# RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Mechanically Strong and Stretchable Polyurethane-Urea Supramolecular Hydrogel Using Water as Additional In-situ Chain Extender

Chao Deng,[a] Yulin Cui,[a] Tingting Zhao,[a] Mei Tan,[a] He Huang[a]* and Mingyu Guo[a]*

Mechanically strong hydrogels have attracted more and more interests because of their various potential applications. However, this is still a great challenge for the supramolecular hydrogels due to the inherent weak character of non-covalent interactions. A novel polyurethane-urea supramolecular hydrogel with excellent mechanical property was accidently developed in our lab during the preparation of waterborne dispersion of polyurethane with excess amount of -NCO groups. Subsequent studies showed that this was because ***multi-urea linkages*** were slowly formed and further chain extension occurred due to the reaction of water with the excessive -NCO groups in the isocyanate prepolymer chains and/or the free diisocyanate. The mechanical properties of the obtained polyurethane-urea supramolecular hydrogels including shear modulus (0.2-0.8 MPa), elongation at break (970%-2420%), tensile strength (3.3-34 MPa) and compression stress (up to 38 MPa) can be adjusted by simply altering the diisocyanate content. Further analysis showed that the elongation ratio and tensile stress at break linearly decreased and increased with increasing hard segment ratio, respectively.

## Introduction

Hydrogels are chemically or physically cross-linked 3D networks which may absorb water from 10-20% up to thousands of times their dry weight.[1, 2] Since the pioneering work of Wichterle and Lim in 1960 on covalently cross-linked polyHEMA hydrogels,[3] and because of the similar softness and water content as natural soft tissues, high permeability for water-soluble nutrients and metabolites, possible biocompatibility, synthetic hydrogels have found great potentials in artificial implants, biomedical devices, tissue engineering and regenerative medicine, etc.[2-16]

Nevertheless, the actual utilization of classic hydrogels has been seriously impeded by their poor mechanical properties. To solve this problem, several types of chemical hydrogels with high mechanical strength were developed during last decades, including covalently cross-linked sliding hydrogel,[17] double-network hydrogel,[18, 19] macromolecular microsphere composite hydrogel,[20] tetra-PEG hydrogel,[21] covalent bond and hydrogen bond cross-linked hydrogel,[22] inorganic clay cross-linked nanocomposite hydrogel,[23] and polyacrylamide-alginate hybrid hydrogel.[13] However, in these chemical hydrogels, the networks are connected by covalent bonds to yield a “permanent” hydrogel and its shape is set at the time of gelation.

In contrast, supramolecular hydrogels or physical hydrogels are tremendously extending our view on new functional hydrogels with great capacity for processability, recycling, self-healing, injectability and so on,[7, 24-26] because in supramolecular hydrogels, the networks are held together by molecular entanglements and/or reversible non-covalent interactions, such as hydrogen-bond, hydrophobic forces, metal-ligand interactions, and host-guest interactions etc. Such features, especially the reversible and dynamic characters are more similar to natural soft tissues, and render supramolecular hydrogels more attractive for bio-medical applications. But problem remains. Most reported supramolecular hydrogels also have low mechanical strength, often like jelly or paste, partially due to the inherent weak character of non-covalent interactions.

It is well-known that polyurethane (PU) or polyurethane-urea (PUU) elastomers are ideal candidates for fabricating tissue engineering scaffolds with mechanical properties akin to strong and resilient soft tissues.[27, 28] Recent years have witnessed an upsurge in interest in PU or PUU hydrogels,[29-32] because of the wide variety of final product properties. As many other supramolecular hydrogels, however, most reported PU or PUU supramolecular hydrogels are also very weak or brittle. Recently, Mather et al. developed a mechanically strong PEG-POSS hybrid polyurethane supramolecular hydrogel whose shear modulus ranged from 0.3 to 4.0 MPa, a range much higher than hydrogels reported previously, but the tensile behaviour of the hydrogel was not mentioned.[31]

Very recently, while making water-dispersible polyurethane adhesives in our lab, very strong and stretchable gels were formed after the samples were left in air for a couple of days up to a week. A careful examination revealed that excess amount of isophorone diisocyanate (IPDI) was added. As a result of this, in the prepared water-dispersible polyurethane dispersions, urea linkages were slowly formed due to the reaction of water with the excess -NCO groups in the polyurethane chains and/or the free IPDI. We came to know later on that the above process happens to be consistent with the recently developed synthetic approach, i.e., formation of urea linkages by in situ chain extension using water, for the preparation of very strong PUU elastomers.[33-35] Herein, we introduced this novel type of tough (i.e., work of extension) and stretchable polyurethane-urea supramolecular hydrogel (PUUS gel) which also holds the advantages of supramolecular materials, such as its easy processability. The aim of this work was to demonstrate the possibilities of this new one-pot synthetic approach to prepare strong and stretchable supramolecular hydrogels using the inherent strong hydrogen bonding interaction of urea groups.

