

Copolymerization and Properties of Multicomponent Crosslinked Hydrogels*

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Abstract A series of multicomponent hydrogels were prepared by the copolymerization of hydrophobic silicon-containing monomer 3-bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate (SiMA) with the solvent-responsive monomers 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl pyrrolidone (NVP) and thermosensitive monomer *N,N*-dimethyl acrylamide (DMA). 2-Hydroxy-2-methyl phenyl acetone (D-1173) was chosen as UV initiator and five different dienes/triene monomers were selected as crosslinking agent in order to select the best crosslinker. The ethanol extraction experiments as well as the FTIR, DSC and TG results showed that the copolymerization was effective. The optical, permeability, and mechanical analysis results demonstrated that the obtained hydrogels were highly transparent with good oxygen permeability and mechanical properties. And the impact of crosslinker on the mechanical properties of the hydrogels was also discussed in detail. The basic results demonstrated that the obtained hydrogels had good stimuli-responsive effects to both pH value and solvent.

Keywords: Multicomponent hydrogel; Silicon-containing monomer; Hydrophilic monomer; Crosslinker; Stimuli-responsive.

INTRODUCTION

Hydrogels have been generally considered as three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining large amounts of water in the swollen state^[1–4]. Hydrogels usually have one or more impressive properties such as biocompatibility, mechanical strength, optical properties, oxygen permeability^[5], etc. A lot of functional hydrogels have been prepared and extensively studied due to the above features and their promising applications in the fields of biomaterials and biotechnologies such as tissue engineering, artificial organs, drug delivery, and contact lens^[6–13].

Recently, stimuli-responsive hydrogels have attracted much attention because they are suitable to be sensors and actuators in biotechnical applications^[14, 15]. Mahdavinia *et al.* synthesized chitosan-g-poly(AA-co-AAm) hydrogels and investigated their pH-sensitivity and capability of ion exchanging^[16]. Pastoriza *et al.* prepared macroporous poly(*N,N*-dimethylacrylamide) hydrogels and found that the solvent response of hydrogels was ascribed to the store and draining capacity of macropores^[17]. Zhao *et al.* prepared polyaspartic acid resin by polysuccinimide (PSI) and found that the water absorbent capacity of the resin was influenced strongly by PSI concentration and terminal pH^[18]. Rajagopal *et al.* prepared a hydrogel using peptides and found the pH-sensitive folding was not only dependent on the net peptide charge but also on the exact position of substitution within the peptide sequence^[19].

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Soft contact lenses are also made of hydrogels that came out later in 1960. Thereafter, the development of contact lenses is heading towards high oxygen permeability^[5, 20–22] and high hydrophilicity^[23, 24]. The conventional hydrogel lenses prepared from hydrophilic monomers such as 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl pyrrolidone (NVP)^[25] have good biocompatibility but limited oxygen permeability. One known way to solve this problem is to add high oxygen permeable silicon-containing monomers^[26–28], which can improve both oxygen permeability and mechanical properties. Silicone materials have become increasingly important as ingredients for preparing hydrogels in biomaterials and biotechnologies^[29–31]. Lai *et al.* prepared two different types of silicone materials^[32–35]. One was polyurethane-polysiloxane prepolymers in which linear polysiloxane was used, and the other was methacrylates with silicon-containing groups in the side chain, such as methacryloxypropyl tris(trimethylsiloxy)silane. Pozuelo *et al.*^[36] compared the transport of oxygen, water and naked ions across aqueous hydrogels and silicone hydrogels. Kaczmarek *et al.*^[37] altered the composition and structure of silicone hydrogels to achieve controlled release of dexamethasone. Wang *et al.*^[38] prepared simultaneous interpenetrating network silicone hydrogels by polymerization of 2-methacryloyloxyethyl phosphorylcholine and vinyl ether terminated polydimethylsiloxane macromonomer.

Crosslinkers, usually containing two or more double bonds, play an important role in bridging linear polymers and forming a crosslinking network^[39, 40]. Argun *et al.* prepared a series of NIPAM hydrogels using four allyl oxygen ethane ammonium bromide and *N,N'*-methylene bisacrylamide (MBA) as crosslinkers and found the crosslinker had influence on the mechanical properties of the hydrogels^[41]. Wei *et al.* used glyoxal bis(diallyl acetal) and MBA as crosslinkers to prepare NIPAM-*co*-AA hydrogels and studied the influence of the nature and content of different crosslinkers on the properties of the hydrogels such as swelling ratio, polymer-water interaction parameter, elastic moduli and effective crosslinking density^[42]. Lou *et al.* discussed the influence of crosslinkers on HEMA hydrogels using five kinds of crosslinkers^[43].

