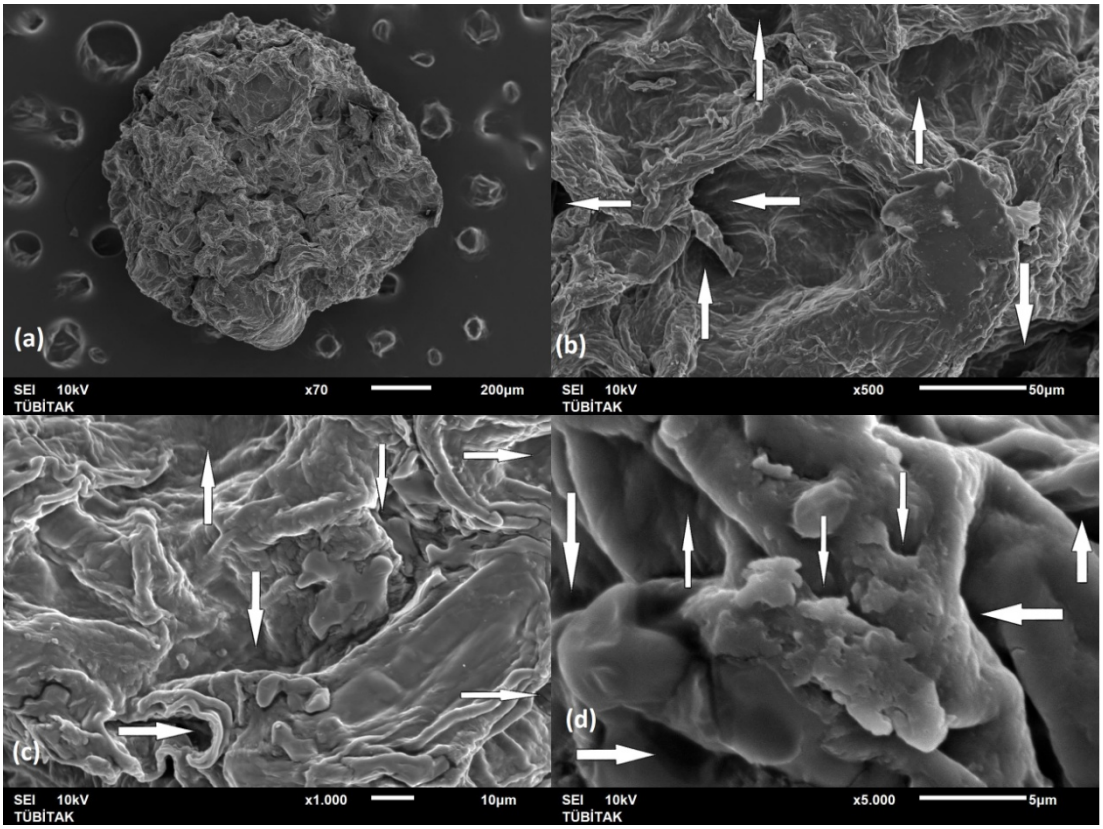


Figure 19. SEM micrograph of porous chitin beads magnified by (a) x70, (b) x500, (c) x1000 and (d) x5000.

Figure 20 illustrates that surface modification on the porous chitin results in the loss of porosity due to the filling effect of the grafted poly(HEMA) chitin.

