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Preparation of hydrogels by photopolymerization of acrylates in the presence of Type I and one-component Type II photoinitiators

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ABSTRACT

Hydrogels were prepared by photoinduced polymerization of poly(ethylene glycol)monoacrylate (PEGMA) and poly(ethylene glycol)diacrylate ($n = 200$ and 700) (PEGDA) with Type I, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (I-2959) and one-component Type II initiators: (9-oxo-9H-thioxanthen-2-yloxy)-acetic acid ($TXOCH_2COOH$) and (9-oxo-9H-thioxanthen-2-yloxy)-sodium acetate ($TXOCH_2COO^-Na^+$). The swelling properties of hydrogels were investigated and observed to be excellent. Smooth morphology and no phase separation were observed from SEM micrographs of the hydrogels.

1. Introduction

The use of UV radiation to achieve polymerization of hydrogels supplies ease of operation, cost effectiveness and fast curing rates at room or physiological temperatures, produces minimal heat and, importantly, is an environmentally friendly technique. In addition, hydrogels, three-dimensional networks of hydrophilic polymers that are able to absorb large amounts of water, can be made to resemble the physical characteristics of soft tissues and they generally exhibit high permeability and good biocompatibility, making these materials attractive for use in tissue engineering applications [1]. Smart hydrogels are the ones that absorb and desorb large quantities of water in response to an environmental trigger such as changes in temperature, pH or concentration of some analyte [2]. In a cured system, an efficient polymerization process requires the presence of a photoinitiator (PI), which is converted into reactive radicals upon exposure to UV–vis light. In vivo applications, difficult polymerization conditions exist because biological systems entail a narrow range of acceptable temperature and pH, as well as an absence of toxic materials such as most monomers and organic solvents. Low light intensity, short irradiation time, physiological temperature, and low organic solvent levels do not damage biological systems [3,4]. All of these support the importance of the photoinitiators' efficiency, since a polymerization reaction initiated by a reactive photoinitiator results in low light intensity, short irradiation time and ambient temperature. Hence, a photoinitiator has high absorption at a specific wavelength of light to produce free radicals to initiate polymerization, which also provides biocompatibility, solubility in water, stability, and cytotoxity [5,6].

Over the last decade, various photoinitiators have been investigated to achieve better photopolymerization. Three major classes of photoinitiation, depending on the mechanism involved in photolysis, are radical photopolymerization through photocleavage, hydrogen abstraction, and cationic photopolymerization [5].

The initiators undergo cleavage to form radicals when exposed to light called 'Type I photoinitiators'. These photoinitiators include aromatic carbonyl compounds such as benzoin derivatives, benzylketals, acetophenone derivatives, and hydroxyalkylphenones [5,7,8]. Acetophenone derivatives, such as 4-(2-hydroxyethoxy) phenyl-(2-hydroxy-2-propyl)ketone (I-2959), have been used as photoinitiators to form hydrogels from acrylated polyethylene glycol (PEG) derivatives in several biomaterial studies [9,10].

Upon UV irradiation, photoinitiators such as benzophenone and thioxanthone as aromatic ketones undergo hydrogen abstraction from a hydrogen-donor as coinitiator to generate a ketyl radical and a hydrogen-donor radical [5,7]. We recently reported the syntheses of thioxanthone acetic acid derivatives as one-component Type II photoinitiators and it was found that they initiate the polymerization much more efficiently than two component systems in which light-absorbing and electron donating acidic sites are composed in independent molecules [11,12]. To increase the solubility of thioxanthone acetic acid derivatives in water, the sodium salt of thioxanthone acetic acid derivatives was synthesized due to the importance of water-soluble polymerization for environmental reasons [13].

