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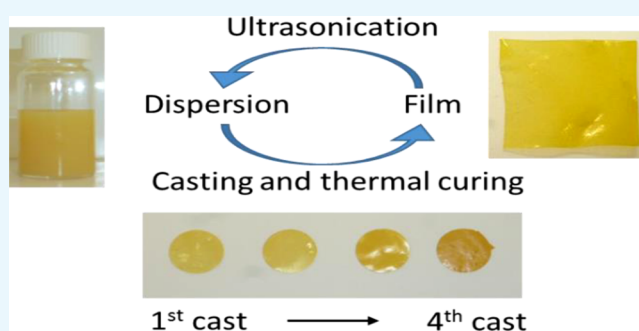
# Water-Reprocessable, Reformable, and Ecofriendly Sustainable Material Based on Disulfide-Cross-Linked Polyethyleneimine

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**ABSTRACT:** A reformable polymer gel material has been developed based on the disulfide cross-linking of low-molecular-weight polyethylenimine (PEI) that can be synthesized through a facile thiolation method and reprocessed through an aqueous method without the use of solvents or additional chemicals. Despite being made with water-soluble PEI, the cross-linked gel shows good mechanical integrity and its properties can be controlled through the fabrication parameters, maintaining the hydrophilic nature of PEI while being sufficiently robust to form a free-standing film that does not dissolve in water. The properties of the gel have been characterized by Fourier transform infrared spectroscopy, thermogravimetry, and dynamic mechanical analyses, showing the effect of parameters such as the degree of thiolation and thermal curing. The reformability of the gel comes from the disulfide cross-links, which can be disrupted and reformed through a simple, aqueous processing method utilizing ultrasonication, creating an aqueous dispersion, which can be recast multiple times with minimal loss in physical properties.



## INTRODUCTION

In recent years, there have been increasing interest in smart sustainable materials based on reversible intramolecular interactions, which provide additional properties such as self-healing or remoldability.<sup>1,2</sup> Such materials capable of autonomous healing of damage are suitable for a variety of applications, such as membranes for lithium batteries, self-healing coatings for corrosion protection and biomedical applications, and for multiple remoldings as an ecofriendly material. Self-healing is a natural phenomenon in living organisms but very challenging to embed in synthetic materials. An ideal self-repairing behavior of materials refers to the ability to theoretically heal themselves endlessly, if the right healing mechanism is applied. Thus, the requisite reversibility can be obtained in such a system either through intrinsic or extrinsic self-healing or rebuilding mechanisms. An intrinsic system could be inbuilt in a material through incorporation of reversible covalent bonds or weaker noncovalent interactions, whereas an extrinsic system would involve external carriers, such as micro/nanocapsules and nanotubes to act as a carrier for active ingredients, which can be released on demand. One of the candidates for such materials is polymeric materials containing disulfide bonds,<sup>3</sup> which have enabled the reformation of damaged polymers under various stimuli such as light and heat. The chemically reversible cross-linking through disulfide bonds is advantageous due to the stability of the disulfide bonds under normal conditions and the fact that the thiol–disulfide exchange reaction proceeds without significant heat effects.

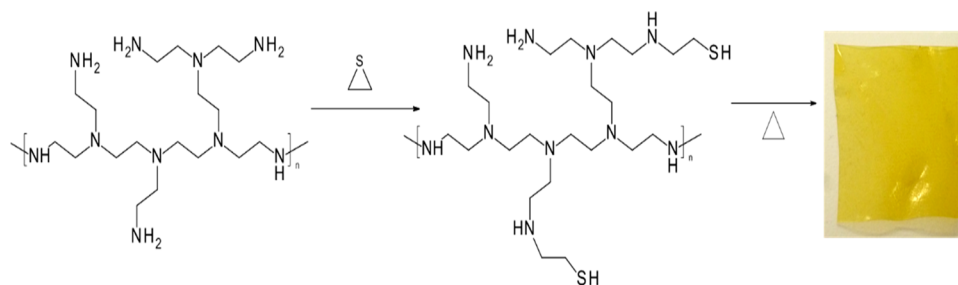
Currently, there are some explorations of polymeric materials containing disulfide bonds in the literature.<sup>4</sup> Disulfide cross-links have been applied to materials such as polyester<sup>5</sup> and poly(ethylene glycol)-based rubber networks.<sup>6</sup> In these materials, the disulfide cross-linking provides reversible covalent bonds, which can impart a degree of self-healing property to the material through the thiol–disulfide exchange reaction. The current studies are mostly aimed at imparting a self-healing property onto polymeric materials; however, such reformable cross-links may also impart recyclability to a polymer material. Most recyclable polymers are thermoplastics; thus, their recycling process involves significant amount of energy required for heating and processing. Using reformable bonds such as disulfides could potentially simplify the recycling process and result in a material that can be recycled at a low cost.

