*Synthesis and Characterization of New Contact lenses Based on 2-Hydroxyethyl methacrylate

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Abstract

In this present work describes the synthesis new soft contact lenses based on 2-Hydroxy ethyl methacrylate monomer.2-Hydroxylethylmethacrylate (HEMA) was polymerized by free radical polymerization in the presence of ethylene glycol dimethacrylate (EGDMA) as acrosslinker and Benzoyl peroxide as initiator. The polymerized materials were characterized fully for its use fullness as an intraocular lens by various techniques. FTIR and ^{1}HNMR were performed to find out the total conversion of monomer 2-Hydroxylethyl methacrylate into hydrogels contact lens. The hydrogels contact lenses were manufactured from different materials, these materials and water content were: copolymerization 2-Hydroxylethyl methacrylate with methacrylic acid (77.1%), Chitosan 82%, Methylacrylate 54%, Ethylhexyl methacrylate 56%.The equilibrium water content (EWC) was measured for all the hydrogels at 34°C and it was observed that the hydrophilic hydrogels swelling more than hydrophobic hydrogels. The oxygen permeability (DK) was measured by Morgan & Efron equation, the results show, the hydrophilic hydrogels display higher oxygen permeability towards the cornea more than hydrophobic hydrogels. The amount of proteins adsorbed on the membrane surface of hydrogels contact lenses was calculated from the concentration of proteins in the SDS solution using a BCA protein assay reagent kit. The results show albumin deposits in higher concentrations on hydrophobic surfaces, as compared to relatively hydrophilic surfaces.The transparency of all hydrogels were examined by using UV-visible spectrophotometer. The results show that all hydrogels contact lenses allowed range of light transmittance 58-94% ,at wave lengths between 400-700nm.

Keywords:Hydrogels;Contact lenses;Protien adsorption ;Oxygen Permability

1-Introduction

The soft contact lens has a flexible property mainly due to retention water. A polymer usually has both hydrophilic and hydrophobic groups. The hydrated state is formed as a result of the interaction between hydrophilic and hydrophobic groups and water. A water molecule is liable to be bound to a polymer or trapped in a small space formed with in the polymer. An hydrated soft contact lens is a typical example of a material carrying bound water, trapped in molecular spaces. In an hydrated soft contact lens of three dimensional network structure,its physical properties are governed by the state of the water within the polymer.[1]

***The Research is apart of on M.Sc. thesis in the case of the Second researcher**

Contact lenses are thin curved disks made out of a clear material[2].These are not implanted devices, used in very close contact with the eye, and their physiological performance depends greatly on the material used to make the lens. Contact lenses are optical devices, usually made of a synthetic polymer, that are placed over the cornea of the eye and remain between the lids and the cornea when the eye blinks. The main purpose of contact lenses is vision correction, but certain types of lenses are often used medically to treat corneal diseases or to protect the cornea in patients with certain eye problems. In the latter cases, the contact lenses are called therapeutic or bandage lenses[3].

Contact lenses have been used to manage corneal disease, in postoperative care,and in vision rehabilitation after disease, surgery, and trauma by serving as a vehicle to deliver drugs, as a bandage, "optically" as a new corneal surface, and as a prosthetic device.A further use of hydrogel contact lenses, which takes advantage of their absorbing properties, is for prolonged delivery of drugs to the eye. Hydrogels have been studied extensively as contact lens materials due to their superior wearer comfort and oxygen permeability compared to hard contact lenses made of (PMMA) Poly methyl methacrylate[4].Hydrogels such as copolymers of 2-hydroxyethyl methacrylate (HEMA) have been widely used, the water content of these lenses varies from 38% to 85% . Copolymerization of various monomers allows the physical and chemical properties such as water content ,refractive index, hardness and oxygen permeability to be controlled[5].

High water content lens materials are obtained by copolymerizing moderately hydrophilic HEMA with highly hydrophilic ionic monomers such as chitosan (Cs), methacrylic acid[6]. The ionic functionality cause these polymers to have high water contents. Thus the different types of contact lenses have distinct surface chemistry based (HEMA) monomer and their characterization by evaluation of some of their properties like water content, oxygen permeability. Where oxygen permeability is different in different contact lenses materials. In conventional hydrogels whatever they have low or high water content, oxygen delivery to the ocular surface takes place mainly through the water phase, so the higher the water content, the higher of the permeability[7].Protein deposition is one of the most frequent contaminants occurring on contact lenses, resulting from the interaction between the tear film and the polymer of a contact lens[8,9].The protective effect and the optical quality of such lenses will be dependent on the absorption characteristics and stability of the UVR filter incorporated in the contact lens matrix, the amount of ultraviolet radiation (UVR) absorbed by a contact lens varies between brands and materials [10,11].However, transmittance properties of contact lenses are of importance for wearers, not only for ultraviolet radiation (UVR) protective properties but also for visual performance[12].The ocular effects of UVR have been studied and it was demonstrated that some pathology of eyelids, cornea, conjunctiva, iris, and lens have a correlation with ultraviolet exposure [13].

In this work, Copolymerization 2- hydroxyethyl methacrylate (HEMA) monomer with different percentages of other monomers and polymers (Cs, MAA, MA, EHMA), hydrogels lenses were prepared by free radical polymerization, and examined effect concentrations of crosslinker ethylene glycol dimethacrylate (EGDMA) on swelling properties of hydrogels contact lenses. In addition Equilibrium water content equation were used to determination the diffusion behavior of water content of the hydrogel contact lenses. And calculated the amount of protein which adsorption on surface contact lenses. And study the oxygen permeability and transmittance for these hydrogels lenses.

2-Expermantal

2-1.The materials

Hydroxylethyl methacrylate HEMA (MERCK), Methyl acrylate MA (ALDRICH), Chitosan Cs (ACROS), Ethyl hexyl methacrylate EHMA (MERCK), Methacrylic acid MAA (MERCK),Sodium hydroxide NaOH (BDH), Acetic acid (BDH), Phosphate buffer saline PBS (HIMEDA), Benzoyl peroxide BPO (HIMEDA),Ethylene glycol dimethacrylate EGDMA (MERCK), Bovine serum albumin BSA (HIMEDA), Sodium dodecyl Sulfate SDS (HIMEDA), 1,6 hexandiol diacrylate HDODA (ALDRICH).

2-2 .Apparatus

(Oven)Trivp International Crop .Italy, (**FTIR 8400S)** Forier Transform infrared spectrophotometer,Shimadzu,Jaban,**(UV-1800PC),**Ultraviolet-visible spectrophotometer, Shimadaz,Italy ,was used to measure transmittance of hydrogel contact lenses .(**UV-1650 PC)** Ultra violet -visible spectrophotometer,Shimadaz Jaban, was used to measure of protein adsorption.**(Hot plate stir)** Bibby Strlintd .UK (**PH meter)**Hanna,Romania,**(Recorded NMR spectra)** using atype of Bruker,Ultra shield 300Mhz,Switzerl and using (DMSO) as asolvent at the university Al-Albyt in the Hashemite Kingdom of Jordan.

2-3 Polymerization of (HEMA)-Based Hydrogels

A (0.015) mol of HEMA with different concentrations of EGDMA (0.0025,0.0037,0.005,0.006.0.007) mol as a crosslinker was polymerized**.** The polymerization was initiated by using 0.0012 mole benzoyl peroxide dissolved in 5 ml DMF was used an initiator.The mixture was refluxing for 6 hrs at 80°C.Nitrogen gas was bubbled through out solutions about 6 hrs.When polymerization has been completed, the hydrogel was removed carefully,and then the hydrogel was dried under vacuum at (37°C) for overnight. The dry hydrogel of each was weighed [14]

2-4 Copolymerization of HEMA

2-4-1 Copolymerization of (HEMA–co-Cs)

2-hydroxyethyl methacrylate with chitosan was copolymerization by using three different percentage molar ratios (10%, 30%, 50%).Cs was dissolved in acetic acid solution as shown in Table(2-1) at room temperature, then the solutions were mixed by mechanical stirring for1 hr. Then the solutions was added to HEMA monomer.Then added 0.0025 mole(EGDMA) as acrosslinking agent 0.0012 mole of BPO dissolved in 5 ml DMF was used an initiator.The mixture was refluxing for 6 hrs at 80°C,nitrogen gas was bubbled through out solutions for about 6 hrs. When polymerization has been complete, the hydrogels was removed carefully,and then the hydrogel were dried in vacuum oven at (37°C) for overnight. The dry hydrogel of each was weighed .[15]

Table (2-1) percentage of Cs in acetic acid

HEMA	Cs %	Wight (gm)	Vml(acetic acid 0.1 mol)
90%	10%	0.2	15
70%	30%	0.6	30
50%	50%	1	50

2-4-2. Copolymerization of (HEMA – co- MAA)

The copolymer was synthesized from reaction of HEMA with MAA by using three different percentage molar ratios (10%,30%,50%).MAA was prepared by naturalization sodium hydroxide before use. Then the solutions was added to HEMA monomer. Then added 0.001 mol (HDODA) as crosslinking agent and 0.0012 mole of BPO dissolved in 5 ml DMF was used an initiator.The mixture was refluxing for 6 hrs at 80°C,nitrogen gas was bubbled through out the solutions for 6 hrs.When polymerization has been complete, the hydrogels were removed carefully,then the hydrogels was dried in vacuum oven at (37°C) for overnight. The dry hydrogel of each was weighed .[14]

2-4-3. Copolymerization of (HEMA-co-MA) , (HEMA-co-EHMA)

The copolymer was synthesized from reaction of HEMA with the monomers (MA,EHMA) by using three different percentage molar ratios (10%,30%,50%), 0.0025 mol EGDMA was added as crosslinking agent and 0.0012 mole of BPO dissolved in 5 ml DMF was used an initiator. The mixture was refluxing for 6 hrs. at 80°C,nitrogen gas was bubbled through out the solutions for 6 hrs.When polymerization has been complete, the hydrogels was removed carefully,then the hydrogels was dried in vacuum oven at (37°C) for overnight.The dry hydrogel of each was weighed.[14]Standard formulations for the four hydrogels used in this study are shown in table (2-2).

