

Preparation and Characterization of PAM/SA Tough Hydrogels Reinforced by IPN Technique Based on Covalent/Ionic Crosslinking

Yali Li, Chaoxia Wang, Wan Zhang, Yunjie Yin, Qingqing Rao

Key Laboratory of Eco-Textile, Ministry of Education, School of Textiles and Clothing, Jiangnan University, Wuxi 214122, China

Correspondence to: C. X. Wang (E-mail: wangchaoxia@sohu.com)

ABSTRACT: In order to fabricate tough hydrogels with superior formability, polyacrylamide/sodium alginate (PAM/SA) interpenetrating polymer network (IPN) hydrogels were produced with ionically crosslinked SA interpenetrated in covalently crosslinked PAM. TGA results show that the heat resistance of PAM/SA IPN hydrogel is improved as compared to that of the individual component. Swelling studies indicate that increasing either chemical crosslinker content or ionic crosslinking via adding more *N,N'*-methylenebisacrylamide (MBA) or SA results in lower ESR. It is concluded by tensile test that loosely crosslinked PAM coupled with tightly crosslinked SA improve mechanical strength for hydrogels based on covalent/ionic crosslinking. PAM/SA hydrogels via “one-pot” method can form different complex shapes with mechanical properties comparable to conventional double network (DN) gels. The fracture strength of PAM_{0.05}/SA₂₀ reaches level of MPa, approaching 2.0 MPa. The work strives to provide method to tune mechanical and physical properties for hydrogels, which is hopefully to guide the design of hydrogel material with desirable properties. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41342.

KEYWORDS: covalent/ionic crosslinking; formability; mechanical properties; swellability; tough hydrogels

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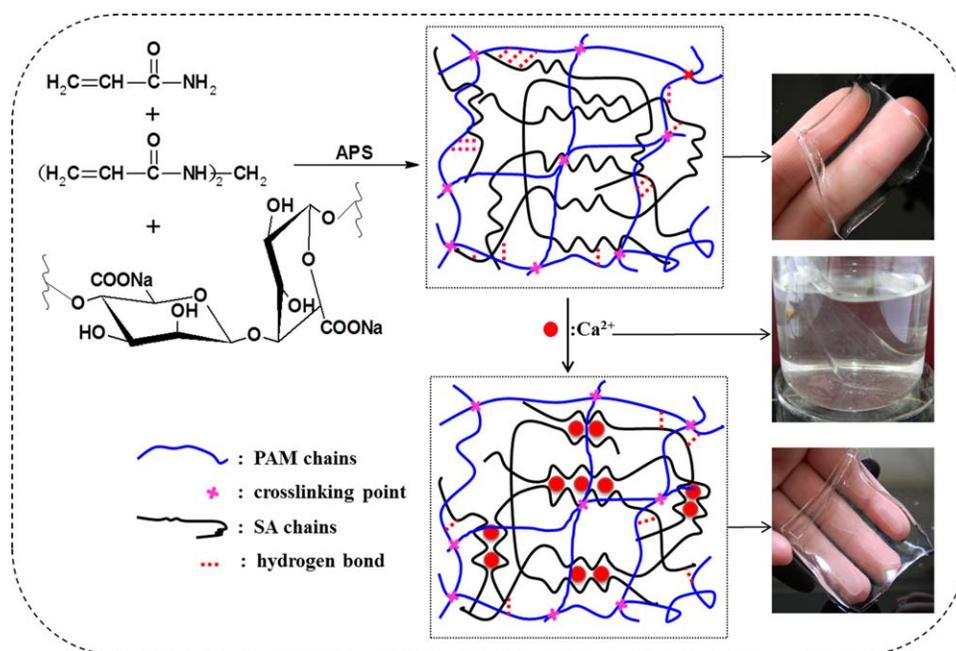
INTRODUCTION

Hydrogels, which can be formed from synthetic and naturally derived polymer, are chemically or physically crosslinked three-dimensional polymer network with unique properties, such as high swelling ratio, soft handle, and special gel-like state. However, hydrogels formulated via conventional way suffer from lack of mechanical strength, exhibiting low tensile and compressive strength (1–100 kPa),¹ which hinders their extensive use as load-bearing material. The poor mechanical properties of these hydrogels are ascribed to irregular crosslinking point between polymer chains, so the stress cannot be evenly distributed and effectively dissipated under external force.