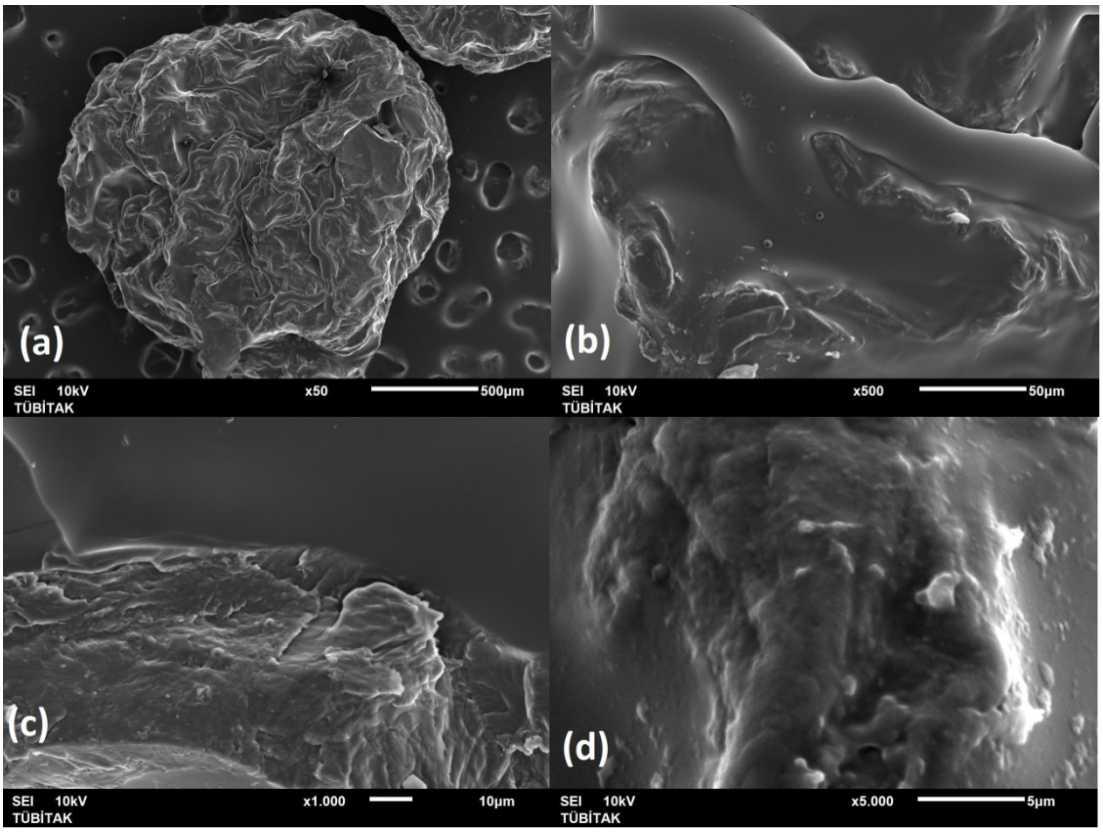


Figure 20. SEM micrograph of porous grafted chitin beads magnified by (a) x50, (b) x500, (c) x1000 and (d) x5000.

3.9 Swelling/Dissolution Properties of Products

Grafting and porosity demonstrated a great effect on the swelling and dissolution properties. The effect of pH on swelling is illustrated in Table 9, 10, 11 and Figure 21, 22, 23, for non porous chitin, non porous chitin-graft-poly(HEMA) (%G= 65%), porous chitin and porous chitin-graft-ply(HEMA) (%G= 515%). Table 9 shows the swelling behaviour of the selected samples in acidic medium, pH=1. The swelling behaviour at pH=1 is also represented graphically in Figure 21.

Table 9. Swelling behaviour of products at pH =1.

Time	**Por.Chi.Not grafted (% swelling)**	**Por.Chi. grafted(515%) (% swelling)**	**Non por.chit.not grafted (% swelling)**	**Non por. Chit. Grafted (65%) (% swelling)**
30 min.	72.1	61.2	8.7	35.6
1hour	80.5	74.3	11.7	45.8
2 hours	85.3	76.1	11.7	62.5
3 hours	85.3	95.4	11.8	63
4 hours	85.4	97.7	11.9	63.2
5 hours	85.5	102.3	12.1	63.4
6 hours	85.7	103	12.1	63.4
24 hours	85.9	103	12.4	63.5