Tabe (2-2) different Copolymer used in this study

Serial No.	HEMA	MA	MAA	Cs	EHMA	Crosslinking
1	90	10	-	-	-	EGDMA
2	70	30	-	-	-	EGDMA
3	50	50	-	-	-	EGDMA
4	90	-	10	-	-	HDODA
5	70	-	30	-	-	HDODA
6	50	-	50	-	-	HDODA
7	90	-	-	10	-	EGDMA
8	70	-	-	30	-	EGDMA
9	50	-	-	50	-	EGDMA
10	90	-	-	-	10	EGDMA
11	70	-	-	-	30	EGDMA
12	50	-	-	-	50	EGDMA

2-5.Swelling measurement

Dried hydrogel pieces were used to determine the water content. the water content was determine by immersing the hydrogel (0.1gm) in 100 ml of distill water for extended period time .Excess water was removed from surface by blotting with lens-cleaning tissue just before measurements. The equilibrium water content in distill water was determined by the ratio of the weight of water in the hydrogel to the total weight of the hydrogel at hydration equilibrium.EWC was calculated using equation.

$$EWC = \frac{Ws-Wd}{Ws} \times 100$$

Where Ws and Wd correspond to the weight of the swollen sample and dried sample, respectively.[16]

2-6.Oxygen permeability

Oxygen permeability is essentially governed by EWC in conventional hydrogels. This occurs since oxygen is able to pass through the water rather than through the material itself. Oxygen permeability is described as the Dk, where D is the diffusivity of the material and k is the solubility of the material. The relationship between EWC and oxygen permeability has been found to be (Morgan & Efron equation):

$$Dk=1.67e^{0.0397EWC}$$

Where'EWC' is Equilibrium water content of the material. The units of Dk are known as Barrer: [17]

$$DK(barrer)=\frac{10^{-11}\ (cm^2 \times mlO_2)}{sec \times ml \times mmHg}$$

2-7.Protien adsorption

The hydrogel membranes were immersed in phosphate buffer solution (PBS, pH7.4) 5ml for 24 hours .After this step soaking the hydrogel membranes in single protein solution of Bovine serum albumin for 3 hours at 34 °C the typical surface temperature of human eye, the concentration of protein solution was 0.5mg/ml .After adsorption the hydrogel membranes were placed gently in to Phosphate buffer saline (PBS) for 5 second to remove excess solution adhering to the hydrogel membranes .The membranes were then inserted into a glass tube containing 1wt% aqueous solution of sodium dodecyl sulfate(SDS) to remove the proteins adsorbed on the membranes. The amount of proteins adsorbed on the membrane surface was calculated from the concentration of proteins in the SDS solution using Bradford assay reagent kit [18].

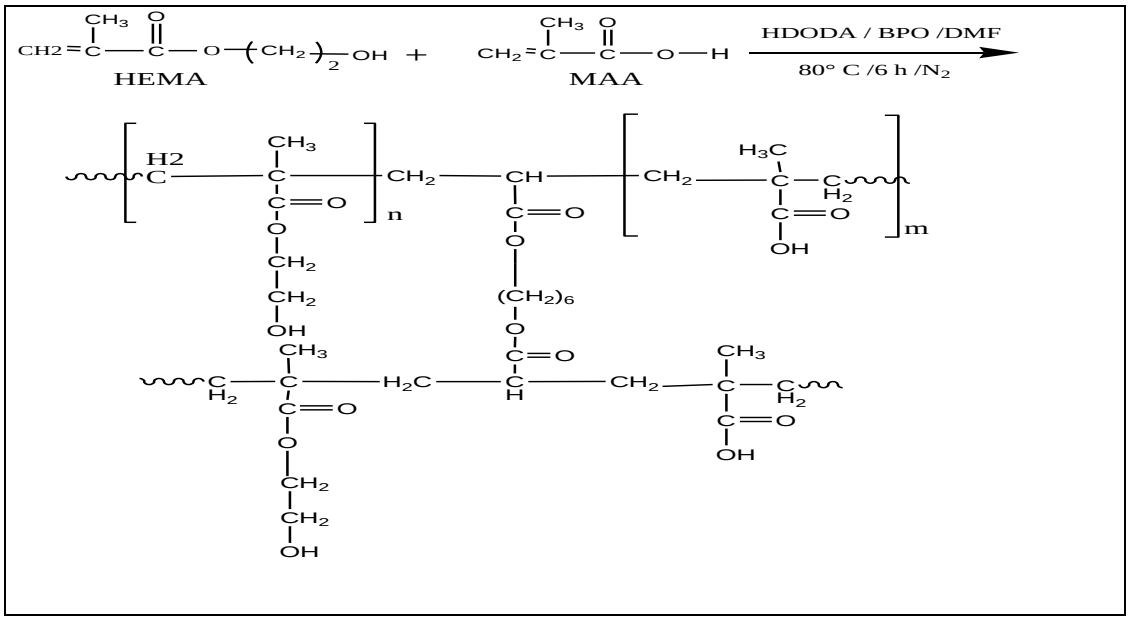
2-8. Transparency measurement

The transparency of the membrane was examined using UV-visible spectrophotometer, sample were prepared by solvent evaporation method and immersed in distall water for 24 hours to reach swelling equilibrium. The measurement were performed from 200 to 700 nm wavelength at room temperature[19].

3-Results and Discussion

3-1-1.Synthesis and Characterization of Hydrogel (HEMA-co-MAA)

The (HEMA-*co*-MAA) was synthesized from the reaction of (HEMA) with (MAA) by using different percentage ratios(10%,30%,50%)in presence of 1,6 hexandiol dimethacrylate(HDODA) as acrosslinker and benzoyl peroxide (BPO) as initiator by refluxing it with DMF as solvent for 6 hrs. The mixture was gently stirred while nitrogen purged through the mixture to remove any dissolved oxygen. This reaction was shown in Scheme (3-1).



Scheme (3-1) Copolymerization and crosslinking of HEMA with meth acrylic acid

FTIR Spectrum

The FTIR Spectrum of (HEMA-co-MAA),is shown in Figure (3-1); which indicates absorption band at 3400-3420cm^{-1} due to (-OH str group in polymer),2940cm^{-1},2830cm^{-1}to (C-H str aliphatic polymer backbone), 1758cm^{-1}(C=Ostr,ester group),1688cm^{-1}to (C=O str carboxyl group),1152cm^{-1} to (C-O-C str) and 1085 cm^{-1}to (-C-O of C-OH str)**.**[20-23]

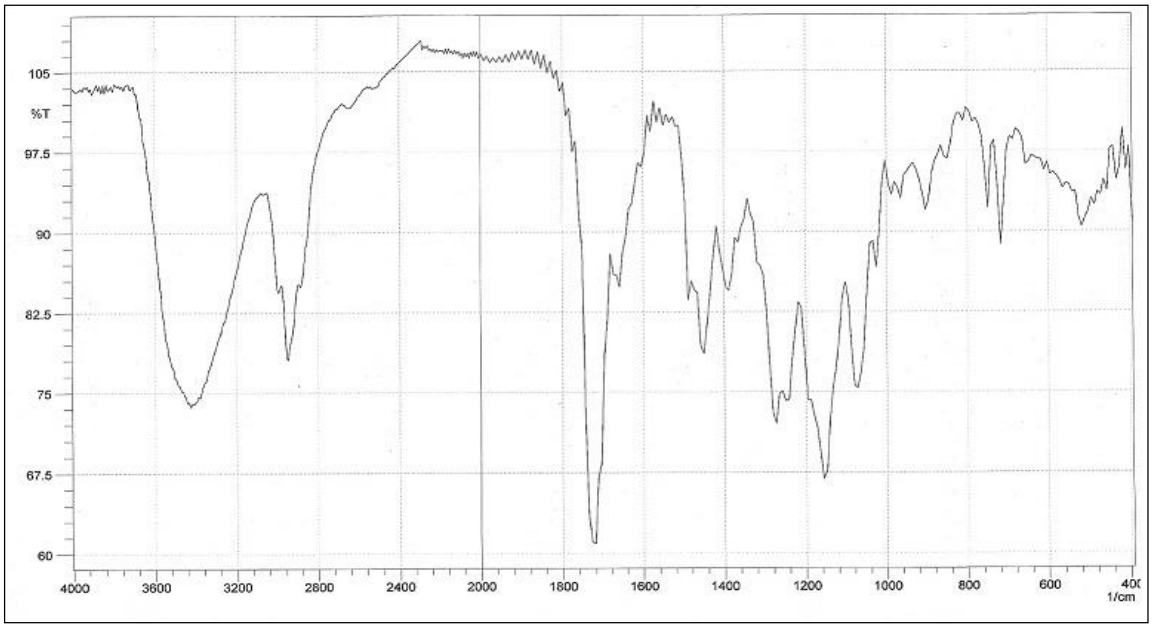


Figure (3-1):FTIR- Spectra of Hydrogel (HEMA–co-MAA)

^{1}H-NMR spectrum

^{1}H-NMR spectrum of (HEMA-*co*-MAA), is shown in Figure (3-2); (s,0.95δ ppm) for (3H,CH_3 HEMA,MAA),(m,1.3-1.9 δ ppm) for (2H,CH_2 HEMA;CH_2 HDODA),(s,3.395 δ ppm) for (2H, CH_2OH,HEMA),(m,3.81-3.94 δ ppm) for (2H, $COOCH_2$ HEMA),(s,4.1 δ ppm) for (2H,$COOCH_2$,HDODA), (s,5.68 δ ppm) for(1H ,OH HEMA), (s,11 δ ppm) for(1H ,COOH).**[20-22]**