Various efforts have been devoted to toughening hydrogels. One approach to modulate hydrogel strength is nanocomposite (NC) technology using inorganic clay as crosslinker instead of organic crosslinker. In NC gels, rigid crosslinking points and flexible crosslinking chains can prevent crack from a single chain spreading over many other chains. Zhu and co-workers^{2,3} have successfully used clay Laponite XLS to enhance tensile strength to 350 kPa. However, strength improvement is restricted by clay content because of high viscosity in presence of high clay concentration. Hydrogels in topological structure using figure-of-eight crosslinkers also present high resistance to extension and volume swelling, up to 20 times longer than its original length

and 500 times that of its original weight. But it only applies to few chemicals with special slide-ring structure.⁴

IPN system is another effective strategy to toughen hydrogels. IPN gels can be divided into full IPN and semi-IPN based on polymer blends in which linear or crosslinked polymers are incorporated into another polymer networks.⁵ Semi-IPN hydrogels based on crosslinked PAM having poly(*N*-isopropylacrylamide) (PNIPAM) inside were reported by Muniz et al. The incorporation of linear PNIPAM improved the mechanical properties of PAM/PNIPAM semi-IPN as compared to the single PAM hydrogel.^{6,7} Zhang et al.⁸ reported PNIPAM/PNIPAM IPN hydrogels with better mechanical strength, and the IPN hydrogels were used for release controlling of 5-fluorouracil. The DN gels using two-step sequential free-radical polymerization method proposed by Gong and co-workers in 2003 are a representative family of IPN hydrogels. Based on DN design principle, they synthesized a series of DN hydrogels, such as poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS)/PAM, methacrylated chondroitin sulfate (MCS)/PAM, poly(2-hydroxyethylacrylate) (PHEA)/PAM, and poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide) (PBDT)/PAM gels.^{9,10} Among them, the most representative PAMPS/PAM exhibits a compressive stress as high as 17 MPa.¹¹ PBDT/PAM DN gel possesses tensile fracture stress of 0.4 MPa, elastic modulus of 0.35 MPa and failure strain of 2200%.¹² Nonetheless, DN gels still exist



Scheme 1. Schematic formation mechanism of PAM/SA IPN hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

some problems which are lack of formability and processability. Recently, there is a trend to toughen hydrogels based on physical crosslinking, such as intermolecular hydrogen bonding researched by Song and Zhang,^{13,14} dipole–dipole interaction focused by Bai,¹⁵ and ionic interaction studied by Sun.¹⁶

The aim of this work was to improve hydrogel strength based on synergetic reinforce using covalently crosslinked PAM and ionically crosslinked SA, taking advantage of toughening mechanism of the DN gels. Here, PAM was chosen as matrix because of its ductility and simple polymerization. SA was used as component of ionically crosslinked network due to its biocompatibility and toxicity. The “one-pot” method reported in this paper is simple, through which hydrogels presented high mechanical strength with excellent formability over conventional DN gels. PAM/SA semi-IPN and IPN hydrogels were fabricated to evaluate the effect of ionic crosslinking on hydrogel properties, especially the mechanical properties. The main parameters affecting mechanical performance of hydrogels, as well as the swelling behavior were researched. The toughening mechanism was elucidated.

EXPERIMENTAL

Materials

Acrylamide (AM, CP grade), *N,N'*-methylenebisacrylamide (MBA, CP grade), ammonium persulfate (APS, AR grade), sodium alginate (SA, CP grade), and calcium chloride (CaCl_2 , AR grade) which used as received were all purchased from Sinopharm Chemical Reagent. Reactive Orange 122 (industrial product) was provided by Sunny-Chem Colors.

Hydrogel Preparation

SA powder, APS were made up in stock solution before use. To prepare hydrogels, specified AM monomer and various amount

of crosslinker (MBA) were dissolved in some deionized water. Then APS solution was added to the above solution, followed by the introduction of SA stock solution along with extra water. After stirring evenly, the reaction solution was transferred into the reaction mould. The reaction was carried out at 60°C in which the final monomer concentration was $2M$, APS concentration was $0.006M$, MBA and SA concentration varied from 0.025 to 1 mol %, 0–20 wt %, respectively. To form ionic crosslinking network, the as-prepared hydrogels were stored in CaCl_2 solution, in which the Ca^{2+} ion behaves as an ionic crosslinker. SA gelled by CaCl_2 was notated as SA/Ca^{2+} . The proposed formation mechanism is shown in Scheme 1. Sample through ionic crosslinking step was referred as IPN. And sample without ionic crosslinking was termed as semi-IPN. Both IPN and semi-IPN need to be stored in deionized water for several days to leach out of the untreated chemicals prior to their characterization. Hereafter, the prepared hydrogels are referred as PAM_a/SA_b , where a is the molar percentage of MBA (mol %) in mol % with respect to AM mole, and b is mass percentage of SA (wt %) in wt % relative to AM mass.

Swelling Studies

Cylindrical gels with the same dimension (15 mm in diameter, 10 mm in length) were stored in deionized water at 25°C until equilibrium. The IPN samples were immersed in 2 wt % CaCl_2 solution for 24 h before test. After swelling, samples were vacuum dried at 60°C . The equilibrium swelling ratio (ESR) is calculated using the following equation:

$$\text{ESR} = \frac{W_e - W_d}{W_d} \quad (1)$$

where W_e and W_d represent the weights of fully swollen hydrogel and dry hydrogel, respectively.

