IDEA

Innovations Deserving Exploratory Analysis Programs

A Novel Durable, Healable, and Conveniently Removable Pavement Marking Material Suitable for Both Permanent and Temporary Marking Uses

Final Report for
NCHRP IDEA Project 219

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NCHRP IDEA Program Final Report

IDEA Project NCHRP-219

Prepared for

The NCHRP IDEA Program
Transportation Research Board
National Academies of Sciences, Engineering, and Medicine

by

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Table of Contents

Acknowledgments

1

EXECUTIVE SUMMARY

A self-healing and conveniently removable pavement marking material (PMM) was developed that can be used for both permanent and temporary applications. Self-healing allows for an increased marking life expectancy compared to existing epoxy systems. Additionally, the convenient removability allows for the marking to be used as a temporary marking for construction projects without damaging the concrete during marking removal when frequently changing traffic diversions. The markings can then be easily removed without employing energy-intensive, expensive, and polluting removal techniques. Using a durable epoxy system also ensures that the marking lasts longer than other temporary marking options and does not fail before construction concludes.

The material is a novel amine crosslinker for a two-part epoxy system with vitrimer properties and a designed sensitivity to mild acidic solutions. Vitrimers have high material strength and longevity like thermosetting polymers due to their similar crosslinked molecular structure, but the links (i.e. chemical bonds) within a vitrimer molecular network are dynamic (instead of permanent). This allows them to become active and undergo dynamic bond-exchange reactions at elevated temperatures rendering the material shape change, repairability, and malleability, all characteristics of a thermoplastic polymer (**FIGURE 1**). In this project, vitrimer properties are introduced by reacting a dialdehyde with a polyamine epoxy curing agent to form reversible imine (N=C) Schiff-base bonds within the epoxy curing agent. The crosslinker also utilizes hydrophilic polyamine compounds. The hydrophilic segments are resistant to water due to the highly crosslinked network but allow for acidic solutions to sever the imine bonds causing swelling of the marking. The water and acid sensitivity were tailored using different hydrophilic polyamines and other non-hydrophilic polyamines resulting in five Schiff-base diamines (SBDAs). The innovation consists of enhanced SBDA catalysts that can cure the resin component of existing epoxy pavement marking materials.
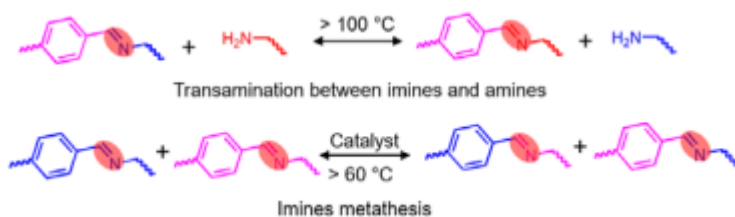
FIGURE 1. Repairing of the epoxy vitrimer marking material based on transamination and imine metathesis.

Curing commercial epoxy resin with any SBDA alone results in a soft, slow-curing product. This is because epoxy PMMs are complex mixtures of a variety of additives to improve curing time, lower the curing temperature, and increase the hardness of the marking. The optimal PMM formulation was developed by investigating the effect that trimethylolpropane triacrylate (TMPTA), 4-nonylphenol (NP), adducting the crosslinker, adjusting the amine-epoxy stoichiometric ratio, and mixing SBDAs and other commercial amines had on curing time and final hardness for this novel crosslinking system. The amine hydrogen equivalent weight (AHEW) was also used to determine the theoretical optimal combination of SBDAs 3, 4, and 5 with commercial diethylenetriamine (DETA). The AHEW value was brought low enough to ensure sufficient no-track curing time while not going too low to diminish the self-healing and convenient removability properties, resulting in a substantial increase in the curing rate.

To verify that the chosen optimal formulations met the standard specifications for construction required by the Minnesota Department of Transportation (MnDOT), the hardness, no-track curing time, and abrasion resistance were tested (**FIGURE 2**). To validate the material tests, all test methods were also conducted with a commercial epoxy PMM to serve as a comparison to the novel formulations. The final novel formulations had slower curing rates compared to the commercial epoxy tested but solidified in under the 30-minute no-track

time requirement and had a final hardness after 3 days of curing similar to the commercial epoxy and greater than the required 80 Shore D hardness. The abrasion resistance of the novel formulations was also comparable to the commercial epoxy and well below the 80 mg/1000 cycles required of epoxy PMMs to meet specifications.
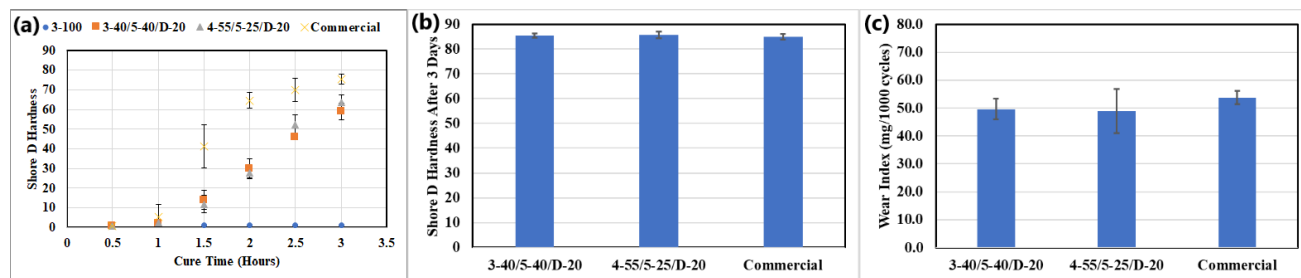
FIGURE 2. (a) Curing rate of the first formulation (3-100), two optimized formulations (3-40/5-40/D-20 & 4-55/5-25/D-20), and the commercial epoxy PMM. (b) Measured hardness after curing 3 days and (c) the wear index of the optimized formulations and commercial epoxy PMM.

Tests were done to confirm the formulation maintained self-healing and convenient removability properties while maintaining resistance to water solubility (**FIGURE 3a, 3b, & 3c**). A significant reduction in the width of micro-cuts in the material was observed when the material was heated to 50°C for 25 minutes. The higher durability formulations resisted water and alkaline solutions but still showed significant softening in a dilute acidic solution. The novel material was applied to the low-volume MnROAD test track (**FIGURE 3d**). The material was also applied to the MnROAD section of I-94 (**FIGURE 3e**). In both MnROAD tests, the novel formulations performed similarly to the commercial formulation after 6 and 4 months of traffic, respectively.
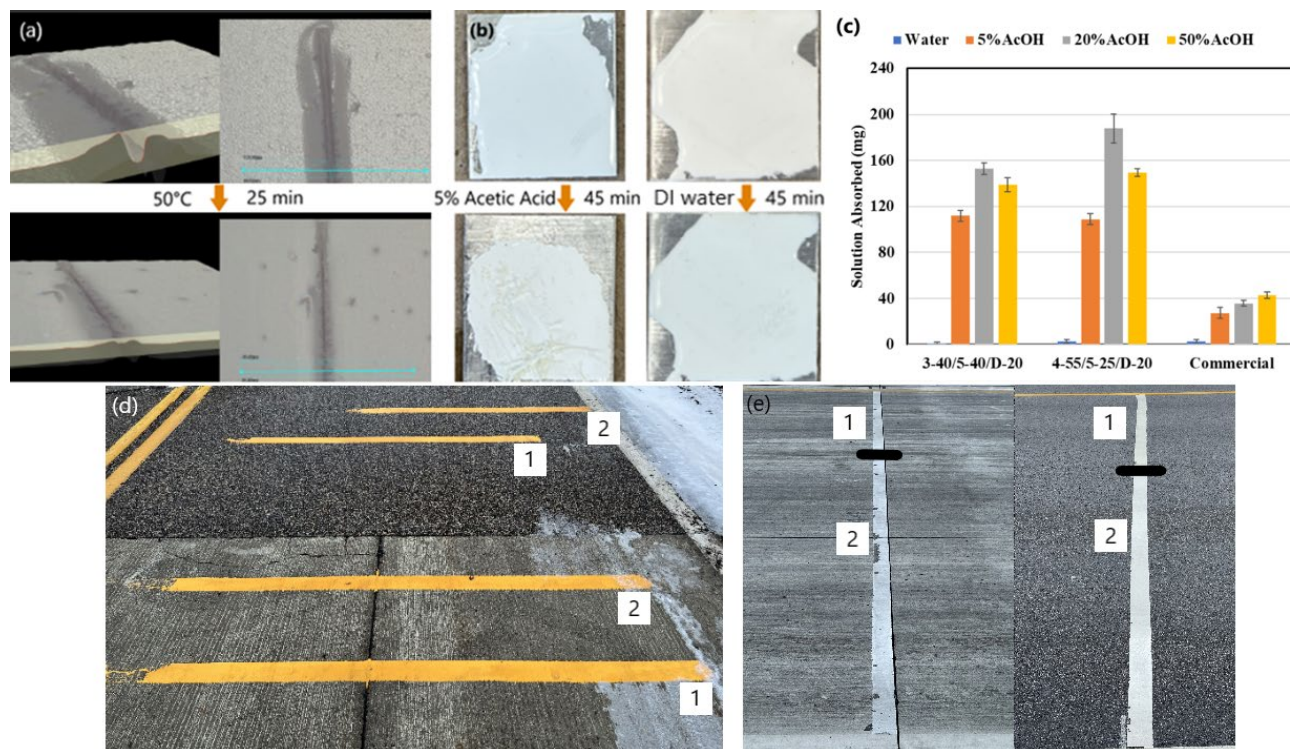
FIGURE 3. (a) Self-healing at 50°C for 25 minutes, (b) removability under 5% acetic acid and DI water after 45 minutes, (c) acetic acid solution and water absorbed after 10 minutes, (d) the material applied to the MnROAD test track after 6 months and (e) the material applied to I-94 after 4 months, where 1 is novel and 2 is commercial.

2

IDEA PRODUCT

PRODUCT CAPABILITIES & SOCIETAL NEEDS

To bridge the technical gaps and meet societal needs, this project is aimed to develop a novel thermally reversible epoxy marking material based on vitrimer chemistry. Specifically, the new epoxy vitrimer system will function as a durable marking material under normal service conditions, exhibit self-healing capability at an adjustable elevated temperature, and show easy removability when subjected to a mild acidic condition. Conventional epoxy marking materials, which are based on polymer crosslinking chemistry, possess high durability but no repairability & poor removability due to their permanently crosslinked structure.

Permanent pavement markings are applied on pavement surfaces for long-term use, whereas temporary markings are used in work zones or other situations to alter normal traffic patterns for a relatively short amount of time. Oftentimes, permanent markings need to be changed or completely removed due to new roadway traffic restrictions or constructions. Many marking removal techniques, including grinding and blasting, are time-consuming and expensive, and usually produce large amounts of noise and dust. The operations often scar the pavement and leave ghost markings on the pavement, which may cause confusion to motorists and lead to traffic accidents. The selective removability of the developed marking material does not need these harsh removal techniques.

Under normal use, pavement markings, temporary and permanent alike, gradually chip away in a continuous, irreversible fashion, eventually necessitating marking replacement. There is no practical and economical method available today to heal the markings when the damages (scratch/cut/dent) on the markings are still insignificant. Such treatment, if available, should markedly extend the lifespan of pavement markings. Therefore, a new long-lasting, healable/repairable, permanent marking material that, when necessary, can also be conveniently removed without scarring the pavement is highly desirable.

To avoid confusion for motorists, old pavement markings need to be removed as soon as possible when new roadway conditions or restrictions are applied. Failure to do so can cause serious traffic accidents. Several marking removal techniques are used, including grinding, high-pressure water jet, hot compressed air/oxygen burning, hydro-blasting, and shot & sand blasting. A survey to study nationwide state DOTs' experience with marking removal shows that grinding is the most used method (7), which is mainly due to its relatively high speed and low cost, despite the ghost stripes left on the damaged pavement by the grinding.

The performance and cost of the different marking removal techniques were reviewed by Cho et al (7). The removal tests were conducted on temporary markings such as traffic paints and temporary tapes. Therefore, the performance is expected to deteriorate, and the cost is expected to increase if permanent marking materials are used as in the tests. It is clear from **TABLE 1** that, even for the temporary markings, the cost of removal is comparable to, in many cases much higher than the cost of marking installation. In addition, almost all the methods involve using brutal force

TABLE 1. Cost of the different marking removal techniques.

Removal	Type	Marking	Marking Size	Cost per Linear Foot
Chemicals	Concrete	Water Based	12 mils	$0.33
	Concrete	Solvent Based	20 mils	$0.41
	Asphalt	Water Based	20 mils	$0.83
	Asphalt	Solvent Based	12 mils	$0.48
Water Blasting	Concrete	Water Based	20 mils	$2.14
	Concrete	Solvent Based	12 mils	$4.39
	Asphalt	Water Based	12 mils	$0.58
	Asphalt	Solvent Based	20 mils	$5.86
	Asphalt	Tape	4 inch	$0.09
Dry Ice Blasting	Concrete	Water Based	12 mils	$3.37
	Concrete	Solvent Based	20 mils	$26.00
	Concrete	Tape	4 inch	$0.06
	Asphalt	Water Based	20 mils	$0.22
	Asphalt	Solvent Based	12 mils	$0.73
Shot Blasting	Concrete	Water Based	20 mils	$0.12
	Concrete	Solvent Based	12 mils	$15.95
	Asphalt	Water Based	12 mils	$3.47
	Asphalt	Solvent Based	20 mils	$0.55
	Asphalt	Tape	4 inch	$0.02
Scarfier	Concrete	Water Based	12 mils	$0.19
Grinding	Concrete	Solvent Based	20 mils	$0.15
Heat Torch	Concrete	Tape	4 inch	$0.11
Grinding	Asphalt	Water Based	12 mils	$0.58
PCD	Asphalt	Solvent Based	20 mills	$0.80
Scarfier	Asphalt	Tape	4 inch	$3.25

Source: Y. Cho, K. Kabassi, Jae-Ho Pyeon, Effectiveness Study on Temporary Pavement Marking Removals Methods, The Charles W. Durham School of Architectural Engineering & Construction, June 2011.

or harsh conditions for good removal results, which inevitably causes pavement damage and environmental/human health concerns.

CONCEPT AND INNOVATION

The repairability/healability of the epoxy vitrimer is achieved through a unique property of vitrimers. Vitrimers resemble conventional thermosetting polymers in terms of their crosslinked molecular structure which imparts the material high strength and longevity. Unlike the conventional ones, the links (i.e. chemical bonds) within a vitrimer molecular network are dynamic (instead of permanent) and they become active and undergo dynamic bond-exchange reactions at elevated temperatures, rendering the material shape change, repairability, and malleability – characteristics of a thermoplastic polymer.

In this project, the dynamic bonds were introduced into the epoxy vitrimer by simply reacting a dialdehyde with a polyamine epoxy curing agent. The imine linkages formed are dynamic bonds that impart repairability/healability to the material. To achieve marking removability, hydrophilic polyamine compounds were used as the primary curing agent. Upon curing, the hydrophilic segments in the highly crosslinked network structure do not markedly alter the water absorption of the marking under normal conditions but can greatly increase water imbibition under acidic conditions. In the latter case, the marking will swell significantly and its bonding to the pavement will be dramatically reduced, resulting in easy removal. Increased ease of removal allows for the epoxy vitrimer to be used for both permanent/durable and temporary markings. The intrinsic properties of epoxy and the added self-repairability are expected to impart this new marking material high durability. In case the marking on the pavement is no longer needed, a simple acidic spray can be applied to loosen the marking from the pavement for removal.

Commercial epoxies, which are usually emulsified bisphenol A epoxies or bisphenol F epoxies (**FIGURE 4a**), were selected. Jeffamine (**FIGURE 4b**) will be used as the major curing agent to react with epoxy at room temperature. Both epoxy resins and Jeffamines are commercially available at relatively low costs. After curing, the hydrophilic Jeffamine segments become less sensitive to water due to the crosslinked structure but can still be greatly influenced by acidic solutions. By varying the hydrophobic epoxy/hydrophilic curing agent mass ratio, the acidic solution sensitivity and hence the removability of the marking can be manipulated to achieve an optimal level. **FIGURE 4c** shows the formation of the reversible imine bonds. **FIGURE 5** demonstrates the reversibility and transfer of chemical bonds at an elevated temperature allowing for the material to flow.
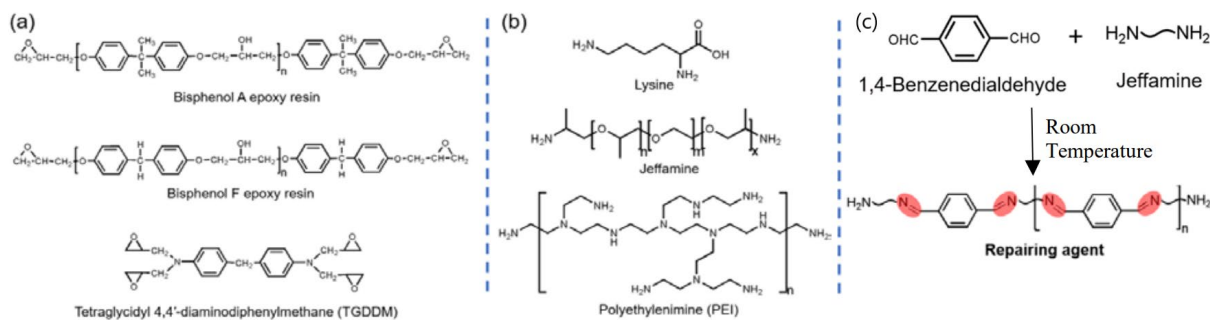

FIGURE 4. Chemical structures of commercial (a) epoxy resins and (b) amines. (c) Direct blending of 1,4-benzenediadehyde with Jeffamine to produce the dynamically exchangeable imine bonds that impart self-repairability to the epoxy vitrimer.
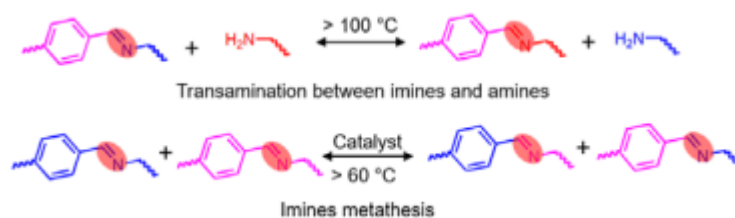

FIGURE 5. Repairing of the epoxy vitrimer marking material based on transamination and imine metathesis.

