Investigation of Optical and Electrical Properties of 2-acrylamido-2-methyl Propane Sulfonic Acid/ 2-Hydroxy Ethyl Methacrylate (AMPS/HEMA) Hydrogel Prepared by Gamma Irradiation

Hamza A. Ghulman[*]

Mechanical Engineering Department, Collage of Engineering and Islamic Architecture, Umm Al-Qura University Makkah, KSA
*Corresponding author: haghulman@uqu.edu.sa

Abstract   Hydrogels from either 2-acrylamido-2-methylpropane sulfonic acid (AMPS) or 2-hydroxyl ethyl methacrylate (HEMA) have been prepared by gamma radiation at irradiation dose of 10 kGy. Different volume ratio (v/v) of the starting materials were used to obtain crosslinked hydrogels of variable compositions and crosslink density. UV-VIS absorption spectra indicated that there is a variation in intensity as well as in optical energy gap with different doping levels. Therefore, values of direct and indirect energy gaps were calculated and discussed. The reflectance and transmittance were collected for the as-prepared hydrogels and analyzed in the incident photon energy range from 0.1 to 1.6 eV at a temperature range 300 to 500 K. The optical investigation revealed that the optical transition is directly allowed.

Keywords: AMPS/HEMA, gamma irradiation, hydrogel, optical and electrical properties

Cite This Article: Hamza A. Ghulman, "Investigation of Optical and Electrical Properties of 2-acrylamido-2-methyl Propane Sulfonic Acid/2-Hydroxy Ethyl Methacrylate (AMPS/HEMA) Hydrogel Prepared by Gamma Irradiation." *American Journal of Materials Science and Engineering*, vol. 6, no. 2 (2018): 31-36. doi: 10.12691/ajmse-6-2-2.

1. Introduction

Commonly**,** Hydrogels are considered a hydrophilic polymer networks which may absorb from 10–20% (an arbitrary lower limit) up to thousands of times their dry weight in water [1,2]. Hydrogels are mostly chemically stable or they may degrade and eventually disintegrate and dissolve. Besides, they are called "reversible," or "physical" gels when the networks are held together by molecular entanglements, and/or secondary forces including ionic, H-bonding or hydrophobic forces. The interest in hydrogels derives from their characteristics, particularly biocompatibility and non-toxicity [3,4]. Hydrogels based on Poly (2-hydroxyethylmethacrylate) (PHEMA) have been effective in ophthalmology field, due to high refractive index at room temperature (n= 1.512), their mechanical stability, and oxygen permeability. Swollen PHEMA possess high light transmission capability in the visible and near-visible region, and its swelling behavior depends on temperature and penetrating solution. Only a limited number of reports are known combining synthetic polymeric hydrogels with opto-electronic materials [5,6,7,8]. The confinement of electro-optical materials in polymeric materials has raised special interest due to their technological applications [9,10]. They are promising devices of light control and electrooptical applications because they can be switched electrically from a light-scattering "off state" to a highly transparent ''on state.'. 2- Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is a relatively strong acid that has a wide variety of applications such as packaging, water absorbents, films foam stabilization,, photographic materials, electrocatalysis, and ion-exchange voltammetry [11-23]. AMPS has received attention in the last few years due to its strongly ionizable sulfonate group. AMPS was selected as ionic comonomer to AAm and the optical properties of solutions incorporating copolymers formed by 2-acrylamido-2-methylpropanesulfonic acid and acrylamide, P(AMPS-AAm) were studied by Valueva et al. [24].

Therefore, attention has recently turned to 2-acrylamido-2-methylpropane sulfonic acid (AMPS^{-+}H) which is a strongly acidic ionic monomer that easily dissolves in water. The polymer properties enhanced by AMPS^{-+}H include hydrophilicity, thermal stability, stability over a broad pH range, resistance to hydrolysis and ionic character. The advantages of this synthetic hydrogel are its softness and flexibility compared to HEMA. Further, any residual unreacted monomer can be more easily removed by water due to the polymerisation is being performed in an aqueous system. The result is that an already hydrated hydrogel is obtained because water is retained within a 3-dimensional crosslinked structure [25].

