Bio-based Non-Isocyanate Polyurethanes as Recyclable and Intrinsic Self-Healing Coating with Triple Healing Sites

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ABSTRACT: Polymer coatings having high amounts of renewable carbon and self-healing properties are highly sought after in a sustainability perspective. We report here the development of bio-/CO_2 derived non-isocyanate polyurethane (NIPU) coating which is recyclable and healable via three different types of healing mechanisms. These NIPUs contain furan rings in their main-chain which after crosslinking with bis-maleimides, form organogel having thermo-reversible sol-gel transition and solvent-borne coatings with improved properties. Judicial selection of the bismaleimide crosslinker structure enabled us to produce recyclable and intrinsic healable coatings mediated by heat (ther-healing), moisture (moisture-healing) and, more interestingly, under dry condition at room temperature (self-healing). The intrinsic moisture-healing property of NIPU based coatings is unprecedented and is mainly due to the presence of hydroxyl functionalities in NIPU structure. The uniqueness of these crosslinked bio-based NIPU recyclable coatings having triple healing sites present in its structure makes these materials potential for sustainable and functional applications.

The thrust towards sustainable functional polymeric materials is continuing to inspire scientific community to exploit renewable resources and to develop smarter technologies. Non-isocyanate polyurethanes (NIPUs) or polyhydroxyurethanes (PHUs) are an emerging class of polymers[1-5] those can be synthesized via catalyst free, atom-efficient, polyaddition reaction of diamines with bis(cylic carbonate)s at moderate reaction conditions. Unlike traditional polyurethanes (PUs), production of NIPUs via polyaddition of cyclic carbonates and amines avoids the usage of toxic phosgene and isocyanate from its production process.[3, 5] Sustainability aspects of such NIPUs can be further improved by the usage of bio-derived diamines or bis(cylic carbonate) monomers, thus reducing the dependency on fossil reserve.[6-11] There are tremendous interests both in academia and industry to utilize NIPUs for many applications where traditional PUs are used currently as well as to explore new applications. NIPUs are already reported to be applied as adhesives[12, 13] and coatings[14, 15] commercially. However, major challenges[16] of using NIPUs as coating materials include low glass transition temperature and poor mechanical properties owing to their lower molecular weight and presence of hydroxyl groups in their structure

as compared to PUs. Post-crosslinking of NIPU is reported[14, 17] to improve their mechanical and chemical properties as coating materials. Additionally, introduction of dynamic-covalent reversible crosslinking[18, 19] via furan-maleimide Diels-Alder (DA) of NIPUs with furan or disulfide chemistry provides NIPU based materials enabled with intrinsic healing, recyclable, and mendable properties.[12, 20-24] Such intrinsic healable coatings are promising material as smart coatings owing to their ability to be repaired under certain external stimuli such as heat. Currently, all reported crosslinked NIPUs required high temperature for efficient healing and there is a strong interest to develop healable NIPU system at room temperature (RT).