LIFE-CYCLE COST ANALYSIS

Four main comparisons between the PMM systems are made in this life-cycle analysis. The first two are comparing the novel epoxy PMM and the commercial epoxy PMM. The performance is considered, including self-healing, abrasion resistance, hardness, curing rate, and convenient removability. The costs of the chemicals used to synthesize the two materials are the second thing considered. The second and third comparisons made are the difference in life-cycle costs between the novel PMM when used as both a permanent and temporary marking compared to commercially used PMMs for both permanent and temporary use. When used as a permanent PMM, the novel epoxy fills the same role as the commercial epoxy so past studies on road scenarios where it is beneficial to use the more durable epoxy PMMs over latex paints can be referenced. When looking at its use as a temporary PMM, the cost of the material, the cost of removal, and the scarring of the pavement were considered.

Performance of Epoxy PMM

The major contributing factors to the performance of the commercial and novel epoxy PMM include self-healing, abrasion resistance, hardness, curing rate, and being conveniently removable (**TABLE 2**). The self-healing properties of the novel PMM are controlled by vitrimer properties, however, both epoxy PMMs experienced relatively minor self-healing when heated above the glass transition temperature (T_g) of the materials. This resulted in similar healing between the two at lower temperatures (~50°C). The abrasion resistance and hardness were also the same between the commercial and novel formulations. The curing rate of the novel PMM is within the requirements for epoxy systems but is still slower than that of the commercial system. For this reason, newly applied markings will need to be coned off for longer to prevent traffic from damaging the coatings. In road tests done so far, both epoxy PMMs experienced a concrete failure resulting in material being removed signifying adequate adhesion to road surfaces. The novel PMM is conveniently removable using acetic acid to soften the coating while the commercial PMM requires more energy to remove from the pavement.

TABLE 2. Property differences between the novel and commercial epoxy PMMs.

	Novel Epoxy PMM	**Commercial Epoxy PMM**
Self-Healing	Vitrimer and T_g Self-Healing at Elevated Temperatures	T_g Self-Healing at Elevated Temperatures
Abrasion Resistance and Hardness	Good Abrasion Resistance and Hardness	Good Abrasion Resistance and Hardness
Curing Rate	Slower Curing Rate	Good Curing Rate
Road Tests (Adhesion)	Good Adhesion to Road Surfaces	Good Adhesion to Road Surfaces
Removability	Softens and Removable using Low Concentration Acetic Acid	Requires Grinding, Scarification, or Water Blasting

Formulation of Epoxy PMM

Another main difference is the formulation. The novel epoxy PMM utilizes a new crosslinker with the existing epoxy resin component of the two-part system. The novel Schiff-base diamine (SBDA) crosslinkers synthesized for this product are not commercially available for purchase but can be synthesized using commercially available chemicals. The percentages of each constitutive chemical that each SBDA is composed of are tabulated in **TABLE 3**. The SBDAs were chemically synthesized in a solvent-free system under vacuum at 80 °C for 3 hours. This process is similar enough to the process for manufacturing the commercial crosslinker that this cost was not considered in calculating the total cost of each SBDA.

TABLE 3. Chemicals used in the synthesis of the SBDAs.

	Chemical	Moles	Molecular Mass	Weight	Weight Percent
SBDA 3	Jeffamine D-230	2 mol	230.00 g/mol	460.00 g	31.61%
	Terephthalaldehyde	3 mol	134.13 g/mol	402.39 g	27.65%
	Jeffamine EDR-148	4 mol	148.20 g/mol	592.80 g	40.74%
SBDA 4	Jeffamine D-230	2 mol	230.00 g/mol	460.00 g	39.69%
	Terephthalaldehyde	3 mol	134.13 g/mol	402.39 g	34.72%
	1,3-Diaminopropane	4 mol	74.125 g/mol	296.50 g	25.58%
SBDA 5	Terephthalaldehyde	1 mol	134.13 g/mol	134.13 g	39.40%
	Diethylenetriamine	2 mol	103.17 g/mol	206.34 g	60.60%

The standard epoxy road marking is 12 mils thick and 4 inches wide which requires approximately 13 gallons of material total per mile (2). This is used to calculate the weight of each chemical required per mile of pavement markings.

The chemical prices were obtained from the largest quantity of chemicals purchasable from laboratory-scale chemical suppliers. Certain chemicals are only purchasable in smaller amounts and are much more expensive compared to the cost of bulk purchasing these chemicals would be. The price of the proprietary resin used in the commercial epoxy PMM could be estimated by looking at the manufacturing of a similar resin from literature, but the price of the possible base chemicals varies enough that the price was taken as the average of the other materials.

To adjust for the lack of prices for bulk materials, the scaling cost of the material is estimated using the bulk prices of similar chemicals. A distinction that must be made between the chemicals is the difference in bulk scaling between metal salts (TiO_2) and organic compounds (all other chemicals) (3). Least squares regression was used to fit pricing data on chemicals that had bulk prices available, and the resulting parameters were averaged to find the bulk discount when ordering a metric ton of each chemical. The bulk cost per kilogram and the cost of material per mile were then calculated for the two novel formulations and the commercial formulation (**TABLES 4, 5, & 6**).

TABLE 4. Total adjusted bulk cost per mile for the 3-40/5-40/D20 novel epoxy PMM.

Novel Epoxy PMM (3-40/5-40/D20)	Weight Per Mile (1.24 g/cm³)	Lab Quantity for Purchase	Cost Per kg	Bulk Discount	Bulk Cost Per kg	Bulk Cost Per Mile
DETA	4.36 kg	15.28kg	$33.70	12.71%	$29.42	$128.26
Jeffamine-D230	1.25 kg	0.474kg	$308.02	44.85%	$169.88	$212.34
Terephthalaldehyde	2.65 kg	0.5kg	$330.00	44.06%	$184.59	$489.16
Jeffamine EDR-148	1.61 kg	4.99kg	$252.51	19.74%	$202.67	$326.30
BADGE	30.30 kg	0.25kg	$160.00	55.28%	$71.55	$2,167.93
4-Nonylphenol	5.31 kg	0.1kg	$570.00	74.12%	$147.49	$783.20

	TiO2	7.77 kg	525kg	$21.15	23.08%	$16.27	$126.41
	TMPTA	7.77 kg	0.5kg	$199.00	44.06%	$111.31	$864.89
						Total	$5,098.49

TABLE 5. Total adjusted bulk cost per mile for the 4-55/5-25/D-20 novel epoxy PMM.

Novel Epoxy PMM (4-55/5-25/D-20)	Weight Per Mile (1.24 g/cm³)	Lab Quantity	Cost Per kg	Bulk Discount	Bulk Cost Per kg	Bulk Cost Per Mile
DETA	3.47 kg	15.28kg	$33.70	13.67%	$29.09	$100.95
Jeffamine-D230	2.16 kg	0.474kg	$308.02	45.81%	$166.91	$360.52
Terephthalaldehyde	2.86 kg	0.5kg	$330.00	45.03%	$181.41	$518.83
1,3-Diaminopropane	1.39 kg	45kg	$63.78	8.77%	$58.18	$80.88
BADGE	30.20 kg	0.25kg	$160.00	56.25%	$70.01	$2,114.24
4-Nonylphenol	5.30 kg	0.1kg	$570.00	75.09%	$142.00	$752.63
TiO2	7.75 kg	525kg	$21.15	23.08%	$16.27	$126.09
TMPTA	7.75 kg	0.5kg	$199.00	45.03%	$109.40	$847.81
					Total	$4,901.95

TABLE 6. Total adjusted bulk cost per mile for the commercial epoxy PMM.

Commercial Epoxy PMM	Weight Per Mile (1.23 g/cm³)	Lab Quantity	Cost Per kg	Bulk Discount	Bulk Cost Per kg	Cost Per Mile
DETA	7.20 kg	15.28kg	$33.70	13.67	$29.09	$209.47
BPA	1.20 kg	2kg	$55.00	28.45	$39.35	$47.22
Proprietary Resin	1.20 kg	-	$173.14	-	$67.69	$81.22
BADGE	29.10 kg	0.25kg	$160.00	56.25	$70.01	$2,037.23
4-Nonylphenol	7.42 kg	0.1kg	$570.00	75.09	$142.00	$1,053.68
TiO2	7.21 kg	525kg	$21.15	23.08	$16.27	$117.30
TMPTA	7.21 kg	0.5kg	$199.00	45.03	$109.40	$788.74
					Total	$4,334.86

Bulk purchasing of raw materials from lab-scale suppliers is still more expensive than the cost of commercial epoxy PMMs from a PMM supplier. A cost report done for the Minnesota Local Road Research Board estimated that the cost of a commercial epoxy PMM system to be $1,822-$2,733 per mile for a minimum distance of 3.75 miles, which is half the cost of the raw materials estimated for commercial epoxy in this report (4). Using the percent difference in the raw material costs calculated in the previous three tables of the novel

PMMs compared to the commercial PMM, an adjusted cost can be determined for the novel PMMs based on the cost of the commercial PMM from the PMM suppliers (**TABLE 7**).

TABLE 7. The price difference between novel epoxies and commercial epoxies.

Formulation	Bulk Lab-Scale Cost Per Mile	Cost Compared to Commercial	Adjusted Cost Per Mile	Adjusted Cost Per Linear Foot
3-40/5-40/D20	$5,098.49	+17.6%	$2,143 - $3,214	$0.41 - $0.61
4-55/5-25/D-20	$4,901.95	+13.1%	$2,061 - $3,091	$0.40 - $0.59
Commercial	$4,334.86	-	$1,822 - $2,733	$0.35 - $0.52

Permanent PMM

When acting as a permanent PMM, the novel formulations would behave the same as a commercial formulation. Work that has already been done to compare epoxy PMM systems to other permanent PMM systems can be used. The types of permanent PMM systems are solvent-based paints, thermoplastics, thermosets, and preformed tapes. The major differences between these systems are their cost and durability (**TABLE 8**). Prices for the different PMMs were determined based on bulk purchases from various PMM suppliers. The cost used for the novel epoxy is the range of prices for the two formulations calculated in the previous section. Prices were adjusted for inflation to May 2022 USD using the Consumer Price Index.

TABLE 8. Cost and durability of permanent PMMs (4).

	Estimated Cost Per Linear Foot	Estimated Life of the Marking (High Traffic)	Estimated Life of the Marking (Low Traffic)
Latex	$0.05 - $0.08	9 months	3 years
Alkyd	$0.05 - $0.08	9 months	3 years
Mid-Durable Paint	$0.14 - $0.17	1 year	3.9 years
Epoxy	$0.35 - $0.52	4 years	4 years
Novel Epoxy	$0.40 - $0.61	4 years	4 years
Tape	$2.59 - $4.57	4 years	8 years
Preformed Thermoplastic	N/A	3 years	6 years

Durable PMMs like mid-durable paint and epoxy are typically used in higher-traffic areas because they need to be replaced less often (**TABLE 9**). Epoxies are especially great for this purpose because a minimal increase in wear is seen as the intensity of traffic increases. So even in high-traffic areas, markings will not need to be replaced more often. In Minnesota, 90% of PMMs used are latex paints in rural low-traffic areas, while 8% are epoxies used in high-traffic areas in and around cities (5). The novel epoxies' increased adhesion to pavement surfaces may further decrease the number of times either formulation needs to be replaced in a 12-year cycle. The annual cost per linear foot is calculated using the higher cost in the range of the estimated cost per linear foot.

TABLE 9. Comparison between epoxy and other PMMs for high volume traffic greater than 10,000 annual average daily traffic (AADT).

	Annual Costs Per Linear Foot	Times Replaced in 12-Year Cycle
Latex	$0.11	16
Alkyd	$0.11	16
Mid-Durable Paint	$0.17	12
Epoxy	$0.13	3
Novel Epoxy	$0.15	< 3 (expected)
Tape	$1.14	3
Preformed Thermoplastic	N/A	4

Temporary PMM

There are PMMs intended specifically for temporary use like temporary tape and temporary raised pavement markers (TRPMs) or additionally permanent PMMs can be used with associated additional removal costs and road damage (**TABLE 10**). The major differences between these systems are the material cost, the cost to remove, and the damage to the pavement. TRPMs are most often used to supplement a line marking for nighttime visibility in construction zones but can be used to simulate a solid line (2). The cost of temporary markings can oftentimes exceed the cost of permanent markings for the added benefit of not damaging new concrete immediately after application. Since temporary markings need to be able to be removed without damaging the surface, they can fail prematurely before construction is complete due to poor adhesion. Using material for temporary pavement markings that costs a similar price and retains the durability of a permanent PMM and retains the durability of an epoxy PMM is greatly beneficial. This is one of the main goals of the novel PMM.

TABLE 10. Cost and pavement damage of temporary PMMs (4).

	Estimated Cost Per Linear Foot	Pavement Damage
Latex	$0.05 - $0.11	Scarification
Epoxy	$0.35 - $0.52	Scarification
Novel Epoxy	$0.40 - $0.61	Minimal
Temporary Tape	$1.90 - $2.59	Minimal
TRPM (2 & 6)	$0.30 - $0.60	Minimal

Conclusion

A life-cycle analysis was conducted to determine the viability of these novel materials in replacing currently existing systems. The similar durability of the novel formulations with additional convenient removability and self-healing properties highlights the materials' potential role as both permanent and temporary marking. Material cost analysis based on scaling up lab-scale suppliers to bulk supplier prices shows that the novel material would potentially cost 13-17% more than current commercial two-part epoxy markings. The novel materials use as permanent markings could potentially decrease the frequency of replacing the markings, saving money from removal and application costs, and decreasing the frequency of lane restrictions on roadways. Use as a temporary marking would reduce the damage to roadways caused by removing permeant marking materials

or reduce costs compared to expensive temporary marking materials. The use of large amounts of acetic acid to remove the coating was also investigated, revealing that acetic acid readily degrades into non-toxic byproducts in the soil, air, and water. Acetic acid was revealed to harm the compressive strength of concrete, but over a much larger time frame than would occur in commercial applications.

INVESTIGATION

CROSSLINKER SYNTHESIS AND CHARACTERIZATION

First Synthesis Trial

All the crosslinkers synthesized are Schiff base diamines (SBDA). In the first synthesis trial, Jeffamine EDR-148 (JA) and terephthalaldehyde (TPA) were used for the synthesis. The reaction mechanism is given in **SCHEME 1**. Briefly, JA and TPA were charged into a flask with different molar ratios and mixed thoroughly. JA was added in excess to consume TPA completely and promote the reaction. After 3h of reaction under 60 °C, the obtained liquid contained both excessive JA and SBDA. The SBDA synthesized by this route was found to gel and solidify after a short period of storage, possibly due to SBDA crystallization. This behavior makes it unsuitable for use in pavement marking because a much longer storage time is required in the industry.
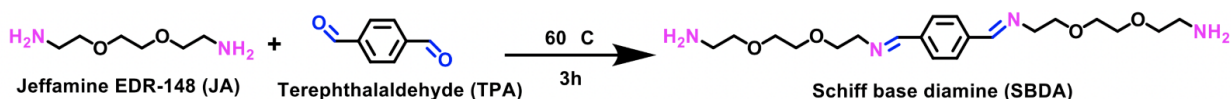
SCHEME 1. Synthesis of the SBDA crosslinker using JA and TPA.

Second Synthesis Trial

In the synthesis second trial, isophorone diamine (IPDA) was used to replace JA in the first trial to synthesize SBDA (**SCHEME 2**). IPDA was reacted with TPA at different molar ratios in an ethanol medium under 60 °C for 24 h. The crude product was rotary evaporated to remove the solvent after the reaction. According to the molar ratio of IPDA/TPA, the products were named IPDA2-TPA1, IPDA3-TPA1, and IPDA4-TPA1, respectively. The excessive IPDA in the latter two products functioned as a reactive diluent for the SBDA, so the apparent viscosity of the products follows the order of IPDA2-TPA1 > IPDA3-TPA1 > IPDA4-TPA1 (**SCHEME 2**, right). **FIGURE 6** shows the Fourier transform infrared spectrometry (FTIR) and nuclear magnetic resonance (NMR) results of the SBDA products. Taking IPDA3-TPA1 as an example, both the FTIR (**FIGURE 1a**) and NMR (**FIGURE 6b**) spectra indicated the consumption of –CHO and the appearance of the imine bonds (N=C), confirming the insertion of the Schiff base structure into the new amine crosslinkers. IPDA2-TPA1, IPDA3-TPA1, and IPDA4-TPA1 all displayed similar spectral characteristics (**FIGURES 6c & 6d**), suggesting that similar products were produced under different reactant molar ratios.
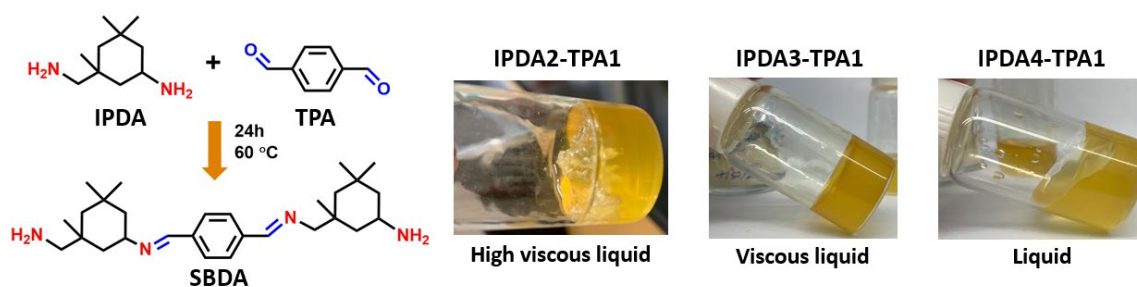
SCHEME 2. Synthesis of the SBDA crosslinker using IPDA and TPA (left) and the synthesized products showing different viscosities under various reactant ratios (right).
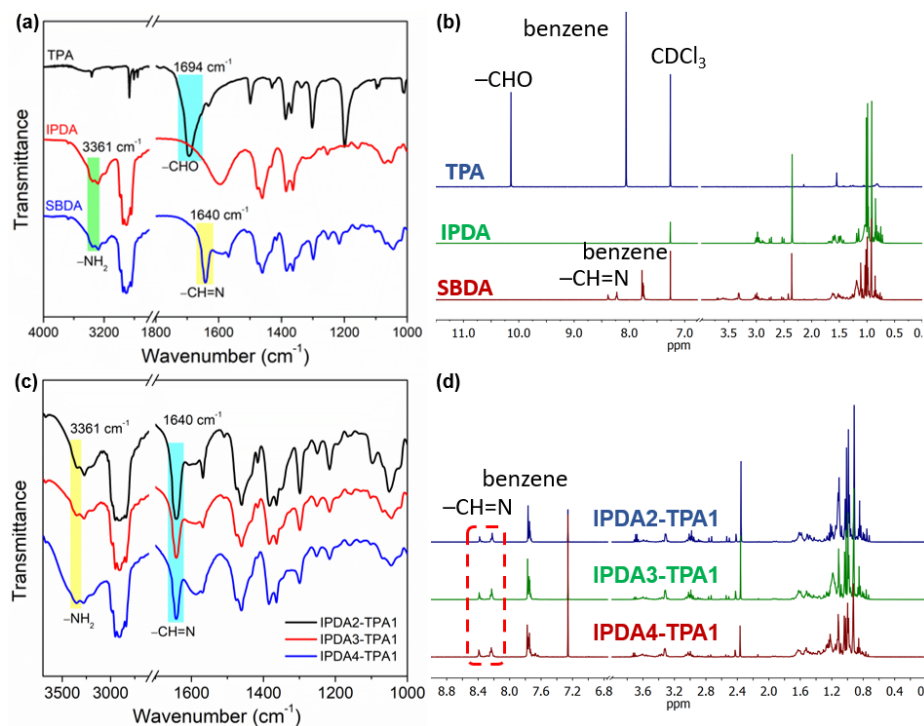
FIGURE 6. (a) FTIR and (b) ^{1}H NMR spectra of TPA, IPDA, and SBDA; (c) FTIR and (d) ^{1}H NMR spectra of SBDAs prepared with different molar ratios of IPDA to TPA.

