

## Self-healing of Poly(2-hydroxyethyl methacrylate) Hydrogel through Molecular Diffusion

(Swa-Pemulihan Hidrogel Poli(2-hidroksietil metakrilat) melalui Penyusupan Rawak Molekul)

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### ABSTRACT

*Synthetic materials that are capable of healing upon damage are being developed at a rapid pace because of their many potential applications. Here, new healing chemically cross-linked hydrogel of poly(2-hydroxyethyl methacrylate) (pHEMA) was prepared. The healing hydrogel was achieved by heating above its glass transition ( $T_g$ ). The intermolecular diffusion of dangling chain and the chain slippage led to healing of the gel. The peaks in attenuated total reflectance (ATR) confirmed that hydrogel was formed while rheological studies had determined the minimum for healing temperature is 48.5°C. The results showed that ratio stress of the healable hydrogel can reach until 92 and 91% of first and second healing cycle, respectively. The morphology of the sample was carried out to evaluate the self-property of hydrogel.*

*Keywords: Chain slippage; intermolecular diffusion; self-healing hydrogel; temperature*

### ABSTRAK

*Keupayaan swa-pemulihan pada bahan sintetik banyak digunakan dalam aplikasi perubatan serta aplikasi-aplikasi yang berkaitan. Suatu hidrogel baharu iaitu poli(hidroksietil metakrilat) telah disediakan melalui tindak balas kimia. Swa-pemulihan hidrogel berlaku apabila diberikan haba melebihi suhu peralihan kaca ( $T_g$ ) dan gel yang telah dipotong bercantum semula melalui proses penyusupan rawak molekul dan penggelinciran rantai. Puncak spektrum yang ditunjukkan dalam ATR mengesahkan proses taut silang yang berlaku dalam hidrogel tersebut. Suhu pemulihan minimum pula telah ditentukan oleh kajian reologi. Hasil ujian tensil membuktikan kekuatan hidrogel pemulihan berupaya mencapai sehingga 92% pada kitaran pertama dan 91% pada kitaran kedua. Ujian morfologi telah dijalankan bagi mengenal pasti sifat pemulihan hidrogel tersebut.*

*Kata kunci: Penggelinciran rantai; penyusupan molekul; suhu; swa-pemulihan hidrogel*

### INTRODUCTION

Self-healing materials possess the ability to repair themselves in response to damage leading to a new route towards safer, longer-lasting products (Blaiszik et al. 2010; Dohler et al. 2013). In recent years there is fast growing interest on a variety of self-healing polymers (Chen et al. 2012; Maes et al. 2012; Murphy & Wudl 2010). Self-healing mechanism in bulk polymer materials are either based on release of repair agents upon damage (Lee et al. 2011) or on the inclusion of latent molecular functionalities in the polymer structure that trigger repair via thermally reversible reactions, hydrogen bonding, ionic arrangements, or molecular diffusion and entanglement (Bergman & Wudl. 2008; Billiet et al. 2013). Of them, self-healing hydrogel has attracted much attention due to their great potential in biomedical applications (Deng et al. 2012; Phadke et al. 2012).

During repair, physical or chemical damage often will cause chain ruptures, resulting in reactive chain ends that significantly contribute to self-healing. Assuming bond cleavage does not occur during damage, chain or intermolecular diffusion is one of the driving forces for self-repairing of polymeric materials and the source of

loose chain ends is chain slippage. It is noticed that many self-healing hydrogels are stimuli-healable hydrogels because their repairing process requires the input of a stimulus to be activated (Deng et al. 2012; Phadke et al. 2012; Tang et al. 2007).

