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Synthesis of Polyurethane from Sustainable Sources

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Honors Research Project

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Contents

Abstract

The current popular production of polyurethanes involves a reaction between various petroleum-based isocyanates and a polyol along with a catalyst; all of which have a negative impact on environmental and human health. The objective of this research project is to eliminate or mitigate the risks and hazards associated with the production and degradation of polyurethane. Hexamethylene diisocyanate isocyanurates (3HDI) are one of the most common isocyanates used in the polyurethane processing industry. 3HDI contains numerous toxins, and it has a negative impact on the environment and human health[1]. It has been found that there are other almost completely organic alternatives to 3HDI. One of these alternatives is a bio-based compound known as 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, or DDI. 3HDI, DDI, and linseed oil were tested as coatings on samples of sheet metal to determine their effectiveness as a coating. Linseed oil was used as a completely organic and unprocessed control. The coatings of each substance were tested in numerous ways including mechanical methods and chemical methods. Mechanical testing including pendulum hardness, cross-hatch adhesion, pencil hardness, and thickness. Chemical testing included chemical resistance, and electrostatic impedance spectroscopy (EIS). The results for each test were analyzed and compared amongst all three coatings. The linseed oil coating performed the worst with significantly lower protection of the metal substrate compared to DDI and 3HDI. DDI performed significantly better than the control coating, but it did not compare to 3HDI. 3HDI had much superior mechanical and chemical integrity results than the possible alternative of DDI. The only test that DDI had similar results with 3HDI was the pendulum test. This study shows that replacing 3HDI completely with DDI would most likely not be successful due to DDI being significantly inferior to 3HDI in mechanical

and chemical aspects. DDI would only be a viable option if the use of the polyurethane would not be affected by a significant decrease in integrity.

Executive Summary

Polyurethane polymers make up an enormous market of product ranging from automobile paint, coatings, adhesives, and much more[2]. Polyurethanes have many different routes of synthesis, but the most important and most widely used method is by reactions between polyols and diisocyanates. Diisocyanates contain two isocyanate functional groups that are highly reactive. Some of the most common isocyanates used in industry include aliphatic isocyanates such as hexamethylene diisocyanate isocyanurates (3HDI), aromatic diisocyanates such as toluene diisocyanate (TDI), and methylene diphenyl diisocyanate (MDI). Most of these are petroleum-based products have an enormous environmental impact on human lives and the surrounding environment. A majority are classified as CMR (carcinogenic, mutagenic, and reprotoxic). Polyurethanes synthesized from various diisocyanates are also toxic to plant and animal life and can pollute groundwater and release toxic amines in the breakdown stages[3]. The purpose of this research project is to investigate a safer and healthier alternative to the more popular petroleum based 3HDI. Hexamethylene diisocyanate is one of the most common compounds found in coatings, especially automotive paint. It is most often inhaled via vapor pathways when being applied as a spray but can also be ingested. 3HDI can also contaminate the water supply and the surrounding soil causing life-threatening effects and even death in nearby wildlife. Some of the adverse effects on human health include nose, eyes, and throat irritation along with pneumonia and difficulty breathing. Studies have shown workers who have developed an allergy and asthma-like symptoms that occur over time to constant exposure to HDI. A safer alternative to 3HDI is another isocyanate-based compound known as 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane or DDI. DDI is almost fully derived from renewable resources and is, therefore,

a suitable replacement for the petroleum-based HDI[4]. Since it is mostly bio-based, it will negate the volatile organic compound (VOC) emissions.

Introduction

Petroleum-based isocyanates are the most commonly used isocyanates to react with polyols to make polyurethanes. One of the most common ones, hexamethylene diisocyanate (HDI), is widely used for various types of coatings for numerous applications. 3HDI is highly reactive and has numerous health and environmental impacts ranging from skin, nose, and throat irritation to water contamination. Dimer fatty acid diisocyanate (DDI) is a nearly completely bio-based alternative that almost eliminates all these negative effects of 3HDI. The chemical structure for the compounds used in this experiment can be seen in the appendix.

Experimental Methods

Formulation & Development

The first step in the experimental procedure was to determine the formulation of the coatings. The normal ratio of isocyanate groups to hydroxyl groups in the coating mixture is set to 1.1, and this was used to calculate the coating mixture by the following procedure[5].