The SBDA synthesized using IPDA and TPA was used to cure two resins. First, IPDA3-TPA1 was used as an amine-type crosslinker to cure a commercial epoxy resin (DER331) with a stoichiometric ratio of the active hydrogen of the amine group to the epoxy group at 1:1. In the second attempt, IPDA3-TPA1 was reacted with pentaerythritol triacrylate (PETA) with a stoichiometric ratio of the amine group to the acrylate at 1:1. It should be pointed out that the reaction between SBDA and PETA is a Michael addition. The crosslinking reactions of IPDA3-TPA1 with both DER331 and PETA were monitored using differential scanning calorimetry (DSC) scanning from 0 to 170 °C at a heating rate of 5 °C/min (**FIGURE 7**). The reaction of SBDA and PETA could start at a sub-ambient temperature and peak at 56.5 °C. Therefore, the curing of PETA with SBDA is achievable at room temperature if sufficient curing time is allowed. In contrast, the reaction of SBDA and DER331 started to take place at an elevated temperature and the reaction peaked at ~99 °C. A transparent SBDA-PETA film was obtained after the sample was left at room temperature for 24 h, while a transparent SBDA-DER331 film was produced via hot pressing at 80 °C for 1 h, 100 °C for 2 h, and 120 °C for 2 h. Both films appeared to be stiff plastics.
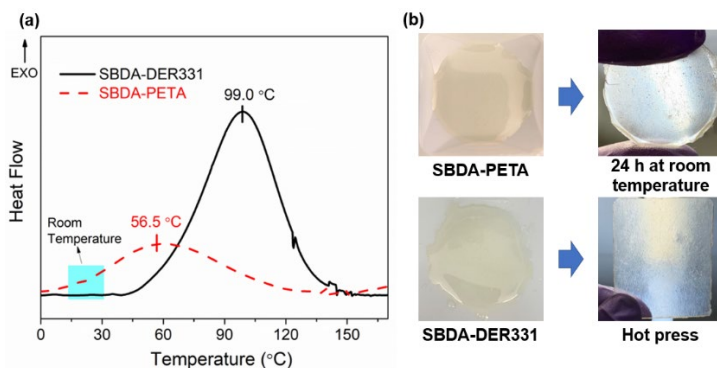

FIGURE 7. (a) DSC thermograms showing the curing process of SBDA-DER331 & SBDA-PETA. (b) Cured samples of SBDA-DER331 & SBDA-PETA under different curing conditions.

13

Third Synthesis Trial

In the third synthesis trial, although IPDA/TPA-based SBDA could remain in its liquid state during storage and could crosslink the epoxy resin, its alicyclic amine had a relatively low reactivity with epoxy at room temperature and therefore required high-temperature curing. To overcome this drawback, two types of Jeffamines, EDR-148 and D-230, were used together to synthesize a mixed Jeffamine-based SBDA in one pot. The reaction mechanism is illustrated in **SCHEME 3**.
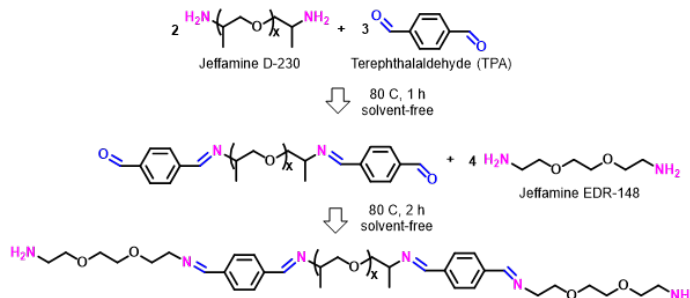
SCHEME 3. Synthetic route of a mixed Jeffamine-based SBDA (D230/EDR148 SBDA).

First, D-230 was reacted with TPA at a molar ratio of 2:3 at 80 °C for 1 h. Subsequently, the residual aldehyde groups were consumed by EDR-148 in the next 2 h of the reaction (**Scheme 3**). The one-pot reaction was a solvent-free system under vacuum, and the molar ratio of amine and aldehyde was 2:1. Different from the second trial, the synthesis of the mixed amine-based SBDA did not need a solvent, and the water produced by the reaction was removed by vacuum to ensure the formation of imine bonds. Also in the previous work, an excessive amount of amine was added as a reactive diluent to manipulate the viscosity of the products. The new mixed Jeffamine-based SBDA was a liquid and its mixture with the viscous epoxy DER331 had a viscosity suitable for processing. Therefore, the excessive amine was not needed and therefore a smaller number of permanent linkages between amine and epoxy were formed during curing, which could enhance the repairability and removability of the marking. **FIGURE 8a** shows the ^{1}H NMR results of the SBDA products. The ratio of peak areas of imine bonds (N=C) and benzene groups was at 1:2, confirming the formation of the Schiff base structure in the new amine curing agents. As shown in **FIGURE 8b**, the mixed amine-based SBDA can be mixed with epoxy DER331 homogenously and transferred into mold easily.
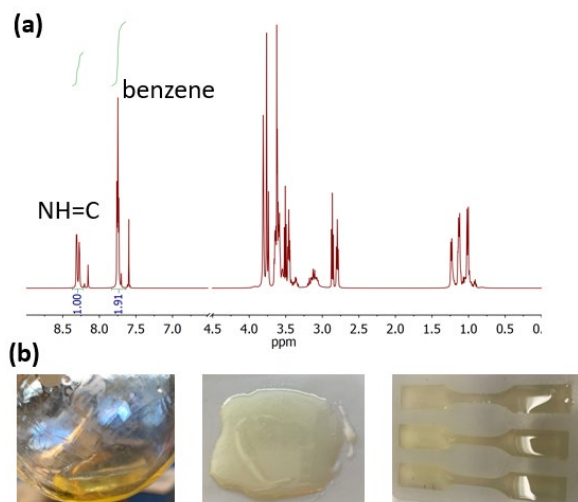

FIGURE 8. (a) ^{1}H NMR spectra of D-230/EDR-148 SBDA; (b) D-230/EDR-148 SBDA, homogenous D-230/EDR-148 SBDA-epoxy DER331 resin, and molded D-230/EDR-148 SBDA-epoxy DER331 test specimens.

The new SBDA was used to cure the epoxy resin. **FIGURE 9a** shows the DSC curing thermograms of epoxy DER331 with the two Jeffamines separately and with the mixed Jeffamine-based SBDA from 0 to 200 °C at a heating rate of 5 °C/min. The curing with Jeffamine D-230 started at a temperature of ~20 °C above room temperature due to the lack of high reactive primary amine in the crosslinking agent. In contrast, the curing with Jeffamine EDR started at room temperature and the reaction proceeded faster. By combining these two Jeffamines, the mixed Jessamine-derived SBDA had a moderate curing reactivity. It could cure epoxy at room temperature, and the incorporation of D-230 chains prevents the resulting SBDA from crystallization. **FIGURE 9b** shows the results of stress relaxation for the epoxies cured by the mixed Jeffamine-based SBDA and by the Jeffamine EDR-148-based SBDA. The relaxation of the former was much faster than that of the latter (1334 s vs 3022 s, when $G(t)/G_0$ reaches $1/e$). This result can be partially attributed to the more flexible chains of D-230 (compared to EDR-148) and a lower crosslinking density of the former. The faster relaxation of the former also indicates its stronger dynamic exchange reactions among the imine bonds.
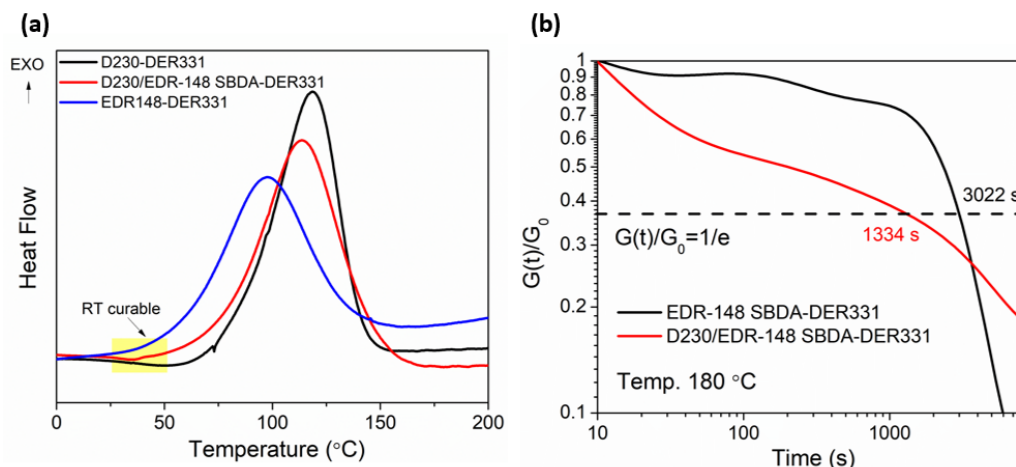

FIGURE 9. (a) DSC thermograms showing the curing process of DER331 epoxy using three crosslinkers and (b) stress relaxation curves of cured epoxies using two different SBDAs.

Fourth Synthesis Trial

In the fourth synthesis trial, Jeffamines EDR-148 was replaced by 1,3-diaminopropane (DAP) in the synthesis of SBDA (**SCHEME 4**). The reason for this replacement is that the mixed Jeffamine-based SBDA was later found to be too water sensitive due to the polyethylene glycol-based EDR-148 (see more discussion in the marking removability section). The new SBDA could be stored in its liquid state for a long time and can be easily mixed with commercial epoxy resin to make pavement markings. The viscosity of the product could be tailored by varying the molar ratio between Jeffamine D-230 and DAP (**SCHEME 4, right**).
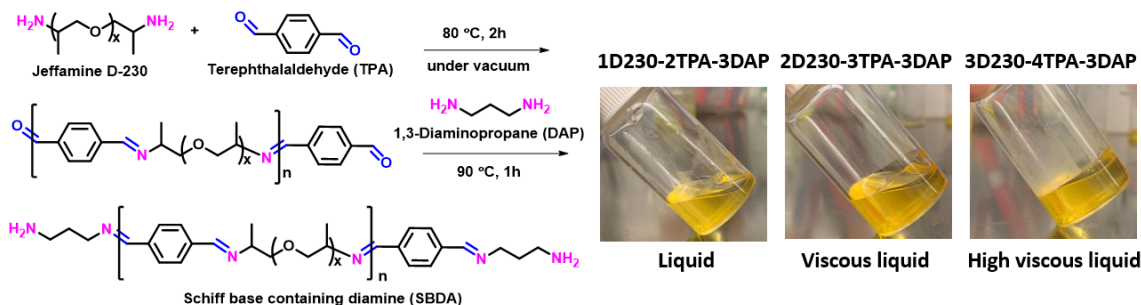
SCHEME 4. Synthesis of the SBDA crosslinker using Jeffamine D-230, TPA, and DAP (left). The synthesized products show different viscosities under various reactant ratios (right).

FIGURE 10 shows the FTIR and NMR results of the new SBDA. In the first step, the aldehyde groups (C=O at 1698 cm^{-1}) of TPA reacted with the amine groups and formed imine bonds (C=N at 1639 cm^{-1}). With

the increasing amount of Jeffamine D-230, the intensity of the C=N peak increased while the intensity of the C=O bond from TPA decreased, indicating the formation of the imine bond and the consumption of the aldehyde. After the second step reaction with DAP, all aldehyde groups were consumed as shown in the FTIR and NMR spectra.
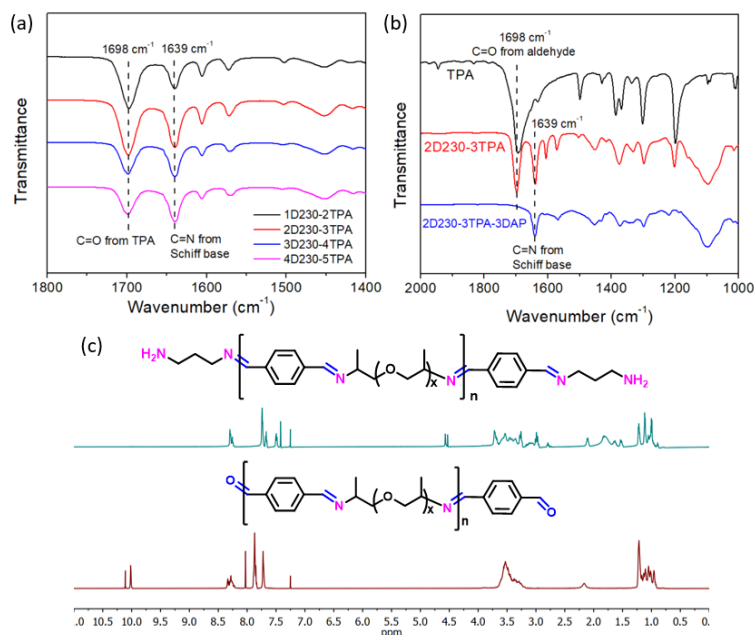

FIGURE 10. FTIR spectra of (a) intermediate product from step 1 with different ratios of Jeffamine D-230 to TPA and (b) TPA, 2D230-3TPA, and 2D230-3TPA-3DAP. (c) ^{1}H NMR of 2D230-3TPA and 2D230-3TPA-3DAP.

The new SBDA crosslinker was used to cure commercial epoxy resin DER331 with a stoichiometric ratio of the active hydrogen of the amine group to the epoxy group at 1:1. The crosslinking reactions of DER331 with both 1D230-2TPA-3DAP and 2D230-3TPA-3DAP were monitored by DSC scanning from 0 to 180 ºC at a heating rate of 5 ºC/min (**FIGURE 11a**). The reaction of SBDA and DER331 could start at a sub-ambient temperature and peak at ~100-110 °C. Therefore, the curing of DER331 with SBDA is achievable at room temperature if sufficient curing time is allowed. A rigid and transparent SBDA-DER331 film was obtained after the sample was left at room temperature for 3 days (**Figure 11b**). To test the inherent properties of SBDA-DER331, the fully cured samples were prepared with a three-stage hot press process: 90 °C for 1 h, 120 °C for 1 h, and 140 °C for 2 h.
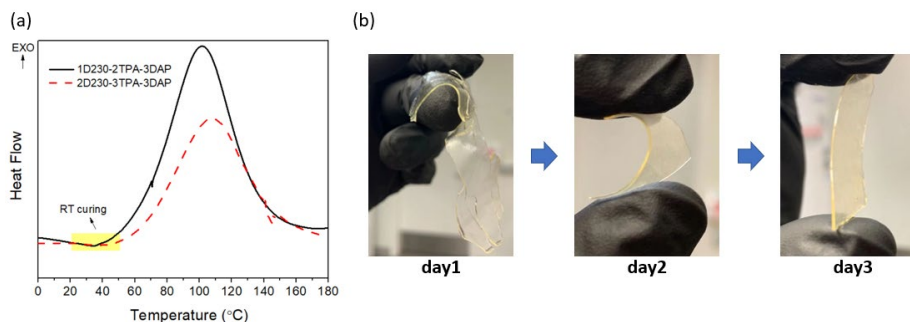

FIGURE 11. (a) DSC thermograms of non-isothermal curing of SBDA-DER331. (b) Samples of SBDA-DER331 cured at room temperature after different curing times.

FIGURE 12 shows the glass transition temperature (T_g) and thermal stability of fully cured SBDA-DER331. The epoxy crosslinked by 1D230-2TPA-3DAP and 2D230-3TPA-3DAP exhibited T_g of 96.5 °C and 80.2 °C,

16

respectively (**FIGURE 12a**). A higher ratio of Jeffamine D-230 in the system resulted in a lower T_g of the cured epoxy due to the Jeffamine's long molecular chain. The thermogravimetric (TGA) curves of the two cured epoxies were similar (**FIGURE 12b**). Both materials showed decent thermal stability below 300 °C. Approximately 20 wt% chars and ashes were left at 800 °C at the end of the test.
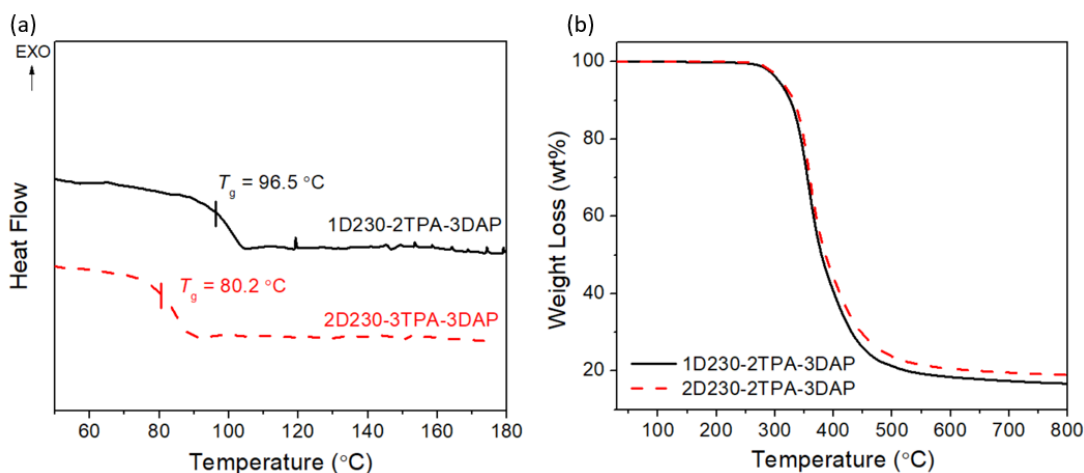

FIGURE 12. (a) DSC curves of the fully cured SBDA-DER331. (b) Thermal stability of SBDA-DER331 characterized from TGA test.

