

Environmental friendly polymers based on schiff-base reaction with self-healing, remolding and degradable ability



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ABSTRACT

In this paper, we have synthesized crosslinked polymers that can be remolded, self-healing and degradable, which provide us more freedom on how to treat the crosslinked polymer after they are damaged or out of use. This type of crosslinked polymer is fabricated by dynamic bonding linkage based on Schiff base reaction between commercial available terephthalaldehyde (A_2) and diamine (B_2) using tri(2-aminoethyl)amine (B_3) as crosslinking agent. The network could be easily tailored by changing the ratio of B_3 to B_2 (R) and increasing R could lead to increasing the crosslinking degree. As a result, the sample could be gradually changed from weak to strong materials with increasing R based on the data of mechanical properties. Most of important, this type of crosslinked polymers could show good self-healing and remolded behavior. The crosslinked sample could also be remolded at 120 °C under hot pressure without the compromise of its mechanical properties and the temperature for self-healing could be controlled from room temperature (~20 °C) to 55 °C based on the different R . In the meantime, they could also be completely degraded into small molecules under the acidic condition for 2 days. All these characters could provide an ideal solution to the crosslinked polymers which is totally friendly to the environment.

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1. Introduction

Nowadays, crosslinked polymers have been widely used in our daily life such as adhesive, coatings and foams due to its shape stability and high mechanical properties [1–7]. However, they suffer one environmental problem that they could not be reused or degradable after they are damaged or out of use [8,9]. Therefore, it is highly desirable to design the environmental friendly crosslinked polymers with ability of self-healing, remolding and degradability at the same time. By this way, people could have great freedom to determine whether the damaged materials could be recycled by the way of being remolded and self-healing, or degraded into small molecules. In present, people have successfully fabricated the polymers having the self-healing and remolding-ability based on the physical and dynamic chemically bonded method [10–15]. For example, polymers with good self-healing and remolding-ability could be fabricated based on the ionic [3] and hydrogen physical interaction [16–19] or the dynamic chemical bonds based on imine

bonds [20], acylhydrazone bonds [21,22], disulfide bonds [23], alkoxyamine bonds [24] and Diels–Alder cycloaddition [25–28]. By comparing these two methods, dynamic chemically bonded method is usually superior to the physical interaction system due to its unstable state upon heating or in solvents which is detrimental to its final mechanical properties. At the same time, polymers with controlled good degradability such as polycaprolactone, have also been successfully synthesized and this kind of polymers based on ester bond could be totally degraded into small molecules under the acidic condition [29–31]. It is interestingly found that polymers having the ability of remolding-ability and self-healing could not finally decompose into small molecules [8,9,32] and the polymers with good degradability lack the ability of being remolded or self-healing. Therefore, it is still difficult to synthesize crosslinked polymers that could have the above three functionalities at the same time. In this paper, we try to use imine bonds formed via Schiff base chemistry to synthesize the crosslinked polymers which could have good ability for being remolded, self-healing and degradable. Imine bonds can be formed between amines and aldehydes by the reversible condensation, one of the oldest and most ubiquitous reactions in organic chemistry. This kind of reaction

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involves two distinct processes: imine condensation/hydrolysis and imine exchange [33–36], which provides the basis for being remolded and self-healing. Recently, Zhang's research group [32] has fabricated the crosslinked polymer based on Schiff reaction, which could be malleable under heat or water. However, the chain in the thermosetting polymers was so rigid that the film sample they provided in the published paper contains several unplasticizing dots in the film after hot pressing, which is detrimental to its final mechanical properties and the ability of self-healing at room temperature might be lost due to its rigid network. In fact, there are a large number of commercially available and inexpensive amines and aldehyde [21,37–39], which provide great freedom to design the polymer to tailor the relationship between the rigidity of chain and the behavior of remolding-ability and self-healing. In this article, we selected terephthalaldehyde (A_2), three different diamines (B_2) and tri(2-aminoethyl)amine (B_3) to build the network for the crosslinked polymers based on the Schiff base. Based on the different mole ratio of B_3 to B_2 (R) and different types of diamines, the sample shows a distinct transformation from weak to strong materials and the temperature for self-healing could also shift from room temperature to about 60 °C. More importantly, the sample could also totally decompose with the presence of water under acidic condition, since imine bonds could be cleaved with the help of water [16]. All these characters could endow this type of polymers as great potential green materials used in a sustainable way.