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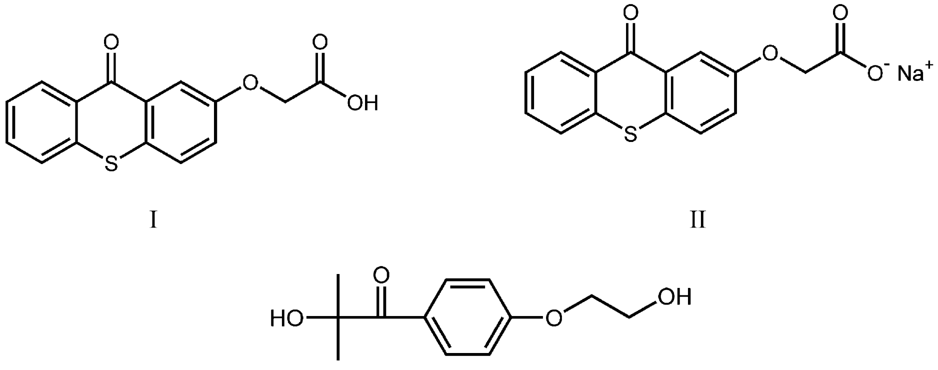


I

II

III

Chart 1. Structure of the photoinitiators.

In this study, we were dealing with the preparation of hydrogels by photoinitiated polymerization and observing the effect of one-component photoinitiators on the curing of PEG acrylates as well as observing the swelling (in water) behaviour of prepared hydrogels. The efficiency of one-component Type II initiators which are used for the preparation of hydrogels was compared with the well-known water-soluble acetophenone derivative Type I initiator, namely I-2959 (Chart 1).

The effect of crosslinked density on the percentage of swelling hydrogels was also investigated by changing the acrylate formulation and composition as well as the type of initiator.

2. Experimental

2.1. Materials

Poly(ethylene glycol)monoacrylate (PEGMA) and poly(ethylene glycol)diacrylate-200 (PEG-200DA) and 700 (PEG-700DA) were obtained from ABCR GmbH & Co.KG and Aldrich. 1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (a water-soluble UV initiator; commercially available as Irgacure-2959 (I-2959)) was purchased from CIBA Speciality Chemicals (Basel, Switzerland), and (9-oxo-9H-thioxanthen-2-yloxy)-acetic acid was synthesized as described previously [11,12].

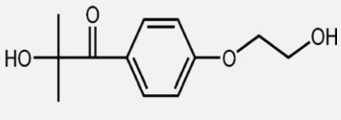
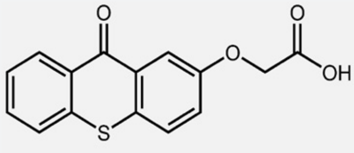
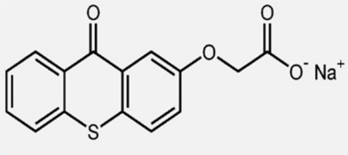
2.2. Instruments

For irradiation in a photopolymerization reaction, a photoreactor consisting of a 400 W medium pressure mercury lamp was used. Light intensity was measured by Radiometer (Macam UV203 Ultraviolet Radiometer).

2.3. Synthesis of (9-oxo-9H-thioxanthen-2-yloxy)-sodium acetate (TXOCH$_2$COO$^-$Na$^+$) [13]

2-(Carboxymethoxy) thioxanthone (0.62 g, 2×10^{-3} mol) was added to equimolar NaOH solution and after the addition, the

Table 1
Formulations, gelation times and conversion percentages of PEGMA, PEG-200DA and PEG-700DA in the presence of initiators.

Photoinitiator	Acrylate system			Gelation times (min)	Conversion (%)
	PEGMA	PEGDA			
		200DA	700DA		
 **I-2959**	99.90	–	–	0.50	100
	89.90	10	–	0.50	100
	79.90	20	–	0.50	100
	69.90	30	–	0.50	100
	89.90	–	10	0.50	99.80
	79.90	–	20	0.50	99.60
	69.90	–	30	0.50	100
 **TXOCH$_2$COOH**	99.90	–	–	2.00	100
	89.90	10	–	1.00	99.90
	79.90	20	–	1.00	94.00
	69.90	30	–	1.00	97.00
	89.90	–	10	1.00	74.80
	79.90	–	20	1.00	76.90
	69.90	–	30	1.00	94.40
 **TXOCH$_2$COO$^-$ Na$^+$**	99.90	–	–	15.00	92.90
	89.90	10	–	5.00	100
	79.90	20	–	3.75	100
	69.90	30	–	2.50	100
	89.90	–	10	8.00	86.30
	79.90	–	20	10.00	90.60
	69.90	–	30	10.00	96.60

