

# Thin, Tough, pH-Sensitive Hydrogel Films with Rapid Load Recovery

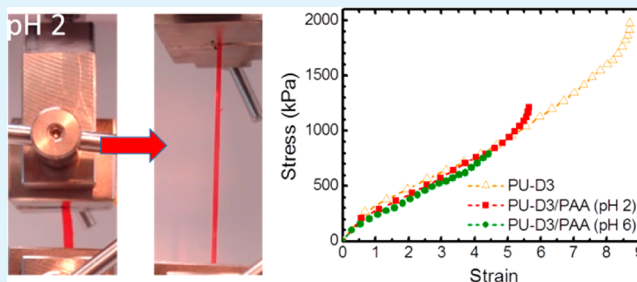
Sina Naficy, Geoffrey M. Spinks,\* and Gordon G. Wallace

ARC Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, New South Wales 2522, Australia

## S Supporting Information

**ABSTRACT:** Stimuli-responsive hydrogels are used as the building blocks of actuators and sensors. Their application has been limited, however, by their lack of mechanical strength and recovery from loading. Here, we report the preparation of pH-sensitive hydrogels as thin as 20  $\mu\text{m}$ . The hydrogels are made of a polyether-based polyurethane and poly(acrylic acid). A simple method was employed to create hydrogels with thicknesses in the range of 20–570  $\mu\text{m}$ . The hydrogel films volume changed by a factor of  $\sim 2$  when the pH was switched around the transition point (pH 4). Tensile extensibilities of up to  $\sim 350\%$  were maintained at each pH, and the average Young's modulus and tensile strength were in the range of 580–910 and 715–1320 kPa, respectively, depending on the pH. Repeated tensile loading and unloading to 100% extension showed little permanent damage, unlike analogous double-network hydrogels, and with immediate recovery (up to 75–85% of the first loading cycle), unlike hybrid ionic–covalent interpenetrating network hydrogels.

**KEYWORDS:** load recovery, pH sensitive, poly(acrylic acid), polyurethane, thin hydrogel, tough



## INTRODUCTION

For artificial muscles to mimic the performance of real muscles, they must generate a large actuation stroke, fast response, direct conversion of chemical energy to mechanical energy, and long cycling life.<sup>1</sup> Hydrogels are a type of stimuli-responsive materials that can fulfill part of these criteria: They are capable of converting chemical energy to mechanical motion, have properties similar to muscle tissue, and can undergo large deformations upon stimulation, generating considerably high stroke.<sup>2</sup> Hydrogels also respond to a wide range of stimuli, such as light,<sup>3,4</sup> temperature,<sup>5,6</sup> pH,<sup>7</sup> solvent composition,<sup>7</sup> chemical species,<sup>8,9</sup> and electrical field.<sup>10–12</sup> A major current limitation, however, is that hydrogels are not particularly fast in responding to these stimulations.<sup>13,14</sup> The volume change associated with hydrogel actuation has a diffusive nature determined by a cooperative diffusion process. The actuation kinetics of hydrogels is characterized by their diffusive characteristic time  $\tau$ , which is related to their smallest dimension  $h$ , so that  $\tau \sim h^2$ .<sup>15</sup> One approach to enhance the response rate of hydrogel actuators is to decrease their size. However, conventional hydrogels are fragile, brittle materials, resulting in catastrophic failure with very small fracture energies ( $\sim 10 \text{ J m}^{-2}$ ).<sup>16</sup> Hence, reducing the size of a conventional hydrogel actuator to improve the response rate increases the likelihood of mechanical failure, limiting the validity of this approach.