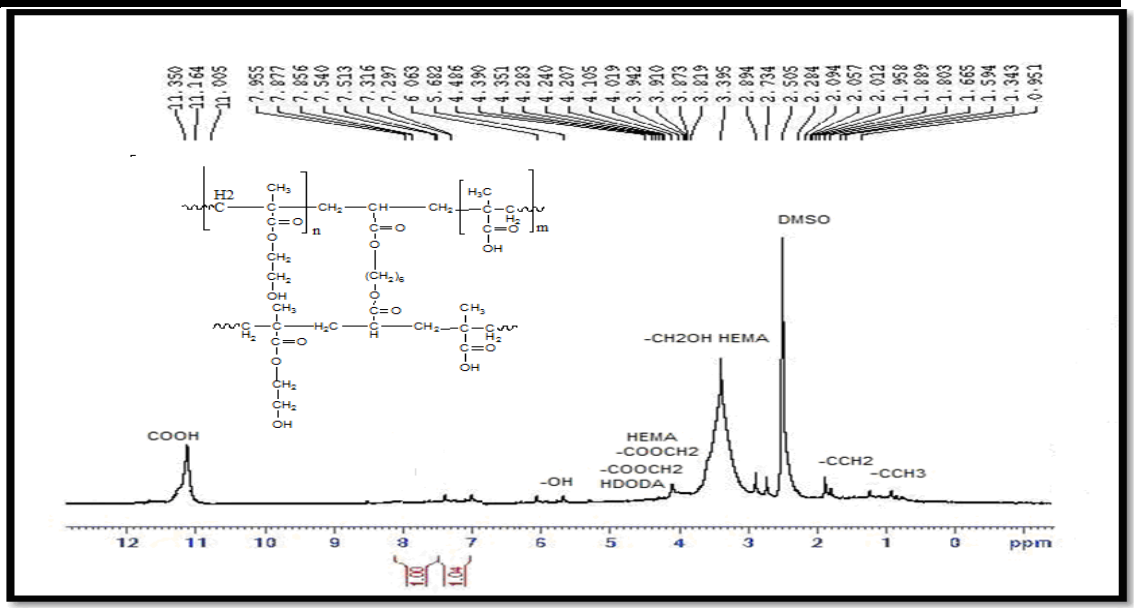
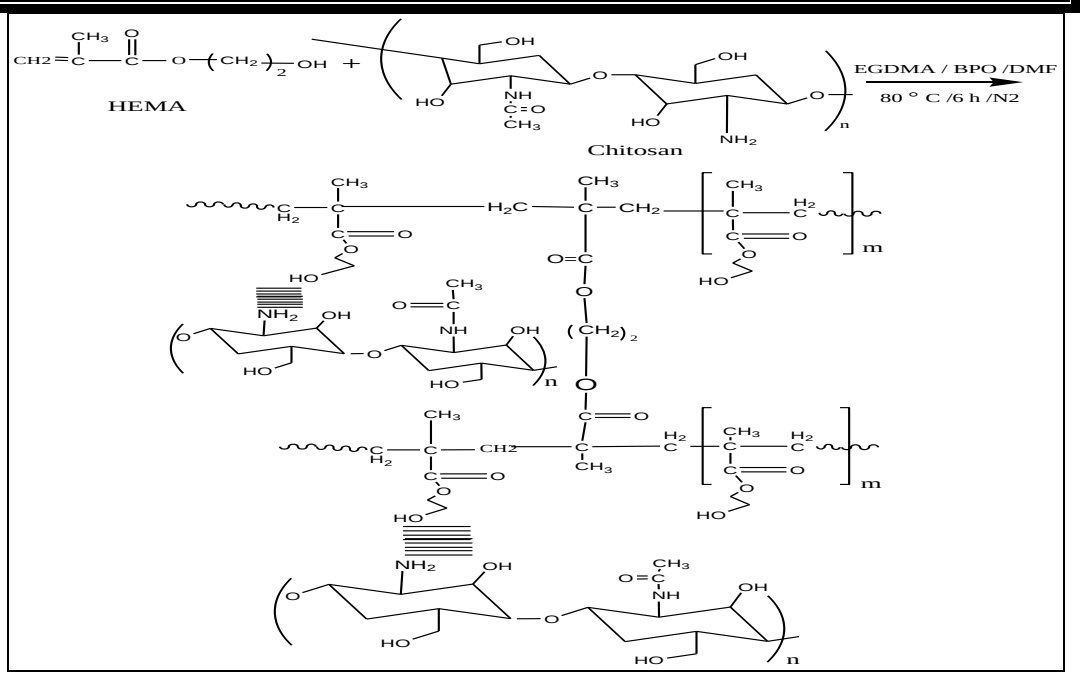


Figure (3-2):^{1}HNMR Spectra of Hydrogel (HEMA- co-MAA)

3-1-2.Synthesis and Characterization of Hydrogel (HEMA-co-Cs)

The (HEMA-co-Cs) was synthesized from the reaction of (HEMA) with (Cs) by using different percentage ratios (10%,30%,50%) in the presence of EGDMA as acrosslinker and BPO as initiator by refluxing it with DMF as solvent for 6 hrs. The mixture was gently stirred while nitrogen purged through the mixture to remove any dissolved oxygen. This reaction was shown in Scheme (3-2).



Scheme (3-2) Copolymerization and crosslinking of HEMA with Chitosan

FTIR Spectrum

The FTIR Spectrum of (HEMA-co-Cs),is shown in Figure (3-3); which indicates absorption band at 3422cm^{-1} due to (-OH str group in polymer), 3380 cm^{-1} to (N-H str of Cs), 2947cm^{-1} ,2885 cm^{-1} to (C-H str of polymer backbone),1720 cm^{-1} to (C=O str, ester group), 1650cm^{-1} to (N-H-C=O) 1164cm^{-1} ,1072 cm^{-1} to (C-O-C str) ,1026 cm^{-1}to (-C-O of C-OH str) and 1118cm^{-1} to (C-N str). **[20-23]**

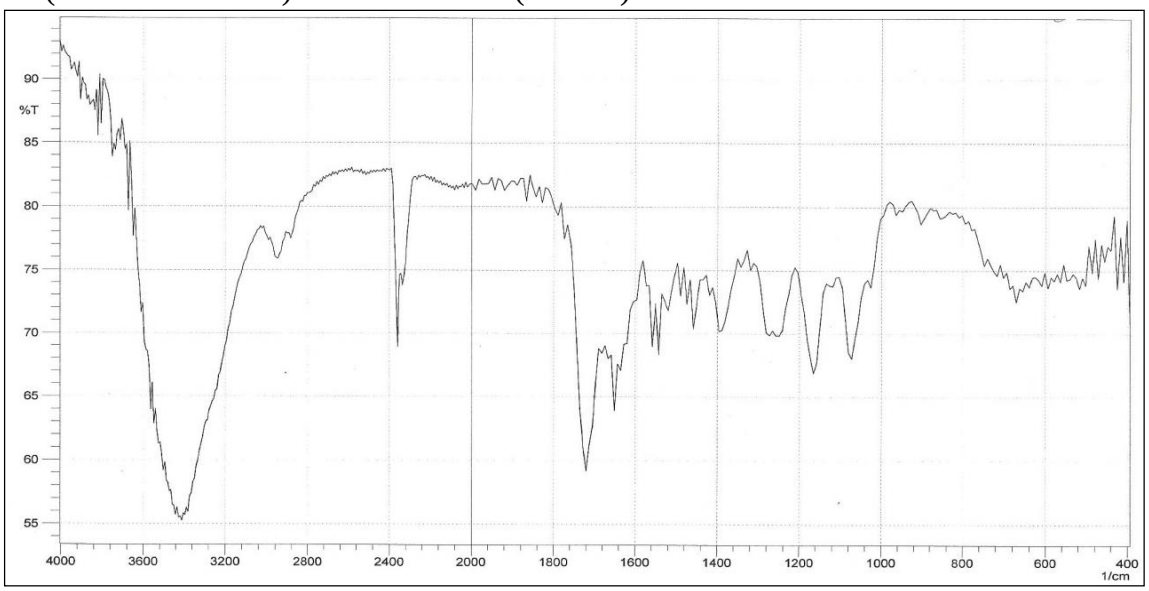


Figure (3-3):FTIR Spectra of Hydrogel (HEMA-co-Cs)

^{1}H-NMR spectrum

^{1}H-NMR spectrum of (HEMA-co-Cs),is shown in Figure (3-4);.(s,0.9δ ppm) for(3H,CH_3 HEMA; CH_3,EGDMA),(m,1.23-1.8 δ ppm) for (2H,CH_2 HEMA;CH_2

EGDMA),(s,2.1 δ ppm) for (3H $COCH_3$), (s,3.4 δ ppm) for (1H OH HEMA),(s,3.58δ ppm) for (2H, CH_2OH,HEMA),(m,3.9-4.0 δ ppm) for (2H,$COOCH_2$ HEMA),(m,4.2-4.8 δ ppm) for (2H,$COOCH_2$,EGDMA), (s,5.58δ ppm) for (1H,NH Cs) [20-22]

