

Effect of Solvent on Swelling, Porosity and Morphology of Transparent Poly (HEMA)

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Abstract: Transparent materials are well known but preparation of transparent poly 2-hydroxyethyl methacrylate {poly (HEMA)} material by varying solvent is a new one and economically reliable. This material is prepared from hydroxyl based monomer HEMA by radical polymerization using benzoyl peroxide (BPO) as initiator and isobutanol, 2-butanol, 1-butanol, hexane and toluene as a solvent. The reaction temperature, time and stirring speed were set at 70°C, 4 hrs and 150 rpm, respectively. The polymer was characterized for functional group by IR spectroscopy. It was observed that the intensity of band at 1637 cm⁻¹, a characteristic band of C=C stretching disappeared indicating that it was completely consumed after polymerization. It was observed that swelling percentage increases with increase as time passes but after a certain time a constant swelling percentage is achieved. SEM pictures reveals that poly (HEMA) prepared by different solvent shows pore with a distinguishable void up to several micrometers. The BET surface area, cumulative pore volume and average pore diameter is greater in poly (HEMA) prepared by hexane as a solvent compared to other solvents. Poly (HEMA) prepared by 1-butanol as a solvent shows higher glass transition temperature compared to other solvents. Poly (HEMA) prepared by different solvents shows 90~94% light transmission property from light transmission measurement and looks transparent.

Keywords: transparent poly (HEMA), radical polymerization, swelling, porosity, morphology

1. Introduction

Hydrophilic polymers prepared from different monomers have been widely investigated in the last decades due to their vast field of application. Poly (HEMA) is a hydrophilic polymer and used as a well bio-compatible material because of its biological inertness, non-toxicity and chemical stability[1-9]. It is also obtained as a hydrogel. This material was first studied by Wicherle that suggested its use as soft contact lenses, but today there are still some difficulties for using them as implant devices because of the low mechanical strength showed by the poly (HEMA) hydrogels [10, 11]. The properties of poly (HEMA) hydrogel are de-

pendent upon their method of preparation, polymer volume fraction, degree of cross-linking, temperature and swelling agent[12-16]. Hydrogel is a class of polymeric material which has the ability to hold substantial amount of water, showing soft and rubbery-like consistency and low interfacial tension[17,18]. The nature of the hydrogel structure, due to its high water content, allows the extraction of the undesirable reaction by-products before implantation and the flow of body fluids between the tissue and implant in vivo. The possibility of fabrication in various geometric forms and the easy alteration of its physical form allow the adjustment of the physical properties according to a specific application. Due to versatile properties of poly (HEMA), it can be used in a wide range of application. Poly (HEMA) contains pendant hydroxyl group

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Table 1. Composition of Poly (HEMA) Prepared by Different Solvents

Expt No.	HEMA (mL)	BPO (g)	1-butanol (mL)	2-butanol (mL)	iso-butanol (mL)	Hexane (mL)	Toluene (mL)
HE1	8	0.1			20		
HE2	8	0.1		20			
HE3	8	0.1	20				
HE4	8	0.1				20	
HE5	8	0.1					90

which is also easily modified and can be used for further application.

The main goal of our study is to develop transparent poly (HEMA) material from hydroxyl based monomer HEMA by varying solvent and also the effect of solvent on swelling, porosity and morphology of poly (HEMA).

2. Experimental

2.1. Materials Used

2-hydroxyethyl methacrylate (HEMA) and benzoyl peroxide (BPO) were both purchase from Aldrich and used without any purification. Isobutanol, 2-butanol, 1-butanol, hexane and toluene were used as a solvent.

2.2. Synthesis Procedure

At first HEMA and BPO in different solvents were mixed together. The mixture solution put in the double walled cylindrical glass jar in nitrogen atmosphere. Nitrogen gas purged for 5 minutes. The cylindrical jar was placed at a temperature of 70°C and was shaken for 4 hr with a shaking speed of 150 rpm. The polymer formed was removed from the glass jar, washed and dried. After drying, poly (HEMA) looks transparent.

Fig. 1 shows the schematic representation of the preparation of poly (HEMA). The composition of poly (HEMA) prepared by different solvent is presented in Table 1.