Tough hydrogels, such as the double-network (DN) systems, are an exception. For instance, the DN hydrogels based on poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and polyacrylamide (PAAm) were found to have high

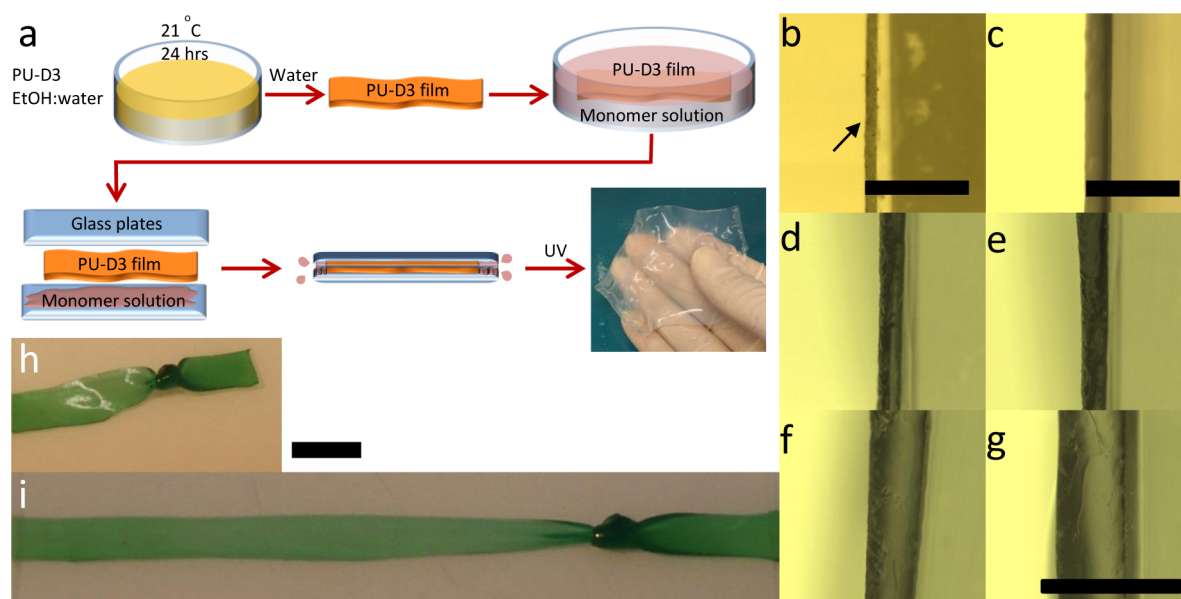
compression and tensile strengths ( $\sim 17$  and  $\sim 0.5$ – $2 \text{ MPa}$ , respectively),<sup>17–19</sup> large strain at break ( $\sim 10$ – $15$ ),<sup>20</sup> and high fracture energies ( $100$ – $1000 \text{ J m}^{-2}$ ).<sup>21</sup> The very high toughness of DN hydrogels was attributed to the breaking up of their tightly cross-linked first-formed network while the second, loosely cross-linked network holds the hydrogel together.<sup>22,23</sup> Consequently, a large damaged area is formed around the crack tip, where energy dissipation occurs.<sup>24</sup> Although this mechanism is the main source of toughness in the DN hydrogels, it also results in an inherent problem with this system: the DN hydrogels are permanently damaged after applying a load.<sup>25</sup> Systematic uniaxial loading and unloading on a PAMPS/PAAm DN hydrogel revealed significant hysteresis during the first cycle because of network chain scission during loading, leading to a decreased shear modulus on the subsequent reloading.<sup>25</sup> In fact, the reloading curve typically follows the previous unloading curve, suggesting permanent damage resulting from load-induced scission of covalent backbone bonds in network strands. This type of permanent damage continues when extension exceeds the historic maximum strain.<sup>26</sup>

Recently, a hybrid hydrogel created from ionically cross-linked alginate and covalently cross-linked PAAm was demonstrated to have both high toughness ( $\sim 9000 \text{ J m}^{-2}$ ) and considerable recovery after loading and unloading.<sup>27,28</sup> Again, the high toughness of this system was attributed to energy dissipation through the unloading of network strands in