The normality of isocyanate groups in DDI is 285.71, meaning that in 285.71g of DDI there is 1 mole of isocyanate (NCO) groups. Likewise, there is 1 mole of hydroxide groups (OH) in 350.63g of castor oil. Knowing this, the following equation was used to calculate the DDI to castor oil ratio:

$$\frac{\mathrm{n(NCO)}}{\mathrm{n(OH)}} = 1.1$$

Knowing that n(NCO) in DDI is 285.71g, n(OH) in castor oil is 350.63g, and the ratio of isocyanates to hydroxides must be 1.1

$$\frac{285.71\mathrm{g}(1.1)}{350.63\mathrm{g}} = 0.896$$

Thus, for every gram of castor oil used, .896g of DDI must be added. The same procedure is done for 3HDI given that n(NCO) in 3HDI is 182.61g:

$$\frac{182.61\mathrm{g}(1.1)}{350.625\mathrm{g}} = 0.573$$

Once the formulation is completed, the two coatings are mixed together at the calculated ratios. The amount of castor oil used was approximately 10g for each coating. For the DDI coating, 10g of castor oil and 9.64g of DDI were mixed in a vial. For the 3HDI coating, 10.02g of castor oil was used along with 5.73g of 3HDI. The 3HDI formulation had trouble mixing together, so acetone was used to help the process. Around 10% of the total weight, or roughly 1.58g, of acetone, was added. The coating was considered mixed by making sure there were no irregularities in the vial and uniformity was clearly visible.

Once the coatings were thoroughly mixed, they were applied to stainless steel samples. This was done using a 20µm manual applicator where the coating mixture was emptied into the applicator until a uniform surface was seen. The applicator was then pulled down the test sheet. This was repeated approximately 10 times for each coating. Once all the samples were coated with the three formulations (including the control linseed oil coating), the samples were left to cure for a couple of days. The DDI and linseed oil samples were cured in an oven to further cure the coating, while the 3HDI samples did not need further curing. Once all the coatings for each sample were ready, the mechanical and chemical testing began.

Mechanical Integrity Testing

Several different testing methods were done in order to test the mechanical integrity of the three coating samples. These tests include pendulum hardness, pencil hardness, gloss, thickness, and cross-hatch adhesion. These tests were completed and then compared for all three coatings.

Pendulum Hardness

The pendulum hardness test involves using pendulum damping testers to determine the hardness of the coatings on each sample. The experiment is set up by setting the test sample on the pendulum displacement scale. The scale sits on a stand that supports the pendulum above the table. The test panel is placed on the panel table, and the pendulum is slowly brought to the surface. The pendulum is then deflected 6º, released, and the time for the amplitude to decrease from 6º to 3º is recorded. This method is known as the König Pendulum Test and is based on off ASTM D4366[6]. The apparatus is the BYK Pendulum Hardness Tester and is seen below in Figure 1.

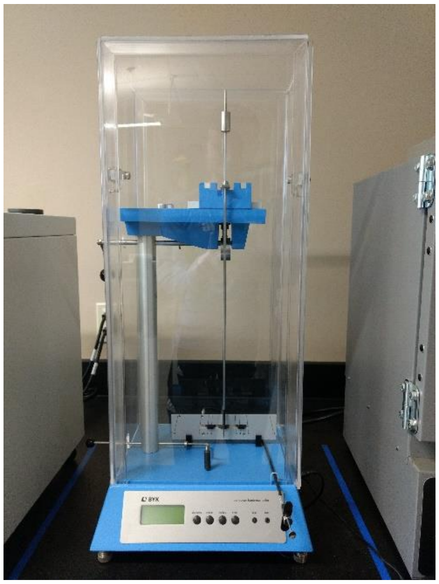
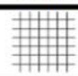
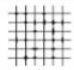
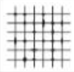
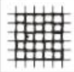
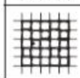
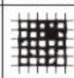
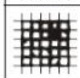
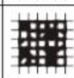
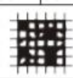


Figure 1. The BYK Pendulum Hardness Tester

Cross Hatch Adhesion

The cross-hatch adhesion test was completed using the Elcometer 1542 Cross Hatch Adhesion Tester. First, parallel scratch lines were made on the surface of the test sample using the Elcometer. Another set of parallel lines was scratched perpendicular and overlapping to the initial lines. The tape was then used to cover the scratched portion of the sample. The tape was removed at an approximately 90º angle and the results were analyzed. This test is done in accordance with ASTM D3359. The table used to analyze the results can be seen below in Table 1.