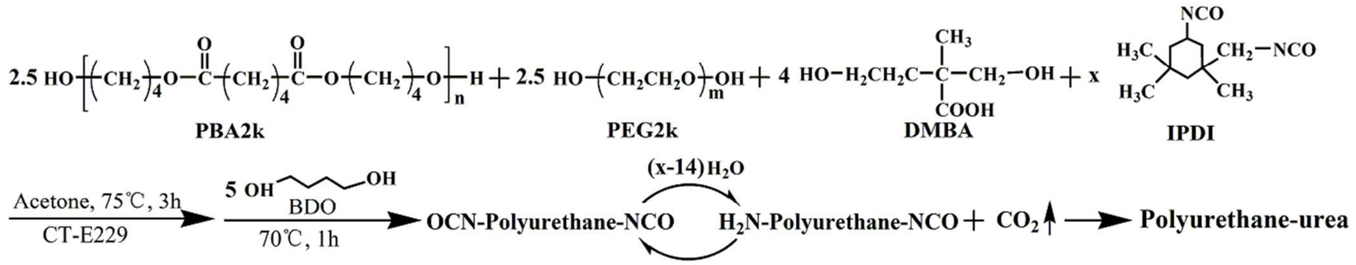
## Experimental Section

### Materials

All reagents were purchased from commercial sources and used without further purification. Poly(ethylene glycol) ($M_w$ = 2000 g/mol, PEG2k) and biodegradable hydrophobic poly(butylene adipate) ($M_w$ = 2000 g/mol, PBA2k) were dried under vacuum at 80 ºC overnight in the presence of $P_2O_5$ before use. Acetone was dried with 4Å molecular sieve before use. CT-E229, an environmental-friendly catalyst, was kindly provided by Newtop Chemical Materials Co., Ltd (Shanghai).

### Synthesis

The polyurethane-urea was synthesized according to the procedure shown in Scheme 1. For example, 2.5 mmol PEG2k, 2.5 mmol PBA2k, 4.0 mmol dimethylolbutanoic acid (DMBA), X mmol IPDI and 15.0 mL acetone were added into a three-necked flask. Catalyst amount of CT-E229 (0.1 g）was then added into the flask and stirred for 10 min at 60 ºC. The reaction mixture was stirred for 3 h at 75 ºC. After that, 5.0 mmol 1, 4-butanediol (BDO) was added and the reaction mixture was stirred for another 1 h at 70 ºC before cooling to 60 ºC. Finally, (X-14) mmol of $H_2O$ was added into the flask under stirring, until the complete conversion (18~60 h according to the total amount of IPDI used) of the -NCO groups verified by FTIR. Solvent (acetone) can be added to adjust the viscosity and to facilitate formation of high molecular weight product.[33] For simplicity, the feed ratios of all the raw materials, except for IPDI and $H_2O$, were kept constant, and the total amount of all the diol molecules was fixed at 14 mmol (Table 1). For comparison, polyurethane hydrogel (PU gel) without urea linkages was also prepared by using 14 mmol of IPDI.



**Scheme 1**. Synthetic procedure of PUU copolymer using water as additional chain extender. In the second step, BDO could also first react with free IPDI and then with the growing chain. In the last step, $H_2O$ could also first react with IPDI yielding one amine group which immediately reacts with any –NCO group attached in the prepolymer chain end or IPDI.

**Table 1.** Chemical compositions of the PU and PUU copolymers.

| | Soft segments | | Hard segments | | | |
|---|---|---|---|---|---|---|
| Sample **[NCO]/[OH]** | PEG2k (mmol) | PBA2k (mmol) | DMBA (mmol) | BDO (mmol) | IPDI (mmol) | $H_2O^b$ (mmol) |
| 14/14[a] | 2.5 | 2.5 | 4.0 | 5.0 | 14.0 | 0.0 |
| 17/14 | 2.5 | 2.5 | 4.0 | 5.0 | 17.0 | 3.0 |
| 19/14 | 2.5 | 2.5 | 4.0 | 5.0 | 19.0 | 5.0 |
| 22/14 | 2.5 | 2.5 | 4.0 | 5.0 | 22.0 | 8.0 |
| 26/14 | 2.5 | 2.5 | 4.0 | 5.0 | 26.0 | 12.0 |
| 32/14 | 2.5 | 2.5 | 4.0 | 5.0 | 32.0 | 18.0 |

[a] The PU hydrogel prepared under equal molar amount of -NCO and -OH groups. [b] The mole amount of water added in the last step was equal to that of the excess amount of IPDI.

### Hydrogel preparation

The final reaction mixture was poured into Teflon mould, where the solvent (acetone, an easy evaporating solvent, instead of DMF, which was used as the solvent to prepare PUU elastomers using water as the in-situ chain extender, was used to facilitate the dry film formation.) evaporated to yield dry films. After fully swelling in a large amount of water, hydrogel films were obtained. For the compression measurements, dry rod samples were first prepared by thermo-compression method in a Teflon mould at 120 ºC, after cooling to room temperature and fully swelling in a large amount of water, rod hydrogel sample with diameter of 24 mm and thickness of 21.5 mm was obtained.

### Characterizations

The water content of the hydrogel samples were calculated according to the following equation:

Water content (wt%) = 100 × ($M_w$ - $M_d$)/$M_w$

where, $M_w$ was the weight of the equilibrium water swelling samples and $M_d$ was the dry weight of the samples.