2. Experimental section

2.1. Materials

Terephthalaldehyde and tri(2-aminoethyl)amine were purchased from TCI Chemical CO., Ltd, hexamethylenediamine, dimethyl formamide (DMF) and dichloromethane were purchased from Sinopharm Chemical Reagent Co., Ltd, and 4,7,10-trioxa-1,13-tridecanediamine and D230 was purchased from Sigma–Aldrich. All the reagents were used as received.

2.2. Preparation of TA-PO (linear polymer-model compound)

1.34 g terephthalaldehyde (TA, 10 mmol) and 2.3 g D230 (10 mmol) were dissolved in 15 mL DMF respectively. Then the monomers were mixed in a 50 mL three-necked flask equipped with a reflux condenser and stirred at 80 °C for 12 h with nitrogen protection. After DMF was removed by reduced pressure distillation at 60 °C, and the product was collected and dried in vacuum oven at 60 °C.

2.3. Preparation of crosslinked polymer films

Based on the above reaction mechanism, the films were prepared in the following process: terephthalaldehyde, tri(2-aminoethyl)amine and diamine with different chain structures (shown in Fig. 1) were dissolved in DMF respectively in proportion as shown in Table S1. The total monomer concentration was kept at about 0.1 g mL⁻¹. Then the mixture was cast onto glass plate and dried in Drying Oven at 80 °C for 12 h to achieve constant weight. The films were named based on the structure of the diamine and the content of the tri(2-aminoethyl)amine. (Where 'cl' represents 'crosslinked', 'PO' represents the chain structure of D230, 'EO' represents 4,7,10-trioxa-1,13-tridecanediamine and 'HM' represents hexamethylenediamine).

2.4. Characterizations

¹H NMR spectra were carried out on a Varian Mercury Plus 400 MHz instrument with tetramethylsilane (TMS) as an internal standard and Dimethyl Sulfoxide-d₆ as the solvent at room temperature.

Fourier transform infrared (FTIR) spectra measurements were carried out on a Perkin-Elmer Paragon 1000 PC spectrometer from 3500 cm⁻¹ to 750 cm⁻¹. 64 scans at a resolution of 2 cm⁻¹ were averaged for each measurement. The samples of terephthalaldehyde and linear polymer were dissolved in CH₂Cl₂ and the solutions were dropped onto KBr plates and dried below an IR lamp. And the sample of the film cl-PO-4 was measured directly.

Differential scanning calorimetry (DSC) analysis was performed using DSC 6200 (Seiko Instrument Inc.) at a heating rate of 10 °C min⁻¹ from -50 to 150 °C and nitrogen flow rate of 50 mL min⁻¹.

The measurement of the mechanical property of films was performed using an Instron 4465 instrument at the crosshead speed of 100 mm/min at room temperature. The film samples with thicknesses of 0.2–0.3 mm were obtained by a solution-casting method. The specimens with widths of 4 mm and lengths of 40–50 mm were cut from the films.

Swelling ratios of the films in deionized water were studied by measuring the weight changes of the films. The weight of the films soaked in the deionized water at room temperature for 24 h was denoted by W₁. Then the wet films were dried under vacuum at 80 °C for 24 h and the weight was denoted by W₂. The SRs were calculated by the following formula:

$$SR = (W_1 - W_2)/W_2$$

The self-healing property of the films was measured with a polarizing optical microscopy (LEICA DM LP) equipped with temperature programmed heating stage (TMS 94) at a heating rate of 10 °C min⁻¹ from 0 to 100 °C.

3. Results and discussion

As shown in Scheme 1, the crosslinked polymers could be synthesized by mixing terephthalaldehyde (A_2), diamine (B_2) and triamine (B_3) using DMF as solvent. By selecting three types of diamine having different degree of hydrophilicity ((3) is hydrophilic and (4) is hydrophobic) and crosslinking degree by changing different R, we have investigated the influence of B_2 structure and crosslinking degree on the physical properties such as swelling ratio, gel fraction and mechanical properties.

3.1. The characterization of polymerization by NMR and FTIR

Since the crosslinked polymer could not be measured by ¹H NMR in solution state, the linear model polymer (TA-PO) was synthesized and characterized by the ¹H NMR spectrum. As shown in Fig. 2B, the typical proton signal at 9.87 ppm corresponding to -CHO on terephthalaldehyde and the signal at 1.73 ppm corresponding to -NH₂ on D230 disappears after polymerization, and a new signal at 7.97 ppm belonging to N=CH- become prominent, which could prove that the linear model polymer has been successfully synthesized through the linkage based on imine bonds.

