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ARTICLE

Revisiting the mechanism of redox-polymerization to build the hydrogel with excellent properties using a novel initiator

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this paper, polyetheramine, a kind of linear epoxy polymer, has been used as both initiator and cross-linker for the synthesis of polyacrylamide hydrogel by means of one pot method, which is a simple, time saving, facile and easily controlled process and the obtained hydrogel showed super stretchable and highly elastic properties. More impressively, only very low content of polyetheramine (0.1wt%) could exhibit greatly enhanced mechanical properties toward polyacrylamide and the properties of hydrogel could be easily tailored by the weight ratio of polyetheramine to acrylamide. These hydrogels could be stretched up to 2000% with a maximal fracture energy up to 3.2MJ/m³. This type of hydrogels could be recovered immediately with low residual strains upon unloading even after 1000% strain. The presence of polyetheramine could create a more homogeneous distribution of crosslinking points and can dissipate the energy effectively, which can be responsible for the improved mechanical properties.

Introduction

Polyacrylamide hydrogels are “soft and wet” materials that consist of three-dimensional cross-linked networks and can absorb a large amount of water while maintain their shapes. Research on this type of hydrogels has been prompted by the potential applications in many fields such as drug-delivery system^{1,2}, sensing devices³ and tissue engineering⁴. The scope of hydrogel applications, however, is often badly limited by their poor mechanical behaviours⁵. One important reason for its low mechanical strength is that the crosslinking points are distributed irregularly and the polymer chains between the crosslinking points have different lengths, the stress cannot be evenly distributed between the polymer chains. When such a gel is deformed, stress is concentrated on the shortest chain which creates a zone of high stress and crack initiation is facile. As a result, the hydrogels exhibit brittle, low-stretchable and poor mechanical properties. In order to improve the homogenous degree of network for the hydrogel, people have applied different strategies for creating highly stretchable hydrogels. For example, double network (DN) gels have been reported to be tough (elastic modulus of 0.1-1.0MPa) and

strong (failure tensile stress 1-10MPa)^{6,7}. The authors usually introduced second monomer or biomacromolecules to design two stepwise-synthesized polymer networks, in which highly and loosely cross-linked networks act as the first and second network, respectively. The synergistic effects of two networks play crucial roles in dissipating crack energy and enhancing the mechanical properties of the hydrogels. Slide ring (SR) gels usually applied new oligomers with pulley effect in the network of hydrogel and the polymer chains could move freely to equalize the tension of the threading polymer chains in the network to improve the mechanical properties of hydrogel^{8,9}. Nanocomposite (NC) hydrogels usually incorporate the inorganic agents (such as clay sheets¹⁰, carbon nanotubes¹¹ and graphene oxide^{12,13} etc.) in the network as crosslinking points to effectively improve the mechanical properties of hydrogels. Based on these published methods, it is found that people usually incorporated foreign component (reactive monomers, oligomers and inorganic agent) to control over the spatial structure of polymer networks across multiple hierarchical length scales, so as that more chains could take part in sustaining and transforming the mechanical loads effectively in the network and improve the final mechanical properties. By now, almost no research work is focused on the possibility for building the hydrogel with strong mechanical properties from the basic initiative mechanism of polymerization since polyacrylamide hydrogel could be theoretically strong based on the facts that the polymer chains usually have strong interactions with each other and the solvent by hydrogen bond and the chain of polyacrylamide is very rigid in the dry state¹⁴. In fact, the peroxydisulfate and water-soluble aliphatic amines redox system is usually applied to initiate the polymerization of

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Electronic Supplementary Information (ESI) available: Synthesis scheme of PEA and ¹H NMR of the obtained PEA, SEM pictures of PEA-0.3wt% hydrogels, and the comparison of the PEA hydrogel and others gels. See DOI: 10.1039/x0xx00000x