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**Figure 1.** PU-D3/PAA hydrogel preparation. (a) Multistep pathway of the preparation method. (b–g) Cross-sectional images of PU-D3/PAA hydrogels with various thickness. The arrow in panel b points to the hydrogel; scale bars in panels b and c are 200  $\mu\text{m}$  and in panels d–g, 1 mm. (h) Knot formed in a fully swollen PU-D3/PAA hydrogel film (pH 6, water content 81%) and then stretched more than 200% (i); scale bar is 1 cm. The hydrogel was colored with a pH-indicator dye.

the tightly cross-linked alginate ionic network with a large load/unload hysteresis. This system has the advantage compared with DN gels of stable mechanical properties on repeated loading and unloading. The recovery was attributed to the reformation of ionic cross-links in the alginate network that had been cleaved during loading. The recovery of ionic cross-links is not instantaneous, however, and a resting or recovery time at zero load is required to fully restore the virgin gel properties. This slow recovery may be problematic in practical applications where external loads are likely to be continually changing.

The goal of the current study was to create thin and tough pH-sensitive hydrogel films with high extensibility that can be loaded and unloaded without permanent damage and show instantaneous recovery. The alginate/PAAm system and most DN hydrogels (e.g., PAMPS/PAAm) are either not pH-sensitive or their mechanical properties have not been extensively reported in both expanded and collapsed states. The hydrogel reported here is made of a commercially available polyether-based polyurethane elastomer into which is imbibed a pH-sensitive polymer, poly(acrylic acid) (PAA). The mechanical properties and swelling degrees were determined in both the collapsed (below pH  $\sim$ 4) and expanded (above pH  $\sim$ 4) states. Moreover, the preparation process proposed here is versatile and enables the creation of micrometer-thickness hydrogels, enabling fast pH response.

## EXPERIMENTAL SECTION

**Hydrogel Preparation.** The preparation of the hydrogels was as follows. HydroMed D3 (AdvanSource, USA; referred to as PU-D3 hereafter) was used as the base polyurethane material. This polymer is a hydrophilic polyurethane, soluble in the mixture of ethanol (EtOH) and water but insoluble in water alone. PU-D3 was dissolved in 95:5 mixture of EtOH and Milli-Q water. The PU-D3 films were prepared using a simple solution-casting method at room temperature ( $21 \pm 2$  °C, 24 h) (Figure 1a). Different concentrations of PU-D3 in EtOH/water (95:5) were used to obtain films with various thicknesses. After evaporation of solvent mixture, water was added on top of the PU-D3 films, allowing them to swell and release from the container. The PU-

D3 films were stored in water for another 3 days, and water was changed on a daily basis. To introduce pH sensitivity into the system, the PU-D3 films were transferred into an acrylic acid (AA) monomer solution. The monomer solution consisted of AA monomer (0.97 M), *N,N'*-methylenebisacrylamide cross-linker (0.17 mol % based on AA), and  $\alpha$ -ketoglutaric acid UV-initiator (0.50 mol % based on AA), all dissolved in water. All chemicals were purchased from Sigma-Aldrich. An adequate amount of sodium hydroxide was added to the monomer solution to fully neutralize the AA monomer because PU-D3 is partially soluble in some organic acids (such as AA monomer). The PU-D3 films were soaked in the AA monomer solution for 2 days and then removed and sandwiched between two glass plates. No spacer was used to separate the plates, but excess monomer solution was used to prevent monomer from being evaporated from the films (Figure 1a). The PAA network was then formed within the PU-D3 film using UV-initiation polymerization (with 240 W power and 300 nm wavelength for 12 h, fan cooled). After polymerization, the PU-D3/PAA hydrogel films were removed from the glass plates and washed extensively with water. More details on the experimental procedure are available in the Supporting Information.