FIGURE 13 shows the tensile properties and thermomechanical properties of fully cured SBDA-DER331. The epoxies cured by both 1D230-2TPA-3DAP and 2D230-3TPA-3DAP displayed decent strength (> 60 MPa). The one cured by 1D230-2TPA-3DAP was tougher with a higher failure strain of 14.6 % (**FIGURE 13a**). It also showed a higher storage modulus (1868.6 MPa) under the service temperature and a higher T_g (107.2 °C) due to its denser network as shown by the dynamic mechanical analysis (DMA) results in **FIGURE 13b**.
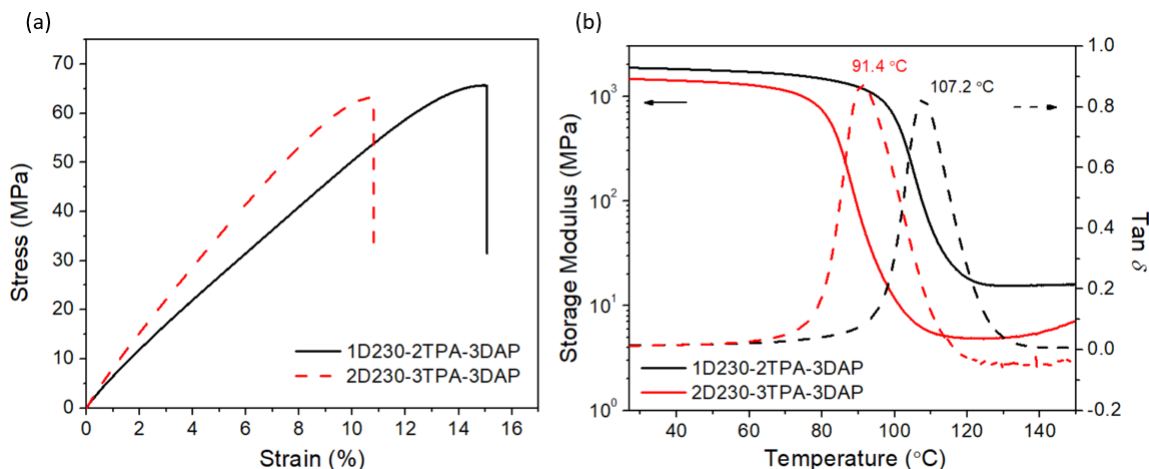
FIGURE 13. (a) Stress-strain curves of SBDA-DER331. (b) Thermomechanical properties of SBDA-DER331 characterized from DMA test.

FIGURE 14 shows the vitrimer properties of the fully cured SBDA-DER331. The relaxation time (τ^*) was determined as the sample relaxed to 1/e of the initial modulus due to dynamic bond exchanges in the network (**FIGURE 14b**). At 150 °C, it took ~5500 s for the epoxy cured by 2D230-3TPA-3DAP to reach 1/e, while the epoxy cured by 2D230-3TPA-3DAP needed more time to relax to 1/e (**FIGURE 14a**). In other words, the SBDA-DER331 pavement marking has good stability under high temperatures. After being immersed in a 20 wt% acetic acid for 3 h, the SBDA-DER331plate sample was partly degraded while it remained unchanged in pure water after the same time (**FIGURE 14c**). Hence, this pavement marking can be easily removable under weak acid conditions.

17

FIGURE 14. (a) Stress relaxation curves of SBDA-DER331. (b) Dynamic bond exchange mechanism of the SBDA-DER331. (c) Degradation of SBDA-DER331 in pure water and 20 wt% acetic acid.

Fifth Synthesis Trial

In the fifth synthesis trial, diethylenetriamine (DETA) and TPA were used for the synthesis in the fifth trial as shown in **SCHEME 5**. DETA was reacted with TPA at a 2 to 1 molar ratio, the product was named DETA2-TPA1. The resulting crosslinker had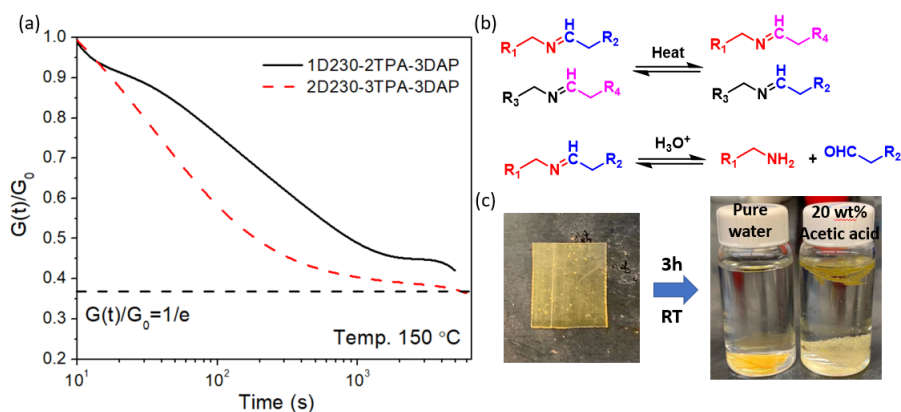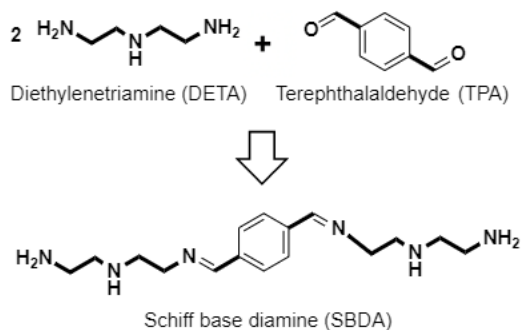 a higher reactivity than all previously synthesized SBDAs but did not contain any Jeffamines to increase the hydrophilicity to improve the convenient removability. The fifth SBDA is viscous but remained in a liquid state for a long time and could be easily mixed with commercial epoxy resins.

SCHEME 5. Synthesis of the fifth SBDA crosslinker using DETA and TPA.

FORMULATION DEVELOPMENT AND OPTIMIZATION

To increase the curing rate, hardness, abrasion resistance, and solvent resistance of the marking material, a formulation that more closely resembled commercial marking materials was developed for the crosslinker and epoxy resin (**TABLES 11 & 12**). The crosslinker consists of an amine mixture with added BADGE to react with 5.53% of the amine functional groups and 4-nonylphenol (NP). The amine mixture is a combination of amine crosslinkers from the third, fourth, and fifth SBDA synthesis trials and a commercial amine DETA. The weight of NP added is twice the weight of the BADGE. The addition of BADGE pre-polymerizes the crosslinker which improves the overall physical properties and allows the epoxy to cure at lower temperatures and higher rates. NP decreases the viscosity of the mixture (facilitating mixing), acts as a hardener, and increases the reactivity of the epoxy. The epoxy resin consists of BADGE, TiO2, trimethylolpropane triacrylate (TMPTA), and a small amount of NP. The TMPTA reacts with the amines in the crosslinker, which helps the epoxy cure at lower temperatures. Enough amine was added to stoichiometrically react with both the epoxy and acrylate functional groups.

TABLE 11. Formulation of the adduct crosslinkers which is dependent on the amine value of the amine mixture.

Amine Mixture	BADGE	NP
Predetermined by the amount of material desired	5.53% Amine Functional Groups	2x BADGE Weight

TABLE 12. Formulation of the epoxy resin. Values in the parentheses are the content ranges given for a commercial pavement marking epoxy resin.

BADGE	TiO2	TMPTA	NP
63.74% (50-75%)	17.85% (10-25%)	17.85% (10-25%)	0.56% (0.1-1%)

The crosslinker is prepared by first heating the SBDAs at 50 °C until liquid if they have crystalized in storage. The crosslinker's ingredients are then measured and mixed using a mechanical mixer at 650 rpm for one minute. The resulting crosslinker does not crystalize at room temperature due to the additives preventing crystallization. The crosslinker is allowed to cure for at least 16 hours at room temperature before being mixed with the epoxy resin. Both the crosslinker and epoxy resin are heated at 50 °C for 20 minutes before mixing, similar to the application process of commercial two-part markings on the pavement. Each of the variables of this formulation, mixing procedure, and application procedure were determined via testing described in the next section.

Pre-polymerization, TMPTA, and DETA Substitution

BADGE was added to pre-polymerize 5.53% of the third SBDA to create an adduct crosslinker to decrease the curing time of the epoxy. The resulting crosslinker was used to cure epoxy resin at 90 °C and had its hardness tested every 10 minutes to determine the degree of cure. The adduct crosslinker solidified 10 minutes quicker than the non-adduct crosslinker and resulted in a harder epoxy after curing at 90 °C for one hour. TMPTA was also added to the epoxy resin to further decrease the time to solidify. This addition solidified the epoxy 10 minutes sooner than just the adduct but also decreased the hardness of the epoxy when curing (**FIGURE 15, left**).

To improve the curing rate and hardness of the epoxy, 10 and 20% of the third SBDA crosslinker were replaced with DETA. The resulting formulations were cured at 90 °C and their hardness was tested every 10 minutes to determine the degree of cure of the epoxy (**FIGURE 15, right**). DETA is a smaller molecule with more amine functional groups, meaning it has a higher amine value than SBDA 3 and results in a more reactive crosslinker. This allows the epoxy to cure faster and produce a greater crosslinking density.

Replacing 10 and 20% of the SBDA with DETA was also tested for the SBDA 3, 4, and 5 epoxies with adduct crosslinkers (**FIGURE 16**). Due to the shorter curing time of the adduct epoxies, these formulations were cured at room temperature and had their hardness measured every 30 minutes for a total of 3 hours. The order of the curing rate for the three crosslinkers is SBDA 3 < SBDA 4 < SBDA 5. This aligns with the amine values of each of the SBDAs, where SBDA 5 has the highest amine value and cures the fastest and SBDA 3 has the lowest amine value and cures the slowest. The SBDA 5 epoxy with 20% DETA had a comparable curing rate to the commercial marking material.
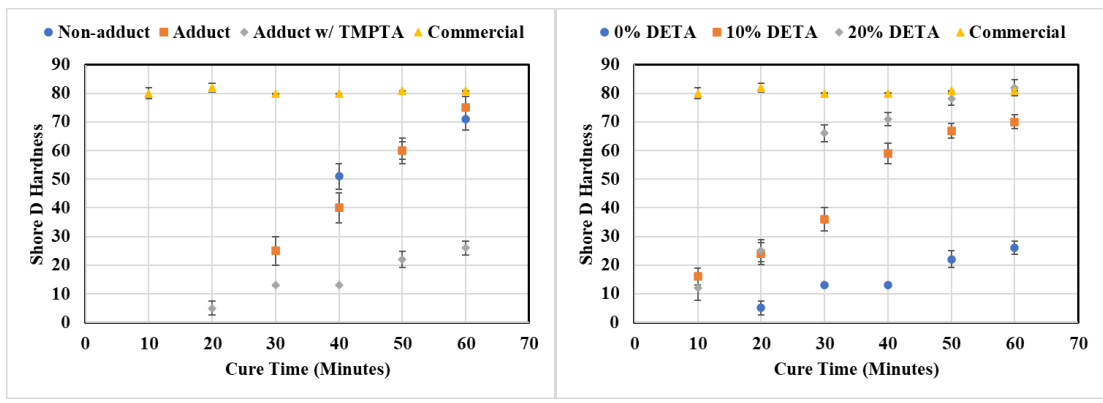
FIGURE 15. (left) 100% third SBDA (3-100) non-adduct, adduct, adduct with TMPTA, and commercial pavement marking material cured at 90 °C. (right) SBDA 3 adduct epoxy with 0%, 10%, and 20% DETA cured at 90 °C.
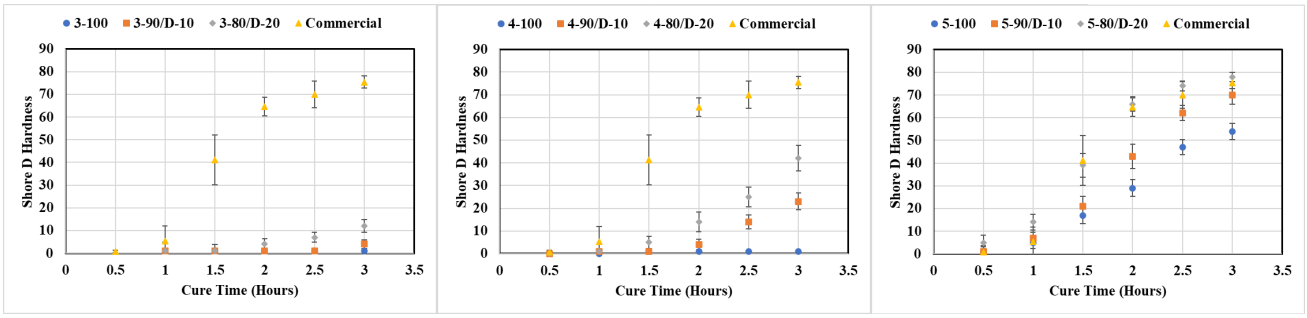

FIGURE 16. (a) SBDA 3, (b) SBDA 4, and (c) SBDA 5 adduct epoxies with 0% DETA (3-100), 10% DETA (3-90 D-10), 20% DETA (3-80 D-20), and full commercial cured at room temperature.

To test the solution resistance of the markings, the material was cured onto 1" square aluminum substrates. The samples were then submerged in various solutions and were scratched with the dull side of a steel blade and had pictures taken before submerging, 10 minutes after submerging, and 45 minutes after submerging. The surface of the coatings was examined to determine the softening due to being submerged in the solution. Three solutions were tested: 5% acetic acid (AcOH), deionized water (DI Water), and sodium hydroxide (NaOH). Due to the nature of the novel imine bonds, the desired condition for the marking would be to swell and soften considerably in AcOH (acidic) and remain durable in DI water (neutral) and NaOH (alkaline) solutions. Due to the qualitative nature of the results from this test, it was just conducted as a preliminary solution resistance test to confirm resistance to DI water and NaOH. Solution absorption and material removal tests are done in the next section, a comprehensive investigation of select formulations and road tests, for a more quantitative comparison between the promising formulations determined in this section and a commercial formulation.

The formulation with TMPTA showed less solution resistance for all three solutions compared to the formulation without TMPTA (**FIGURE 17**). This follows the trend shown in the generally decreased hardness when TMPTA was added. Both 100% SBDA 3 formulations showed considerably more softening in acetic acid when compared to DI water and a NaOH solution.
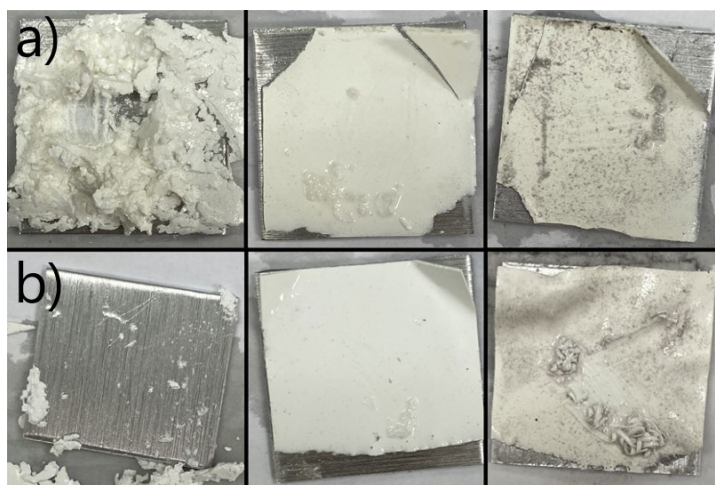
FIGURE 17. SBDA 3 coatings (a) without TMPTA and (b) with TMPTA after being exposed to 5% acetic acid (left), deionized water (middle), and 5% NaOH (right) for 45 minutes.

The adduct formulations softened more when submerged in acetic acid compared to DI water and NaOH solutions. Increasing the amount of DETA in the formulation increased the solution resistance of the coating to all three solutions (**FIGURE 18**).
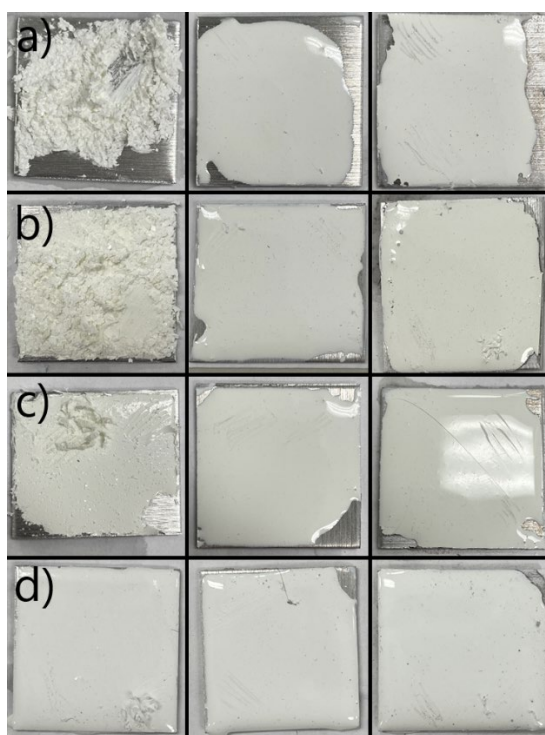
FIGURE 18. SBDA 3 adduct coatings with (a) 100% SBDA 3, (b) 90% SBDA 3 10% DETA, (c) 80% SBDA 3 30% DETA, and (d) a commercial road marking material after being exposed to 5% acetic acid (left), deionized water (middle), and 5% NaOH (right) for 45 minutes.

Even though substituting SBDA 3 for DETA increases the solution resistance of the coatings, the 100% SBDA 3 adduct performed better than the 50% SBDA 3 50% DETA non-adduct (**FIGURE 19**). Pre-polymerizing the crosslinker into a crosslinker adduct improved the solution resistance of the coatings by a greater degree than substituting DETA.

FIGURE 19. SBDA 3 (a) 100% SBDA 3 adduct and (b) 50% SBDA 3 50% DETA non-adduct coatings after being exposed to 5% acetic acid (left), deionized water (middle), and 5% NaOH (right) for 45 minutes.

