New Thermally Remendable Highly Cross-Linked Polymeric Materials

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ABSTRACT: Two new remendable highly cross-linked polymers, **2ME4F** and **2MEP4F**, were prepared without solvent. Solid-state NMR (nuclear magnetic resonance) was used to study the thermal reversibility of Diels−Alder (DA) cross-linking, and it was found that DA connections and disconnections of both polymers are thermally reversible. Differential scanning calorimeter and dynamical mechanical analysis were applied to study thermal and mechanical properties of these materials, and it is found that the glass transition temperature (T_g) of **2ME4F** is about 30−40 °C and that of **2MEP4F** is about 80 °C. A qualitative study of the healing efficiency of **2MEP4F** showed that cracks can be healed effectively with a simple thermal healing procedure. This process can be repeated to heal cracks multiple times.

Introduction

During past decades, highly cross-linked polymers have been widely studied as matrices for composites, foamed structures, structural adhesives, insulators for electronic packaging, and other applications.[1] The densely cross-linked structures are the basis of superior mechanical properties such as high modulus, high fracture strength, and solvent resistance. Though these are commendable properties, highly cross-linked polymeric engineering materials are also notorious for their brittleness and propensity to crack. The ultimate cause of failure of all structural materials is due to initiation and growth of cracks, often hidden within the bulk and ultimately leading to their catastrophic failure.[2]

A substantial effort has been spent to find effective ways for crack-healing of polymeric materials during the past decades.[3] Based on the mechanism of linear polymer chain interpenetration at interfaces, techniques of crack-healing of linear polymers have been well established, such as hot plate welding and small molecule induced crack-healing.[4] However, crack-healing of cross-linked polymers is still a fairly new research field. Crack-healing of a composite of linear polymer and thermoset was reported.[5] However, only 1.7% of the fracture energy was recovered after annealing of fractured solid interfaces without any surface treatment or new monomers. Several years ago, the concept of self-repair was introduced to heal cracks by embedding hollow fibers that can release repair chemicals when a crack propagates.[6] In 2001, the crack self-healing ability of an epoxy resin composite was reported by White et al., consisting of a clever use of a catalytic network formation of an encapsulated add-monomer, which is held within a capsule embedded in the epoxy matrix.[7] However, it was not clear how efficient multiple self-healing was.

Retro-Diels−Alder cycloadditions have been studied for decades.[8] Since the early days of the application of the Diels−Alder (DA) cycloaddition to the synthesis of thermally reversible cross-linked polymers,[9] many studies have been reported in this area.[10,11]

Reversibly cross-linked polymers using the retro-DA reaction have been reported by Small, Loy, and their colleagues.[11] For their application of debonding adhesives, liquid monomers were required, and Si−O−C bonds are essential to achieve liquids at room temperature. However, it is well-known that Si−O−C bonds are susceptible to acid- or base-catalyzed hydrolysis,[13] and potentially biodegradable polymers have been reported recently based on this feature of Si−O−C bonds.[14] Furthermore, only soft materials, with Young's modulus of 29−36 MPa and compressive strength of less than 1 MPa,[11c] were reported, which are not suitable for engineering materials.

In our previous work,[12] the concept of debondable adhesives[11] was taken one step further, and a remendable plastic was reported. It was found that the energy to break DA adducts is much lower than that to break all the other covalent bonds, and the retro-DA reaction was found responsible for crack propagation. When the sample was reheated, the furan and maleimide moieties were found to reconnect again and the cracks healed or fractures mended. On the basis of this concept, a transparent organic polymeric material was developed that could repeatedly mend or "remend" itself under mild conditions. The "intermonomer" linkages were formed by DA cycloadditions that disconnected upon heating to 120 °C and above and reconnected upon cooling. It was found that this process was fully reversible and could be used to restore a fractured part multiple times, and it did not require additional ingredients such as a catalyst, additional monomer, or special surface treatment of the fractured interface. At the end of that paper, we suggested that a colorless maleimide monomer and a process to make polymeric materials without solvent (the methylene chloride) would be essential features of the next generation of this type of polymeric material.