The hard segment (HS) ratio was defined as the weight ratio of IPDI and DMBA, BDO and $H_2O$ (in the PUUS case) to that of the copolymer, and the weight of $CO_2$ gas formed in the last step (Scheme 1) was excluded. Infrared spectra were collected on Nicolet 6700 Spectrometer by coadding 32 scans with a resolution of 4 cm$^{-1}$. Rheology measurements were performed on a HAAKE Rheometer (RS 6000) with a parallel plate accessory (20 mm in diameter). All the tensile tests were carried out in air, at room temperature, using a universal tensile machine (KJ-1065B, Kejian-tech, China) with a 50 N loading cell. The cross-head speed of the tensile measurements was 50 mm/min. Compression measurements were carried out on universal tensile machine (WDT-2000, Kaiqiangli Testing Instruments Co.) with a 20 kN loading cell, and the cross-head speed was 5 mm/min. Both the tensile and compression stresses are obtained by stress = F/$S_0$, where F is the load applied on the specimen and $S_0$ is the original cross-sectional area of the specimen. RPA 2000 rubber process analyser was used for rheological temperature sweeps (25 ºC to 150 ºC, 3 ºC/min) with a frequency of 1 Hz and strain amplitude of 3%. Thermogravimetric analysis (TGA) was carried out on a Pyris 1 TGA instrument. Disc samples cut from films were heated at 10 ºC/min under nitrogen atmosphere.

## Results and Discussion

As shown in Scheme 1, the synthetic procedure was a simple one-pot with three steps reaction without any purification process, and each step was monitored by the determination of isocyanate group using the di-n-butylamine-acetone method associated with infrared spectroscopy (IR) until a desired stoichiometry was reached (Fig. S1 in ESI).[36] Here, hydrophilic PEG2k and biodegradable PBA2k were used as the soft segments, DMBA and BDO as normal chain-extender. Water was added in the last step as an additional in-situ chain extender for the generation of urea linkages, stronger H-bonding units than urethane groups.[35] The synthesis strategy was to first create isocyanate end-capped prepolymer by letting diol-terminated molecules react with IPDI and then the isocyanate terminated prepolymers were further chain-extended by adding water in the last step.

All the diol molecules were completely consumed in the first two steps. Therefore, when water was added in the last step, corresponding amine group was formed upon reaction with remained isocyanate groups, and the amine group then reacted with other isocyanate groups in the prepolymer chain end or free IPDI, resulting in a urea linkage. These reactions repeated until all the –NCO groups transformed to urea linkages. Fig. 1 showed the normalized FTIR spectra of the PU ([NCO]/[OH] = 14/14) and PUU ([NCO]/[OH] > 14/14) samples. It can be observed that as increasing [NCO]/[OH] ratio while water was added as the in-situ additional chain extender, the weak shoulder centered around 1650 cm$^{-1}$ increased in intensity. At the same time, the intensity of the N-H stretching region between 3100 and 3500 cm$^{-1}$ also increased. These demonstrated that more and more urea linkages were formed with increasing [NCO]/[OH] ratio, because the total amount of diol molecules were kept constant (14 mmol, Table 1) for all the samples. Previous studies have shown that the urea-urea hydrogen bond is much stronger than the corresponding urethane-urethane hydrogen bond.[33-35] And it is generally acceptable that one of the driving forces for phase separation of PU or PUU is strong hydrogen bonding interactions between urethane and/or urea groups. Hence, it may be safe to presume that the higher hydrogen bonding strength and higher driving force for phase separation of shorter hard segments would result in improved mechanical properties of the resulting supramolecular hydrogels.