**Mechanical Testing.** Mechanical tensile testing was conducted on the fully swollen PU-D3 and PU-D3/PAA hydrogel ribbons (5 mm width and 10 mm gauge length) equilibrated at two different pH's (pH 2 and 6). All mechanical tests were performed in air and at room temperature using a universal mechanical tester (Shimadzu EZ-L) with a 10 N load cell at a constant strain rate of 0.3  $\text{min}^{-1}$ . The water loss was measured to be less than 5% during the course of the experiments. To measure energy dissipation and hysteresis of the hydrogels, consecutive loading–unloading tensile tests were performed at three different strain rates (i.e., 0.3, 1, and 3  $\text{min}^{-1}$ ) using the 10 N load cell. To prevent excessive water loss from the samples over the longer period of measurements, oil was applied on the surface of the hydrogel specimens.

Fracture energy ( $G_c$ ) of the hydrogels was also measured under two different pH conditions using a trouser-type tear test. All tests were conducted on  $7.5 \times 50 \text{ mm}^2$  specimens with a 30 mm central cut. The legs of specimens were then pulled apart (10  $\text{mm min}^{-1}$ , room temperature), and the fracture energy was calculated using  $G_c = 2F/h$ , where  $F$  is the applied force during crack propagation and  $h$  is the sample thickness.

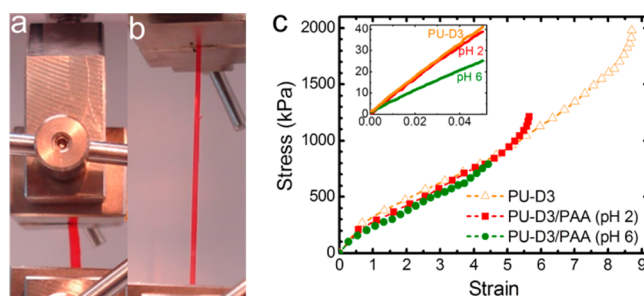
## RESULTS AND DISCUSSION

The water-swollen PU-D3 films had a water content (WC) of  $58 \pm 1\%$ . Depending on the initial thickness of the starting PU-D3 film, PU-D3/PAA hydrogels with different thicknesses, as small as  $\sim 20 \mu\text{m}$  and up to  $570 \mu\text{m}$ , were successfully produced (Figure 1b–g). Although the swelling ratio of PU-D3 hydrogel films remained pH-independent over the entire pH range of 1–11 ( $Q \sim 2.40 \pm 0.05$ ), the PU-D3/PAA hydrogels were pH-sensitive, with their swelling ratio almost doubled when pH changed from 2 to 6 (Figure S1). The swelling ratio of PU-D3/PAA hydrogels equilibrated at pHs below 4 was  $\sim 2.75 \pm 0.25$ , which then increased to  $\sim 5.63 \pm 0.66$  as the pH exceeded the transition point (pH  $\sim 4$ ). The fully swollen PU-D3/PAA hydrogel films could also withstand high levels of deformation, such as elongation and torsion (Figure 1h,i and Movie S1 in the Supporting Information).

Although similarly thin and tough hydrogels have been reported previously, their preparation requires more elaborate techniques. For example, DN hydrogels as thin as  $\sim 30 \mu\text{m}$  were synthesized using a three-step polymerization process.<sup>18</sup> Thin PAMPS films were first prepared between two glass plates separated by a spacer followed by a salt-controlled swelling process in AAm monomer solution to prevent the thin PAMPS films from excessive swelling and breakage. After polymerization of AAm, the film was re-soaked again in the AAm monomer solution, and a third polymerization step was used to make the final thin PAMPS/PAAm DN hydrogel.<sup>18</sup> The second and third polymerizations were required to generate sufficient PAAm content needed for toughening. In contrast, the robust hydrophilic polyurethane films used in the present study allowed a simple two-step preparation of thin hydrogels suitable for rapid pH response. The diffusion coefficient was found to be  $\sim 3.58 \times 10^{-7}$  and  $\sim 1.14 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  when the pH was switched from 2 to 6 and from 6 to 2, respectively. Assuming  $\tau \approx h^2/D$ , where  $\tau$  is the characteristic response time and  $h$  and  $D$  are the sample thickness and nominal diffusion coefficient, respectively, then  $\tau$  will be around 10 s for a 20–34  $\mu\text{m}$  thick hydrogel film.