In view of the above, the present study attempts to explore the optical and electrical properties of HEMA by forming hydrogel with AMPS using gamma irradiation.

2. Experimental Set up

Materials:

2.1. AMPS

2-acrylamido-2-methyl propane sulfonic acid produced by Merck, Germany, Molecular formula $C_7H_{13}NO_4S$, M.wt.= 207.25 g/mol, was used without any purification.

2.2. HEMA

2- hydroxy ethyl methacrylate (HEMA) was supplied in the form of liquid by Fluka chemical with acetylation degree of 14%. The viscosity average- molecular weight is 70000 kDa.

2.3. Gamma Radiation Source

Irradiation of samples was carried out using ^{60}Co gamma source installed at the National Centre for Radiation Research and Technology (NCRRT), Egypt with a dose rate of 5.54 kGy/h using doses ranged from 5 kGy to 30 kGy.

2.4. Preparation of AMPS / HEMA Hydrogel

2-acrylamido-2-methyl propane sulfonic acid (AMPS) at a concentration of 50 % (w/v) was prepared by dissolving AMPS powder in bi-distilled water and from this precursor different composition ratios of AMPS/HEMA (V/V) were prepared. AMPS/ HEMA mixture with a total volume of 10 mL was transferred into a 20 cm^3 glass tube, closed tightly and then subjected to different doses of γ- irradiation (3 kGy- 30 kGy) at fixed irradiation rate (5.54 kGy/h).
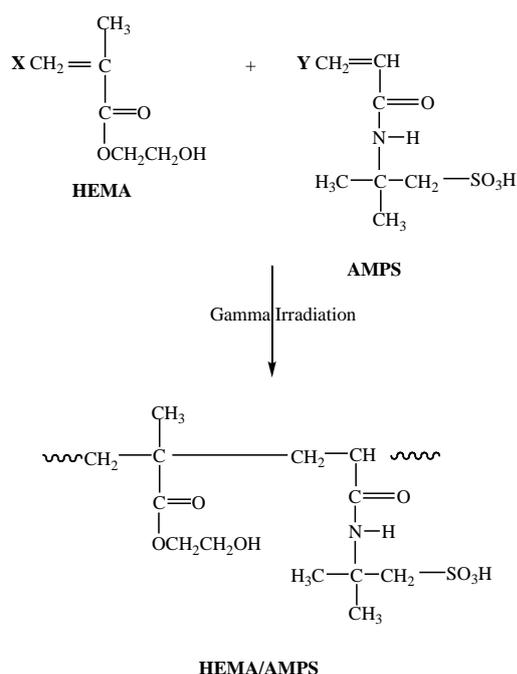
Scheme 1. The proposed mechanism of prepared HEMA/AMPS hydrogel using gamma irradiation

HEMA is a hydrophilic, hydrolytically stable derivative of acrylate with a primary hydroxyl (OH) functionality at the end of an ethyl spacer**.** Accordingly, HEMA and AMPS are of interest as their copolymerization leads to an amphoteric hydrogel incorporating hydroxyl functionality along with $-NH_2$ and $-SO_3H$ groups. Scheme 1 illustrates the copolymerization reaction of AMPS with 2-hydroxyethylacrylamide (HEMA).

2.5. Measurement

A Shimadzu model UV-1650PC UV-visible double beam spectrophotometer was employed to collect the reflectance and transmittance spectra over the incident photon energy of the wavelength range from 500 to 1060 nm.

2.6. Physical Characteristics

Solution casted polymer films were clear and transparent, but brittle in the dry state. When hydrated, the films became more flexible. For hydrogels with high contents of AMPS (e.g., 80 wt%), the swelling results in a soft gel which disintegrates easily, whereas intact flexible film derive when using less than 20% of AMPS. Films containing 20% AMPS were relatively breakable when hydrated and were unable to withstand rough handling.