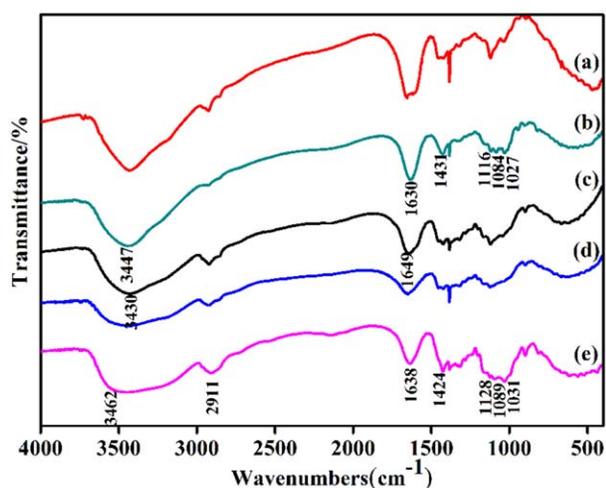


Figure 1. FTIR spectra of (a) PAM/SA IPN, (b) SA/Ca²⁺, (c) PAM, (d) PAM/SA semi-IPN, and (e) SA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile Measurement

Tensile test was performed using a KD II-0.05 tester (Shenzhen, China) with tensile velocity of 30 mm · min⁻¹. Each sample was tested at least three times. The tensile strength is under maximum stress sustained during the test, and elongation stands for fracture elongation. The hydrogel samples were cut into strips (5 mm in width, 50 mm in length) with thickness measured by a DUALSCOPE MPO gauge. For these IPN samples, the as-prepared hydrogels were immersed in 2 wt % CaCl₂ solution for 24 h. For these semi-IPN samples, the as-prepared hydrogels were directly used after surface washing with deionized water and then blotting with filter paper. The elastic modulus (*E*) is determined by the slope of linear dependence from the stress-strain curve over the strain ratio of 0–10%.^{7,17}

FTIR Analysis

The Fourier Transform Infrared (FTIR) spectra were obtained on a NICOLET is10 spectrometer in the range of 400–4000 cm⁻¹ for 32 scans. The dry hydrogels were pressed into disk with KBr powder before data collection.

Thermal Analysis

TGA/SD TA851e was used for thermal analysis of SA/Ca²⁺, PAM, and PAM/SA IPN hydrogels under nitrogen atmosphere. Samples weighting 5–10 mg were heated from ambient temperature to 800°C at heating rate of 20°C · min⁻¹.

RESULTS AND DISCUSSION

Infrared Spectroscopic Analysis

To characterize the structure of prepared hydrogels, the FTIR spectra of SA, PAM, SA/Ca²⁺, PAM/SA semi-IPN, and PAM/SA IPN were included in Figure 1. In Figure 1(e), SA exhibits a broad band at 3462 cm⁻¹ responsible for the stretch vibration of –OH group, a sharp peak at 2911 cm⁻¹ assigned to C–H stretch vibration, two peaks at 1638 and 1424 cm⁻¹ account for antisymmetric and symmetric stretch of –COO⁻. From Figure 1(b), SA/Ca²⁺ shows wavenumber shift associated with –COO⁻ groups,¹⁸ and a narrower band for O–H stretch at 3447 cm⁻¹, suggesting that some groups on SA chains involve in crosslink-

ing with Ca²⁺ for SA/Ca²⁺ network. The narrower band for O–H stretch and significantly reduced peak intensity at 2911 cm⁻¹ for C–H stretch maybe because the stretch vibrations of C–H and O–H groups on hexatomic ring were restricted by three-dimensional network of SA/Ca²⁺. But for PAM/SA semi-IPN and PAM/SA IPN, peaks assigned to C–H stretch vibration nearby 2911 cm⁻¹ are remarkable. In the spectra of PAM, the overlapped peak nearby 1649 cm⁻¹ belongs to C=O stretch and N–H bend vibration, which also occurs in the spectra of PAM/SA semi-IPN and PAM/SA IPN. Meanwhile, the peak at 3430 cm⁻¹ depicts vibrational peak of N–H. The various peaks mentioned above could be also detected in PAM/SA semi-IPN and PAM/SA IPN, confirming the presence of PAM and SA in the polymer hydrogels. Moreover, the adsorption peaks nearby 3400 cm⁻¹ for –OH or –NH₂ groups, coupled with peaks nearby 1600 cm⁻¹ for –COO⁻ and –NH₂ groups are slightly deflected, confirming the occurrence of new hydrogen bonds between –COO⁻ or –OH on SA and –CONH₂ on PAM, which is in accordance with the results reported by Solpan.¹⁹

Thermal Analysis

Figure 2 contains typical curves of thermograms for SA/Ca²⁺, PAM, and PAM/SA IPN hydrogels. And temperature for maximum weight loss rate (*T*_{max}) and half life (*T*_{1/2}) are used to evaluate the thermal performance.