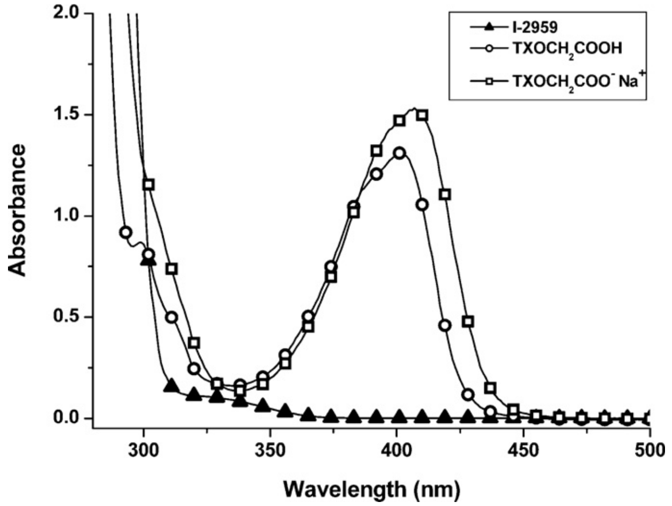


Fig. 1. The absorption spectra of photoinitiators [4×10^{-4} M], namely TXOCH$_2$COOH, TXOCH$_2$CO$^-$Na$^+$ and I-2959 in DMSO.

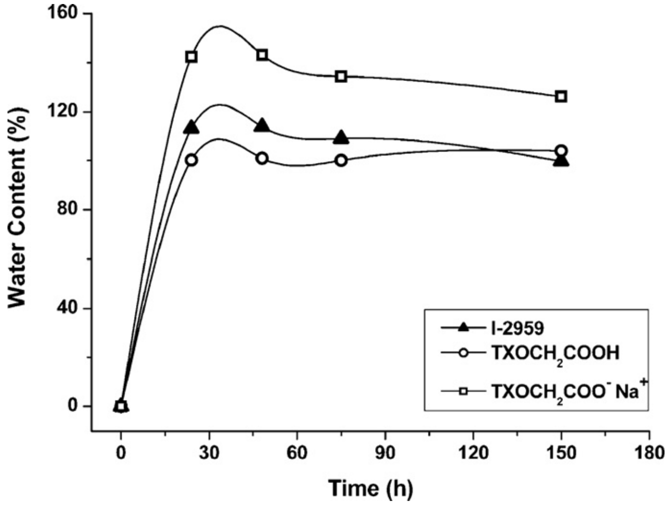


Fig. 2. Swelling behaviour of the hydrogels obtained by photoinitiation with different photoinitiators in PEGMA.

reaction mixture was refluxed at 100 °C for 24 h after which it was left to stand at room temperature overnight. The suspension was filtered and the solvent was removed by evaporation. The resulting yellow solid was dried in vacuum to obtain the desired compound.

UV (water): $\lambda_{max}(\varepsilon) = 409$ nm ($3800\ \mathrm{L\,mol^{-1}\,cm^{-1}}$). ^{1}H NMR (D$_2$O): δ 8.07–6.63 (m, 7H, aromatic), 4.41(s, 2H, CH$_2$). IR (KBr): 3057 (aromatic), 2980 (aliphatic), 1628 (s, C=O), 1590 (C=C).

Elemental analysis $C_{15}H_9NaO_4S$: Calc, C: 58.44; H: 2.94; S: 10.40 found, C: 57.84; H: 3.24; S: 9.77.