FT-IR was further used to characterize this linear model polymer after the reaction between A_2 and B_2 . As shown in Fig. 2C, there is a distinct C=O stretch absorption band at 1693 cm⁻¹ in the IR spectrum, which is attributed to terephthalaldehyde. After polymerization, a new absorption band at 1643 cm⁻¹ corresponds to the C=N stretch of the newly formed imine bond has become

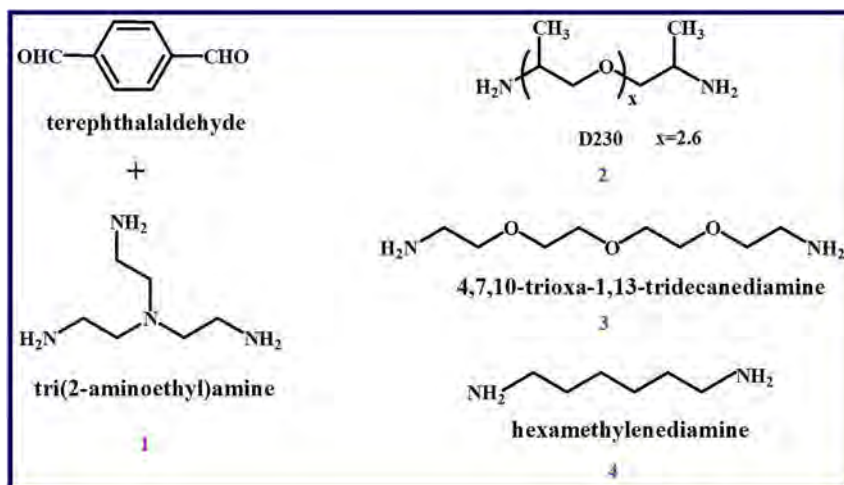
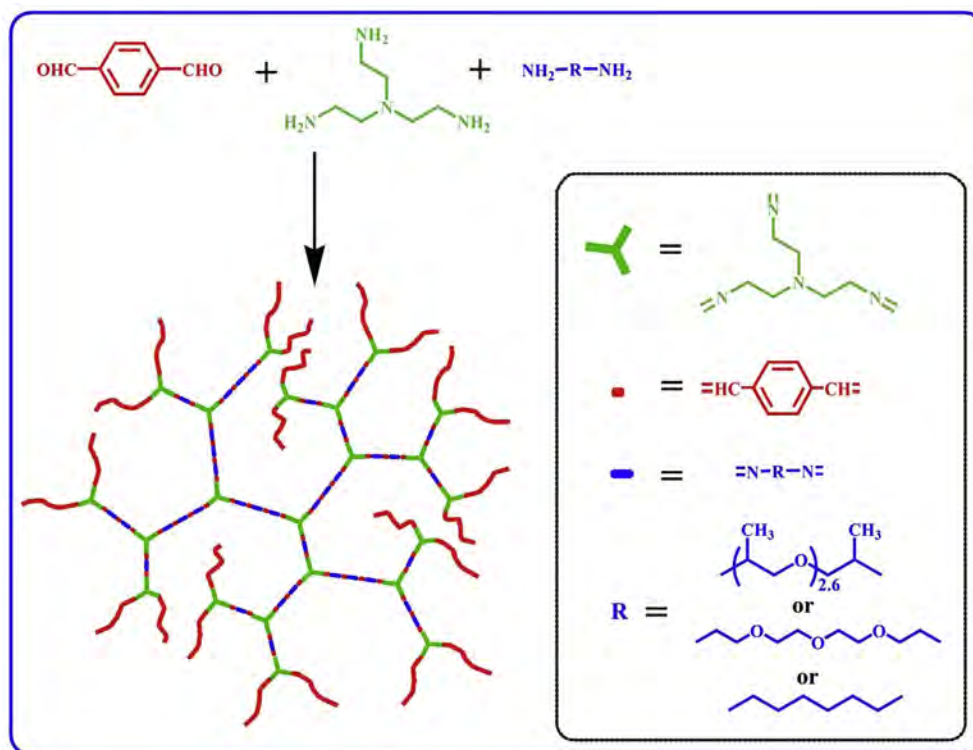


Fig. 1. Molecular structures of building units for the crosslinked polymer films.



Scheme 1. Structure of the crosslinked polymer films.

prominent in the FT-IR spectra of linear polymer, while the C=O stretch absorption band is barely detectable, which indicates the consumption of aldehyde groups and the formation of imine links after the polymerization. In the same way, this phenomenon is also observed in the FT-IR spectrum of cl-PO-4, indicating the successful formation of imine links in the crosslinked polymer.