From Figure 2, PAM gives 50% residue at *T*_{1/2} = 377°C and undergoes three main decomposition stages at 200–330, 330–480, and 480–800°C. Weight loss in the first stage could be related to the degradation of PAM side chains,²⁰ resulting in the formation of imide with ammonia release from every two amide groups. The subsequent weight loss indicates that polymer backbone of PAM breaks and more extensive thermal degradation of imides occurs.^{16,19} SA/Ca²⁺ shows *T*_{1/2} = 481°C. Weight loss below 200°C attributes to the loss of water. The sharp weight loss between 200 and 337°C with 33% weight loss is speculated for the thermal degradation of carboxyl group on side chains, resulting in CO₂ releasing.¹⁶ The weight loss above 337°C ascribes to more extensive degradation of backbone, as char yields. The temperature of 10% weight loss (*T*_{10%}) for

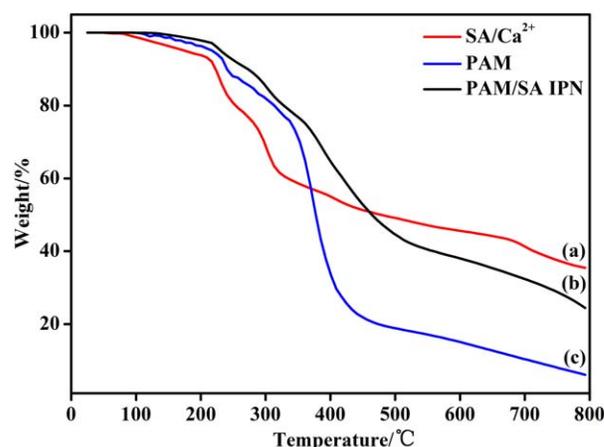


Figure 2. TGA spectra of (a) SA/Ca²⁺, (b) PAM/SA IPN, and (c) PAM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

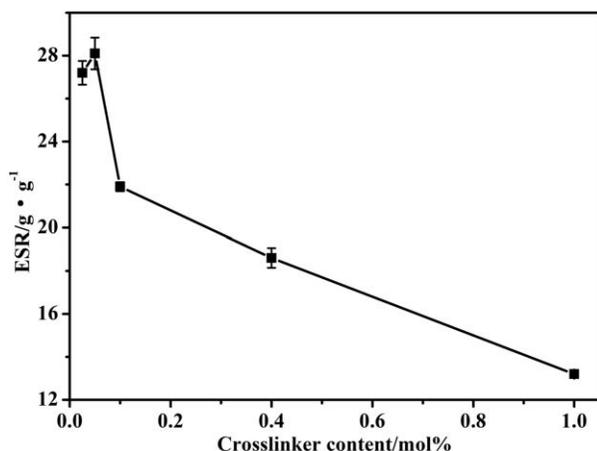


Figure 3. ESR of PAM_a/SA₅ semi-IPN hydrogels as function of crosslinker content.

PAM and SA/Ca²⁺ is 241 and 223°C, respectively, implying that the thermal stability of PAM is higher than SA/Ca²⁺. The $T_{10\%}$ of PAM/SA IPN is 275°C, by contrast, presenting higher than that of the individual component. Compared to PAM of $T_{max} = 377^\circ\text{C}$ coupled with SA/Ca²⁺ of $T_{max} = 305^\circ\text{C}$, the T_{max} for PAM/SA IPN is shifted to a higher temperature of 385°C. These results indicate that the heat resistance of PAM/SA IPN is improved, which may be due to the synergistic improvement of IPN network formed by PAM and SA/Ca²⁺.^{21,22}

Comparison of Swellability

Swellability, which relates to expansion of polymer network promoted by chain expansion, is among the most important properties used to assess hydrogels, reflecting the network density. From Figure 3, it is noteworthy that the increase of crosslinker content leads to a decline in ESR, except at MBA 0.025 mol %. This is because that at very low MBA dosage, the formation of hydrogel network is incomplete. As MBA further increases from 0.05 to 1 mol %, ESR declines from 28 to 13 which attributes to the denser network caused by the increasing chemical crosslinker content.