The PU-D3/PAA hydrogel films were transparent and homogeneous when examined with light microscopy, as shown in Figure 1. Some surface features were observed in these micrographs, but they were due to cutting artifacts. The amount of PAA incorporated into the PU-D3 film was estimated to be approximately 18% compared to the mass of PU-D3 determined from the mass increase after soaking the film in water and then in the AA monomer solution. In comparison, maximum toughening for DN gels occurs with a large excess of the second, loose network compared to the first, tight network. Extensive soaking of the PU-D3/PAA films in EtOH/water (95:5), which is a good solvent for both PU-D3 and noncross-linked PAA, left particles of highly swollen material that are likely the remnants of the lightly crosslinked PAA network.

Figure 2 shows images of a PU-D3/PAA hydrogel (250  $\mu\text{m}$  thick) fully swollen in acid before and during the tensile test. Typical tensile curves of PU-D3/PAA hydrogel films under the two different pH conditions are shown in Figure 2c along with the PU-D3 film equilibrated in water. All three samples show remarkably similar stress–strain curves, indicating that the polyurethane network is mechanically dominant. The main differences relate to the breaking stress and strain, which decrease with increased swelling. The elastic modulus (Figure



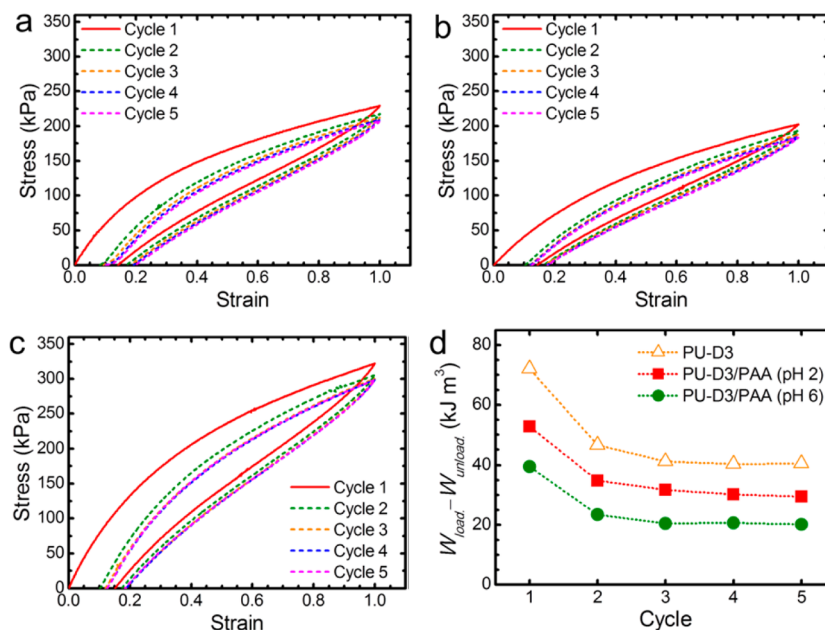
**Figure 2.** Tensile performance of the PU-D3/PAA hydrogel films. (a) PU-D3/PAA hydrogel (pH 2) before the test and (b) during the tensile testing. The hydrogel was colored with a pH-indicator dye. (c) Stress–strain curves of PU-D3/PAA hydrogels at pH 2 (squares) and 6 (circles). Included for comparison is the PU-D3 film (open triangles) equilibrated in deionized water.