Mixing Temperature and Amine-Epoxy Ratio

Different mixing temperatures were tested to see their effect on the curing rate of the epoxies. 100% DETA formulations were prepared and the crosslinker and epoxy resin were separately heated simultaneously at the desired temperature for 20 minutes before being mixed. The resulting epoxies were cured at room temperature for 3 hours. Even though all the epox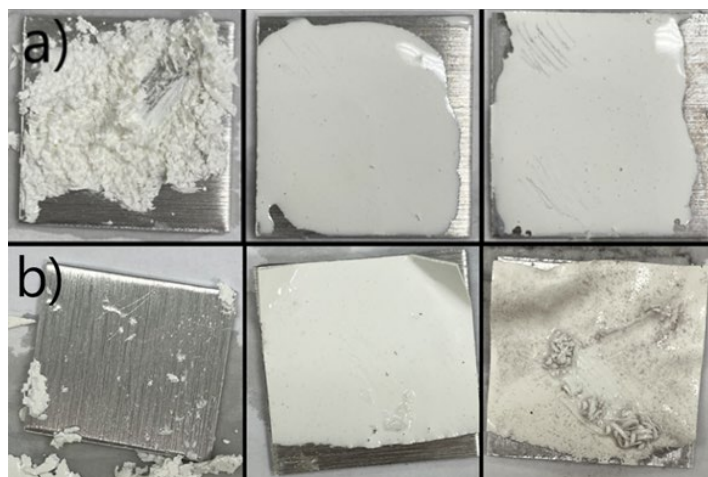ies were cured at room temperature, the initial heating kickstarted the curing rate of the epoxies over the entire 3-hour curing process. This resulted in quicker curing at higher preheating temperatures (**FIGURE 20**).
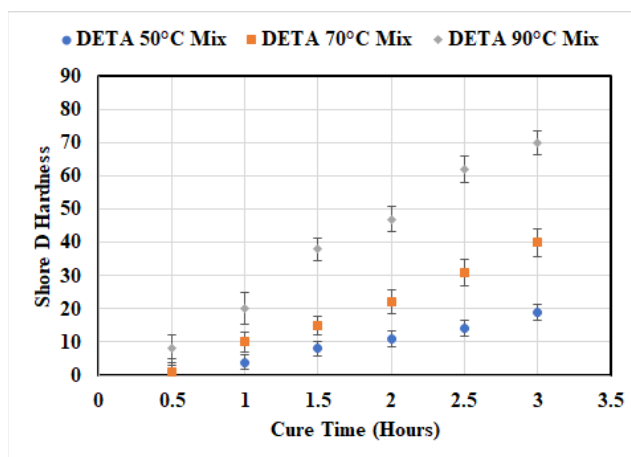
FIGURE 20. 100% DETA adduct epoxies mixed at 50, 70, and 90 °C and cured at room temperature for 3 hours.

The ratio of amine functional groups to epoxy functional groups (amine-epoxy ratio) in the formulations was tested to determine its effect on the curing rate. 100% DETA epoxies with amine-epoxy ratios of 0.96:1 and 1.29:1 were mixed at 90 °C and cured at room temperature for 3 hours. The 0.96:1 amine-epoxy ratio is based on a 1:1 amine-epoxy value formulation without considering the extra epoxy groups brought in when pre-polymerizing the crosslinker. The 1.29:1 amine-epoxy ratio is based on a 1:1 amine-epoxy ratio where the epoxy groups from the pre-polymer are considered as well as the extra amine added to react with the acrylic functional groups in the TMPTA in a 1:1 ratio. The resulting 1.29:1 amine-epoxy ratio epoxy cured quicker than the 0.96:1 amine-epoxy ratio epoxy (**FIGURE 21**).
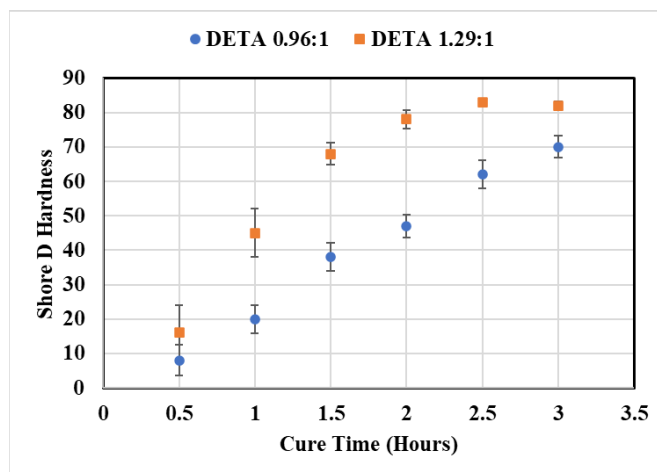
FIGURE 21. 100% DETA adduct epoxies with amine-epoxy ratios of 0.96:1 and 1.29:1 mixed at 90 °C and cured at room temperature for 3 hours.

The effect that the amine-epoxy ratio had on epoxies was also tested in an SBDA-containing epoxy formulation containing 40% SBDA 3, 40% SBDA 5, and 20% DETA (3-40 5-40 D-20). That formulation was prepared with 0.96:1 and 1.29:1 amine-epoxy ratios, mixed at 50 °C, and cured at room temperature for 3 hours. The results agreed with the 100% DETA epoxies. The 1.29:1 amine-epoxy ratio epoxy cured quicker than the 0.96:1 amine-epoxy ratio epoxy (**FIGURE 22**).
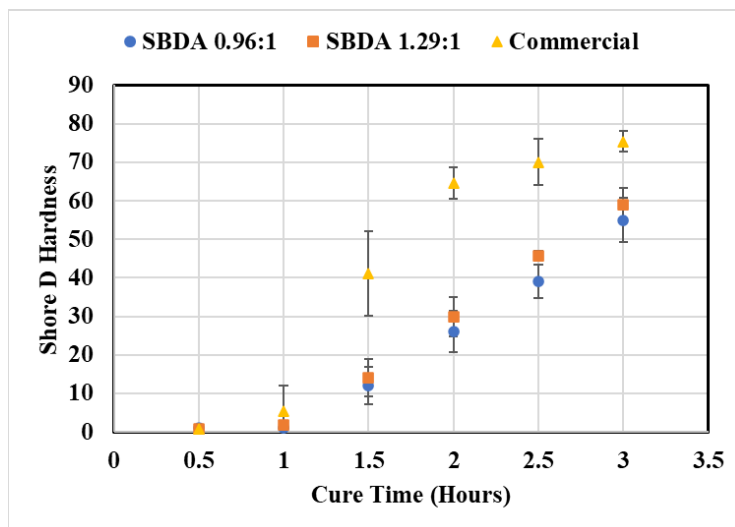
FIGURE 22. 3-40/5-40/D-20 epoxies with amine-epoxy ratios of 0.96:1 and 1.29:1 mixed at 50 °C and cured at room temperature for 3 hours.

Mixing SBDAs and DETA

Up to this point, all tests were done with the SBDA synthesized in the third synthesis trial (SBDA 3). Before mixing the various SBDAs, they are characterized on their own using the optimal formulations determined previously with different amounts of DETA substituted. Adduct epoxies were prepared for SBDA 3, 4, and 5 with 0, 10, and 20% of the SBDA replaced by DETA to investigate the new SBDA's solution resistance. Pre-polymerizing the crosslinker resulted in all the epoxies tested showing no softening after being submerged in deionized water for 45 minutes (**FIGURE 23, left**).

More pronounced differences were seen when those same formulations were submerged in a 5% acetic acid solution. The same trend of substituting more of the SBDA with DETA continues as less material is removed

the more DETA is added. The trend of the higher amine value SBDA showing less softening is also seen, although the softness of the SBDA 4 epoxies is very similar to the SBDA 3 epoxies (**FIGURE 23, right**).

When mixing formulations with two SBDAs in equal amounts, the resultant epoxy would cure at a rate between the individual epoxies (**FIGURE 24**). The same trend was seen in epoxies that had 20% DETA added to them as well. 3-40 5-40 D-20 cured at a rate between 3-80 D-20 and 5-80 D-20.

Crosslinkers containing equal portions of SBDA 3 and 5 as well as SBDA 4 and 5 were tested for their removability with 0 and 20% DETA. Of these formulations, 3-40 5-40 D-20 showed the most promising removability in a 5% acetic acid solution while not softening in DI water or a 5% NaOH solution (**FIGURE 25**). This formulation also showed a quick curing rate similar to that of the commercial road marking material.
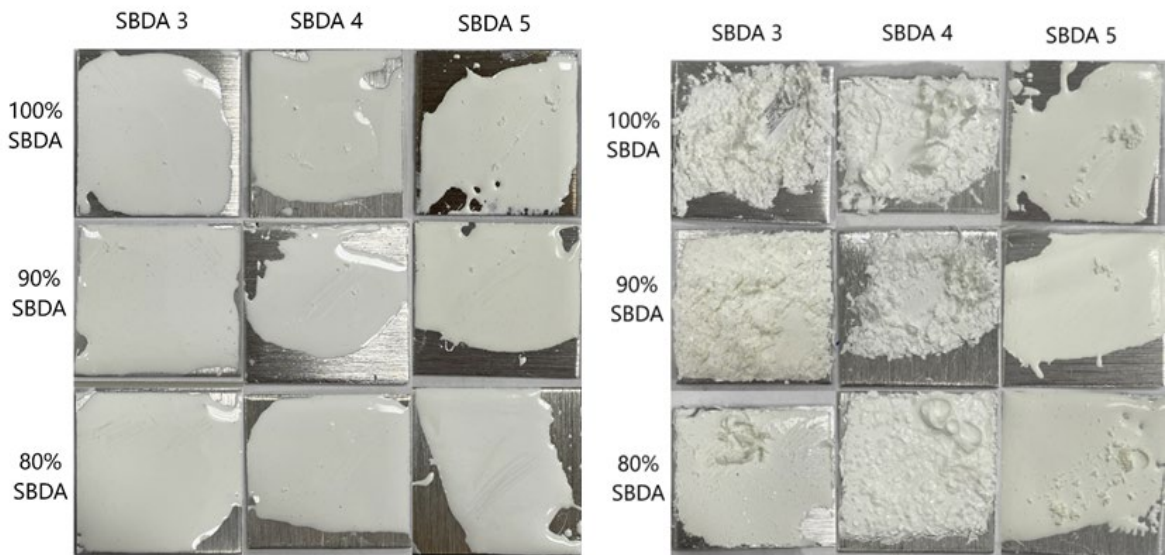

FIGURE 23. (left) Epoxy formulations after being submerged in DI water for 45 minutes and scratched. (right) Epoxy formulations after being submerged in 5% acetic acid for 45 minutes and scratched.
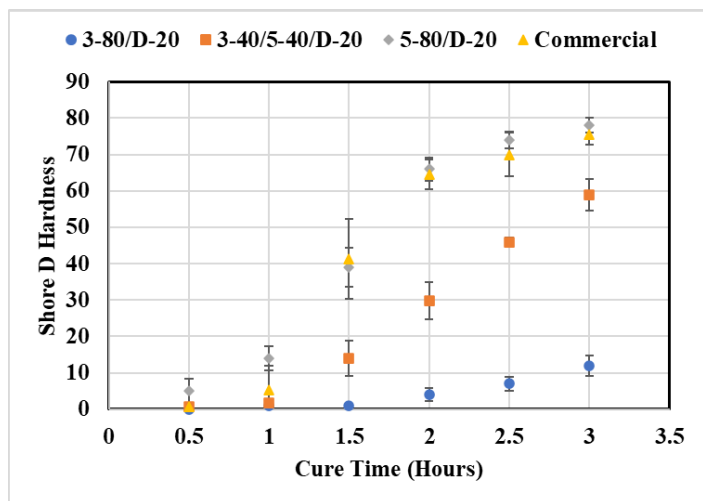

FIGURE 24. SBDA epoxies with 20% DETA, one fully SBDA 3, one half SBDA 3-half SBDA 5, and the last fully SBDA 5.
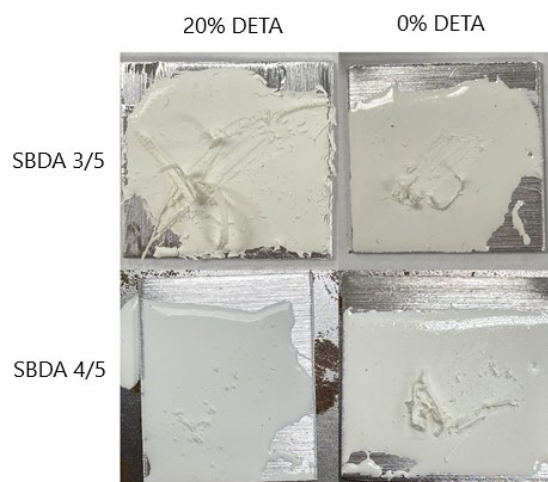
FIGURE 25. SBDA 3 & 5 and SBDA 4 & 5 mixtures with 0 and 20% DETA after being exposed to a 5% acetic acid solution for 45 minutes.

The amine hydrogen equivalent weight (AHEW) is a measurement of the weight of the crosslinker required to reach one mol of amine functional groups. It is the inverse of the amine value, so the lower the AHEW the higher the amine value, which also considers the difference in hydrogen between primary and secondary amines. Generally, the lower the AHEW value a crosslinker has, the quicker the formulation cures. The curing rate of an SBDA mixture can be estimated by first calculating the AHEW value expedites finding promising formulations (**FIGURE 26**). All amine mixtures previously tested with an AHEW near or below 43 had sufficient curing rates and hardness. Promising new formulations with low enough AHEW values can then be calculated and tested.
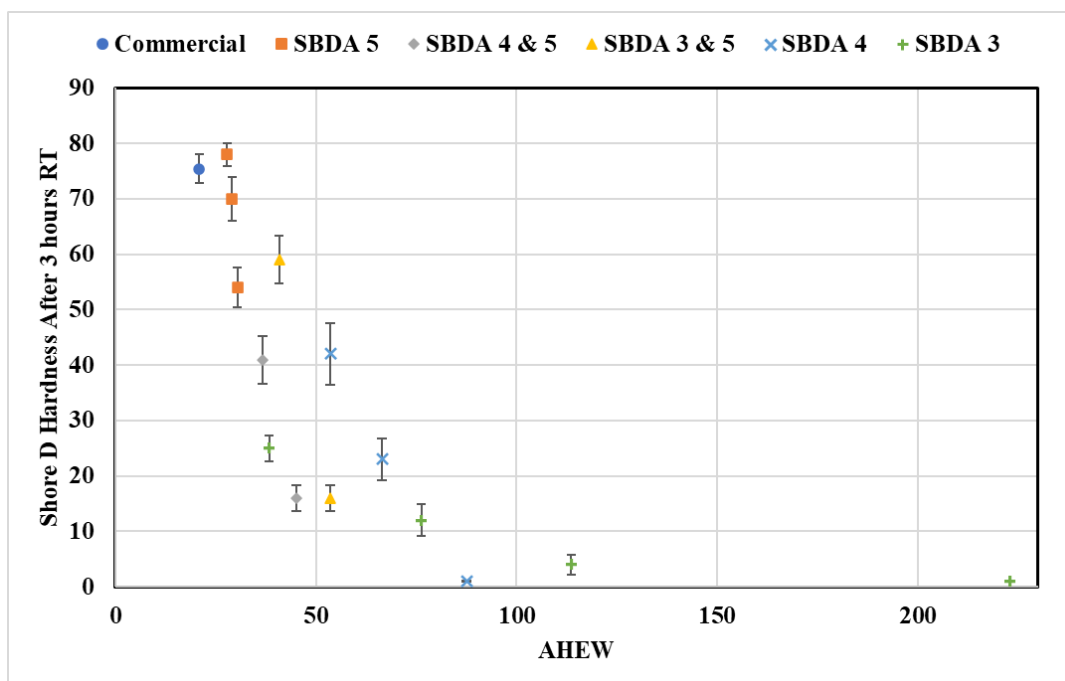
FIGURE 26. The AHEW values of the different SBDAs and multiple SBDA mixtures are graphed against the hardness of the resultant epoxy after curing at room temperature for 3 hours. Formulations that have two SBDAs contain an equal weight of each SBDA. The rightmost point is 100% SBDA and the points to the left are 10%, 20%, and 50% DETA, respectively. The multiple SBDA mixtures skip the 10% DETA formulation.

COMPREHENSIVE INVESTIGATION OF SELECT FORMULATIONS AND ROAD TESTS

Of the synthesized SBDA crosslinkers, SBDA-3 and SBDA-4 showed considerably better removability under weak acetic acid solutions compared to SBDA-5. These two SBDAs were used as the base for the road test formulations and mixed with SBDA-5 to increase the curing rate, with the addition of 20% commercial crosslinker DETA, the amount of SBDA-5 used could be reduced allowing for more SBDA-3 and -4 in the formulations. This resulted in the two formulations used in the road tests, 3-40/5-40/D-20 and 4-55/5-25/D-20. These two formulations were tested for sufficient curing rates, hardness, abrasion resistance, solvent resistance, convenient removability using acetic acid, and self-healing.

Curing Rate and Hardness

The two SBDA-based formulations had very similar curing rates, which was expected due to their selected similar AHEW values (**FIGURE 27**). The 4-55/5-25/D-20 formulation showed a slightly faster curing time with a higher hardness after 3 hours than the 3-40/5-40/D-20 formulation.
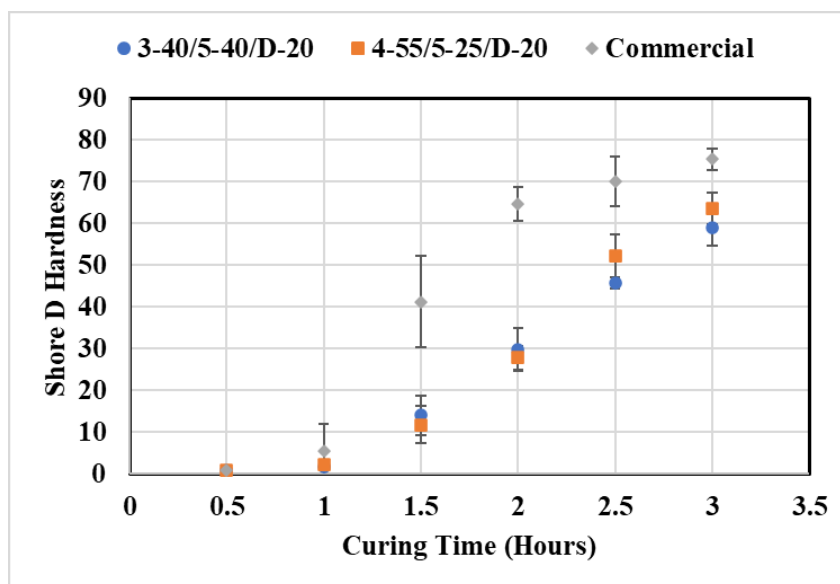
FIGURE 27. Curing rate of selected SBDA-based formulations for their AHEW values.