3.2. Gel fraction and the swelling ratio

In order to characterize the network for materials at different R, the Gel fraction and swelling ratio were applied to measure the crosslinking degree. Fig. 3A, B and C illustrates the gel fraction of the films after immersion in DMF. It shows that the polymers could

only be swollen in DMF due to the formation of the crosslinked network and the solvent resistance is improved with increasing B_3 . R for the observed sample is selected between 3/5.5 and 6/1 and it is observed that the gel fraction is shifted around 90%. Take the cl-PO as an example, as shown in Table S2, the gel fraction was observed to increase from 87.9 to 95.8%, as R was increased from 3/5.5 to 6/1, which indicates that the crosslinking degree was increased with increasing B_3 . Fig. 3D, E and F shows the results of swelling ratio for three samples having different diamines. In contrast to the results of gel fraction, it is found that B_2 monomer has a significant influence on swelling ratio. The swelling ratio of B_2 having ethylene oxide structure is much larger than the others. By comparing the films having different B_2 at the same R, the

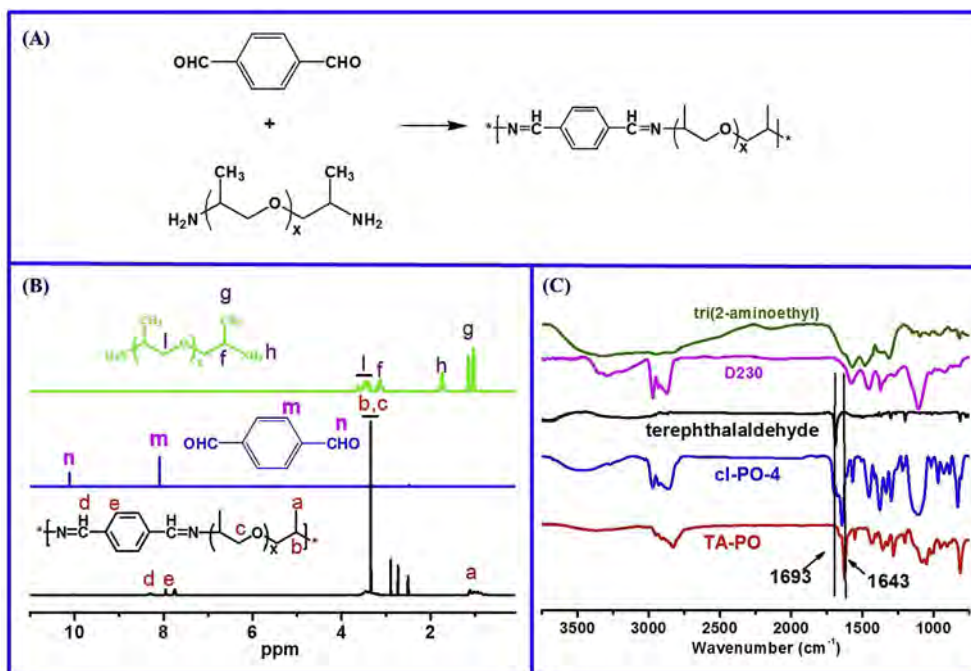


Fig. 2. (A) Synthesis process for model polymer, (B) ^1H NMR spectra of linear model polymer (TA-PO) (The signals between 2.89 and 2.69 ppm correspond to the residual DMF in the sample and the peak at 2.49 ppm belongs to DMSO- d_6), D230 and A_2 , (C) FT-IR spectra of TA, D230, tri(2-aminoethyl), TA-PO and cl-PO-4.