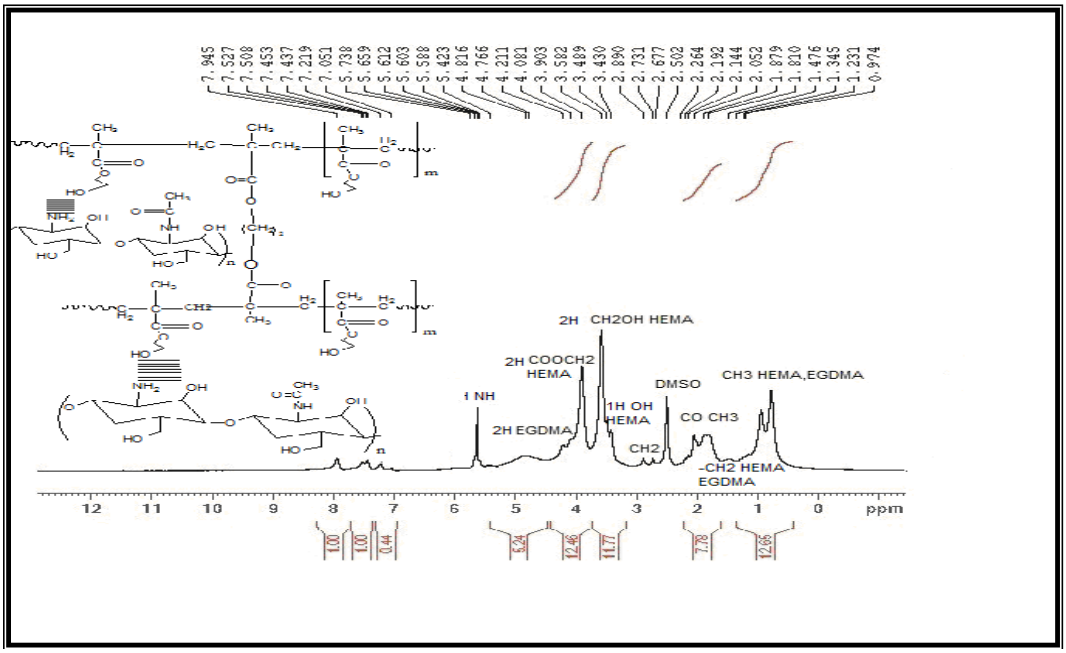
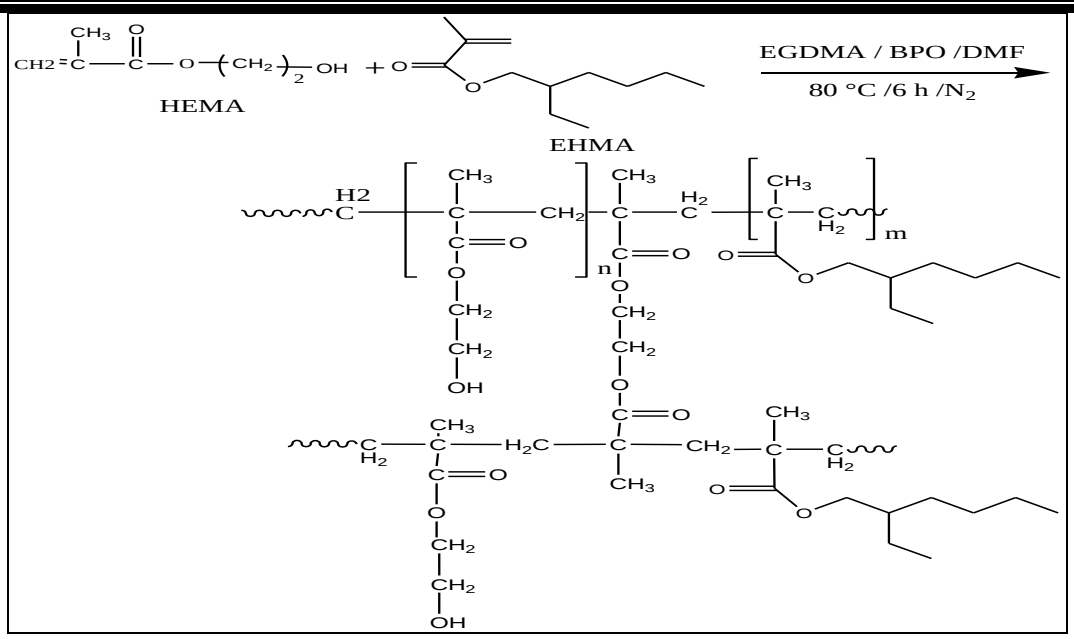


Figure (3-4):^{1}HNMR Spectra of Hydrogel (HEMA-co-Cs)

3-1-3 .Synthesis and Characterization of Hydrogel (HEMA-co-EHMA)

The (HEMA-co-EHMA) was synthesized from the reaction of (HEMA) with (EHMA) by using different percentage ratios (10%,30%,50%) in the presence of EGDMA as acrosslinker and BPO as initiator by refluxing it with DMF solvent for 6 hrs .The mixture was gently stirred while nitrogen purged through the mixture to remove any dissolved oxygen. This reaction was shown in Scheme(3-3).



Scheme (3-3) Copolymerization and crosslinking of HEMA With Ethylhexyl methacrylate

FTIR Spectrum

The FTIR Spectrum of (HEMA-co-EHMA),is shown in Figure(3-5) ;which indicates absorption band at;3433 cm^{-1} due to (-OH str in polymer), 2947cm^{1}, 2885cm^{-1} to (C-H str of polymer backbone),1728cm^{-1} to (C=O str,ester group),1080cm^{-1},1157cm^{-1} to(C-O-C str) and 1077 cm^{-1} to (-C-O of C-OH str). **[20-23]**

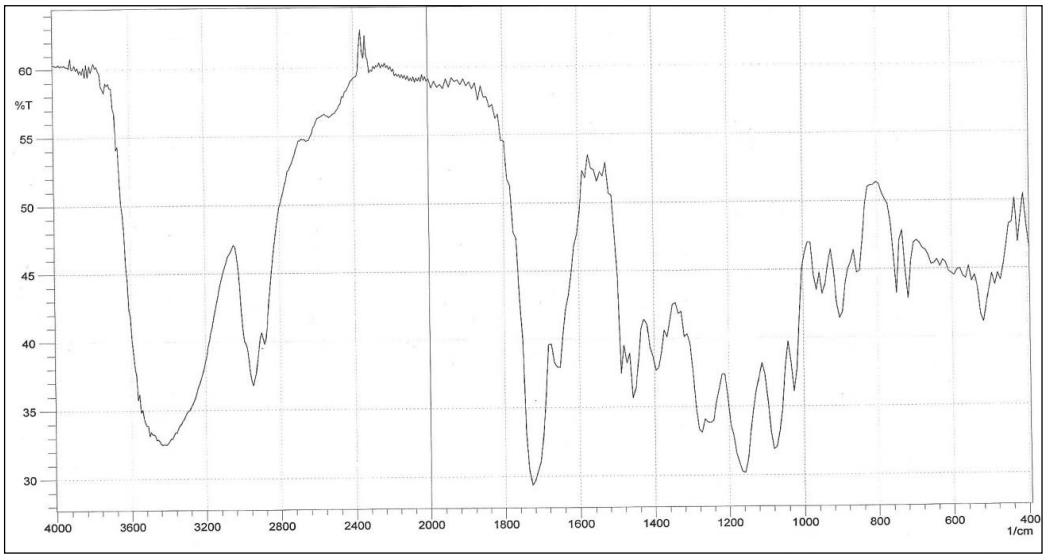


Figure (3-5):FTIR- Spectra of Hydrogel (HEMA-co-EHMA)

^{1}H-NMR spectrum

^{1}H-NMR spectrum of (HEMA-co-EHMA), is shown in Figure (3-6); (m,0.4-0.9δ ppm) for (3H,CH_3 HEMA; CH_3,EGDMA),(m,1.2-1.7 δ ppm) for (2H,CH_2 HEMA;CH_2 EGDMA),(s,3.3 δ ppm) for (1H OH ,HEMA), (s,3.5δ ppm) for(2H,

CH_2OH,HEMA),(s,3.9 δ ppm) for(2H, $COOCH_2$ HEMA), (m,4.4-4.7 δ ppm) for (2H,$COOCH_2$,EGDMA).[20-22]

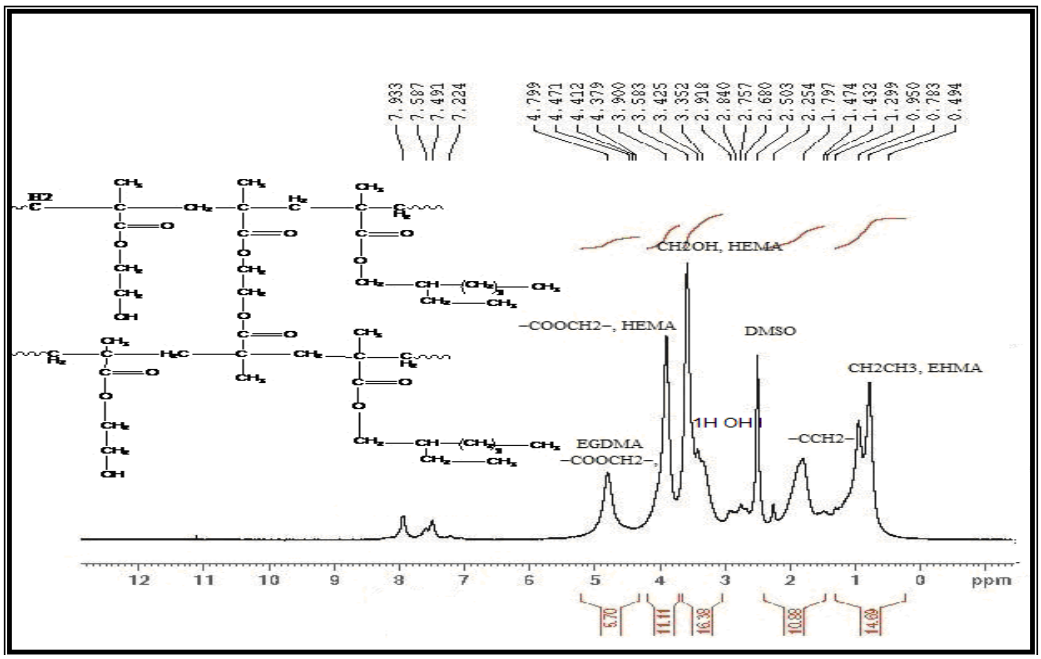
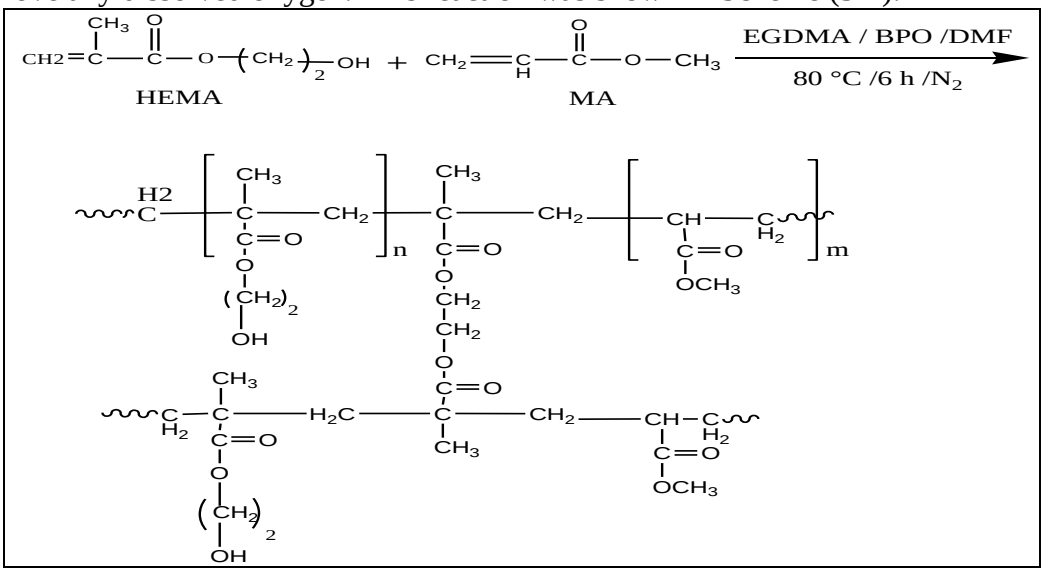