Polymers such as polyethyleneimines (PEIs) are interesting as they are potentially biodegradable, have low toxicity, and possess antibacterial property. Whereas linear PEI is solid at room temperature, branched PEI is liquid at all molecular weights. Nevertheless, PEI does not possess suitable mechanical properties for applications requiring mechanical stability; because of their hydrophilic nature they are water-soluble and thus generally find applications derived from its polycationic character.<sup>7–9</sup> In some studies,<sup>10,11</sup> chemical modification of PEI

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**Figure 1.** Synthesis of the disulfide-cross-linked PEI.

has been carried out, and in this regard, disulfide cross-linking has also been applied to PEI<sup>12</sup> for gene delivery applications. However, there are comparatively less studies on the use of branched PEI as building blocks for a mechanically stable, bulk polymer material. Wang et al. used a PEI–copper complex as a basis for a supramolecular polymer that is UV-healable;<sup>13</sup> however, because of the hydrophilic nature of PEI, such a supramolecular approach may result in a material whose mechanical integrity can be compromised due to excess moisture. In this regard, an approach based on covalent bonds such as disulfides may provide a more robust, mechanically stable material.

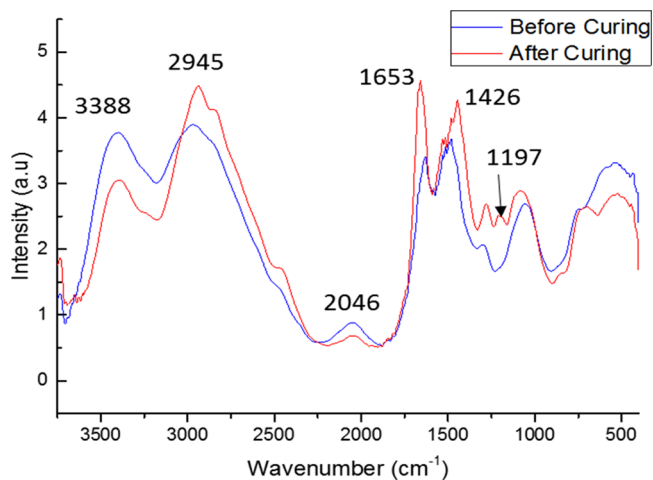
PEIs have several advantages as a base material for disulfide cross-linkings because they are widely available and can be readily thiolated through their amine functionalities, which will provide facile, low-cost fabrication of such materials. The amine groups of PEI also form hydrogen bonds between the polymer chains, which would complement the disulfide cross-links in providing strength to the material as a gel. In this contribution, we investigate the potential use of disulfide-cross-linked PEIs as a reformable gel through the disruption and reformation of the disulfide bonds. The cross-linked polymers show good mechanical properties, which would enable their use as bulk material; whereas at the same time, they can be recycled by simple, low-cost methods using only water and ultrasonication and recast into films with minimal loss in physical integrity, resulting in a material with a longer life cycle due to this recyclability.

## RESULTS AND DISCUSSION

**Synthesis of Disulfide-Cross-Linked PEI.** In this study, the disulfide-cross-linked PEI was obtained by direct thiolation using ethylene sulfide, and by increasing the amount of the thiolating agent, it produces a sticky, yellow solid, which is water-dispersible but which can be cast and cured to produce a solid, water-insoluble film (Figure 1). To achieve this, it was necessary to use a larger quantity of ethylene sulfide (1:5 ratio of the ethylene sulfide to amine units in PEI) in the thiolation reaction. Use of a lower amount of thiolating agent (ethylene sulfide) resulted in a sticky, soft material, which does not cure into a mechanically robust film. This observation indicates that due to the low molecular weight of the starting PEI, sufficient cross-linking needs to exist to obtain a robust film.

When a 1:5 ratio of the ethylene sulfide to amine units was used, a sticky yellow solid is obtained, which can be dispersed in water/methanol (50:50) and cast into a solid, flexible film. The film was soft but did not show self-healing at room temperature, which indicates that the cross-linking of the PEI prevents significant intramolecular movements of the PEI chains and thus the gel does not flow. Photoacoustic Fourier

transform infrared (PA-FTIR) analysis of the material shows peaks attributed to PEI at 3388  $\text{cm}^{-1}$  (N–H stretching), 2945  $\text{cm}^{-1}$  (C–H stretching), 1653  $\text{cm}^{-1}$  (N–H bending), 1426  $\text{cm}^{-1}$  (C–H bending), and 1100–1300  $\text{cm}^{-1}$  (C–N stretching). In addition, there was also a peak at around 2046  $\text{cm}^{-1}$ , indicative of S–H groups in both the cured and uncured samples (Figure 2). After curing, a new peak can be observed at