It has also been reported that crack healing takes place in polymer matrix when a damaged material is annealed above the glass transition temperature where 'intermolecular diffusion' of dangling chain at interface occurs henceforth leading to entanglement couplings (Dohler et al. 2013; Wool 1994). The healing behaviour is accelerated at higher temperature because of the enhanced intermolecular diffusion of dangling chain at interface. Not only a single crack but also mechanically induced damages such as crazes and micro-voids are also healed by means of chain inter-diffusion above  $T_g$  for various polymers including semi-crystalline polymers such as polyethylene and polypropylene (Begley et al. 2008; Yajuan et al. 2012). Further, the 'dangling chains' in the gel, defined as the chain segments whose one end is not connected to the network, are responsible for repairing nature, because the dangling chains exhibit segmental interdiffusion like liquid at a local scale (Radi et al. 2013; Yamaguchi et al. 2009).

Here, we report the discovery of self-healing poly(2-hydroxyethyl methacrylate) (pHEMA) hydrogel prepared with chemically cross-linked conditions at temperatures above minimum healing temperature, exhibiting both good self-healing capability and mechanical strength. This finding is important because pHEMA hydrogel has been extensively studied and considered as one of the hydrogels most suitable for biomedical and tissue engineering applications.

## EXPERIMENTAL DETAILS

### MATERIALS

Monomer 2-hydroxyethyl methacrylate (HEMA) with  $M_w$  130.14 g/mol, potassium persulfate, (KPS ACS reagent with  $M_w$  270.32 g/mol), L-cystine (with  $M_w$  240.30 g/mol) and solvent dimethyl sulfoxide (DMSO with molecular weight 78.13 g/mol) were purchased from Sigma Aldrich (Malaysia). All chemicals were used as received.

### HYDROGEL PREPARATION

The stock solutions were prepared using the following concentrations: KPS in water (0.00012 mg/5 mL), L-cystine in DMSO (0.0004 mg/40 mL) and HEMA (4 M). The hydrogel without dye were prepared in aqueous solutions at 22°C in the presence of 0.09 M KPS initiator, 4 M HEMA monomer and 0.04 M L-cystine cross-linker. In another beaker, the hydrogel with dye was prepared exactly similar to the procedure before (Belma 2000; Zhao et al. 2012). Using Rhodamine B as dye, the diffusion can be more clearly seen. After mixed up all the materials above, the dye (0.02 g/3 mL) was added and allowed the mixture solution to be stirred for a while. Then, the reaction was carried out in the beaker and the solution was then poured into a petri dish. The polymerization was conducted at 45°C for 5 h.

### HEALING PROCEDURE

The gel was cut into two pieces using scissors and two halves from each of the original hydrogels were put together rapidly to have their freshly created fracture surfaces brought into contact at 60°C for 5 h. These healing procedure experiments were totally done in the same size of petri dish.

### MECHANICAL MEASUREMENT

The dried gel was cut into dumbbell shape and was tested with Testometric M500-50CT Universal Testing Machine. Tensile test were performed on gel before and after healing condition. The load cell used was 10 kN with speed 15 mm/min. This mechanical testing was done on 5 samples for each condition. Dimension with all length ratios used confirm to the standard of American Society for Testing and Materials (ASTM D5045-99 2007). In order to evaluate the healing behaviour quantitatively, healing efficiency can be expressed as the percentage ratio of ultimate tensile

strength,  $R(\sigma)$ , before ( $\sigma_{initial}$ ) and after healing ( $\sigma_{healed}$ ) as shown in (1) (Yamaguchi et al. 2009).

$$R(\sigma) = \frac{\sigma_{healed}}{\sigma_{initial}} \times 100. \quad (1)$$

### CHARACTERIZATION OF THE GEL BY ATTENUATED TOTAL REFLECTANCE (ATR)

ATR spectra of pure HEMA, gel before healing and after healing were recorded with Spectrum ASCII PEDS 400 ATR Spectrometer to carry out the spectral analysis. The gel first was cut into cubic shape and dried in the oven and then only was sent to the analysis. All spectra were recorded at room temperature within range 4000-650  $\text{cm}^{-1}$ .

### RHEOLOGICAL MEASUREMENT

The temperature sweep measurement were performed on Anton Paar Rheoplus/32 Rheometer with oscillatory measurements at 1 Hz, while the temperature was increased at the rate of 5°C/min between 25 and 180°C and the thickness dimension used was 1 mm.