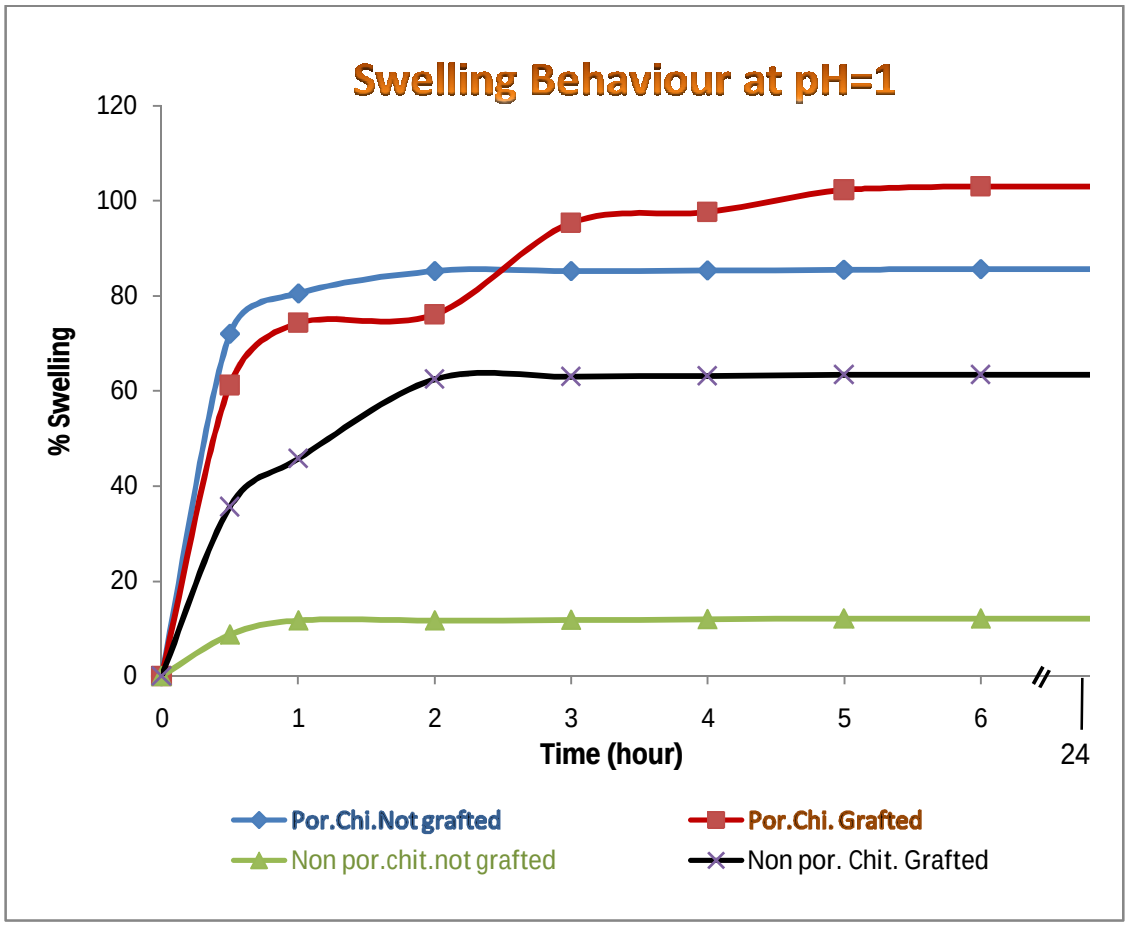


Figure 21. Swelling behaviour of products at pH =1.

It can be followed from Table 9 and Figure 21 that porosity has a drastic effect on the % swelling value. While non porous chitin beads reach equilibrium swelling within 1 hour with 12% swelling, the porous counterparts reach equilibrium % swelling value of 85 within an hour.

It can also be noted that poly(HEMA) grafted beads swell more than the non grafted ones whether porous or non porous. Equilibrium % swelling value of the chitin-graft-poly(HEMA) of the non porous and porous samples have been determined as 63% and 103% respectively.

A similar effect of porosity and grafted poly(HEMA) chains on % swelling can be observed at pH=7 and at pH=11 in Table 10 and Figure 22 and Table 11 and Figure 23 respectively. Highest swelling for the porous grafted and non grafted and non porous grafted samples was observed at pH=11. Non porous non grafted chitin beads on the other hand did not swell at pH=11. Higher swelling at pH=11 of the grafted products should be due the presence of carboxylic acid groups of HEMA. Hence both modifications carried out, namely introducing porosity and chemical modification by grafting poly(HEMA) improved swelling behaviour considerably.

Table 10. Swelling behaviour of products at pH =7.