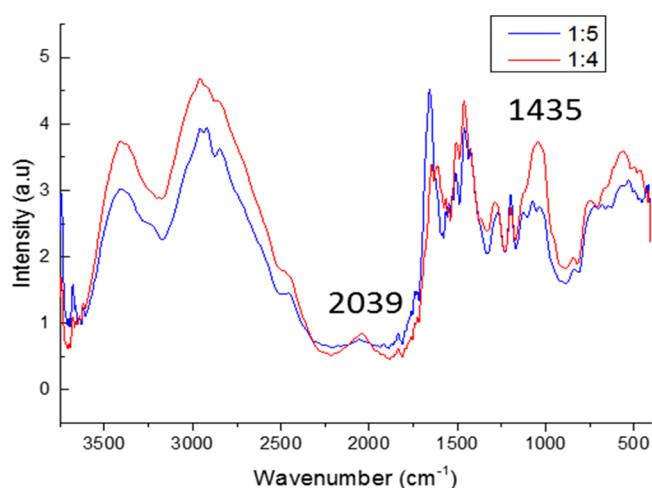


**Figure 2.** PA-FTIR spectra of the thiolated PEI before and after thermal and UV curing.

1197  $\text{cm}^{-1}$ , which is likely due to the cross-linking resulting in a shift of the C–N stretching peak, and this is accompanied by a slight shift in most of the other peaks. The bands due to C–H and C–N also increased in intensity, whereas there was a decrease in intensity in the amine peak at 3388  $\text{cm}^{-1}$ , which indicates reduced hydrogen bonding as the cured sample would have a more rigid structure compared with the uncured sample. The peak due to S–H at 2046  $\text{cm}^{-1}$  shows a reduction after curing but is still present, which indicates that some free S–H still exists in the material after curing; however, its intensity has decreased, indicating the formation of disulfide bonds. The presence of remaining thiol groups may be beneficial for reforming the material as it provides additional cross-linking points when the material is redispersed and recast. The expected peak due to disulfide (S–S) bonds is at around 500–550  $\text{cm}^{-1}$  and is very broad, and because of the broadness of the peak in this area, no single peak has been isolated. Despite this, there was an increase in intensity around the area, which indicates the presence of an S–S peak within the broad peak.

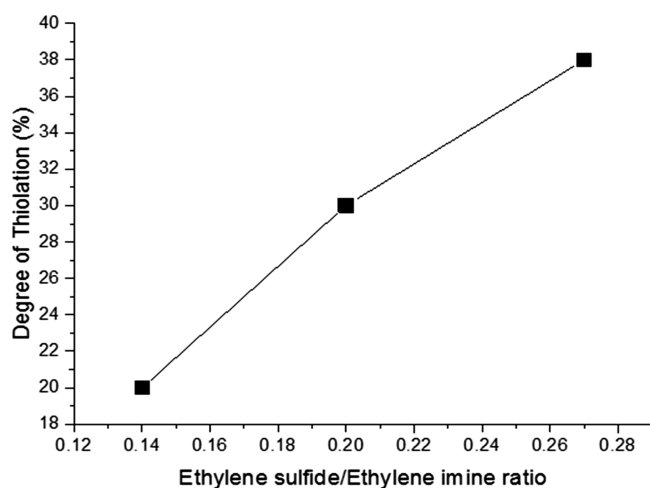
**Effect of the Ratio of Ethylene Sulfide/Ethylene Imine Units.** As previously mentioned, varying the amount of ethylene sulfide in thiolation resulted in materials with differing physical appearance. At low thiolation levels with the ratio of

the ethylene sulfide to amine units of below 1:7, a viscous, sticky soft solid is obtained, which does not cure into a solid film upon thermal curing. Increasing the amount of ethylene sulfide, with the ratio of the ethylene sulfide/ethylene imine units of 1:5, resulted in a sticky, glue-like solid, which can be thermally cured into a solid, flexible film. Further increasing the ethylene sulfide/ethylene imine ratio to 1:4 also resulted in a sticky solid, which can be cured into a film, but the film was noticeably stiffer. This shows that the physical properties of the material can be controlled through the amount of thiolating agent, as higher amounts of thiol groups would mean a more solid material due to the higher number of disulfide cross-links. Furthermore, a PA-FTIR comparison of the samples made with the 1:4 and 1:5 ratios (after curing) in Figure 3 shows an increase in the peak due to thiols at 2039 and 1435  $\text{cm}^{-1}$  due to the C–N stretching, which indicates a greater degree of thiolation in the sample.



**Figure 3.** PA-FTIR spectra of disulfide-cross-linked PEI with the 1:5 and 1:4 ratios of the ethylene sulfide/ethylene imine units.

This is supported by the degree of thiolation calculated from elemental analysis (based on the sulfur/carbon ratio, assuming two carbons per ethylene imine unit) in Figure 4, which shows an increase in the sulfur content of the polymer with the increasing ratio of ethylene sulfide. However, the degree of



**Figure 4.** Degree of thiolation of the disulfide-cross-linked PEI.

thiolation obtained from elemental analysis (based on the sulfur/carbon ratio) seems to be higher than what would be expected based on the ratio of the initial reagent. Because the yield of thiolation was around 65–75%, this indicates that the reaction led to partial thiolation (with some PEI molecules not thiolated); however, it is likely that the unmodified PEIs were more soluble and thus removed during precipitation and washing, and thus the thiolated PEIs that were retained contain a higher degree of thiolation.