### MORPHOLOGICAL OBSERVATION

Photographs showing the self-healing of pHEMA hydrogel were taken in transmitted light and under UV lamp.

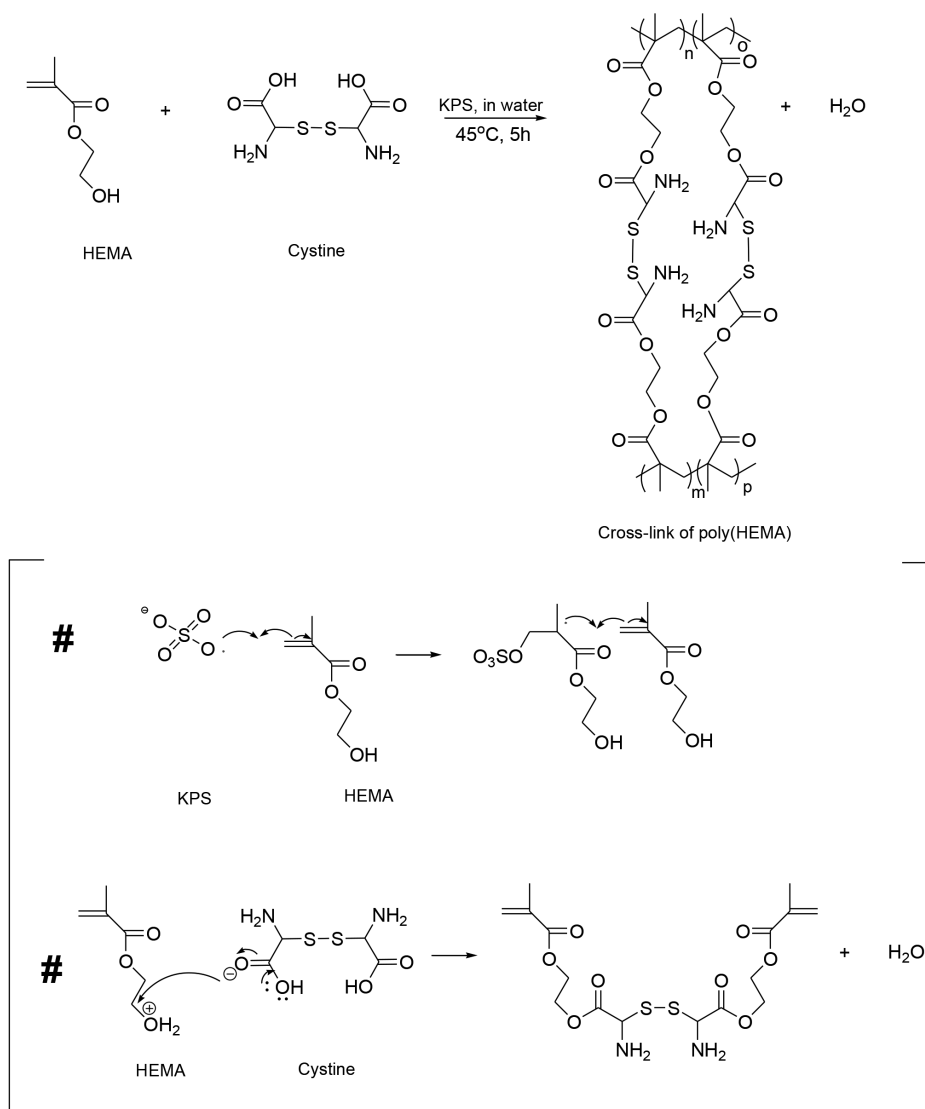
## RESULTS AND DISCUSSION

A self-healing system in hydrogel materials was achieved by reptation of dangling side chains (or chain slippage) through the network to the damage area for healing recovery (Yamaguchi et al. 2009). This system based on cross-linked hydrogel of poly(2-hydroxyethyl methacrylate) was prepared.