Self-healing coatings with multiple healing sites are rare. We hereby report the synthesis of novel bio-based NIPUs containing furan in their main-chain enabling these NIPU-polymers to crosslink using bis(maleimides) via Diels-Alder (DA) chemistry to produce organogel with thermo-reversible sol-gel transition, recyclable coatings and finally to make intrinsically healable coatings. Judicious selection of bis(maleimides) allowed such crosslinked coatings to have three types of healing sites that enable the coatings to heal triggered by heat, moisture and at room temperature in the absence of moisture.
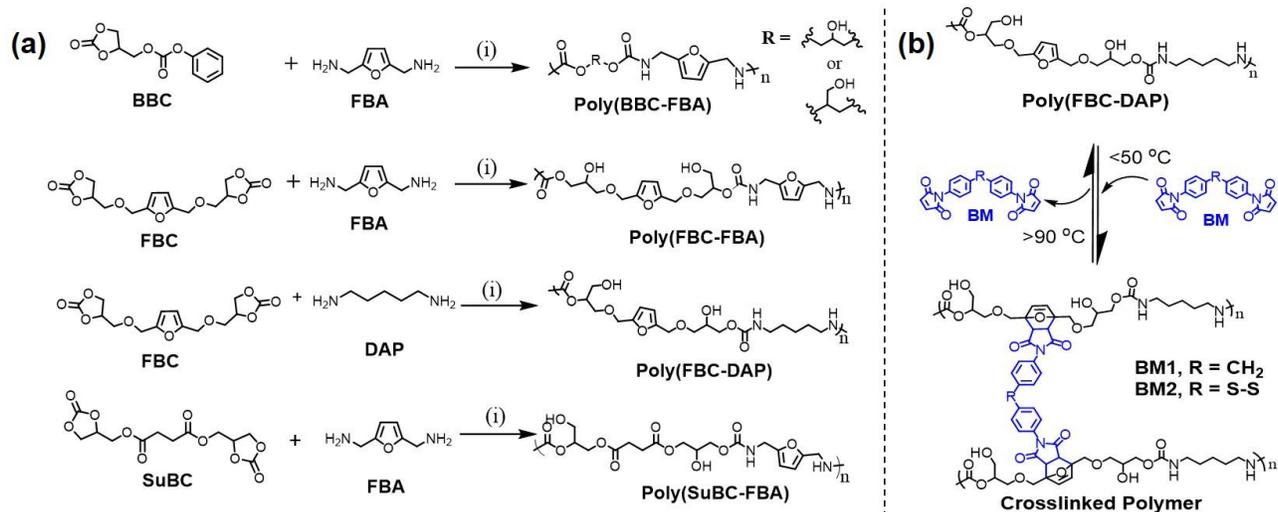
Scheme 1. (a) Synthesis of main-chain furan containing NIPUs by utilizing furan based bis(cyclic carbonate) and diamine. (i) DMF, 70 °C, up to 48 h; (b) Diels-Alder (DA) and retro-Diels-Alder (rDA) thermo-reversible reactions of poly(FBC-DAP) crosslinked with commercial bis-maleimides.

Four different novel NIPUs namely poly(BBC-FBA), poly(FBC-FBA), poly(FBC-DAP), and poly(SuBC-FBA) were synthesized (Scheme 1a) in house according to the literature[25-27] by the reaction of phenoxycarbonyloxymethyl ethylene carbonate (BBC) or hydroxymethylfuran bis(cyclic carbonate) (FBC) or succinate bis(cyclic carbonate) (SuBC) synthesized and commercially available 2,5-bis(aminomethyl)furan (FBA) or 1,5-diaminopentane (DAP) in dimethylformamide (DMF) at 70 °C to yield 71 - 97% of polymers.

^{1}H NMR analysis of purified NIPUs confirmed their chemical structures with no residual monomer, polymerization solvent, and phenol (the by-product from polymerization of BBC) as impurity (Supporting Information, Figure S1). Size Exclusion Chromatography (SEC) analysis showed that the M_n of the NIPUs were in between 4,900 g.mol^{-1} to 10,900 g.mol^{-1} and the dispersity (Đ) were in between 1.5 to 2.0, which are in agreement to the theoretical $\overline{M_n}$ derived from degree of advancement of the reaction (p = 0.923 – 0.972) and degree of polymerization ($\overline{X}_{2n}$ = 13 – 36) determined by ^{1}H NMR (Figure S2-S5, Table S1). The lower degree of polymerizations and low molecular weight characteristics of these polymers were most probably due to the stoichiometric imbalance of monomers, partial conversions in aprotic solvent, where the polymer chain mobility is limited by the presence of strong inter- and intra-chain hydrogen bonding, and possibly due to the side reaction such as amidation of ester bonds as highlighted by Cornile et al.[28]

The bio-/renewable content of the NIPUs synthesized were very high by considering the fact that 2,5-bis(hydroxymethyl)furan, the precursor of FBC, and 2,5-bis(aminomethyl)furan (FBA) can be obtained from 5-hydroxymethylfufural (HMF), a bio-based rigid molecule readily derived from carbohydrates[29-31] and by utilization of

CO$_2$[32, 33]. Other key chemical building blocks e.g. succinic acid, glycerol carbonate and 1,5-diaminopentane (DAP)[29, 34] used for the synthesis of polymers are also known to be derived from different bio-sources.