Table 1 shows the description for each outcome of the cross-hatch adhesion test

Surface	Description	ISO/JIS	ASTM
	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	0	5B
	Detachment of flakes of the coating at the intersections of the cuts. A cross cut area not significantly greater than 5% is affected.	1	4B
 	The coating has flaked along the edges and/or at the intersections of the cuts. A cross cut area significantly greater than 5%, but not significantly greater than 15% is affected.	2	3B
 	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross cut area significantly greater than 15%, but not significantly greater than 35%, is affected.	3	2B
 	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross cut area significantly greater than 35%, but not significantly greater than 65%, is affected.	4	1B
	Any degree of flaking that cannot be classified even by classification 4 (1B).	5	0B

Pencil Hardness

The Pencil Hardness Test is based off ASTM D3363[7] and helps determine the hardness of the coatings. It involves using a set of calibrated drawing pencils containing a scale of hardness seen in Figure 2. The BYK Pencil Hardness Tester was used to scratch the surface of each sample using pencils of various hardness. The BYK Pencil Hardness Tester can be seen below in Figure 3. Abrasive paper is also used to flatten the tip of each pencil to help ensure a 45^{0}angle scratch on the film.

$$\underbrace{6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H}_{\text{Softer} \qquad\qquad\qquad\qquad \text{Harder}}$$

Figure 2. The scale of levels of hardness for the pencil hardness tests

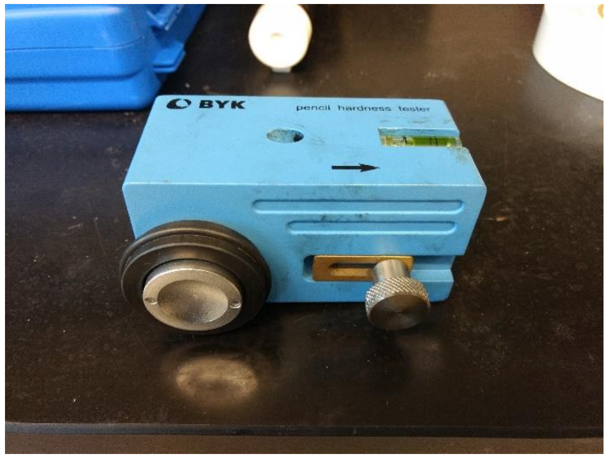


Figure 3. The BYK pencil hardness tester

Thickness

The thickness of each coating was analyzed to determine if they were consistent with each other. This was measured using a thickness meter. The thickness was measured at three different points of the coating on each test specimen in order to determine an average thickness for each sample.

Chemical Integrity Testing

Chemical integrity tests were also conducted to determine more than just mechanical components of the coating. A couple of the testing methods that were completed were electrochemical impedance spectroscopy (EIS) and chemical resistance. These tests were conducted for three samples for each different coating to find a consistent result.

Chemical Resistance

The chemical resistance testing was conducted with a simple rag and two different chemicals. Ethanol and methyl ethyl ketone (MEK) were used to determine the effectiveness of the coatings on coming in contact with chemicals. The rag was soaked with one of the two substances, and the coated samples were rubbed with a decent amount of pressure. A movement up and back down was counted as 1, and it was repeated until the coating degraded down to bare metal. This test is based off of ASTM D5402[8].

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance is normally measured by applying an alternating current (AC) potential at different frequencies to an electrochemical cell and then measuring that same current through the cell. This allows the measurement of the quality of a coating on a test sample. A current is induced on the sample and a circuit is applied. This results in the coating creating a high electrical resistance across the whole of the coating. The coating starts to degrade and deform in the corrosion process, which allows water and other electrolytes to infiltrate the corroded part of the coating. Thus, the electrical resistance of the coating is reduced.