### PROPOSED MECHANISM OF 2-HYDROXYETHYL METHACRYLATE HYDROGEL

Scheme 1 represents the proposed mechanism of pHEMA hydrogel by free radical polymerization. Mechanism that we have proposed below shows two possible reactions. The radical that produced from initiator will attack the C=C of monomer. Therefore, once polymerization completed, spectrum for C=C at 1637  $\text{cm}^{-1}$  (Figure 1(a)) will disappear as shown in the ATR spectra (Figure 1(c)). Besides, the second possible reaction is condensation process between hydroxyl group of the HEMA with carboxylic acid of the cystine forming ester bond which it is in agreement with the previous study reported (Bhalekar et al. 2013). In addition, the elements for breaking and reformation of disulphide bond on the hydrogel for thermally healing system will be explored in the future.

The ATR spectra of pure monomer, L-cystine and pHEMA hydrogel; before and after healing condition are shown in Figure 1. Peak 1637  $\text{cm}^{-1}$  (in Figure 1(a)) which corresponds to C=C stretch for pure monomer was



SCHEME 1. Proposed mechanism of poly(HEMA) hydrogel

invisible after the hydrogel was formed (Figure 1(c)). The stretching vibration band of C=O was observed at  $1718\text{ cm}^{-1}$ ; the characteristic absorption band of C-O was observed at  $1155\text{ cm}^{-1}$ ; the distortion vibration bands of methyl and methylene were observed at  $1275$ ,  $1246$  and  $1017\text{ cm}^{-1}$  (Zhang et al. 2014). Besides, spectrum for gel after healing condition (Figure 1(d)) was seen to have no difference with gel before healing condition (Figure 1(c)) and this indicates that the chemical structure of the gel remained the same.

#### RHEOLOGICAL STUDY OF PHEMA HYDROGEL

The formation of pHEMA hydrogel was further investigated with rheological properties. Figure 2 shows the curve of storage modulus  $G'$  and loss modulus  $G''$  of the gel at increased temperatures before and after healing condition. In our work, the storage modulus decreases with temperature for both samples and remains a constant

value at high temperature, which is known plateau modulus. This is attributed to the existence of a permanent network, prohibiting the macroscopic flow (Yamaguchi et al. 2009). In agreement with ATR results, this shows that the present hydrogel system displays a predominantly solid-like behaviour. As known, the storage modulus can be used to measure the extent of gel network formation. Note that cross-linked polymers do not 'flow' because the entanglements are chemical covalent links and therefore they have a rubbery plateau up to the decomposition temperature (Ferry 1980; Lesueur 2009) as shown in Figure 2. Both storage ( $G'$ ) and loss modulus ( $G''$ ) decrease with an increase of the gel temperature ( $45^\circ\text{C}$ ) indicates that the molecules had started to vibrate until the point where the rubbery plateau was constant and stabilize. At this point, the molecules are 'free' and the reptation process begins which contributed to the healing process. In comparison with  $G''$ , the higher  $G'$  value of the gel means the stronger gel intensity (Tang et al. 2007).