In this work, silicon-containing monomer was added to the conventional HEMA and NVP copolymer hydrogels and DMA was added to ensure the water content of the hydrogels. The efficiency of copolymerization and the properties of the obtained hydrogels such as the optical, mechanical and oxygen permeation properties were studied in detail. Moreover, different types of crosslinkers were used in the hydrogels to evaluate their impact on the mechanical properties and heat stability of the hydrogels. The basic research showed that the prepared hydrogels presented multiple stimuli-responsive behaviors.

EXPERIMENTAL

Materials

3-Bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate (SiMA, CAS No: 69861-02-5) was purchased from Cornelius Specification Ltd. 2-Hydroxyethyl methacrylate (HEMA) was obtained from BASF Chemical Co. *N,N*-Dimethyl acrylamide (DMA) was bought from Aldrich Chemical Co. *N*-Vinyl pyrrolidone (NVP), ethyleneglycol dimethacrylate (EGDMA) and 2-hydroxy-2-methyl benzene acetone (D-1173) were purchased from TCI (Shanghai) Development. Methylacrylic acid allyl ester (AMA), 1,6-hexanediol diacrylate (HDDA), *N,N'*-methylene bisacrylamide (MBA) and trimethylolpropane triacrylate (TMPTMA) were got from Aladdin Chemical Reagent Co. Ethanol was purchased from Sino Pharm Chemical Reagent Co. Some of the chemicals were purified by distillation under reduced pressure before use.

Preparation of Multicomponent Copolymer/Hydrogel

For preparing hydrogels, the photoinitiator D-1173 and crosslinker were added in flask first. And then HEMA, NVP, SiMA were added in orders. At last, certain amount of DMA was added into the mixture. The percentage of each component is listed in Table 1. The formulation mixture was stirred in dark for two hours in beaker at room temperature. And then the mixture was UV initiated for copolymerization in double stack polypropylene molds for three hours at room temperature. The newly formed copolymer was purified by extraction with ethanol for sixteen hours and then hydrated in boiling water for four hours. The obtained hydrogels were preserved in phosphate buffered saline.

Table 1. The copolymerization formulations for the multicomponent hydrogels with different percentages of hydrophobic monomer SiMA

Hydrogel	0	I	II	III	IV	V
SiMA (%)	0	10	20	30	40	50
HEMA (%)	59.5	52.5	45.5	38.5	31.5	24.5
NVP (%)	25.5	22.5	19.5	16.5	13.5	10.5
DMA (%)	15	15	15	15	15	15
AMA (%)	1	1	1	1	1	1
D-1173 (%)	0.2	0.2	0.2	0.2	0.2	0.2

Measurements of Extractables

The obtained film was dried to constant weight in vacuum oven, and the dry weight M_1 was measured. And then the dried film was extracted with ethanol for sixteen hours, and dried to constant weight again. The dry weight M_2 was measured. The extractables (β) was calculated by the following equation: $\beta = [(M_2 - M_1)/M_1] \times 100\%$.

Measurements of Equilibrium Water Content

The obtained film was dried by vacuum oven, and the dry weight G_1 was accurately measured. Then the dried film was boiling water hydrated for 4 h. The film was placed between two pieces of filter paper to blot up the water on the surface. Finally, the wet weight G_2 was measured. The water content (η) was calculated by the following formulation: $\eta = [(G_2 - G_1)/G_1] \times 100\%$.

Fourier Transform Infrared (FTIR) Spectroscopy

The formulation mixture and extractables with ethanol were characterized by a Nicolet 5700 FTIR spectrometer using the KBr pellet technique.

Differential Scanning Calorimetry (DSC)

The glass-transition temperatures (T_g) of hydrophilic homopolymers, silicone homopolymer and the target copolymers were measured using a modulated DSC (Modulated DSC-8230, TA Instruments) coupled with a refrigerated cooling system. Nitrogen was used as purge gas and cooling gas at the flow rate of 20 mL/min and 100 mL/min respectively. These hydrogels were heated from $-50\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ at a heating rate of 2.5 K/min .

Thermogravimetric Analysis (TG)

The heat stability of multicomponent copolymers was characterized using thermogravimetric analysis (NETZSCH TG209). The sample was heated from $50\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$ and the heating rate was 10 K/min with the protection of nitrogen atmosphere.

Measurements of Optical Properties

The average transmittance of visible light of the hydrogels was measured using a721 spectrophotometer at the range from 440 nm to 800 nm. The refractive index was measured using a WYA (2WAJ) Abbe refractometer. The power was tested using JD-2100 Full-automatic Focimeter. Definition was evaluated by the results of back vertex power, cylinder vertex power and cylinder axial position.

Measurements of Mechanical Strength

The elastic modulus and elongation at break were measured using a Labthink XLW Auto Tensile Tester at a stretching rate of 100 mm/min .