Thermogravimetric analysis (TGA) of the cured films in Figure 5 shows that the thermal stability of the material is not affected by the degree of thiolation. Both samples at thiolation ratios of 1:4 and 1:5 (which are able to be cast into solid films) show the same main degradation temperature at around 245  $^{\circ}\text{C}$ ; however, the sample with higher thiolation (38%) shows a higher amount of residue due to the higher sulfur content. In addition, the mass loss below 150  $^{\circ}\text{C}$  (which is likely due to water adsorbed by the hydrophilic PEI) is greater for the sample with lower thiolation (1:5 ratio) at around 15% mass, whereas the sample with higher thiolation (1:4 ratio) shows lower amount of water content of around 10%. The gradual nature of this mass loss also indicates that the water is bound to the PEI by hydrogen bonding, as the mass loss continues beyond 100  $^{\circ}\text{C}$  up to 160–170  $^{\circ}\text{C}$ . Differential scanning calorimetric (DSC) analysis of the films did not show any distinct transitions in the sample. On the basis of the literature,<sup>14</sup> branched PEI is expected to have a  $T_g$  of around  $-47$   $^{\circ}\text{C}$ ; however, the disulfide-cross-linked gels did not show any clear  $T_g$  within the temperature range analyzed. This may be due to variation in the number of cross-links between the PEI molecules, resulting in a broader transition, which could not be accurately determined from the DSC result. Both samples show a slight transition at around 42  $^{\circ}\text{C}$ ; however, because the samples are soft and rubbery at room temperature, this is unlikely due to  $T_g$  and thus may be attributed to a cluster transition which indicates a loss in long-range ordering.<sup>15</sup> There is also a small endothermic peak at 100  $^{\circ}\text{C}$ , which is likely due to water; however, in the sample with higher thiolation (1:4), this peak has been shifted to around 124  $^{\circ}\text{C}$ , which indicates that the higher cross-linked sample may retain water more strongly.

Dynamic mechanical analysis (DMA) at 25  $^{\circ}\text{C}$  and under varying relative humidity (RH) conditions in Figure 6 shows that the disulfide-cross-linked PEIs have good mechanical properties comparable to those of ionomer gels and are strongly affected by water. For this analysis, the samples have been thermally cured for 1 h at 90  $^{\circ}\text{C}$  prior to the analysis to induce cross-linking of thiol groups. It is likely that at a low RH the disulfide-cross-linked PEI is very rigid due to the combination of disulfide cross-linking and hydrogen bonding between the amines, and because of the hydrophilicity of PEI, the presence of water significantly plasticizes the material with a significant reduction of storage modulus with increasing humidity. From the experiment, it was observed that more significant changes in the mechanical properties of the material occur at a higher RH, with relatively little change between 0 and 25% RH, even for the sample with the lowest degree of thiolation. However, at a higher RH of 50% and above, a significant difference can be observed between the samples depending on the amount of the thiolating agent. A comparison of PEI samples with different ratios of ethylene sulfide/amine units shows that at 1:6 ratio (lowest degree of thiolation) the material obtained was mechanically weak and susceptible to

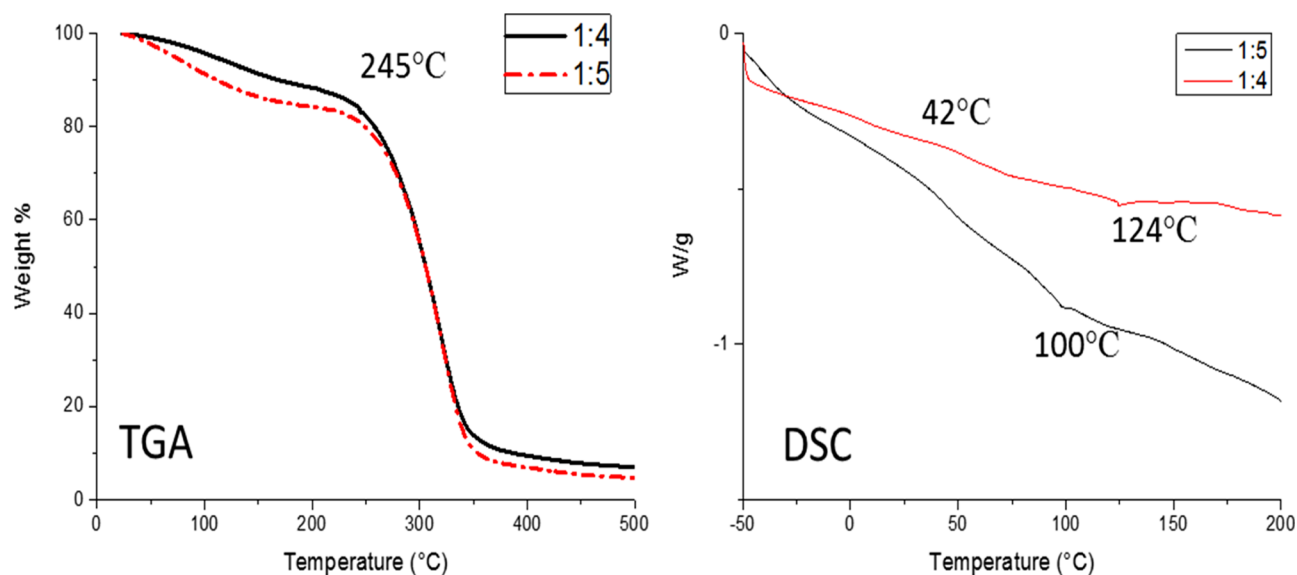


Figure 5. TGA and DSC analyses of the disulfide-cross-linked PEI with 1:5 and 1:4 ratios of the ethylene sulfide/ethylene imine units.