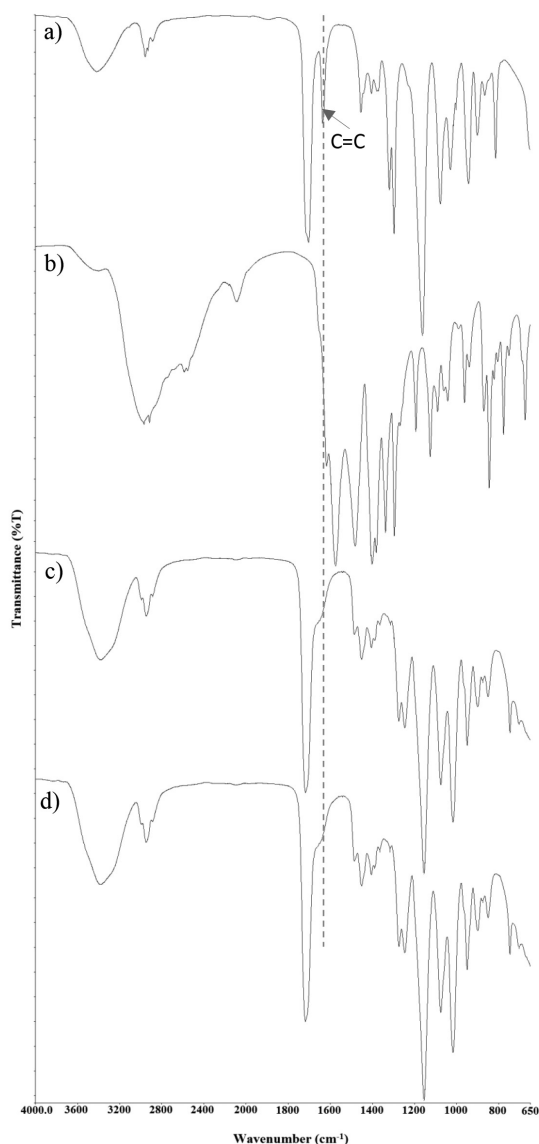


FIGURE 1. ATR spectra in the region  $4000\text{--}650\text{ cm}^{-1}$  recorded at room temperature of a) 2-hydroxyethyl methacrylate, b) L-cystine, c) gel before healing and d) gel after healing

Besides, we can also determine the minimum healing temperature used in the experiment (Lesueur 2009). From the graph, the minimum healing temperature is shown to be around  $48.5^{\circ}\text{C}$  (Figure 2(b)) to  $49^{\circ}\text{C}$  (Figure 2(a)). Since the healing process known to start at  $48.5^{\circ}\text{C}$ , thus the healing temperature used in this experiment which at  $60^{\circ}\text{C}$  is adequate to trigger the molecular for reptation and diffusing to the affected area. In addition, the little difference between the transition temperature before and after healing may suggest that there is no further curing or crosslinking in the sample. Instead, the healing process might occur due to the chain slippage and intermolecular diffusion of dangling chain (Dohler et al. 2013; Moura et al. 2007).

#### THE HEALING EFFICIENCY OF SELF-HEALING HYDROGEL

The self-repairing property is evaluated quantitatively by tensile testing employing repaired samples by the butt-joint technique at the cut surface (ASTM D5045-99 2007). The stress-strain curves of different conditions or cycle hydrogel were obtained as shown in Figure 3.

From Table 1, we can see the pattern of healing in hydrogel. The healing efficacy of hydrogel decreased as the number of cycle increased. Nevertheless, the percentage of healing was still considered relatively high due to little difference between them and the original sample. In the first and second healing cycle, the healing percentages are 92 and 91%, respectively. These percentages of healing indicate that the strength of this poly(HEMA) hydrogel is considerable (Deng et al. 2012).

Again, this might be due to the intermolecular diffusion and chain slippage of entanglement chain during healing process. Healing recovery has been shown to achieve by rearranging polymer chains at ambient or elevated temperatures. According to Wool's (2008, 1993) theory, the crack healing via molecular inter-diffusion in polymeric material involves the process of surface rearrangement, wetting, diffusion and randomization that takes place across the micro-fine crack. In similar concept,

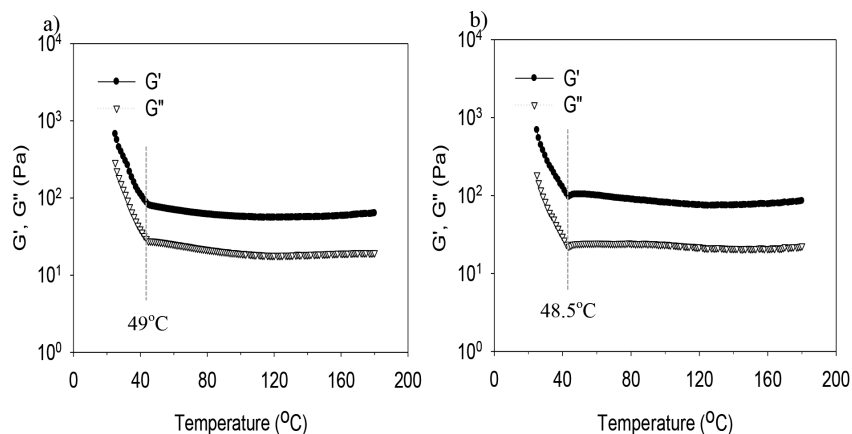


FIGURE 2. Temperature dependence of storage modulus  $G'$  and loss modulus  $G''$  of a) gel before and b) after healing at a heating rate  $5^{\circ}\text{C}/\text{min}$