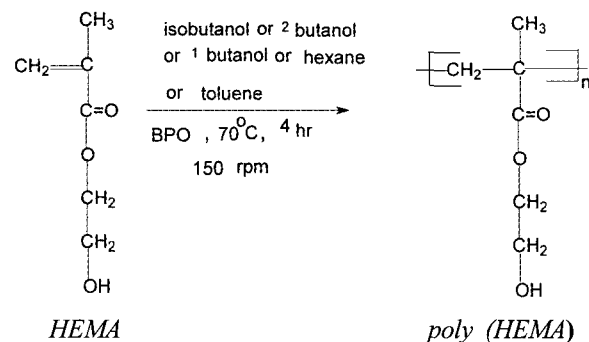


Fig. 1. Reaction scheme for the Preparation of transparent poly (HEMA) from HEMA.

2.3. Preparation of Film for Light Transmission Measurement

Dried poly (HEMA) prepared by different solvents were dissolved in ethanol as a solvent and stirred for 1 hr in a magnetic stirrer. After stirring, the clear solution of poly (HEMA) was decanted. The clear solution was put into the film forming chamber and kept it at room temperature for drying. After drying, the film was removed from the film forming chamber. The film looks transparent.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The identification of characteristic absorption bands concerned with the vibrations of functional groups present in the molecules was based on the FTIR analysis. Fig. 2(a, b, c, d, e and f) represents the FTIR spectra of HEMA, HE1, HE2, HE3, HE4 and HE5, respectively. The characteristic IR peak of HEMA in Fig. 2(a) are 3435 cm⁻¹ for -OH, 1720 cm⁻¹ for -C=O,

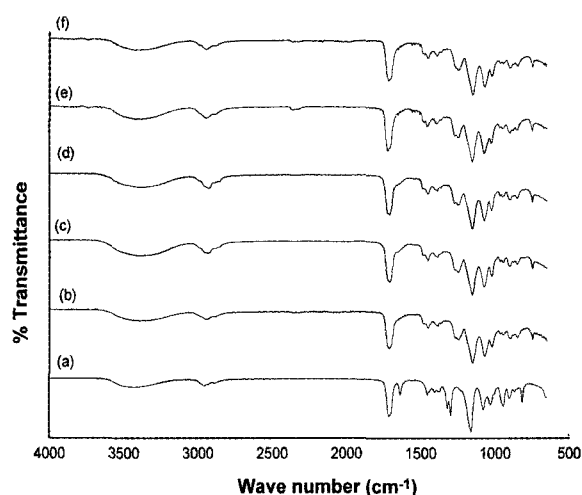


Fig. 2. FTIR spectra of (a) HEMA (b) HE1 (c) HE2 (d) HE3 (e) HE4 and (f) HE5.

1637 cm^{-1} for $-\text{C}=\text{C}$, 1079 cm^{-1} for $-\text{C}-\text{O}$ of $-\text{COH}$ and 1162 cm^{-1} for $-\text{C}-\text{O}-\text{C}$ group. The characteristics IR peak of HE1, HE2, HE3, HE4 and HE5 in Fig. 2(b, c, d, e and f) are $\sim 3435 \text{ cm}^{-1}$ for $-\text{OH}$, $\sim 1715 \text{ cm}^{-1}$ for $-\text{C}=\text{O}$, $\sim 1071 \text{ cm}^{-1}$ for $-\text{C}-\text{O}$ of $-\text{COH}$ and $\sim 1158 \text{ cm}^{-1}$ for $-\text{C}-\text{O}-\text{C}$ group.

There is no peak of $-\text{C}=\text{C}$ observed at 1637 cm^{-1} in Fig. 2(b, c, d, e and f). It indicates vinyl double bond totally consumed after polymerization. The $-\text{CH}_2$ rocking peak of methacrylic polymer was also observed at 749 cm^{-1} in Fig. 2(b, c, d, e and f), respectively.