Time	Por.Chi.Not grafted (% swelling)	Por.Chi. grafted (515%) (% swelling)	Non por.chit.not grafted (% swelling)	Non por. Chit. Grafted (65) (% swelling)
30 min.	63.1	62.6	7.8	50.0
1 hour	81.5	65.1	7.9	55.4
2 hours	82.3	65.4	7.9	60.8
3 hours	82.5	65.6	8.0	61.3
4 hours	82.6	65.9	8.0	61.5
5 hours	82.7	66.1	8.0	61.7
6 hours	82.9	66.2	8.0	62.0
24 hours	83.1	73.6	8.1	62.6

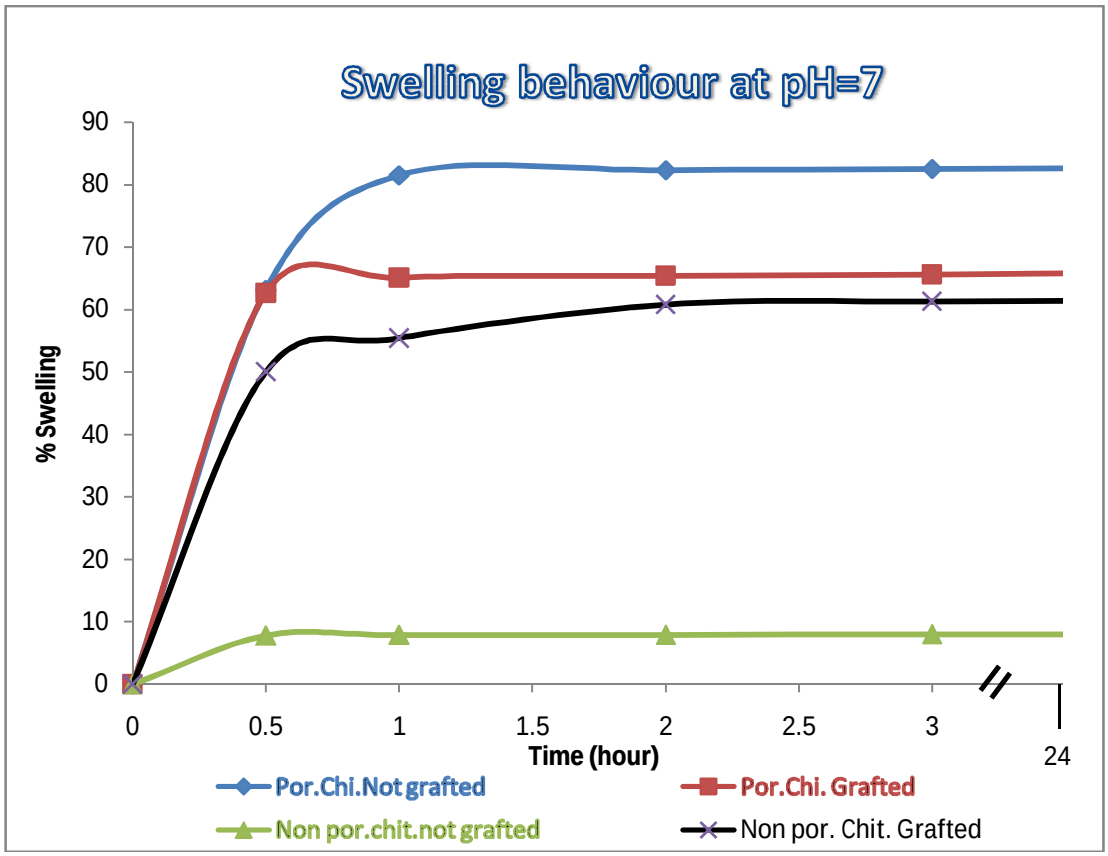


Figure 22. Swelling behaviour of products at pH =7.

Table 11. Swelling behaviour of products at pH =11.

Time	Por.Chi.Not grafted (% swelling)	Por.Chi. grafted (% swelling)	Non por.chit.not grafted (% swelling)	Non por. Chit. Grafted (% swelling)
30 min.	128.3	101.8	0.5	57.5
1 hour	128.5	145.5	0.7	69.0
2 hours	128.8	153.6	0.9	69.4
3 hours	129.2	160.3	1.1	71.3
4 hours	129.9	160.8	1.3	73.3
5 hours	130.1	161.6	1.3	74.8
6 hours	130.5	163.2	1.4	75.0
24 hours	135.7	169.4	1.7	78.6