Wool and O'Connor (1983) proposed a reptation mode; in which an interface between the fracture surfaces was formed by random walk chains or moving polymer that from a tube-like region and diffusion by reptation across a polymer-polymer weld line before the chains form new physical crosslinks (Pavlos 2010). The crack healing

process was described schematically as shown in Figure 4 (Dohler et al. 2013).

#### MORPHOLOGICAL OBSERVATION OF PHEMA HYDROGEL

This 'healing capability' of the self-healing hydrogel was further verified using optical microscopy. Figure 5

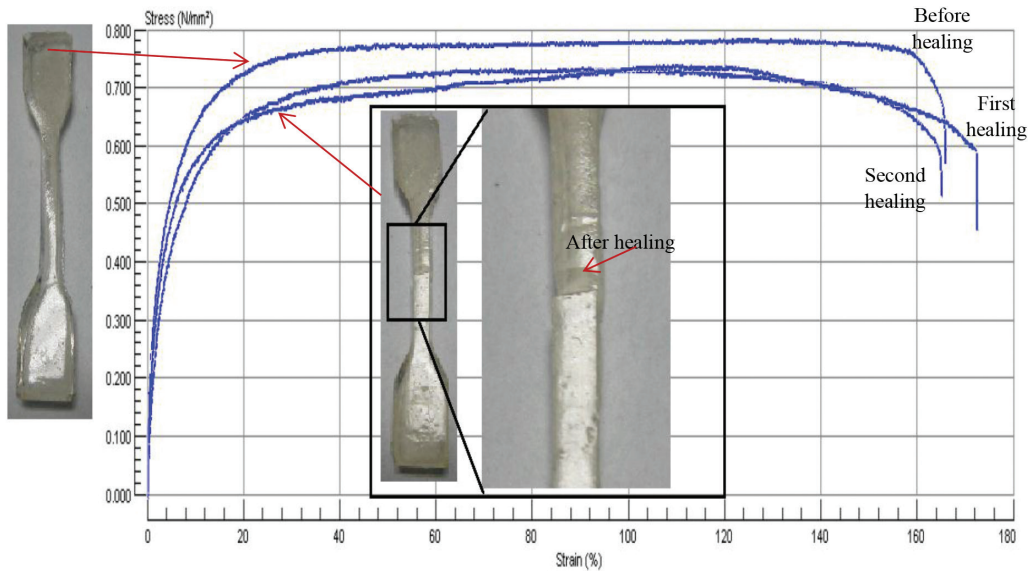


FIGURE 3. Stress-strain curves of sample before healing, first and second healing

TABLE 1. The percentage of ratio stress at before and healable hydrogel condition

Cycle	Ultimate tensile stress (N/mm <sup>2</sup> )	$R(\sigma) = \frac{\sigma_{healed}}{\sigma_{initial}} \times 100$
Before healing	0.7800.20	100%
First healing	0.7200.10	92%
Second healing	0.7100.20	91%