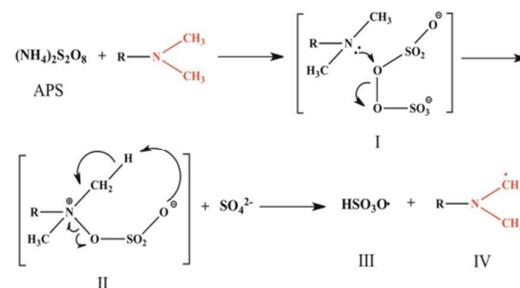
hydrogel via contact charge transfer complex (CCT) and cyclic transition state (CTS) which is still the most commonly used initiator nowadays^{15, 16}. As shown in Scheme 1, lone pair electrons of nitrogen atoms firstly attack the persulfate and the unstable intermediate I, II and sulfate ion are created. Then oxygen anion of sulfate in intermediate II abstracts a hydrogen from dimethyl group. Consequently, the free radicals III and IV that are responsible for initiating the polymerization are formed. Peroxydisulfate can also be decomposed into free radicals itself. But this process usually needs a high temperature (usually above 70 °C) or takes a long time. Aliphatic amine like N,N,N',N'-tetramethylethylenediamine (TEMED) with a tertiary amine structure can react with peroxydisulfate immediately when they are mixed together then the free radicals are created which can initiate the vinyl polymerization even below room temperature. By revisiting the mechanism of polymerization, we found that the tertiary amine from TEMED has two important functions in polymerization. One is to catalyze the radical polymerization occurred at lower temperature and the other is used as an anchor to grow the chain of polyacrylamide. Wang et al. has reported that using graphene peroxide^{17, 18} and macromolecular micropores¹⁹ as poly initiating and crosslinking centers to build tough and super-resilient hydrogels. Inspired by their pioneered work, if we designed the polymer having tertiary amine units to take part in polymerization acting as catalyst (accelerator), is it possible that such polymers could also be acted as initiating and crosslinking centers to build the network for hydrogel? And what are effects of this novel catalyst on the mechanical properties? In this paper, we firstly synthesized linear epoxy polymers having tertiary amine and investigated the possibility of using poly (ether amine) (PEA)²⁰ as the initiating and crosslinking agent to prepare hydrogels. It is unexpectedly found that only 0.1wt% PEA could result in crosslinked polyacrylamide with extraordinary mechanical properties. Such big difference comes from the different molecular weight and high molecular weight of accelerator could be acted as both accelerator and crosslinking agent to build the homogeneous network of polyacrylamide with great improved mechanical properties considering the fact that the networks built by the macromolecular crosslinking agent are lack of short chains and could be more homogeneous than those based on the small molecular crosslinking agent.

Results and discussion

Formation of PEA gels.

The PEA was firstly synthesized by using polyethylene glycol diglycidyl ether (PEO-DE) as difunctional epoxy macromonomer and 3-(dimethylamino)-1-propylamine (DMPA) as diamine (Figure S1). Under the refluxing condition,

the polymerization process was carried out in ethanol with no small molecule generated. The product was confirmed by ¹H NMR (Figure S2). Because of the effective nucleophilic addition/ring-opening reaction, which possesses characterization of “click chemistry”, it's easy to synthesize PEA under mild condition. As illustrated in Scheme 1, lone pair electrons of nitrogen atoms from PEA firstly attack the persulfate and the unstable intermediate I, II and sulfate ion are created. Then oxygen anion of sulfate in intermediate II abstracts a hydrogen atom from dimethyl group of PEA. The free radicals III and IV that are responsible for initiating the polymerization are formed. By this way, PEA could be directly used as the macro initiator and cross-linker for the free radical polymerization of acrylamide. The fabrication processes are illustrated briefly here: firstly, variable molar ratios of PEA and AAm monomers were dispersed in deionized water under ultrasonication to obtain a transparent aqueous dispersion. Then it was bubbled with nitrogen gas for 30 min to remove oxygen. Subsequently, APS was added to the system at 0 °C and stirred for another 10 min. Next, the solution was deaerated under reduced pressure. The polymerization was performed at room temperature for 24h without adding any other cross-linkers or accelerators. For comparison, the conventional chemically cross-linked PAM-MBA hydrogels by adding N,N,N',N'-methylenebis(acrylamide) (MBA, crosslinked agent) and TEMED were also prepared. The formulation of the component for preparation of hydrogel is listed in Table 1 and its preparation process is illustrated in Scheme 2.

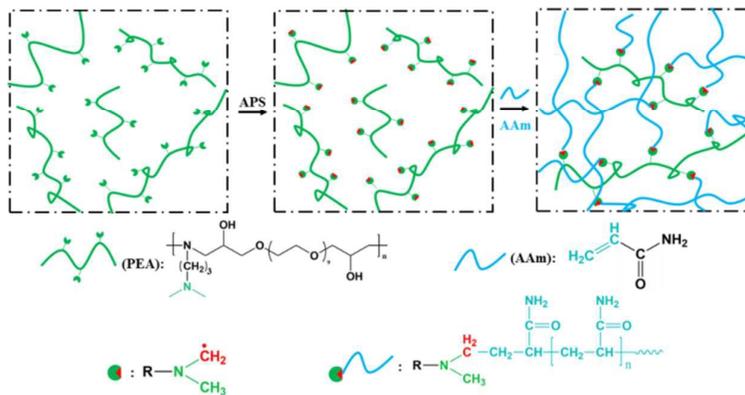


Scheme 1. The initiation mechanism of the system persulfate tertiary amine.

