Starch-based physically cross-linked self-healing hydrogel

Highlights

Mechanically tough self-healing hydrogels have attracted tremendous attraction in recent years owing to their flexibility and excellent deformation-resistance. In this work, we have synthesized a bio-based self-healing hydrogel by incorporating starch onto a hydrophobically associated (HA) domain. The inclusion of physically cross-linked starch onto the HA-poly(acrylamide) (PAM) chain enhanced the mechanical strength of the hydrogel and this enhancement depends on dose level of starch. The ductile and tough HA-PAM network could bear stress and recombine the damage zones within a short time, and hence exhibit noteworthy self-healing ability. Moreover, the introduction of the reversible and physically cross-linked starch network was unable to eliminate self-healing attribute of the HA-PAM network completely. Most importantly, synthesized hydrogel was dimensionally stable after swelling and exhibited noteworthy mechanical strength under such conditions. Thus, this work provides a novel starch incorporated mechanically tough, self-healing hydrogel that can hopefully enrich the current hydrogel research and expand its practical application spectrum.

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5.1. Introduction

Chapter 4 demonstrates the fabrication of a starch-based mechanically tough hydrogel by using a double network (DN) strategy. This is one of the most effective ways to protect the hydrogel network from breakage and provide mechanical stability. Although, the presence of chemically cross-linked DN can provide noteworthy toughness but it is not able to recover the damage zone spontaneously to introduce self-healing ability. But only mechanical stability unable to fulfill the demand of some applications, and they need some smart properties like self healing ability, shape memory property, etc. [1]. These issues compel the researchers to investigate new design strategy to incorporate these smart properties in hydrogel. Thus, in this chapter we have demonstrated the fabrication of a starch-based self-healing mechanically tough hydrogel.

Although a few hydrogels with similar properties are reported in literature but still, it is a challenging task to obtain a self-healing hydrogel with high strength and stretch ability. DN hydrogels [2], hydrophobically associated (HA) hydrogels [3], nanocomposite hydrogels [4], etc. are such kinds of hydrogels. Among all these, the HA hydrogel has received immense importance owing to achieve remarkable mechanical property and satisfactory self-healing ability. Beside these, such hydrogels can also be prepared by using simple polymerization protocols. Usually, HA hydrogels are constructed by a micellar copolymerization reaction between a hydrophilic monomer and a hydrophobic monomer in the presence of a surfactant. The physical cross-linking that occurs between the monomers and the surfactant molecules promotes the formation of reversible polymeric chains and thus three-dimensional hydrogel networks with self-healing ability are created [3, 5-6]. As an example, a melt processable self-healing hydrogel was constructed using acrylic acid and n-octadecyl acrylate as the hydrophilic and hydrophobic monomers, respectively, in the presence of a surfactant [7]. This hydrogel showed temperature-sensitive shape-memory property. Similarly, a graphene oxide-HA hydrogel was prepared by Cui et al. with the mechanical strength of 243 kPa. This hydrogel showed excellent recyclability in wastewater treatment due to retention of the mechanical property after swelling along with noteworthy self-healing ability [3]. But the use of only synthetic monomers restricts their widespread uses. To overcome this drawback in this chapter we aimed for synthesizing a bio-based self-healing hydrogel by incorporating starch onto a physically cross-linked HA domain. Moreover, to enhance the mechanical strength, various toughing mechanisms have been adopted by different

researchers. Among these, combinations of two networks in a single hydrogel termed as DN hydrogel as stated in **Chapter 4,** have generally been adopted. But chemically cross-linked DN [8] and hybrid physically-chemically cross-linked DN [9] are not able to exhibit efficient self-healing ability. Thus, to provide efficient self-healing ability with high mechanical strength, starch without any cross-linker was introduced in the HA domains. The gelatinization of starch results in hydrogen bonding association, and the introduction of it in the HA networks contributes towards the enhancement of the mechanical strength of the hydrogel. Due to its high molecular weight, it can act as a framework to bear stress and hence, can enhance the mechanical strength of the hydrogel. Moreover, HA-poly(acrylamide) (PAM) network can also bear the stress and promote self-healing ability as well as impart fatigue resistance. Most importantly, the mechanical property of the hydrogel can be retained even after swelling. This would be one of the most interesting and unique properties of the synthesized hydrogel. From our best knowledge, starch-containing HA self-healing hydrogel has not been reported so far. Thus, a novel starch containing mechanically tough fully physically cross-linked, self-healing hydrogel with retention of toughness even after swelling is reported in this chapter. The simple one-pot polymerization process, further, leads to the development of a new generation of starch containing self-healing tough material.

5.2. Experimental

5.2.1. Materials

Various chemicals including tapioca starch, ammonium per sulfate (APS), and *N, N*-methylene bis acrylamide (MBA), were used as the same grade and specifications as mentioned in **Chapter 2.**

Acrylamide (AM) is procured from SRL. It is an odorless solid with molecular weight 71.08 g/mol and density 1.13 g/cm³. It is a white odorless solid soluble in water and several organic solvents and used as the monomer for preparation of the hydrogel.

Stearyl methacrylate (SMA) is a long carbon chain containing monomer with molecular weight 339 g/mol and density 0.9±0.1 g/cm^3. It was received from Sigma-Aldrich and was used without any further purification.

Sodium dodecylbenzene sulfonate (SDBS) is a light yellow sand-like solid with molecular weight 348.48 g/mol. It was purchased from Sigma-Aldrich and used as a surfactant.

5.2.2. Methods

5.2.2.1. Synthesis of the self-healing hydrogel

The starch containing self-healing hydrogel was prepared by using a simple "one-pot" copolymerization technique. Briefly, the predetermined amount of starch was mixed with the calculated amount of distilled water in a three-necked round bottom flask. The reactant was stirred with a gradual increment of temperature up to 60–65 °C and continued still the solution became transparent. The resulting solution was then gradually cooled down to 45 °C and at that temperature, hydrophilic monomer, AM (1.8 g in 5 mL water) and the hydrophobic monomer, SMA (0.4 g) were mixed into it. Subsequently, 0.4 g of SDBS was added to the resulting solution and stirred at 50–55 °C for 3 h to make a uniform solution. Finally, to initiate the polymerization, an aqueous solution of APS (0.06 g in 1 mL water) was added under N_2 atmosphere at 70 °C. The reaction was allowed to proceed up to the formation of a stable gel and the desired hydrogel was obtained after cooling at room temperature. Different compositions of the hydrogels were prepared with different amounts of starch and encoded as SAS1, SAS2, SAS3 and SAS4. The compositions of the constituents used in the formation of these hydrogels are tabulated in **Table 5.1**. A hydrogel without using the surfactant was also prepared in the same way as above and encoded as SASW hydrogel.

Table 5.1. Compositions of the synthesized self-healing hydrogel.