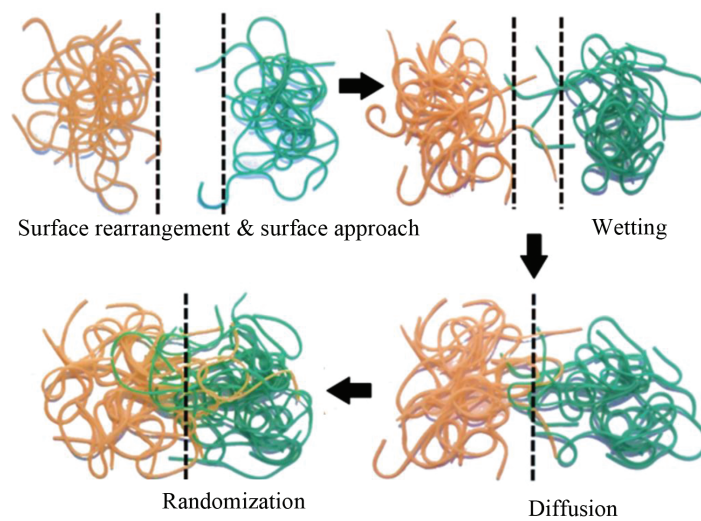


FIGURE 4. Schematic of self-healing mechanism of the self-healing hydrogel (Dohler et al. 2013)

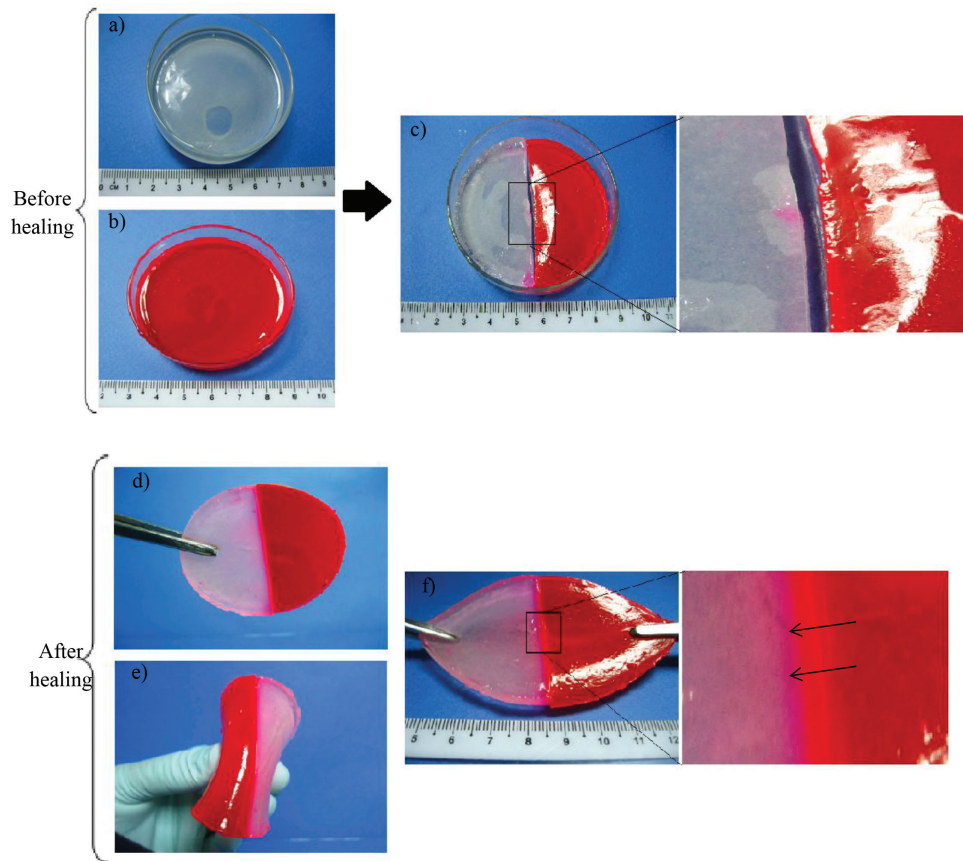


FIGURE 5. Photograph of the hydrogel before and after healing process; a) Hydrogel without dye, b) Hydrogel with Rhodamine B dye and c) the cut sample brings into contact. Hydrogel still d) merged together when e) bending forces and f) stretching forces were given to the healable hydrogel