3.2. Swelling Behaviors and Density of Poly (HEMA)

Swelling behaviors of polymer was observed gravimetrically. The water content (S_w) of the swollen polymer was calculated from the following expression[19]

$$S_w = [(m_t - m_0) / m_0] \times 100\% \quad (1)$$

where m_t is the mass of the swollen polymer at time t and m_0 is the initial mass of the dry polymer. Swelling behavior of HE1, HE2, HE3, HE4 and HE5 prepared by different solvent is given in Fig. 3. It is shown in Fig. 3 that the swelling percentage increased with time but after a while constant percentage swelling is

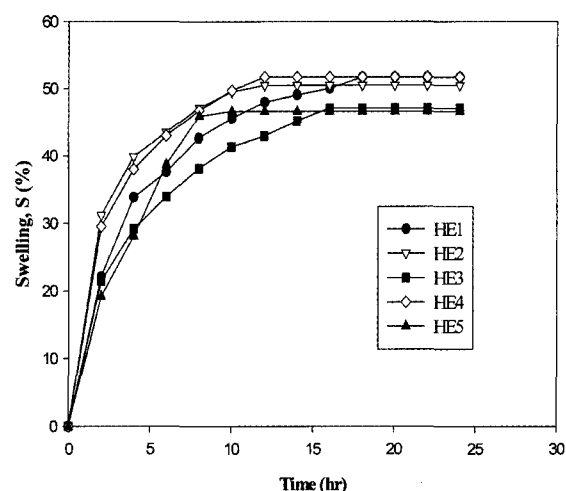


Fig. 3. Plot of swelling (S %) as a function of time of HE1, HE2, HE3, HE4 and HE5.

Table 2. Equilibrium Swelling, S (%) and Density of Poly (HEMA) Prepared by Different Solvents

Expt No.	Equilibrium swelling, S (%)	Density (g/mL)
HE1	51.73	0.823
HE2	50.49	0.740
HE3	47.11	0.695
HE4	51.75	0.770
HE5	46.6	0.975

achieved. This value of swelling percentage may be called equilibrium mass swelling. During the polymerization, the polymer formed is precipitated resulting in a solid material. The equilibrium swelling and density of poly (HEMA) prepared by different solvent is given in Table 2.

Comparing HE1, HE2 and HE3, the equilibrium swelling is greater in HE1, may be more branched solvent used in the polymerization. However, poly (HEMA) is able to absorb water and water remains filling the intermolecular spaces of the polymer network. In case of HE4 and HE5, the equilibrium swelling is greater in HE4, may be due to less solubility parameter of hexane compared to toluene which is used as a solvent in the polymerization. The solubility parameter of poly (HEMA) and solvents are given in Table 3.

Table 3. Solubility Parameter of Different Components

Component	Solubility parameter (cal/cm ³) ^{0.5}
poly (HEMA)	13.30
isobutanol	11.10
2-butanol	10.85
1-butanol	11.30
Hexane	7.3
toluene	8.9

The density of poly (HEMA) for HE1 and HE3 decreases according to equilibrium swelling as it is seen in Table 2. The density of HE5 is greater compared to HE4, may be due to more polar solvent used in the polymerization.

3.3. Scanning Electron Microscopy

The surface morphology of HE1, HE2, HE3, HE4 and HE5 are given in Fig. 4(a, b, c, d and e), respectively.

The SEM image of HE1, HE2, HE3, HE4 and HE5 in Fig. 4(a, b, c, d and e) indicates that pores are present on the surface of poly (HEMA) with a distinguishable void up to several micrometers. It is seen in Fig. 4 that HE2 shows larger pore compared to HE1 and HE3. This can be explained on the basis of the solubility parameter. The solubility parameter [20,21] of isobutanol, 2-butanol and 1-butanol are 11.10, 10.85 and 11.30 (cal/cm³)^{0.5}, respectively. So, 2-butanol is less polar compared to isobutanol and 1-butanol. Hence, addition of less polar solvent compared to more polar solvent to the polymerisation mixture causes the formation of larger size of voids. It is also seen in Fig. 4 that HE5 shows larger pore compared to HE4. The solubility parameter of hexane and toluene are 7.3 and 8.9, respectively. Although the toluene is more polar than hexane, HE5 shows larger pore, may be due to larger amount of toluene is used in the polymerization as shown in Table 1.