Sample code	Starch (g)	Water (mL)	SMA (g)	AM (g)	SDBS (g)	APS (g)
SAS1	0.6	6	0.4	1.8	0.4	0.060
SAS2	0.9	9	0.4	1.8	0.4	0.060
SAS3	1.2	12	0.4	1.8	0.4	0.060
SAS4	1.5	15	0.4	1.8	0.4	0.060
SASW	1.2	12	0.4	1.8	---	0.060

5.2.3. Structural analysis

FTIR spectra of the self cross-linking hydrogels were recorded using the same instrument and same condition as mentioned in **Chapter 2** (**Section 2.2.3**).

5.2.4. Determination of thermal properties

The differential scanning calorimetry (DSC) study was performed by DSC 6000 instrument (PerkinElmer, U.S.A.) at a heating rate of 10 °C min^{-1} with the N_2 flow rate of 30 mL min^{-1} from the temperature range of −70 to +120 °C. The thermogravimetric analysis (TGA) of the hydrogel was done by using the same instrument and same condition as mentioned in **Chapter 2** (Section **2.2.3**).

5.2.5. Determination of mechanical properties

The tensile measurements of the prepared hydrogels were performed using the same Universal Testing Machine (UTM) as described in **Chapter 4**, at a crosshead speed of 200 mm min^{-1}.

5.3.6. Compression study

The compression test was conducted using UTM with a 5kN load cell (ZwickRoell, Z005TN Proline).

5.3.7. Impact resistance study

The impact strength of the synthesized hydrogel was determined by using an impact tester (S C Dey & Co.) by the standard falling ball method using 850 g weight.

5.2.8. Swelling study

The swelling study of the synthesized self-healing hydrogel was determined using the same method as mentioned in **Chapter 2**.

5.2.9. Determination of self-healing ability

The healing ability of the hydrogels was evaluated by cutting the gel specimens into six pieces and allowed to reconnect by simply joining the pieces at room temperature without any external stimuli. After the gels were completely healed, the tensile strength was measured at the same crosshead speed (200 $mm.min^{-1}$) using the same UTM instrument.

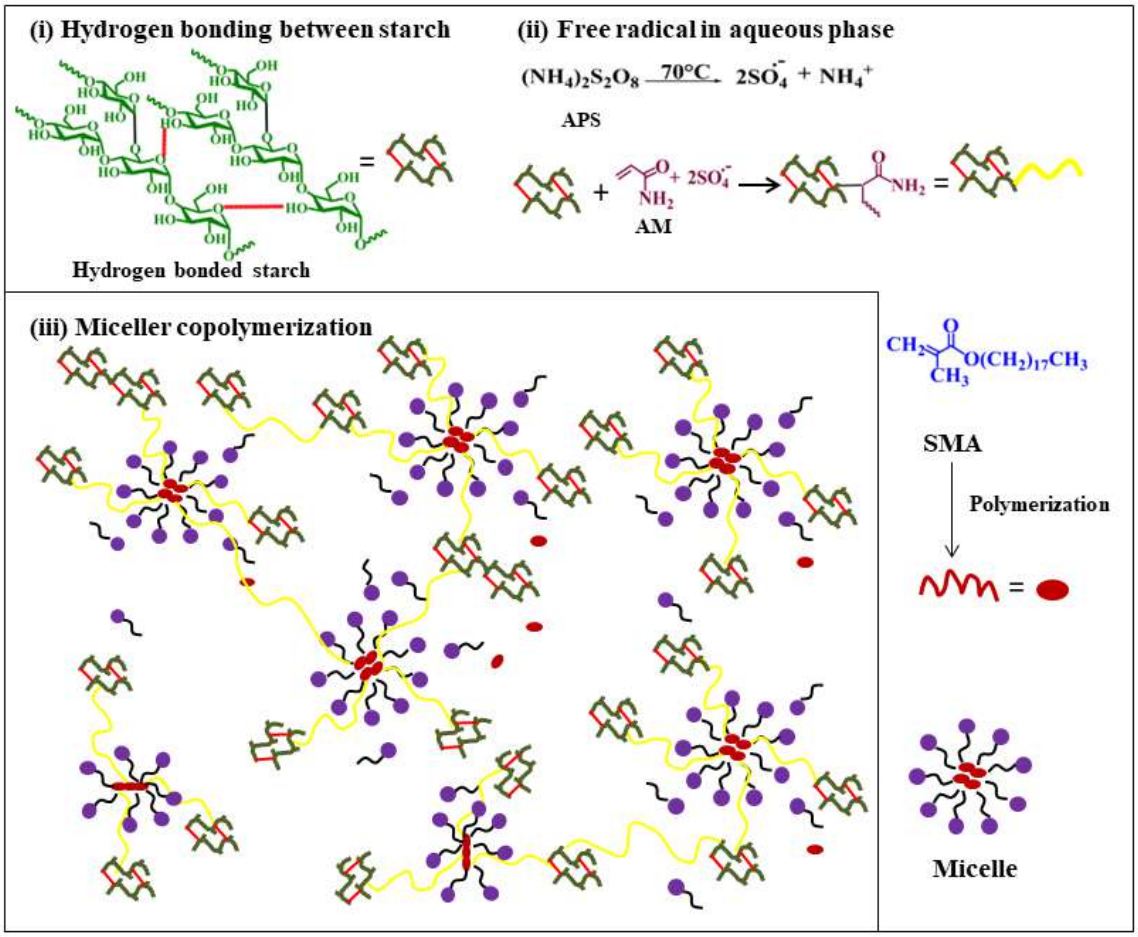
The following equation was used to determine the healing efficiency of the hydrogels.

Healing efficiency (%) = 100 × [tensile strength (after healed)/tensile strength (before healed)] ----------Eq. 5.1

5.3. Results and Discussion

5.3.1. Synthesis of the self-healing hydrogel

To fabricate mechanically strong self-healable physically cross-linked hydrogel, starch was introduced in the HA-PAM networks (**Scheme 5.1**).



Scheme 5.1. Preparative scheme and possible structure of the self-healing hydrogel.

The gelatinization of starch creates hydrogen bonding among the hydroxyl groups. The HA-PAM network was prepared using a micellar copolymerization reaction between PAM and SMA in the presence of surfactant, SDBS to achieve the desired hydrogel. In this polymerization process, the hydrophobic monomer, SMA is solubilized in the SDBS micelle, whereas the hydrophilic AM monomer was dissolved in water. The initiator (APS) initiates the polymerization of AM and several active chain radicals of AM were created through the free radical addition polymerization process [10-12]. Moreover, the possibility of radical formation on the hydroxyl groups of starch and free radical grafting of PAM chains onto the starch backbone cannot be ruled out completely. However, the presence of surface-active agent like SDBS lowers the surface energy at the interface and

thereby facilitating the radicals from the water-soluble initiator and AM active chains to the hydrophobic monomer. So SMA radical is activated in the interface to propagate the hydrophobic chains through polymerization process.