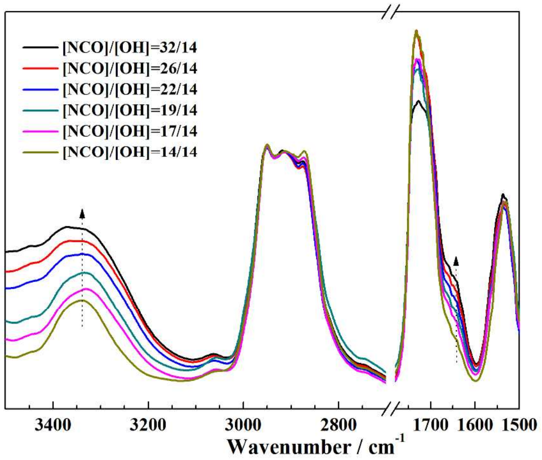


**Fig. 1** Normalized FTIR spectra of the PU ([NCO]/[OH] = 14/14) and PUU samples ([NCO]/[OH] > 14/14) ratios.

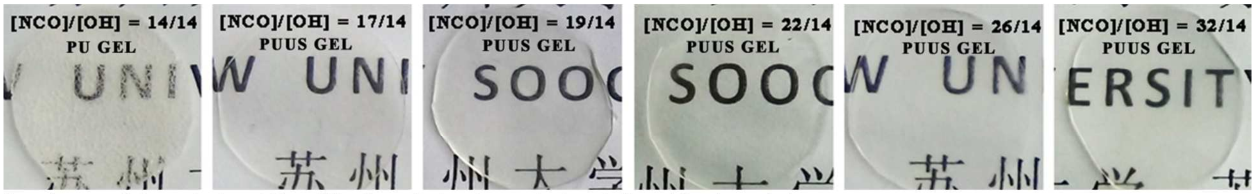


**Fig. 2** Photo images of the PU hydrogel ([NCO]/[OH] = 14/14) and PUUS hydrogels ([NCO]/[OH] > 14/14).

Journal Name RSCPublishing

ARTICLE

Fig. 2 showed photographs of the PU hydrogel ([NCO]/[OH] = 14/14) and PUUS ([NCO]/[OH] > 14/14) hydrogels with various [NCO]/[OH] ratios. One can see that the PU hydrogel was opaque, and its surface looked very coarse with plentiful cracks. It was also too weak and brittle to do mechanical measurements, such as rheology or tensile-test. While, all the PUUS hydrogels showed transparent character, and their surfaces were smooth and compact. They also showed unexpected mechanical properties. For example, Fig. 3 showed the photo images of the biaxial stretching and loading-unloading behaviours of a PUUS ([NCO]/[OH] = 22/14) hydrogel film. As shown in Fig. 3a and movie-S1 in ESI, the transparent 60×60×1.5 mm hydrogel film can be stretched to several times of its original size without fracture. Meanwhile a 75×15×1.5 mm hydrogel strip even can withstand 6.2 kg of loading and return to its original size immediately after unloading (Fig. 3b and movie-S2 in ESI). More surprisingly, the hydrogel rod with diameter of 24 mm and thickness of 21.5 mm can even bear more than 1.6 tons loading (Fig. 3c and Fig. S2 in ESI) without break, and still can almost return to its original state within 10 min after unloading (Fig. 3c).

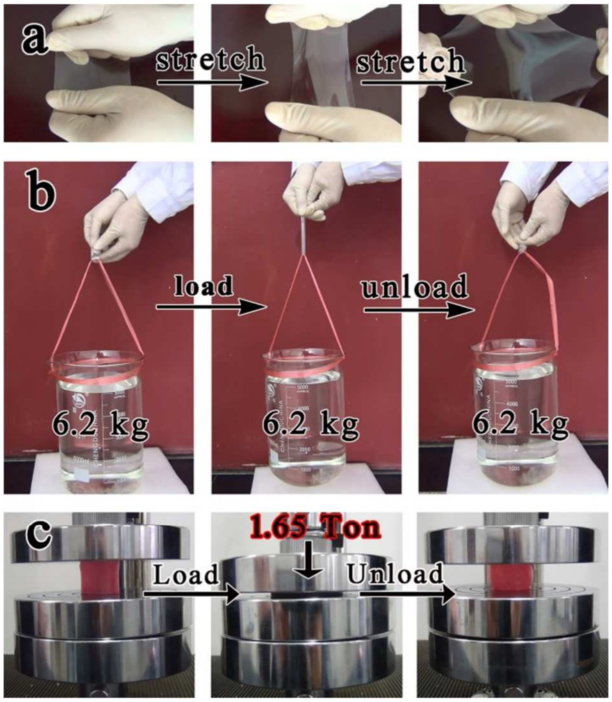


**Fig. 3** Photo images of the (a) stretching, (b) loading-unloading and (c) compression of the hydrogel films with [NCO]/[OH]= 22/14. In Figure c, the hydrogel was dyed with Rhodamine B for clear observation.

In order to get detailed mechanical properties of the PUUS hydrogels with various [NCO]/[OH] ratios, dynamic oscillation rheology measurements were first carried out. The existence and extent of the linear viscoelastic regime were determined by measuring the dynamic shear storage modulus (G') and loss modulus (G"), as a function of strain ($0.01 < \gamma < 10$) at an angular frequency of 6.28 rad/s. All the measurements were carried out within the linear viscoelastic range, where G' and G" were independent of strain.

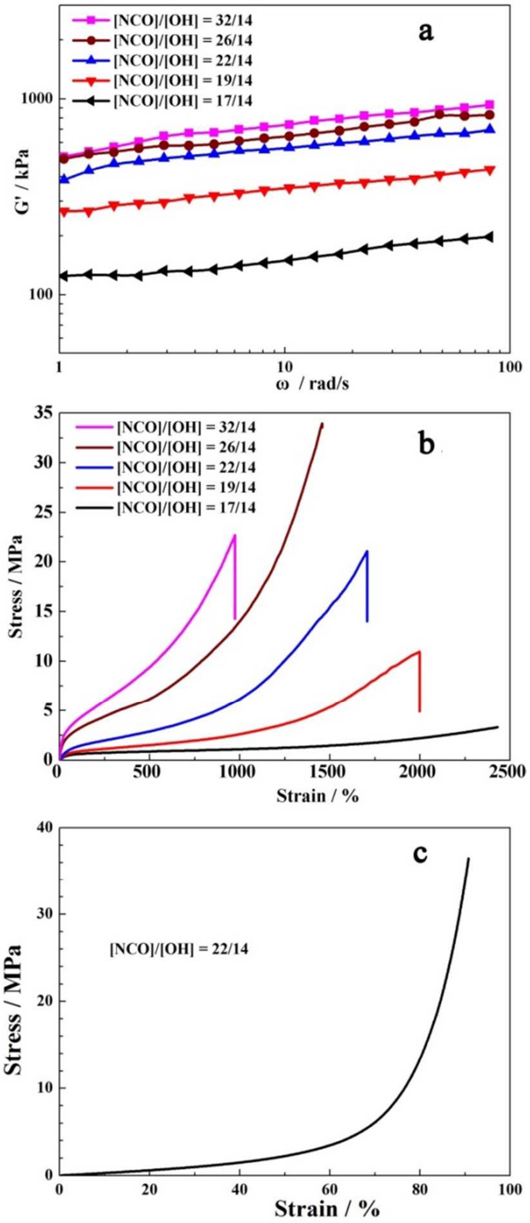


**Fig. 4** (a) rheology, (b) tensile-test and (c) compression measurements of the PUUS hydrogels with various [NCO]/[OH] ratios as the insets shown.