The set-up of the experiment begins with clamping an electrochemical glass cell to the test specimen. This set-up can be seen in Figure 4(a-b). A rubber O-ring is placed in between the cell and the coated sample to prevent any leakage of the solution inside the cell. The cell is filled up with 3.5% sodium chloride solution. Once the set-up of the experiment is completed as shown below, the solution is set to sit for 30 minutes before the first data set is taken. A Gamry Reference 600 System is used to run the EIS measurement. The frequency of the measurement is measured between 0.01 Hz to 10^6 Hz with an open circuit potential of 0.1mV. Once the measurement is complete, the data is recorded. Once the first measurement is completed, the reference and counter electrodes are removed and set aside for the next data measurement. The next measurements are taken at 1, 3, 7, and 14-day intervals for a total of 5 EIS measurements. Bode plots are constructed in order to analyze the data. The x-axis is the frequency in hertz, and the y-axis is the impedance modulus |Z| in ohm-cm^2. Impedance is the resistance that is encountered when a current flow through the circuit that is set up in the experiment. Duplicates are tested for each coating sample to ensure good testing results.

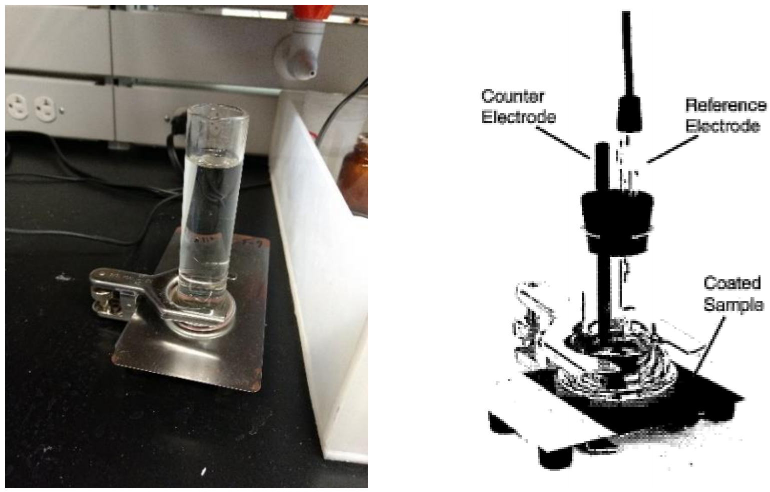


Figure 4. (a) The electrochemical cell and (b) the coated test sample set-up for EIS including the reference and counter electrodes.

Data & Results

DDI was investigating in this project to determine a safer and healthier alternative to the more toxic 3HDI. Linseed oil was used as the base case constant coating that 3HDI and DDI were compared to. Linseed oil was set as the constant because it is a naturally organic coating that has polymer-forming properties. The testing of the pendulum hardness, chemical resistance, and thickness measurements were taken 3 times. The average of these 3 was then taken. The pencil hardness and cross-hatch adhesion tests were taken only once. The results of the mechanical testing and chemical abrasion testing are seen below in Table 2. The EIS results are compiled below in Figure 5, where two EIS tests for each compound were conducted.

Mechanical Integrity Test Results

The mechanical integrity test consists of the general coating tests that were conducted for this experiment. These are pendulum hardness, cross-hatch adhesion, pencil hardness, and thickness tests.

Pendulum Hardness Test Results

The results of the pendulum hardness test can be seen below in Table 2. Three tests were conducted at the same parameters for each of the 3 coatings. The linseed oil coating showed the worst results out of the three. Linseed oil had a 16.33s result on the pendulum hardness test. DDI had an average pendulum hardness of 69.33s, while 3HDI had 78.67s.

Cross Hatch Adhesion

Crosshatch adhesion was completed once for each sample. The results of the test were determined using Table 1. Linseed oil had the best result of 5B, meaning that the edges of the cuts were completely smooth, and none of the squares of the lattice are detached. DDI was found to be

0B, where almost all of the coating was peeled off. 3HDI had a result of 3B, where the cross-cut area is only affected between 5-15% with flakey edges and intersections.

Pencil Hardness

The pencil hardness test was also conducted only once per coating sample. The linseed oil resulted in a 4H hardness level. DDI had the same result as the linseed oil, while 3HDI was not scratched by the hardest lead hardness of 9H.

Thickness

The thickness of the coatings was measured prior to all testing in order to pick samples that had relatively the same amount of thickness uniform throughout the sample. The linseed oil test sample had an average overall thickness of 19.77µm. The DDI and 3HDI coated samples had average thicknesses of 14.00µm and 18.13µm.