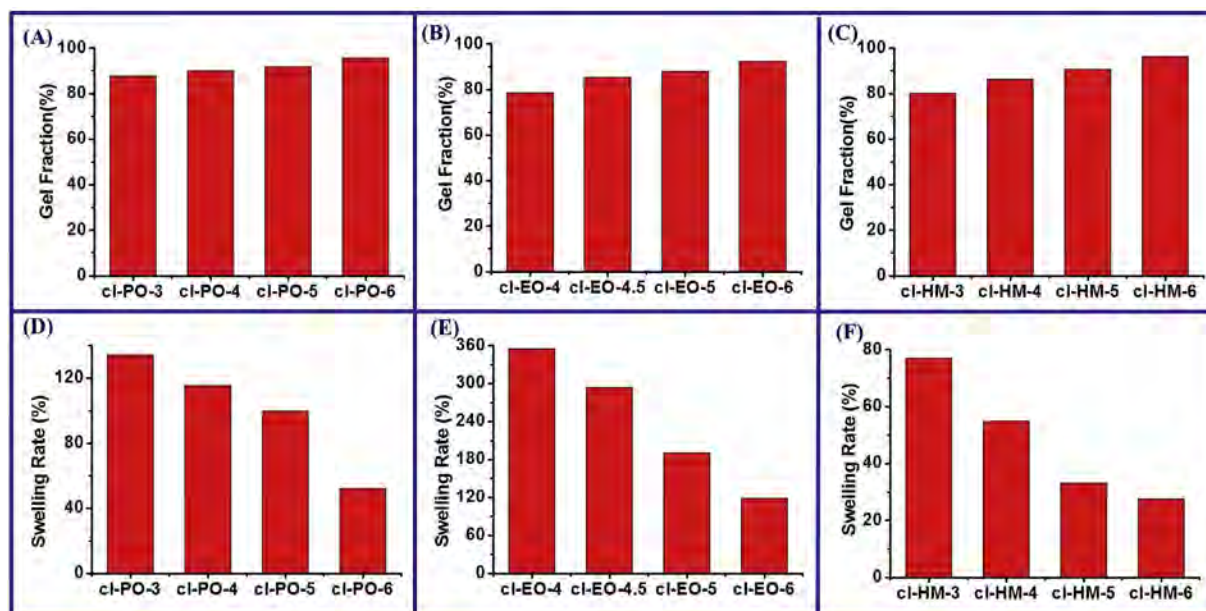


Fig. 3. Gel fraction (A, B and C) and the swelling ratio (D, E and F) of the films with the different composition.

hydrophilicity of chain has a significant influence on swelling ratio. For example, as R is about 4/4, the swelling ratio of cl-PO-4, cl-EO-4 and cl-HM-4 is 111.6%, 355.1% and 55.1% and hydrophilic diamine (4,7,10-trioxa-1,13-tridecanediamine) (3) shows the most swelling ratio, which indicates that ethylene oxide (EO) units in 4,7,10-trioxa-1,13-tridecanediamine(3) is conducive for the solvent to enter into its network to increase the swelling ratio. In addition, the crosslinking degree also has a close relationship with the swelling ratio. For example, with R increasing from 3/5.5 to 6/1, the swelling ratio increases from 52.2 to 134.3% for the cl-PO sample.

3.3. Mechanical properties of films

It is found that the crosslinking degree and the type of diamine have a profound effect on the swelling properties of the sample. Therefore, it is necessary to investigate the relationship between the mechanical properties and different crosslinking degree and the type of diamines. The mechanical properties of samples were then studied under the tensile mode. For each sample, three strips were measured and the average values were used to draw the stress–strain curves. Fig. 4 presents the typical stress–strain curves