Measurements of Oxygen Permeability

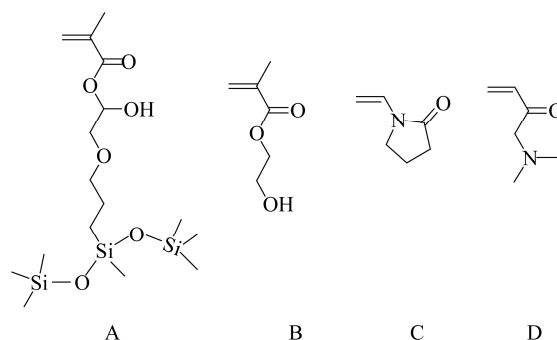
The oxygen permeability coefficient of the hydrogels was measured using an oxygen permeation analyzer (201T Oxygen permeameter) via AC polarography.

Measurements of Geometric Parameters

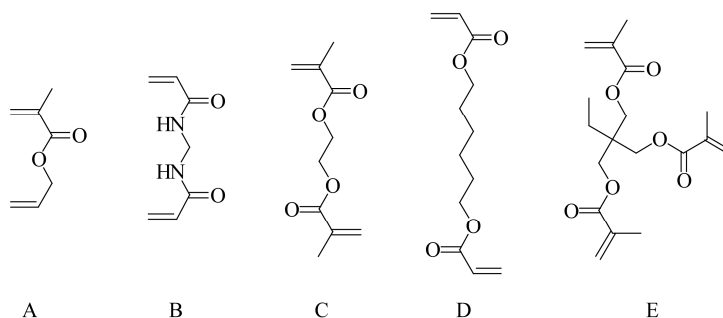
The diameter and the center thickness of the hydrogels were measured using a PDP-4025W projection comparator with one hundred times of magnification. Ten samples were measured from each series of hydrogels in order to get the average value and standard deviation.

RESULTS AND DISCUSSION

In order to prepare multicomponent hydrogels, it is important to make sure all the monomers were copolymerized together into one relatively homogenous system. In this paper, bulk polymerization was adopted because all the monomers were miscible together without help of solvent. UV radiation was adopted to initiate the copolymerization since UV initiated polymerization is much faster and easier to control compared to thermal initiated polymerization. Four different monomers listed in Scheme 1 were selected for making copolymers. Among them, SiMA is a hydrophobic monomer with high oxygen permeability, HEMA and NVP are hydrophilic monomers with solvent-responsive characteristics, and DMA is also a hydrophilic monomer with thermo sensitivity. Five different types of multicomponent hydrogels named hydrogel I to V were prepared using the formulations listed in Table 1. The percentages of SiMA increased from 10% to 50% and the percentages of HEMA and NVP decreased correspondingly. In order to compare the crosslinking effect of different crosslinkers, five different kinds of crosslinkers listed in Scheme 2 were used and another series of hydrogels named VI to X were prepared using the formulations listed in Table 2. In this table, the percentage of each monomer was fixed and five different crosslinkers were added at a molecular ratio of olefinic functional groups from 0.1% to 1.3%.



Scheme 1 The molecular formulas of four monomers used for preparing multicomponent hydrogels: (A) hydrophobic and high oxygen permeability monomer, 3-bis(trimethylsilyloxy) methylsilylpropyl glycerol methacrylate (SiMA), (B) solvent-responsive monomer, 2-hydroxyethyl methacrylate (HEMA), (C) solvent-responsive monomer, *N*-vinyl pyrrolidone (NVP) and (D) thermo-sensitive monomer, *N,N*-dimethyl acrylamide (DMA)



Scheme 2 The molecular formulas of five crosslinkers used for preparing crosslinked hydrogels: (A) methacrylic acid allyl ester (AMA), (B) *N,N'*-methylene bisacrylamide (MBA), (C) ethyleneglycol dimethacrylate (EGDMA), (D) 1,6-hexanediol diacrylate (HDDA) and (E) trimethylolpropane triacrylate (TMPTMA)

Table 2. The copolymerization formulations for the multicomponent hydrogels with different types of crosslinkers

Hydrogel	VI	VII	VIII	IX	X
SiMA (%)	50	50	50	50	50
HEMA (%)	24.5	24.5	24.5	24.5	24.5
NVP (%)	10.5	10.5	10.5	10.5	10.5
DMA (%)	15	15	15	15	15
Crosslinker	AMA	MBA	EGDMA	HDDA	TMPTMA
D-1173 (%)	0.2	0.2	0.2	0.2	0.2

Because it is impossible to achieve 100% conversion of the monomer in the bulk polymerization, the typical way is to extract unreacted monomer using water or solvent. The ratio of the extractables is directly decided by the extent of copolymerization. The hydrogel II in the Table 1 (20 wt% SiMA) was adopted to study relationship between the amount of the extraction residues with different reaction time, and the results are shown in Fig. 1, where ethanol was used as the extraction solvent to remove small molecular residues. It is clear that as the UV-cured reaction time increased, the amount of the extractables decreased at a near linear trend. When the reaction time reached 180 min, the extractables was only about 4%, which indicated that the reaction was almost completed.