2c, inset) was the lowest in the most highly swollen PU-D3/PAA at pH 6 ( $Q = 5.3$ ) because of the dilution of elastically active network strands. However, almost identical moduli were observed for PU-D3 and PU-D3/PAA at pH 2 despite the different swelling of  $Q = 2.4$  and  $3.1$ , respectively. It is possible that internetwork bonds, such as the hydrogen bonding that occurs between protonated carboxylic acid groups and poly(ethylene oxide), may compensate for the increased swelling. For the PU-D3/PAA hydrogel at pH 2 (with water content of 68%), the tensile strength  $\sigma_b$ , elongation at break  $\epsilon_b$ , and Young's modulus  $E$  were  $1321 \pm 221$ ,  $4.31 \pm 0.65$ , and  $912 \pm 70$  kPa, respectively. In comparison,  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  were  $717 \pm 112$ ,  $3.49 \pm 0.80$ , and  $580 \pm 44$  kPa, respectively, for the hydrogels equilibrated at pH 6 (WC  $81 \pm 1\%$ ). The native PU-D3 equilibrated in water (WC  $58 \pm 1\%$ ) had  $\sigma_b$ ,  $\epsilon_b$ , and  $E$  of  $1980 \pm 225$ ,  $8.70 \pm 0.73$ , and  $942 \pm 40$  kPa, respectively. Compared to the other thin, tough hydrogel films, our current system was pH-sensitive, exhibited high extensibility within the range of other thin DN hydrogels ( $\sim 3$ – $5$  vs  $\sim 1$ – $12$ ),<sup>18,19</sup> and had relatively high moduli ( $\sim 580$ – $950$  kPa vs  $\sim 100$ – $1700$  MPa).<sup>19,20</sup> Figures S2–S5 in the Supporting Information provide a mechanical properties comparison between these and other materials.<sup>29</sup>

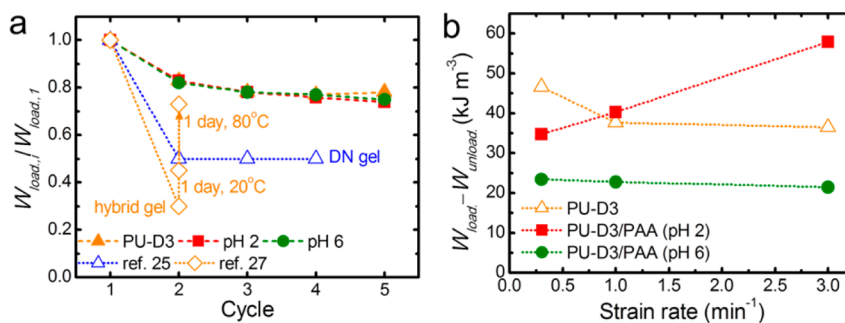
The differences noted in terms of breaking stress and strain of the hydrogels were further evaluated using fracture toughness tests. Trouser-type tear tests were used to measure the fracture energy of the PU-D3/PAA hydrogel equilibrated at pH 2 and 6. The fracture energies calculated were  $3964 \pm 1278 \text{ J m}^{-2}$  for samples at pH 2 and  $472 \pm 40 \text{ J m}^{-2}$  for samples at pH 6. Tear tests on the water-swollen PU-D3 samples were not successful because of their high toughness. The energy dissipated during the tensile testing until mechanical failure occurs is sometimes used as a measure of toughness and was estimated by calculating the area under the tensile curve (work of extension  $W_{\text{load}}$ ). The  $W_{\text{load}}$  values decreased with increased swelling in the order of PU-D3 ( $7600 \pm 570 \text{ kJ m}^{-3}$ ) > PU-D3/PAA at pH 2 ( $3787 \pm 617 \text{ kJ m}^{-3}$ ) > PU-D3/PAA at pH 6 ( $1812 \pm 800 \text{ kJ m}^{-3}$ ). The  $W_{\text{load}}$  measured here is similar to those of other tough hydrogels, such as DN hydrogels ( $\sim 2 \times 10^3$  to  $2 \times 10^4 \text{ kJ m}^{-3}$ ) and nanocomposite hydrogels ( $\sim 10^3$ – $10^4 \text{ kJ m}^{-3}$ )<sup>16</sup> (Figure S4).

The mechanism of toughening in DN and hybrid hydrogels has been associated with energy dissipation by network strand scission, as indicated by the nature of repeated loading and unloading tests. In both cases, a load–unload hysteresis indicates energy dissipation that correlates with toughness.