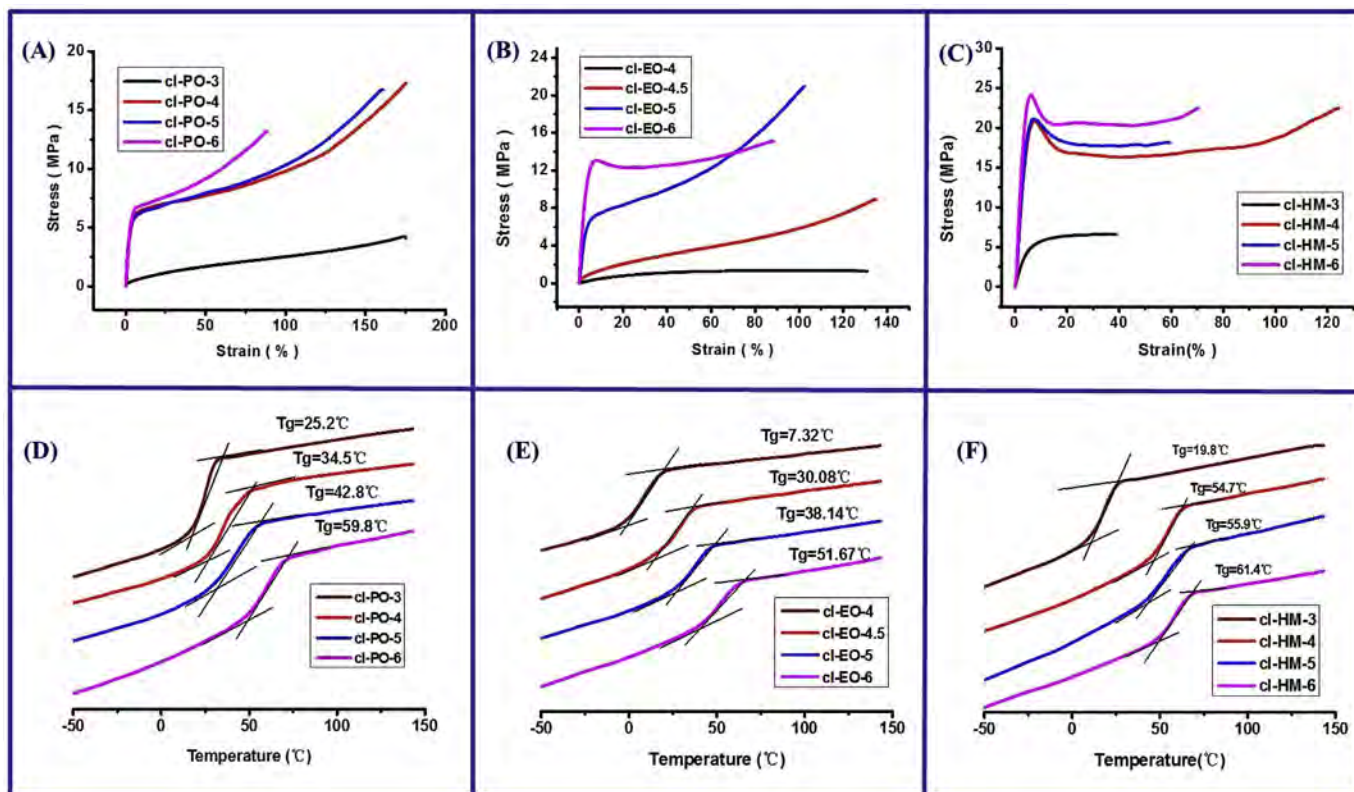


Fig. 4. Stress–strain curves and T_g of cl-PO series (A, D), cl-EO series (B, E) and cl-HM series (C, F).

for the samples of cl-PO, cl-EO and cl-HM series and the average young's modulus, max stress and elongation at break are listed in Table S3. As shown in Fig. 4 and Table S3, it is found that both the type of diamine and crosslinking degree greatly affect the mechanical properties. For different R, it is found that samples are initially very weak as the ratio is below 4/4. For example, the strength at tensile was only observed at 4.2 MPa as R is 3/5.5 in the series of cl-PO. With increasing R from 3/5.5 to 5/2.5, the strength of the sample was gradually increased with maximum data observed at 16.7 MPa, accompanied by a little reduction in the elongation at break from 174.7% to 161.5% for cl-PO. Since the sample with low R has a low crosslinking degree, chains in the network have great freedom to move, which could not efficiently sustain and spread the strength of loading. With the gradual increasing ratio, the network could help the chain effectively transfer the loading. Therefore, the strength would be gradually increased. With further increasing R from 5/2.5 to 6/1, the movement of chain among the network is prohibitively limited, which finally results in the reduction of elongation at break from 161.5% to 88.5% for cl-PO. Therefore, the mechanical properties of the sample could be tailored based on the different R.

For the three types of diamine, cl-HM shows the strongest in the mechanical properties as compared with other two systems. For example, as R is about 4/4, the strength at yield is about 325.9 MPa for cl-HM, higher than cl-PO (142.6 MPa) and cl-EO (4.5 MPa) respectively. Such results could be related with the chain rigidity of diamine. More hydrophilicity could facilitate the chain movement, which results in softening the polymers with reduced mechanical. This proposal is also supported by the measurement of glass transition temperature (T_g) of the samples with three different B₂. Fig. 4D, E and F shows the results of T_g obtained from the DSC measurements. As shown in Fig. 4D, E and F, it is found that cl-HM

shows the highest T_g at the same R among the three samples. For example, T_g for cl-HM is observed at 54.7 °C as R is 4/4, which is higher than cl-PO (34.5 °C) and cl-EO (7.32 °C), respectively. With increasing R, T_g is progressively increased and difference for T_g of different diamine is reduced and T_g for cl-HM is still the highest data at the same R. Therefore, the results from DSC are in agreement with those from the mechanical properties and the swelling ratio.

3.4. Remolding and self-healing ability of films

The reprocessing ability for the crosslinked samples could be assessed by two methods. One is self-healing properties and the other is remolding ability. Both of them could be used to characterize the samples' recycling ability since the samples were built based on dynamic reversible bonds which can be proved as shown in Fig. S1 and S2.