In this work, we report two remendable cross-linked polymeric materials based on thermally reversible DA cycloaddition. These materials are hard, *colorless*, and transparent at room temperature and do not require solvent for the polymerization processes.

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Experimental Section

Furan monomer (**4F**) was synthesized as described in the Supporting Information of our previous work.[12] Monomer 1,8-bis(maleimido)-3,6-dioxaoctane (**2ME**) was synthesized according to the literature.[15] All other reagents, *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, dimethylformamide (DMF), Ac_2O, Et_3N, $Ni(OAc)_2 \cdot 4H_2O$, $SOCl_2$, CH_2Cl_2, toluene, pyridine, and furfuryl alcohol, were purchased from Aldrich, Fisher, or Acros and used without purification.

Elemental analysis was provided by Desert Analytics (Tucson, AZ). Solution NMR spectra were obtained on a Bruker 400 MHz NMR instrument. The solid-state NMR spectrum was obtained on a Bruker Avance 300 NMR instrument.

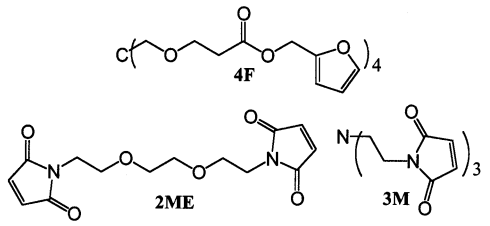
Differential scanning calorimeter (DSC) data were obtained on a Thermal Analysis MDSC 2920 with scan rate of 10 °C/min. Dynamic mechanical analysis (DMA) data were obtained on a TA Instrument DMA 2980 with scan rate of 1 °C/min and frequency of 1 Hz. The ultrasonic testing was performed in accordance with ASTM E494-95 at a frequency of 5 MHz with a Compuscope 8012 12 bit A−D 100 Megasample/second two-channel card with a Matek Instruments TB-1000 Gated Amplifier Toneburst card. Compression testing was performed according to the ASTM D695 protocol on an Instron Floor Model (TT). A Hopkinson bar test was also conducted to obtain compression data according to the conditions and procedures described in the literature[17] with 0.5 in. diameter bars (designed and built at the University of California, San Diego, by Prof. Nemat-Nasser and J. Isaacs) and a Nicolet 4094B data acquisition system. Compact tension specimens with a drilled hole were used to obtain critical load data. Testing was performed on an Instron model 5544 using a crosshead speed of 0.1 mm/min, and specimens were held in place by C-clamps during testing. All mechanical tests were performed at 24 ± 1 °C. During crack-healing, specimens were held in place with a 1-in. hose clamp. The clamp pressure was insignificant, sufficient only to prevent lateral displacement of the fracture surfaces.

Synthesis of 1,8-Bis(maleimido)-1-ethylpropane (2MEP). To a solution of 36 g (0.37 mol) of maleic anhydride and 70 mL of *N*,*N*-dimethylformamide (DMF) in a 500 mL three-neck round-bottom flask with magnetic stirring, 20 mL (0.17 mol) of Dytek-EP (Aldrich) was added dropwise. The temperature of the solution was kept below 85 °C. Stirring was continued for 2 h after addition at 75 °C. Then, 64 mL of acetic anhydride, 8 mL of triethylamine, and 0.4 g of nickel acetate tetrahydrate were added in one portion to the solution. Stirring was continued for about 2 h at 80 °C. Water (100 mL) was added, and the solvent was distilled under vacuum at 60 °C. The residue was redissolved in 500 mL of CH_2Cl_2 and washed with H_2O (3 × 300 mL). The organic layer was collected and shaken with about 200 g of silica gel. The solvent from the filtered solution was evaporated, and the residue was purified by chromatography on a short silica gel column using ethyl acetate as solvent. The solvent was removed on a rotary evaporator, and crystallization from 50% ethyl acetate and 50% hexane was carried out to afford white crystals (21 g, 42%); mp 82−84 °C. ^{1}H NMR ($CDCl_3$): 6.61 (4H, s); 3.76−3.3 (3H, 3m); 2.19−1.56 (4H, 4m); 0.70 (3H, t). ^{13}C NMR ($CDCl_3$): 171.09; 170.59; 134.08; 133.85; 50.32; 34.88; 29.97; 25.58; 10.78. FT-IR: 3102; 1705; 1407; 1189 cm^{-1}. UV−vis: 237; 296 nm. Elemental analysis: Calcd: C, 59.52; H, 5.38; N, 10.6. Found: C, 59.68; H, 5.38; N, 10.38.

