Structure-property Relationship Study of Polyimine-based Dynamic Covalent Networks and Their Applications Towards Functional Composites

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Thesis Abstract

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Structure-property Relationship Study of Polyimine-based Dynamic Covalent Networks and Their Applications Towards Functional Composites

Thesis directed by Dr. Wei Zhang

This thesis aimed to address fundamental study and related applications of covalent adaptable networks (CANs), focusing on polyimine materials.

Crosslinked polyimine represents a novel class of covalent adaptable network, which exhibits room temperature repairability, catalyst-free malleability, recyclability, and robust mechanical properties. Polyimine network prepared from commercially available monomers (terephthaldehyde, diamine and triaminotriethylamine) have been investigated including solvent and concentration effect on their physical properties. Monomer concentration and solvent properties directly control reaction rates and influence solvent diffusion into polymer chains and interfacial interactions during the polymerization progress, a range of mechanical properties can be obtained in different solvents from the same monomer composition, thus determining the morphology evolution and properties of polymers.

Next, we turned our attention to design fully rehealable and recyclable electronic skin by introducing silver nano-particles into polyimine networks. Such electronic skin has tactile, flow, temperature, and humidity sensing capabilities. Full recyclability has been demonstrated by simply soaking the whole device in one of the starting monomer at room temperature even without any stirring.

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I would also like to acknowledge the contributions of my collaborators. My collaborators helped with designing projects, identifying applications, and showed me how to understand

materials from engineering aspects. I would like to thank Professor Jianliang Xiao, Professor Rong Long, Professor Yifu Ding, Professor Kai Yu and Professor Sehee Lee, and particularly their students: Zhanan Zou, Mengyuan Wang, Luxia Yu, Justin Whiteley, Drew Hanzon, and Xu He.

Thank you to my family, and especially my parents, for supporting me education and living expenses. Lastly, a special recognition will be delivered to my fiancée, Lin Yuan, who has been behind me all the way. Thank you for everything; I could not have done this without you.

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CHAPTER 1

Recent Development in Covalent Adaptable Network

1.1 Background information on CAN

Covalent Adaptable Networks (CAN) are crosslinked polymers through reversible covalent bonds, and have many specific structural properties that can be utilized for various material applications.[1] Since these polymers have covalent crosslinks that are easily reversible, they can positively respond to external stimulus, leading to their dynamic properties as compared to traditional polymers. CANs can be deformed to on-demand appearances through breakage and reformation of their covalent bonds under various chemical/physical stimuli.[2] CANs have desirable characteristics since they are easily reversible, and can be recycled/processed into new materials. Their capability of being fabricated into any desired shape, their recyclability and the malleability allow them to be used for various purposes. As a result, these polymers have found considerable applications in various industrial processes.

Polymers can be categorized into two major groups: thermosets and thermoplastics (Figure 1.1), which are mainly used for different functions due to their intrinsic characteristics. Thermoplastics can be reshaped while thermosets cannot be reprocessed and recycled once they are cured. The advantage of thermoplastic polymers is their reprocessibility which allows them to be reused and recycled. On the other hand, thermosets are advantageous in terms of thermal stability. Celluloid was the first thermoplastics developed in 19th century. However, it is no longer widely used due to the high flammability and high production cost.[3] Thermoplastic elastomers or polymer composites were then developed as part of thermoplastic compounds possessing more desirable characteristics. Thermoplastic elastomers show advantages typical of both rubbery and plastic materials. Thermoplastic elastomer materials can be remolded, extruded and recycled, which allows applications in many important fields including aerospace, as adhesives or coating agent.[4]

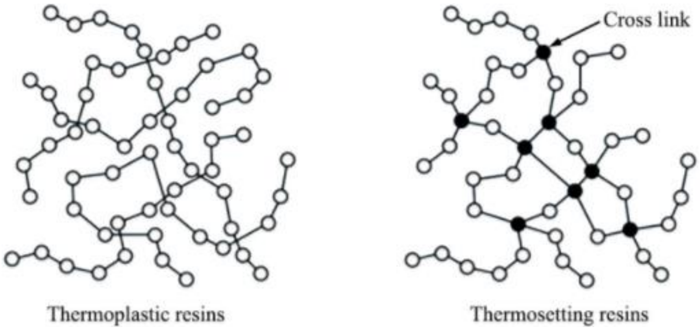

Figure 1.1 Illustration of the difference between thermoset and thermoplastic. The figure was reproduced from ref. [5]

Thermoplastics don't undergo permanent change and can be reprocessed and recycled. The easy reprocessibility of thermoplastics upon heating allows them to be fabricated into any desirable shape.[4] However, their inferior mechanical strength and thermal/chemical stability oftentimes limit their applications. In some industrial applications, thermosets are preferred due to their high thermal stability and high resistance to chemical corrosion.

CANs' unique properties, combining the advantages of both thermosets and thermoplastics, make them a novel type of polymer materials with good mechanical strength and reprocessibility and adaptability to change of external environment. For example, elevated temperature triggers reversible formation of covalent bonds, allowing the change of polymer structures to acquire a new state. The dynamic bonds in the CANs can break/form locally, making the whole process desirable and efficient.[6] The classifications of CANs, their unique characteristics, and the resultant products after introducing stimulus are compared. Industrial applications and the process of different products will also be discussed.

Two main types of reactions have been utilized to develop CANs, which are reversible exchange reactions and reversible addition reactions (Figure 1.2). In reversible addition reaction, dynamic equilibrium is established between the reactants and the products. In condensation reactions, uptake and release of molecules are involved and the equilibrium position is the key in the process of crosslinking. Dynamic characteristics of the resultant materials are determined by the forward and reverse kinetics as well as the equilibrium shift of the reaction.

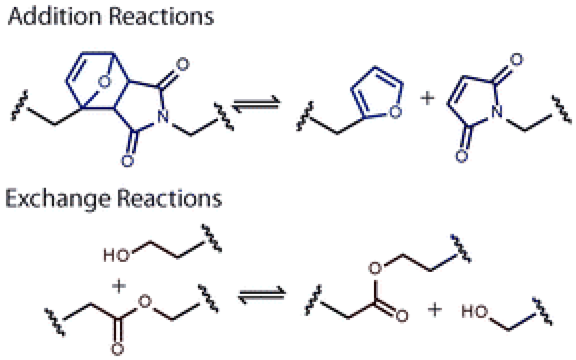

Figure 1.2 Reversible addition reaction, result in breaking and reforming of the polymer backbone (Diels-Alder reaction as an example). In contrast, reversible exchange reaction, result in bond rearrangement or shuffling without a disruption in connectivity (transesterification reaction as an example). Figure reproduced from ref.[7]

In contrast, in exchange reactions, the crosslink densities are conserved since the cleavage and reformation of bonds proceed simultaneously. The active functional group in the backbone of the polymer is the only one that is interfered in the reaction. Lower molecular weight is desirable in the formed product to allow reversibility of the cross-links and the mobility of the functional groups.[8] Therefore, step growth network is the most desirable in the studies due to its rapid arrangement of the bonds in the crosslinking parts. To understand the formation and the structure of CANs, vitrimers based on transesterification and Diels Alder reaction will be discussed as representative examples.

The stress relaxation of CANs based on transesterification is dependent on the chemical reactions taking place and not the friction of the chains similar to that of vitreous silica. Stress relaxation behavior and the activation energy of CANs rely on the catalyst used, organic or inorganic. When synthesizing such polymers, the viscosity-temperature has to be considered to allow the development of easily manipulated polymers.[9] Brutman et al synthesized a hydroxyl-terminated Polylactic acid (PLA), by incorporating ester groups between crosslinks and polymerized with a difunctional isocyanate. As a result, the products exhibited a very short characteristic relaxation time.[10] In the case of step-growth Diels Alder based CANs, the equilibrium conversion of the dienophile / diene groups decrease with temperature change, and in some cases network can depolymerize and flow as liquid with sufficient heating.[12]

In CANs, the crosslink density is the key factor determining the polymers' properties. The mechanical behavior can be understood by applying the elasticity theory that accurately describes the predicted characteristic of a given material. Transient modulus behavior is the key in all the properties of CANs as it determines the density of the crosslinks.

Stress relaxation is another important feature for CANs as it determines the bond arrangement in the materials.[11] The stress relaxation is determined by the kinetic energy of the molecules which is temperature dependent.

1.2 Applications of CANs

It has been recognized that CANs have great potential in materials development due to their unique features. Thermal stability and creep resistance are among the favorable properties that make CANs unique and desirable in various polymer reactions. The solubility and remoldability of the polymers allow various scientific research institutions and industries to work with these polymers. Photopolymers can be utilized in making 3D objects such as stereolithographic through the dual cure mechanism. The reversible crosslink formation upon heating makes the polymers desirable since their healing process is rapid as compared to the traditional polymers. The versatility of the CANs allows welding and injection molding of the powder to any desirable shape. The key parameters controlling the kinetics, as well as the final strength of the welding, are the concentration of the transesterification catalyst and the concentration of hydroxyl groups present in the network.[8]

Covalent bonding of CANs allows them to have unique mechanical properties which are highly desirable for various industrial applications. Electronic devices use CANs to protect them from physical damages and environmental corrosions. Such applications include the circuit board in which in case of any defects they can be easily fixed due to the existence of reversible dynamic bonds in the polymer bases. Thermal CANs have also been employed in hot-melt adhesives[13] and hot -melt inks[14], where the materials are treated in a liquid state and then cooled to form on-demand solid shapes.