Even though the curing rate of the novel formulations is not as quick as the commercial formulation, when the markings reach a more complete cure after 3 days, the hardness of the two novel formulations is on par or greater than the commercial formulation (**FIGURE 28**). A p-value of 0.52 was calculated using ANOVA analysis denoting there is not enough of a significant statistical difference between each formulation to reject the null hypothesis.
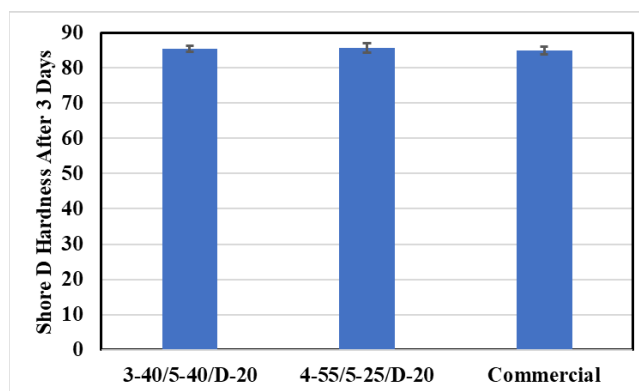
FIGURE 28. Shore D Hardness of 3-40/5-40/D-20, 4-55/5-25/D-20, and commercial formulations after 3-days

26

Solution Resistance

FIGURE 29 shows the removability of SBDA-based and commercial formulations. Each formulation was scratched with the dull side of a steel blade, submerged in the solution for 10 minutes, scratched again, submerged for an additional 35 minutes, and then scratched again. Weights of each sample were taken before and after the coatings were scratched. All formulations showed good solution resistance to DI water and 5% NaOH solution, with high enough hardness that negligible amounts of material were removed. The state of the coatings at 0 minutes is taken as the baseline before the solutions impact the coating properties. The 5% acetic acid solution imparted minor softening on the commercial sample, but large ribbons of the SBDA-based formulation samples were removed when scratched. In the SBDA-based formulations, the surface of the coating softened and started flaking away before even abrading the surface. This demonstrates the potential for an increase in ease of removal as the coatings soften when exposed to 5% acetic acid. A larger decrease in the area of the 4-55/5-25/D-20 formulation after being submerged in acetic acid for 45 minutes shows greater removability than the 3-40/5-40/D-20 formulation, even though both formulations showed similar softening when submerged in acetic acid.
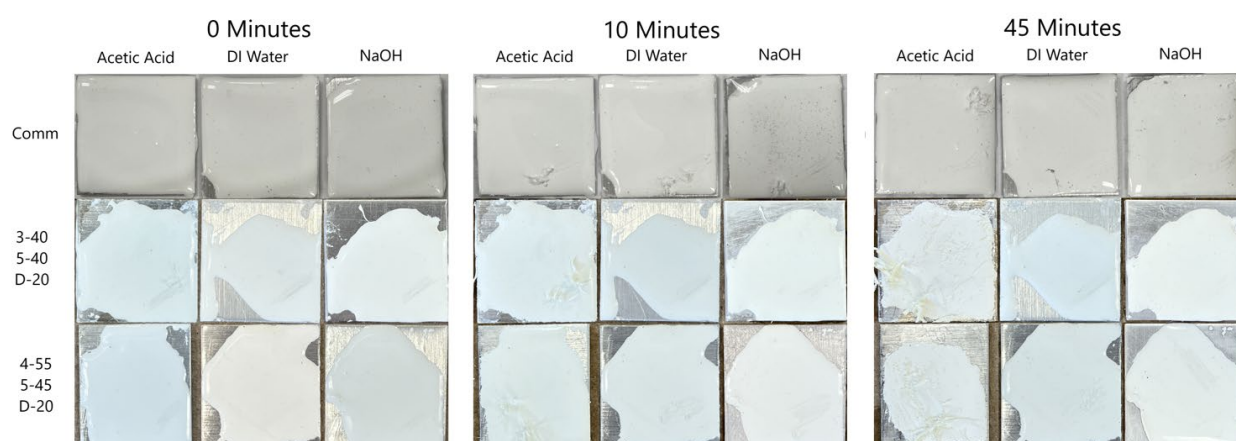

FIGURE 29. Pictures of the markings after being submerged in 5% AcOH solution for 0 minutes, 10 minutes, and 45 minutes. The samples were scratched before taking each of the images.

To quantify the removability, the amount of material lost when scratching was recorded in **FIGURE 30**, showing a negligible loss of material when submerged in DI water and NaOH even after 45 minutes. Because the manual scratching cannot be precisely repeated on each coating sample, the weight losses should only be used as an indication of general trends. The formulations, without first being submerged in solutions, lost on average 0.2 mg of material, meaning that no softening was seen in the DI water and NaOH solutions. The 3-40/5-40/D-20 and 4-55/5-25/D-20 formulations showed similar weight loss when submerged in acetic acid due to the similar softening seen in the two formulations. **FIGURE 31** shows the weight increase before and after the samples were submerged in the solution. The weight loss in the NaOH solution is due to the reaction between the NaOH and the aluminum substrate producing hydrogen gas and, therefore, was not included in the corresponding figure. The weight gain in the SBDA-based samples shows the absorption of the acetic acid solution, while the negligible change in weight when submerged in DI water shows good water resistance. The 4-55/5-25/D-20 formulation not increasing in weight during the 35-minute submerging test may be because of the loss of material seen in **FIGURE 29** rather than the sample not absorbing the acetic acid solution. In the two SBDA-based samples submerged in acetic acid, the rough surface is due to the coating flaking off and a reduction of the area can be seen. (**FIGURE 32**). The greater reduction in the area of the 4-55/5-25/D-20 sample can be attributed to better removal in acetic acid than the 3-40/5-40/D-20 sample.
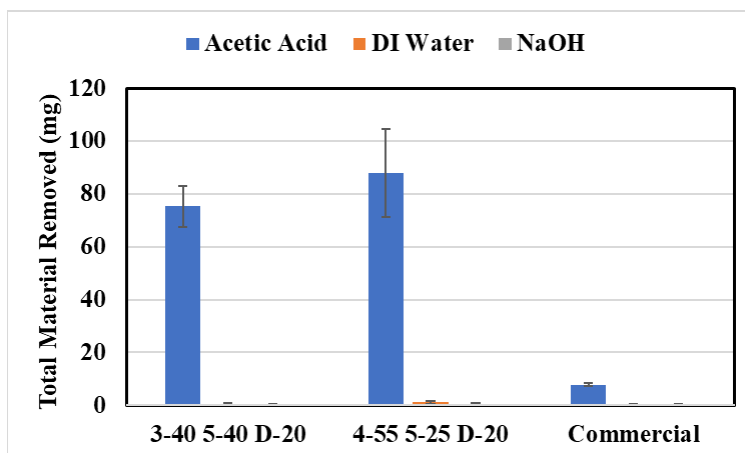
FIGURE 30. Material loss of the two SBDA-based coatings before and after being scratched after being submerged in the solution for different periods.
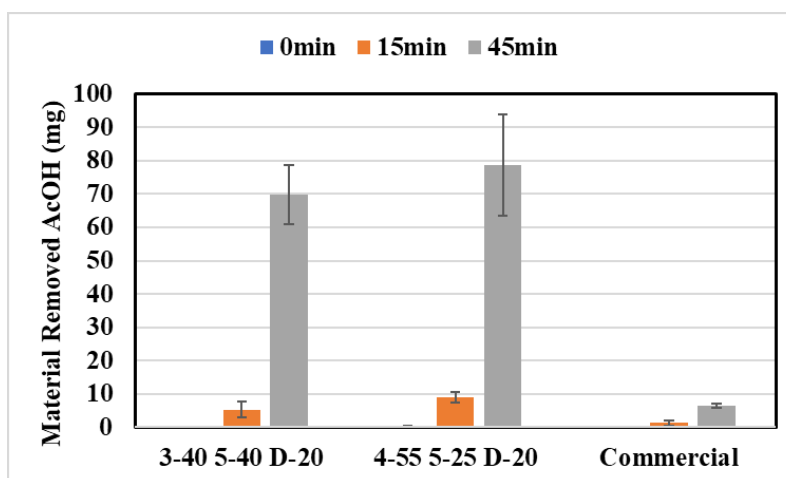
FIGURE 31. Solution absorbed by the two coatings after being submerged in various solutions for 10 minutes, an additional 35 minutes, and total.

FIGURE 32. Surface roughness of 3-40/5-40/D-20 (left) and 4-55/5-25/D-20 (right) after being submerged in 5% acetic acid for 45 minutes.

Self-Healing

To determine the self-healing properties of each formulation, epoxy was applied to an aluminum substrate at a thickness of 0.5 mm. The surface was then scratched and self-healed at 50 °C for 25 minutes. The width and geometry of the scratch were observed before and after heating with a KEYENCE VHX-7100 microscope

to determine the repair ratio and develop surface maps of each scratch (**FIGURE 33**). The repair ratio was calculated using the initial and final widths of the cuts before and after self-healing.
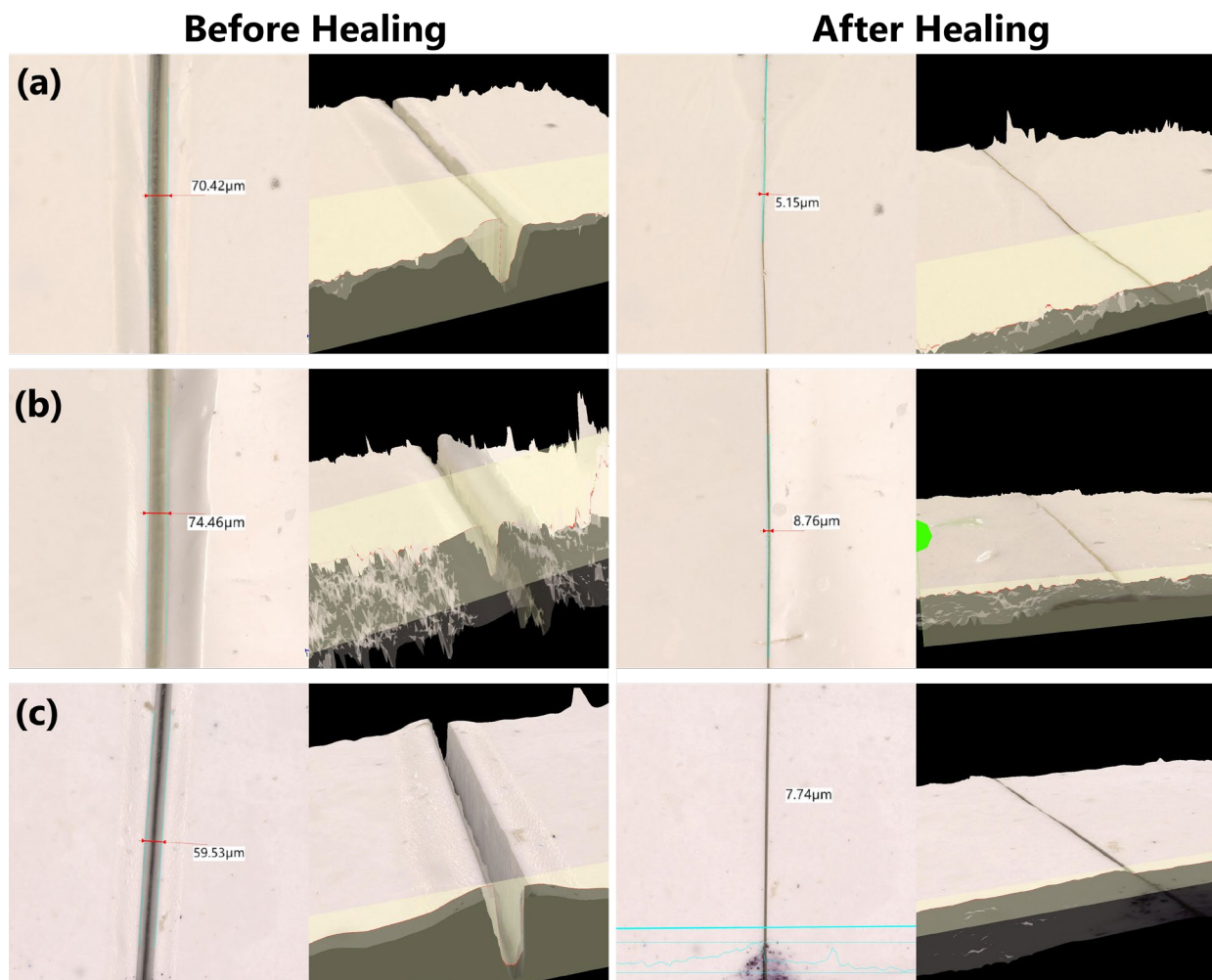
FIGURE 33. Scratch width and generated surface maps before and after heating at 50 °C for 25 minutes of the (a) 3-40/5-40/D-20, (b) 4-55/5-25/D-20, and (c) commercial formulations 3 days after application.

Vitrimer materials have two thermal transition points, the glass transition temerature and the temperature at which bonds are dynamically exchanged. The dynamic exchange temperature is typically higher than the glass transition temperature. Both contribute to the self-healing of the epoxies. At 50 °C, the main factor affecting self-healing is the glass transition temperature. After completely curing, the two novel formulations and commercial formulation all showed good self-healing. The width of the scratch for all three formulations was significantly reduced (**FIGURE 34**). A p-value of 0.54 was calculated using ANOVA analysis denoting there is not enough of a significant statistical difference between each formulation to reject the null hypothesis.

The geometry of the cut is an important factor in whether a cut can self-heal or not. This is because there needs to be material deposited on either side of the cut to flow back into the cut when heated. A distinction then needs to be addressed about the shape of cracks that occur on markings in the field. When abraded, while being driven over, microcracks occur below the surface of the marking. In this scenario, the microcracks would have sufficient material above them to flow and self-heal. Other methods of repair that would work for all damage

include applying wet mixed material over the marking or heating pre-cured material over existing markings, introducing material that can flow and self-heal.
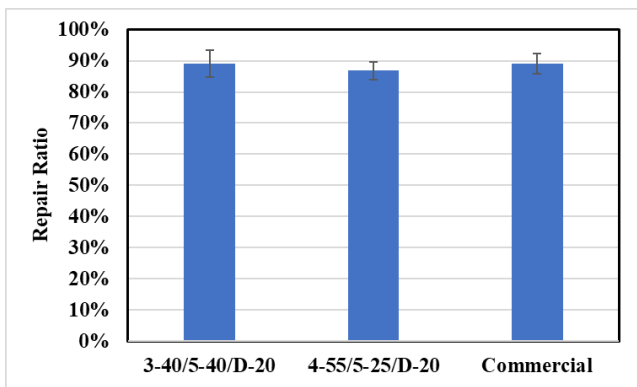
FIGURE 34. The repair ratio for each formulation after curing for 3 days.

Abrasion Resistance

A 3-40 5-40 D-20 formulation and commercial formulation were prepared. The epoxies were applied to a 100 by 100 mm aluminum plate with a hole cut in the middle and rounded edges. The Taber Rotary Abrader (Model 5155) was loaded with a 1000 g load per arm using CS 17 abrading discs. The weight and thickness of each of the samples were measured before testing and every 1000 cycles. Every 1000 cycles the abrader discs were resurfaced using an S-11 resurfacing disk for 45 cycles. The abrader was run at 75 cycles per minute and the vacuum nozzle was set at 100% and placed 3 mm above the sample to remove material. This was done for a total of 5000 cycles for each sample. **FIGURE 35** shows the condition of the samples before and after 5000 cycles.
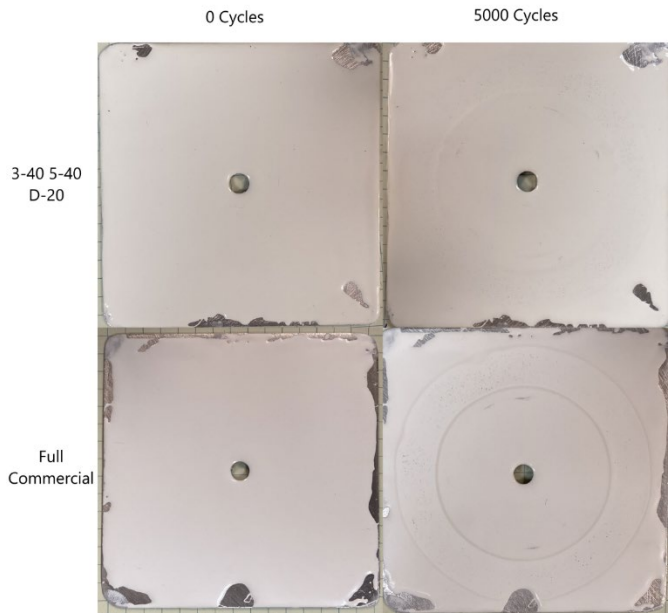
FIGURE 35. The 3-40 5-40 D-20 and commercial formulations before and after 5000 abrasion cycles.

The 3-40 5-40 D-20 and commercial perform very similarly having a wear index of about 50 mg/1000 cycles (**FIGURE 36**). The first data point collected for each of these samples was removed as an outlier. A p-value of 0.73 was calculated using ANOVA analysis denoting there is not enough of a significant statistical difference between each formulation to reject the null hypothesis.
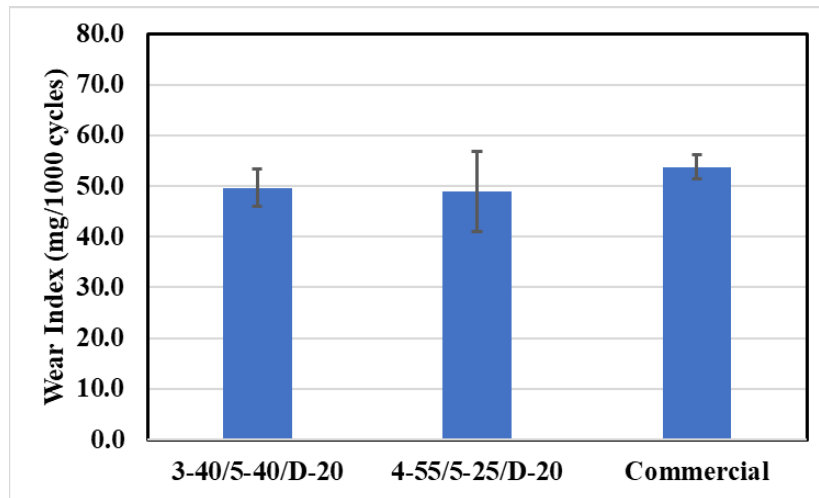
FIGURE 36. Wear index and standard deviation of the commercial and 3-40 5-40 D-20 formulations.