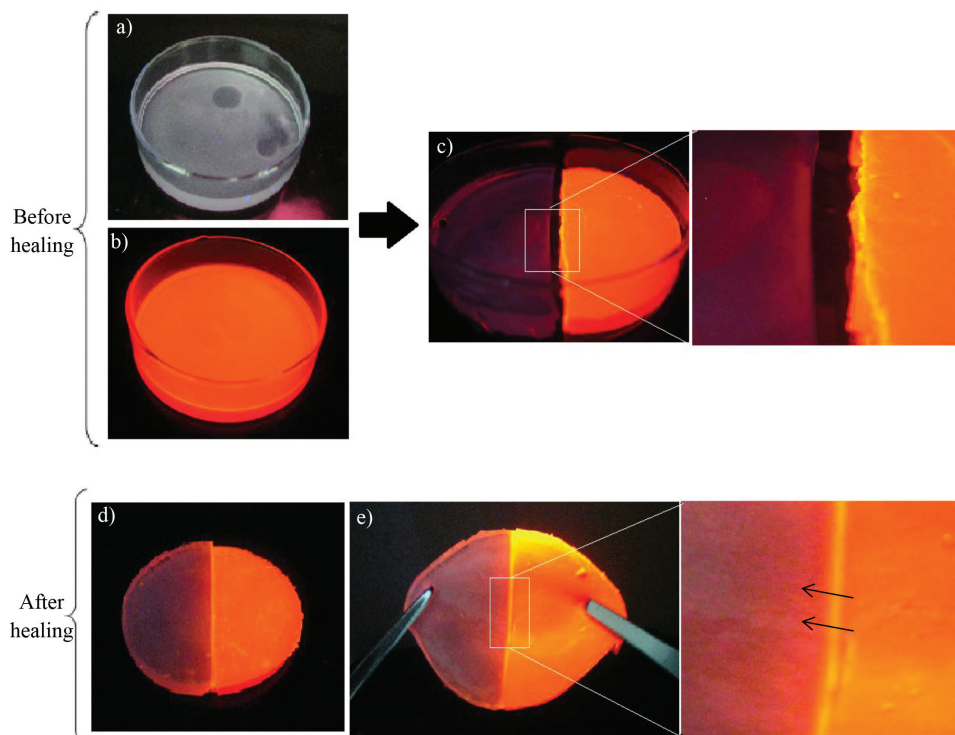


FIGURE 6. Photograph before and after healing process under UV lamp a) Hydrogel without dye, b) Hydrogel with Rhodamine B, c) Hydrogel after being cut, d) Hydrogel after merged together and e) when stretching forces were applied

shows characteristics optical micrographs of the healable hydrogel. The cut region is clearly seen (Figure 5(a)-5(c)) and after healing at 60°C for 5 h, this cut is apparently healed; in which the cut surface was filled up and brought into contact (Figure 5(d)). The self-healed, one-piece hydrogel could withstand several kinds of mechanical forces without failure at the interface, such as bending and stretching to a large extension (Figure 5(e)-5(f)).

Other than camera, the photos were also taken under UV lamp (Figure 6(a)-6(e)). UV lamp was used to enhance the fluorescence characteristics so that the diffusion would be clearly seen. The steps in UV lamp mode were the same as in the transmitted light mode; i.e. freshly prepared hydrogel without dye (Figure 6(a)) and hydrogel with dye, Rhodamine B (Figure 6(b)). The samples were cut and brought into contact (Figure 6(c)). Moreover, under UV lamp, we can emphasise the intermolecular diffusion due to the healing process when the healable hydrogel (Figure 6(d)) is applied as stretching forces (Figure 6(e)).

### CONCLUSION

In summary, chemically cross-linked poly(HEMA) hydrogel prepared using the free radical polymerization method can self-heal at given temperature. The self-healable hydrogel is mechanically strong and this is exhibited by the highest fracture stress reported so far. Our study suggested that intermolecular diffusion of dangling chain contributed to this self-healing of hydrogel. Moreover, chain slippage might have occurred and caused the pHEMA hydrogel to become healable. This discovery is important because pHEMA hydrogel is economical, easy to produce and has great potential for biomedical applications due to its biocompatibility and nontoxicity. The discovery of self-healing ability adds a new value to this old hydrogel.

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