Crosslinking can be used to increase thermal stability of chromophore alignment, which are reversible when subjected to change in temperatures.[15] Such alignment reduces the object volume and improves its stability in the long run. Healing of material in case of any problem is also aided by the Diels-Alder reaction in some examples. Electro-optical devices require cladding to minimize loss of light as they travel within the tube and such protection is provided by thermally reversible materials. Gel reversion is also utilized to improve the toughness and durability of materials and in case of any crack, the material can fully recover due to its healing property.[9]

The gap between thermoplastics and thermosets can be effectively bridged by CANs. More research on the properties and the applications of CANs is necessary to allow maximum utilization of their properties in different industries. The chemical component of CANs and their reversible characteristics are the major considerations in their widespread applications. Since these materials can adapt to various environments, more research will allow more applications of the product in the industries.

Philippe et al. found out that rubbers had the ability to heal themselves and gain their initial shapes after subjection to stress.[16] Rubber-like properties of various polymers were investigated while subjected to both stress and temperature changes and their behavior studied. The authors compared the properties of supramolecular network with those of cross-linked rubbers and their behavior when subjected to stress. Montarnal et al. also reported the study of crosslinks and their properties in various materials using the epoxy network. The effect of temperature changes on the equilibrium point and the effect of viscosity were discussed in the article as well, which demonstrated that the same reaction happens in a highly crosslinked step-growth polymer to yield dynamic behavior at elevated temperature. The advantages of the reversible links are also discussed by the authors.[17]

Kandambeth et al. report covalent organic frameworks and their applications in separation applications as well as the limitations of using these components.[18] The chemical stability and mechanical stability allow them to be efficient in various industrial applications such as waste management like the removal of dye particles in water and in pharmaceutical industries. Scott et al. investigated the limitations of cross-linked polymers when subjected to stress. Covalently cross-linked networks are also discussed and their reversible nature when subjected to photo mediation. Reversible backbone cleavage of the materials is also discussed and its implications on the nature and properties of the materials when subjected to various stresses and tensions are elaborated. The as-prepared specimens can heal themselves due to the existence of dynamic cross-linked polymeric network.[19] Finally Chen et al. investigated photoinduced plasticity in cross-linked polymers that can heal themselves even under mild conditions. With intensive research, several self-healing materials have been developed through reversible DA reactions. Challenges experienced by the maleimide monomers were also illustrated which includes instability at higher temperatures that causes melting of the material.

Different kinds of CANs containing various dynamic bonds have been applied to many technological applications, which exhibit excellent mechanical strength, thermal stability and solvent resistance. However, the processing of these polymers typically requires high temperature or relies on catalyst. Taynton at el. presented catalyst-free malleable polyimines made from three commercial available monomers at room temperature which fundamentally behave like a classic thermoset.[20] In the next chapter, one of the fundamental study on malleable polyimines will be discussed.

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CHAPTER 2

The Solvent and Monomer Concentration Effect for The Physical Properties of Malleable And Recyclable Polyimine Thermosets

(Manuscript published under the "Tuning the physical properties of malleable and recyclable polyimine thermosets: the effect of solvent and monomer concentration" title in *RSC Advances* 7 (76), 48303-48307, coauthored with C Xi, W Doro, T Wang, X Zhang, Y Jin, W Zhang)

2.1 Abstract

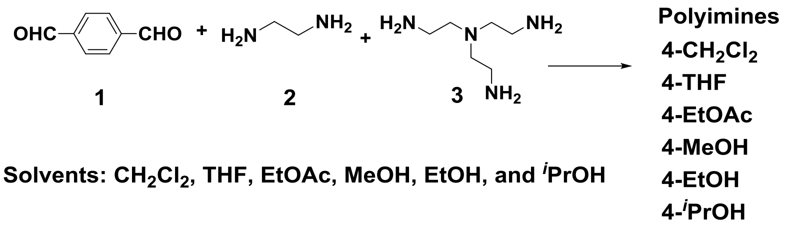
Cross-linked polyimine represents a novel class of covalent adaptable network, which exhibits room temperature repairability, catalyst-free malleability, recyclability, and robust mechanical properties. Herein, we investigated the morphological, mechanical, and thermal property changes of polyimine films under different reaction conditions. Both weak and brittle polyimine films with Young's modulus of 0.029 GPa and tough materials with Young's modulus of 2.04 GPa, have been obtained from the same monomer combinations but under different concentration and solvent. The study of polymerization reaction shows that morphology evolution and thus property changes in polyimines are determined by the combined effect of solvent choice (e.g. diffusion) and polymerization rate. Such polyimines can be fully recycled and repeatedly reshaped many times with application of only heat, showing their immense value in developing sustainable materials.

2.2 Introduction

Dynamic polymers linked by reversible bonds have attracted great attention due to their self-healing properties and responsiveness to external stimuli.[1-3] Recently, Covalent Adaptable Network (CAN) polymers that are crosslinked by dynamic covalent bonds[4-6] have emerged as a novel class of dynamic polymers.[7,8] They behave like classic thermosets at room temperature, but can undergo microscopic stress relaxation and materials flow under external stimuli (e.g. heat, light). Therefore, they exhibit combined properties of classic thermosets and thermoplastics: they have excellent mechanical properties of thermosets due to the crosslinked nature of polymer networks, yet they are reprocessible, repairable and recyclable like thermoplastics due to the reversible chemical bonds connecting monomers. A variety of CANs have been developed utilizing reversible Diels–Alder (DA) reactions,[9-11] transesterification,[12-19] olefin metathesis,[20,21] disulfide chemistry[22-27] and Schiff base reactions.[28-32] Among them, polyimines prepared from simple imine condensation[33] are of particular interest since they can achieve stress relaxation and material flow in the absence of a transition metal catalyst, and can be reshaped, reprocessed, and repaired upon application of only heat or water, the greenest possible approaches available so far. In addition, the commercial availability of various amines and aldehydes promises ready tunability of the polyimine properties through judicious selection of monomers. Previously, we have reported inexpensive, catalyst-free polyimine network materials that exhibit Arrhenius-like malleability in response to heat and can be recycled and reshaped at an ambient temperature using only water.[30] Through variation of diamine monomers, we were able to obtain polyimines with a wide range of thermal, mechanical, and moisture-induced properties, such as semicrystalline polymers with high strength and thermal stability, and elastomeric materials with low temperature malleability.[31] Such polyimines have been used as binder materials to form fully recyclable carbon fiber reinforced composites (CFRCs) that exhibit excellent moldability, weldability and easy repair of delamination damage through a simple heat-pressing process.[29] Recovery of full-length fiber, as well as complete recovery and reuse of the polyimine binder materials has been achieved by taking advantage of the reversibility of imine bonds under external trigger, in this case the addition of excess monomer. The malleability of polyimines has also enabled dry processing of a thin electrolyte membrane for solid state lithium batteries through hot iso-static pressing of polyimine powder and the glass-ceramic solid electrolyte.

2.3 Results and discussion

During the process of preparing polyimine samples for various applications, we found that the solvent has a profound effect on the morphology and mechanical properties of the materials. Strong defect-free polymer film or powder can be formed from the same monomer combinations but in different reaction solvents. For example, polymerization of 3:0.9:1.4 molar ratio of terephthaldehyde, diethylenetriamine, and triethylenetetramine in mixed solvents of dichloromethane, ethyl acetate and ethanol provided a homogeneous polymer film after slow evaporation of the solvents, whereas polymer powder was obtained when ethyl acetate was used as the sole solvent. This result shows that reaction conditions are critical to obtain a polymer with suitable properties. Herein, we present how the reaction conditions (solvent choice and monomer concentration) affect the morphology, mechanical properties, and moisture sensitivity of polyimine films. Aprotic and protic solvents with different polarities were used as the reaction media, and the properties of resulting polyimines were systematically studied. Solvents directly interact with monomers and polymer chains to influence both reaction kinetics and polymer film formation and further the physical properties of materials.



Scheme 1. The synthesis of polyimines **4** in various solvents.

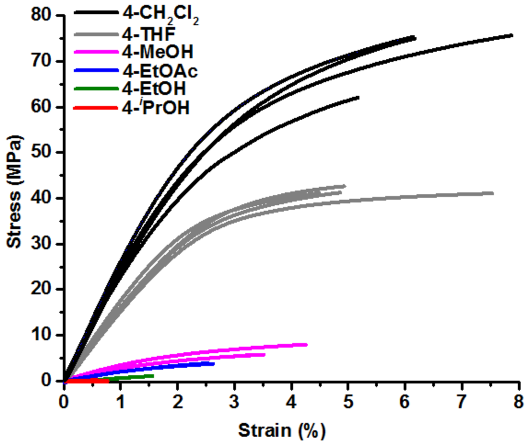


Figure 2.1 Stress-strain curves of polyimine films prepared in different solvents.