Figure (3-6):^{1}HNMR Spectra of Hydrogel (HEMA-co-EHMA)

3-1-4.Synthesis and Characterization of Hydrogel (HEMA-co-MA)

The (HEMA-co-MA) was synthesized from the reaction of (HEMA) with (MA) by using different percentage ratios(10%,30%,50%) in the precence of EGDMA as acrosslinker and BPO as initiator by refluxing it with DMF as solvent for 6 hrs. The mixture was gently stirred while nitrogen purged through the mixture to remove any dissolved oxygen. This reaction was shown in Scheme (3-4).



Scheme (3-4) Copolymerization and crosslinking of HEMA with methacrylate

FTIR Spectrum

The FTIR Spectrum of (HEMA-*co*-MA) ,is shown in Figure (3-7); which indicated absorption band at; 3417cm^{-1} to (-OH str), 2916 cm^{-1} to (C-H str of polymer backbone), 1720 cm^{-1}to (ester group, C=O),1157cm^{-1} ,1080 cm^{-1} to (C-O-C str) and 1026 cm^{-1} to
(-C-O of C-OH str)**.** [20-23]

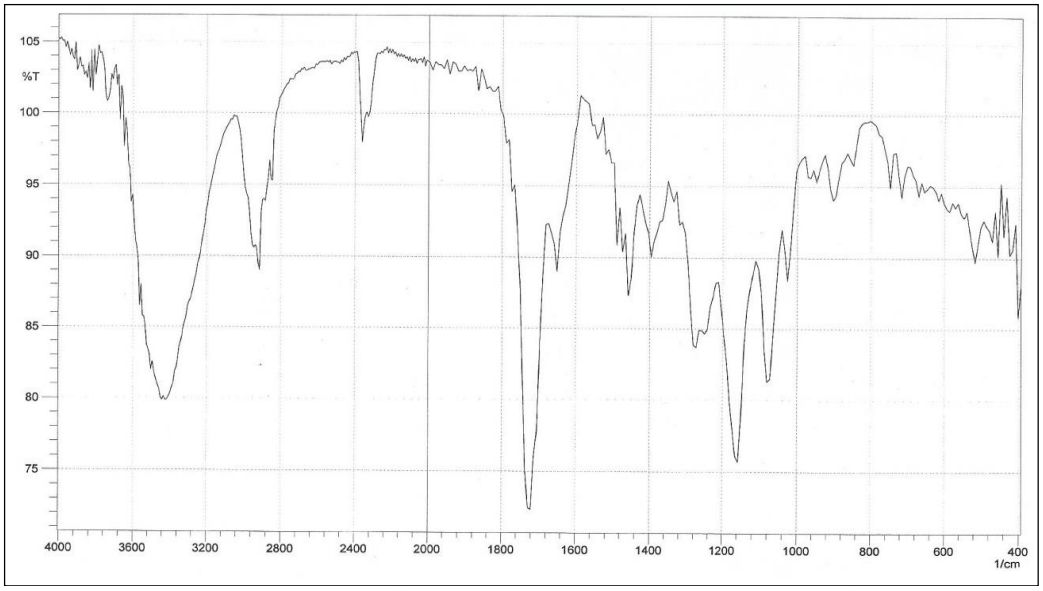


Figure (3-7):FTIR- Spectra of Hydrogel (HEMA-co-MA)

^{1}H-NMR spectrum

^{1}H-NMR spectrum of (HEMA-co-MA), is shown in Figure (3-8) ;(m,0.7-0.9δ ppm) for (3H,CH_3 HEMA; CH_3,EGDMA),(m,1.2 -1.8 δ ppm) for (2H,CH_2 HEMA;CH_2 EGDMA),(m,3.3-3.49 δ ppm) for (1H ,OH HEMA), (s,3.5δ ppm) for (2H, CH_2OH, HEMA),(s,3.9δ ppm) for (3H,-OCH_3),(s,4.3 δ ppm) for (2H, $COOCH_2$ HEMA),(s,4.79δ ppm) for (2H,$COOCH_2$,EGDMA). [20-22]

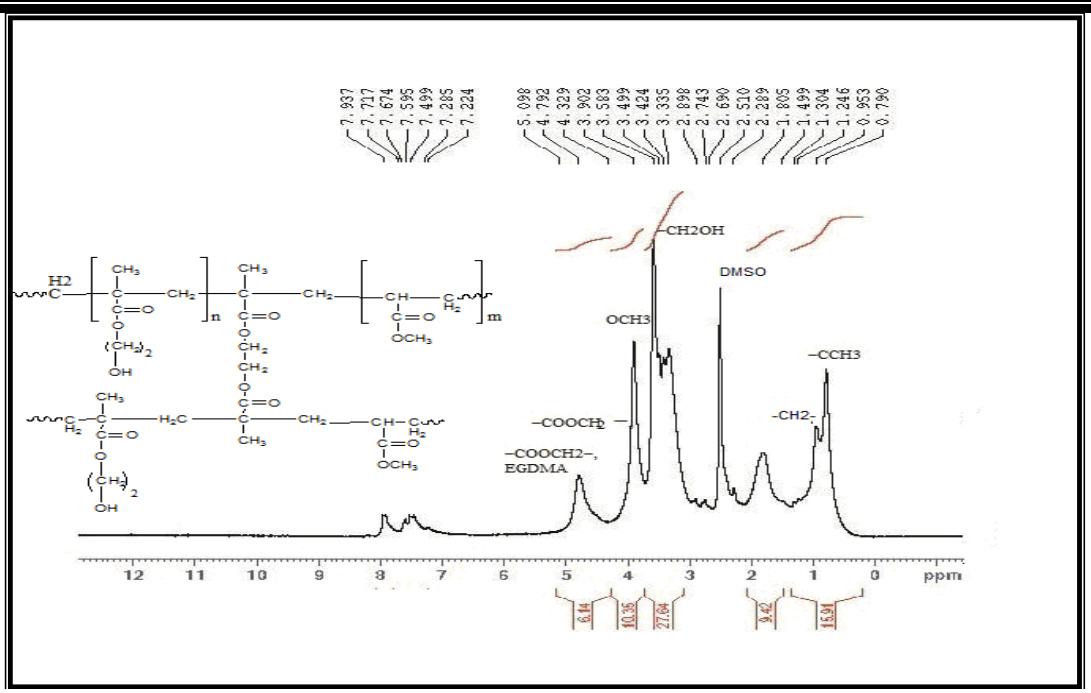
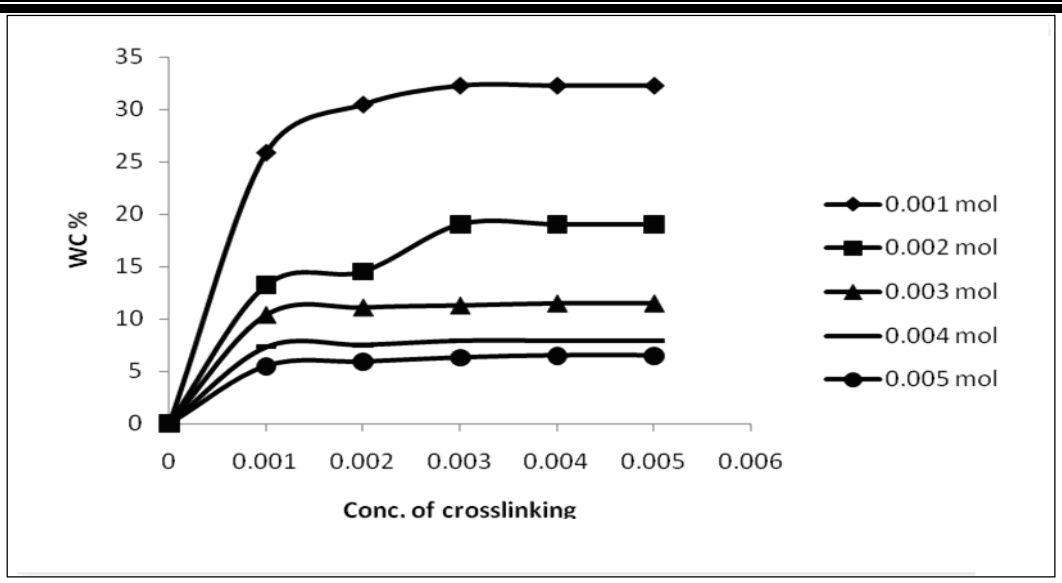


Figure (3-8):^{1}HNMR Spectra of Hydrogel (HEMA–co-MA)

3-2. Water Content

3-2-1 Effect of Crosslinking Ethylene glycol dimethacrylate on Swelling Hydrogel 2-Hydroxyethyl methacrylate (HEMA)

Figure (3-9) represents the water content to time for different concentrations of ethylene glycol dimethacrylate. In these experiments, crosslinker EGDMA concentrations were changed among (0.0025,0.0037,0.005,0.006.0.007) moles .As the amount of EGDMA increases the water content of the hydrogel composite decreased because of the molecules of the crosslinking are placed between the chains of monomers. A higher amounts of crosslinker produces larger degrees of polymer chains branching generates an additional network [24]. The results show that only 0.0025mol EGDMA is sufficient for hydrogel PHEMA which increases water content to 38% .