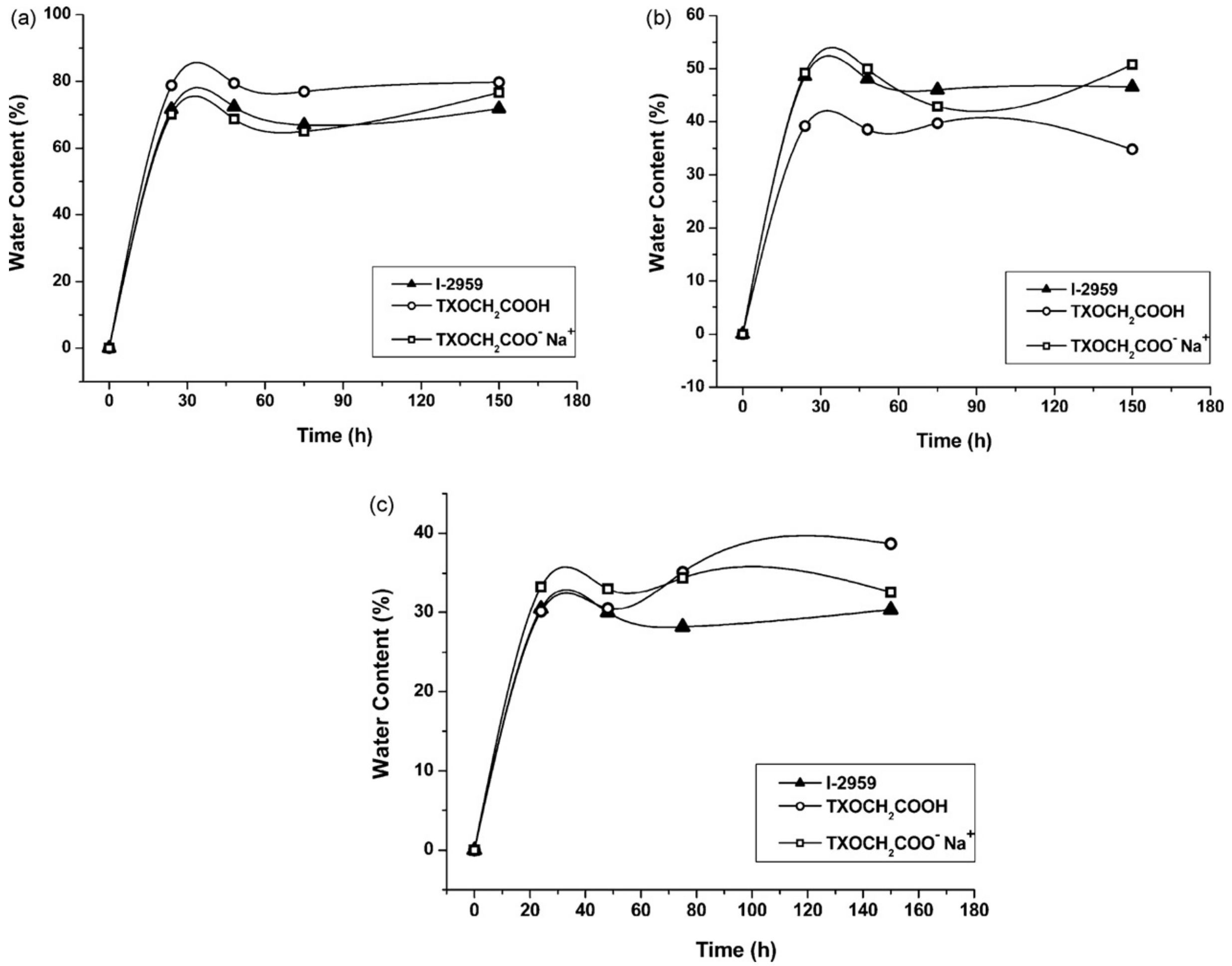


Fig. 3. Swelling behaviour of the hydrogels obtained by photoinitiation with different photoinitiators (PI = 0.1%, w/w) in 89.9% PEGMA: 10% PEG-200DA (a), in 79.9% PEGMA: 20% PEG-200DA (b), and in 69.9% PEGMA: 30% PEG-200DA (c).