Thus, PAM chains can join the SMA chains through free radical polymerization process in the interface and generates hydrophobic blocks. These hydrophobic SMA blocks are distributed as randomly within the PAM backbones [13]. This whole process created a block copolymeric structure along with the hydrogen bonding associated starch moieties that resulted in the desired self-healing hydrogel (**Scheme 5.1**). Interestingly, compared with the other chemically cross-linked hydrogels, this work provides a fully physically cross-linked starch containing self-healing hydrogel without the inclusion of any additional chemical cross-linker. The presence of starch enhances the mechanical strength and HA-PAM introduces self-healing ability to the hydrogel. After the breakage of the hydrogen-bonded starch network, the strong and reversible HA network dissipates energy and bears the stress to reconstruct the whole 3D network. Thus, it showed self-healing ability without exposure of any external stimuli.

5.3.2. FTIR spectral study

Figure 5.1. (**a** and **b**) represents the FTIR spectra of starch and three compositions of the self-healing hydrogel.

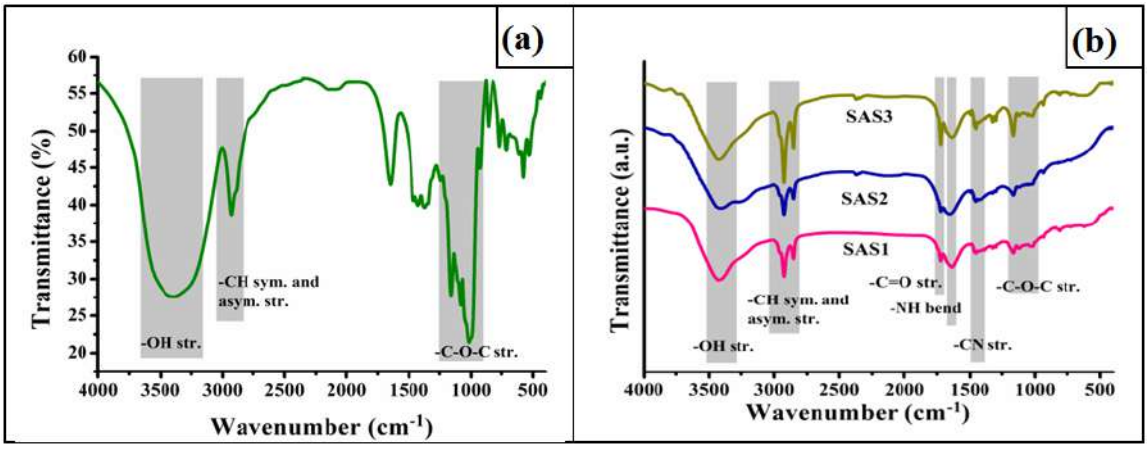


Figure 5.1. FTIR spectra of (a) starch, and (b) SAS1, SAS2, and SAS3.

The characteristic peaks represent the interaction between starch, AM and SMA. The broad absorption band present in the region of 3517–3293 cm^{-1} represents the -OH stretching frequency of starch [14]. The peaks present at 2963 cm^{-1} and at 2831 cm^{-1} represent the –CH asymmetric and symmetric stretching frequencies, respectively which

are the important bands for starch, AM, and SMA moieties. Moreover, the high intensity of this band represents the presence of a large alkyl chain within the hydrogel network. The adsorption peak at 1725 cm^{-1} can be assigned to the CO stretching frequency of both SMA and AM moieties. Further, the band at 1633 cm^{-1} represents the -NH bending vibrations of the amide group, present in AM moiety. Therefore, these peaks provide evidence for the presence of both PAM and SMA chains. Yet, the absorption band present at 1461 cm^{-1} can be assigned to –CN stretching vibration of amide groups of PAM chains [15]. Furthermore, the absorption band present at 1165–1020 cm^{-1} is assigned to the –C–O–C– linkage of starch chains [16]

5.3.3. Thermal properties

Figure 5.2.a depicts the DSC traces of the synthesized hydrogel. The glass transition temperature (T_g) values obtained from the DSC analyses are tabulated in **Table 5.2**. The first T_g of the hydrogels showed negative values, and the reason is due to the presence of long SMA flexible moieties [17]. Moreover, there is also presence of another T_g which is due to the presence of starch and PAM in the range of 96.81-110.69 °C. Thus, DSC data provide evidence of the presence of two different phases in the hydrogel.

Table 5.2. Glass transition temperatures of the hydrogels obtained from DSC.

Parameter (°C)	SAS1	SAS2	SAS3
Tg_1	-30.66	-29.92	-29.85
Tg_2	110.69	105.85	96.81

The thermograms of TGA and the first derivative (DTG) for all the compositions of the hydrogel and tapioca starch are displayed in **Figure 5.2.b** and **c**. The thermogram of starch has two distinct weight loss regions. The first one is due to the moisture or absorbed water and the other peak is due to the degradation of the starch backbone [18]. Further, the degradation due the starch moiety is clearly observed in all three compositions of the hydrogel. The degradation of the hydrogels at around 405–415 °C is due to the decomposition of PAM chains [19]. There is a little weight loss in the range of 420–465 °C, which might be due to the degradation of SMA moieties [20]. The SMA moiety degradation is combined with the degradation of PAM moiety, as supported by the literature reports [20]. These hydrogels were degraded at 515 °C which corresponds to the liberation of carbon dioxide. The production of carbon dioxide as a byproduct is

due to the degradation of PAM moieties [20].

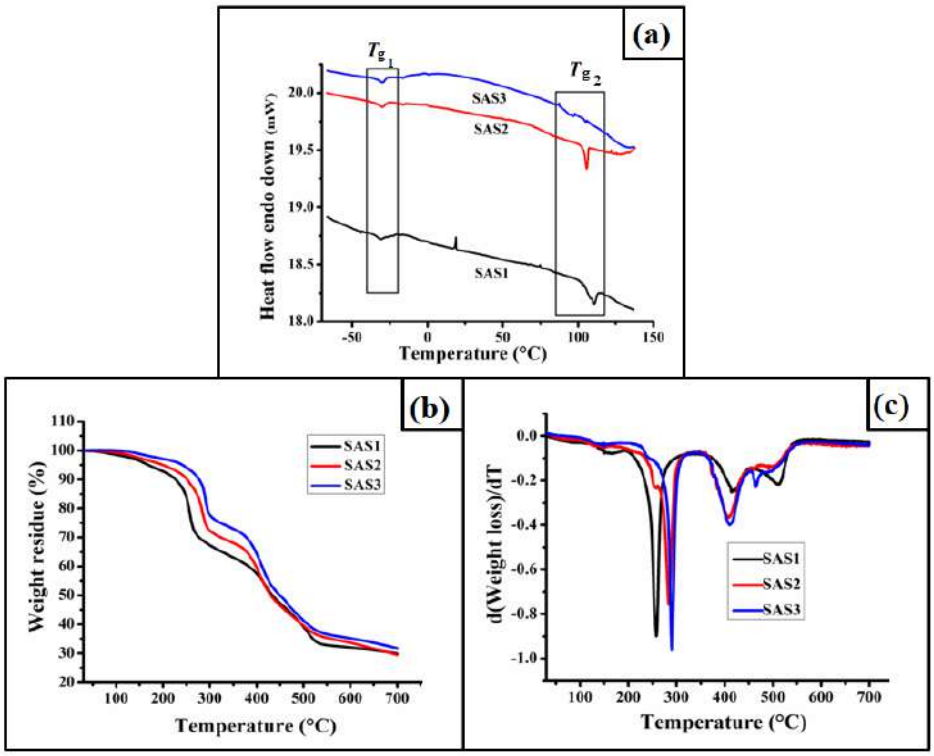


Figure 5.2. (a) DSC curves of SAS1, SAS2 and SAS3; (b) TGA thermograms, and (c) DTG curves of SAS1, SAS2, and SAS3.