2.7. Water Adsorption

The conductivity of protons depends on the ability of the membrane to remain hydrated especially at elevated temperatures. It is expected that water uptake to increase with increasing wt% of the hydrophilic AMPS in the copolymer and a maximum took place for membranes comprising 80% AMPS. This may be also related to the increase in $SO_3^-H^+$ content in the copolymer.

3. Results and Discussion

The most direct method to investigate the band structure of polymers is the measurement of the UV-Vis. absorption spectrum of this material. In the absorption process, an electron is excited from a lower to higher energy state by absorbing a photon of known energy. The changes in the transmitted radiation can decide the types of possible electron transitions. Fundamental absorption is referred to as band-to-band or exaction transition. The fundamental absorption shows a sudden rise in absorption, known as absorption edge, which can be used to determine the optical band gap ($E_g = hc/\lambda$). Absorption is expressed in terms of a coefficient α (absorption coefficient), which is defined as the relative rate of decrease in light intensity. The absorption coefficient α was calculated from the absorbance (A), where $\alpha = 2.303A/x$ and x are the sample thickness.

Absorption coefficient for polymer materials can be related to the energy of the incident photon as follows [26]:

$$(\text{ahu}) = \text{b}(\text{hu} - \text{E}_\text{g})^\text{r} \text{ for hu} > \text{E}_\text{g}. \tag{1}$$

$$(\text{ahu}) = 0 \text{ for hu} < \text{E}_\text{g}. \tag{2}$$

Where β is a constant, E_g is the optical energy gap and r is an exponent that can take the value 1, 2, 3, 1/2 and 3/2, depending on the nature of the electron transitions responsible for optical absorption. It is well known that r takes the value of 1/2 in case of direct electronic transition across direct energy gap in the k space and 2 in case of indirect electronic transition across indirect energy gap. Davis and Shalliday [27] reported that near fundamental band edge, both direct and indirect transitions occurs and can be observed by plotting $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{1/2}$ versus photon energy ($h\upsilon$).

Figure 1 shows a plot of $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) which can be used to calculate its optical energy gap and the relevant values are shown in the figure.

The nature and width of the band gaps can be evaluated form both Figure 1 a and Figure 2 and the absorption edge values were obtained by extrapolating the linear portions.

The indirect band gap values were obtained from the plots of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ as the absorption coefficient of indirect electron transitions depends on the phonon assistance while direct band gap values were obtained from the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (Figure 1).

The values of direct and indirect band gap are displayed in Figure 2. It is apparent that the direct and indirect band gap values showed a decrease with the increase in doping level. This decrease may be attributed to the formation of defects in the polymeric matrix. These defects produce the localized states in the optical band gap. These overlaps are responsible for decreasing energy band gap when temperature is increased in the 2-acrylamido-2-methyl propane sulfonic acid (AMPS) polymer matrix [28].