2.4. Synthesis of hydrogels

Photocurable formulations were prepared gravimetrically by dissolving the initiators in the neat (solvent-free) monomers. Formulations were irradiated to form hydrogels with a 400 W medium pressure mercury lamp with a water cooling system in an air atmosphere until gellation occurred. Light intensity was measured as $I = 390\ \mathrm{W/m^2}$. Polymers were dried in a vacuum incubator at room temperature. Conversions were calculated for all samples gravimetrically.

2.5. Swelling studies

The swelling characteristics of the gels were investigated for at least three samples at room temperature. Samples of the cured polymer with a mass of 0.9 ± 0.1 g were placed into a beaker which was then filled with distilled water. Periodically, the samples were blotted free of surface water with filter paper, and the wet weight of the gel sample was measured. The samples were re-submerged in fresh distilled water. The swollen masses of the hydrogels were then compared with their dry masses in order to calculate the equilibrium water content (EWC) with the formula in Eq. (1):

$$\mathrm{EWC}\,(\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

W_d and W_s are the weight of the dry and swollen hydrogels, respectively. This process was continued until the sample appeared to have dissolved or for up to 150 h.

3. Results and discussion

3.1. Photopolymerization reactions

Photoinitiated polymerization of PEGMA was achieved for various formulations which consisted of either PEG-200DA or PEG-700DA as the crosslinking agents in the presence of $\mathrm{TXOCH_2COOH}$, $\mathrm{TXOCH_2CO^-Na^+}$ and I-2959 as initiators. The effect of the concentration of crosslinking agents on the hydrogel properties was also investigated. PEG-200DA and PEG-700DA were chosen as the crosslinking agents due to good solubility in PEGMA monomer. Polymerization studies were performed for various concentrations of the crosslinking agents, starting from 10 to 30%. The gravimetrically determined conversions of monomer to polymer are tabulated in Table 1.

Prepared formulations (see Table 1), which consist of various compositions were irradiated by medium pressure mercury light in an air atmosphere at room temperature. The concentration of photoinitiators was constant for all formulations (0.1%, w/w). Absorption properties of initiators in DMSO are given in Fig. 1.

Although the inhibition of oxygen on polymerization is very important, the hydrogels were prepared in an air atmosphere. I-2959, which can be classed as a Type I initiator, was chosen because Type I photoinitiators usually have very short triplet lifetimes, therefore do not suffer extensively from oxygen inhibition [5,7,14]. However, this is not the case for Type II systems which involve a bimolecular reaction between the triplet initiator and the synergist [7]. Nevertheless, in this study, one-component Type II initiators