**Figure 3.** PU-D3/PAA hydrogel films equilibrated at pH (a) 2 and (b) 6. (c) PU-D3 films equilibrated in water were subjected to consecutive loading–unloading cycles of 100% stretch. (d) Hysteric dissipated energy during each load–unload cycle ( $W_{\text{load}} - W_{\text{unload}}$ ). Strain rate:  $0.3 \text{ min}^{-1}$ .



**Figure 4.** (a) Loading work of consecutive loading cycles,  $W_{\text{load},i}$  normalized to the loading work of first cycle,  $W_{\text{load},1}$  (squares: PU-D3/PAA at pH 2; circles: PU-D3/PAA at pH 6; filled triangles: PU-D3 in water). Data extracted from refs 25 (PAMPS/PAAm DN, open triangles) and 27 (alginate/PAAm hybrid, diamonds) are presented for comparison. For the latter, the second loading cycle was either performed immediately following unloading or after a 1 day recovery period at zero load and the temperatures indicated. The maximum strains at which experiments were performed are 1 for the PU-D3-based samples, 0.6 for the DN hydrogel (note, DN hydrogel was tested in compression), and 6 for the hybrid hydrogel. (b) Hysteric dissipated energy during the second loading cycle ( $W_{\text{load}} - W_{\text{unload}}$ ) as a function of strain rate.

The reloading curve of a DN gel typically follows the previous unloading curve, indicating that the original loading had induced network chain scission and permanently reduced the cross-linking density. In contrast, the reloading of the ionic-covalent networks can be close to the previous loading curve when a suitable recovery time at zero stress is allowed.<sup>27</sup> The latter is interpreted as slow recovery of ionic cross-links that are cleaved during the loading process.

Cyclic tensile testing of the PU-D3/PAA hydrogels displayed almost no change in network properties upon immediate reloading. Figure 3 shows the performance of PU-D3 and PU-D3/PAA hydrogels equilibrated at pH 2 and 6 and tested for five cycles, where the sample was stretched to 100% of its initial length during the loading cycles ( $\epsilon = 1.0$ ). The dissipated energy per unit volume (area between the loading and unloading curves:  $W_{\text{load}} - W_{\text{unload}}$ ) during the first cycle of loading–unloading increased in relative order of increasing toughness: PU-D3 > PU-D3/PAA (pH 2) > PU-D3/PAA (pH 6) (Figure 3d). The dissipated energy in the second cycle was found to be lower than that of the first cycle for all samples but

remained approximately constant for subsequent cycles. The fractional hysteric energy dissipations (normalized to  $W_{\text{load}}$ ) were considerably smaller than those of alginate/PAAm hybrid hydrogel and PAMPS/PAAm DN gels.<sup>25,27</sup> Interestingly, all loading cycles had a similar shape, although it was offset somewhat by permanent strain during prior loading. The permanent strain offset was largest between cycles 1 and 2 and thereafter it was quite small so that cycles 2–5 were almost identical. These results indicate some rearrangement in the network structure during the first cycle without a permanent change in cross-linking density.

The extent of recovery on repeated loading and unloading for various tough gels can be illustrated from the ratio of work of extension during each loading cycle ( $W_{\text{load},i}$ ) to the first cycle ( $W_{\text{load},1}$ ), as shown in Figure 4a. All three PU-D3-based systems showed identical behavior, with a 20% decrease in the work of extension during the second loading and little further decrease in cycles 2–5. In contrast, DN hydrogels showed a large decrease in the work of extension of over 50% in the second loading cycle for strains to just 60% (open triangles in Figure

4a).<sup>25</sup> Recovery studies of alginate/PAAm hybrid hydrogels show the work of extension in the second loading cycle to be as small as 30% of the initial loading work when reloaded immediately after unloading (at maximum strain of 600%). However, the work of extension increased to ~75% of the initial value for long holding times (1 day) at an elevated temperature (80 °C) between the unloading and reloading (diamonds in Figure 4a).<sup>27</sup>