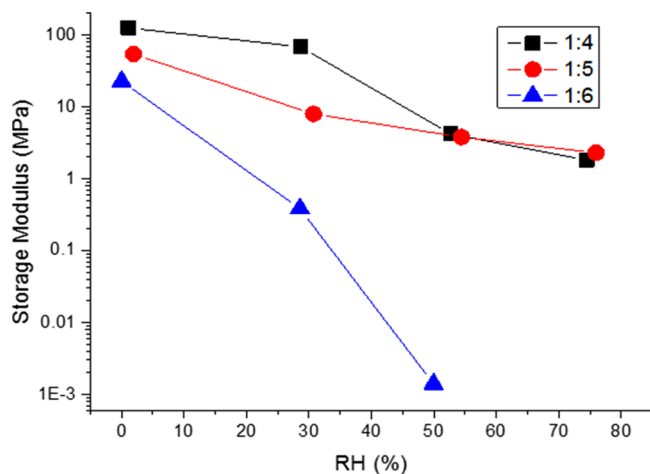


Figure 6. DMA analysis of the disulfide-cross-linked PEI.

breakage at 50% RH and above but those with an ethylene sulfide/amine ratio of 1:5 or higher show sufficient mechanical integrity at 80% RH with little difference between samples made with the 1:5 and 1:4 ratios of the thiolating agent. This observation confirms that increasing the amount of thiolating agent resulted in an increased storage modulus, as can be expected due to the increased amounts of disulfide cross-links.

However, it was also noted that although the gel with 1:5 ratio retained its mechanical integrity at 80% RH when subjected to immersion in water for prolonged periods it was not able to retain its shape and was susceptible to breakup. This is likely due to the hydrophilic nature of the PEI resulting in a very high water uptake, causing the disruption of the gel structure. However, the gel with 1:4 ratio was sufficiently robust to immersion in water and did not disrupt, indicating this ratio to be an optimum degree of thiolation with improved stability and high degree of cross-linking. Because of the highly

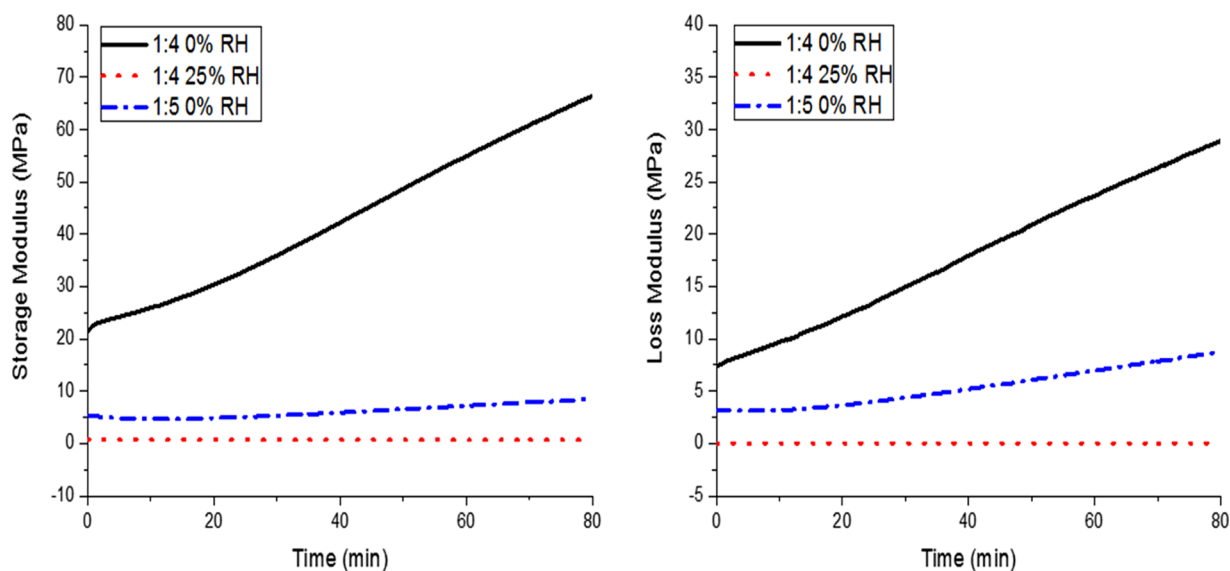


Figure 7. Storage modulus and loss modulus of the gels when held isothermally at 80 °C and at 0 and 25% RH.

hydrophilic nature of the PEI, the gel shows a very high water uptake of 180%.

**Effect of Cross-Linking.** The thiolated PEI obtained after synthesis was a soft, sticky solid resembling adhesives in physical appearance. This material can then be dispersed in water/methanol and cast, and after thermal curing at 90 °C for 1 h, a solid, flexible gel is obtained. DMA of the film in Figure 7 shows that this thermal treatment needed to be done under dry conditions to improve the mechanical properties of the film, as shown by isothermal DMA at 0 and 25% RH. At 0% RH, the storage modulus and loss modulus of the gel increase linearly over time; however, at 25% RH, there was no visible increase in the storage and loss moduli over the same time period. This may be due to the plasticizing effect of water in this material as the gel remains very hygroscopic due to its PEI building blocks.