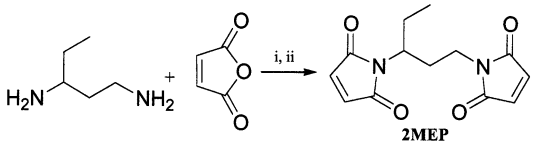
Synthesis of Polymer 2ME4F. A typical procedure is as follows: 1.004 g (1.35 mmol) of monomer **4F** and 0.831 g (2.76 mmol) of monomer **2ME** (powder) were mixed together in a glass test tube. Air trapped inside was removed by vacuum. The mixture was then heated to 125 °C on a silicon oil bath for about 20 min. The solid dissolved into the liquid in about 5 min. The resulting gel was then cooled to about 40 °C in 12 h to obtain a colorless, transparent material.

Synthesis of Polymer 2MEP4F. A typical procedure is as follows: 7.154 g (9.61 mmol) of monomer **4F** and 5.038 g (19.21 mmol) of monomer **2MEP** (powder) were mixed together in a glass test tube. Air trapped inside was removed by vacuum. The mixture was then heated to 115 °C in a silicone oil bath for about 20 min. The solid dissolved into the liquid in about 3 min. The resulting gel was cooled to about 40 °C in 12 h to obtain a transparent, colorless material.

Chart 1



Scheme 1. (i) DMF; (ii) DMF, Acetic Anhydride, Triethylamine, Nickel Acetate Tetrahydrate



Results and Discussion

Chart 1 depicts three monomers used in this and previous work. Maleimide monomer **3M** and furan monomer **4F** were used to make polymer **3M4F** in our previous work.[12] Maleimide compounds usually have high melting points. The tris(maleimide) reported in our previous work,[12] **3M**, has a melting point of 113 °C. Because of their high melting points, maleimide monomers are difficult to dissolve in furan monomers. In our previous work,[12] the maleimide monomer was dissolved in methylene chloride first, and the solvent was evacuated after mixing with the furan monomer. However, polymerization starts as soon as solvent is being removed, and residual solvent in the material makes the processing procedure difficult. To avoid the necessity of diluents, low melting point maleimide derivatives were required. Even though Si−O bonds were previously used to obtain low melting maleimide compounds,[11,13] as mentioned in the Introduction, the hydrolytic stability is marginal, and the stiffness of the resulting material falls short of common engineering polymeric materials.

Several maleimide compounds have been reported in the literature.[15] In this work, maleimide monomer **2ME** and **4F** were used to make polymer **2ME4F** and maleimide monomer **2MEP** (shown in Scheme 1) and **4F** were used to synthesize **2MEP4F**. With ethylenedioxy units, compound **2ME** has a melting point of 92 °C, which is much lower than that of the tris(maleimide) **3M** (mp 113−114 °C). As shown in Scheme 1, a bis(maleimide) with a branch and potential chiral center, **2MEP**, was synthesized, and the melting point was found to be as low as 82 °C, even though there are only three bridge carbons. Both of these two bis(maleimide) compounds were mixed with liquid furan monomer (**4F**) and heated to about 20−30 °C above their melting points. Both materials can be processed in the pregel as well as in the gel state, and hard polymers are formed upon cooling.