All NIPUs synthesized showed good thermal stability as observed from thermogravimetric analysis (Supporting Information, Figure S1b). Poly(BBC-FBA), poly(FBC-FBA), poly(FBC-DAP), and poly(SuBC-FBA) showed decomposition temperatures with 5% weight loss under air at 177 °C, 240 °C, 210 °C, and 220 °C respectively. The glass transition temperatures (T$_g$) of poly(BBC-FBA), poly(FBC-FBA), poly(FBC-DAP), and poly(SuBC-FBA) are 40 °C, 38 °C, 15 °C and 33 °C, respectively, as determined by differential scanning calorimetry (Supporting Information, Figure S1c). The highest T$_g$ of poly(BBC-FBA) among all NIPUs could be due to the presence of smaller repeat unit structure that imparts rigidity into the polymer coupled with the higher molecular weight. In contrast, the flexible aliphatic component in the main-chain in poly(FBC-DAP) imparts flexibility to the polymer to bring down T$_g$ below room temperature.

The water absorptions of NIPUs were determined by measuring the weight change of polymers over three days in a humidity chamber (relative humidity >95%). Poly(FBC-DAP) with flexible backbone showed the highest water absorption with weight gain of 29%, followed by 24%, 19%, and 14% found for poly(SuBC-FBA), poly(BBC-FBA), and poly(FBC-FBA), respectively. DSC analysis on moistened NIPUs revealed broaden and lower T$_g$ peaks (Supporting Information, Figure S8). Both poly(FBC-DAP) and poly(SuBC-FBA) showed significant decreases in T$_g$ (up to 18 °C) owing to the absorbed water acting as plasticizer (i.e. hydro-plasticization). In contrast, other NIPUs with more rigid backbone exhibited smaller decrease in T$_g$. In general, most of these polymers are sticky either at RT

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or slightly elevated temperature due to their low T_g and, therefore, needed to be crosslinked to be used as coatings like traditional solvent borne coatings.

Interestingly, due to the presence of furan in their main-chain all these polymers were able to react with bismaleimides (BM) via furan-maleimide Diels-Alder (DA) reaction to yield crosslinked network containing DA adduct (Scheme 1b). Considering thermo-reversible nature of furan-maleimide reaction (i.e. DA and retro-Diels-Alder (rDA)), the mentioned polymers are potential for different interesting class of materials. In the presence of organic solvent, production of such network yielded thermo-reversible self-standing organogel as shown in Figure 1a for poly(BBC-FBA) and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BM1) system. The isolated self-standing organogel was not soluble further in excess DMF or DMSO, where the precursor polymer poly(BBC-FBA) was easily soluble. DA adduct formation by the reaction of poly(BBC-FBA) and BM1 in DMF (84 wt% solvent) at furan:maleimide ratio of 1:0.5 at 50 °C in 18 h was measured in a NMR tube using NMR spectroscopy by measuring the disappearance of maleimide protons (7.09 ppm, 63% conversions) against mesitylene as an internal reference (Supporting Information, Figure S9). The rDA reaction of the same system was confirmed by ^{1}H NMR analysis after heating the organogel at 110 °C for 1 h to yield >82% of the original furan structure and maleimide and in easily flowable solution form. However, this solution again turned into the gel upon heating at 50 °C for 1 h or upon storage at RT overnight. Similar DA and rDA reactions were observed for poly(FBC-FBA), poly(FBC-DAP), and poly(SuBC-FBA) with BM1 under the same conditions, albeit with different rates of reaction (Supporting Information, Figure S10-S16). Time for gelation, crosslink density and gel strength of all these organogels were dependent on furan to BM ratio, type of polymer and BM used, temperature of reaction, and polymer concentration.