Figure(3-9)Effect of Crosslinker EGDMA Concentration on the Swelling Behavior of Hydrogel 2-Hydroxyethyl methacrylate (HEMA)

3-2-2.Effect of Methacrylic acid on Water Content of Hydrogel HEMA

Figure (3-10) represents the water content to time for different percentage of methacrylic acid. Hydrophilic monomer that has been very successfully used in contact lens hydrogels is methacrylic acid (MAA).When added to a soft lens polymer formulation, it results in a soft lens with ionised groups (negatively charged) with in the polymer matrix, allowing the lens to absorb more water.The higher the amount of MAA, the higher the EWC of the resulting polymer or lens, that's allowing oxygen permeability to increase significantly. Once HEMA/MAA lenses have been manufactured they need to be ionised (ie; the hydrogen atom in the carboxyl group is removed). The conversion of the carboxyl group (CO_2H) to the more hydrophilic ionised form (the carboxylate anion, CO_2-) produces an increase in water content. This is commonly achieved by treated MAA with sodium hydroxid, the carboxylic acid groups are neutralized, as illustrated in the following equation:

$$R\text{-}CO_2H + NaOH \rightarrow R\text{-}CO_2Na + H_2O$$

Unlike the un reacted methacrylic acid moieties, the sodium methacrylate groups are ionized, with the negative methacrylate ions being counter balanced by the positive charge in the sodium ions. However, this negative charge causes the carboxyl ate ions to repel each other often referred to as ‘expanding the network’. This has the effect of allowing the network to take in more water. If the polymer was not ionized, then the material would have an unexpanded network whose water content was similar to that of PHEMA[25].

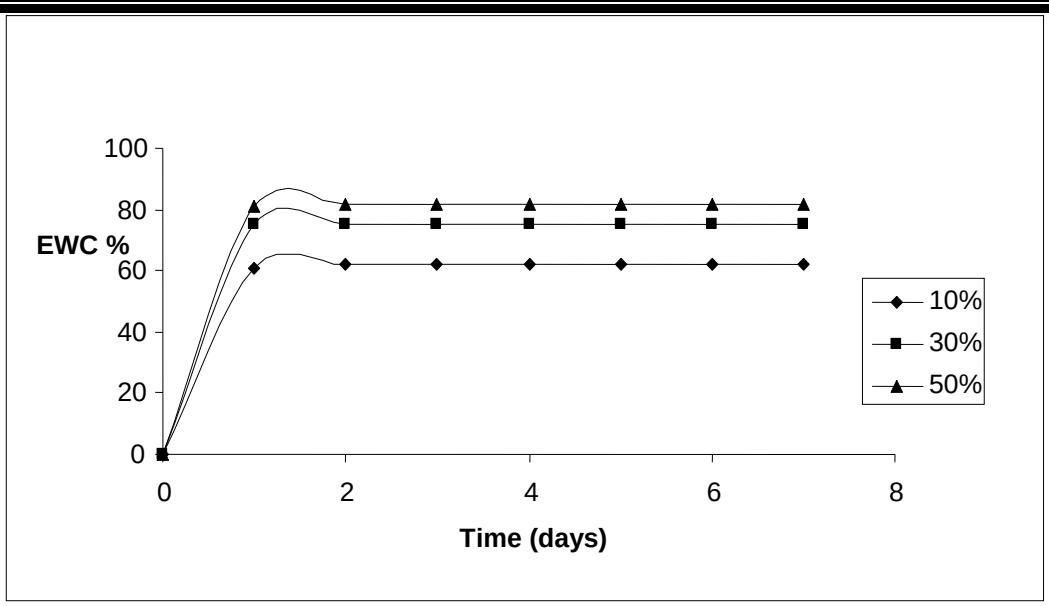


Figure (3-10) Equilibrium Water content (EWC) for different ratios of MAA (10%,30% ,50%)

3-2-3.Effect of Ethylhexyl methacrylate and Methylacrylate on Water Content of Hydrogel HEMA

Figure (3-11) and (3-12) represents the water content to time for different percentages of ethyl hexyl methacrylate and methyl acrylate .The water content of the hydrogels can be decreased by increasing the amount of EHMA and MA because of the hydrophobic monomers contain many methyl group that make swelling behavior and the expansion water of the polymer network very poorer and kept its chain rigid in resulting hydrogel[26].

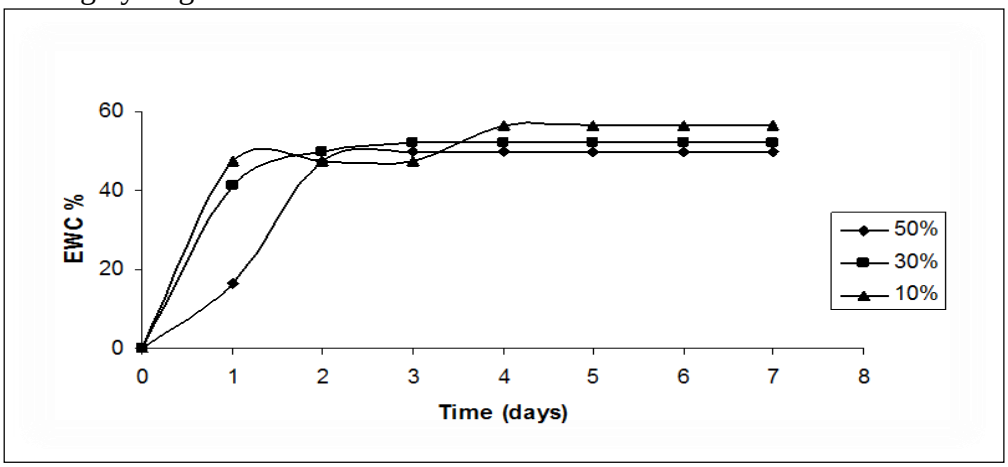
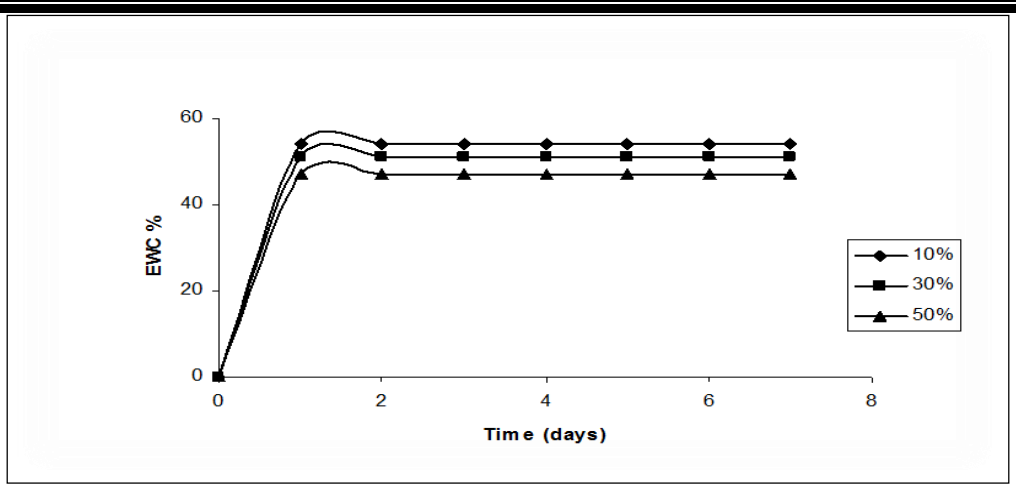


Figure (3-11) Equilibrium Water content (EWC) for different ratios of EHMA (10%,30% ,50%)



Figure(3-12)Equilibrium Water content (EWC) for different ratios of MA (10%,30% ,50%)

3-2-4. Effect of Chitosan on Water Content of Hydrogel HEMA

Figure (3-13) represents the water content to time for different percentages of chitosan .the water content of the hydrogel PHEMA increases when adding chitosan because of contain (–OH) groups can make hydrogen bonding with water molecule and increases water content to 82% ;clearly that the hydrophilic monomer used to increase the ability of a hydrogel to take up more water.[27]

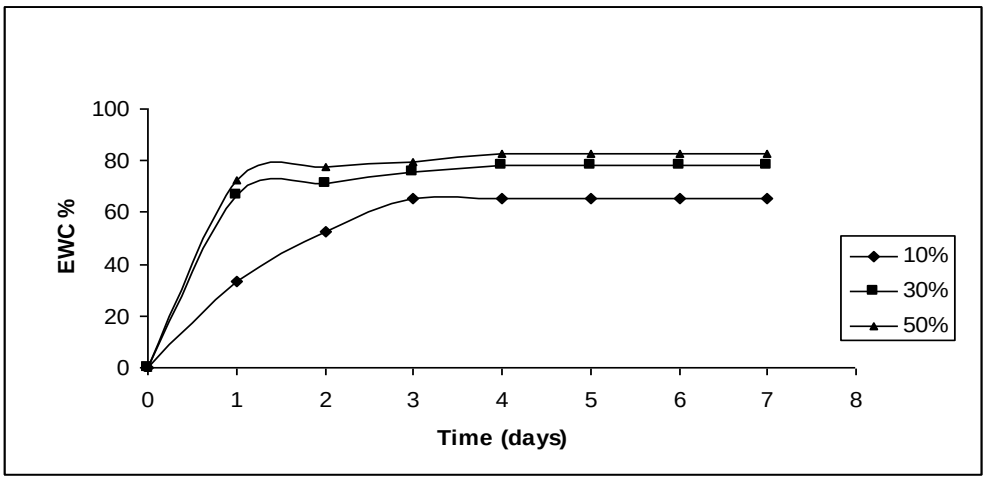


Figure (3-13) Equilibrium Water content (EWC) for different ratios of Cs (10%,30% ,50%)

3-3. Effect adsorption of protein

Bradford assay, originally, is one of the popular methods to determine protein concentration. It relies on the formation of a complex between brilliant blue dye and proteins in solution. The free dye exists in four different ionic forms. The more anionic blue form binds to proteins and has an absorbance at 590 nm. The protein concentration can be evaluated by determining the amount of dye in the blue ionic form and by measuring the absorbance of the solution at 595 nm using a spectrophotometer [28] .The dye binds mostly to arginine, tryptophan, tyrosine, histidine, and phenylalanine residues of the protein[29].Most researchers use BSA as the protein standard since it is inexpensive and easily available, One advantage of this method is its compatibility with reducing agents used to stabilize proteins in solution, further advantage is the possibility to measure high molecular weight (M.Wt) proteins since the dye does not bind to peptides with low M.Wt [28,29].The limitation of Bradford assay is the incompatibility with low concentration of detergents, which are routinely used to solubilize membrane proteins.