5.3.4. Mechanical properties

The presence of starch with the HA network helps to achieve outstanding mechanical properties in the 'as prepared' hydrogels. **Figure 5.3.a** depicts the typical stress-strain profiles of five hydrogels with different compositions. It is found that the tensile strength of SAS1 was only 0.083±0.006 MPa, though it exhibits maximum strain of 3948±237%. In contrast, the stress of SAS3 reached up to 0.26±0.0195 with 2561±158.65% strain. Thus, these results indicate that starch has a noteworthy contribution to the mechanical strength. The mechanical strength of these hydrogels increases with the increase in amount of starch, while elongation decreases with the increase in the amount of starch. **Figure 5.3.b** showed the digital photographs of the three compositions of the hydrogel. From the figure it is clearly seen that, with increasing amount of starch the hydrogel could exhibit an ordered structure.

To examine the mechanical strength of the synthesized hydrogels, the stretching test was also performed. **Figure 5.4.(a** and **b)** represents the single knot stretching, while **Figure 5.4.c** represents the tensile stretching undergoing in the UTM machine. The mechanical

stretching results clearly showed that the hydrogel is mechanically strong to withstand any kind of external force. The mechanical strength of the hydrogel is further tested by lifting the dead weight of 0.5 kg by the strip of the hydrogel. From **Figure 5.4.d,** it is seen that a piece of SAS3 with 0.17 g can lift to a weight of 0.5 kg, which indicates the incredible mechanical strength of the hydrogel. In addition to these, the hydrogel is strong enough to prepare different geometrical shapes like star and heart (**Figure 5.4.e** and **f)**.

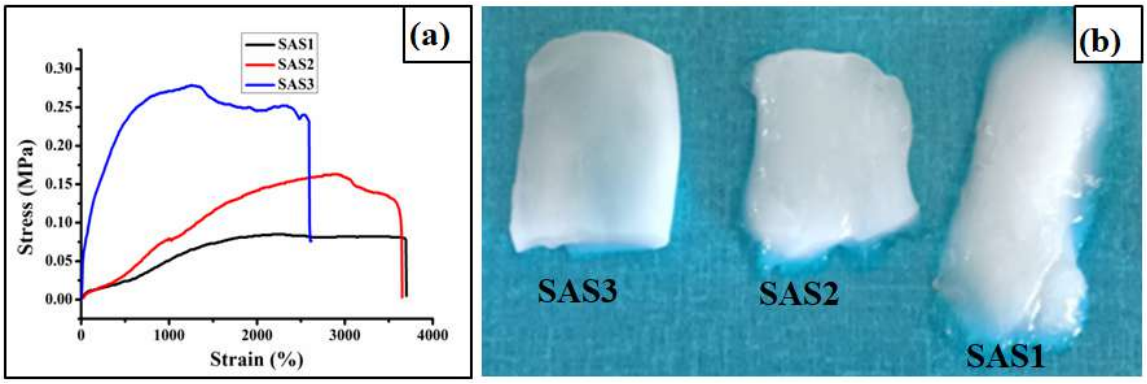


Figure 5.3. (a) Stress-strain profiles of the hydrogels, and (b) digital photographs of three compositions of the hydrogel.

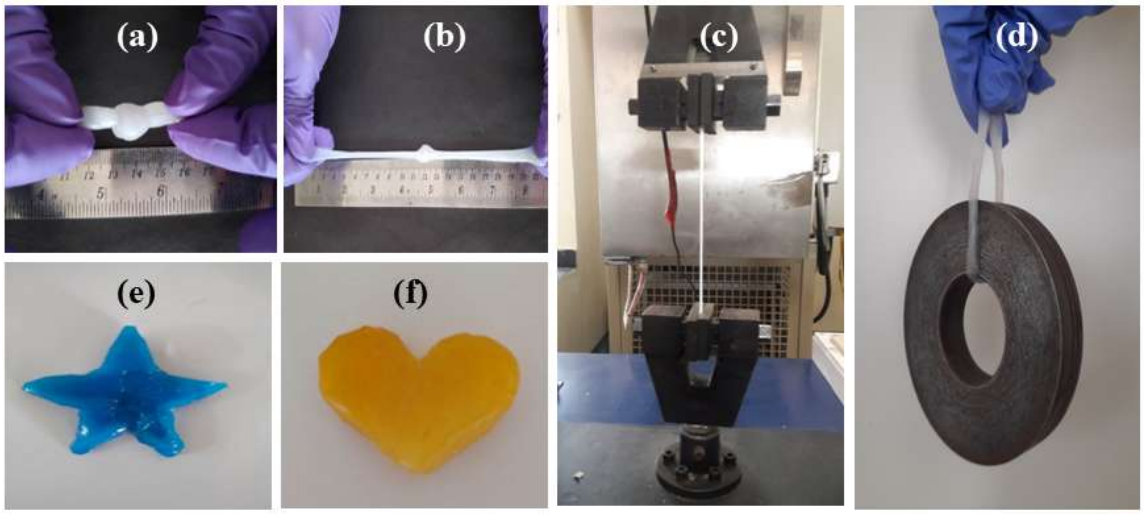


Figure 5.4. (a–b) Single knot stretching, (c) tensile stretching in UTM machine, (d)SAS3 (0.17 g) lifting a weight of 0.5 kg, (e) SAS3 as star shape, and (f) SAS3 as heart shape.

In addition to the high strength, the hydrogel also showed shape recovery property, and upon removal of the external force, the gel quickly recovers to its original shape, indicating the shape-recovery ability of the hydrogel without using any external stimuli. **Figure 5.5.a** represents the hydrogel before deformation, **Figure 5.5.b** represents the hydrogel in the time of deformation and **Figure 5.5.c** represents the hydrogel after

deformation upon the removal of external force. It is clearly seen from these figures that the hydrogel can retain its original shape after the deformation. Most impressively, the mechanical property of a piece of SAS3 was tested by hitting it with a weight of 2 kg. The weight was kept above the hydrogel for 30 min and then hit 10 times to examine its load bearing and impact capacity. It was found that there was no observable damage after the test, as shown in **Figure 5.5.g**. Thus, these results provide evidence that the inclusion of a ductile HA network with strong physical cross-linking helps to dissipate energy and thus improve the mechanical strength of the hydrogel.