Conduction in the surface layers of AMPS based polymer material is often sensitive to ambient humidity and surface contamination. The surface resistivity is determined from the flow of current between two electrodes in contact with one surface of a thin specimen of AMPS based polymer material. The valency electrons in the polymer chains (with a few exceptions) are localized in covalent bonds between pairs of atoms. The small currents which are observed to flow in weak fields arise from the movement of electrically charged species present as structural defects and impurities. The concentration of defects increases as the temperature rises, so that the resistivity falls (Figure 3). Exposure to ionizing radiation and absorption of AMPS based polymer can also lead to an increase in the concentration of charge carriers which is associated with increase in conductivity.
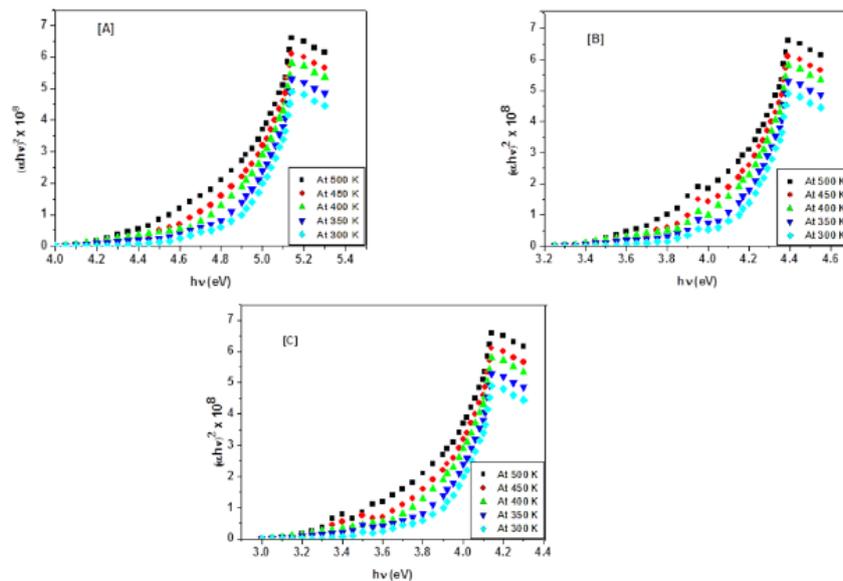
Figure 1. $(\alpha h\upsilon)2$ vs. $h\upsilon$ (photon energy) for 2-acrylamido-2-methyl propane sulfonic acid (AMPS)/HEMA hydrogel at different composition ratios A) 80: 20 HEMA/ AMPS, B) 50: 50 HEMA/ AMPS, C) 20: 80 HEMA/ AMPS
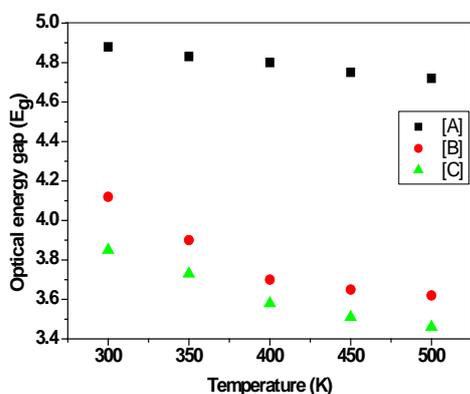
Figure 2. Optical energy gap vs. temperature for 2-acrylamido-2-methyl propane sulfonic acid (AMPS)/HEMA hydrogel at different composition ratios: A) 80: 20 HEMA/ AMPS, B) 50: 50 HEMA/ AMPS, C) 20: 80 HEMA/ AMPS
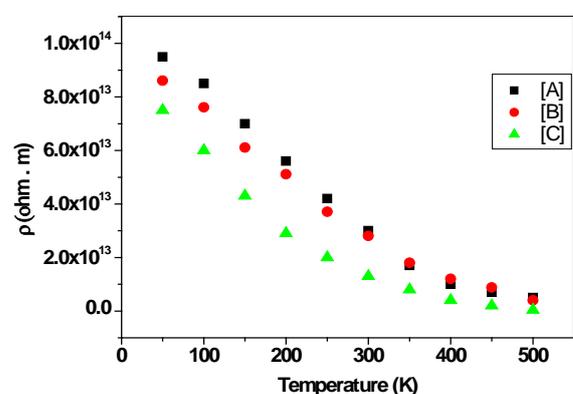
Figure 3. Resistivity vs. temperature for 2-acrylamido-2-methyl propane sulfonic acid (AMPS)/HEMA hydrogel at different composition ratios: A) 80: 20 HEMA/ AMPS, B) 50: 50 HEMA/ AMPS, C) 20: 80 HEMA/AMPS

Based on the increased water content of the AMPS copolymers in saturated water vapor atmosphere, we anticipated high ionic conductivity. AMPS-HEMA copolymer containing 80% AMPS were too soft when hydrated to allow rough handling, as were 20% copolymer although to a lesser extent. Consequently, copolymer had to be handled carefully to prevent tearing, and impedance measurements were difficult since the voltage-measuring pins of the conductivity cell could easily penetrate/puncture the films if too much pressure was applied. As AMPS content to increased from 20 to 80% the ionic conductivity increased. Considering the physical characteristics associated with various levels of AMPS, 80% AMPS is the maximum level that provides an easily handled hydrated membrane, and gives rise to maximized conductivity we can expect from a copolymer film containing these two polymers.