In a typical procedure, the monomers, terephthaldehyde (**1**), ethylenediamine (**2**), triethylenetetramine (**3**), in a 1.00 : 0.30 : 0.47 molar ratio, were dissolved in a solvent and the solution was added to a box-shaped tray (9 cm x 9 cm x 2 cm) made by folding silicone-coated paper. The solvent was then allowed to evaporate in a fume hood under ambient conditions. A total of six different solvents, methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), ethyl acetate (EtOAc), methanol(MeOH), ethanol (EtOH), and isopropanol (^{i}PrOH) were tested (Scheme 1). In CH_2Cl_2 and THF, homogeneous polymer films with smooth surfaces were obtained, whereas in other solvents, films with rough surfaces formed. In all cases, the polyimine films (**4**) were heat-pressed at 78 ℃ for 3 h, at 95 ℃ for 1 h, and finally at 105 ℃ for 1 h before being subjected to various property tests. The mechanical properties of the polyimine samples were investigated by measuring stress–strain curves (Figure 2.1). As shown in table 2.1, a wide range of tensile strength (69 MPa to 0.2 MPa) was observed for the polyimines prepared in different solvents. The polymer films, **4-CH_2Cl_2** and **4-THF**, obtained in CH_2Cl_2 and THF exhibit significantly higher tensile strength, 69 MPa and 42 MPa, respectively, compared to the samples prepared in other solvents. The polyimine samples obtained in this study generally don't deform much before break, showing elongation at break from 0.7% to 6.4%. The polyimine **4-^{i}PrOH** prepared in isopropyl alcohol exhibits the worst performance, weak and brittle, with tensile strength of 0.23 MPa (300 times lower than **4-CH_2Cl_2**) and elongation at break of 0.7%. Table 2.1 summarizes the solvent properties and mechanical properties of polyimines. It appears that vapor pressure of the solvents and surface tension have some effect on the mechanical properties of the resulting polyimine samples. The order of tensile strength of polyimines (**4-CH_2Cl_2**>**4-THF**>**4-MeOH**>**4-EtOAc**>**4-EtOH**>**4-^{i}PrOH**) follows the order of vapor pressure and surface tension of the solvents (CH_2Cl_2> THF > MeOH, EtOAc>EtOH>^{i}PrOH).

Table 2.1 Summary of properties of solvents

Solvents	**CH_2Cl_2**	**THF**	**EtOAc**	**MeOH**	**EtOH**	**^{i}PrOH**
v_p (KPa)	58.2	21.6	12.6	16.9	7.87	6.02
μ (Debye)	1.6	1.75	1.78	1.7	1.69	n/a
η (mPa s)	0.41	0.46	0.42	0.54	1.07	2.04
γ (mN/m)	27.2	26.5	23.4	22.1	22	20.9

The vapor pressure (25 ^oC) is denoted with v_p, the dipole moment (25 ^oC) with μ, the viscosity (25 ^oC) with η, and the surface tension (25 ^oC) with γ unless otherwise indicated.Total five samples were examined for each polyimine prepared in a different solvent.

It has been known that solvent retention in polymer films can cause plasticization and significantly affect the physical properties.[34] To investigate the possible inclusion of the solvents in polyimine samples, we conducted thermal gravimetric analysis (TGA). TGA shows <2% weight loss at 200 ℃ and <3% weight loss before their decomposition (232-243 ℃), indicating the presence of a minimal amount of residual solvents in the polyimine films (Figure 2.2). Therefore, the effects of retained solvents on the mechanical properties of polyimines would be negligible.

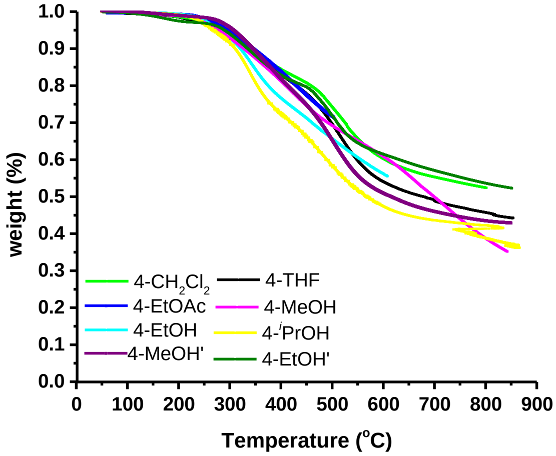


Figure 2.2 TGA plots of polyimines.

Since mechanical properties are closely related to molecular weight and crosslinking density of polymers, we next studiedthe possible solvent effect on the monomer conversion. It should be noted that the same monomers and crosslinker in thesame stoichiometric ratio were used in all the entries; therefore, the crosslink density is mainly controlled by the monomer conversion in different solvents. We estimated the aldehyde conversion by analyzing 13C magic-angle spinning solid-state NMR spectra of the best-performing 4-CH2Cl2 and the worst performing 4-iPrOH (Fig. 2.9 and 2.10). Our analysis shows that 98% aldehyde conversion was achieved in CH2Cl2, whereas only 94% aldehyde conversion was reached in isopropyl alcohol. The polyimines are formed through condensation of equimolar quantities of amine and aldehyde groups (step-growth polymerization), thus the 4% lower conversion of aldehyde monomers would decrease the polymerization degree and average molecular weight by 3-fold, which has significant negative effect on the mechanical properties. This result is consistent with our mechanical test, which shows much poorer mechanical properties of 4-iPrOH compared to those of 4-CH2Cl2.

We next examined the morphological features of the polyimine samples, which are also known to greatly affect mechanical properties of polymers. The polyimine morphologies were investigated by analyzing scanning electron microscopy (SEM) images of both the surface and cross section. As shown in Fig. 2.3, the SEM images of the surfaces of polyiminefilms show drastically different morphologies. The polyimine films 4-THF and 4-CH2Cl2 prepared in THF and CH2Cl2 showcoherent smooth surfaces, whereas the surfaces of polyimines4-EtOAc, 4-iPrOH, 4-MeOH, 4-EtOH prepared in EtOAc, iPrOH,MeOH, and EtOH are relatively rough, consisting of agglomerated micron-sized spherical particles likely caused by phaseseparation. The polyimine morphologies shown in cross sectionSEM images (Fig. 2.7) agree well with their correspondingsurface morphologies, indicating these samples have homogeneous phases. Flattened particles were observed on the surfaceof some samples (e.g. 4-MeOH, Fig. 2.3), but not at cross section,suggesting it is likely caused by the contact point pressure during heat-press.

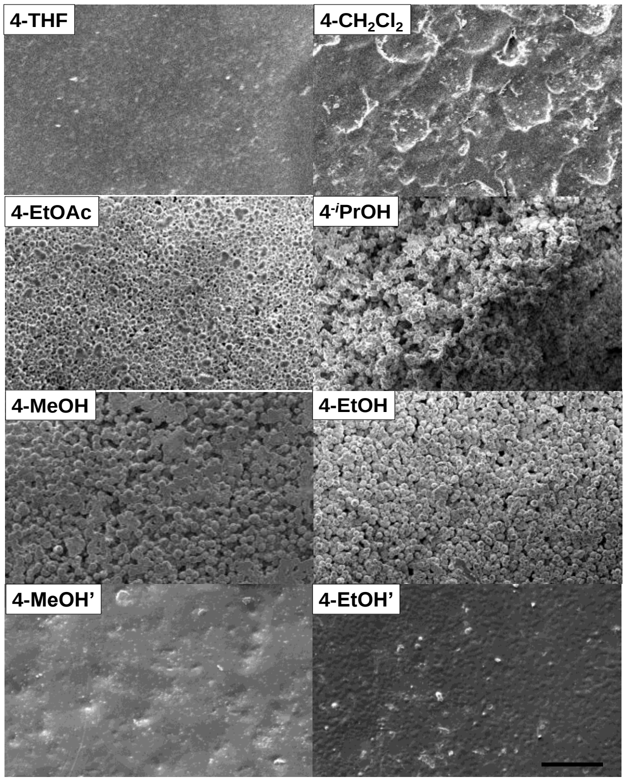


Figure 2.3 Surface SEM images of polyimine films. Scale bar is 50 μm.

It is plausible that agglomerates in polyimines 4-EtOAc, 4-iPrOH, 4-MeOH, 4-EtOH loosely bound to the neighboring particles mostly through van der Waals forces, causing their poor mechanical performances. Such morphological differences directly affect moisture sensitivity of polyimines. 4-THF and 4-CH2Cl2 with relatively seamless smooth surfaces show only 14% and 6% weight gain when they were soaked in deionized (DI) water for 24 h. By contrast, polyimines 4-MeOH, 4-EtOH, 4-EtOAc, 4-iPrOH, which show obvious surface porosities, absorb DI water of 59–262 wt% when treated under the same conditions.