Solid-state ^{13}C NMR spectra of polymer **2ME4F** and **2MEP4F**, as a function of thermal cycling, are shown in Figures 1 and 2. In our previous work,[12] it was shown that unreacted or disconnected furan units have ^{13}C NMR peaks at chemical shifts of ca. 111 and 150 ppm which shift to lower values upon cycloaddition. These results are of diagnostic value to monitor the change of

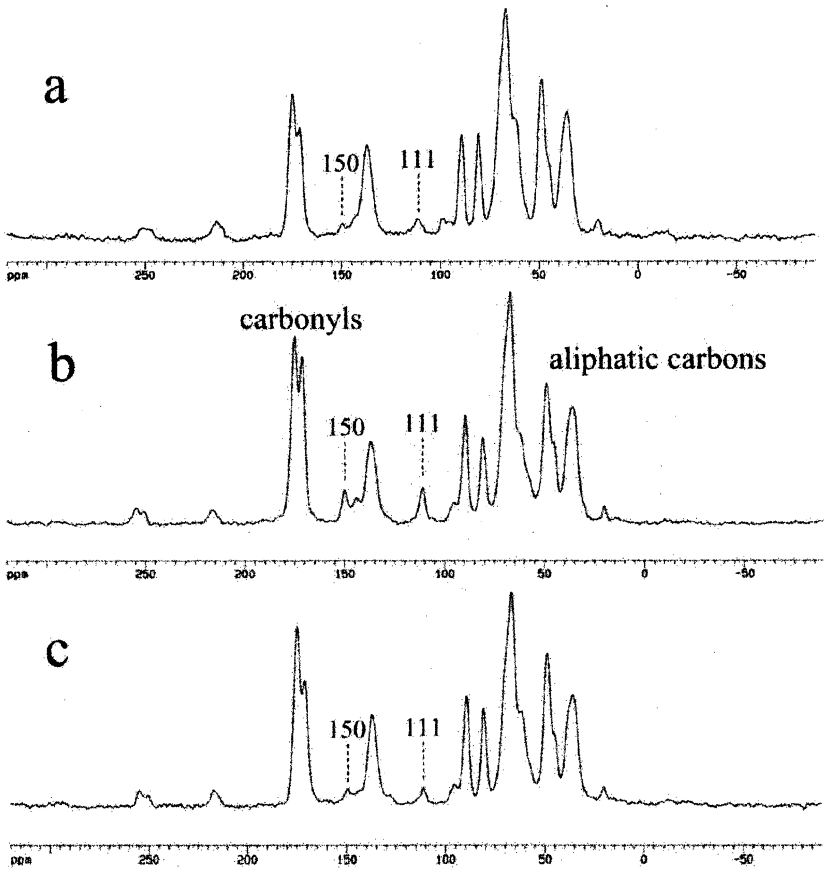


Figure 1. Solid-state ^{13}C NMR of **2ME4F**: (a) fully polymerized; (b) sample of (a) heated to 130 °C and then quenched in liquid nitrogen; (c) samples of (b) heated to 80 °C and then cooled to room temperature.

cross-linking. As shown in Figures 1a and 2a, there are two small peaks at ca. 111 and 150 ppm resonances on both spectra, which means that most furan unites have reacted in the current polymerization process for both **2ME4F** and **2MEP4F**. The reason for the residue of furan units might be that DA cycloaddition happens as soon as maleimide compounds dissolve in the furan compound, and the mixture is not as homogeneous as the one formed with the help of a solvent. The reversibility of both polymers was also studied by solid-state ^{13}C NMR. For **2ME4F**, the polymer was heated to 130 °C for 25 min, followed by quenching in liquid nitrogen to produce a material with the solid-state ^{13}C NMR spectrum shown in Figure 1b. Polymer **2MEP4F** was heated to 140 °C for 25 min, followed by quenching in liquid nitrogen, and the solid-state ^{13}C NMR spectrum of the product is shown in Figure 2b. It is clear that in both Figure 1b and Figure 2b the intensity of the ca. 111 and ca. 150 ppm resonances are now much higher, indicating more of unreacted furan moieties. Furthermore, the intensity of the two peaks for maleimide carbonyl groups changes. After heating and quenching, the peak at higher field, ~172 ppm, which belongs to unreacted maleimide carbonyls,[12] increases. This indicates that there are many more unreacted maleimide moieties. The same samples were heated to 90 °C and cooled to 30 °C in 6 h to repolymerize. Their solid-state ^{13}C NMR spectra are shown in Figures 1c and 2c. Since the latter are essentially identical to the spectra in Figures 1a and 2a, respectively, the simplest interpretation demands that disconnected linkages had reconnected, which was also observed in our previous work.[12]