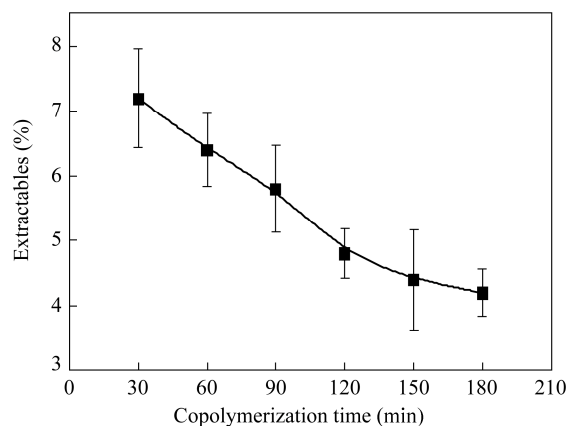


Fig. 1 The percentage of extractables of the hydrogel II (20 wt% SiMA) as the function of UV-cured copolymerization time

Figure 2 shows the FTIR spectra of the mixture of the monomers and the extractables, respectively. The disappearances of Si—C stretching vibration peak at 1260 cm^{-1} and Si—O—Si peak at 1070 cm^{-1} in the spectrum of extractable residues in comparison with that of the mixture of the reaction monomers illustrated that the silicon-containing monomer was copolymerized into the copolymer. The peaks in the range of $2967\text{--}2807\text{ cm}^{-1}$, $1452\text{--}1032\text{ cm}^{-1}$, $850\text{--}767\text{ cm}^{-1}$ as well as C—N stretching vibration at 1297 cm^{-1} and C=C peak at 1636 cm^{-1} were all disappeared, which meant most of the hydrophilic monomers were involved in the copolymerization. The characteristic peak of monosubstitute benzene ring at $850\text{--}767\text{ cm}^{-1}$ was disappeared which meant the initiator reacted completely. From the above analysis, it is clear that the majority of the monomers was involved in the copolymerization and the copolymerization was effective.

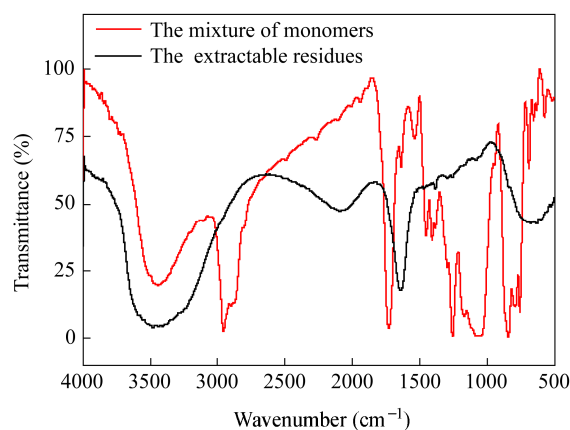


Fig. 2 FTIR spectra of the mixture of the reaction monomers and extractable residues

Figure 3 shows the modulated DSC analysis for homopolymers of PHEMA, PVP, PDMA and PSiMA at the temperature range from $-50\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$. PHEMA and PSiMA had no obvious glass transition temperature as shown from Figs. 3(a) and 3(b), while the glass transition temperatures of PVP and PDMA were $184\text{ }^{\circ}\text{C}$ and $129\text{ }^{\circ}\text{C}$, respectively as shown in Figs. 3(c) and 3(d). The glass transition temperatures we measured for PVP and PDMA were close to the values reported by other references or polymer vendors^[44, 45].