Our study shows that solvents have significant effects on the surface roughness, film morphology and moisture sensitivity. In all the cases, the polymerization started as homogeneous solution. In CH2Cl2 and THF, no phase separation was observed and the mixtures remained clear throughout the polymerization process until the evaporation of the solvents to form transparent and relatively tough films. In protic solvents MeOH, EtOH and iPrOH, milky gels were formed in the course of polymerization and brittle opaque films were obtained. Obvious polymerization-induced phase separation (yellow precipitation) was observed in EtOAc, resulting in a polyimine film with powdery composition. Although the imine linkages are reversible and theoretically allow materials flow at certain conditions, our attempts to obtain homogeneous films similar to 4-THF and 4-CH2Cl2 by post-treatment of the polyimine films (heat pressing under high pressure and high temperature above their Tg) were unsuccessful. Heat-pressing of 4-iPrOH film at a pressure of 8.9 MPa (170 C, 10 min) led to a brittle film with dark brown color. We did not try longer pressing time or higher temperature, since the change of the film color from bright yellow to dark brown is likely due to the occurrence of possible side reactions. At this stage, we have not yet developed suitable conditions to erase the solvent effect by simple post-treatment method (e.g. heating), and changing the reaction solvent appears a more viable approach to engineer the properties of polyimine films. Likely, imine exchange reactions are limited to contact points and the system is unable to reach global materials flow under the applied conditions.

Since the dynamics of phase separation and gel-formation are controlled by reaction rate and monomer concentrations in the early stage, and solvent diffusion and interfacial tension in the late stage, we studied the effect of monomer concentration on the polymer morphology in different solvents. We increased the monomer concentration by two folds and carried out the polymerization under the same conditions as previously described. In CH2Cl2, higher monomer concentration induced more rapid imine condensation, which is exothermic, leading to boiling of the solvent and formation of polyimine film with many entrapped bubbles. In EtOAc, at increased monomer concentration, the reaction was rapid and immediate, and massive precipitation was observed upon mixing the monomers. Interestingly, in contrast to the results from low monomer concentration experiments in MeOH and EtOH, at higher monomer concentration, transparent and homogeneous films (4-MeOH0 and 4-EtOH0) were obtained (see SEM in Fig. 2.3), which show excellent mechanical properties. The tensile strength of 4-MeOH0 and 4-EtOH0 are 39 MPa and 33 MPa, which are increased 6-fold and 28-fold compared to those of 4-MeOH and 4-EtOH, respectively (Fig. 2.4). They also exhibit greatly enhanced Young's moduli, 1.80 GPa and 2.04 GPa (up to 22 fold increase) for 4-MeOH0 and 4-EtOH0, respectively. Correspondingly, 4-MeOH0 and 4-EtOH0 show much reduced moisture sensitivity compared to 4-MeOH (12 wt% vs. 59 wt%) and 4-EtOH (22 wt% vs. 106 wt%). Our study clearly indicates that the solvent properties and reaction kinetics are critical to the dynamics of phase separation and morphology evolution of polyimine films and thus their mechanical properties. Although, vapor pressure of the solvents and surface tension could have some effect on the mechanical properties of the resulting polyimine samples as mentioned previously, it is more likely a combined effect of various parameters including reaction rate, diffusion of solvent, solubility of polymers, and interactions between polymers and solvents.

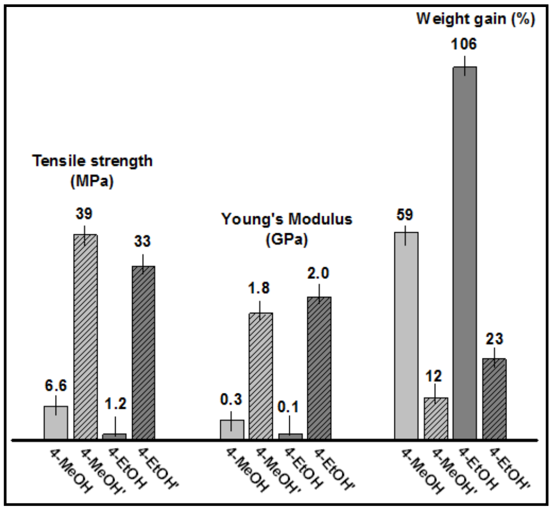


Figure 2.4 Comparison of tensile strength, young's modulus and weight gain (after soaking in DI water for 24 h) of 4-MeOH, 4-EtOH, 4-MeOH', and 4-EtOH'.

Since solvents have significant effects on reaction kinetics,[35] we next monitored the reaction progress in different deuterated solvents, CD2Cl2, THF-D8, and CD3OD using model compounds, 4-bromobenzaldehyde and ethylenediamine by 1H NMR spectroscopy under the same monomer concentrations as the polyimine formation. The monomer conversions were then calculated based on 1H NMR signal integration and plotted against time as shown in Fig. 2.5. Our study shows that the reaction rate is the highest in methanol, in which the polymerization provides weak and brittle film with micrometer range heterogeneity. Much lower reaction rate was observed in THF, in which smoother polyimine film with higher mechanical properties can be obtained. These results indicate that phase separation and chemical reaction are in competition, and the morphology is determined by the combined effect of solvent choice (e.g. diffusion) and polymerization rate. At high reaction rate, the growth of polymer network is fast, leading to rapid sol–gel transition prior to phase-separation. At very low reaction rate, the growth of polymer network is slow and the reaction mixture remains homogeneous for prolonged time due to the mutual solubility of constituents, leading to delayed phase-separation. However, for intermediate rates, the phase separation can be initiated prior to sol–gel transition, leading to much coarser phase-separated domains as shown in 4-EtOAc, 4-iPrOH, 4-MeOH, 4-EtOH.

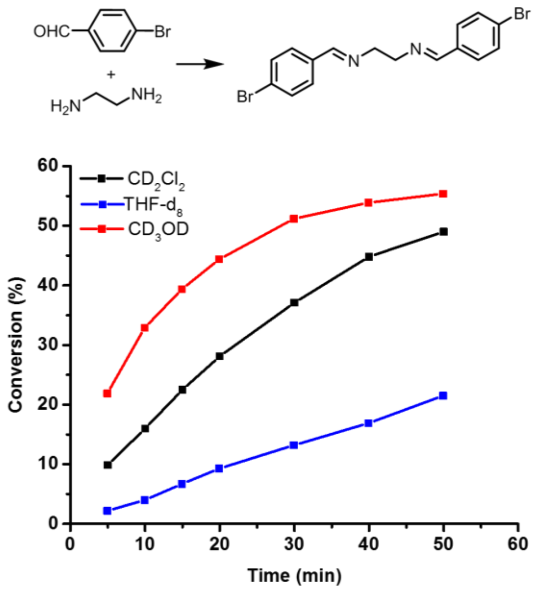


Figure 2.5. Imine condensation reaction progress monitored by 1H NMR spectroscopy using condensation between 4-bromobenzaldehyde and ethylenediamine as a model reaction.

These polyimines can be completely degraded by adding diamine monomer, and recycled to form new batch of polyimine films. They can also be welded and reshaped in any desirable shape for multiple times by simple application of heat. As a proof of concept demonstration, we reshaped a strip of polyimine 4-EtOH0 by simple heating. As shown in Fig. 2.6, the polyimine strip can be repeatedly reshaped to a bent circle or a multiple time upon heating and cooling. The sample was twisted into a fusilli shape at high temperature, and was subsequently cooled down to a hard-thermoset object. It can be twisted back to the original straight shape by heating and cooling.

Figure 2.6 Reversible shaping of polyimine thermoset by simple heating.

2.4 Conclusion

We have demonstrated how solvent choice and monomer concentration affect polyimine morphology and mechanical properties. Monomer concentration and solvent properties directly control reaction rates and influence solvent diffusion into polymer chains and interfacial interactions during the polymerization progress, thus determining the morphology evolution and properties of polymers. A range of mechanical properties can be obtained in different solvents from the same monomer composition. Tough polyimine materials with excellent Young's modulus of 2 GPa was obtained in ethanol, highlighting the great potential of these malleable and recyclable thermosets in materials development. We also briefly demonstrated the malleability of a polyimine sample by repeatedly reshaping it between a circular shape and a fusilli-shape. The knowledge gained in this study would be of great importance to future development of polyimine thermoset materials targeting various potential applications.

2.5 Experimental Details

2.5.1 Polyimine materials preparation

Polyimine preparation at low monomer concentration: To a solution of ethylene diamine (**2**, 0.268 g, 4.46 mmol) and tris(2-aminoethyl)amine (**3**, 1.02 g, 6.976 mmol) in a solvent of choice (45 mL) was added terephthalaldehyde (**1**, 2.00 g, 14.9 mmol). The mixture was vigorously stirred until the solution became translucent and yellow-to-orange in color. The solution was then poured into a tray made from silicone-coated release paper (with approximate dimensions 9 cm x 9 cm x 2 cm). The volatiles were allowed to evaporate in a fume hood overnight at room temperature. The resulting polyimine film was heat pressed at 78 ℃ for 3 h, at

95 ℃ for 1 h, and finally at 105 ℃ for 1 h using a top platen-heated hand-operated heat press under nominal pressure.