The fast and significant recovery of the PU-D3/PAA hydrogels after tensile loading and unloading suggests different toughening mechanisms than those occurring in DN and hybrid ionic-covalent hydrogels. The absence of recovery in DN systems is taken as evidence for permanent scission of covalent network strands, whereas the time-dependent recovery of ionic-covalent hybrid networks has been interpreted as the gradual reformation of ionic cross-links. In both cases, the unloading of network strands in the tighter network is assumed to be the main contributor to energy dissipation and toughness. The fast recovery and relatively small loading-unloading hysteresis reported here for PU-D3 and PU-D3/PAA hydrogels may be tentatively associated either with a viscoelastic energy dissipation process or with the unloading of network strands because of the dissociation and/or reorganization of physical cross-links in the tightly cross-linked PU-D3 network. If the latter process dominates, then the physical cross-links must reform rapidly on unloading. Cyclic load/unload testing was performed at three different cross-head rates to assess viscoelasticity effects (Figure 4b). The hysteresis energy of the PU-D3/PAA equilibrated at pH 2 was found to increase with increasing testing speed, suggesting a viscoelastic dissipation mechanism. However, the PU-D3 and PU-D3/PAA samples tested at pH 6 showed a slight decrease or no change in hysteretic energy dissipation with increasing rates. It must be concluded that energy-dissipation processes other than viscoelasticity must be operating in these materials. The difference in strain-rate behavior noted for the PU-D3/PAA samples equilibrated at the two different pHs may be due to hydrogen bonding between carboxylic acid groups and ethylene glycol units that form at pH's lower than 4. More comprehensive experiments are required to fully understand these effects. Further testing is currently underway to assess these possible toughening mechanisms.

Overall, the robust mechanical performance of the PU-D3/PAA hydrogels appears to originate from the PU-D3 part, whereas the pH sensitivity and high swellability are the result of the PAA network.

## CONCLUSIONS

Exploiting the mechanical performance of a hydrophilic rubber as the base material has allowed us to create a versatile stimuli-sensitive material well-suited for sensors and actuators. We report a simple process to produce pH-sensitive hydrogel films as thin as 20  $\mu\text{m}$  with excellent mechanical properties. Polyether-based polyurethane was used to create thin and robust films followed by incorporating a pH-sensitive poly-(acrylic acid) network. The approach differs from that used to create double-network hydrogels wherein two relatively brittle hydrogel networks are combined to create a tough gel. Here, we start with a low-swelling and tough elastomeric network and incorporate a second hydrophilic network. The result is an increase in swelling compared to the starting material and the ability to use external pH (in the range 2–6) to change the degree of swelling. Little change in modulus occurred as a result

of PAA incorporation, although the toughness decreased particularly in the high-swelling PU-D3/PAA samples equilibrated at pH 6. Even under this condition, however, the toughness and swelling degree were comparable with some DN hydrogels. The mechanisms of toughening were dominated by the processes occurring in the mechanically dominant polyurethane network and may be related to dissociation or reorganization of physical bonds. The rate of network reformation on unloading was high, as cycling loading-unloading tests showed little change on repeated cycling (especially after the first cycle) without any recovery period.

The hydrogel system introduced here is one of a few demonstrations of a tough and pH-sensitive hydrogel prepared as thin films and with ability to undergo multiple cycles of loading and unloading with minimal change in its mechanical performance. The preparation process was shown to be simple and versatile, allowing creation of hydrogels with a range of thickness, from micrometer to millimeter, with the likelihood of response times in the tens of seconds.

## ASSOCIATED CONTENT

### Supporting Information

Video showing the formation of a knot on the hydrogel film followed by stretching the film; experimental details; swelling ratio of PU-D3 and PU-D3/PAA hydrogels equilibrated at different pH's; and comparison between mechanical performance of the hydrogel reported here and other conventional and tough hydrogels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [gspinks@uow.edu.au](mailto:gspinks@uow.edu.au).

### Notes

The authors declare no competing financial interest.

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