The self-healing process was investigated after cutting a small scratch into the crosslinked polymer film by a surgical blade. Afterwards, the film with crack was put onto the heating stage with a heating rate of 10 °C min⁻¹ and photos were taken at different temperature using optical microscopy during the heating process to observe the evolution of the crack. For example, when the sample of cl-PO-4 was heated to about 24 °C, the crack on the film became smaller, and almost disappeared at 33 °C, as shown in Fig. 5C, indicating that the cross-linked films could be self-healed at room temperature. In all cases, the crosslinked sample network did not melt during the healing process. Therefore, the above described healing is based on an intrinsic self-healing capability of materials based on the dynamic reversible reaction between aldehyde groups and amine. Table S4 illustrates the initial and final temperatures to complete the process of self-healing process for the sample having

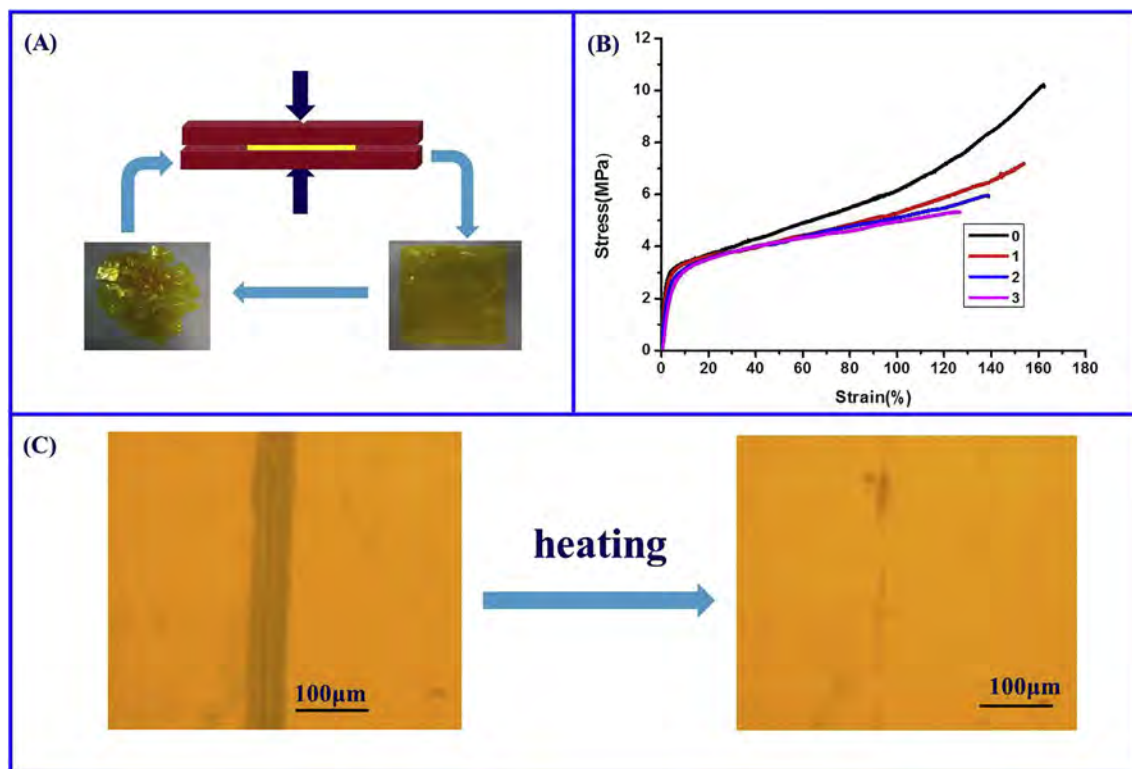


Fig. 5. (A) Recycling study: the process of heat press polymer pieces into solid film, taking the sample cl-PO-4 for example. (B) Stress–strain curves of the samples shown in Fig. 5A. (C) Digital images for healing process of cl-PO-4. The photo of the film with a crack at 0 °C (left) and at 33 °C (right).

different crosslinking degree and different types of diamines. It is found that both of these two factors could also obviously affect the temperatures range to finish the self-healing process. Take the cl-PO as examples, it is observed that both the initial and final temperatures are increased from 20 °C to 38 °C and 25 °C to 50 °C, respectively, as R is increased from 3/5.5 to 6/1. Such phenomena could be explained by the ability for chain movement in the network, considering the chain's movement is important parameter for the self-healing behavior. As shown in the results of DSC (Fig. 4), it is found that T_g is increased with increasing R, which means that the chain could not easily move as T_g is increased. Therefore, high temperature is needed to give the chain more energies to move together to facilitate the self-healing process. For the type of diamine, cl-HM also shows the highest healing temperature. For example, cl-HM's healing temperature range is found between 36 °C and 55 °C, which is much higher than cl-EO and cl-PO at the same R. This result is also closely related with chain movement. As shown in the results of DSC, cl-HM's chain show the highest rigidity based on the data of T_g . Therefore, the chains in cl-HM's network need higher temperature to move together for the healing process. Therefore, based on the analysis of self-healing behavior for the crosslinked polyimine, it is found that the healing temperature range could be tailored by choosing different R and the different type of diamines, which is especially useful for the applications with special requirement in the healing temperature.