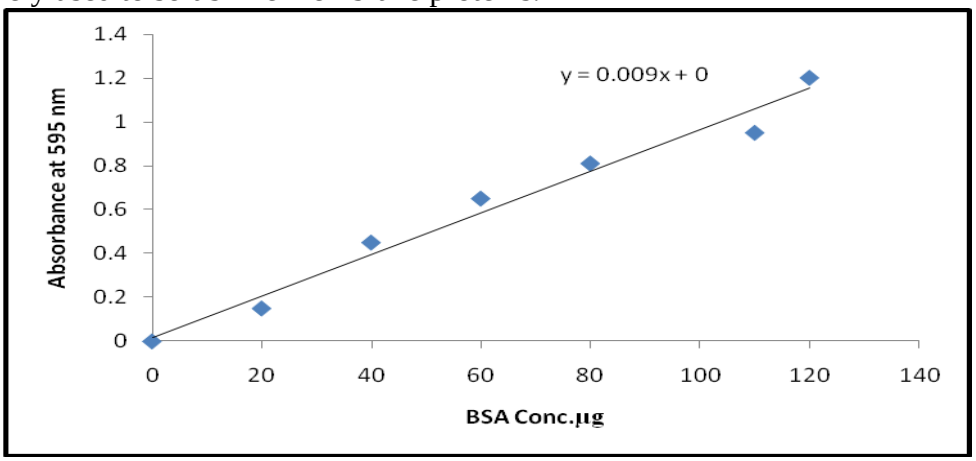


Figure (3- 14) Calibration curve for BSA at λ_{max} 595 nm

In This work used Bovine serum albumin Because the BSA are very similar in the shape and physicochemical properties to human serum albumin, due to the similarity of HSA and BSA, and the relative availability and lower cost of BSA, many in vitro studies have used BSA as a surrogate for HSA.[30,31]

albumin has a negative charge in the tear film, the relative charge of the material substrate is also highly relevant for the level of deposition. Albumin deposition can be minimized if the material exhibits a net negative charge, is relatively hydrophilic and exhibits a high water content, that result show BSA adsorbed in highest concentrations
in MA followed by EHMA, with the lowest albumin uptake reported for the most negatively charged substrate Co(HEMA-MAA) .

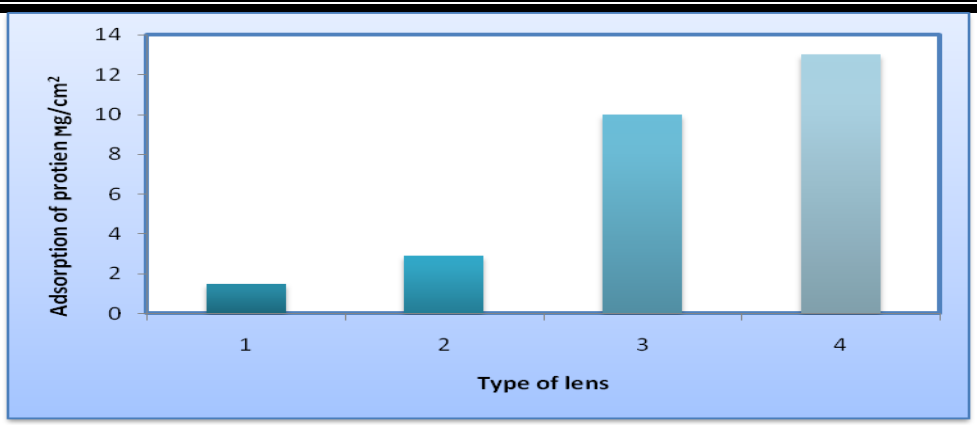


Figure (3-15) Effect of Albumin Deposition on Hydrogel Contact Lens.Where 1- (HEMA-Co-MAA) 2-(HEMA-co-Cs) 3- (HEMA-co-EHMA) 4- (EHMA-co-MA)

3-4. Oxygen permability of contact lenses

It is well known, that contact lenses must transmit enough oxygen towards the cornea, in order to allow the cornea to maintain its normal oxygen uptake rate,is necessary to avoid discomfort ,swelling of the cornea and other, more severe eye irritations ,Thus the determination of oxygen-transmissibility (Dk/L) and permeability (Dk) has become very important in the development of new contact lens materials,its water content and hydration, the overall oxygen concentration of the lens as well as the oxygen consumption rate of the cornea are the principal factors that affect oxygen transport across the contact lens. Oxygen permeability is essentially governed by EWC in conventional hydrogels. This occurs since oxygen is able to pass through the water rather than through the material itself. Oxygen permeability is described as the Dk, where D is the diffusivity of the material and *k* is the solubility of the material. The relationship between EWC and oxygen permeability has been found to be (Morgan & Efron equation)[17].

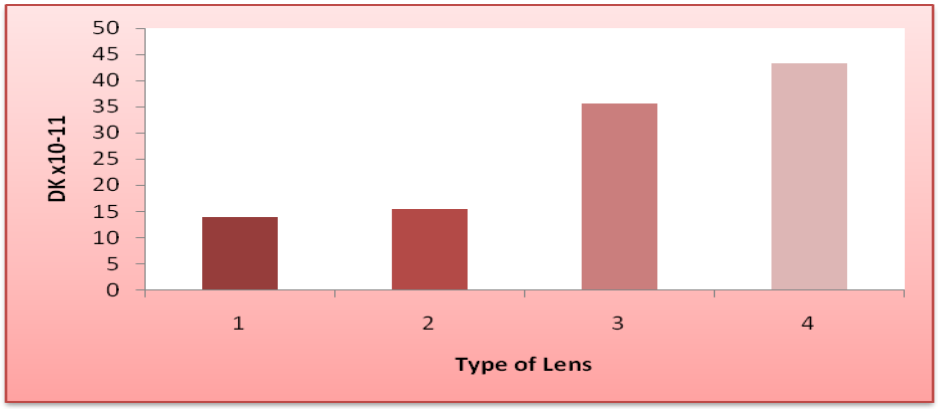


Figure (3-16)Effect of Lens Materials on Oxygen Permability.Where 1-(HEMA-co-MA) 2- (HEMA-co-EHMA) 3- (HEMA-co-MAA) 4- (HEMA-Co-Cs).

3-5 . Transparency of Contact Lenses

The electromagnetic spectrum is a wide array of diverse waves, including short waves, infrared rays, X-rays, and gamma rays. A small part of it is the visible

spectrum. The visible light spectrum is the only portion of the total electromagnetic spectrum we can see. It occupies wavelengths of approximately (400 to 700) nm .The UVR spectrum is subdivided into three bands: UVC (100–280 nm), UVB (280–315 nm) and UVA (315–400 nm).[32,33] UVB radiation has also been considered as the range 280–320 nm and UVA 320–400 nm[34] .Previous studies evaluating the efficacy of UV absorbing soft contact lenses in reducing UV transmittance have found ranging from 1 to 95.5% in the UVA wavelengths, with UVB attenuation ranging from 0 to 30%, depending on lens type. These studies incorporated either a single or double beam spectrophotometer However, wavelengths below 180 nm (vacuum UV) are of little practical biologic significance since they are readily absorbed in air. The transmittance spectra in the range 200 to 700 nm are the mean transmittance spectrum for each type of lens, general measurement as to the amount of UV radiation transmitted by a specific lens type over specific spectrum[35].The synthesized polymer must be transparent in order to be suitable for contact lenses. Figures (3-17) to (3-20) show the transmittance of monomers employed in contact lenses should be as compatible a possible to avoid phase separation .The results show that all contact lenses tested allowed relatively uniform range of transmittance of approximately 58-94% ,at wave lengths between 400-700nm and below 240 nm there was less than 1% transmittance for all contact lenses.

Our results indicated that all contact lens tested provide some ocular protection against UVA, UVB and UVC .The results shows at 240 nm (UVC) showed transmission between (1-8)%. Currently UVC transmittance is not considered as ocular health concern as only small amounts of radiation in the UVC range reach the earth's surface due to filtering effects of the ozone layer[36].Depletion of the ozone layer is actually thought to increase the transmittance of wavelengths in the UVA and UVB range[37].

The percentages of light transmission at 290 nm for (HEMA- co-Cs), (HEMA-co MA), (HEMA-Co-EHMA), give the light transmission between (0.1-11%) of light transmission. The percentage of light transmission through the (HEMA-co-MAA) is (13.4%) higher than other hydrogels contact lenses tested at the same wavelength.

The percentages of light transmission at 400 nm (HEMA-co-Cs) and (HEMA-co-MAA) give the lowest light transmission (58%,67%) respectively was lower than hydrogels lenses tested (HEMA-co-MA) and (HEMA-co-EHMA) (94%, 88%) respectively at the same wavelength.