Table 1. Compositions of reactants for the synthesis of the hydrogels including the conventional chemically cross-linked hydrogels using organic MBA cross-linker (PAM-MBA), and PEA-PAM hydrogels with PEA as the cross-linker.

Sample ^a	AM/g	PEA/g	APS/g	TEMED/ μL	MBA/ g	Water content
PEA-0.1	5	0.005	0.0019	0	0	70%
PEA-0.3	5	0.015	0.0057	0	0	70%
PEA-0.5	5	0.025	0.0095	0	0	70%
PEA-1	5	0.051	0.0193	0	0	70%
PEA-5	5	0.263	0.0997	0	0	70%
PAM-MBA	5	0	0.015	4.8	0.004	70%

^aThe letter n of PEA-n represents the weight ratio of PEA.



Scheme 2. Schematic models of the PEA-PAM hydrogels preparation process.

Mechanical properties of PEA hydrogels.

As vividly shown in Fig.1, the as-prepared PEA-PAM hydrogels appeared soft, resilient, tough and completely transparent. They could be bent, knotted, compressed or stretched dozens of times and recover to its initial state immediately after unloading. In addition, these PEA hydrogels didn't dissolve after immersing in large excesses of water for a week. Instead, they could absorb tens of hundreds percentage weight of water compared to their dried state and displayed equilibrium swelling phenomena. These results demonstrate that the stable cross-linking networks were formed. Therefore, we can conclude that in sharp contrast to conventional hydrogels, the as-prepared PEA-PAM hydrogels showed extraordinary mechanical properties.

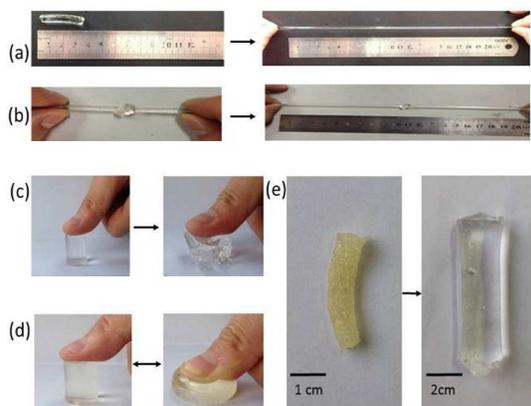


Fig.1 Digital photos of the prepared PEA-0.3wt% hydrogels. The hydrogels could withstand (a) ultrastretching, (b) knotting, (d) compression. Left picture in (e) is frozen-dried sample and the right is the sample immersed in water for a week. Picture (c) is the conventional PAM hydrogel cross-linked by MBA and is so brittle that it's easily broken under compression.

To further verify that the material synthesized is indeed a crosslinked gel instead of a viscoelastic polymer solution, we turned to dynamic rheology measurement on the three samples: a PEA-PAM gel, linear polyacrylamide (PAM), and a conventional PAM-MBA hydrogel. As shown in **Fig.2**, two different types of rheological response were observed, based on the data from the storage modulus G' and loss modulus G'' as functions of frequency (f). For the linear PAM, the sweeping frequency has a profound effect on both the storage modulus G' and loss modulus G'' and it was observed that G' is increased and G'' is decreased with increasing frequency, which is characteristic viscoelastic materials. However, for the conventional PAM-MBA hydrogel and PEA-PAM gel, they show similar behaviors in rheological response which is quite different from that for linear PAM. It is found that both G' and G'' are nearly independent of frequency with G' exceeding the G'' by a factor of 20 over the entire frequency range. Taken these two important characters together, it could be obtained that PEA-PAM hydrogel shows gel like behaviour due to its cross-linked structure based on the results obtained from dynamic rheology study²¹.

We also immersed the as-prepared PEA-PAM hydrogel in urea solution (pH=11) which is a well-known chemical for breaking

hydrogen bonds and hydrophobic interactions²² to verify whether our PEA-PAM is chemically cross-linked. After swelling in urea solution for 1 week (refresh the solution every equilibrium rather than dissolving in the solution with its original cylindrical shape, as shown in **Fig. 2**, and the result

other day), the obtained transparent hydrogel also reached an swelling

convinced us that our PEA-PAM hydrogel is actually chemically cross-linked.

