

## PUBLISHED VERSION

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**Water-reprocessable, reformable, and ecofriendly sustainable material based on disulfide-cross-linked polyethyleneimine**

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**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.

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

**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

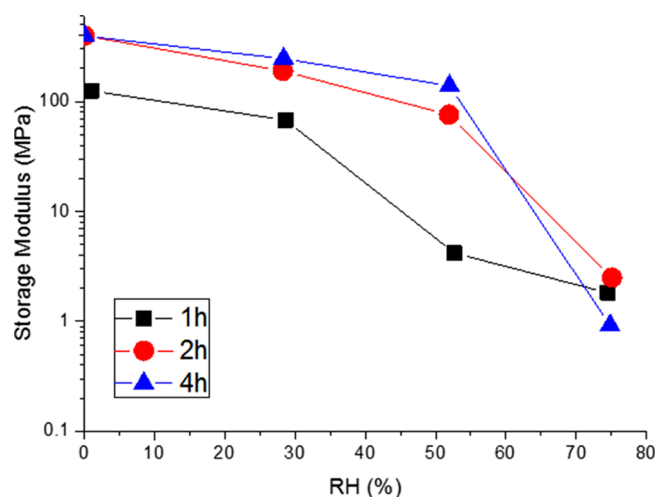


Figure 8. Effect of the thermal treatment time on the mechanical properties of the gel (1:4 thiolation ratio).

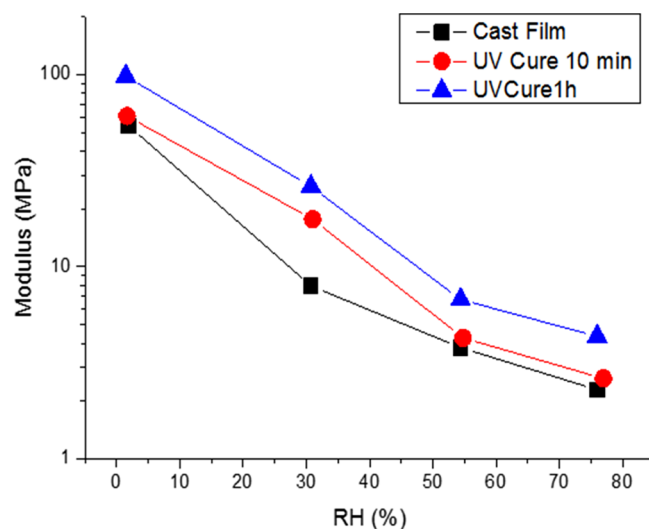
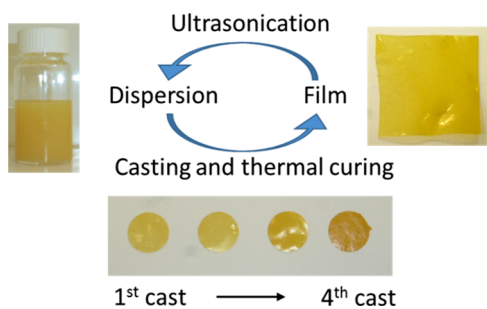


Figure 9. Effect of UV curing (at room temperature) on the disulfide-cross-linked PEI (1:4 thiolation ratio).

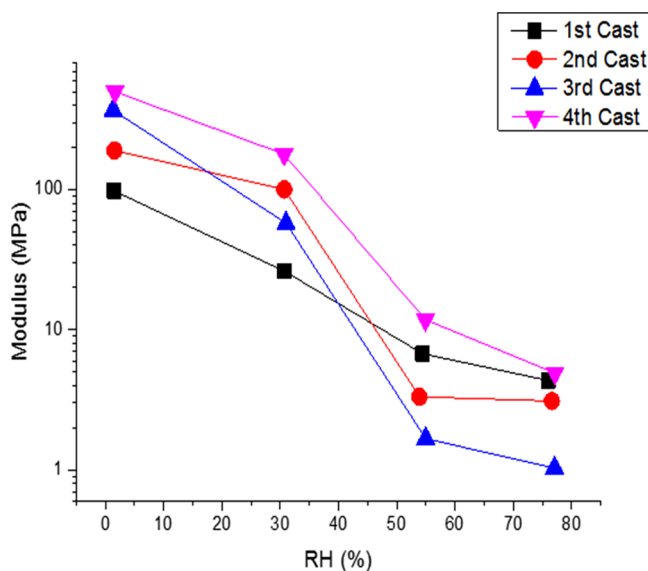
curing, which changes the material from a sticky glue-like material to a solid film. Despite its sensitivity to RH, when sufficiently cross-linked, the PEI retains its solid form even after being immersed in water due to the presence of the disulfide cross-links. Other studies with disulfide-bonded materials 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.

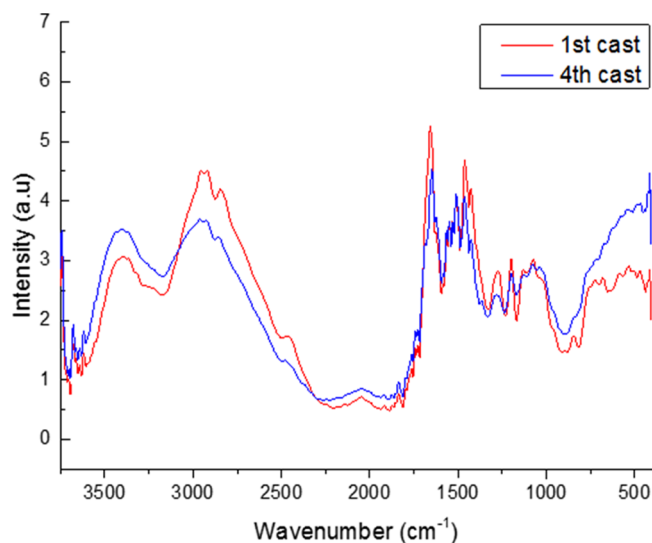
would be expected with the sample contains more disulfide cross-links. Through this facile process, a dispersion can be obtained, which is highly stable, with no signs of precipitation or separation after prolonged storage at room temperature.

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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