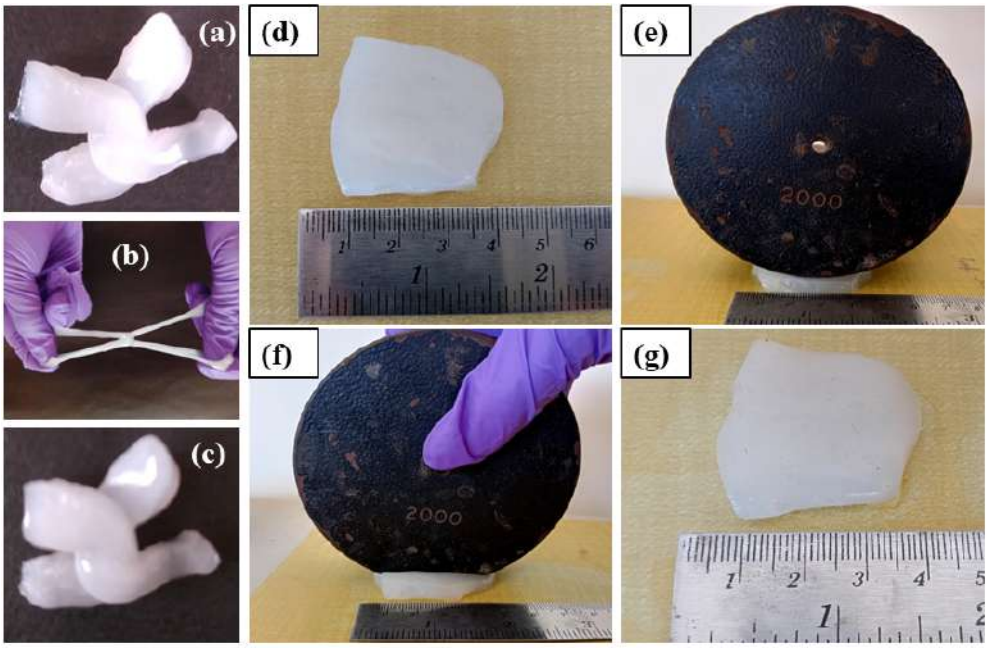


Figure 5.5. (a) Visual inspection before stretching, (b) hydrogel in the time of stretching, and (c) recovered shape after stretching; digital photographs of (d) a piece of SAS3 (thickness 5 mm), (e) weight of 2 kg is placed onto it for 30 min, (f) hit by the weight 10 times, and (g) no observable damage after the test.

5.3.5. Compression study

Compression measurement was also conducted for the synthesize hydrogel to evaluate the compressive strength. **Figure 5.6** represents the force-deformation curves for all the hydrogels with 80% of deformation. It is clearly seen from the figure that the force required deformation of the sample enhanced with increasing amount of starch, and SAS3 exhibited the highest compressive force (34.973 kPa). However, the forces required for SAS2 and SAS1 were found to be 20.054 kPa and 18.048 kPa, respectively. These results showed that the compressive strength of the hydrogel is remarkably high

with high amount of starch. Thus, the interpenetrating starch has great influence on compressive strength, and it showed linear relationship with tensile strength.

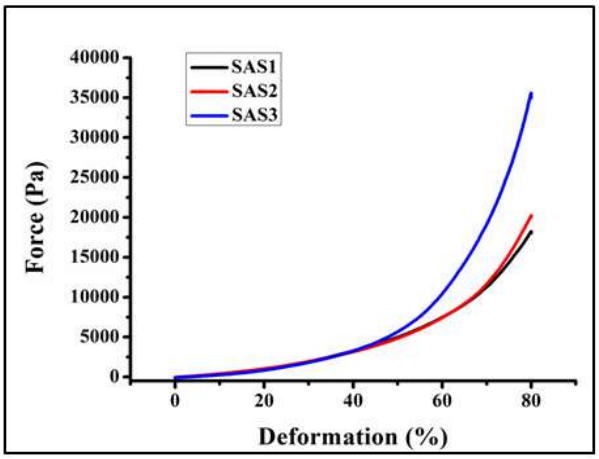


Figure 5.6. Force-deformation graphs for the hydrogels

5.3.6. Impact resistance study

The impact resistance determines the capacity of a substance to withstand a sudden applied force by dissipating it throughout the matrix [21]. All the hydrogels can withstand impact energy of 1.93 kJ/m^2 without cracking for several times. The impact resistance ability was found to be 13 cycles, 19 cycles and 27 cycles for SAS1, SAS2, and SAS3, respectively. These results showed that, impact resistance ability of the hydrogel followed a similar order as the tensile strength. Thus, this study further supports the enhancement of the strength of the hydrogel with the increase in amount of the starch.

5.3.7. Swelling of the hydrogel

Figure 5.7.a depicts the swelling ability of the synthesized hydrogel. The swelling study indicated that the water absorption capacity of the hydrogel was very poor, and the highest amount of water absorption was found to be 32.4±1.5 g/g, in the case of SAS1. However, the swelling ability decreases with the increase in amount of starch and thus the absorption was found to be in the order SAS1 > SAS2 > SAS3 (**Figure 5.7.a**). The lowering of swelling ability with the increase in starch amount may be due to high cross-linking density in the resulted hydrogel, which arises due to interpenetration of starch chains with the HA domains. The cross-linking density was enhanced through the high chain entanglements with the hydrogel bonding and thereby making dense network structure. Thus, hindering the entrapment of the water molecule in the hydrogel cage

results in lowering water absorption capacity [22]. Moreover, the hydrophilicity of starch is lower than the synthetic PAM. Hence, the introduction of starch lowers the swelling ability of the resulted hydrogel. Most importantly, the hydrogel is stable after equilibrium swelling for a week and showed notable mechanical property. However, absorbed water decreases the mechanical strength than the original one as shown in **Figure 5.7.b**. The tensile strength of swelled SAS1 was found to be 0.052±0.002 MPa, while the values were 0.10±0.025 MPa and 0.19±0.032 MPa for SAS2 and SAS3 swollen gels, respectively. Thus, these results showed that the hydrogels can show noticeable mechanical strength even after swelling. Further, it indicates the stability of the physical cross-linking network in the presence of water for a week, even after equilibrium swelling. The digital photographs of the hydrogel before and after swelling are shown in **Figure 5.7.c** and **d**. Thus, the hydrogel can attain a considerable amount of mechanical strength even at swollen state and this unique and extraordinary property makes the hydrogel suitable for various applications.