Adhesion to Concrete

To determine the adhesion to concrete, acetic acid solutions were applied to the markings and various methods were used to remove the markings. A single strip of PTFE tape was placed down across the long side of a concrete block near the edge to create a side in which the marking would not adhere and could be peeled off. Duct tape strips were placed perpendicular to mark the boundaries of the samples (**FIGURE 37**). The duct tape used was 5.8 mils thick, so 4 layers were applied to reach near the desired coating thickness of 20 mils. The mixed epoxy was then poured and dragged flat using a steel scraper in a drawdown method. The samples were allowed to cure for 3 days before testing.
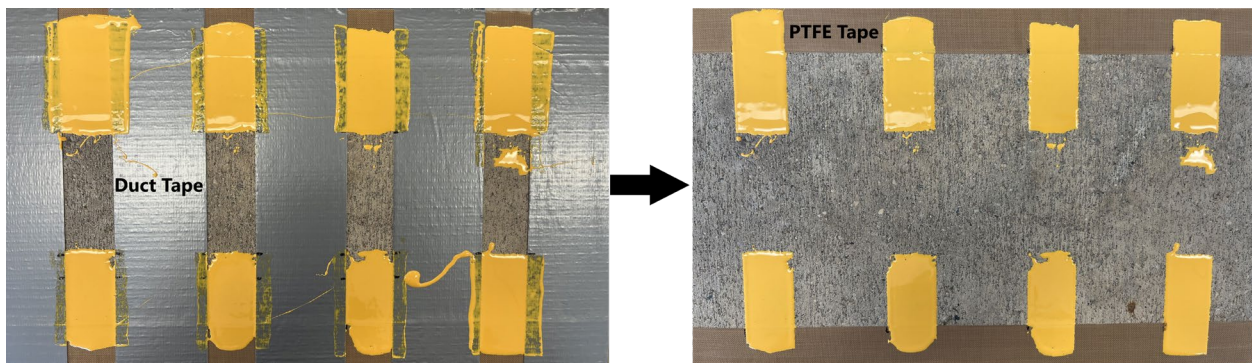
FIGURE 37. Coatings of the desired thickness after being drawn down and after removing the duct tape after allowing the markings to cure.

A variety of concentrations of acetic acid (5, 20, and 50%) were applied for 60 minutes before removal testing of the coatings was conducted. Two main tests conducted were a removal test and a crosshatch adhesion test. For the removal test, a steel razor scraper was used to pry at the coating after exposing it to a solution. The crosshatch adhesion tests were conducted based on ASTM D3359. The surface was thoroughly cleaned and a cut in an 'X' shape was made down to the substrate. After soaking in acetic acid for 10 minutes, the surface was dried, and fresh tape (3M™ All Purpose Duct Tape DT8) was placed on top of the marking. After 90 seconds the tape was removed, and any removal or damage was noted.

Both formulations proved to be very difficult to remove when both dry and after soaking for one hour in 10% acetic acid, so a blade was used to forcefully chip away the concrete underneath the coating. The 4-55/5-25/D-20 formulation had large ribbons of material removed from the coating which indicates softening on the surface, but the solution was unable to penetrate to the adhesive layer with the concrete (**FIGURE 38a***)*. The

commercial formulation did not have any measurable decrease in strength after soaking in the acetic acid solution (**FIGURE 38b**).
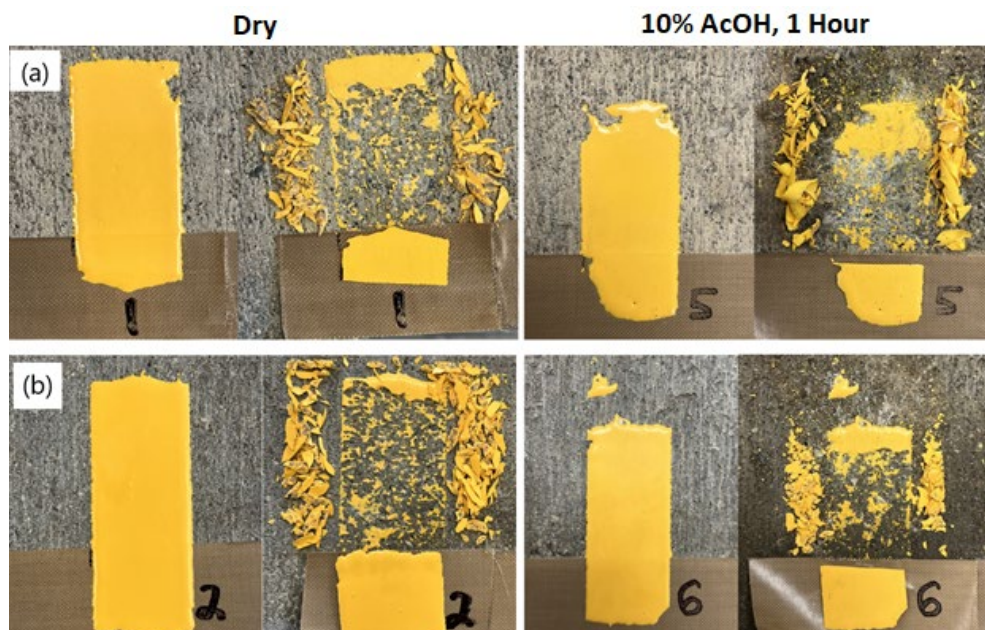
FIGURE 38. (a) 4-55/5-25/D-20 formulation; (b) commercial formulation. Before and after chipping away the coating when dry and after soaking in a 10% solution of acetic acid for one hour.

The adhesion to concrete was also tested using the crosshatch test. This test was done with the same coating four times with the conditions as follows: dry, 5%, 20%, and 50% acetic acid solution. The only damage observed by removing the tape was in the 4-55/5-25/D-20 formulation after having the 5% acetic acid solution applied, a 1 mm chip was observed slightly left of the center of the 'X'. Finally, the markings were scratched with a blade. This resulted in easy removal of the soft surface of the 4-55/5-25/D-20 surface and chipping of both formulations near the center (**FIGURES 39, 40**). Still, the acetic acid solution is unable to penetrate deeper into thicker coatings without first abrading the softened top surface.
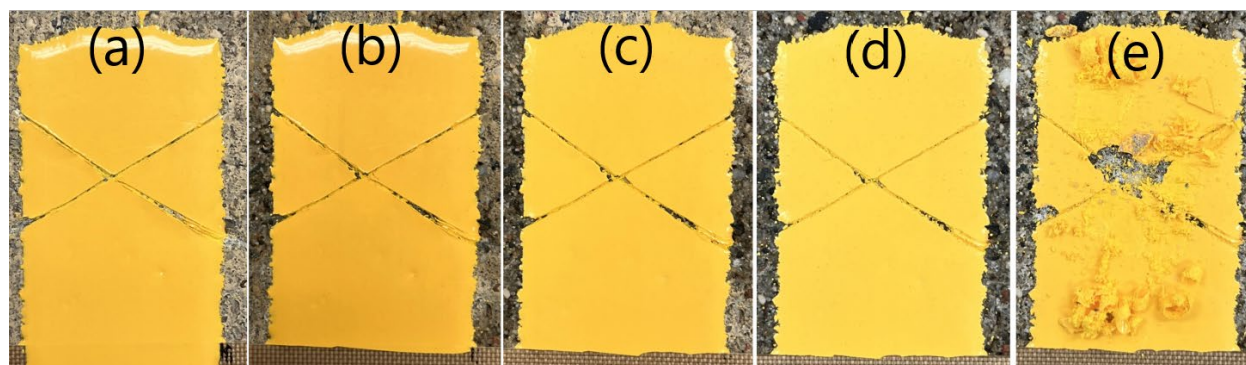
FIGURE 39. The 4-55/5-25/D-20 formulation after the tape was removed for the (a) dry and (b) 5%, (c) 20%, and (d) 50% acetic acid solution, and (e) after scratching with a steel blade.

FIGURE 40. The commercial formulation after the tape was removed for the (a) dry and (b) 5%, (c) 20%, and (d) 50% acetic acid solution, and (e) after scratching with a steel blade.

NDSU Road Test

Two novel epoxy formulations and one control commercial epoxy were applied to a roadway near Thorson Maintenance Center on the NDSU campus. Pictures were taken a couple of days after application in October 2021, after winter six months later in April 2022, and a full year after application in October 2022. The reduction of surface area that the markings co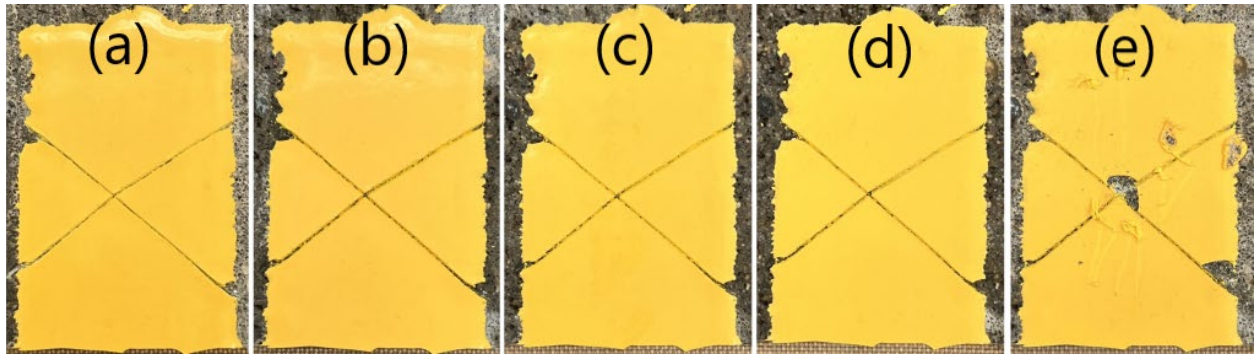ver was examined using ImageJ software and the general state of the markings was examined. Three formulations were used: 3-40/5-40/D-20, 4-55/5-25/D-20, and the commercial formulation. The markings have experienced heavy vehicle traffic from the maintenance center, various types of precipitation, snow removal including plowing and rotary brushes, and de-icing measures like salting. **FIGURE 41** compares the overall condition of the markings 6 months and 12 months after the initial application.
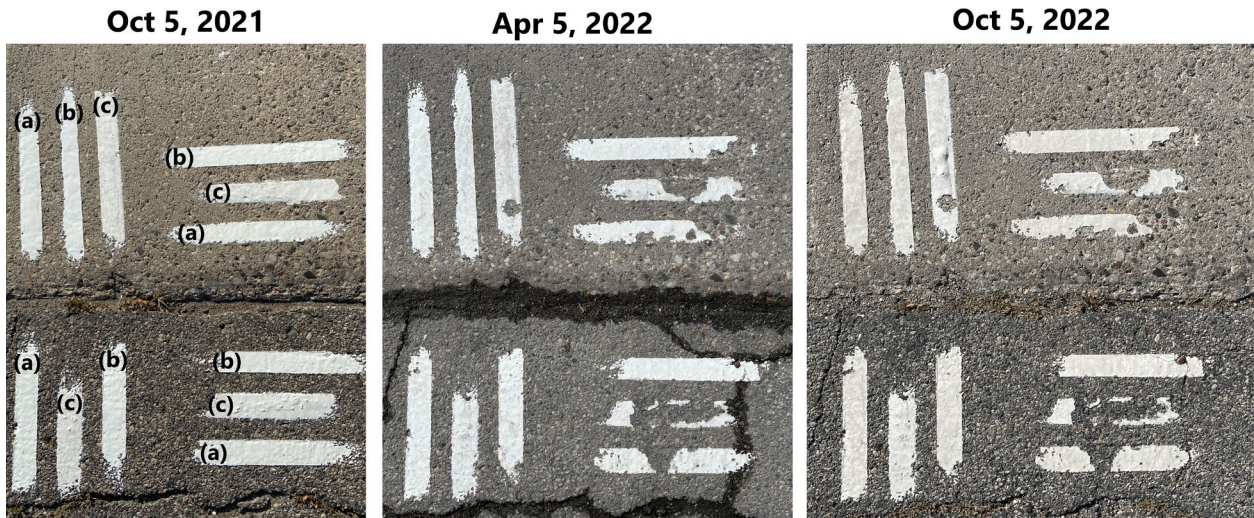
FIGURE 41. (a) 3-40/5-40/D-20, (b) 4-55/5-25/D-20, and (c) commercial markings applied to the concrete. The traffic direction is vertical.

During the first six months over the winter, a great amount of surface area was removed from the markings. This amount of removal is greater than what is expected in commercial applications due to the markings being applied thicker than a typical epoxy marking. This thickness allows snow removal plows to chip away pieces of the markings that extend further away from the road surface. The markings painted transverse to the traffic direction had more area removed over the study. This is expected as markings transverse to the traffic direction are expected to see accelerated wear due to their orientation causing more traffic to drive over the markings.

For all directions and pavement types, the commercial epoxy had the most material removed, followed by the 3-40/5-40/D-20 novel formulation, with the 4-55/5-25/D-20 formulation losing the least area (**FIGURE 42**). The failure of the markings most likely occurred at the concrete rather than the adhesive surface. It is then possible that the commercial formulation had more area removed because it was thicker in some areas.

The second six months of testing took place over the summer months. Compared to the material lost over the winter, very little area was removed over the summer (**FIGURE 42**). This is due to snow and ice removal techniques that are used to clear pavement, which greatly damages the pavement marking materials. The markings are also more brittle when exposed to cold weather conditions during the winter resulting in pavement marking chipping of the pavement, a brittle mode of failure.
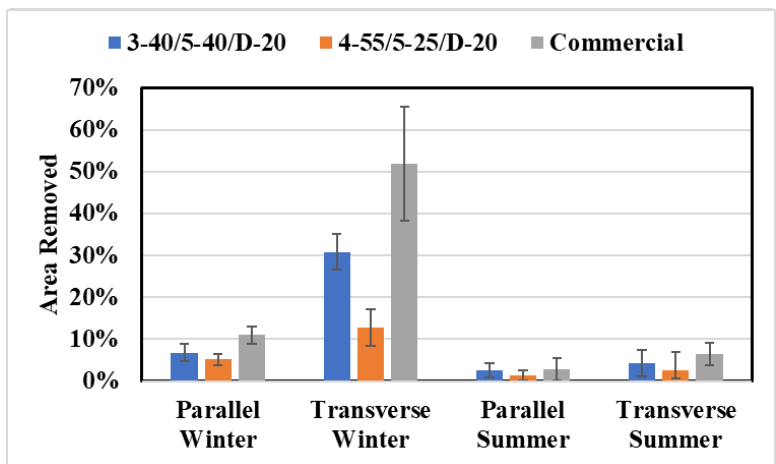
FIGURE 42. Area removed during the first 6 months over the winter and during the second 6 months over the summer.

MnROAD Road Test

To get a better idea of the novel markings' durability when experiencing actual road conditions, the materials were applied at the MnROAD test track and the MnROAD test section of I-94. The markings were applied to the newest concrete and hot mix asphalt (HMA) available on both sites. The MnROAD test track site is closed to public traffic, instead a semi-trailer truck circles the track simulating traffic of a rural low-volume road. The I-94 test track is split into two sections, traffic is diverted to the test section to wear that section down under interstate traffic conditions (high-volume) and is diverted to the main interstate to investigate the condition of the test section. For the test track, all markings were applied on the trafficked side of the road, the truck only drives clockwise on the inner loop. The 4-55/5-25/D-20 and commercial markings were applied transverse to the traffic direction to experience accelerated wear. Two markings of each formulation were applied, one on concrete and one on hot mix asphalt (HMA) on 7/14/2022 (**FIGURE 43**).
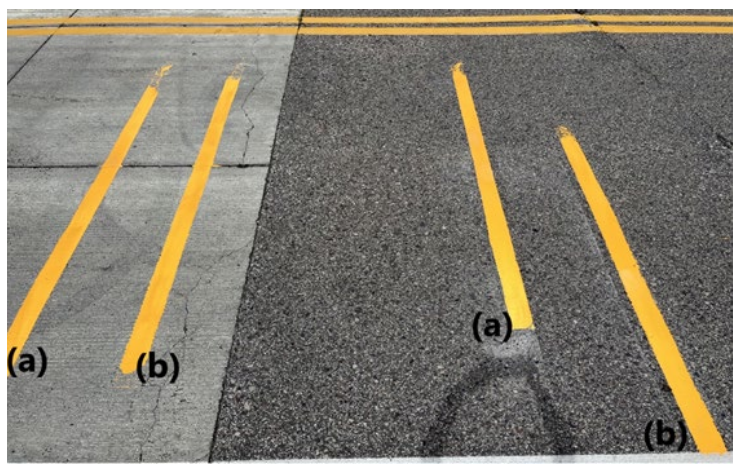
FIGURE 43. Markings of (a) 4-55/5-25/D-20 and (b) commercial formulations on the MnROAD test track.

For the test section of I-94, the 4-55/5-25/D-20 formulation was applied to the passing lane and the

commercial formulation was applied to the driving lane on 9/26/2022. Again, one marking of each formulation was applied on concrete and one on HMA (**FIGURE 44**).
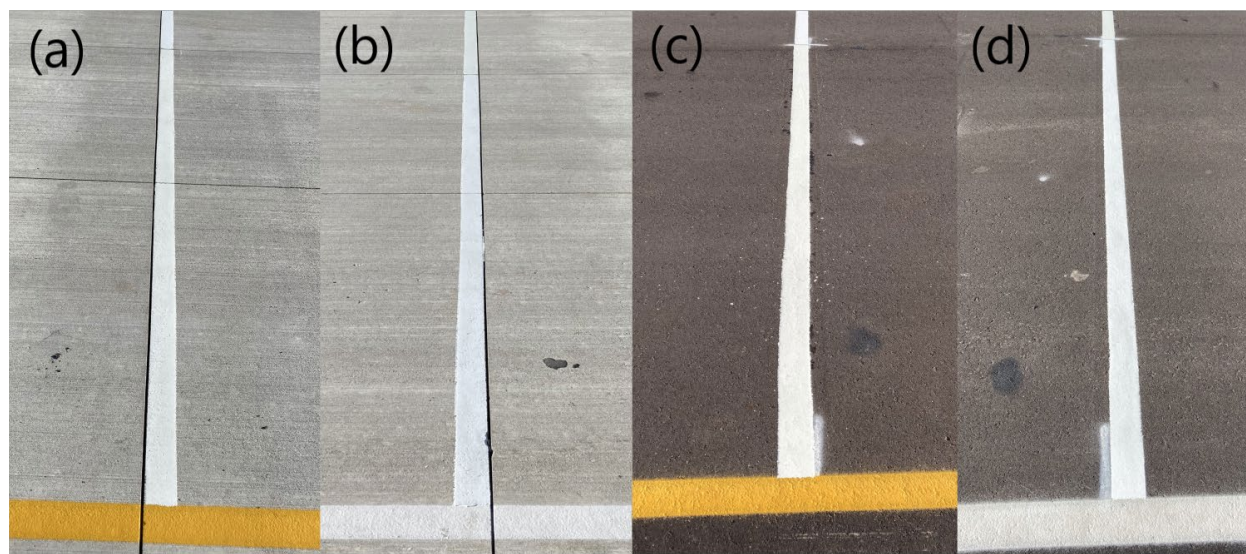
FIGURE 44. Markings applied to the test section of I-94. (a) 4-55/5-25/D-20 on concrete, (b) commercial on concrete, (c) 4-55/5-25/D-20 on HMA, and (d) commercial on HMA.