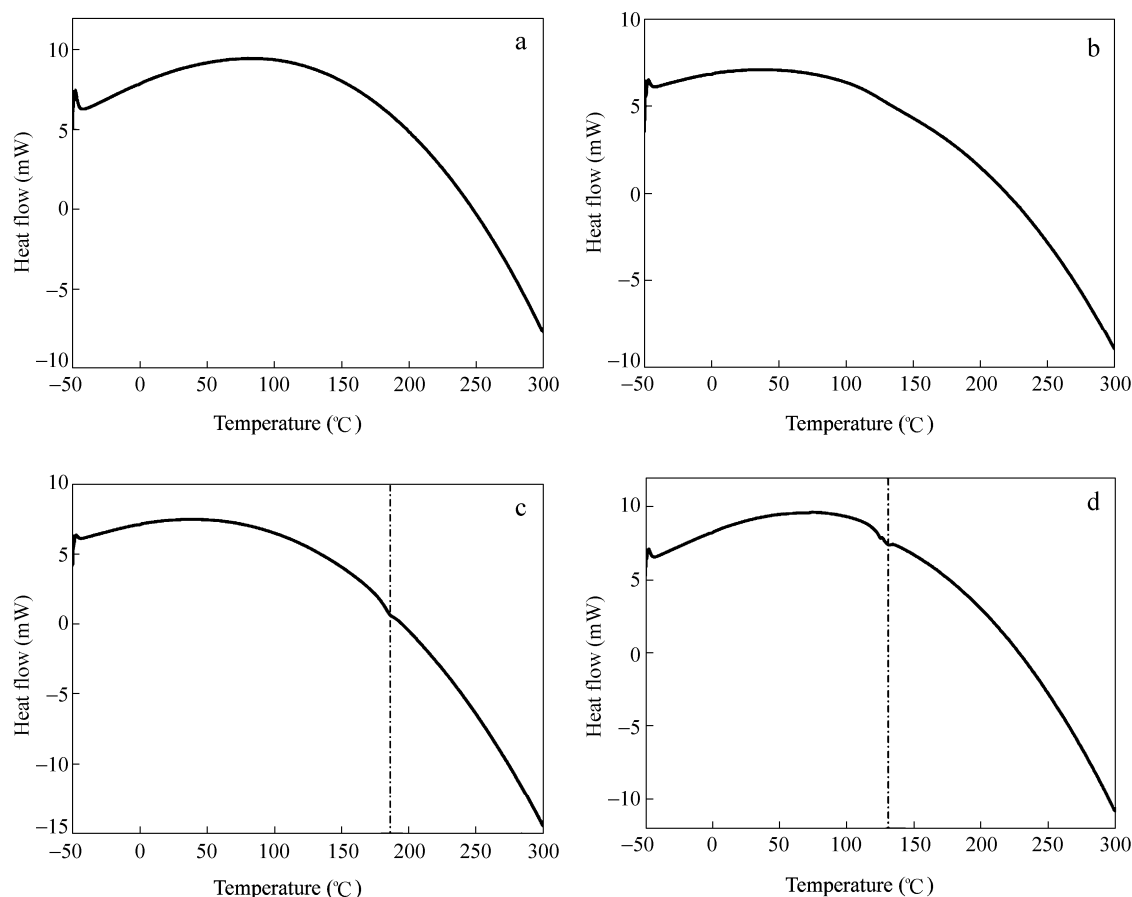


Fig. 3 DSC results of homopolymers: (a) PSiMA, (b) PHEMA, (c) PVP and (d) PDMA

Figure 4 shows modulated DSC analysis for resultant copolymers with different SiMA contents. As shown in Fig. 4, no obvious glass transition temperature was observed in all these copolymers when different percentages of SiMA were added. It indicated that rather than a mixture of homopolymers, the resultant products were well copolymerized.

Figure 5(a) shows TG analysis for the resultant copolymers with different SiMA contents. There was no obvious weight loss before the temperature of $250\text{ }^{\circ}\text{C}$. When the temperature reached about $280\text{ }^{\circ}\text{C}$, the weight lost dramatically, which meant the decomposition and the pyrolysis of the molecular chain started at this temperature. The TG analysis of the copolymers with different crosslinkers also showed no big difference as shown in Fig. 5(b). The heat stability of all these hydrogels was similar and not influenced by either the percentage of SiMA or the type of the crosslinker.

When the copolymers were hydrated by pure water, the obtained hydrogels had transparent appearance seen with naked eyes. The full optical tests were performed on the hydrogels and the results are shown in Table 3. The light transmittances of the hydrogels were higher than 95% and they were not influenced by the content of SiMA component. The definition was measured and calculated to rate the quality of the hydrogel. The

definitions was around 2–3, which means they are good/excellent materials for making contact lens (The values of definition have 15 grades, in which grade 1 indicates that the hydrogel is the best material used as contact lens while grade 15 means the worst). The refractive index of the hydrogels increased with the increase of SiMA percentage. Because the silicon-containing monomer was more hydrophobic than those hydrophilic monomers, the water content decreased with the increase of SiMA content.

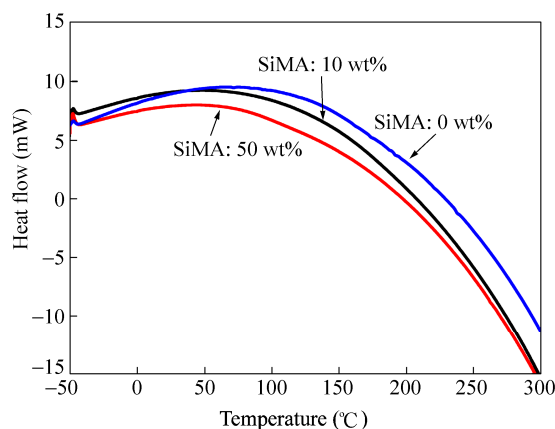


Fig. 4 DSC results for copolymers with the SiMA percentages of 0 wt%, 10 wt% and 50 wt%