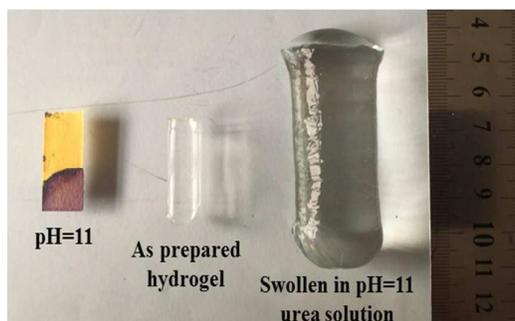


Fig.2 Immersing the as-prepared PEA-0.3wt% hydrogel in urea solution (pH=11)

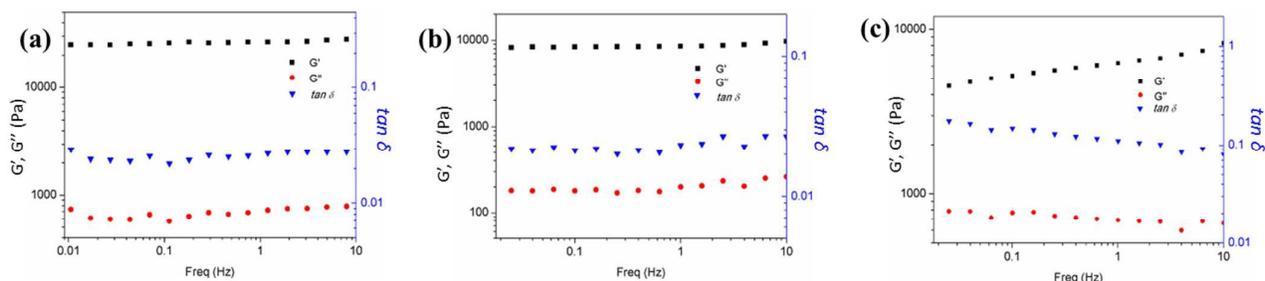


Fig.3 Dynamic rheology of PEA-PAM gels (a) compared with that of PAM-MBA gels (b) and linear neat PAM (c). Storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$) as a function of frequency (f). Reaction conditions: PEA content 0.3wt%, water content of each sample ~ 70 wt%.

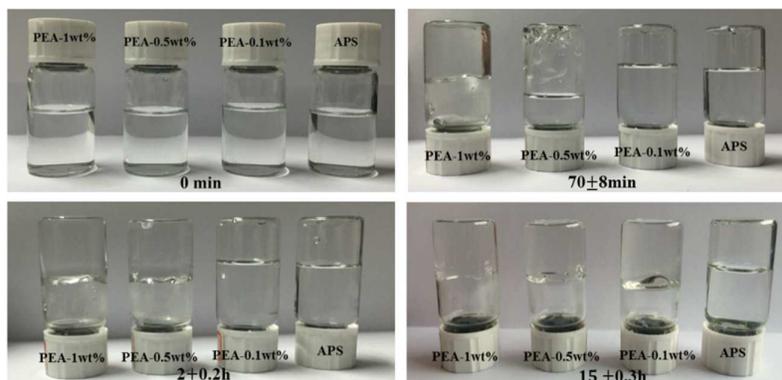


Fig.4 Effect of PEA content on polymerization rate. PEA-0.1wt%, PEA-0.5wt% and PEA-1wt% were synthesised, the reactant compositions were listed in **Table 1**. For comparison, we also mixed AAm aqueous solution with APS (APS content was 0.5mol% relatively to AAm monomer) and no other cross-linker or accelerator was added.

To get a deeper understanding of what role is PEA playing in the system, we studied the effect of PEA content on polymerization rate. As we can observe from **Fig.4**, for PEA-1wt%, the polymerization happened after 70min; for PEA-0.5wt%, about 2h; for PEA-0.1wt%, about 15h; and for APS,

the polymerization cannot be initiated at room temperature. The result suggests that PEA is an important part in this system and the polymerization cannot be initiated without PEA at room temperature.