Figure 4 compares ESR of hydrogels between samples through or without ionic crosslinking which reveals an opposite trend as SA content increases. Although physical reinforcements caused by the entanglements of SA inside PAM contribute to a decrease in the degree of swelling,²³ ESR presenting an increasing trend is ascribed to the hydrophilia of $-\text{COO}^-$ and $-\text{OH}$ groups on SA. But for IPN hydrogels, ESR decreases with the increase of SA. Therefore, these results confirm that the higher crosslinking density caused by ionic crosslinking between SA and Ca²⁺ with increasing SA dosage outweighs the contribution of hydrophilia SA. Meanwhile, hydrogels without ionic crosslinking exhibit much higher ESR in comparison with that of the corresponding IPN hydrogels. When the amount of SA is 15 wt %, the ESR of semi-IPN hydrogel can reach up to 46, that is, four times higher than that of the corresponding IPN hydrogel.

The above results demonstrate that, for IPN hydrogels, increasing either chemical crosslinker content or ionic crosslinking via adding more MBA or SA results in lower ESR.

Tensile Testing

Effect of Crosslinker Content on Tensile Properties. The mechanical properties for hydrogels are essential parameters to investigate when used as load-bearing material. As PAM_{0.025}/SA₅ hydrogel is proteiform, extremely unsuitable for tensile test, Figure 5 represents tensile properties for semi-IPN hydrogels with various crosslinker contents from 0.05 to 1 mol %. Under tensile strains, these hydrogels sustain an elongation up to 1000% or even higher before fracture. Meanwhile, the fracture strength can reach up above 200 kPa, which is higher than 100 kPa of conventional hydrogels.¹

Usually, a denser network leads to higher mechanical strength.²⁴ Whereas the experiment performed here shows an opposite result. Two factors contribute to hydrogel strength are proposed: one is crosslinking density which is reflected by swelling degree, and the other is movement of polymer chains which is supposed to slow crack propagation. The decrease of tensile strength as MBA increases may be better understood by taking into account the polymer chains' movement. Denser network responsible for higher crosslinking density will result in lower average molecular length between crosslink points and, therefore, weaken movement of polymer chains. When the gel is stretched, the short-chain network ruptures because of the ineffective dissipation of energy stored between crack tips. But for the longer chain, the crack propagates through polymer chains' movement related to their flexibility. The higher stress at lower crosslinker content demonstrates that flexibility dominates in the strength of chemical crosslinking PAM hydrogels.

The elastic modulus, also known as Young's modulus, is one of the indexes for evaluating material's stiffness which is proportional to the crosslinking density. From Figure 5, a steady increase in elastic modulus can be seen for semi-IPN hydrogels with increasing crosslinker dosage. From Figure 3, we can confirm that the lower swelling ratio caused by the augment of crosslinker content indicates a higher crosslinking density, which means the material becomes more rigid, resulting in the improvement of elastic modulus.⁷

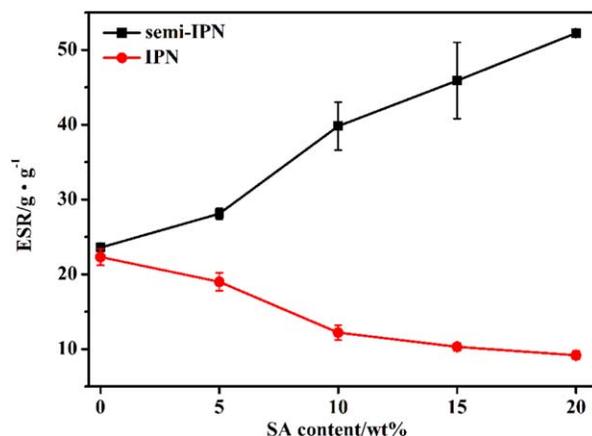


Figure 4. ESR comparison of PAM_{0.05}/SA_b semi-IPN and IPN hydrogels as function of SA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