The studied samples consist of AMPS polymer layer and are shown schematically in Figure 4. Light incident on AMPS polymer surface reflects from all layers; the absorption within layers as well as the reflection from the interface contribute to the measured reflectance and transmittance spectra.

We estimated the optical constants of AMPS polymers using fittings to dielectric functions model for a layer. The reflectance and transmittance spectra for the polymers are exhibited in Figure 4, Figure 5, respectively, along with fittings to the multilayer Drude-Lorentz model as discussed below. All layers contribute to these spectra, with the electrochromic contribution most evident in the visible-region transmittance spectra. As is known from spectroelectro-chemistry, the neutral state shows a strong optical transition at about 2.5 eV, due to the transition of the undoped polymer. This feature is seen in our transmittance data as a deep minimum at this energy. In the infrared region, the spectrum is affected by all materials in the sample. The polymer prevents any transmission at energies lower than 0.3 eV and has high reflectance at energies lower than about 0.4 eV, especially in the polymer that is highly transparent; the infrared-active vibrational modes of the polymer are evident between 800 and 1600.
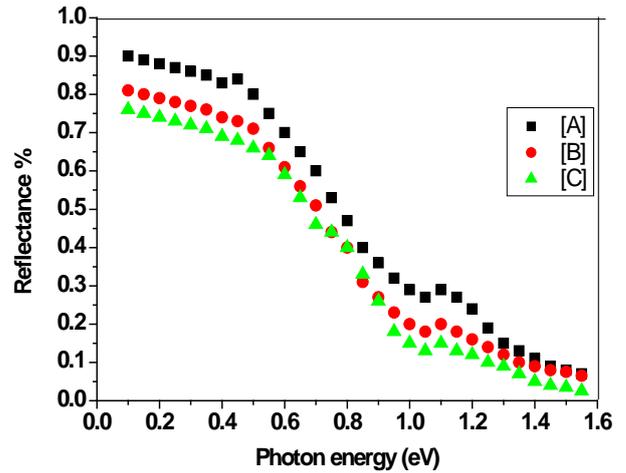

Figure 4. Reflectance vs. hυ (photon energy) for 2-acrylamido-2-methyl propane sulfonic acid (AMPS)/HEMA hydrogel at different composition ratios: A) 80: 20 HEMA/ AMPS, B) 50: 50 HEMA/ AMPS, C) 20: 80 HEMA/ AMPS

Figure 5. Transmittance vs. hυ (photon energy) for 2-acrylamido-2-methyl propane sulfonic acid (AMPS)/HEMA hydrogel at different composition ratios: A) 80: 20 HEMA/ AMPS, B) 50: 50 HEMA/ AMPS, C) 20: 80 HEMA/ AMPS
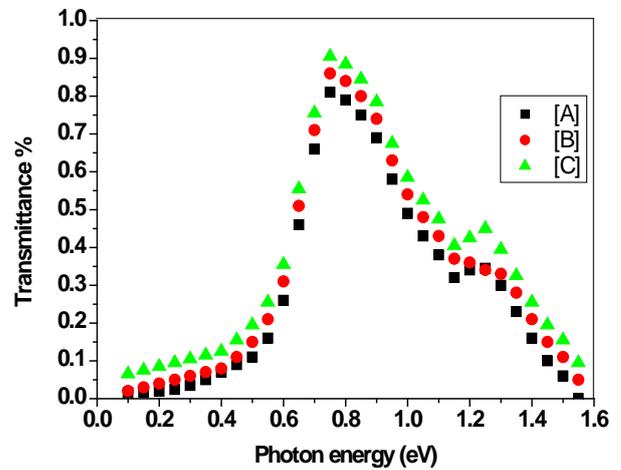
Table 1. Optical energy gap for specimen A, B, and C at different temperature

Optical energy gap (eV)	300 K	350 K	400 K	450 K	500 K
Specimen A (80: 20 HEMA/ AMPS)	4.88	4.83	4.80	4.75	4.72
Specimen B (50: 50 HEMA/ AMPS)	4.21	3.90	3.70	3.65	3.63
Specimen C (20: 80 HEMA/ AMPS)	3.85	3.75	3.58	3.51	3.46

Table 2. Resistivity for specimen A,B, and C at different temperature.