Furthermore, the result in Figure 7 is consistent with that obtained previously in FTIR analysis. Analysis of uncured samples shows a very low modulus, which indicates that little cross-linking occurs during thiolation; thus, cross-linking has to be performed postsynthesis via thermal curing. Holding the sample isothermally at an elevated temperature and under anhydrous conditions resulted in an increase in the modulus over time, which indicates the formation of cross-links in the sample. The samples with a higher degree of thiolation show a more rapid increase in modulus upon thermal treatment; however, they still show the presence of un-crosslinked thiol after 1 h of thermal curing at 80 °C. This means that the thermal curing can be carried out for a longer period to further improve the mechanical properties of the gel. PEIs with higher thiolation ratio (1:4) show a greater increase in the storage and loss moduli upon further thermal treatment, whereas those with lower thiolation (1:5) show only a marginal increase, which is consistent with FTIR analysis showing a larger excess of unreacted thiol in the higher thiolation sample. This observation indicates that the degree of cross-linking increases linearly with time and although 1 h was sufficient to cross-link the sample with a lower degree of thiolation ratio, the sample with a higher degree of thiolation can be treated further to improve its mechanical properties, whereas beyond the optimal treatment time, further annealing will result in increasing stiffness, as indicated by the increase in the loss modulus in the sample with 1:5 thiolation ratio. Thus, the longer thermal treatment time should result in a more highly cross-linked material that retains its mechanical properties better at increased humidity or temperature, with a noticeable increase in the storage and loss moduli with the thermal treatment time. However, on the basis of the results shown in Figure 8, it appears that for the 1:4 ratio sample after 2 h there was no longer a significant gain in mechanical properties; instead, the film became more brittle and thus showed lowered mechanical properties at a high RH, as it is more susceptible to cracking when swollen.

Mechanical analysis also shows that UV curing can also be used to induce cross-linking to improve the mechanical properties of the film. As can be seen from Figure 9, the use of UV curing (after 1 h of thermal curing at 80 °C) enhances the mechanical properties of the gel. The hydrophilic nature of PEI is retained in the disulfide-cross-linked PEI regardless of the curing method, with the modulus decreasing in the similar fashion with increasing RH due to the plasticizing effect of water.

**Reformability of the Disulfide-Cross-Linked PEI.** In this study, a disulfide-cross-linked PEI was formed by thermal

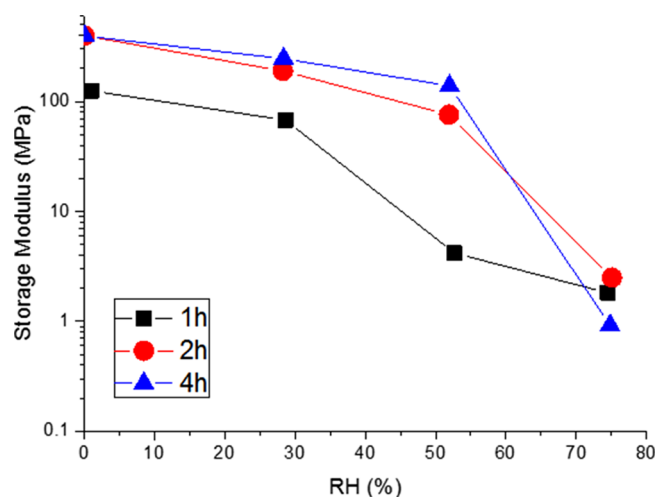


Figure 8. Effect of the thermal treatment time on the mechanical properties of the gel (1:4 thiolation ratio).

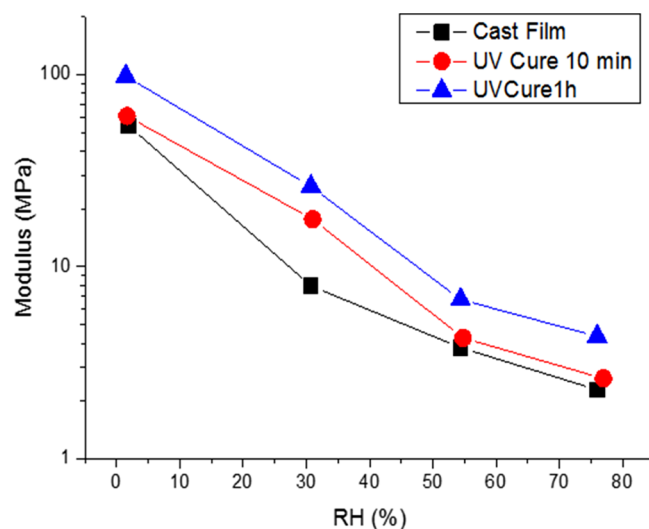
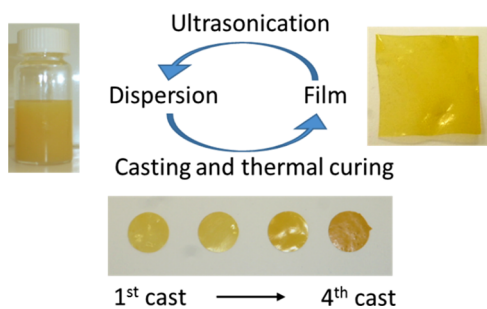


Figure 9. Effect of UV curing (at room temperature) on the disulfide-cross-linked PEI (1:4 thiolation ratio).