Furthermore, when a solution of poly(BBC-FBA) and BM1 was applied on a substrate and dried at 50 °C for 12 h, it produced a crosslinked, hard, uniform, non-tacky, and glossy NIPU coating film. This coating can be applied to different substrates including steel, aluminium, glass and wood (Figure 1b). The mechanical properties of crosslinked dry NIPU coating films were then evaluated for pencil and pendulum (König, oscillation time) hardness and adhesion pull-off strength according to ASTM methods (Supporting Information, Table S2). In general, coating films produced from poly(BBC-FBA) and poly(FBC-FBA) showed higher pencil hardness (up to HB) and pendulum hardness (up to 181 s) than coating films produced from poly(FBC-DAP) and poly(SuBC-FBA) most probably owing to their higher T_g. Interaction of such coating films on aluminium substrate (one of the most difficult substrates to coat) was evaluated by the measurement of pull-off strength. Coating films produced from all NIPUs showed high adhesion strengths (5.70 MPa to 6.11 MPa) on aluminium substrate,

which is attributed to the hydrogen bond interaction of –OH and –OCONH- groups of NIPU to the substrate. This makes such NIPUs an attractive candidate for industrial coating applications.
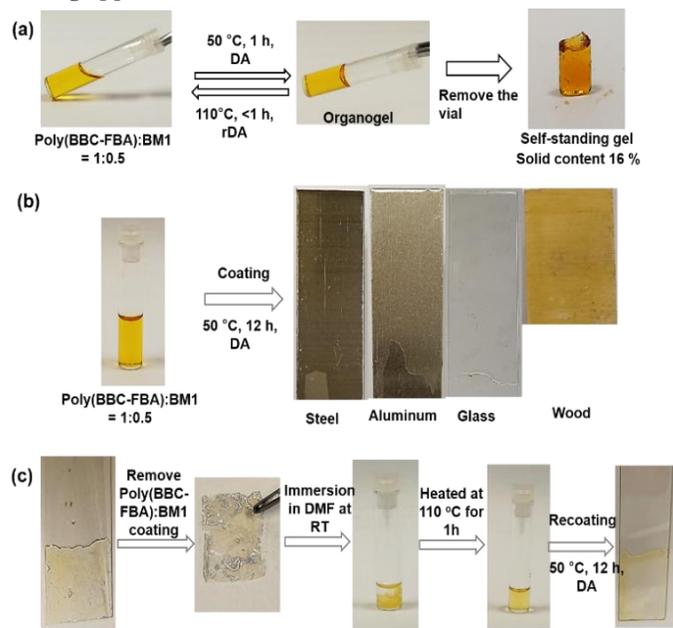

Figure 1. a) Production of poly(BBC-FBA) organogel (in DMF) via DA reaction of NIPU and de-gelation via rDA, b) production of crosslinked NIPU coating on steel, aluminium, glass and wood, c) recycling of crosslinked poly(BBC-FBA) coating via rDA and DA.

The recyclability of such crosslinked dry NIPU coatings was then evaluated by the application of rDA reaction conditions (Figure 1c). A peel off crosslinked NIPU coating film, which was insoluble in any of the organic solvents tested, produced polymer solution after heating at 110 °C for 1 h in DMF. The polymer solution was then applied to recoat the substrate. This process was repeated several times, though the coating films turned darker over time likely due to the oxidation of furan containing polymer chains.