Chemical Integrity Test Results

The chemical integrity test results consist of chemical resistance testing and EIS. EIS was conducted over a 2-week period starting with 30min, 1 day, 3 days, 7 days, and 14 days. The results of both are seen in Table 2 and Figure 5.

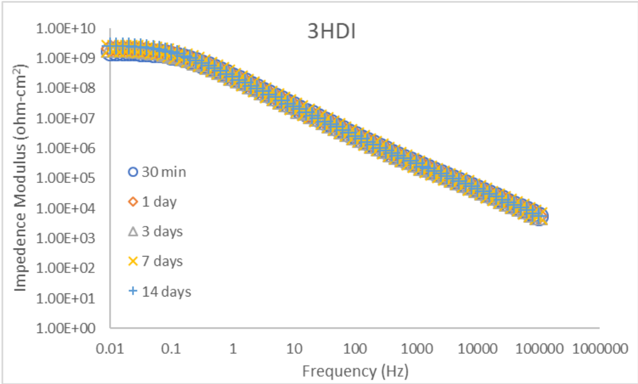
Chemical Resistance

The chemical resistance tests were conducted using methyl ethyl ketone (MEK) and ethanol. The test was conducted 3 times for each sample, and the average was taken. The linseed oil required roughly 10 counts to remove the coating. DDI required about double the amount, roughly 21.67 counts. 3HDI performed the best because it resisted up to 200 and did not lose any protection of the metal.

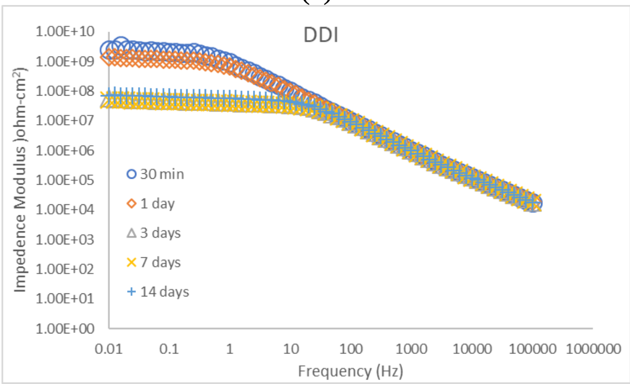
Electrochemical Impedance Spectroscopy (EIS)

EIS was used to analyze the corrosion resistance of the coating on each of the panels[9]. The frequency indicated the corrosion resistance, and the impedance to 0.1 Hz are shown in Figure 5. Over periods of time, water and other substance penetrate coatings to form new interfaces under the coatings. This causes corrosion to occur. The impedance data that is obtained from Figure 5 can be interpreted using a simple circuit shown in Figure 6. This circuit represents a failed coating where C_C is the capacitance of an intact coating. The failed coating is represented by C_{dl} and R_{ct} in parallel with each other. C_{dl} is the capacitance of the double layer coating, and R_{ct} represents a kinetically controlled charge-transfer reaction[10]. The double layer comes from the coating itself and the electrolyte solution that has formed from degradation over time. EIS data estimates these parameters such as pore resistance and capacitance, and these are then evaluated to determine the degree to which the coating has failed[11].

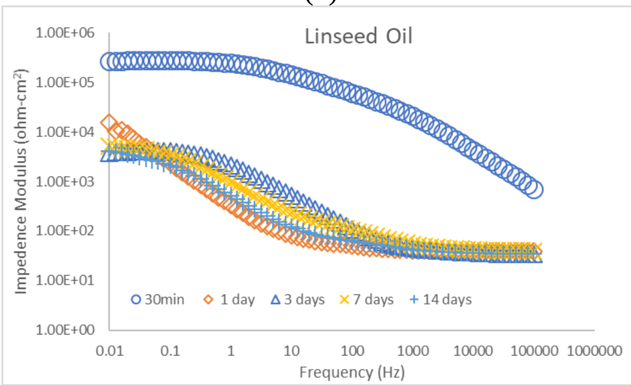
The inverse of capacitance is the impedance. Therefore, when the impedance is decreasing, the capacitance is increasing. Looking at the plots in Figure 5 and focusing on 3HDI, the results are almost exactly the same for all time frames. There is almost no change in the effectiveness of the coating in 14 days compared to 30 minutes; therefore, the coating is holding up very well. Looking at DDI, the impedance has significantly decreased at the 3-day mark. Linseed oil; however, has shown the greatest rate of decrease in impedance. The impedance decreased significantly after one day and continued to decrease afterward.