Fig. 4a showed the log-log plots of shear modulus G' (corresponding loss modul G" can be found in Fig. S3 in ESI) as a function of frequency $\omega$ at a fixed strain, $\gamma = 1\%$. The shear modulus of the PUUS hydrogel increased from ~0.2 to ~0.8 MPa, a range comparable to most previously studied tough hydrogels, as the [NCO]/[OH] ratio increased from 17/14 to 32/14. The sample with highest [NCO]/[OH] ratio (32/14) gave the largest G', ~0.8 MPa. While, the tensile tests showed a little bit different trend. As shown in Fig. 4b and Table 2, with increasing [NCO]/[OH] ratio from 17/14 to 26/14, the elongation at break decreased from 2420% to 1450%, a range comparable to highly stretchable hydrogels reported so far, whereas the tensile stress at break increased from 3.3 MPa to 34 MPa, a range much higher than previously reported famous high mechanical strength hydrogels, including sliding hydrogel (<20 kPa),[37] double-network (DN) hydrogel (<3.8 MPa),[38] tetra-PEG hydrogel (<200 kPa),[39, 40] hydrogen-bond and covalent bond cross-linked hydrogel (<1.8 MPa),[22, 41, 42] and inorganic clay cross-linked nanocomposite hydrogel (<1 MPa).[23, 43] With further increase of the [NCO]/[OH] ratio to 32/14, the elongation and tensile stress at break decreased but its tensile stress in the experimental range (strain from 0 to 970%, Fig. 4b) was still always higher than all other samples. Compression mechanical properties are also very important for the actual utilization of hydrogels, thus, for simplicity and to protect the machine, PUUS hydrogel with [NCO]/[OH] = 22/14, the one with middle mechanical strength, was chosen for the compression measurement. As shown in Fig. 4c, the hydrogel can bear a compression stress of 36.8 MPa with strain of 90.7% and compression force of 1.65 tons (16.5 kN, Fig. S2 in ESI) without breaking. This stress is much higher than all that of strong hydrogels reported in literature at the same strain (<17 MPa with a strain of 90%[18]). Of special note, here, the compression force was already very close to the up limit of the machine (20 kN), and thus to protect the machine, we did not get the strain and stress or force at break.

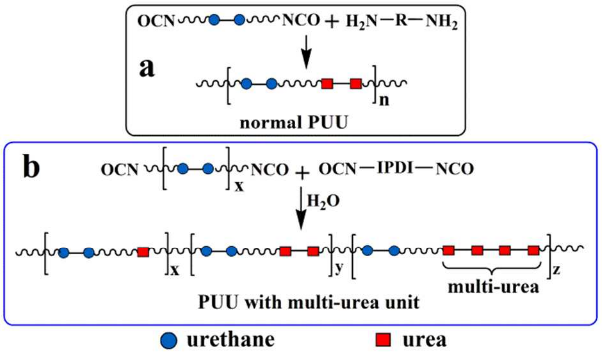
**Table 2.** Hard segment ratio of the PUU copolymers, stress and elongation at break and water content of the respective PUUS hydrogels.

| Sample [NCO]/[OH] | HS ratio[c] (wt%) | Stress at break (MPa) | Elongation at break (%) | Water content (wt%) |
|---|---|---|---|---|
| **14/14[a]** | 29 | Unavailable[d] | Unavailable[d] | 66.0 |
| **17/14** | 32 | 3.3 | 2410 | 61.7 |
| **19/14** | 34 | 11.0 | 1990 | 53.8 |
| **22/14** | 36 | 21.0 | 1700 | 52.3 |
| **26/14** | 39 | 34.0 | 1450 | 46.0 |
| **32/14** | 43 | 22.7 | 970 | 45.5 |

[c] The hard segment (HS) ratio was defined as the weight ratio of IPDI and DMBA, BDO and $H_2O$ (in the PUUS case, [NCO]/[OH] > 14/14) to that of the respective copolymer, and the weight of $CO_2$ gas formed in the last step was excluded. [d] The sample is full of cracks and too brittle to get the data.

All the above excellent mechanical properties were dependent on the soft/hard segment ratio of PU and PUU in the hydrogel, and corresponded well with previously reported thermoplastic elastomer using water as the in-situ chain extender.[33, 34] It is well known that, PU and PUU elastomers always contain soft segments (SS) and hard segments (HS). The SS gives the material its elastic properties, while the HS provides the physical strength.[35] As shown in Table 1, for all the samples, the molar amounts of the soft segments (PEG2k and PBA2k) and normal chain extenders (DMBA and BDO) were constants, and all the hydroxyl groups had been completely consumed in the first two steps. Thus with increasing [NCO]/[OH] ratio, although the HS fraction formed from the urethane linkages was a constant, the HS fraction formed from urea linkages increased. This was also confirmed by the results shown in Fig. 1. Herein, we may conclude that the higher HS fraction formed from urea linkages, stronger hydrogen-bond groups than urethane groups, should be the main contributor to the dramatically increase of the mechanical properties with increasing [NCO]/[OH] ratio.