The self-healing property was attributed to the reversible reaction between aldehyde groups and amidogen. With the temperature rising, the decrease of crack in this stage was caused by the compression formed at the back of interface. When the temperature continued to increase, the liberated polymer chain could move together and form new imine bonds to connect the polymer chains together and totally heal the crack.

The remolding ability of films was also carried out via hot

compression molding at an elevated temperature. In this process, we use cl-PO-4 as a typical example to illustrate the remolding behaviors. As shown in Fig. 5A, pieces of broken samples were reprocessed at 120 °C for 5 min under a pressure of 10 MPa and a solid polymer film was re-formed. Then the remolded film was cut into pieces again, and the remolding process was repeated two times. Fig. 5B shows the mechanical properties of the remolded films and it is found that the remolded samples exhibit fairly good mechanical properties even through three generations of recycling. Therefore, the cross-linked polymer films could be reprocessed with maintaining good mechanical properties.

3.5. The degradable ability of polymer

Since imine bonds could be cleaved with the help of water [16], we designed the following process to test the degradable ability of the crosslinked polymer based on imine linkage. The samples of the films about 10 mg were immersed into 10 mL of buffer solution (pH = 1) at room temperature and it was observed that the films were gradually disintegrated after 48 h and a little precipitates were formed in the solution, as shown in Fig. 6A and B. This phenomenon could be explained by the character of the imine bonds which could be hydrolyzed with the presence of water with acid catalysis [23].

In order to further investigate the undissolved substance, ^1H NMR was carried out to characterize the structure of the precipitate. As shown in Fig. 6C, the typical proton signal at 9.87 ppm was observed, which is corresponding to $-\text{CHO}$ from terephthalaldehyde after degradation tests and this result could prove that the $\text{N}=\text{CH}-$ bond has successfully been decomposed into small molecules. Therefore, the polymers have good degradability after immersion in the acidic water in addition with good self-healing and remoldability.

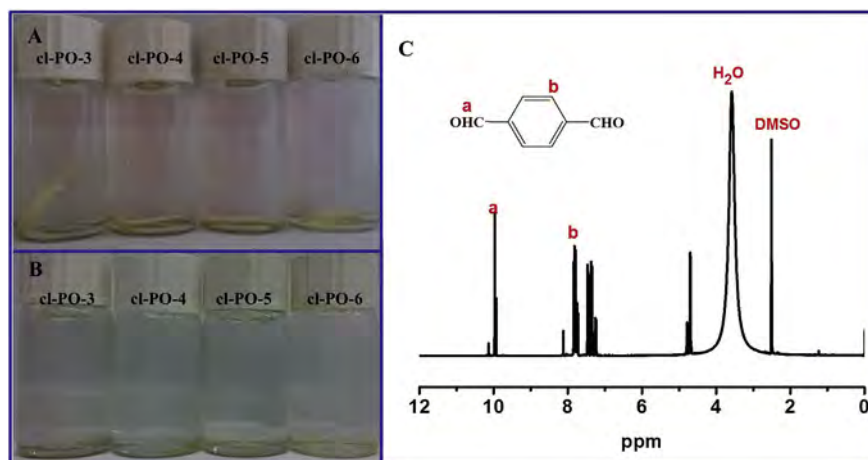


Fig. 6. Acid treatment for the films of cl-PO (A) before and (B) after 48 h, (C) ^1H NMR spectrum of the precipitate after degradation.

4. Conclusions

We prepared a series of cross-linked polymer films based on the Schiff-base reaction using terephthalaldehyde (A_2), tri(2-aminoethyl)amine (B_3) and diamine (B_2) with different chain structures. The obtained films could have tunable mechanical properties by adjusting the cross-linking degree and different B_2 . For example, the tensile strength shows an obvious increase from 4.3 to 165.6 MPa with reduced strain at break from 174.7 to 88.5% as R increases from 3/5.5 to 6/1 for cl-PO series. More importantly, the cross-linked polymer films possessed good self-healing ability and the temperature for self-healing could be tailored by adjusting R and type of diamine. The crosslinked samples could also be thermally remolded to produce new sample without any catalyst. By these two methods, this type of crosslinked polymer could prolong its service life, which provides good solution for the unrecyclable problem about the crosslinked polymer. Besides, the polymer films could be degradable under water with acid catalysis. All in all, this work demonstrated an effective method to produce eco-friendly and recyclable cross-linked polymer films with tunable mechanical properties.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.01.050>.

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