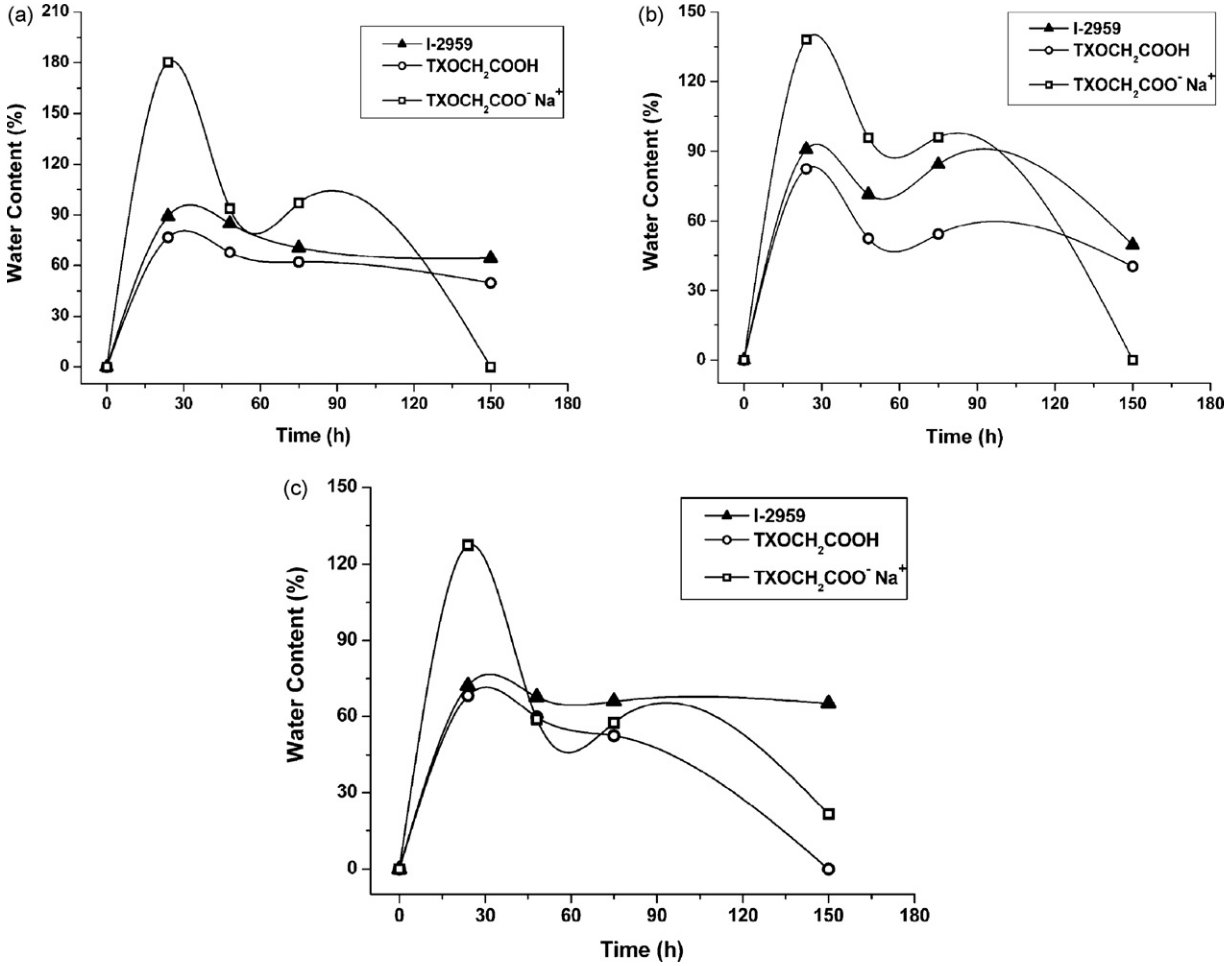


Fig. 4. Swelling behaviour of the hydrogels obtained by photoinitiation with different photoinitiators (PI = 0.1%, w/w) in 89.9% PEGMA: 10% PEG-700DA (a), in 79.9% PEGMA: 20% PEG-700DA (b), and in 69.9% PEGMA: 30% PEG-700DA (c).