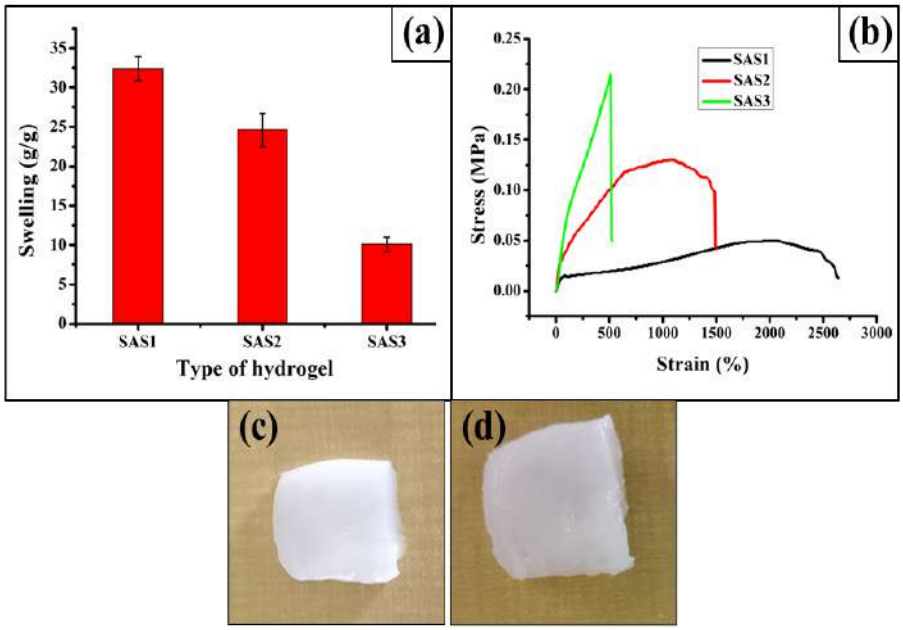


Figure 5.7. (a) Swelling ability, (b) stress-strain profiles after swelling of the hydrogels, (c) photographs of hydrogel before swelling, and (d) photographs of hydrogel after swelling.

5.3.8. Self-healing ability

The physically cross-linked HA domain provides satisfactory self-healing ability to the synthesized hydrogel. To investigate this self-healing ability of the hydrogel six separate

pieces (**Figure 5.8.a**) are allowed to physically join together at room temperature. It was found that the hydrogel showed satisfactory self-healing ability and the healed gel can withstand its own weight as shown by the alternative two colors (**Figure 5.8.b**). Moreover, the healed gel was inseparable even after bending and twisting as well as on stretching (**Figure 5.8.c-e**). The combination of self-healing and freely shapeable properties of the hydrogel can be utilized for different purposes. As an example, we made some English alphabets as shown in **Figure 5.8.f** by utilizing such properties.

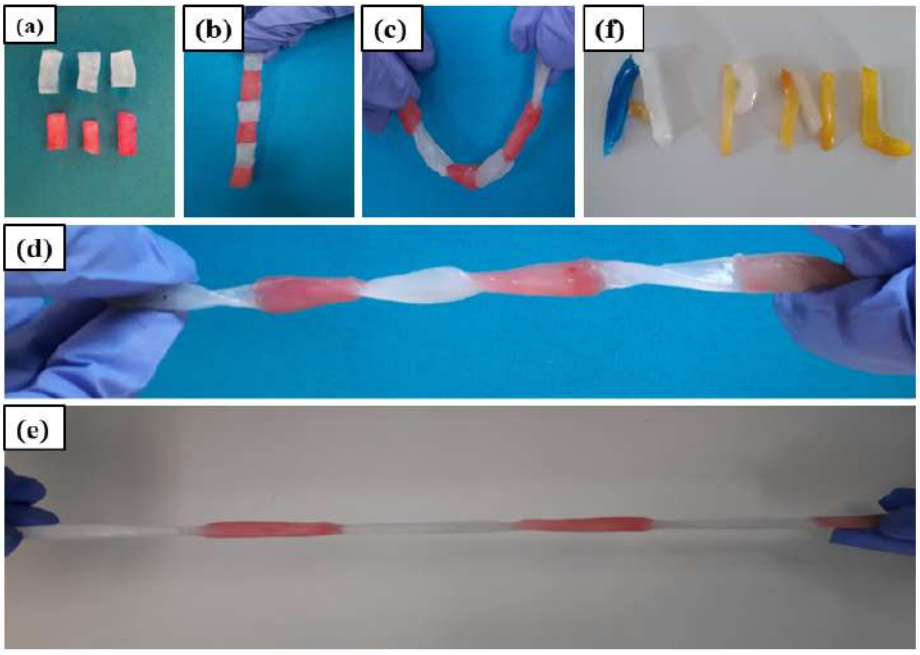


Figure 5.8. Self-healing properties of SAS3 at room temperature (a) six pieces of SAS3, (b) the healed hydrogel that can bear its own weight, (c) the healed gel can be bent without breakage, (d) can be twisted stretching without breakage, (e) high stretching of the healed hydrogel, and (f) combination of self-healing and free shapeable property to make the alphabets.

Further, we evaluated the healing efficiencies of all three hydrogels by the tensile strength measurements. **Figure 5.9.a** showed that healed SAS1 achieved mechanical strength of 0.072±0.004 MPa with a healing efficiency of 86.89%. The healing efficiency decreases with the increase in amount of starch and was found to be 75.59% and 57.88% for SAS2 and SAS3, respectively (**Figure 5.9.b**). These results demonstrate that the physically cross-linked network is responsible for the self-healing property of the hydrogel and the introduction of starch diminished its healing efficiency. The interpenetration of starch decreased the probable interaction between the physically cross-linked networks to form new HA domains and thus leading to low healing

efficiency. However, the addition of starch was unable to vanish the healing ability of the gel completely, and a satisfactory amount of healing efficiency was observed in the case of SAS3 even in the presence of 35.29% starch. Although the healing efficiency of SAS3 was much lower than SAS1, the tensile strength of the healed SAS3 was much higher than the healed SAS1 and the elongation at break showed a similar trend before and after healing. However, the hydrogel with 40.54% of starch was not able to show proper self-healing ability even after 2 h, as shown in **Figure 5.9.d**.