Polyimine preparation at high monomer concentration: The above procedure was followed but the concentrations of monomers were increased 2.5 time: ethylene diamine (**2**, 0.6721 g, 11.15 mmol), tris(2-aminoethyl)amine (**3**, 2.54 g, 17.44 mmol), terephthalaldehyde (**1**, 5.00 g, 37.25 mmol), and solvent (45 mL) were used.

2.5.2 SEM images of polyimine samples

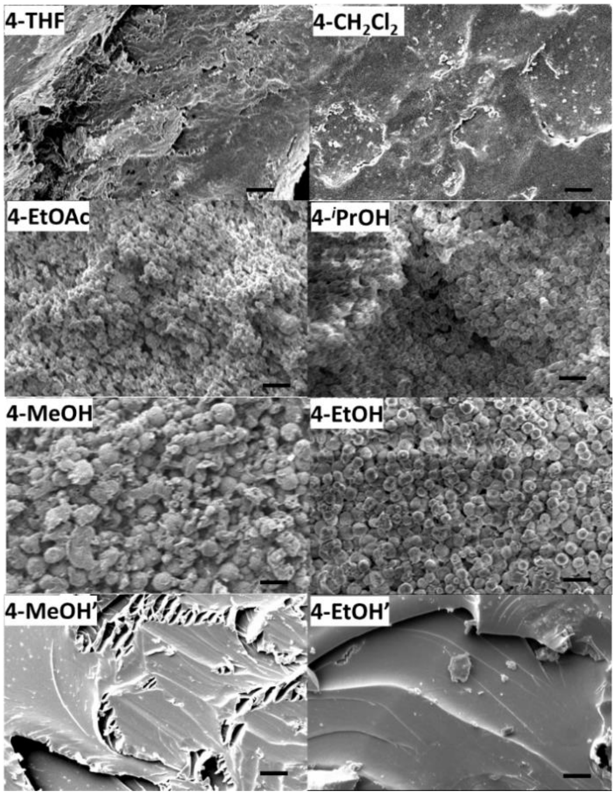


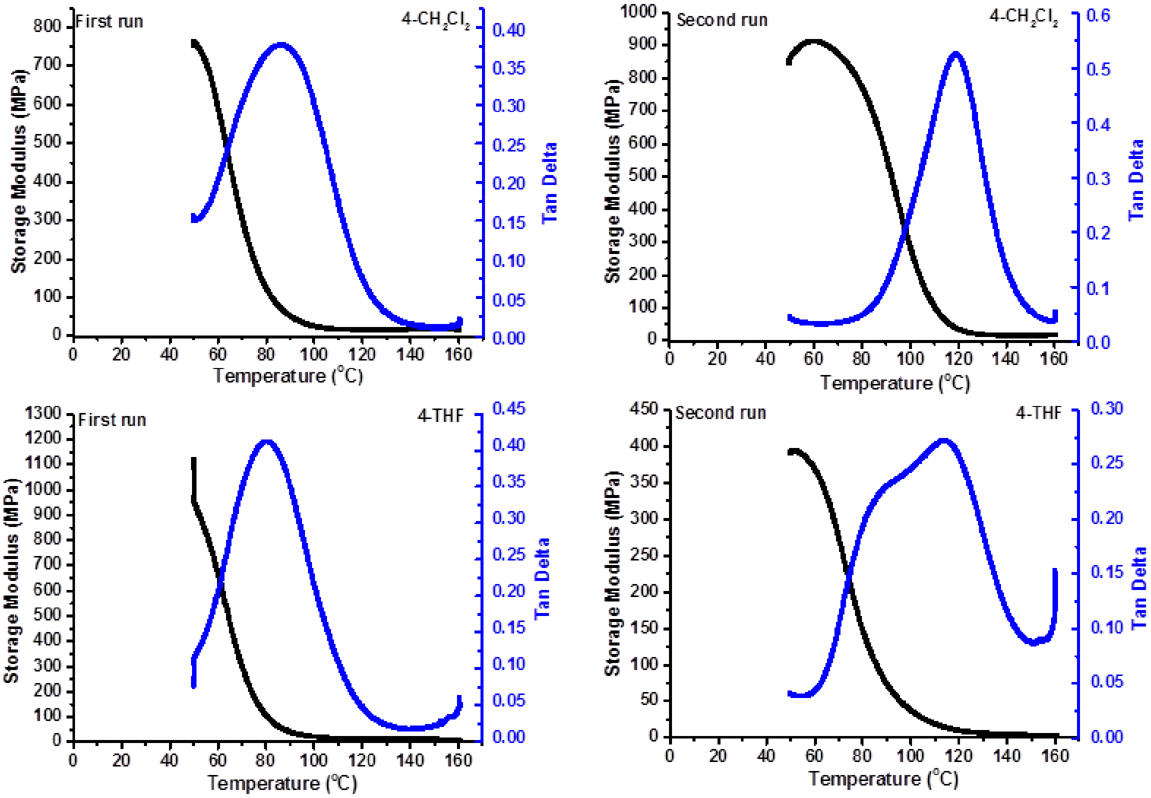
Figure 2.7 Cross section SEM images of the polyimine films.

2.5.3 Mechanical tests of polyimine films

DMA Tension tests: A dynamic mechanical analysis (DMA) instrument (Model Q800, TA Instruments, New Castle, DE, USA) was used to carry out tension tests at room temperature (24.6 ℃ locally). All samples were cut into dog-bone shapes with the size of 30 mm x 4 mm (length x width), and stretched under a constant loading rate (2 MPa/min) until broken. For the wet tensile measurements, pre-cut samples in the same shape were soaked in DI water for 24 h. After being removed from the water, each sample was blotted dry with paper towel, loaded into the DMA instrument, and then tested under the same method.