To assess the mechanical properties of the novel PEA-PAM hydrogels, a set of mechanical tests was performed. **Fig. 5a** shows the uniaxial tensile strain-stress curves of PEA-PAM hydrogels at a crosshead speed of 100 mm min^{-1} with different amounts of PEA and the tensile modulus and the toughness were summarized in **Fig. 5b**. The weakest one was found for the conventional PAM-MBA hydrogel, which was brittle and fractured at a low elongation (only 200% of its original length) with a tensile strength of 30kPa. Further increasing the content of MBA, the PAM-MBA hydrogel would become more brittle with substantially decreasing of elongation at break, though the elastic modulus would increase. That can be ascribed to the irregularly distributed crosslinking points. Consequently, the polymer chains between the crosslinking points have different lengths, the stress cannot be evenly distributed between the polymer chains. When PAM-MBA hydrogel is deformed, stress is concentrated on the shortest chain which creates a zone of high stress and crack initiation is facile. Thus, the hydrogels exhibit brittle, low-stretchable and poor mechanical properties²³. By contrast, when PEA is incorporated into the polyacrylamide, PEA-PAM hydrogels show quite different behaviours in mechanical properties with great reinforced effect. More impressively, with the presence of only 0.1wt% PEA content relative to AAm monomer, the mechanical properties were greatly enhanced and the hydrogel was very tough and stretchable with a fracture stress of 336kPa at an elongation of 1072%, which is 11.1 and 5.1 times more than the conventional PAM-MBA hydrogel respectively. Each curve of the PEA-PAM hydrogels shows an initial linear region with a high slope (elastic region) followed by a decrease in slope and a subsequent elongation region up to the break point. The S-shaped tensile stress-strain curve is typical of elastomeric materials²⁴. Increasing of PEA content from 0.1wt% to 5wt% could result in the following phenomenon: (1) the corresponding ruptured strain increases from 1072% and 3450%, which is obviously higher than the SR and most of the clay and graphene based hydrogels. (2) Their toughness increased firstly and then declined the maximum data 3.06 MJ m^{-3} observed for the sample with 0.3wt% PEA. The toughness of PEA-PAM hydrogel was tens or even more than one hundred times higher than that of the conventional cross-linked PAM-MBA hydrogel (about 0.03 MJ m^{-3} for the sample in this paper).

(3) The tensile strength decreased from 336 to 91kPa. (4) The modulus decreased from 0.98MPa to 0.26MPa. Based on the mechanical properties of the hydrogel, it is found that the PEA-PAM hydrogel became softer with increasing PEA content. The possible reason is that PEA content is quite low that causes the relatively low chemically crosslinking density. In the PEA/PAM hydrogel, the PAM network is the backbone and the physical interactions like hydrogen bonds and entanglements between PAM chains mainly contribute to the mechanical properties²⁵. That's why there is the presence of necking phenomenon in the tensile stress-strain curves (**Fig. 5a**) and very obvious hysteresis in the cyclic loading-unloading curves (**Fig. 6a**). PEA acts as not only a macromolecular crosslinker but also an initiator, the double roles make PEA different with common crosslinkers. As reported by Feng et al.^{26, 27}, increasing PEA content means increasing the initiator concentration, which causes the rate of PAM polymerization increased. On the other hand, the molecular weight of single PAM chain decreases with the increasing of PEA. So the length of PAM chains between adjacent crosslinking points also decreases, which impairs the physical interactions of PAM chains. In the mean time, the PEA chain is too soft and flexible to form a rigid crosslinking center. Therefore, the modulus and tensile strength of the PEA/PAM gels decreases, while the elongation increases with increasing PEA content, which is contrary to the usual crosslinker.

By comparison of PEA hydrogels and those successfully enhanced hydrogels (like DN, NC and SR gels), several following advantages could be obtained. (1) Instead of small molecular accelerator (TEMED) and cross-linked agent (MBA), we use macromolecular PEA which could be acted as both initiating and crosslinking center and this novel and facile method has not been reported by now to the best of our knowledge. (2) The reinforced behaviour is highly effective. The presence of very low content of PEA (for example 0.1wt%) would result in the pronounced reinforced effect. Considering that the content of graphene in graphene/PAM^{12, 13} hydrogels and clay in LDH²³ NC hydrogels is usually above 5wt%, which is much higher than the PEA content. The results demonstrated that building the hydrogel with improved mechanical properties from the basic initiative mechanism of polymerization maybe a more effective way.