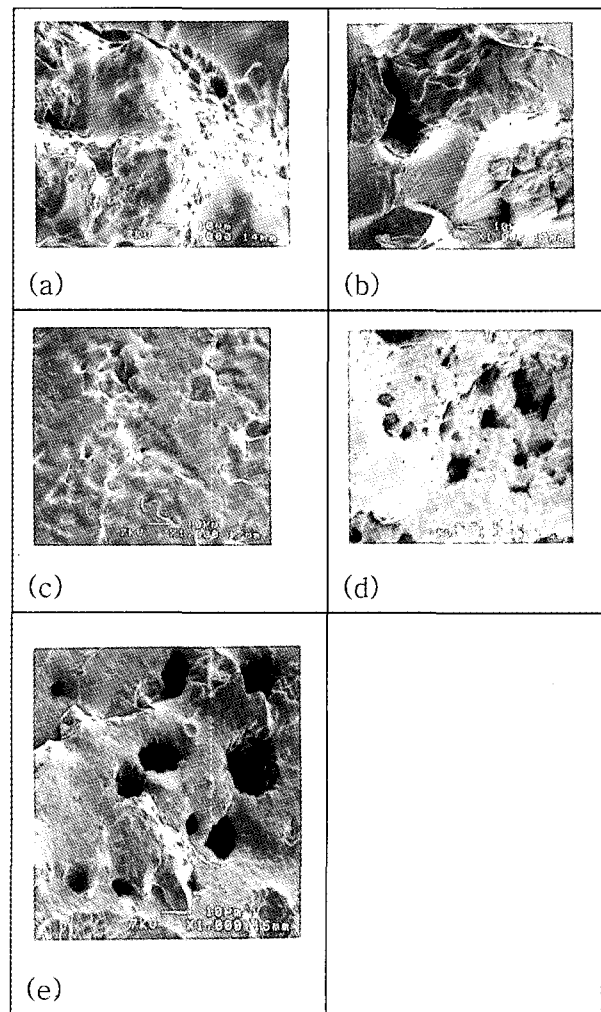


Fig. 4. SEM pictures of (a) HE1 (b) HE2 (c) HE3 (d) HE4 and (e) HE5.

3.4. BET Surface Area, Cumulative Pore Volume and Average Pore Diameter

The surface area measurements, based on single point nitrogen adsorption (BET) method, were conducted using monosorb surface area analyzer, Quantachrome Corporation, USA, based on dynamic adsorption/desorption technique.

Fig. 5 represents the plot of average pore diameter versus cumulative pore volume of HE1, HE2, HE3, HE4 and HE5. It is seen in Fig. 5 that pores of HE4 are present in the higher pore volume domain whereas pores of HE5 are present in the lowest pore volume domain. The BET surface area, cumulative pore vol-

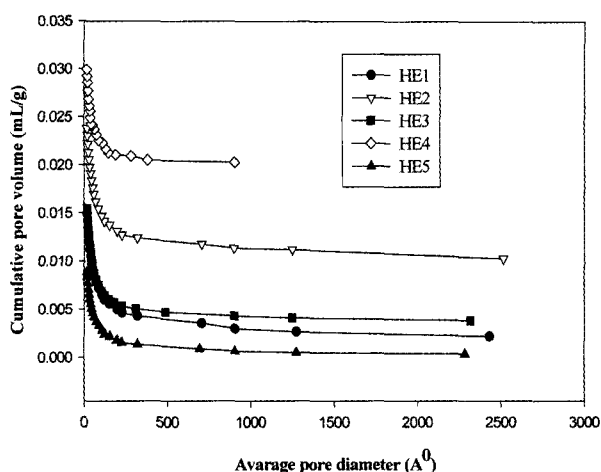


Fig. 5. Plot of cumulative pore volume as a function of average pore diameter of HE1, HE2, HE3, HE4 and HE5.