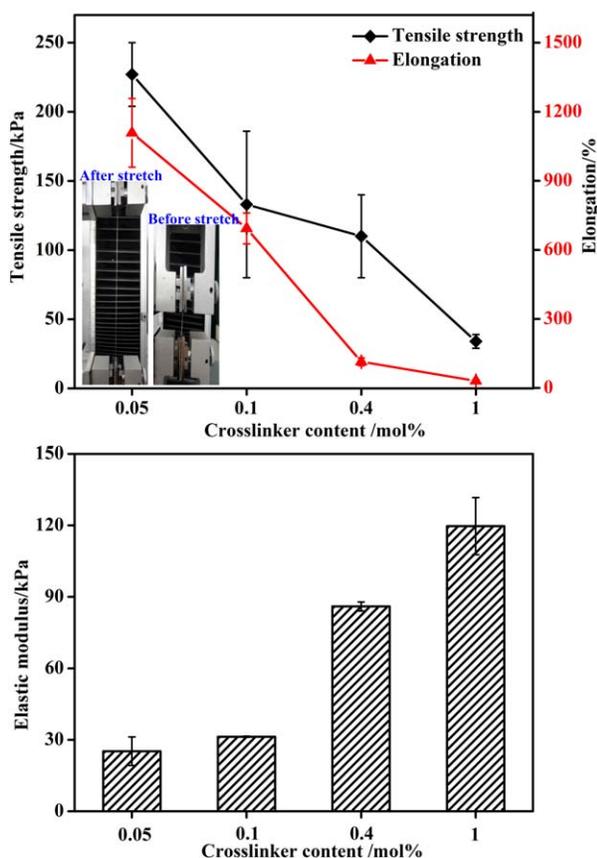


Figure 5. Tensile properties of PAM_{0.05}/SA₅ semi-IPN hydrogels with various MBA contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Ionic Crosslinking on Tensile Properties. SA composed of mannuronic acid and guluronic acid residues can gelate in presence of Ca²⁺, producing changes in network structure, consequently affecting mechanical properties. PAM_{0.05}/SA₅ and PAM_{0.1}/SA₅ through or without ionic crosslinking were used to investigate the effect of ionic crosslinking on tensile

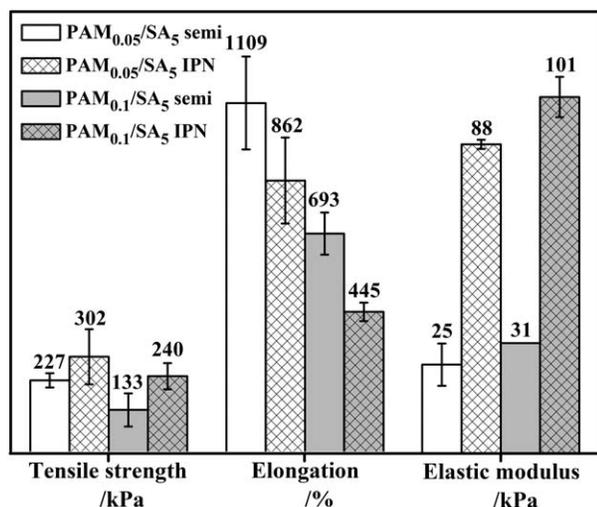


Figure 6. Comparison of tensile properties through or without ionic crosslinking.

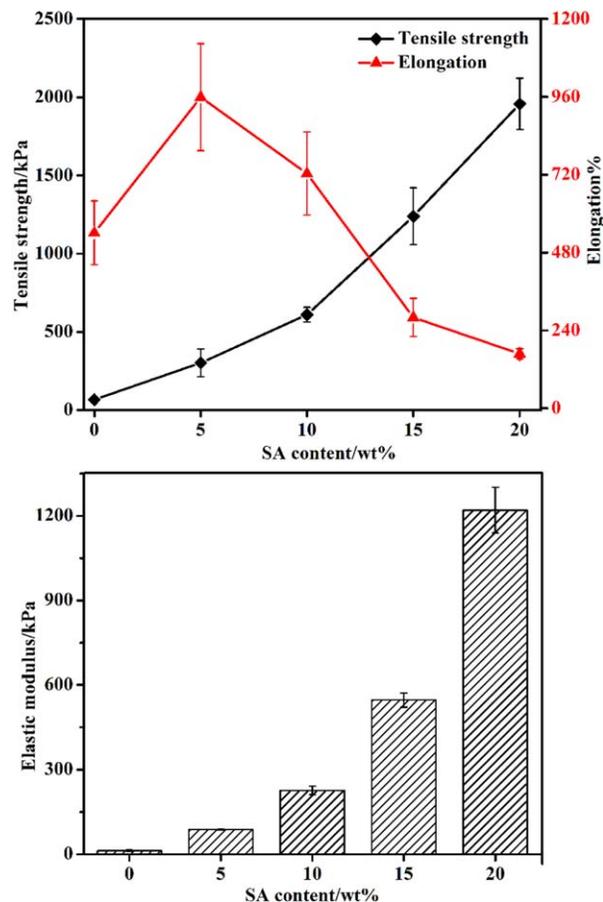
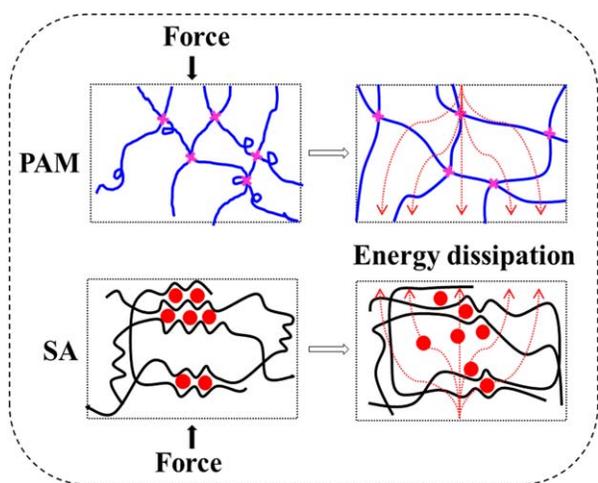