(a)



(b)



(c)

Figure 5 The EIS results for (a) 3HDI, (b) DDI, and (c) linseed oil

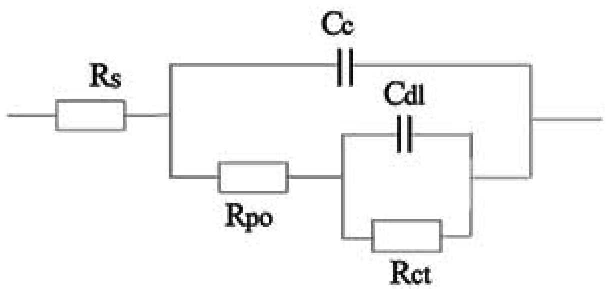


Figure 6. The simplified circuit for a failed coating

Table 2 shows the results of the integrity tests on the coating

	Linseed Oil		DDI		HDI	
Pendulum Hardness	16.33		69.33		78.67	
Pencil Hardness	4H		4H		9H+	
	ethanol	MEK	ethanol	MEK	ethanol	MEK
Chemical Resistance	10.33	5.00	21.67	6.33	200+	200+
Thickness (um)	19.77		14.00		18.13	

Table 3 shows the raw data of the results of the general coatings tests

	Linseed Oil		DDI		3HDI	
Pendulum Hardness (1)	7		90		91	
2	19		62		97	
3	23		56		48	
Pencil Hardness	4H		4H		9H+	
Chemical Resistance	ethanol	MEK	ethanol	MEK	ethanol	MEK
1	15	5	24	6	200+	200+
2	5	4	22	6	200+	200+
3	11	6	19	7	200+	200+
Cross Hatch Adhesion	5B		0B		3B	
Thickness (1) (um)	20.8		14.4		15.1	
2	20.2		16.2		18.6	
3	18.3		11.4		20.7	

Discussion & Analysis

The results of mechanical integrity tests can be seen in Table 1 and Table 3. The pendulum hardness test shows that 3HDI had the highest hardness level. A higher hardness signifies an increase in damping time. The damping time can be influenced by several factors including hardness, elasticity, the coefficient of friction, and the shore of the sample. DDI had a similar hardness of 69.33, which is not very far off. However, linseed oil had a significantly lower hardness of 16.33. This shows promising results that DDI could be an alternative to 3HDI. The pencil hardness test showed that 3HDI is very resistant to all the lead that was used in the test. The surface of the coating did not scratch for any hardness. DDI and linseed oil, on the other hand, scratched at a lead hardness of 4H.

The chemical integrity tests are also found in the same tables but also Figure 5 for the EIS results. The chemical resistance test had a slightly negative impact on the practicality of replacing 3HDI with DDI. 3HDI had very positive results in chemical resistance. For both MEK and ethanol, the coating never diminished. DDI, however, failed after roughly 22 swipes for ethanol and 6 for MEK. Linseed oil was even worse with only 10 rubs for ethanol and 5 for MEK. This shows why 3HDI is used so extensively in the industry.

The EIS results were also in favor of 3HDI. The results show why 3HDI is so widely produced and used extensively in the industry. The EIS results show that the coating performed and protected as it should over the entire course of the test. The impedance data practically remained constant throughout the entirety of the 2 weeks. The DDI coating, however, dropped impedance on the 3rd-day test. This means that the capacitance shot up due to the coating failing and allowing water or other electrolyte-filled substances to penetrate the coating. The control coating, linseed oil, performed the worst out of the 3 coatings. The impedance dropped, and the coating failed just after one day in the test.

This study investigated the possible alternative of replacing 3HDI with DDI as a diisocyanate group in the production of polymers. Polyurethanes are manufactured by the reaction between polyols and diisocyanates. 3HDI is one of the most widely used diisocyanates in the industry, but it is also a very toxic substance as it is petroleum based and non-renewable. DDI was investigated as an alternative because it is a renewable and almost completely organic isocyanate. Linseed oil was used as a control because it is a completely organic and natural coating. Mechanical and chemical integrity testing was completed in order to determine the effectiveness of these three coatings against a metal substrate. Linseed oil performed the worst with poor mechanical and chemical integrity. 3HDI performed very well in both categories, especially in chemical integrity. The possible alternative, DDI, performed slightly worse in certain categories and significantly worse in others in comparison to 3HDI. The hardness of the coating proved significantly worse in the pencil hardness test but almost similar in the pendulum hardness test. However, the chemical resistance proved much better in the 3HDI coating. Both linseed oil and DDI coatings failed early in the test with MEK. They performed slightly better with ethanol, but the 3HDI coating was no comparison with not failing at all for either substance.