Thermo-healing properties of side-chain and some main-chain furan containing polymers, were reported before.[35-37] Therefore, thermo-healing property of crosslinked coatings produced using our novel main-chain furan containing NIPUs and BM1 was investigated by a scratch test followed by heating (Supporting Information, Scheme S1). A solution of NIPU and BM1 (with furan:maleimide ratio of 1:0.5) was applied on a glass substrate using an applicator followed by drying in an oven at 50 °C for at least 24 h to produce crosslinked, dry, hard, uniform, non-tacky, and glossy NIPU coating films (thickness ~30 μm). The absence of DMF in the coating films after drying was confirmed by the ^{1}HNMR analysis after CDCl$_3$ extraction of dry film. Indeed the damaged (5 μm thick) lines of crosslinked (and dry) NIPU coating film got repaired after heating at 120 °C

for 1 h (Figure 2 and Supporting Information, Figure S17-S18)). This was due to the rDA reaction that produced de-crosslinked coatings followed by the network re-formation upon storage at RT. However, time required for full recovery was slightly dependent on the actual polymer structure used. Coatings produced from poly(FBC-DAP), and poly(SuBC-FBA) were repaired in less than 1 h, whereas crosslinked poly(BBC-FBA) and poly(FBC-FBA) only showed partial recovery at that time. The other possible healing mechanism, say, transcarbomoylation is ruled out here as it requires high temperature as high as 150 °C and often the presence of a catalyst.[24]
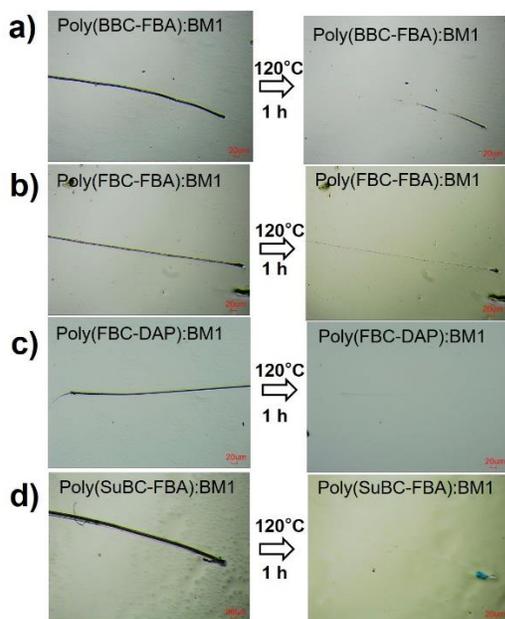

Figure 2. Microscopic images of thermo-healing of scratched crosslinked dry coating films produced from a) poly(BBC-FBA) and b) poly(FBC-FBA), c) poly(FBC-DAP) and d) poly(SuBC-DAP) and BM1 with furan:maleimide ratio of 1:0.5 (applied on glass substrate for better microscopic visibility) at 120 °C.

However, considering real/practical applications, we were always keen to develop coating formulations having self-healing property under mild temperature for an infinite number of cycles without requiring any healing agents. To our surprise, we have observed that highly crosslinked dry coating films (crosslink densities of 2.57 to 3.94 mmol/cm³ as determined from previously reported method on NIPU,[38] see Supporting Information for more details) produced from poly(FBC-DAP) and poly(SuBC-FBA) using BM1 as crosslinker (furan:maleimide = 1:0.5) exhibited intrinsic self-healing property to recover fully at 23 °C within 1 h (Figure 3, Figure S21 and see video in Supporting Information). Further detailed investigation however confirmed that crosslinked poly(FBC-DAP) and poly(SuBC-FBA) films healed at RT only in the presence of

higher humidity (>70 %). These crosslinked coatings did not heal at RT when kept under dry argon condition for 7 days (Supporting Information, Figure S19).
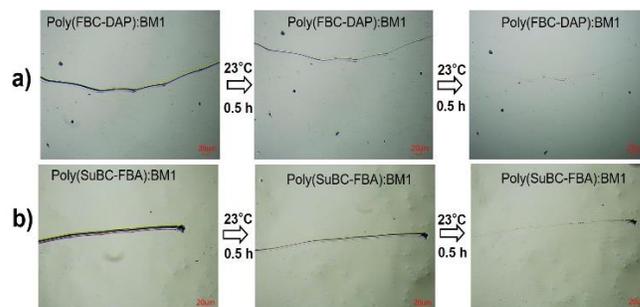