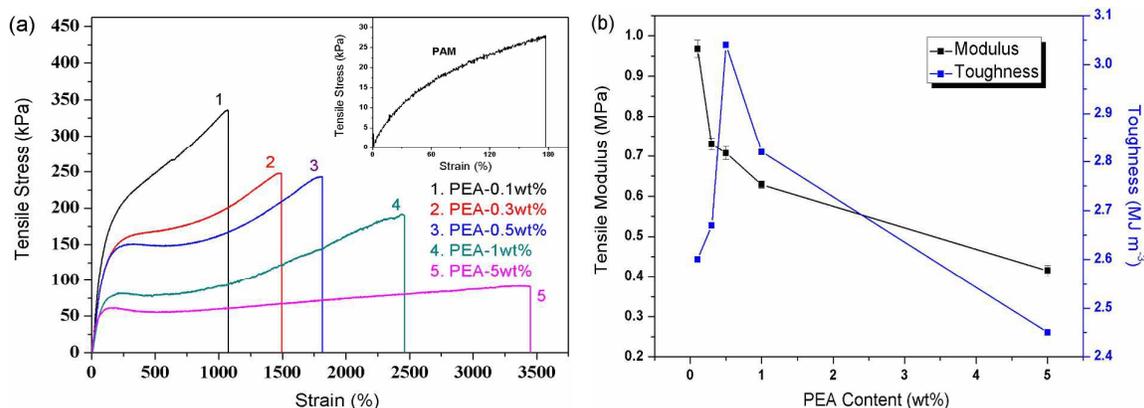


Fig.5 (a) Stress–strain curves for PEA-PAM hydrogels with different content of PEA. (b) Dependence of tensile modulus and toughness on the PEA content. The error bars correspond to the standard deviation obtained from at least three samples.

Besides the tensile tests, the loading–unloading properties of the as-prepared PEA hydrogels were investigated to reveal the energy dissipation mechanism of these hydrogels. **Fig. 6a** shows the loading–unloading curves at different strains (200%, 500%, 800% and 1000%) of PEA-0.3wt%. For example, when the strain is fixed at 200%, the residual strain was negligible and the elastic recovery was 95%. With increasing fixed strain, the residual strain is also increased and the degree of recovery could still be kept at 88% even at 1000% strain. In addition, it is also observed that the loading and unloading ways of stress–

strain curves show the obvious hysteresis loops and the area for this loop is increased with increased strain, which indicates that the PEA-PAM hydrogel can dissipate energy effectively²⁸. The hydrogen bond ruptures as well as the disentanglements of PAM chains and the slippage of PEA chains may contribute to the hysteresis loops. And the rupture of covalent bonds in the network may cause the permanent damage. The energy dissipation helps the PEA-PAM hydrogel improve the mechanical properties effectively. **Fig.6b** shows that the loading–unloading is actually an irreversible process.

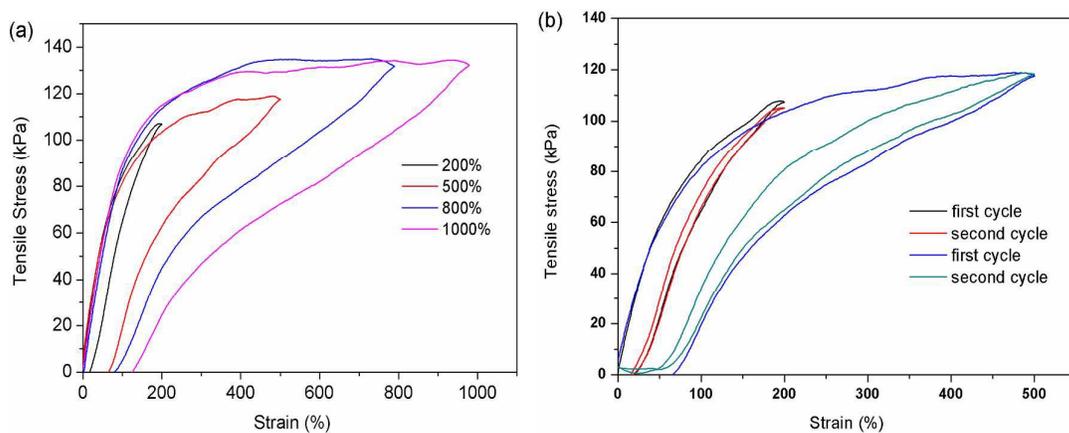


Fig.6 Loading–unloading test under various conditions: (a) Loading–unloading tests of PEA-0.3wt% under different strain (200%, 500%, 800%, 1000%); (b) First and immediate second loading–unloading cycles of PEA-0.3wt% gels with different maximum stretch. Water content was fixed at 70%.