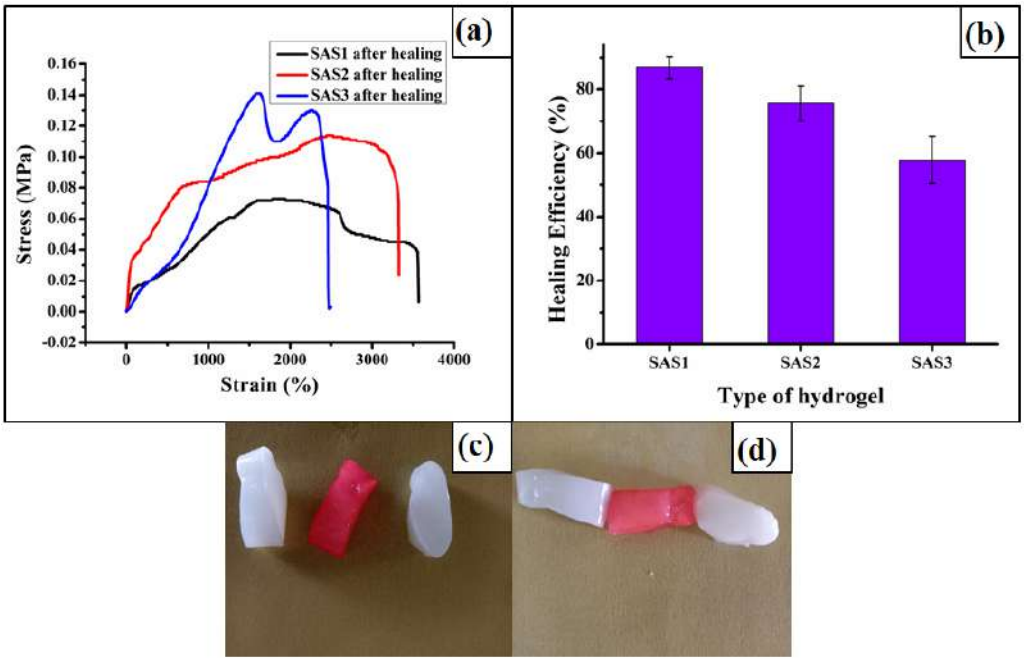


Figure 5.9. (a) Tensile strength of the healed hydrogel, (b) healing efficiency of the synthesized hydrogel, digital photographs of (c) three pieces of SAS4, and (d) hydrogel without proper healing of the cut pieces, after 2 h

5.3.9. Toughening and self-healing mechanism

To reduce the brittleness and enhance the mechanical strength of the conventional hydrogel, different strategies have been adopted over the decades. Among these, only chemically cross-linked, physically-chemically cross-linked, and physically-physically cross-linked methodologies have been accepted, broadly. To evaluate the toughening mechanism of the synthesized starch containing self-healing hydrogel, we have compared thoroughly the different toughening mechanisms.

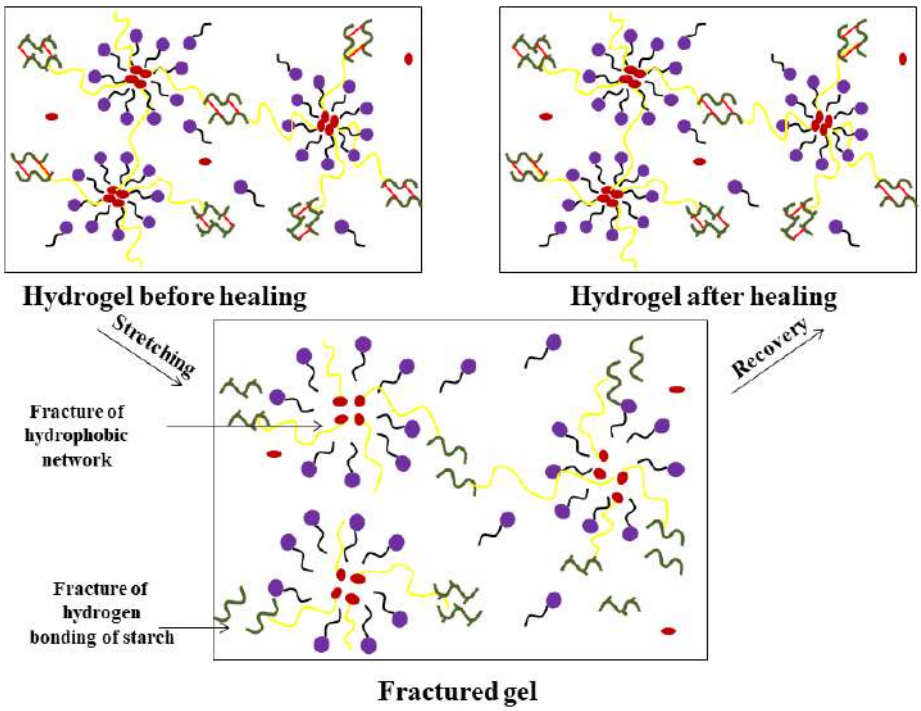
In case of chemically cross-linked gels, the toughness mechanism is mainly based on the concept of "sacrificial bonds". Briefly, the first network is made up of strong polyelectrolytes that undergo permanent breakage upon deformation and these broken

blocks serve as the sacrificial bonds to protect the second network. Thus, the first network increases the resistance of the whole gel network against the crack formation by creating a huge damage zone [9]. Moreover, the permanent damage of the first network leads to irreversible dissipation of energy in hysteresis measurement [23, 24].

But in case of physically-chemically cross-linked DN hydrogel, the first network is physically linked via hydrogen bonding or ionic interaction. For example, in case of agar/PAM gels as reported by Chen et al., the first network is formed by physically cross-linked agar, while the second network is formed by chemical cross-linker MBA cross-linked PAM. This work suggested that the toughening phenomenon is mainly based on the "chain-pulling-out" mechanism [9]. According to this mechanism, during the deformation agar network did not fracture into small fragments, instead the agar network progressively pulls out from the aggregated agar helical bundles. This continuous fracture process leads to the hybrid hydrogel towards a velocity-dependent fracture process. The damage zone can recover under the use of heat energy as the stimulus or after loading during a certain time interval and thus exhibit self-recovery property. Hence, from both the chemically-chemically DN and chemically-physically DN gels, the toughness originates from the first network, but the soft PAM network unable to bear the stress. Moreover, when this soft PAM is replaced by a physically cross-linked HA network, the hydrogel showed slightly higher mechanical strength than the agar/PAM gel and showed self-healing ability without any external stimuli within 24 h, as reported by Chen et al. [25].

Our starch containing physically cross-linked self-healing hydrogel also showed a similar effect, and the incorporation of starch showed a noteworthy effect on the mechanical strength. The mechanical strength of the hydrogel was enhanced with the increase in starch amount. Similar observation was also reported by Shang et al. in case of self-healing hydrogel [26]. This suggests that the presence of starch with the HA network contributes towards the enhancement of the mechanical properties of the hydrogel. Actually, the starch hydrogen bonded network acts as the "sacrificial" physical network that protects the HA network. Moreover, it may also act as the "load carriers" to effectually withstand the large deformation. The strong hydrogen bonded starch networks also act as a "scaffold" to successfully transfer the stress throughout the whole three-dimensional network of the hydrogel. However, the reversible and noncovalent HA-PAM network can also bear stress and combination of both physical networks contributes towards the enhancement of mechanical strength.