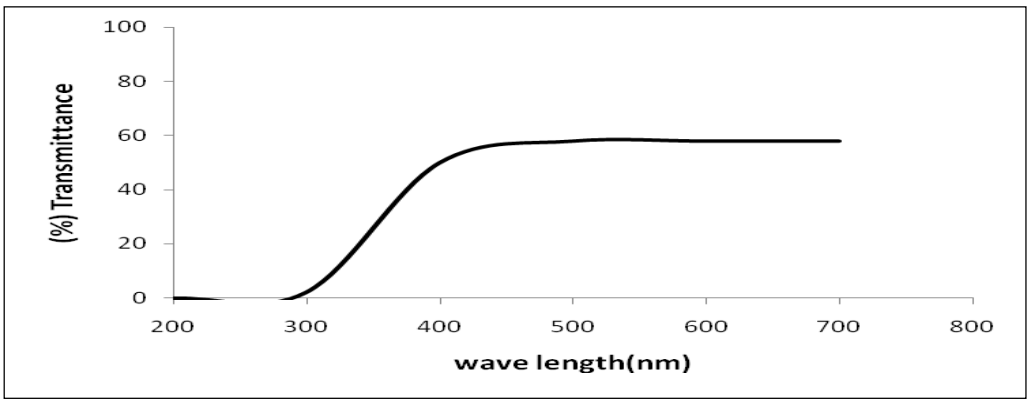


Figure (3-17)Transmittance of Copolymer(HEMA-co-Cs) in the visible light wave range of 400-700 nm

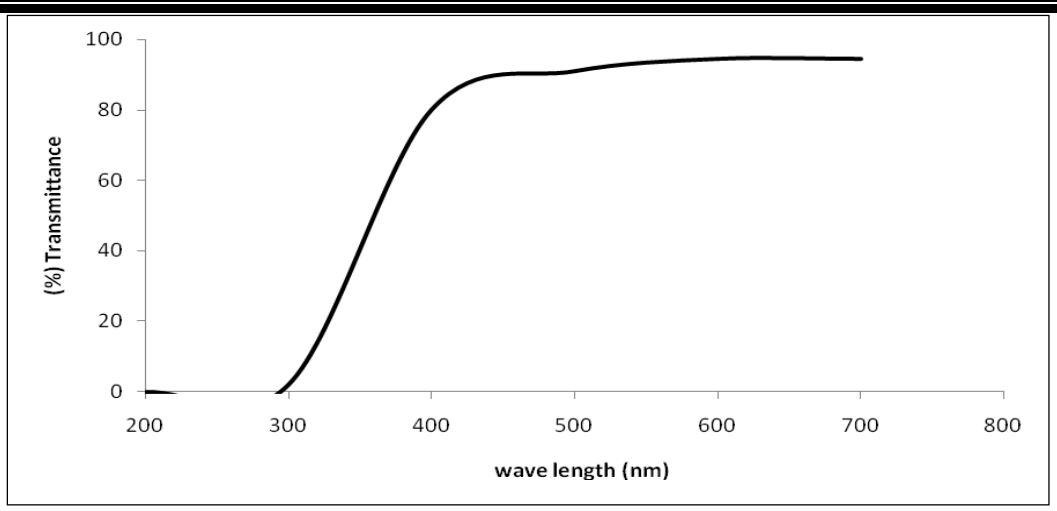
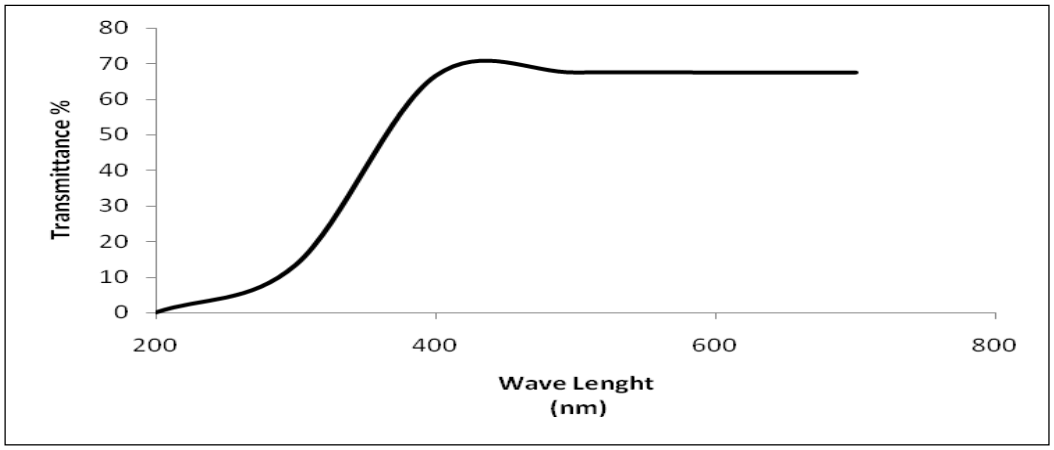
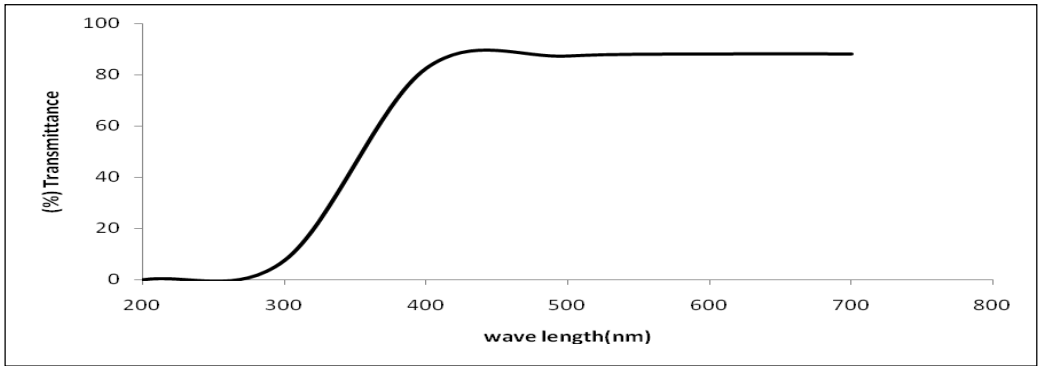


Figure (3-18) Transmittance of Copolymer (HEMA-co-MA) in the visible light wave range of 400-700 nm



Figure(3-19)Transmittance of Copolymer(HEMA-co-MAA) in the visible light wave range of 400-700 nm



Figure(3-20) Transmittance of Copolymer (HEMA-co-EHMA) in the visible light wave range of 400-700 nm

Conclusions

IR ,[1]HNMR confirmed the chemical structure of hydrogel contact lenses based on HEMA,EHMA monomers, transmittance of light (%T) was studied by UV Spectrophotometer. The results show when increase the concentrations of crosslinker, the percentage of water content decreases because of decreases in free –OH groups because of restriction, the variation in the water content of hydrogels contact lenses was successfully obtained with used of controlled amounts of other monomers as co monomers. Co monomers in hydrogels increased the percentage of water content, when contain hydrophilic groups in the polymer hydrogels inverse hydrophobic group which decrease the water content. A hydrogel with a high water content is generally more advantageous in increasing permeability ,biocompatibility and transmittance visible light of lenses.

The oxygen permeability (Dk) increases logarithmically with increasing water content of hydrogel contact lenses which permeability as much as necessary oxygen and carbon dioxide to promote normal corneal metabolism. Protein adsorption of hydrogel contact lenses shows that albumin deposits in higher concentrations on hydrophobic surfaces as compared to relatively hydrophilic surfaces.
. In the visible light wave range shows all hydrogel contact lenses exhibited light transparency .UV coated soft contact lenses are effective and highly recommended to protect the internal structure of the eye. However, the external structures of the eye such as the conjunctiva and eyelids remain at risk and would continue to benefit from the use of UV blocking sunglasses.

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*تحضير وتشخيص انواع جديدة من العدسات الملامسة بالاعتماد على 2-هيدروكسي ايثايل ميثا أكريليت

تاريخ الاستلام : 2013\9\15 تاريخ القبول : 2013\11\27

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الخلاصة :

في هذا البحث تم تخليق عدسات ملامسة لينة جديدة بالاعتماد على 2-هيدروكسي ايثايل ميثا أكريليت 2-Hydroxyethylmethacrylate(HEMA) بواسطة بلمرة الجذور الحرة بوجود اثيلين كلايكول داي ميثا اكريليت و1,6هكسان دايول داي ميثا اكريليت كعوامل شابكة و بنزويل بيروكسايد كبادئ للتفاعل.الهلاميات الناتجة شخصت بواسطة تقنيات FTIR و^{1}HNMR التي أستخدمت لمعرفة التحولات الكلية للمونمر HEMA الى هلاميات العدسات الملامسة.

تم تصنيع هلاميات العدسات الملامسة من مواد مختلفة .وهذه المواد والمحتوى المائي هي :
2-هيدروكسي ايثايل ميثا اكريليت /ميثا اكريلك اسد (77.1%)
2-هيدروكسي ايثايل ميثا اكريليت /الكايتوسان (82%)
2-هيدروكسي ايثايل ميثا اكريليت /ايثايل هكسايل ميثا اكريليت (56%)
2-هيدروكسي ايثايل ميثا اكريليت/مثايل اكريليت (52%)
تم قياس المحتوى المائي لكل التراكيب الهلاميات المحضرة بدرجة حرارة 34م° وتبين أن انتفاخ الهلاميات القطبية اكثر من الهلاميات الغير قطبية .

تم قياس نفاذية الاوكسجين (DK) بواسطة معادلة Efron &Morgan واظهرت النتائج أن الهلاميات القطبية تسمح بنفاذ أوكسجين الى القرنية أكثر من الهلاميات الغيرالقطبية .

تم قياس كمية البروتين الممتز على سطح غشاء هلاميات العدسات الملامسة من تركيز البروتين في محلول SDS بأستخدام كاشف اختبارالبروتين BCA. أظهرت النتائج أمتزاز البروتين بتراكيز عالية على السطوح الغير قطبية نسبة الى السطوح القطبية. تم فحص الشفافية لجميع الهلاميات بأستخدام مطيافية الاشعة الفوق البنفسجية المرئية بدرجة حرارة الغرفة بمدى من الاطوال الموجية واظهرت النتائج ان كل الهلاميات تسمح بنفاذ الضوء من (58-94%).

الكلمات المفتاحية : هيدروجيل ، عدسات لاصقة ، امتزاز البروتين ونفاذية الاوكسجين

***البحث مستل من رسالة ماجستير للباحث الثاني .**