In order to gain insight into the excellent properties of PEA-PAM hydrogels, we studied the polymer molecular mobility by means of crosslinking density. The S-shaped strain–stress curves of PEA-PAM gels indicate they are similar to that of

cross-linked natural rubber, which is well explained by the classical theory of rubber elasticity as followed²⁹:

$$\sigma = \phi N_0 k T (\lambda - \lambda^{-2})$$

where N_0 , ϕ , k , T and λ are the cross-linking density of the hydrogels, a prefactor, Boltzmann's constant, the absolute temperature, and the extension ratio, respectively. Here, we adopted $\lambda = 3$ and the corresponding stress at 200% elongation; $\phi = 1$ and $T = 298.15\text{K}$. From **Fig. 5a**, the calculated N_0 values for all the PEA hydrogels are summarized in **Fig. 7a**, it is found that the crosslink degree for PEA hydrogel is relatively low²³. For example, N_0 for the sample with 0.1wt% PEA is only about 27mol m^{-3} . With increasing PEA content from 0.1wt% to 5wt%, N_0 is further gradually decreased from 27 to 8.8mol m^{-3} . Such change in the crosslinking degree could be in agreement with the results obtained from the strain-stress tests, which supports that increasing PEA content could result in lower crosslinking degree.

The time constants of the swelling process depend on both the hydrogel thickness and the network topology³⁰. We used same sizes of hydrogel samples for swelling tests to study the crosslinking degree. The neat PAM hydrogel did not swell but degenerated and partly dissolved in water. In contrast, all of the PEA-PAM hydrogels did not dissolve but were highly swelled, maintaining their original shape very well. This suggests the occurrence of a stable 3D crosslinked network structure consisting of PEA and PAM chains. Moreover, as shown in **Fig. 7b**, the swelling ratio for the hydrogel with 0.1wt% PEA was about 2200%. With increasing PEA content up to 5wt%, the swelling ratio was gradually increased up to 4600%, which supports that more PEA content could result in lower crosslinking degree.

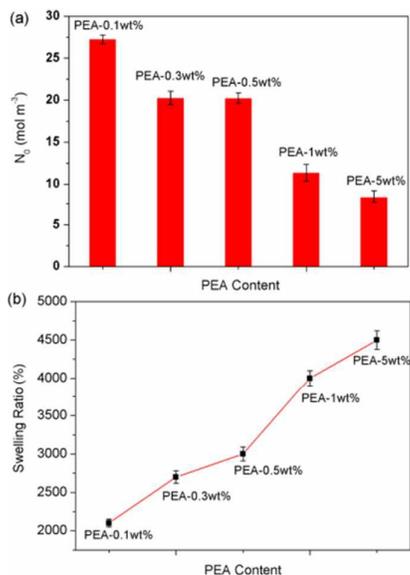


Fig. 7 (a) Cross-linking density of the prepared hydrogels. (b) Swelling ratio (Q) of the prepared PEA-0.3wt% hydrogels.

We also investigated the effects of PEA and APS content for the mechanical properties of PEA-PAM hydrogels. Firstly, the PEA content was fixed at 0.3wt% relatively to AAm monomer (5g). The ratio of APS/PEA was changed from 0.5-4. And the water content was 70%. As shown in **Figure S3**, with increasing the content of APS, the obtained hydrogels became softer with a longer elongation at break. That may be because when there is excessive persulfate, the persulfate radicals would compete with tertiary amine to initiate the polymerization, resulting in the declining of crosslinking density thus the obtained hydrogels become softer. So it's important to control the content of APS in order to get a mechanically strong PEA-PAM hydrogel. Next, we controlled the APS content and changed the PEA content from 0.1wt% to 1wt%. In **Figure S4**, the results show that with increasing of the PEA content, the tensile modulus decreases slightly and the elongation at break extends slightly. Increasing PEA content, the strong interactions between polyacrylamide chains is impaired and the flexibility and mobility of the network are intensified, which lead to the softened phenomenon.

Conclusion

In summary, we have initially designed a novel method to produce the hydrogel with excellent mechanical properties, where PEA having the tertiary amine structures could be used as both the initiation and cross-linking point for the production of PAM hydrogels. As a result, it is found that the hydrogel showed a super stretchability and high elasticity at extremely low PEA content. In these novel PEA-PAM hydrogels, PAM chains were grafted from the tertiary amine dangling on the PEA chains to form a homogenous cross-linking structure. This kind of hydrogels also has good elastic properties. The homogeneous crosslinking structure, the existed strong physical interactions of PAM chains and the effective energy dissipation are the possible reasons for the improved mechanical properties. Moreover, the mechanical properties of hydrogel could be easily controlled by the amount of PEA. Increasing PEA content could make the hydrogel softer with higher stretchability. To the best of our knowledge, such simple method for preparing the hydrogel with super stretchability and high elasticity has never been reported, which could provide new clue to understand the mechanism for the production of hydrogel with excellent mechanical properties.