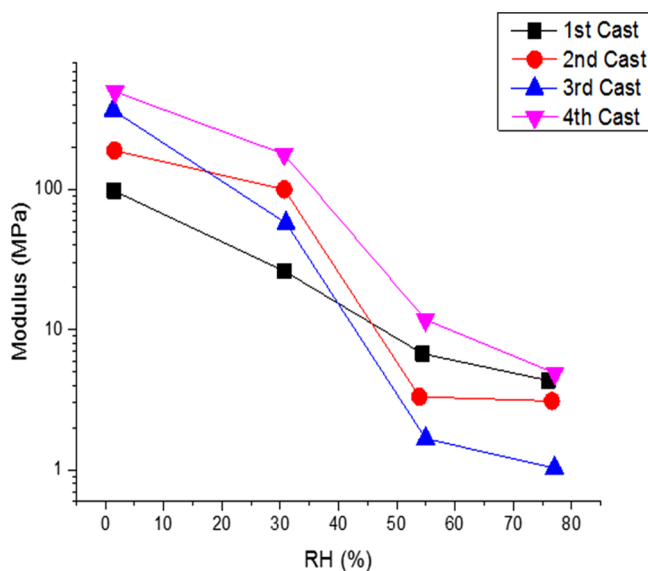
curing, which changes the material from a sticky glue-like material to a solid film. Despite its sensitivity to RH, when sufficiently cross-linked, the PEI retains its solid form even after being immersed in water due to the presence of the disulfide cross-links. Other studies with disulfide-bonded materials have shown the possibility of self-healing;<sup>6</sup> however, the disulfide-cross-linked gel did not seem to show fusion or self-healing when treated with heat or UV light. This may indicate that in these gels the high amounts of disulfide cross-linking may prevent sufficient molecular movements to allow some flow to occur for the material to fuse. However, when the gel was put in water, vigorous shear (by ultrasonication) appears to be able to break the material and resolubilize the disulfide-cross-linked PEI into an aqueous dispersion (Figure 10). This indicates that although after curing the material was sufficiently cross-linked to hold the low-molecular-weight PEI units in place, ultrasonication in water appears to break the disulfide cross-linking and resulted in a dispersion similar to that of the material prior to the initial casting into film. Furthermore, more vigorous shearing (longer time and larger amplitude of ultrasonication) is needed to redisperse the sample with higher thiolation, as



**Figure 10.** Schematic of the redispersion and recasting process and the physical appearance of the film after multiple casting.

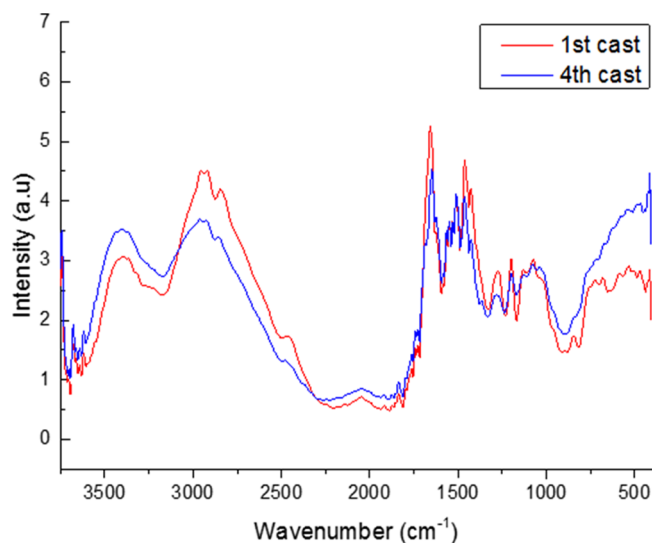
would be expected with the sample contains more disulfide cross-links. Through this facile process, a dispersion can be obtained, which is highly stable, with no signs of precipitation or separation after prolonged storage at room temperature.

This aqueous dispersion can then be recast into a solid film, and this process was repeatable multiple times without an apparent decline in the film's physical properties. DMA analysis of the films made by subsequent casting shows that under dry conditions (Figure 11) the films made from repeated casting



**Figure 11.** DMA analysis of multiple casting of the disulfide-cross-linked PEI film.

become stiffer but also appear to be more sensitive to increased humidity. This observation indicates that ultrasonication did not completely break the disulfide bonds and thus recast films contain a more highly cross-linked material. It is likely that the structures of the recast films contain domains of denser, higher cross-linked areas, which did not fully solubilize from the previous cast film during ultrasonication. These domains would be bound together by the solubilized PEI upon curing, resulting in a stiffer material due to the domains but with greater sensitivity to moisture due to the less cross-linked matrix between these domains. Although there was a slight darkening of the film upon multiple recasting (which is likely due to the thermal curing step after each recast), PA-FTIR analysis of the recast film (Figure 12) shows very little differences between the films after multiple casting indicating the chemical structure of the films does not change upon recasting as the process is



**Figure 12.** PA-FTIR spectra of the thiolated PEI after multiple casting.

affected mainly by breaking and reformation of the disulfide bonds.