The markings were then investigated on 1/10/2023 for damage. After 6 months, the markings on the low-volume test track have not experienced any visible wear (**FIGURE 45**). The dark spot on the commercial marking on concrete, and any darkness in general, is mud that has temporarily been deposited on the marking.

FIGURE 45. Markings of (a) 4-55/5-25/D-20 and (b) commercial formulations on the MnROAD test track after 6 months of low-volume traffic.

Similar to the low-volume test track, both markings applied to the HMA on the high-volume test track experience no visible wear (**FIGURE 46**). However, both markings applied to the concrete experienced chipping in the direction that traffic comes from. The commercial formulation experienced more area loss than the novel formulation, but this is to be expected because the driving lane experiences more traffic than the passing lane. Overall, the novel formulation is holding up well to the MnROAD road tests compared to the NDSU road test due to the improved application techniques.

FIGURE 46. Markings applied to the test section of I-94. (a) 4-55/5-25/D-20 on concrete, (b) commercial on concrete, (c) 4-55/5-25/D-20 on HMA, and (d) commercial on HMA after 4 months of high-volume traffic.
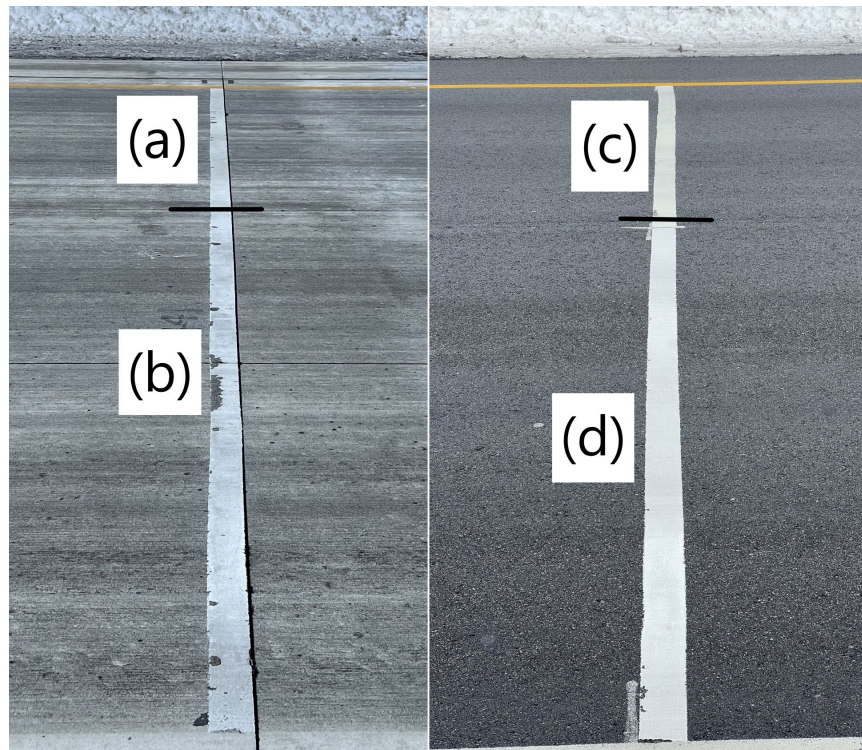
PLANS FOR IMPLEMENTATION

The new marking material that was developed in this project can be used in the construction, transportation, and airport industries. The key audiences for this research are federal and state DOTs, researchers/engineers in the transportation industry, marking manufacturers, and academia. We are working with NDSU Research and Creativities on the potential IP protection of the product. After the decision on IP protection is made by NDSU, the results from this project will be shared in the public domain. Publications including full and summary reports of the research, peer-reviewed journal articles, and conferences/seminars are planned to disseminate knowledge afterward.

In a collaborative effort with MnDOT, the material has been applied to the MnROAD test track and test section of Interstate 94 (**FIGURES 47 & 48)**. Collaborate efforts were also made with the marking industry to ensure the developed material met durability and curing requirements and that the novel material was compatible with current epoxy systems and applications equipment. The developed material is compatible with current pavement marking application systems. Each part of the two-part epoxy is poured into separate tanks, where it is heated, and then sprayed through a static mixing nozzle onto the pavement. The novel material just makes modifications to the crosslinker (part B) and utilizes an existing commercial epoxy resin (part A). The crosslinker is compatible with most commercial epoxy resin components with minor changes to the mixing ratio, which can be easily implemented during application without changing the novel material. Changes in material properties are expected when changing epoxy resin, but the final material should still meet the requirements of the system that the inserted epoxy resin is from.

FIGURE 47. Pavement application on MnROAD test track.

FIGURE 48. Application of the marking at the MnROAD I-94 test section.

A life-cycle analysis was conducted to determine the viability of these novel materials in replacing currently existing systems. The similar durability of the novel formulations with additional convenient removability and self-healing properties highlights the materials' potential role as both permanent and temporary marking. Material cost analysis based on scaling up lab-scale suppliers to bulk supplier prices shows that the novel material would potentially cost 13-17% more than current commercial two-part epoxy markings. When used as a permanent marking, the material could potentially decrease the frequency of replacing the markings, saving money from removal and application costs, and decreasing the frequency of lane restrictions on roadways. Use as a temporary marking would reduce the damage to roadways caused by removing permeant marking materials or reduce costs compared to expensive temporary marking materials. The use of large amounts of acetic acid to remove the coating was also investigated, revealing that acetic acid readily degrades into non-toxic byproducts in the soil, air, and water. Acetic acid was revealed to harm the compressive strength of concrete, but over a much larger time frame than would occur in commercial applications.

We plan to continue to work with Amy Beise (NDDOT) and Ben Worel (MnROAD) to find opportunities to implement the new marking material in new transportation projects. We have also proposed a plan (to

MnDOT/LRRB 2022 RFP) to further improve the properties and simplify the implementation of the new marking. This plan focuses on reducing the cost of the material by skipping the laboratory synthesis and developing a new method to synthesize the vitrimer epoxy on-site during application. A new epoxy can also be added to enhance the vitrimer behavior of the marking and achieve even higher self-repairing efficiency. The properties of the final vitrimer epoxy marking are affected by the content of each ingredient in the system. By adjusting the ingredient ratios, the thermal and mechanical performance, adhesion to the pavement, repairability, and removability of the markings can be manipulated to achieve an overall optimal level. The material and installation costs are expected to be further reduced after the plan is completed.

CONCLUSIONS

A crosslinker was developed to cure epoxy vitrimer PMMs optimized for durability, self-healing, and convenient removability. This was accomplished by imbuing the material with reversible imine bonds (N=C) and a hydrophilic molecular backbone which allowed the severing of these bonds in dilute acidic solutions while maintaining resistance to water and alkaline solutions. The reversible nature of the bonds also allowed for the material, when heated, to relax and flow allowing for the material to repair itself. Laboratory tests were used to confirm an abrasion resistance under 80 mg/1000 cycles, a Shore D hardness above 80 after 3 days, and a no-track time under 30-minute, standards commonly shared between various state DOTs. The markings applied to the MnROAD low-volume test track and high-volume section of I-94 have experienced little wear over the past 6 and 4 months of traffic, respectively. What wear the markings have experienced, mostly on the high-traffic concrete, are similar between the novel and commercial formulations. Future field evaluation of these markings will be done according to guidelines set out by the AASHTO NTPEP pavement marking materials committee.

This project demonstrated the possibility and viability of vitrimer systems to be adopted for PMM applications, allowing for both increased marking durability through self-healing and the ability to be conveniently removable, thus for use as both a permanent and temporary marking. Presently, harsh removal techniques are used that are expensive, energy-intensive, and environmentally damaging. A conveniently removable epoxy PMM allows for the use of a durable marking in temporary applications that can be removed without damaging the newly applied pavement. Improving the durability of markings is an effective method of reducing both material and application costs, as the markings last longer and do not need to be replaced as often. The synthesis of the crosslinker utilizes chemicals that are already used in other commercial applications and are therefore commonly available. The crosslinker may also be used to cure the epoxy resin of existing two-part epoxy PMM systems. Comprehensive cost analysis shows favorable results for the implementation of the new marking material, but there is still room for improvement in both costs and self-healing properties.

A plan has been proposed to further improve the properties and simplify the implementation of the new marking material. This involves reducing synthesis costs by implementing a method of synthesizing the vitrimer epoxy on-site. This will also allow for greater control over the ratio of reversible imine bonds and the density of the crosslinked network by controlling the ratio between the reactants. Another method of giving the material vitrimer properties will also be introduced to further enhance the self-repairing performance. The markings can be manipulated to achieve optimal thermal and mechanical performance, adhesion to the pavement, repairability, and removability by adjusting these ingredient ratios. The material and installation costs are expected to be further reduced after the plan is completed. The removal process will be further developed and current pavement marking removal equipment can be adapted for the easy removal of these markings, perhaps as easy as switching the solvent to a weak acetic acid solution.

INVESTIGATORS' PROFILES

Dr. Long Jiang: Dr. Jiang is a Professor in the Department of Mechanical Engineering (ME) at NDSU. His academic background is concentrated on polymer materials science. He has extensive experience in synthesizing and testing multifunctional polymeric materials including polymer fiber composites, nanocomposites, and polymer blends/alloys. His recent research focus is to develop biobased, multifunctional polymer composite and nanocomposite resins for structural, electrical, and coating applications. Dr. Jiang's research work in the polymer composite field has been widely recognized by researchers from academia and industry alike with a Google Scholar citation over 3,000 times since 2018. He has served on review panels for more than 60 scientific journals and many funding agencies.

Dr. Jinwen Zhang: Dr. Zhang is a Professor in the School of Mechanical and Materials Engineering (MME), Washington State University (WSU). His diverse educational background and extensive research experience have prepared him well for interdisciplinary and cross-disciplinary research. Specifically, his research focuses on the synthesis of novel polymer materials from renewable feedstocks, toughening and reinforcing of polymers, and novel recycling of composite materials. He was awarded Gold Medalist in Excellence in Government Awards 2013 (Federal Executive Board). He has published 100+ peer-reviewed journal papers, 1 edited book, and 11 book chapters. He also has 5 granted US patents and 7 pending patents. Since 2004, he has been funded for ~$7M from federal/state funding agencies and private industry. In recent 7 years, Dr. Zhang has been studying epoxy vitrimers and has achieved significant progress.

Dr. Mijia Yang: Dr. Yang is an Associate Professor in the Civil & Environmental Eng. (CEE) department of NDSU. With extensive practical experience in concrete materials and applications, he has worked on dozens of projects as a principal investigator, including accelerated pavement repairs, electrically conductive fly ash geopolymer concrete, and its application in revealing highway markings after snow. Dr. Yang has published over 50 refereed and conference publications and reports in the field of structural engineering, impact mechanics, composite materials, and structural testing. Dr. Yang is a registered professional engineer in the state of Ohio, and the recipient of the 2005 Philip E. Rollhaus, Jr. Roadway Safety Essay Contest.

Dr. Zhibin Lin: Dr. Lin is an assistant professor in the Department of Civil and Environmental Engineering (CEE) at NDSU. His research areas focus on the durability of concrete structures, and advanced engineering materials with applications to civil infrastructures, including the durability of concrete under freeze-thaw and overweight vehicles, and structural coatings. Dr. Lin is an active member of several technical committees and serves as a member of the editorial board of three international journals. He is the secretary of the American Concrete Institute Committee 523, and a member of subcommittees 447 and 446. He has worked on durability-related pavement projects, including "Concrete Surface with Nano-Particle Additives for Improved Wearing Resistance to Increasing Truck Traffic".

Dr. Zhang at WSU has access to a wide spectrum of polymer synthesis and characterization equipment through the Composite Materials and Engineering Center, Franceschi Microscopy and Imaging Center, and Center for NMR Spectroscopy. Drs. Jiang, Yang, and Lin at NDSU have access to a wide range of processing & characterization equipment specialized in composites, construction & transportation material research. This equipment is available through several different departments/research centers including CCE, Center for Nanoscale Science and Engineering (CNSE), ME, and Electron Microscopy Center (EMC).

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Program Steering Committee: NCHRP IDEA Program Committee

Month and Year: October 2022

Title: A Novel Durable, Healable, and Conveniently Removable Pavement Marking Material Suitable for Both Permanent and Temporary Marking Uses

Project Number: 219
Start Date: October 25, 2019
Completion Date: December 31, 2022

Product Category: Pavement Marking

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TITLE:
Durable, Healable, and Conveniently Removable Pavement Marking

SUBHEAD:
A highly durable pavement marking material was developed with self-healing properties and selective removability for both permanent and temporary applications.

WHAT WAS THE NEED?
Under normal use, pavement markings, temporary and permanent alike, gradually chip away in a continuous, irreversible fashion, eventually necessitating marking replacement. There is no practical and economical method available today to heal the markings when the damages (scratch/cut/dent) on the markings are still insignificant. Mechanical grinding and various types of blasting (e.g., sandblasting and water blasting) rely on intensive mechanical energy to physically destruct and remove the marking materials, along the way causing environmental impacts (energy consumption, noise, vibration, dust) and leaving damaged pavement surface.

WHAT WAS OUR GOAL?
Our goal was to develop a new long-lasting, healable/repairable, permanent marking material that, when necessary, can also be conveniently removed without scarring the pavement.

WHAT DID WE DO?
- New crosslinking agents were synthesized to cure epoxy pavement marking material systems showing vitrimer properties.
- Formulations were developed to help this new material reach the properties necessary to meet commercial specifications while also expressing strong self-healing and selective removability properties.
- The material was applied to test tracks to determine the in-field performance of the material and on a real-world project on a section of the interstate system.

WHAT WAS THE OUTCOME?

A pavement marking material (PMM) was successfully developed that demonstrated self-healing and convenient removability while meeting durability specifications issued by DOTs.

- The solution resistance of the synthesized amine was able to be tailored by selecting base monomers.
- Vitrimer amine crosslinkers were proven to be able to be formulated to meet the curing rate, hardness, and abrasion resistance requirements of epoxy PMMs.
- The durability and self-healing/selective removability properties needed to be balanced to optimize the novel properties of the material while still meeting material specifications.

WHAT IS THE BENEFIT?

Self-healing allows for the material to have greater durability and a longer lifespan compared to conventional epoxy pavement markings. Conditional removability allows for durable epoxy to be used as temporary markings with increased ease of removal. These beneficial properties were added to epoxy PMMs without a significant increase in cost and without any changes to application methods. Any DOT or business that utilizes epoxy pavement markings for roadways, parking lots, or airports can benefit from this developed material. The chemistry explored may also be further developed to give self-healing and convenient removability properties to other thermosetting PMM systems (i.e. polyurea, polyester, polymethyl methacrylate).
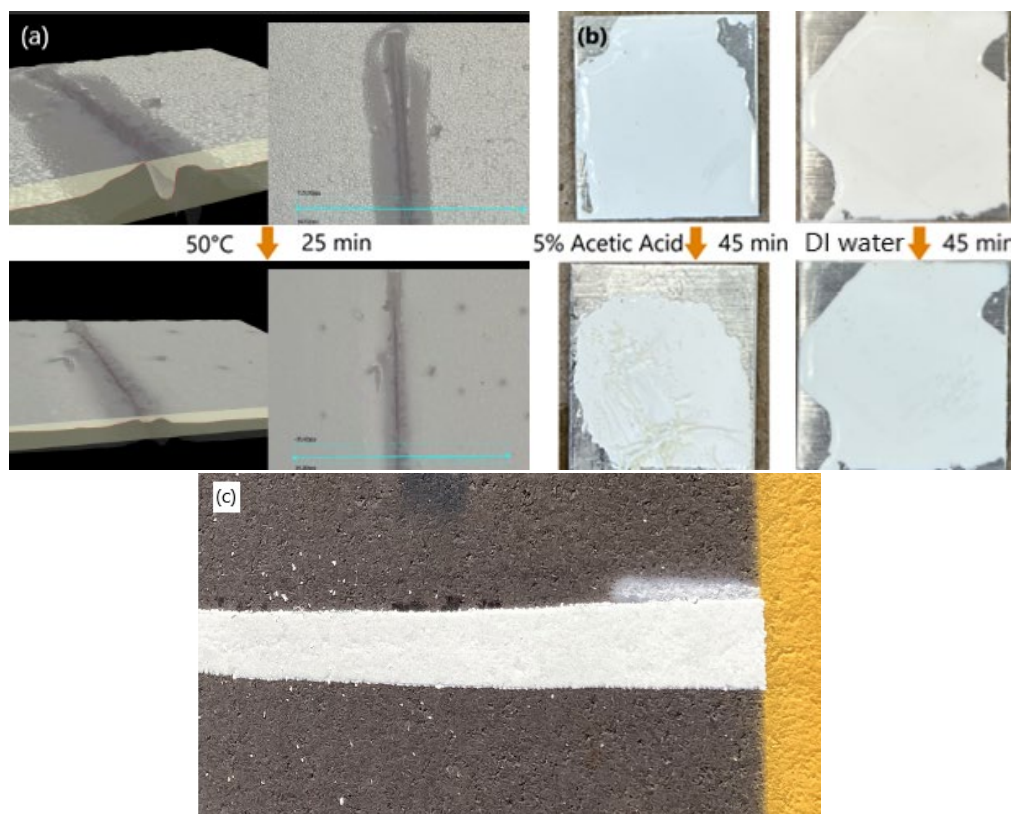
LEARN MORE

We plan to set up a website to disseminate the knowledge learned from this project after IP protection is completed.

To view the evaluations:

xxx@xxx.xxx

IMAGES

(a) Self-healing, (b) convenient removability, and (c) novel epoxy PMM applied on asphalt.