2.5.4 Characterization of thermal properties of polyimines

Determination of glass transition temperature: Glass transition temperatures (T_g) of the samples were determined using a DMA instrument (Model Q800, TA Instruments, New Castle, DE, USA). Samples were mounted between film tension fixtures and tested under the following parameters: Test Mode DMA Multi-Frequency – Strain; Strain 0.0250 %; Preload force 0.1000 N; Force track: 125%; Equilibrate at 60 ℃; Isothermal for 5.00 min; Ramp 3.00 ℃/min to 160.00 ℃. The data of the first measurement was used to determine the T_g.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Tan Delta
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200
300
400
500
600
700
800
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0
20
40
60
80
100
120
140
160
Second run
4-CH_2Cl_2
Storage Modulus (MPa)
Tan Delta
Temperature (°C)
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100
200
300
400
500
600
700
800
900
1000
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
20
40
60
80
100
120
140
160
First run
4-THF
Storage Modulus (MPa)
Tan Delta
Temperature (°C)
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100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0
20
40
60
80
100
120
140
160
Second run
4-THF
Storage Modulus (MPa)
Tan Delta
Temperature (°C)
0
50
100
150
200
250
300
350
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450
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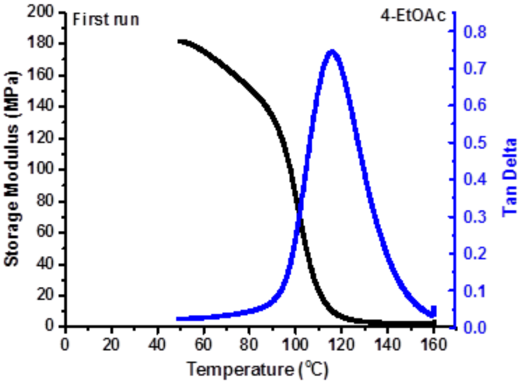
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0.8
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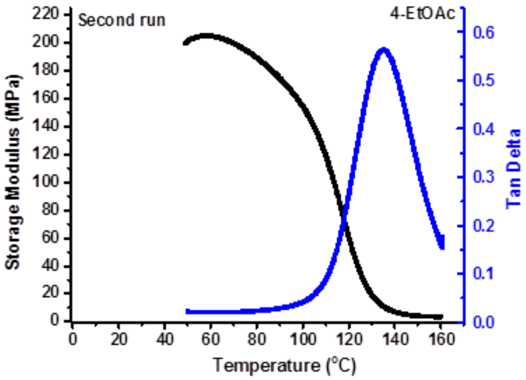
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0.1
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0.6
Temperature (°C)
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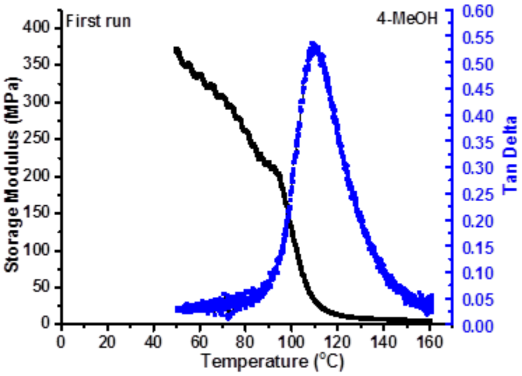
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0.15
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0.25
0.30
0.35
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0.50
0.55
0.60
Temperature (°C)
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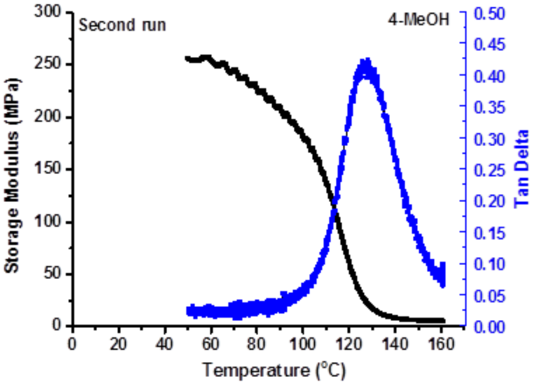
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200
250
300
Tan Delta
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0.20
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0.50
Temperature (°C)
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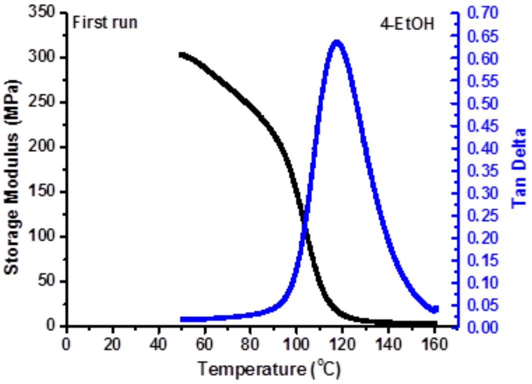
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300
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Tan Delta
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0.40
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0.60
0.65
0.70
Temperature (°C)
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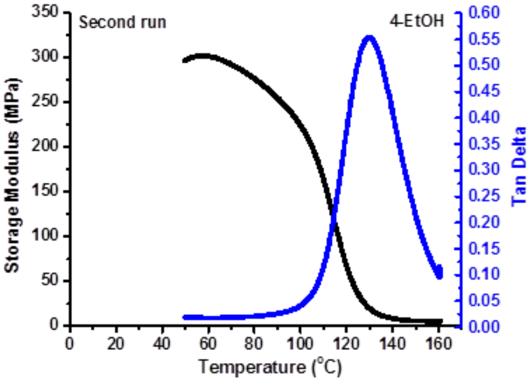
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250
300
350
Tan Delta
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0.05
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0.15
0.20
0.25
0.30
0.35
0.40
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0.55
0.60
Temperature (°C)
0
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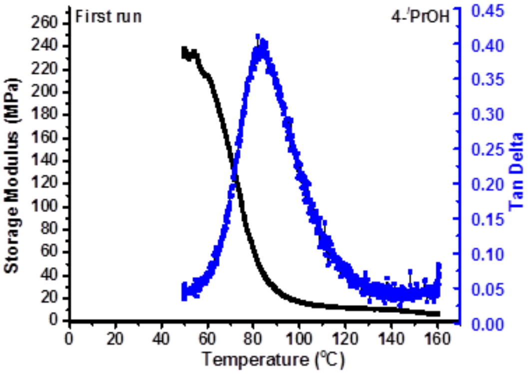
160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100
120
140
160
180
200
220
240
260
Tan Delta
0.00
0.05
0.10
0.15
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0.25
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0.35
0.40
0.45
Temperature (°C)
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20
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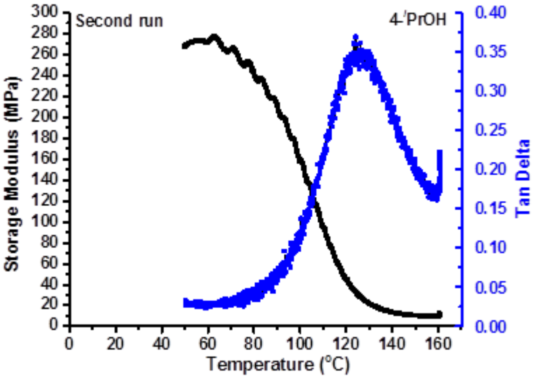
140
160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4-^{i}PrOH
Storage Modulus (MPa)
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160
180
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240
260
280
300
Tan Delta
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
Temperature (°C)
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140
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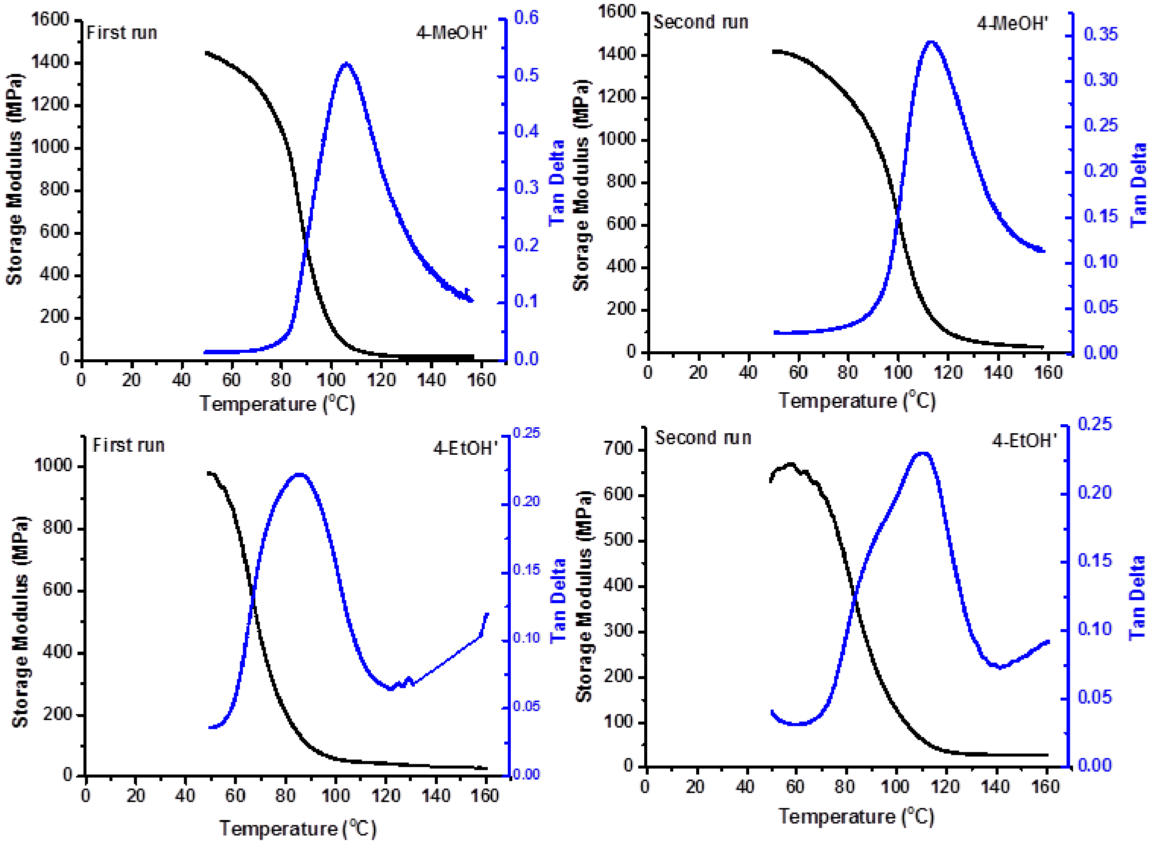


Figure 2.8 The DMA scans of polyimines.

2.5.5 Thermal Gravimetric Analysis of polyimines

Samples were run on a TA Instrument Q-500 series thermal gravimetric analyzer with samples held in a platinum pan under nitrogen atmosphere. A 10 K min^{-1} ramp rate was used.

2.5.6 Moisture sensitivity of polyimines

Pristine polyimine films were prepared in the manner describe above. The swelling study was performed by placing a dog-bone shape pre-tared sample of each polyimine in a 20 mL screw cap vial filled with DI water. Samples were soaked in DI water for 24 h. Upon removal of the samples from the water, the samples were blotted dry and weighed within 1 minute to minimize the ambient drying of the swollen polymer films.