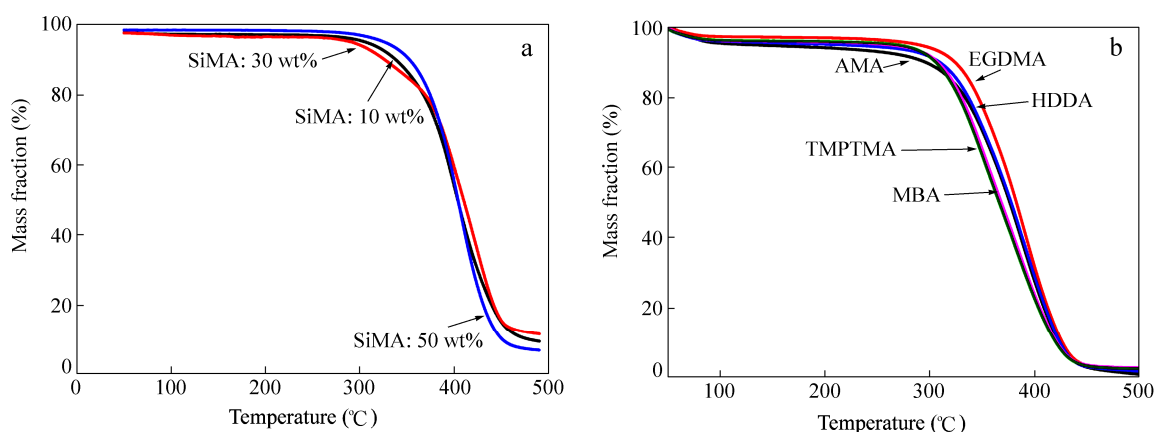


Fig. 5 (a) TG results for the copolymers listed in Table 1 with the SiMA percentages of 10 wt%, 30 wt% and 50 wt%, (b) TG results for the copolymers listed in Table 2 with different crosslinkers

Table 3. Optical and oxygen permeability properties of the hydrogels

SiMA content (wt%)	10	20	30	40	50
Light transmittance (%)	98.3	96.9	97.8	98.2	99.0
Definition	2.7	3.2	3.1	3.8	2.8
Refractive index	1.331	1.360	1.382	1.399	1.430
Oxygen permeability coefficient [10^{-11} cm ² /s]	19.6	18.2	17.9	20.4	35.7

A relatively high permeability to oxygen could effectively avoid corneal diseases^[46]. The conventional hydrogel was made of HEMA, mainly in the form of homogeneous transparent gels^[47–50]. But the oxygen permeability coefficient of PHEMA hydrogels was about 7×10^{-11} cm²/s, which was considered rather low and limited its application to a long-term wear. As shown in Table 3, when the percentage of SiMA monomer of the hydrogel was 50%, the oxygen permeability coefficient was 35.7×10^{-11} cm²/s, which reached about five folds higher than that of the conventional ones. All these results meant that the hydrogels might be good candidate for contact lens.

Mechanical properties were crucial factors for the applications of hydrogels. Figure 6(a) shows the relationship between elastic modulus and the SiMA content. The elastic modulus increased with the increase of SiMA content. Figure 6(b) shows the relationship between elongation at break and the SiMA content. There was no an obvious tendency of elongation at break with the change of the SiMA content. The results in Fig. 6(b) showed fine elasticity that the hydrogel can be horizontally stretched more than two folds.

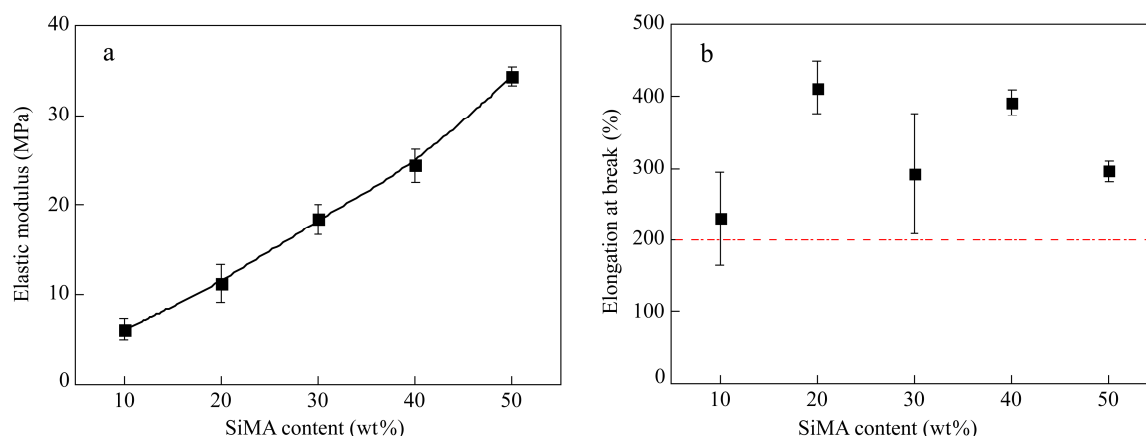


Fig. 6 Dependence of mechanical properties on the SiMA content of hydrogels (a) elastic modulus and (b) elongation at break