Compared with the PU supramolcular hydrogel obtained in this study and other conventional supramolecular hydrogels formed from linear PUU copolymers, the excellent mechanical properties of the present PUU ones are amazing. As shown in Table 2, the PUUS hydrogel with 32 wt% HS ratio could be elongated 24 times of its original length, while the PU sample with 29 wt% HS ratio was too brittle to be cut and clamped to do tensile test. Besides, as the HS ratio increased from 32% to 39%, a narrow HS ratio range of only 7% difference, the stress at break increased 10 times (from 3.3 MPa to 34 MPa). We also tried to use isophorone diamine (IPDA, a small diamine molecule with similar chemical structure as IPDI) or and 1, 2-ethanediamine as the chain extender instead of water in the last step, but only viscous water solution was obtained after the dry PUU film was immersed in large amount of water, indicating dissolution of the diamine chain extended PUU copolymers in water. Although more experiments and characterizations are needed to clarify the detailed mechanism, one may get some primary clues from Scheme 2. Traditional linear PUU copolymers were often prepared by one-pot with a two-step reaction procedure as shown in Scheme 2a. In this case, –NCO end-capped polyurethane prepolymers were obtained in the first step, then the prepolymers were further chain-extended by small diamine molecules yielding the final PUU copolymers which in fact were bis-urea and bis-urethane alternately segmented linear copolymers (Scheme 2a). While in our case, the story was totally different. As shown in Scheme 1 and Scheme 2b, although only similar –NCO end-capped polyurethane prepolymers and free IPDI existed in the last step before addition of water, the formation of urea units after addition of water was rather complicated. Because any –NCO group attached in the prepolymer chain end or free IPDI can slowly react with $H_2O$ yielding one $-NH_2$ group, and the formed $-NH_2$ group could immediately react with any other –NCO groups attached in the prepolymer chain end or IPDI yielding one urea group. Thus, in the present case, the resultant PUU polymer was in fact a bis-urethane, urea, bis-urea and multi-urea segmented linear copolymer. And with increasing [NCO]/[OH] ratio, more or longer multi-urea linkages formed.[35] And so, we may conclude that the formation of these multi-urea linkages should have profound influences on the improvement of the mechanical properties of the present PUUS hydrogels.



**Scheme 2.** Schematic representation of the formation of (a) normal PUU and (b) PUU with multi-urea linkages in the backbone.

A detailed analysis of the data presented in Table 2 reveals another interesting behaviour of the present PUUS hydrogels as shown in Fig. 5. Fig. 5a and Fig. 5b showed the hard segment ratio effect of the PUU copolymers on the elongation and tensile stress at break of the obtained PUUS hydrogels, respectively. Fig. 5a clearly showed that the elongation at break almost linearly decreased with increasing HS ratio. While, for the tensile stress, the stress at break linearly increased as the HS ratio increased from 32 % to 39%. As far as we know, this may be the first supramolecular hydrogel sample whose mechanical properties can be quantitatively tuned, and therefore may provide useful reference for the rational design of other PUUS hydrogels with exceptional mechanical property.

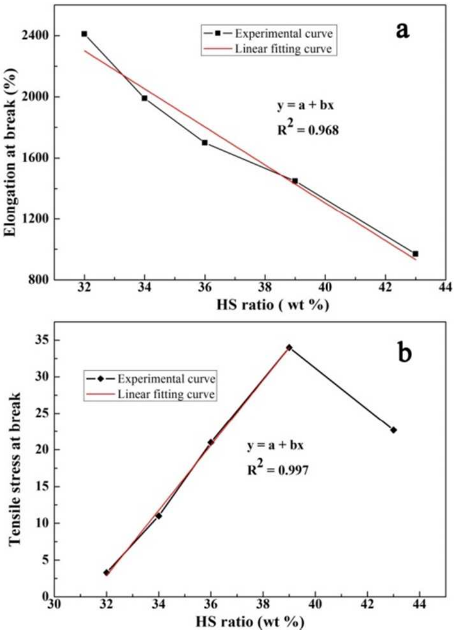


**Fig.5** HS ratio effects on the (a) elongation and (b) tensile stress at break of the PUUS hydrogels. Note: linear fitting was conducted on the Origin Pro 8 system, and the first four data were linear fitted in the tensile stress case (b).

In addition to the above mentioned excellent mechanical properties, another advantage of the present PUUS hydrogel is its easy processability due to the dynamic and reversible cross-linking character. The as prepared viscous PUU solution (Fig. S4 in ESI) can be stored for several months without obvious change. Thus films can be easily prepared by solution casting method, and fibres can also be obtained by wet-spinning, such as electro-spinning technique (as shown in Fig. 6).

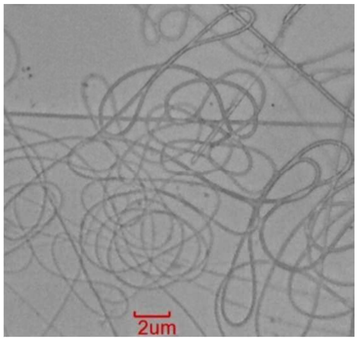


**Fig. 6** Microphotograph of the electro-spinning fibres of PUU sample with [NCO]/[OH] ratio of 22/14 from its acetone solution.