Figure 3. Microscopic images of moisture-healing of scratched crosslinked dry coating films produced from a) poly(FBC-DAP) and b) poly(SuBC-FBA) and BM1 with furan:maleimide ratio of 1:0.5 (applied on glass substrate) at room temperature and at relative humidity of 70-90% (the scattered black dots are deliberately placed for easy tracking of healing scratched sites).

To our knowledge this is the first report of moisture-healing property of NIPU based coatings. Intrinsic moisture-healing property of polyelectrolytes[39, 40], boronic-ester polymers[41, 42] and some polyurethane-polyureas[43, 44] were only very recently reported. Moisture-healing property of these NIPU based coatings was due to the presence of different polar groups especially –OH groups in its structure. This is a characteristically different property of NIPUs in comparison to traditional polyurethanes (PUs). Absorption of moisture by NIPUs from air interrupts hydrogen bonding within the polymer network leading to increase in flexibility of the polymer network and increased molecular motion and diffusion which could also be called as hydroplasticization. The decrease in pendulum hardness from $105 \pm 3s$ to $76 \pm 4s$ was found for poly(FBC-DAP)-BM1 coating after exposure of the coating with high humidity (RH>95%) for 2 days (Supporting Information, Table S2). In contrast, poly(BBC-FBA) and poly(FBC-FBA) with high T_g showed minimal decrease in hardness and no self-healing after the exposure to moisture for 2 days (Supporting Information, Figure S20). This was supported by a moisture absorption test for crosslinked NIPUs in a humid chamber (RH > 95%). It was found that crosslinked poly(FBC-DAP) showed high weight change (8.4%) as compared to crosslinked poly(BBC-FBA) (0.5%) after 1 week. This could be attributed to the presence of longer flexible units in between each crosslinking point for poly(FBC-DAP) and poly(SuBC-FBA) based coatings in comparison to coatings produced from poly(BBC-FBA) and poly(FBC-FBA). This moisture effect on T_g in crosslinked poly(FBC-DAP) with BM2 was observed by DSC (Supporting Information, Figure S24). The T_g of dry crosslinked polymer was observed at around 53 °C and it decreased to about 23 °C after moistened. The decrease in T_g allowed

higher polymer chain mobility that resulted in more efficient healing of polymer.

In order to prove the role of hydroxyl groups in the moisture-healing of crosslinked NIPUs, we functionalized the hydroxyl groups in poly(FBC-DAP) with acetyl groups or palmitic groups (Supporting Information, Figure S6-S7) and subsequently crosslinked it with BM1. The NIPU functionalized with acetyl groups (T_g = 14 °C) showed a marginal moisture-healing of coating with a decrease in scratch line width from 4 μm to 2 μm (Supporting Information, Figure S22) as the carbonyl of acetyl group could still be able to form hydrogen bonding with water. On the other hand, no healing was observed for NIPU with longer and more hydrophobic palmitic groups (Supporting Information, Figure S22), which minimize the hydrogen bonding between polymer chains and water.