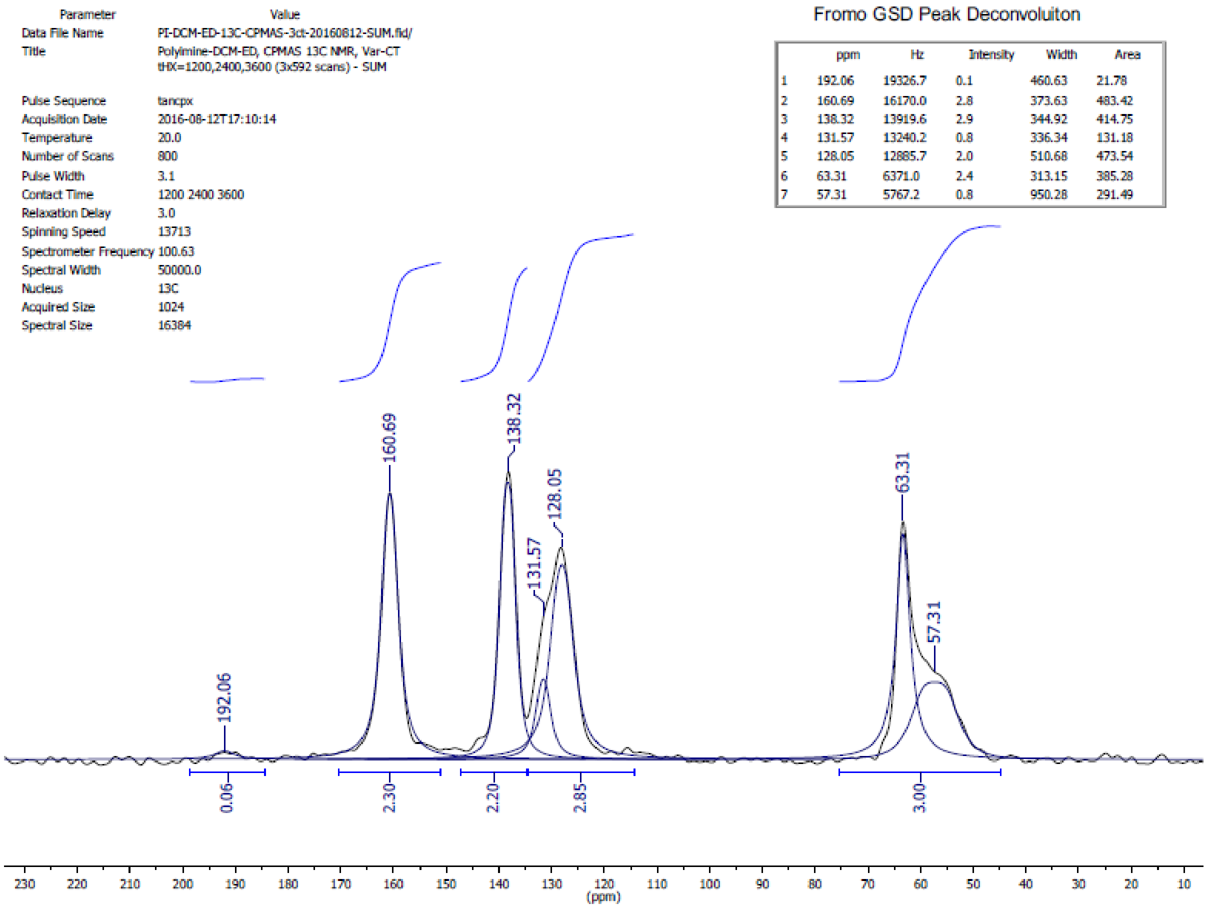
Table 2.2 Summary of mechanical properties of polyimines.

	Pristine samples		**After soaking in DI water**		
polyimines	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Weight gain (%)**	**Tensile strength (MPa)**	**Elongation at break (%)**
4-CH$_2$Cl$_2$	69±6	6.4±1.3	6.5±1.8	29±1	2.3±0.3
4-THF	42±1	4.6±0.2	14±3	9.7±0.4	2.9±0.5
4-EtOAc	3.8±0.7	2.3±0.3	138±18	1.6±0.1	1.9±0.3
4-MeOH	6.6±0.8	3.8±0.5	59.3±4.3	3.8±0.5	2.2±0.1
4-EtOH	1.2±0.1	1.42±0.08	106.45±6.5	0.85±0.1	1.65±0.15
4-^{i}PrOH	0.23±0.01	0.7±0.1	262±19	0.185±0.15	1.1±0.1
4-MeOH'	39±5	4.2±0.3	12.2±1.0	21.8±1.2	5.21±0.8
4-EtOH'	33±1	4.6±0.7	23±2	10.7±1.4	5.9±0.3

2.5.7 NMR spectra of selected compounds

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-State, Cross-Polarization Magic Angle Spinning (CPMAS), ^{13}C NMR spectroscopy was performed using a Varian INOVA-400 spectrometer (Agilent Technologies, Inc.) operating at 100.63 MHz for ^{13}C observation. The probe incorporates a 5 mm Magic Angle spinning module and coil assembly designed and constructed by Revolution NMR, Inc. (Fort Collins, CO), capable of spinning up to 13 KHz with Zirconia rotors (also from Revolution NMR, Inc.). Spectra were acquired using cross-polarization spin-lock and decoupling R_f field of 80.5 KHz, and TPPM (Time Proportional Phase Modulation) decoupling was applied during signal acquisition. Chemical shifts were referenced using the absolute, calibrated spectrometer configuration frequency and magnetic field offset, such that the aldehyde carbon peak appears at 191 ppm. Sample spinning frequencies from 10.5-11.57 KHz were employed with the sample oriented at the magic angle

(54.736 degrees, relative to the magnetic field axis, calibrated using the ^{79}Br spinning sideband pattern of KBR). To effect the uniform cross-polarization of ^{1}H magnetization to all ^{13}C nuclei, spectra were acquired using multiple cross-polarization contact times among 1.2, 2.4 and 3.6 mSec and these were summed to yield the final spectra. These optimal contact times were determined using variable contact-time experiments and were chosen to obtain uniform excitation across all carbon atoms in the molecules of polyimine samples.



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Number of Scans	800
Pulse Width	3.1
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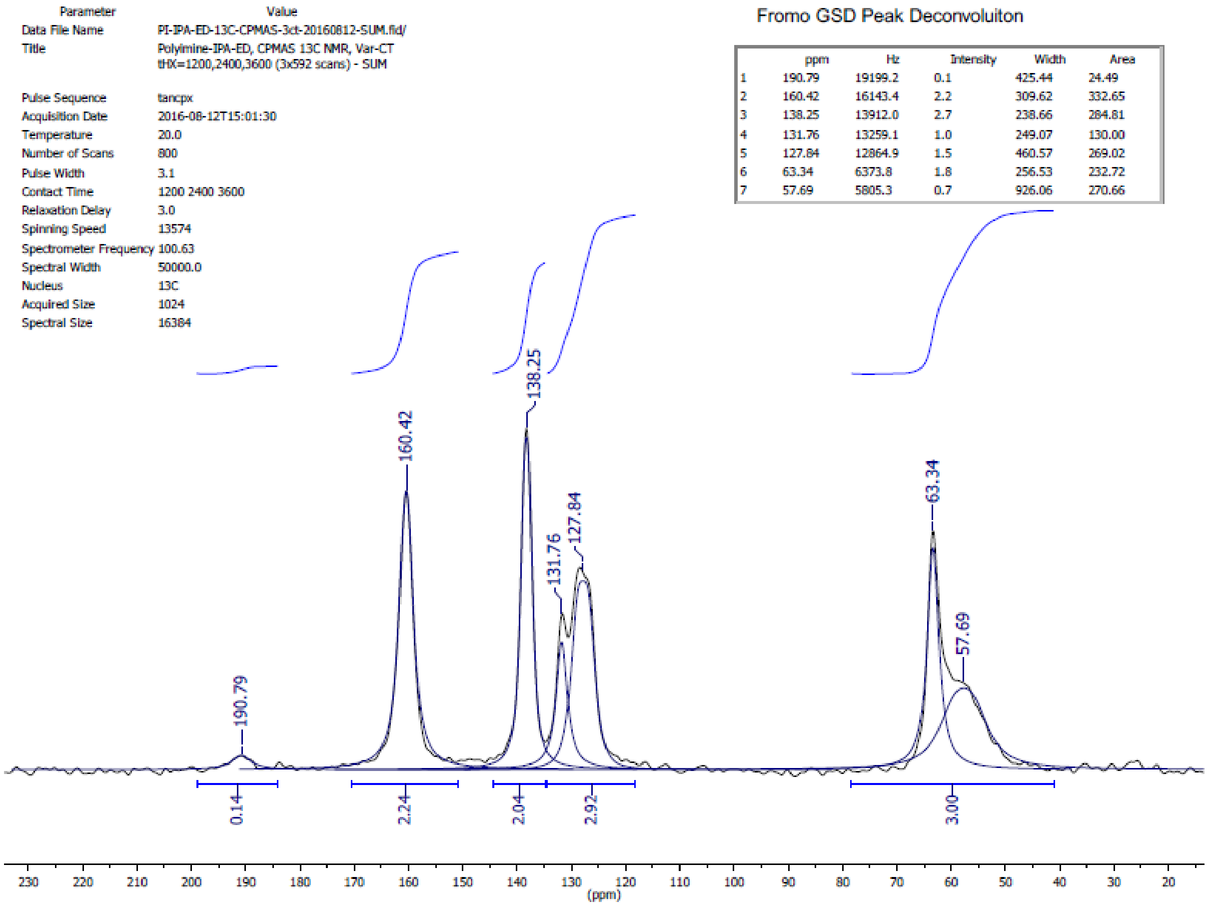
Relaxation Delay	3.0
Spinning Speed	13713
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	16384

Fromo GSD Peak Deconvoluiton

	ppm	Hz	Intensity	Width	Area
1	192.06	19326.7	0.1	460.63	21.78
2	160.69	16170.0	2.8	373.63	483.42
3	138.32	13919.6	2.9	344.92	414.75
4	131.57	13240.2	0.8	336.34	131.18
5	128.05	12885.7	2.0	510.68	473.54
6	63.31	6371.0	2.4	313.15	385.28
7	57.31	5767.2	0.8	950.28	291.49

Figure 2.9 ^{13}C NMR spectrum of 4-CH_2Cl_2 dry sample.