## CONCLUSIONS

We have shown the fabrication of a mechanically stable gel based on disulfide cross-linking of low-molecular-weight PEIs. Because of the nature of the gel, it can be reformed into a dispersion via a facile, aqueous-based process with no additional chemical reaction and recast directly from this dispersion to obtain a gel film with no discernible loss in mechanical properties. Elemental analysis and PA-FTIR analysis show that the degree of thiolation can be controlled through the amount of thiolating agent, and DMA analyses confirm that the mechanical properties of the gel are affected by the curing conditions, degree of thiolation, and RH. Although the gel exhibits the hydrophilic nature of PEI (and thus shows a very large water uptake), it retained its mechanical integrity under high humidity conditions and was sufficiently robust to remain solid when immersed in water. The use of disulfide cross-linking enables the gel to be redispersed by a facile ultrasonication method in water and recast into a gel again with minimal loss in physical properties. This approach allows the fabrication of a mechanically stable polymer from low-molecular-weight components, which is recyclable through multiple cycles, potentially allowing significant advantage in waste management. With further improvement in its stability to water sorption and barrier properties, such recyclable and ecofriendly materials offer an attractive option for applications, such as short-term packaging, where current recycling techniques are less cost-effective due to the low cost of conventional materials.

## EXPERIMENTAL SECTION

**Materials.** Branched PEI (MW 700), ethylene sulfide, tetrahydrofuran (THF), hydrochloric acid (HCl), and methanol were purchased from Aldrich and used as received. Deionized water was obtained using a Milli-Q system.

**Thiolation of PEI.** Prior to thiolation, PEI was neutralized by diluting it in deionized water and titrating with a solution of 0.1 M HCl until the pH of the solution was neutral. The water was then removed by evaporation under reduced pressure to yield a viscous yellow liquid. In a typical thiolation procedure,

the neutralized PEI (4.2 g of 0.1 mol ethylene imine units) was then added to 20 mL of dry methanol and transferred to a round bottom flask and flushed with nitrogen. Ethylene sulfide (1.2 g, 0.02 mol) was then added dropwise with stirring, and the solution was stirred at room temperature under nitrogen for 72 h. Upon completion, the polymer was precipitated in THF and then reprecipitated with methanol and THF to remove unreacted ethylene sulfide. The polymer was then dried under reduced pressure to obtain a sticky yellow solid (yield: 4.06 g, 75%).

**Casting of Thiol-Functionalized PEI.** The thiolated PEI was then dispersed in deionized water by ultrasonication with a QSonica ultrasonic processor to produce an aqueous dispersion. The dispersion was then cast in a Teflon mold and dried slowly at room temperature to produce a film. The dried film was then thermally treated at 90 °C for 1 h to induce cross-linking and produce a solid, clear yellow film. In the case of UV-cured films, the thermally cured film was further cured by UV irradiation under a UV lamp (254 nm) for 1 h.

To investigate the reversibility of disulfide bonds and for subsequent recasting, the cast film was cut into small pieces and put into deionized water. A polymer dispersion was obtained by subjecting the polymer in water to ultrasonication (3 × 20 min ultrasonication with a 20/10 s on/off pulse), which can then be recast into film using the same method as previously described.

**Analysis of Disulfide-Cross-Linked PEI.** PA-FTIR analysis was carried out by a Nicolet Magna-IR Spectrometer 750 equipped with a photoacoustic cell using a carbon black reference. DSC measurement was conducted using TA Instruments Discovery DSC. The instrument was calibrated for baseline and cell constant prior to running the experiments. The samples were sealed in hermetic aluminum pans for use in the DSC experiment, and an empty pan was used as the reference. The temperature range for the experiment was from -70 to 200 °C, with a heating rate of 10 °C/min and under a controlled nitrogen gas flow rate of 50 mL/min. For kinetic study, the samples were held isothermally at 125, 135, and 145 °C for 45 min under a flow of nitrogen. TGA was performed using a TA Instruments Discovery TGA with an aluminum pan. The samples were subjected to a 10 °C/min ramp rate from 100 to 550 °C under a nitrogen atmosphere. DMA was conducted using the TA Instruments Q800 DMA equipped with a humidity accessory. The storage and loss moduli of the gel samples were determined under controlled humidity between 0 and 80% RH, with 30 min equilibration time upon changing the RH. The polymer films were cut into strips of around 5 × 20 mm<sup>2</sup> and measured at an amplitude of 10 μm and a preload force of 0.0100 N. Elemental analysis was performed at University of Queensland Microanalytical Services.

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

PEI: polyethyleneimine; DMA: dynamic mechanical analysis; PA-FTIR: photoacoustic infrared spectroscopy

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