Mechanical properties of these two polymers have been tested at room temperature and are shown in Table 1, together with data for polymer **3M4F**.[12] For all three polymers, the densities are between 1.31 and 1.37 g/cm^3, and Poisson ratios are also very similar, from 0.32 to 0.37. The mechanical properties of **2MEP4F** are lower than, but close to, those of **3M4F**. Young's modulus of **2MEP4F** is as high as 4.41 GPa, and the specific strength is as high as 180 MPa. Both of these are similar to, or higher than, those of widely used epoxy resins and unsaturated polyesters[12] whose typical Young's modulus are in the range of 2−4 GPa and compression stresses are 80−200 MPa. However, the mechanical properties of **2ME4F** are weaker than those of **3M4F** and **2MEP4F**. A reasonable conjecture for this result is the presence of the ethylenedioxy soft unit in monomer **2ME**. The Young's modulus and compressive strength of **2ME4F** and **2MEP4F** are about 2 orders of magnitude higher than those reported in silicon-based DA polymers.[11c] The specific modulus (modulus divided by density) of **2ME4F** and **2MEP4F** (3.40 and 3.16 GPa/(g cm^3), respectively) are about 15 times higher

Table 1. Mechanical Testing of Polymer 2MEP4F and 3M4F

		3M4F	2MEP4F	2ME4F
ultrasonic testing	density (g/cm^3)	1.34	1.31	1.33
	Poisson ratio	0.32	0.36	0.37
	Young's modulus (GPa)	4.70	4.41	3.6
compression testing	Young's modulus (GPa)	4.55[a]	4.14[a]	3.4[b]
	specific modulus (GPa/(g cm^3))	3.40	3.16	
	ultimate tensile (MPa)	241[a]	234[a]	
	strain to failure (%)	25[a]	24[a]	
	strength at yield (MPa)	121[b]		116[b]

[a] Hopkinson bar testing. [b] ASTM D695.