Finally, in an effort to impart moisture-independent intrinsic self-healing property to our NIPU based coatings, aromatic disulfide-containing bismaleimide, bis(p-maleimidophenyl) disulfide (BM2) was selected as crosslinker. Though dynamic disulfide exchange reaction was exploited previously to create self-healing polymers[24, 26, 45-51], usage of BM2 for main-chain furan containing NIPUs imparts dual dynamic covalent reactions i.e. thermo-reversible furan-maleimide and –S-S– disulfide exchange reaction. Therefore, finally highly crosslinked coating film (crosslink density of 2.54 mmol/cm³) produced using poly(FBC-DAP) and BM2 showed healing at low humidity conditions (RH<24%) as described in Figure S23. However, in a complete dry condition, under dry argon atmosphere, this crosslinked coating film showed slow healing as demonstrated in Figure 4. The healing efficiency of aromatic disulfides-containing polymer is known to be highly dependent on the main-chain structure as reported previously.[46] Further studies are on-going to optimize the polymer structure for improved self-healing efficiency at RT. In this case, the crosslinked coating produced using poly(FBC-DAP) and BM2 crosslinker were able to show three different i.e. thermo-healing and moisture-healing and self-healing properties (Figure 5). This could be used as healable and easily-recyclable thermoset materials.
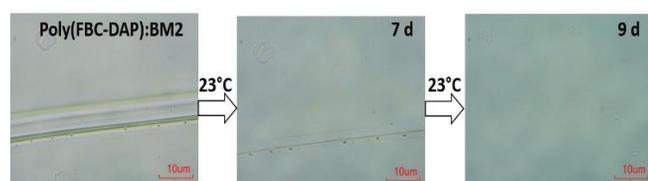

Figure 4. High magnification microscopic images of self-healing of scratched crosslinked dry coating films produced from poly(FBC-DAP) and BM2 with furan:maleimide ratio of 1:0.5 after 7 days and 9 days at RT under argon atmosphere.
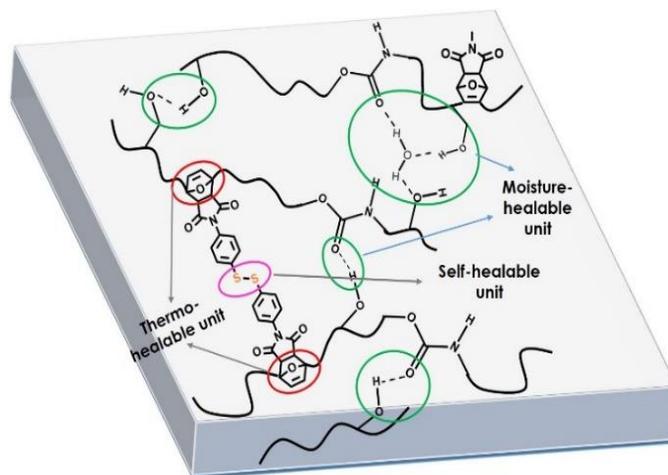

Figure 5. Functionalities enabling crosslinked NIPU coatings thermo-healable, moisture- healable and self- healable (ester bond are omitted from the polymer structure to impart simplicity).

In conclusion, we have developed novel main-chain furan containing bio-based NIPUs and crosslinked materials therefrom with recyclability and self-healing properties[26, 52]. Judicial selection of bismaleimides structure enabled us to produce intrinsic healable coatings, where healing is mediated by heat, moisture and self-healing even at room temperature under dry conditions. Hydro-plasticization and the moisture-healing property of NIPU based coatings are reported for the first time and these properties of NIPU are mainly due to the presence of hydroxyl groups in its structure, which makes NIPU characteristically different from the traditional polyurethanes (PUs). Effect of T_g and chain-flexibility on healing performance is also demonstrated by detailed investigation. These results highlight the value of combining different dynamic reversible crosslinking approaches to create functional coating materials.

ASSOCIATED CONTENT

Supporting Information. Experimental details, ^{1}H NMR spectra of polymers, DSC plots of polymers, microscopic images on thermo-healing and self-healing of crosslinked NIPU coatings. This material is available free of charge via the internet at http://pubs.acs.org.

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P.S. Choong has prepared the polymers, performed characterization with all the analysis, and drafted the manuscript. N.X.

Chong and E.K.W. Tam have synthesized monomers and polymers. A.M. Seayad, J. Seayad, and S. Jana have provided intellectual input and manuscript preparation. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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