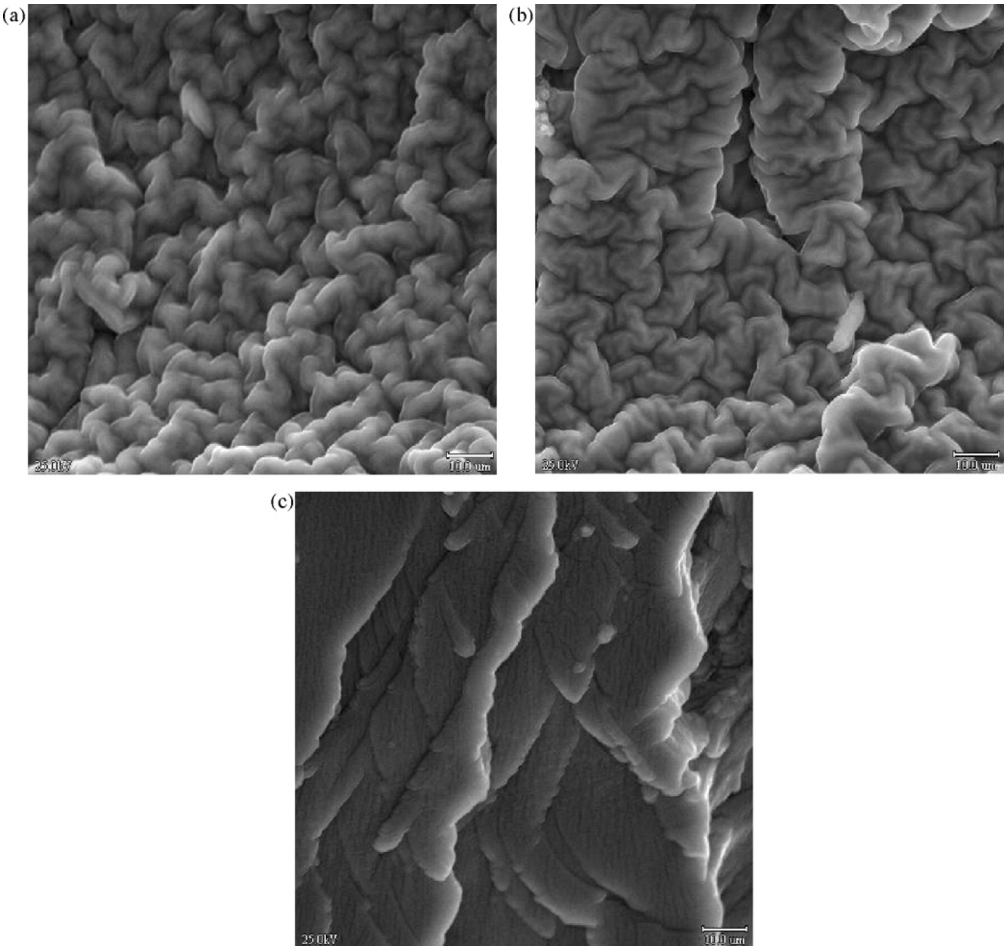


Fig. 5. SEM micrographs for hydrogels obtained by photoinitiation with different photoinitiators: $TXOCH_2COO^-Na^+$ (a), $TXOCH_2COOH$ (b), and I-2959 (c) in PEGMA system.

were used without adding any coinitiator and experiments were performed in air. A tertiary amine was deliberately not added to the formulations due to its plasticizing ability which would reduce the degree of cure and the molecular weight of the polymer.

As can be seen from Table 1, addition of diacrylate, PEG-200DA led to an increase in crosslinking density, and rapid curing was achieved in a short irradiation time. When a higher molecular weight of PEG-700DA was added to the formulations, gelation times were not changed for $TXOCH_2COOH$ and I-2959 but retardation of gelation time for $TXOCH_2CO^-Na^+$ was observed (see Table 1).

3.2. *Hydrogel swelling behaviour*

Hydrogel swelling properties are affected considerably by several factors such as the properties of the monomer solution, the