Our synthesized hydrogel showed noteworthy self–healing ability even after incorporation of a large amount of starch. However, as this starch network has no contribution to the self-healing property of the hydrogel and hence full recovery was not possible to achieve after damage. Moreover, the decrement of the healing efficiency with the increase in starch amount reveals that the starch network is unable to recover automatically. This observation suggests that the reversible, non-covalent physically cross-linked HA-PAM network is responsible for the self-healing ability of the hydrogel [8]. After breakage, the reversible strong hydrophobic interactions between the alkyl groups of the SMA chains and the SDBS micelle can rapidly reconstruct upon deformation without any external stimuli and provide self-healing ability within 20 min. Moreover, the HA network also bears the stress after the breakage of the starch containing physical network and the combination of these leads to the enhancement of the mechanical strength. Thus, along with the self-healing ability, the ductile and soft HA network also contributes towards the tensile strength of the hydrogel. Thus, this mechanistic pathway provides a starch containing hydrogel with high mechanical strength and high stretch ability that can be self-healed without the use of any external stimuli. The schematic representation of the fracture and self-healing process of the hydrogel is represented in **Scheme 5.2**.



Scheme 5.2. Schematic representation of the fracture and self-healing process of SAS3.

To provide the evidence for the presence of HA network we have conducted the experiment without addition of the surfactant. It was found that the hydrogel without surfactant was not possible to carry out the mechanical test as no ordered stable dimension was formed (**Figure 5.10.a**). Further, this hydrogel was also unable to exhibit high stretch ability. This observation proves that the hydrophobically associated domain could be formed only in the presence of surfactant, and this surfactant has noteworthy contribution for the polymerization process. Without surfactant, even in the presence of higher carbon containing SMA, the hydrogel was unable to process high stretch ability (**Figure 5.10.b-d**). Thus, this experiment provides the evidence for micellar polymerization and only in the presence of the surfactant, the polymerization could be successfully performed.

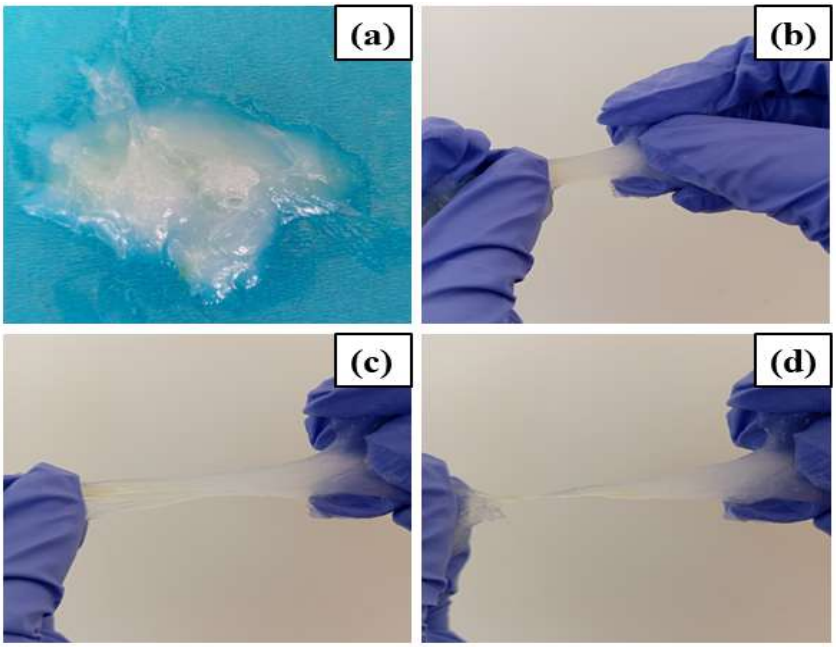


Figure 5.10. (a) SASW hydrogel, and (b–d) stretching of SASW hydrogel.

5.3.10. Comparison of present self-healing hydrogel with other reported hydrogels

To investigate the effectiveness of our synthesized hydrogel as a mechanically tough self-healing material, we have compared its various properties with reported hydrogels. However, it is to be remembered that different hydrogels have been synthesized under different experimental conditions for various purposes; hence it is quite complicated to exactly compare their properties. Although lots of self-healing hydrogels have been reported in the last few decades, but stimulus dependence healing ability and long recovery time restricted their applications. For example, an Agar/PAM DN hydrogel

with high toughness (500–1000 J/m^2) was fabricated by Chen et al., which exhibited temperature-dependent self-healing ability and hence restricted its applicability [9]. Wang et al. prepared an amphiphilic terpyridine-based molecule incorporated hydrogel that can exhibit radically induced healing ability [27]. Moreover, requirement of short healing time is one of the most important properties for practical applications of hydrogels. But most of the reported hydrogels required long healing time. For example, HA agar/PAM gel reported by Chen et al. possesses healing time of 24 h [25].

In contrast, our starch containing HA hydrogel can be self-healed within 20 min at room temperature without the application of any external stimuli, which may extend its applicability. Moreover, it is seen that our SAS1 hydrogel can receive higher healing efficiency though it possesses relatively lower mechanical strength than the above-reported hydrogels. However, in case of SAS3, a much higher tensile strength was noticed than SAS1, though the healing efficiency was lower. Thus, it is seen that the properties of our synthesized hydrogel can be tuned according to the specific applications. Moreover, all the hydrogels possess higher elongation at break which was several times higher than the above-reported hydrogels. Most importantly, our synthesized hydrogel can retain its stability as well as mechanical strength after swelling in water for 1 week or so, which is one of the most interesting properties of this hydrogel. Above all, our synthesized hydrogel is a bio-based starch containing hydrogel, and amount of starch has noteworthy influence on the mechanical property. All these results support that our synthetic strategy is a promising route to synthesize a bio-based self-healing hydrogel with high mechanical strength that can be widely used for various practical applications.

5.4. Conclusion

In this work, we introduce a new design strategy to fabricate a self-healing bio-based hydrogel consisting of both HA domains and physically cross-linked starch. The addition of starch enhanced the mechanical strength of the hydrogel, but the self-healing ability is reduced. Moreover, the addition of starch also makes the hydrogel bio-based. The physically cross-linked HA network introduces shape-recovery property along with superior self-healing property via reversible chain reconstruction. The mechanical property of the hydrogel was greatly affected by the amount of starch and enhanced with the increase in its amount. Additionally, due to its reversible and physically cross- linked

network structure, the damaged hydrogel can reconstruct within 20 min at room temperature without the exposure of any external stimuli. Moreover, the one-pot polymerization reaction leads to the formation of a hydrogel with a free shapeable property. Most importantly, the hydrogel can retain a satisfactory amount of mechanical strength along with the absorbed water. Thus, this work provides a new bio-based soft-but-tough hydrogel containing starch with desired properties via a simple one-pot polymerization technique. Most importantly, along with the formation of a novel starch containing self-healing hydrogel, this work helps to understand the toughness mechanism of a fully physically cross-linked hydrogel network and hence enriching the knowledge of existing hydrogel research.

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