Resistivity ρ(ohm.m)	50 K	100 K	150 K	200 K	250 K
Specimen A (80: 20 HEMA/ AMPS)	9.50E13	8.50E13	7.00E13	5.60E13	4.20E13
Specimen B (50: 50 HEMA/ AMPS)	8.61E13	7.61E13	6.11E13	5.11E13	3.71E13
Specimen C (20: 80 HEMA/ AMPS)	7.50E13	6.00E13	4.30E13	2.90E13	2.00E13
Resistivity ρ(ohm.m)	300 K	350 K	400 K	450 K	500 K
Specimen A	3.00E13	1.70E13	1.00E13	7.00E12	5.00E12
Specimen B	2.81E13	1.80E13	1.20E13	8.80E12	4.00E12
Specimen C	1.30E13	8.00E12	4.00E12	2.00E12	4.00E11

In the high absorption regions (linear increase in α with increase in incident photon energy), the relationship between the absorption coefficient and the incident photon energy is governed by the relation shown in Eq. 3 [29,30].

$$\alpha = \mathbf{B}\left(\mathbf{h}\upsilon - \mathbf{E_g}\right)^{\mathbf{n}}/\mathbf{h}\upsilon, \qquad (3)$$

where B is a constant that depends on the transition probability, E_g is the width of the band gap, and n is an index that characterizes the optical absorption processes in (AMPS) polymer. Analysis of experimental results show that a proportionality exist between the absorption coefficient and the frequency of the photon energy in the form $(h\upsilon - E_g)^n$. The exponent n can take one of the four values: 2, 1/2, 3 and 3/2, which define the type of the optical transition. Theoretically n is equal to 2, 1/2, 3 or 3/2 for the indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions, respectively [31].

On other hand, the usual method for determining the type of optical transition includes plots of $(\alpha h\upsilon)1/n$ as a function of incident photon energy $h\upsilon$. These proportionalities gives a set of plots with four values of the exponent n: $(\alpha h\upsilon)^{1/2}$ - $h\upsilon$, of $(\alpha h\upsilon)^2$ - $h\upsilon$, of $(\alpha h\upsilon)^{1/3}$ - $h\upsilon$ and of $(\alpha h\upsilon)^{2/3}$ − $h\upsilon$. One of these plots satisfies the widest linearity of data, and hence its exponent determines the type of the optical transition.

In the present study, values of n indicate that the dominant transition is direct-allowed. A plot of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$ is shown in Figure 4. In this work, the optical band gaps were calculated by linear fitting in the high absorption regions. These fits intersect the $h\upsilon$-axis at the values of the optical band gap widths, and show that the direct allowed band gap width of AMPS based polymer decreases with the increase in the temperature.

4. Conclusions

AMPS was chosen based on the sulfonic acid groups contained in its structure, which are responsible for proton conductivity. HEMA was chosen as a comonomer because it is water-insoluble and provides mechanical stability. Solution casted films were found to be brittle in the dry state.

Hydrogels with only 20 wt% AMPS exhibited poor ionic conductivity. Increasing AMPS content to 80 wt% greatly improved the conductivity. Physical properties also need to be improved as they suffer brittleness in the dry state which limits an easy handling and processing of resulting membrane electrode assemblies.

The optical band gaps can be calculated by linear fitting in the high absorption regions. These fits intersect the $h\upsilon$-axis at the values of the optical band gap widths, and show that the direct allowed band gap width of AMPS based polymer decreases with increase in the temperature.

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