Experimental

Materials

Polyethylene glycol diglycidyl ether (PEO-DE, $M_n=500\text{g/mol}$), N,N' -Dimethyl-1,3-propyldiamine (DMPA, 98%) were purchased from Sigma-Aldrich. Acrylamide (AAm),

N,N,N',N'-tetramethylethylenediamine (TEMED, 99%), ammonium peroxydisulfate (APS), N,N,N',N'-methylenebis(acrylamide) (MBA) and ethanol were of analytical pure reagent (A.R.) grade supplied by Sinopharm Chemical. All chemicals were used as received. In all of the experiments, deionized water was used.

Preparation of PEA

The reaction was conducted in a 100-mL two-necked flask equipped with a nitrogen inlet tube and a reflux condenser. PEO-DE and DMPA were added to the flask in equal molar ratio. Then, ethanol was added to dissolve these monomers. The total monomer concentration was kept at 0.5g/mL. The mixture was refluxed for 10h. Then, the reaction mixture was poured into n-hexane. After removing the supernatant, the product was collected and dried in oven. The weight averaged molecular weight M_w and the polydispersity index M_w/M_n were measured by GPC in the mobile phase of tetrahydrofuran (THF). The results showed that M_w was about 1.2×10^4 g/mol and M_w/M_n was about 1.5. Yield of PEA was nearly 98%.

Preparation of PEA-PAM Hydrogels

First, the PEA was dispersed in deionized water under ultrasonication to obtain a transparent aqueous dispersion. Then it was purged with nitrogen gas for 30 min to remove oxygen. After the monomer AAm (30wt% in total amount) and the initiator APS had been added at 0°C, the system was stirred for 10 min to yield a homogeneous dispersion which was then deaerated under reduced pressure to remove the excess gas. The pre-gel solution was transferred into a test tube with an inner diameter of 6 mm and a length of 10 cm. The gelation was performed at room temperature for 24h. The reactant compositions were listed in Table 1.

Mechanical Tests of PEA-PAM Hydrogels

Uniaxial tensile tests were conducted with an Instron 4465 electronic universal testing machine (Instron Corporation, MA, USA) at a crosshead speed of 100 mm min⁻¹, a load cell of 2 kN, temperature of 25°C, initial gauge length of 40mm. The cylindrical samples were formed in the glass tube with a diameter of 6 mm and a length of 10cm. The tensile strain is defined as the change in the length relative to the initial gauge length, and the breaking tensile strain is the tensile strain at which the sample breaks. Stress and strain between 10-30% were used to calculate the initial elastic modulus. At least three specimens per experimental point were tested in all mechanical measurements to obtain reliable values. Loading-unloading tests were performed by performing subsequent trials immediately following the initial loading with the same specimen at a crosshead speed of 100mm min⁻¹. The gel specimens were coated with a thin layer of silicon oil to prevent the evaporation of water during the tests.

Rheological property measurements

Rheological properties of neat PAM, conventional PAM-MBA hydrogel, and PEA-PAM hydrogels were conducted with TA ARES-G2 rheometer using parallel plates of diameter 20 mm at 25°C. The gap between the two parallel plates was set at 1 mm. The frequency sweep was performed over the frequency range of 0.001-10 Hz at a fixed strain of 0.5%.

Equilibrium swelling ratio of hydrogel

For determining the equilibrium swelling ratio (Q) of hydrogels, the as-prepared hydrogels were first lyophilized in freeze-drying equipment for 1 week. Then, certain amounts of dried hydrogels were immersed into the DI water until the hydrogels achieved an equilibrium swelling state in sealed containers at room temperature for 1 week. Afterwards, the equilibrium swollen hydrogels were taken out, after removal of excess surface water with a filter paper, and weighed. The Q is calculated from the equation:

$$Q = \frac{W_e - W_d}{W_d} * 100\%$$

where W_e and W_d represent the weights of the hydrogel at swelling equilibrium state and the dried hydrogel, respectively.

Acknowledgements

We thank the National Nature Science Foundation of China (No.51473901) and National Basic Research Program of China (Grant No.2011CB606003) for the support.

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Table of Contents. We propose a novel and facile approach to prepare excellent hydrogels by using PEA as initiating and crosslinking centers.