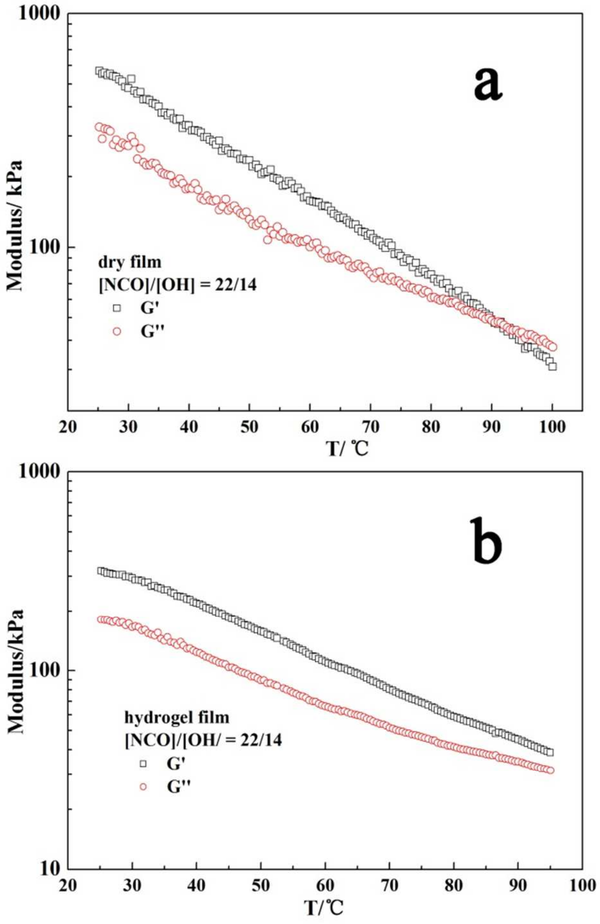


**Fig. 7** Temperature dependent rheology experiments of (a) the dry and (b) hydrogel films.

Further, as shown in Fig. 7a, temperature dependent rheology experiment of dry PUU film with [NCO]/[OH] ratio of 22/14 showed that both G' and G" decreased with increasing temperature, and a cross temperature was observed at about 90 ºC, which was much lower than its degradation temperature (~250 ºC, Fig. S5 in ESI). Below the cross temperature, the behaviour of the PUU dry film was mainly elastic (G' > G"), and above this temperature the behavior changed to be viscous (G" > G').[44] Similar behaviour can also be observed for PUU dry films with other [NCO]/[OH] ratios (Fig. S6 in ESI). These results demonstrated the typical thermoplastic nature of the present PUU material will greatly facilitate the manufacture of hydrogel products by injection, extrusion and compression moulding, etc. At the same time, contrary to most other PU or PUU supramolecular hydrogels which generally turn to sol at higher temperatures, the present hydrogel showed high thermal stability by keeping its gel state (G' > G") up to temperature as high as 95 ºC (Fig. 7b).

## Conclusions

In summary, a novel type of transparent polyurethane-urea supramolecular hydrogel (PUUS gel) with excellent mechanical properties and easy processability has been reported, using water as the additional in-situ chain extender to form urea linkages. The mechanical properties, in terms of shear modulus (0.2-0.8 MPa), elongation at break (from 970% to 2420%), tensile strength (from 3.3 to 34 MPa) and compression stress (up to 36.8 MPa), of PUUS gel could be easily controlled to a great extent by simply altering the [NCO]/[OH] ratio. The elongation and tensile stress at break can even be quantitatively tuned. The superior mechanical characteristics of the present PUUS hydrogels could be ascribed to the formation of unique multi-urea linkages in the last synthetic step. Besides, the present linear PUU polymers can be dissolved in many organic solvents, such as acetone, methanol, ethanol, DMF and so on, and thus could be made into different forms by various manufacturing methods including solution casting, electro-spinning, injection, extrusion and compression moulding etc. So far, no other supramolecular hydrogels have been reported to possess all these features, making this supramolecular hydrogel an unprecedented one. This study provided a simple and mild avenue to the formation of mechanical strong and stretchable PUU supramolecular hydrogels, which of course would promote their applications in various areas, and the results may also provide useful theoretical references for the rational design of other PUU supramolecular materials with exceptional/designed mechanical property. Our current efforts are focused on increasing the equilibrium water content of the resultant supramolecular hydrogels and exploring applications and realizing other functionalities of this supramolecular hydrogels, such as self-healing and shape-memory functions.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (NSFC, No. 21274102 and 21074087).

## Notes and references

[a] Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, JiangSu 215123, China.
E-mail: hehuang@suda.edu.cn, guomingyu@suda.edu.cn

† Electronic Supplementary Information (ESI) available: Fig. S1-S5 and movie S1 and S2. See DOI: 10.1039/b000000x/