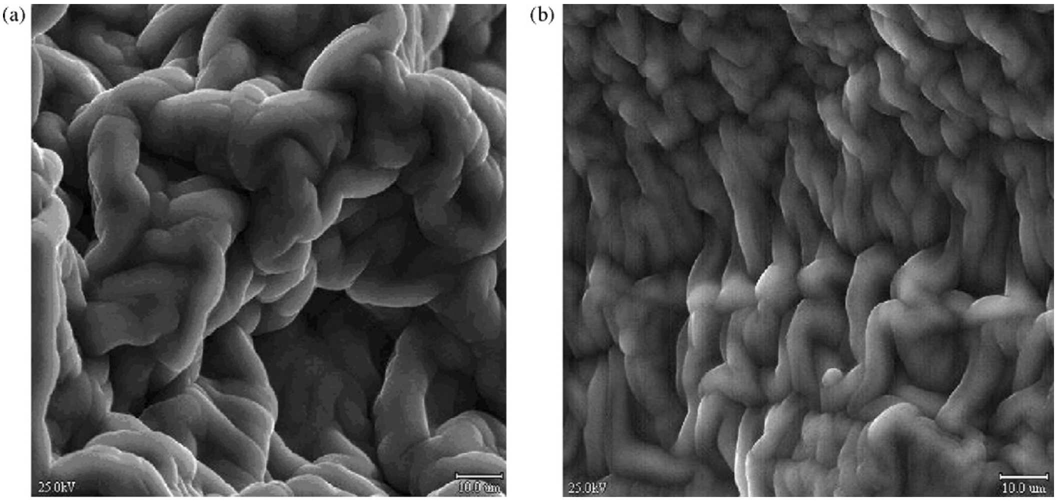


Fig. 6. SEM micrographs for hydrogels obtained by photoinitiation with different photoinitiators: $TXOCH_2COO^-Na^+$ (a) and $TXOCH_2COOH$ (b), in 69.9% PEGMA: 30% PEG-200DA system.

conditions of photopolymerization and the medium. A fundamental relationship exists between the swelling of a polymer in a solvent. The percentage of swelling is the most important parameter in swelling studies. The swelling behaviour of all hydrogels was evaluated using Eq. (1).

Fig. 2 gives the swelling behaviour of the hydrogels obtained in the presence of initiators, namely I-2959, $TXOCH_2COOH$ and $TXOCH_2COO^-Na^+$ for PEGMA. Maximum swelling levels were obtained in the first 25 h for all hydrogels then all hydrogels started to lose water.

The hydrogels which were prepared with $TXOCH_2COO^-Na^+$ had the highest degree of swelling. It is known that fast polymerization rates lead to less swelling. The reason for this is that higher monomer to polymer conversion in a short time induces more extensive crosslinking of the polymer, and makes the diffusion of water inside the network more difficult. The swelling properties of hydrogels containing PEG-200DA were changed by the concentration of PEG-200DA; when PEG-200DA is added to the hydrogel system, it is known that there is a change in the swelling ratio of the hydrogels, due to a decrease in the hydrophilic group number.

Increasing the diacrylate content in the formulations led to a decrease in the degree of swelling of the hydrogel (see Fig. 3).

Experimental studies were conducted to investigate the network structure of loosely crosslinked PEG hydrogels formed by the addition of PEG-700DA.

Gelation time was longer for $TXOCH_2COO^-Na^+$ compared to the formulation which consisted of PEG-200DA. The swelling degree of the hydrogels prepared in the presence of PEG-700DA was found to be much higher than formulations containing PEG-200DA (see Fig. 4).

A good inverse relationship was found between swelling and gelation times and the water content percentage went up for all formulations containing various amounts of PEG-700DA. This must be due to the structure of the crosslinking agent which has a longer and more flexible chain structure, compared to PEG-200DA. Flexibility of the PEG-700DA segment of the gel increases the swelling rate. Its longer chain length provides a larger space among prepared hydrogels. As a result, water diffuses into the gel structure more easily and in higher amounts. The most effective initiators were found to be $TXOCH_2COO^-Na^+$ and $TXOCH_2COOH$, respectively. The initiator influences not only the polymerization speed but also the structure and the uniformity of the hydrogel. Efficient initiators will cause inhomogenity of the hydrogels due to the accumulation of polymerization heat, while the less efficient ones may lead to a smooth free radical reaction and a homogenous hydrogel.

The three micrographs of the results of electron scanning microscopy of the hydrogels are shown in Figs. 5 and 6.

The three micrographs indicate a smooth morphology and no phase separation.

4. Conclusion

Poly(ethylene glycol)-based hydrogels were prepared using the photoinitiated polymerization method. Type I and one-component Type II photoinitiators were employed for the preparation of PEG-based hydrogels and the efficiency of the photoinitiators was also tested. The effect of molecular weight of diacrylate on the swelling properties of hydrogels was determined and it was found that PEG-700 DA led to an increase in the swelling rate due to the longer and flexible chain structure. In conclusion, photochemically prepared poly(ethylene glycol)-based hydrogels exhibited water uptake properties extremely well. These hydrogels may find use as drug delivery depots and/or biomedical materials due to their good swelling characteristics.

Acknowledgements

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