Because normally it is difficult to crosslink multiple monomers with different polarity and solubility to form a relatively homogeneous hydrogel, it is important to choose the suitable crosslinker. Five different types of crosslinkers with the molecular ratio of alkylene groups from 0.1% to 1.3% were added to evaluate their crosslinking effect in forming hydrogels. It was clear for all the five different types of crosslinkers, that the elasticity modulus increased (Fig. 7a) and the elongation at break decreased (Fig. 7b) as the ratio of crosslinker increased. This was because the crosslinking degrees of hydrogels increased with the increase of crosslinker, and higher crosslinking degrees resulted in the higher elasticity modulus and lower elongation at break.

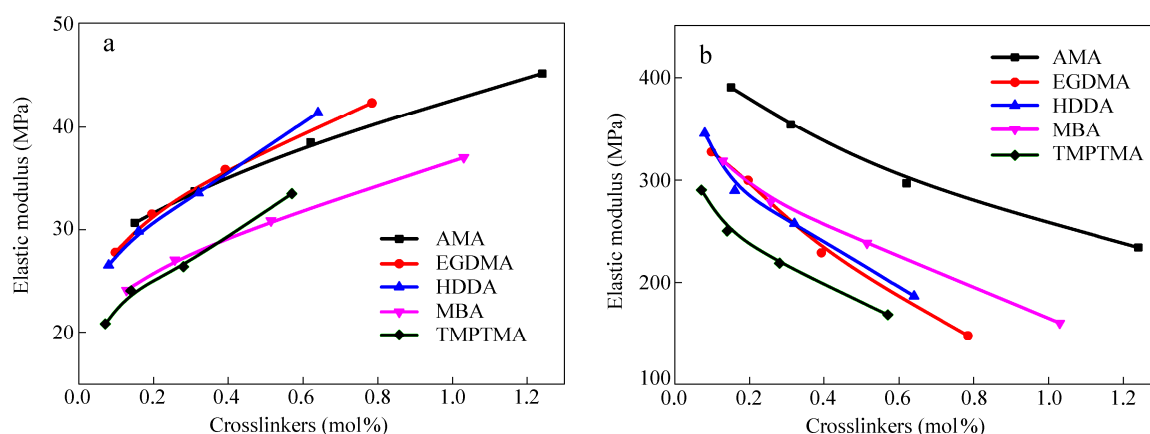


Fig. 7 (a) The statistical curves show the relationships between elasticity modulus and the molecular ratio of alkylene group in crosslinkers; (b) The statistical curves show the relationships between elongation at break and the molecular ratio of alkylene group in crosslinkers

Figure 8(a) shows the influence of the crosslinkers on the extractables. It is obvious that as the content of the crosslinker increased, the amount of extractables decreased. And among all the crosslinkers, the hydrogels crosslinked by TMPTMA have the biggest amount of extractables. Figure 8(b) shows the relationship between

equilibrium water content and crosslinkers. The water contents of the hydrogels crosslinked by AMA or MBA were higher while the water contents of those crosslinked by EGDMA, HDDA and TMPTMA were lower.

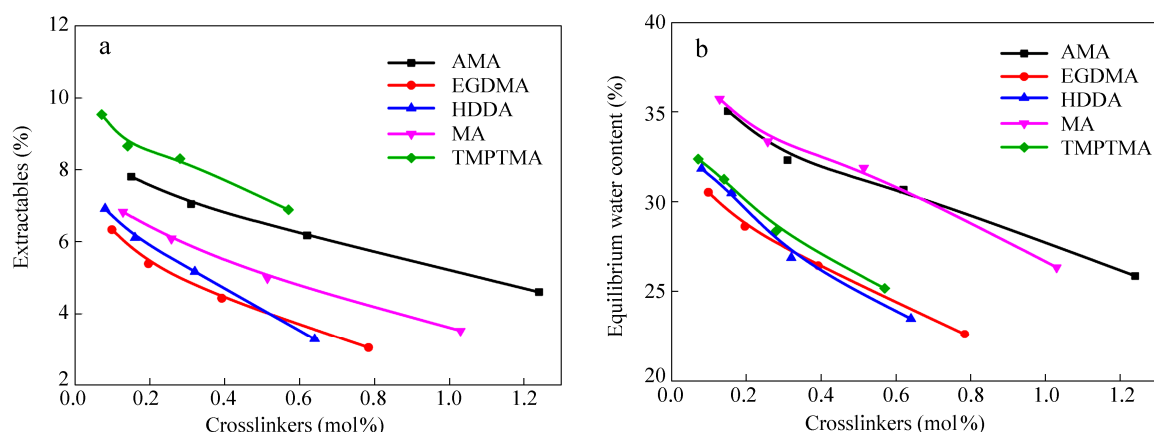


Fig. 8 (a) The statistical curves showing the relationship between extractables and the molecular fraction of alkylene group in crosslinkers, (b) the statistical curves showing the relationship between equilibrium water content and the molecular fraction of alkylene group in crosslinkers