ume and average pore diameter of HE1, HE2, HE3, HE4 and HE5 are given in Table 4. Comparing HE1, HE2 and HE3, the BET surface area and cumulative pore volume is higher in HE2, may be due to more solubility parameter difference between poly (HEMA) and 2-butanol compared to poly (HEMA) and isobutanol or 1-butanol as seen in Table 3. The higher surface area may be due to the decrease in the size of the macrosphere. Comparing HE1 and HE3, HE1 shows lower surface area and cumulative pore volume, although solubility parameter difference between poly (HEMA) and isobutanol is greater compared to poly (HEMA) and 1-butanol. This may be due to the branching of alcohol. 1-butanol is linear alcohol whereas isobutanol is branched alcohol. The average pore diameter of HE2 is higher compared to HE1 and HE3. This can be explained on the basis of the solvent property which is used during the polymerization. The formation of larger morphological units is promoted a formation of larger size of the voids due to addition of poor soluble solvent to the polymerization mixture. Comparing HE4 and HE5, The surface area and pore volume is higher in HE4, may be due to more solubility difference between poly (HEMA) and hexane as it is seen in Table 3. Hexane is less polar than toluene. The average pore diameter is higher in HE4 compared to HE5, may be due to introduction of the

Table 4. BET Surface Area, Cumulative Pore Volume and Average Pore Diameter of HE1, HE2, HE3, HE4 and HE5

Expt No.	BET surface area (m ² /g)	Cumulative pore volume (mL/g)	Average pore diameter (Å)
HE1	15.0167	0.014840	54.31
HE2	16.4411	0.023782	78.80
HE3	15.8360	0.015870	52.49
HE4	17.5723	0.029918	102.14
HE5	10.9654	0.008838	44.68

Table 5. Glass Transition Temperature (T_g) of HE1, HE2, HE3, HE4 and HE5

Expt No.	T_g (°C)
HE1	78.63
HE2	131.80
HE3	147.27
HE4	61.90
HE5	98.27

less polar solvent during polymerization.

3.5. Differential Scanning Calorimetry

The glass transition temperatures (T_g) of poly (HEMA) prepared by different solvent were determined by use of a Shimadzu DSC 50 thermal analyzer system. All samples were tested on aluminum pans at a heating rate of 10°C/min under dry N₂ gas (30 mL/min) and a temperature range from 10 to 200°C. The values of T_g are given in Table 5. The glass transition temperature (T_g) of poly (HEMA) prepared by different solvents were determined from the DSC thermograms. The values of T_g are given in Table 5. It is seen in Table 5 that T_g value of HE1 is lower compared to HE2 and HE3, may be due to branched solvent used in the polymerization. Comparing HE1, HE2 and HE3, the T_g value of HE3 is higher, may be due to more polar solvent 1-butanol used in this study. 1-butanol is diffused faster compared to 2-butanol and isobutanol. The butanols follow the logic mentioned above where most complicated structure has the lowest T_g and the straight chain has the highest T_g . It is also seen in Table 5 that the T_g value of HE5 is greater compared to HE4. This

may be explained on the basis of the solvent polarity. HE5 is prepared in presence of toluene as a solvent whereas HE4 is prepared in presence of hexane as a solvent. Hexane is very poor soluble solvent whereas toluene is a moderately poor soluble solvent. Poor soluble solvent can not diffuse out very rapidly, thus a significant reduction of T_g occurs.

3.6. Light Transmission Property of Poly (HEMA)

A Topcon transmittance meter (Model No: TM-1) with a sensitivity of 5 nm was used to study the light transmission property of poly (HEMA) prepared by different solvent. The percentage of light transmission in HE2, HE3 and HE5 are 92%, 94% and 90%, respectively. According to ASTM test (ASTM D-1003), light transmission percentages above 85% are usually accepted as transparent. Poly (HEMA) prepared by different solvent looks transparent from direct observation also.

4. Conclusions

From the IR spectroscopy, we can say that vinyl double bond of HEMA is totally consumed after polymerization to form poly (HEMA). The equilibrium swelling is greater in HE4 (51.75%) whereas it is lower in HE5. Comparing HE1, HE2 and HE3, the SEM image of HE2 shows larger pore whereas HE3 shows smaller pore. Comparing HE4 and HE5, SEM image of HE5 shows larger pore. The BET surface area, cumulative pore volume and average pore diameter is greater in HE4 whereas it is lower in HE5 also. The glass transition temperature is higher in HE3 compared to HE1, HE2, HE4 and HE5. The percentage of light transmission of HE2, HE3 and HE5 are 92%, 94% and 90% from light transmission experiment. Poly (HEMA) prepared by different solvent looks transparent and could be further applicable as a transparent hydrophilic material for medical application.

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