1. A. S. Hoffman, *Adv Drug Deliver Rev*, 2002, **54**, 3-12.
2. B. Balakrishnan and R. Banerjee, *Chemical Reviews*, 2011, **111**, 4453-4474.
3. O. Wichterle and D. Lim, *Nature*, 1960, **185**, 117-118.
4. K. L. Shantha, P. Ravichandran and K. P. Rao, *Biomaterials*, 1995, **16**, 1313-1318.
5. Z. S. Liu and P. Calvert, *Adv Mater*, 2000, **12**, 288-291.
6. S. Kiyonaka, K. Sada, I. Yoshimura, S. Shinkai, N. Kato and I. Hamachi, *Nat Mater*, 2004, **3**, 58-64.
7. N. M. Sangeetha and U. Maitra, *Chem Soc Rev*, 2005, **34**, 821-836.
8. L. Yu, H. Zhang and J. D. Ding, *Angew Chem Int Edit*, 2006, **45**, 2232-2235.
9. P. Calvert, *Adv Mater*, 2009, **21**, 743-756.
10. B. V. Slaughter, S. S. Khurshid, O. Z. Fisher, A. Khademhosseini and N. A. Peppas, *Adv Mater*, 2009, **21**, 3307-3329.
11. Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara and T. Aida, *Nature*, 2010, **463**, 339-343.
12. J. N. Hunt, K. E. Feldman, N. A. Lynd, J. Deek, L. M. Campos, J. M. Spruell, B. M. Hernandez, E. J. Kramer and C. J. Hawker, *Adv Mater*, 2011, **23**, 2327-2331.
13. J.-Y. Sun, X. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. Suo, *Nature*, 2012, **489**, 133-136.
14. K. Y. Lee and D. J. Mooney, *Chemical Reviews*, 2001, **101**, 1869-1879.
15. Y.-m. Chen, J.-j. Yang, Y. Osada and J. P. Gong, *Chinese J Polym Sci*, 2011, **29**, 23-41.
16. M. Tan, T. T. Zhao, H. Huang and M. Y. Guo, *Polymer Chemistry*, 2013, **4**, 5570-5576.
17. Y. Okumura and K. Ito, *Adv Mater*, 2001, **13**, 485-487.
18. J. P. Gong, Y. Katsuyama, T. Kurokawa and Y. Osada, *Adv Mater*, 2003, **15**, 1155-1158.
19. T. Nakajima, T. Kurokawa, H. Furukawa, Q. M. Yu, Y. Tanaka, Y. Osada and J. P. Gong, *Chinese J Polym Sci*, 2009, **27**, 1-9.
20. T. Huang, H. Xu, K. Jiao, L. Zhu, H. R. Brown and H. Wang, *Adv Mater*, 2007, **19**, 1622-1626.
21. T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M. Shibayama and U.-i. Chung, *Macromolecules*, 2008, **41**, 5379-5384.
22. L. Tang, W. Liu and G. Liu, *Adv Mater*, 2010, **22**, 2652-2656.
23. K. Haraguchi and T. Takehisa, *Adv Mater*, 2002, **14**, 1120-1124.
24. X. Yan, F. Wang, B. Zheng and F. Huang, *Chem Soc Rev*, 2012, **41**, 6042-6065.

25. A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew Chem Int Edit*, 2008, **47**, 8002-8018.
26. L. Yu and J. Ding, *Chem Soc Rev*, 2008, **37**, 1473-1481.
27. Z. Ma, Y. Hong, D. M. Nelson, J. E. Pichamuthu, C. E. Leeson and W. R. Wagner, *Biomacromolecules*, 2011, **12**, 3265-3274.
28. P. N. Coneski and J. H. Wynne, *Acs Appl Mater Inter*, 2012, **4**, 4465-4469.
29. J. H. Park and Y. H. Bae, *Biomaterials*, 2002, **23**, 1797-1808.
30. X. J. Loh, S. H. Goh and J. Li, *Biomaterials*, 2007, **28**, 4113-4123.
31. J. A. Wu, Q. Ge and P. T. Mather, *Macromolecules*, 2010, **43**, 7637-7649.
32. X. Gu and P. T. Mather, *Rsc Advances*, 2013, **3**, 15783-15791.
33. J. O. B. Asplund, T. Bowden, T. Mathisen and J. Hilborn, *Macromolecules*, 2006, **39**, 4380-4385.
34. E. Yilgor, M. Isik and I. Yilgor, *Macromolecules*, 2010, **43**, 8588-8593.
35. J. O. B. Asplund, T. Bowden, T. Mathisen and J. Hilborn, *Biomacromolecules*, 2007, **8**, 905-911.
36. F. S. Jun Xiong, Hongguang Du, *Chin. J. Anal. Lab.*, 2007, **26**, 73-76.
37. K. Mayumi, M. Tezuka, A. Bando and K. Ito, *Soft Matter*, 2012, **8**, 8179-8183.
38. A. Nakayama, A. Kakugo, J. P. Gong, Y. Osada, M. Takai, T. Erata and S. Kawano, *Adv Funct Mater*, 2004, **14**, 1124-1128.
39. T. Sakai, Y. Akagi, T. Matsunaga, M. Kurakazu, U.-i. Chung and M. Shibayama, *Macromol Rapid Comm*, 2010, **31**, 1954-1959.
40. K. Fujii, H. Asai, T. Ueki, T. Sakai, S. Imaizumi, U.-i. Chung, M. Watanabe and M. Shibayama, *Soft Matter*, 2012, **8**, 1756-1759.
41. H. Gao, N. Wang, X. Hu, W. Nan, Y. Han and W. Liu, *Macromol Rapid Comm*, 2013, **34**, 63-68.
42. J. Zhang, N. Wang, W. Liu, X. Zhao and W. Lu, *Soft Matter*, 2013, **9**, 6331-6337.
43. K. Haraguchi and H. J. Li, *Angew Chem Int Edit*, 2005, **44**, 6500-6504.
44. Y. L. L. L. Yang, L. S. Wang, A.Q. Zhang, *Polym. Chem*, 2014, **5**, 153-160.