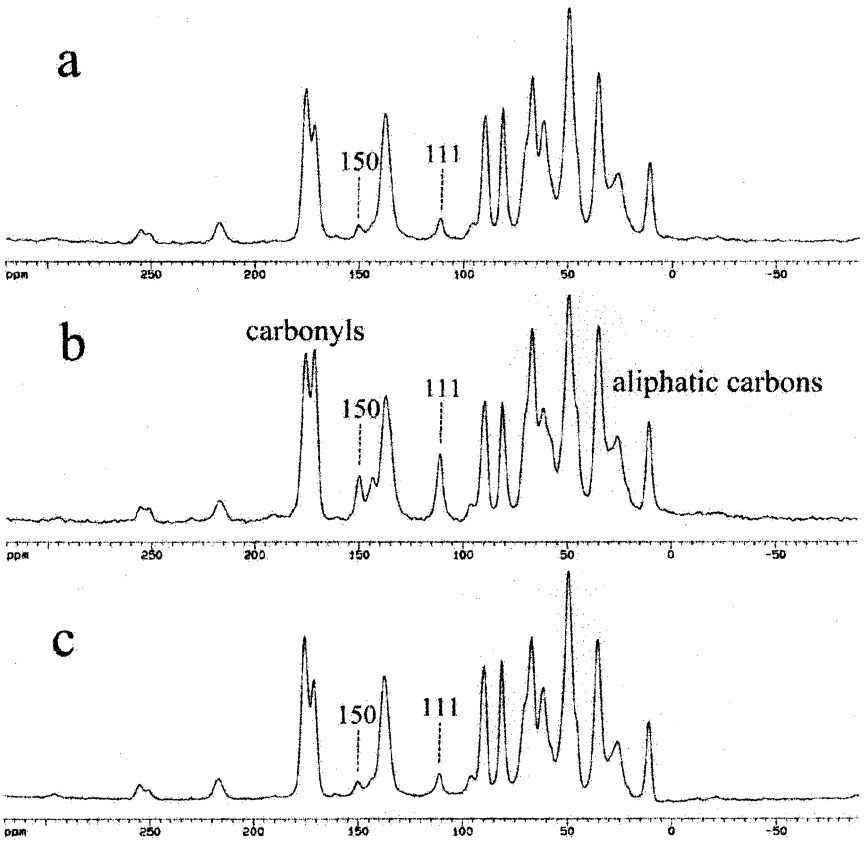


Figure 2. Solid-state ^{13}C NMR of **2MEP4F**: (a) fully polymerized; (b)sample of (a) heated to 150 °C and then quenched in liquid nitrogen; (c) samples of (b) heated to 90 °C and then cooled to room temperature.

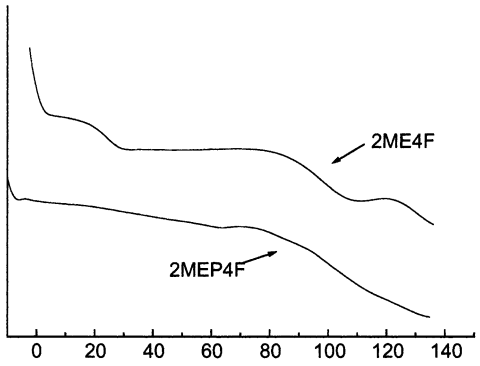


Figure 3. Results of DSC obtained on **2ME4F** and **2MEP4F**.

thanthe materials reported in ref 11c (ca. 0.22 GPa/(g cm^3)).

To test the thermal properties of both polymers, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were carried out. The DSC results of **2ME4F** and **2MEP4F** are shown in Figure 3. It can be seen that the DSC curve of polymer **2ME4F** has three transitions that start at 21, 93, and 120 °C. The lower transition at 21 °C might be due to the movement of ethylenedioxy segments. Also as shown in Figure 3 are only two transitions at about 86 and 120 °C for polymer **2MEP4F**. The transitions that start at 110−120 °C have already been assigned to be the retro-DA cycloadditions.[12]

DMA results are shown in Figure 4. In Figure 4a, it can be seen that even though the storage modulus of **2ME4F** at 30 °C is as high as 2.87 GPa, it starts dropping at that temperature, indicating that the material starts softening and the tan δ peak shows at 59 °C. This result matches previous DSC data, which also show a transition at around 20−30 °C. From Figure 2b, it can be seen that storage modulus of **2MEP4F** starts at 4.46 GPa. The onset point of glass transition is at about 78 °C and the peak of tan δ shows at 95 °C, which also matches previous DSC data, with a transition at about 86 °C. For comparison, DMA results of **3M4F** are shown in Figure 2c. It can be seen that the transition also starts at about 84 °C, and the peak of tan δ appears at 100 °C.

Regarding the healing/mending efficiency of both polymers, polymer **2ME4F** softens and can be remolded at 160 °C, while polymer **2MEP4F** exhibits the same behavior at a temperature above 180 °C. However, the quantitative study of healing efficiency of polymer **2ME4F** was not successful because the shape of the specimens changed before it reached the healing temperature. To determine the fracture-mending efficiency of polymer **2MEP4F**, tests were performed using compact tension test specimens.[16] In our previous work,[12] specimens fractured (failed) into two pieces. The resulting pieces were held together with a simple hose clamp to heal/mend the crack. However, it was essentially impossible to perfectly match the two halves, and healing/mending efficiencies were thereafter affected. To overcome this problem, compact tension specimens in this work were machined as shown in the diagram in Figure 5, in which a hole was drilled in the middle of the specimens to stop crack-propagation.