Figure 7. Tensile properties of IPN hydrogels with various SA contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

properties. As shown in Figure 6, PAM_{0.05}/SA₅ exhibits large stretchability up to 1109% and fracture strength of 227 KPa in the absence of Ca²⁺. While in presence of Ca²⁺, hydrogel sustains higher fracture strength and elastic modulus than those without Ca²⁺. Meanwhile, the same results can be observed for PAM_{0.1}/SA₅. After ionic crosslinking, the SA chains are trapped in the PAM network and form additional network. And the additional network can bear load and assist in energy dissipating to a large zone during the fracture process, which results in the high mechanical strength observed in the series of PAM/SA IPN hydrogels. Moreover, the elastic modulus of hydrogel through ionic crosslinking is higher than that without ionic crosslinking, which can be related to the additional crosslink points provided by the crosslinked SA network. As ionically crosslinked SA leads to an increase in the crosslink density throughout the gel structure which is derived in Figure 4, then the denser network implies higher elastic modulus.

Effect of SA Content on Tensile Properties of IPN Hydrogels.

Figure 7 illustrates the dependence of tensile properties on SA content. From the figure, incorporation of SA into PAM gels improves the tensile strength which attributes to the entanglement of SA with PAM networks. Tensile strength increases by increasing SA concentration, while elongation diminishes corresponding. At higher SA content, the additional network



Scheme 2. Energy dissipation of single network. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

produced by SA in presence of Ca^{2+} becomes compact which contributes to energy dissipating, as a result, hydrogels may sustain high fracture stress. It is astonishing that the fracture strength of $\text{PAM}_{0.05}/\text{SA}_{15}$ and $\text{PAM}_{0.05}/\text{SA}_{20}$ hydrogels reach

level of MPa. Due to denser network caused by augment of SA content, the elastic modulus increases as increasing SA content. The modulus of $\text{PAM}_{0.05}/\text{SA}_{15}$ is nearly six times larger than that of $\text{PAM}_{0.05}/\text{SA}_5$.

Toughening Mechanism

In DN gels, one ductile network is loosely crosslinked within another tightly crosslinked network. The speculated reason of toughness improvement for DN gels is that tightly crosslinked network dissipates strain energy and the loosely crosslinked network supports high strains.²⁵ In contrast, IPN hydrogels based on covalent/ionic crosslinking here is composed of a tighter crosslinked SA network within a loosely crosslinked PAM network. The decline in crosslinking density of PAM leads to longer unbounded sections between crosslinking points. So the applied load can be distributed effectively through movement and deformation of polymer chains as seen in Scheme 2, which improves the resistance ability of stress concentration. The tough network with loose crosslinking is parallel with DN gels. Even the fracture strength of as-prepared $\text{PAM}_{0.05}$ can reach up to 120 kPa, which confirms this result. On the other hand, denser network of SA trapped in PAM network unzips over a large zone before network fracture. The synergistic effect of covalent/ionic crosslinking between two networks facilitates efficiently energy transfer.