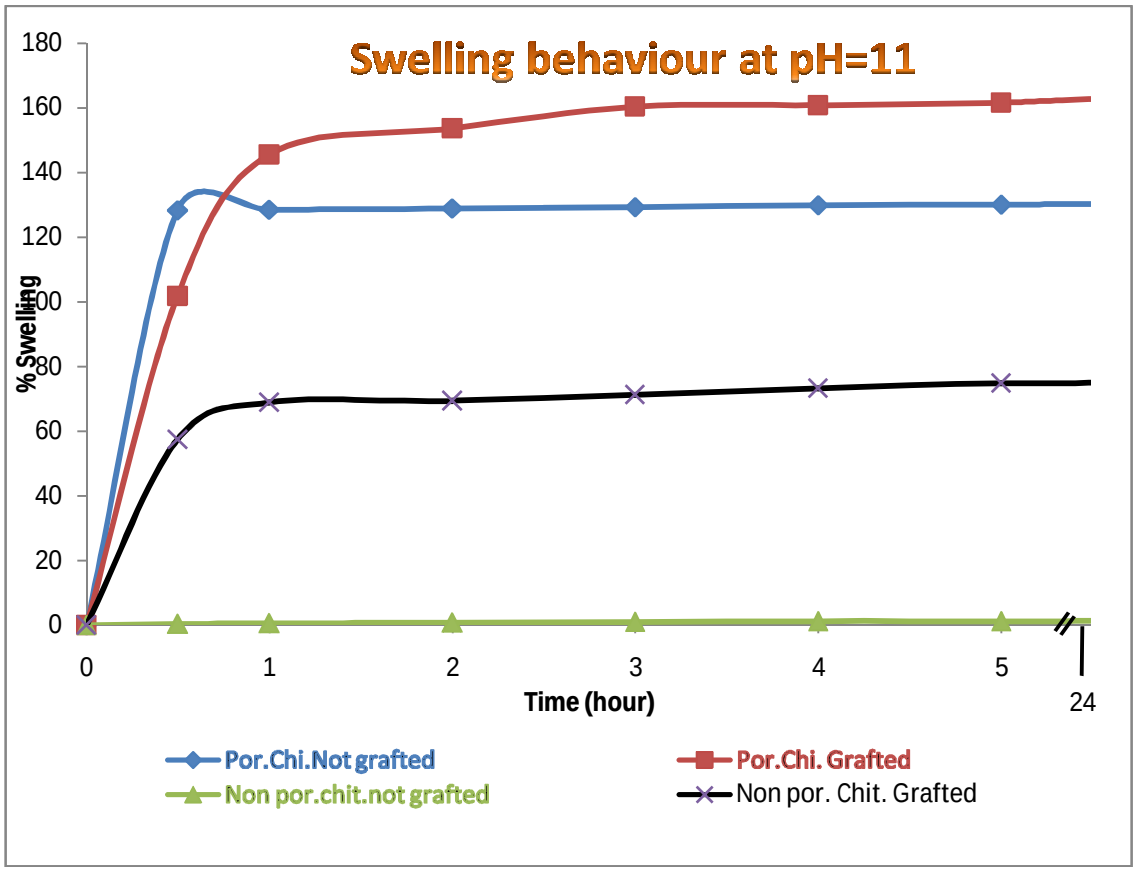


Figure 23. Swelling behaviour of products at pH =11.

Chapter 4

CONCLUSION

Poly(2-hydroxyethaylmethacrylate) poly(HEMA) can be grafted on to non porous and porous chitin beads to produce chitin-graft-poly(HEMA).

The maximum grafting value achieved on the non porous chitin beads is 65%, while it is 515% for poly(HEMA) grafting carried out on porous beads. The optimum grafting conditions are 35 °C, 3 hour reaction time, 0.1 g porous chitin beads prepared from 1% (w/v) chitin solution, 0.5 g CAN initiator and 8 mL from HEMA monomer to give 515% grafting yield.

Introducing porosity onto chitin beads improved the swelling properties considerably. Grafting the beads with poly(HEMA) whether porous or non porous also produces an improvement in the swelling capacity when compared to non grafted samples. While non porous chitin beads swell to a small extent at all pH values, the porous beads swell up to 85%, 83% and 135% at pH=1, pH=7 and pH=11 respectively. The porous grafted product with grafting yield = 515% swells up to 169% at pH=11, the non porous grafted one with grafting yield = 65% swells up to 78%. The decrease in crystallinity during the treatment to create porosity should also contribute to increased swelling ability of the porous beads.

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