A sharp precrack was created in the tapered samples by gently tapping a fresh razor blade into a machined "starter notch". Application of a load in the direction perpendicular to the precrack to the point at which the fracture toughness limit was exceeded beyond the

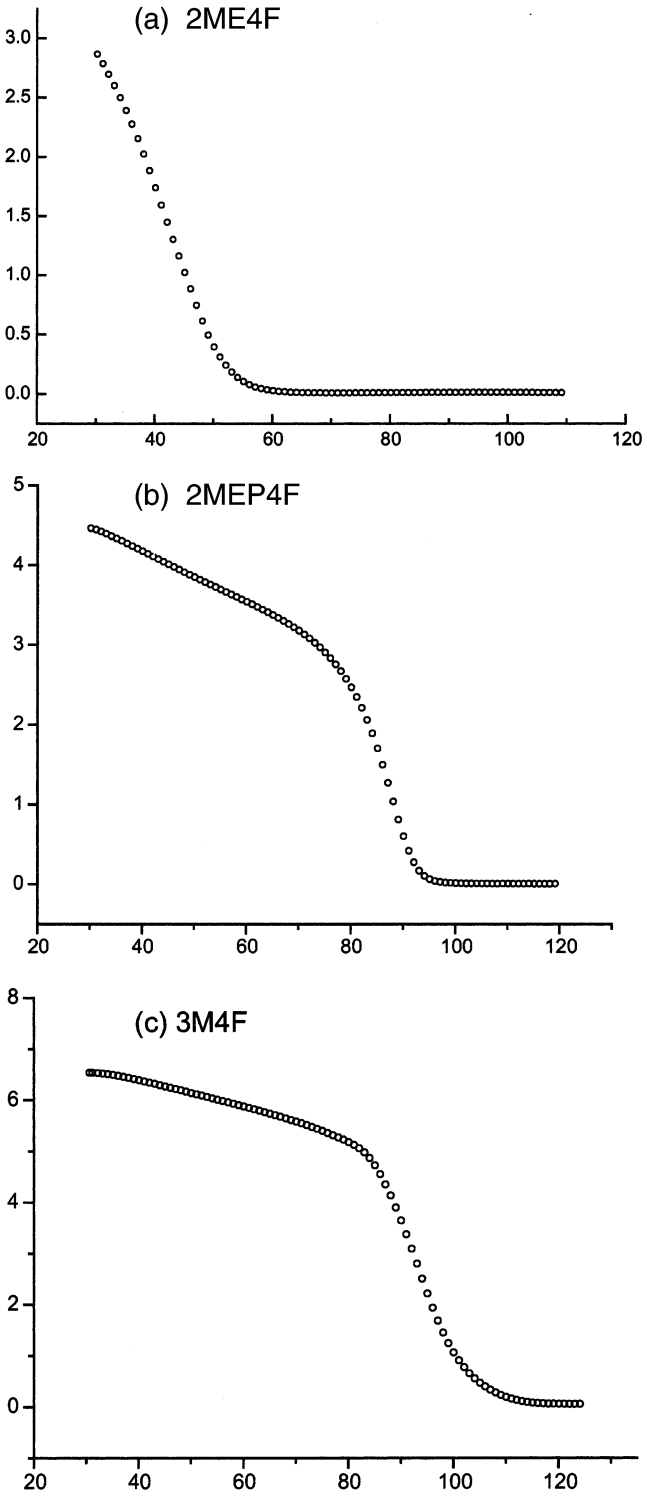


Figure 4. Results of DMA obtained on polymers (a) **2ME4F**, (b) **2MEP4F**, and (c) **3M4F**.

critical load, which is about 62 N, the specimen fractured and the crack was stopped by the hole. Load vs displacement results are shown in Figure 6. Because the drilled hole might lie within the volume associated with the stress concentration introduced by the notch, the critical load value should be considered as an estimation of fracture toughness. Additional studies are required to resolve this issue.