Parameter	Value
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Pulse Width	3.1
Contact Time	1200 2400 3600
Relaxation Delay	3.0
Spinning Speed	13574
Spectrometer Frequency	100.63
Spectral Width	50000.0
Nucleus	13C
Acquired Size	1024
Spectral Size	16384

Fromo GSD Peak Deconvoluiton

	ppm	Hz	Intensity	Width	Area
1	190.79	19199.2	0.1	425.44	24.49
2	160.42	16143.4	2.2	309.62	332.65
3	138.25	13912.0	2.7	238.66	284.81
4	131.76	13259.1	1.0	249.07	130.00
5	127.84	12864.9	1.5	460.57	269.02
6	63.34	6373.8	1.8	256.53	232.72
7	57.69	5805.3	0.7	926.06	270.66

Figure 2.10 ^{13}C NMR spectrum of 4-^{i}PrOH dry sample.

2.6 Reference

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Chapter 3

Conclusions and Potential Applications

3.1 Overview of current work

Properties of crosslinked catalyst free polyimine network prepared from commercially available monomers (terephthaldehyde, diamine and triaminotriethylamine) have been investigated including solvent and concentration effect on their physical properties.[1] We have demonstrated monomer concentration and solvent properties directly control reaction rates and influence solvent diffusion into polymer chains and interfacial interactions during the polymerization progress, thus determining the morphology evolution and properties of polymers. A range of mechanical properties can be obtained in different solvents from the same monomer composition. Another fundamental research performed is moisture sensitivity study by varying diamine monomers (hydrophobic or hydrophilic) used in the polymer networks.[2] We have demonstrated that a variety of commercially available diamines can provide a wide range of thermal, mechanical and moisture sensitivity properties for this type of malleable polyimine networks because of the presence of hydrophilic and hydrogen bonding amine moieties in their backbones. The applications of polyimines have also been explored. We developed repairable woven carbon fiber reinforced composite (CFRC) with full recyclability using polyimine as a binder to mold and weld woven carbon fiber composite materials, which can be directly recycled and reused by soaking CFRC into amine solution (Figure 3.1).[3] Defects of CFRCs can be easily repaired through simple heat-press process. Polyimines have also been used in the development of fully rehealable and recyclable electronic skin by introducing silver nano-particles into polyimine networks. Such electronic skin has tactile, flow, temperature, and humidity sensing capabilities

(Figure 3.2).[4] Polyimine based electronic skin can be easily custom-fit onto a person's wrist. Upon damage, the materials can be rehealed by simple treatment of the crack with a small amount of monomer solution. Moreover, the rehealed materials exhibit very similar mechanical properties and sensing performance. Also, full recyclability has been demonstrated by simply soaking the whole device in one of the starting monomer at room temperature even without any stirring. The materials slowly dissolve into soluble oligomers and precursors while leaving AgNPs sink to the bottom of the vessel.

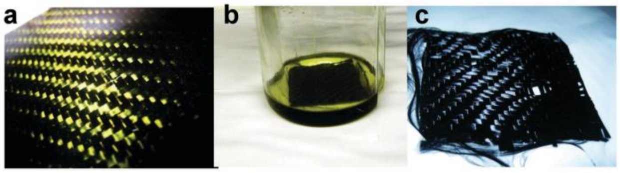

Figure 3.1 Composite recycling and repairing. a) Pristine CFRC sheet. b) CFRC immersed in neat recycle solution. c) Woven carbon fiber material removed from recycle solution

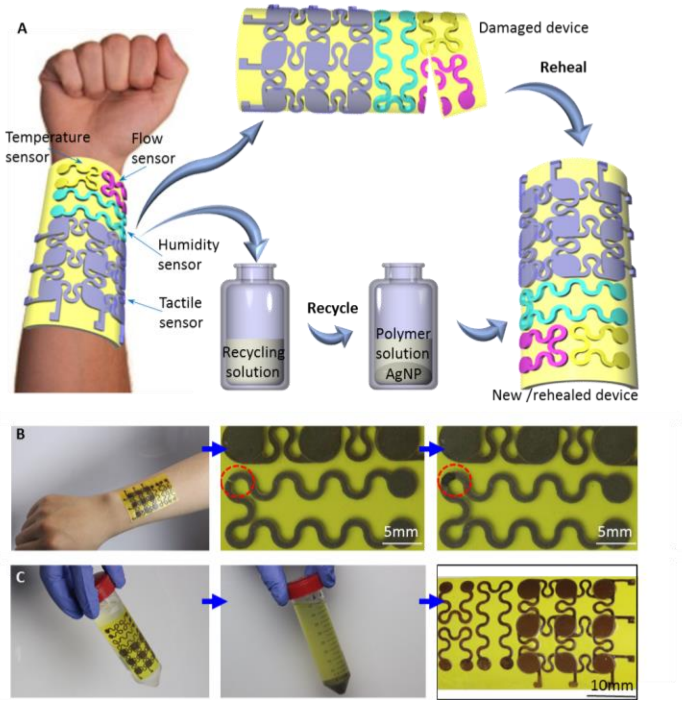

Figure 3.2 Rehealable, fully recyclable and malleable electronic skin (e-skin). (A) Schematic illustration of rehealability and full recyclability of the e-skin. (B) The

malleable e-skin can be conformally mounted onto a human arm (left). When mechanically cut broken (middle), the e-skin can be rehealed by applying a small amount of rehealing agent and heat pressing (right). (C) The e-skin can be fully recycled using the recycling solution (left), yielding the solution with dissolved oligomers/monomers and AgNPs at the bottom (middle). The solution and AgNPs can be reused to make a new e-skin (right).

3.2 Other potential Applications

3.2.1 Advanced composite materials.

We reported the development of carbon fiber reinforced polyimine composite materials by using exchangeable nature of imine chemistry to obtain self-healing and recycling abilities. Such composite was prepared by soaking carbon fiber into a solution containing monomers and allowing the polymerization and evaporation of all volatiles at room temperature overnight to evaporate all solvent. In order to shorten the processing time, we also explored solid-state method mixing method for the fast manufacturing of polyimine based carbon fiber reinforced polyimines. In this dry approach, carbon fibers were sandwiched between two layers of freshly-prepared polyimine powder and heat-pressed to form CFRCs. Under the temperature higher than Tg (85℃), fast processing time can be achieved using high pressure heat-press instrument to apply different heating temperature and processing time. In-situ repair and recyclablility will also be investigated.

3.2.2 Mixed Matrix Membranes.

In the past few years, two-dimensional nanosheets materials have been widely developed in the field of materials science, nanotechnology and chemistry, such as TiS_2, WS_2, $MoSe_2$, MoS_2 and WSe_2.[5,6,7,8,9] Ultrathin 2D nanosheets have shown remarkable physical, chemical and electronical properties. However, these materials have the common disadvantages: those materials/devices generally don’t have flexibility or recyclability, which brings limitations to their applications and raises costs. Graphene oxide based self-healing nanocomposite hydrogels were prepared for biomedical appliations (Figure 3.3).[10] Formation of various hybrids by combining 2D nanosheets with polyimines either through aforementioned wet-chemistry approach or dry-press method would be viable, which opens new way for developing advance materials with malleable, repairable and recyclable properties based on covalent dynamic chemistry.

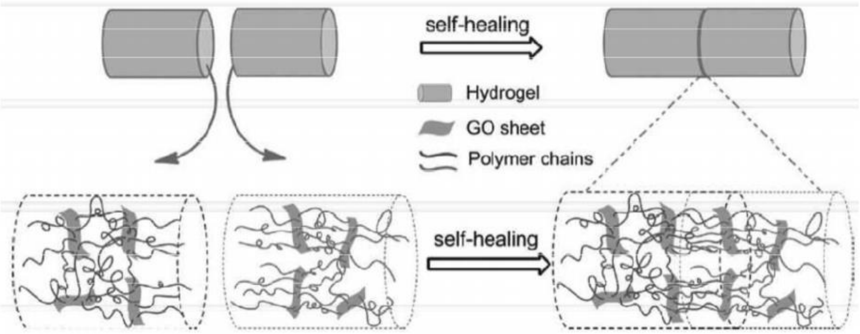

Figure 3.3 The proposed self-healing mechanism of Graphene oxide composite hydrogels. Figure adapted from ref. 10

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