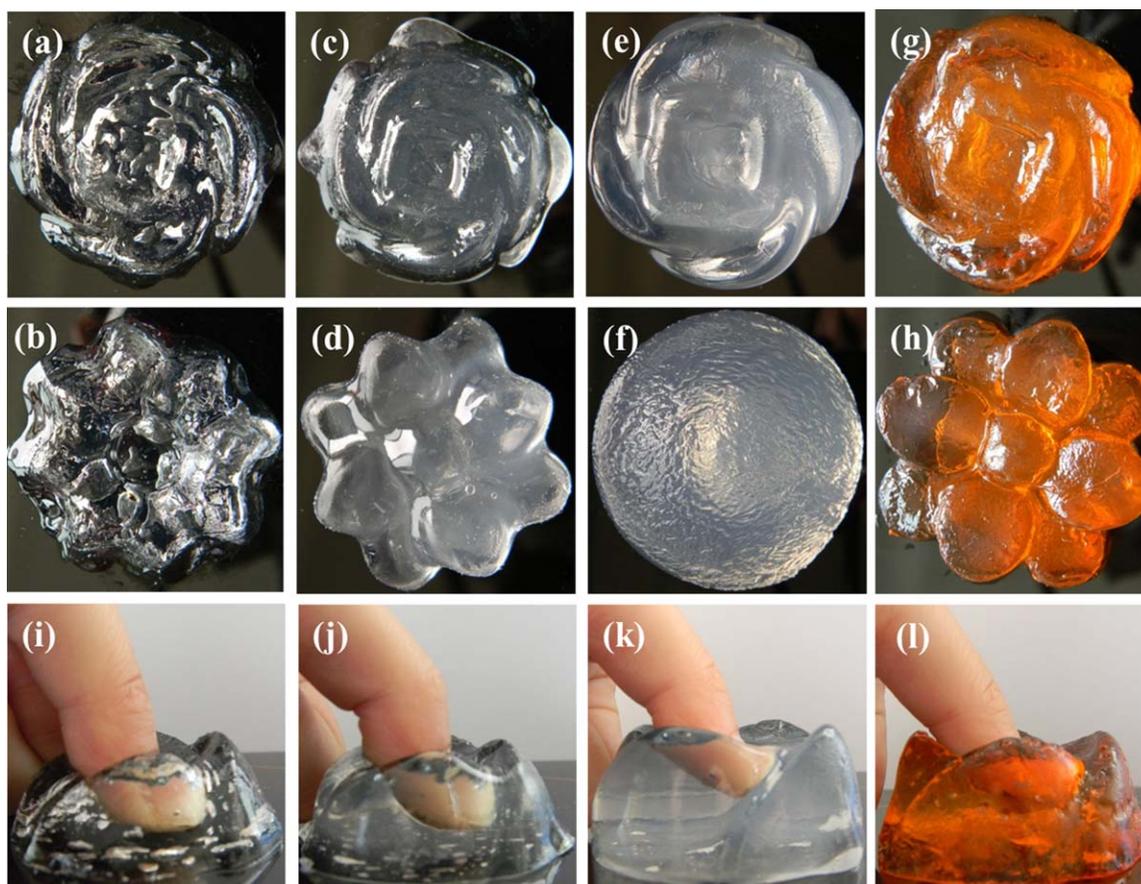


Figure 8. The pictures of hydrogels with different shapes: (a) and (b) represent $\text{PAM}_{0.05}$; (c) and (d) denote $\text{PAM}_{0.05}/\text{SA}_{10}$ semi-IPN; (e) and (f) are $\text{PAM}_{0.05}/\text{SA}_{10}$ IPN; (g) and (h) stand for dyeing $\text{PAM}_{0.05}/\text{SA}_{10}$ IPN; (i), (j), (k) and (l) represent $\text{PAM}_{0.05}$, $\text{PAM}_{0.05}/\text{SA}_5$ semi-IPN, $\text{PAM}_{0.05}/\text{SA}_{10}$ IPN and dyeing $\text{PAM}_{0.05}/\text{SA}_{10}$ IPN hydrogels under finger compression. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Formability

The conventional DN gel is fabricated via two-step sequential polymerization process. And the first network which determines the shape behaves too fragile and weak to handle owing to its brittleness. So it is less likely to remain intact before the second step. While PAM and PAM/SA semi-IPN hydrogels prepared here via “one-pot” method can form different shapes as Figure 8 exhibited, which shows that formability of this covalent/ionic crosslinking hydrogel is introduced by the flexible and soft matrix network. After stored in CaCl_2 solution, PAM/SA IPN hydrogels are endowed with superior mechanical properties as can be felt through simple compression by finger. Furthermore, PAM/SA IPN hydrogels can present a ball-like shape as seen in Figure 8(f) which cannot be formed via conventional DN method.²⁶ This facile method utilizes ductile PAM as matrix, and SA is ionically crosslinked within PAM network to enhance mechanical strength, avoiding two-step polymerization, thereby simplify the process. Moreover, PAM/SA IPN hydrogels can absorb dyestuff, presenting colorful owing to their reversible swellability, which will expand their application for different fields, such as the removal of heavy metal ions and dyes.¹⁹ Compared to those hydrogels with low mechanical strength, the PAM/SA IPN hydrogels can be circularly used.

CONCLUSIONS

In this research, PAM/SA semi-IPN and IPN hydrogels were successfully synthesized through IPN technique with PAM as matrix and SA as interpenetrated component. The unique network structure of covalent/ionic crosslinking for PAM/SA IPN hydrogels endows them with higher tensile strength and lower ESR than the corresponding semi-IPN hydrogels. The presence of SA or ionically crosslinked SA in PAM/SA hydrogels improves tensile strength. Elastic modulus of PAM/SA hydrogel is improved with increasing either MBA or SA content, while tensile strength increases with decreasing MBA content and increasing SA dosage. Tensile testing demonstrates that flexibility dominates in the strength of chemical crosslinking PAM network, and denser network of SA trapped in PAM network synergistically reinforces PAM/SA hydrogels. PAM/SA hydrogels via “one-pot” method exhibit excellent formability over conventional DN gels. The fracture strength of PAM_{0.05}/SA₂₀ approaches 2.0 MPa which is comparable to DN gels.

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