After failure, the specimen was held by a clamp and placed in a thermal chamber at 115 °C for 30 min to heal the crack. The time for the specimen to reach

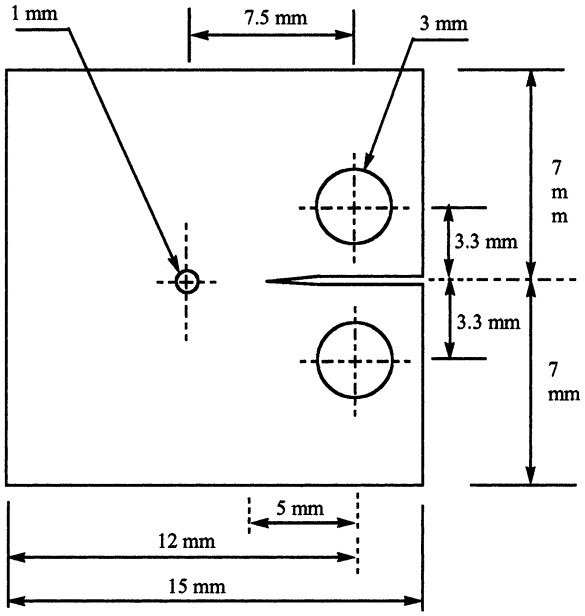


Figure 5. Diagram of compact tension specimens (thickness: 6 mm).

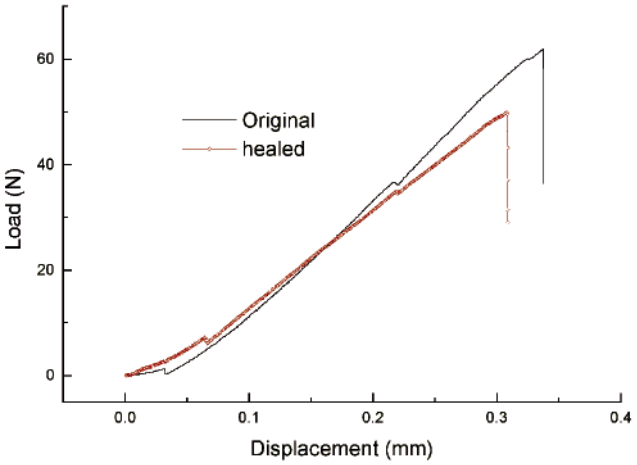


Figure 6. A typical load vs displacement diagram of fracture toughness testing of compact tension test specimens of polymer **2MEP4F**. The original and healed fracture toughness were determined by the propagation of the starter crack along the middle plane of the specimen at the critical load.

thermal equilibrium with the chamber was ca. 15 min. The specimen was then cooled in the chamber to 40 °C in 6 h to fully repolymerize the material. Minimal pressure was provided by the clamp, although some pressure arose from the thermal expansion of the polymer. During this treatment, only the cracks were mended—the starter notches were not affected. The same fracture tests were also carried out in an effort to study the healing efficiency. Representative load–displacement curves for a polymer specimen are plotted in Figure 6, showing recovery of about 81% of the original fracture load, and an average of 80% was achieved from three independent specimens (83%, 81%, and 76%). Usually, the second crack propagated along the original crack plane. An identical heating/cooling procedure was applied to heal the second crack. The average of second mending efficiency achieved was 78% of the original load, as determined from three independent specimens (79%, 79%, and 76%). This result indicates that the material can be healed efficiently multiple times. Because the parameter of critical load

can be influenced by several factors, such as crack length and crack bluntness, the healing efficiency reported here should be regarded as an estimate. More quantitative experiments will be undertaken in future work.

Conclusion

Two new thermally remendable highly cross-linked polymers, **2ME4F** and **2MEP4F**, were synthesized in neat form. Polymer **2ME4F** with soft ethylenedioxy chains exhibits a T_g of about 30−40 °C, while the T_g of **2MEP4F** is about 80 °C. It was found that the DA cross-links of both polymers are thermally reversible and can be used to remend fractured parts. The preliminary study of the healing/mending efficiency of 2MEP4F shows that, qualitatively, cracks in this material can be recovered effectively after a simple thermal healing procedure, and this process can be repeated.

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