Figure 9(a) shows the relationship between the diameter of the hydrogel and the SiMA ratio. The diameter decreased with the increase of SiMA content, but the decrease of the diameter slowed down with the increase of the SiMA content from 40 wt% to 50 wt%. Figure 9(b) shows the relationship between the center thickness of the hydrogel and the SiMA content. The center thickness decreased when the SiMA content increased. The change trends of the diameter and the center thickness were consistent which meant that the volume of the hydrogel became smaller with the increase of the SiMA content.

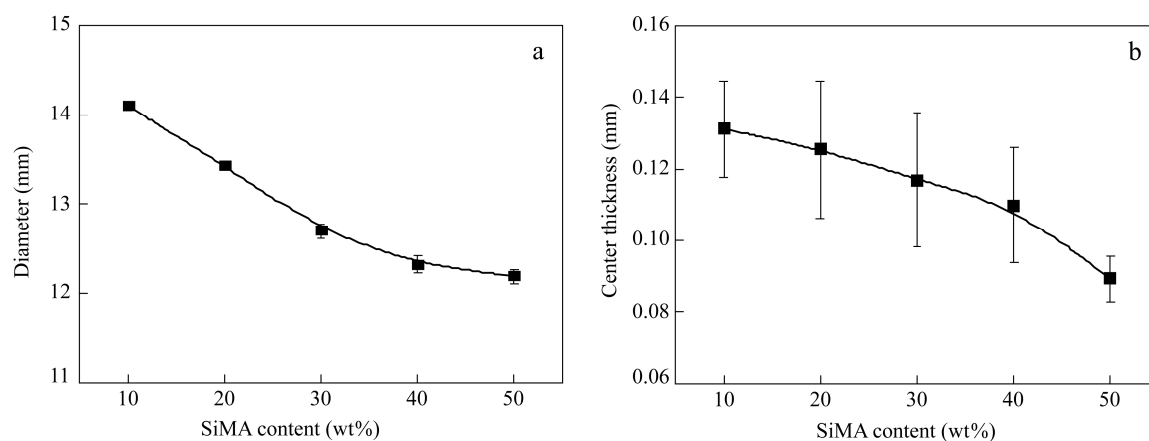


Fig. 9 (a) Diameter of multicomponent hydrogels as a function of the SiMA content and (b) Center thickness of multicomponent hydrogels versus the SiMA content

Since the multicomponent hydrogels were copolymerized using different stimuli-sensitive monomers, they might present different stimuli-responsive behaviors. The basic research showed that they had remarkable base-responsive and ethanol-responsive properties. The hydrogel containing 50 wt% of SiMA and 0.2 wt% of AMA was chosen to study their stimuli-responsive behavior. As shown in Fig. 10(A), the hydrogel swelled about 1.8 times bigger in the pH = 14 solution, after the gels were soaked in the solutions of different pH values for 4 h. And Fig. 10(B) shows the hydrogel swelled about 1.6 times bigger in the solvent of ethanol after the gels were also soaked in different solvents for 4 h.

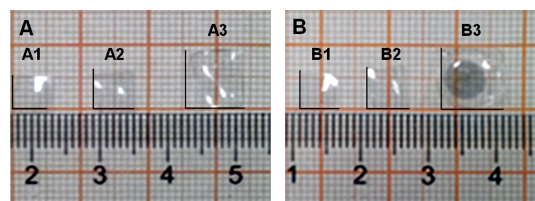


Fig. 10 (A) The sizes of multicomponent hydrogels in the solution of different pH values: (A1): pH = 1, (A2): pH = 7 and (A3): pH = 14, (B) the sizes of multicomponent hydrogels in different solvents: (B1) H₂O, (B2) *n*-Hexane, (B3) ethanol

Based on the above researches, the multicomponent hydrogels were good candidate for biomaterials and might have broad applications in drug delivery, contact lenses, artificial tissues and so on.

CONCLUSIONS

A series of multicomponent copolymers were prepared by the copolymerization of silicon-containing monomer SiMA with hydrophilic monomers HEMA, NVP, DMA together. FTIR, DSC and TG analyses demonstrated that the copolymerization reaction was complete, and the obtained materials existed as relatively homogeneous copolymers with good heat stability. The optical, oxygen permeation and mechanical tests showed that the obtained hydrogels possess good light transmittance, improved oxygen permeability, high mechanical strength, and good elongation at break. The basic results also demonstrated that the obtained hydrogels had good stimuli-responsive effect to solvent and pH values.

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