Conclusion

The almost completely organic DDI substance was investigated as a possible alternative to the more toxic 3HDI isocyanate in the production of polyurethanes. Linseed oil was used as a completely organic control coating. Coatings were applied to metal substrates made from 3HDI, DDI, and linseed oil to test the effectiveness against corrosion. Chemical and mechanical testing was conducted on all 3 coatings once they were applied. The results of the testing and coating performance were analyzed. It was determined that the control, linseed oil, performed the worst with almost no protection of the metal substrate. DDI performed better than the control; however, it was still significantly worse than 3HDI. There is a reason that 3HDI is so widely used as the main isocyanate component in the production of polyurethanes, and that is because it has very good mechanical and chemical integrity. DDI is not a good alternative for the more toxic 3HDI, because it does not offer similar performance as a coating. Although it is organic and better for the environment, it will not perform nearly as well as the popular 3HDI. Another healthy alternative will need to be investigated in order to completely replace 3HDI as one of the main components in polyurethane production.

References

1. Abadin, H.; Spoo, W. Agency for Toxic Substances and Disease Registry **1998**.
2. Cornille, A.; Auvergne, R.; Figovsky, O.; Boutevin, B.; Caillol, S. European Polymer Journal **2017**, 87, 535–552
3. Noreen, A.; Zia, K. M.; Zuber, M.; Tabasum, S.; Zahoor, A. F. Progress in Organic Coatings **2016**, 91, 25–32.
4. Guan, J.; Song, Y.; Yin, X.; Zuo, M.; Zhao, Y.; Tao, Z.; Zheng, Q. Industrial & Engineering chemistry Research **2011**, 6517–6527
5. ASTM Standard D1652, 2011, “Epoxy Content of Epoxy Resins”, ASTM International, University of Akron, OH, 2011, DOI: 10.1520/D1652-11E01, www.astm.org
6. ASTM Standard D4366, 2016, “Pendulum Damping Tests”, ASTM International, University of Akron, OH, 2016, DOI: 10.152/D4366-16, www.astm.org
7. ASTM Standard D3363, 2011, “Film Hardness by Pencil”, ASTM International, University of Akron, OH, 2011, DOI: 10.1520/D3363-05R11E02, www.astm.org
8. ASTM Standard D5402, 2015, “Solvent Resistance of Organic Coatings Using Solvent Rubs”, ASTM International, University of Akron, OH, 2015, DOI: 10.1520/D5402-152, www.astm.org
9. Zhang, C.; Wang, H.; Zhou, Q. Progress in Organic Coatings **2019**.
10. Zhang, C.; Wang, H.; Zeng, W.; Zhou, Q. I&EC Research **2019**.
11. Cheng Zhang. Pigmented Polyurethane/Polysiloxane Hybrid Coatings for Corrosion Protection. Master of Science, University of Akron, Akron, OH, May, 2017.

Appendix

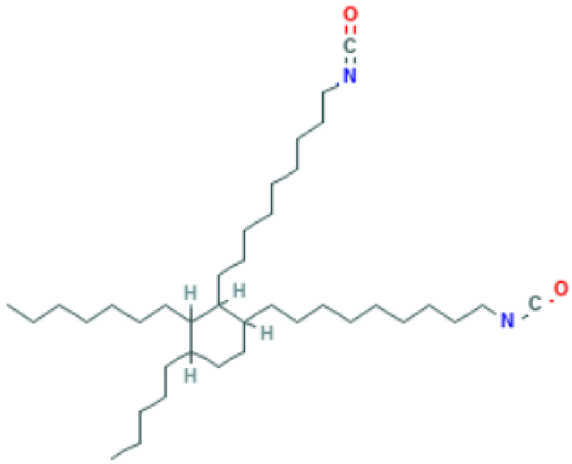


Figure A1- The chemical structure for DDI

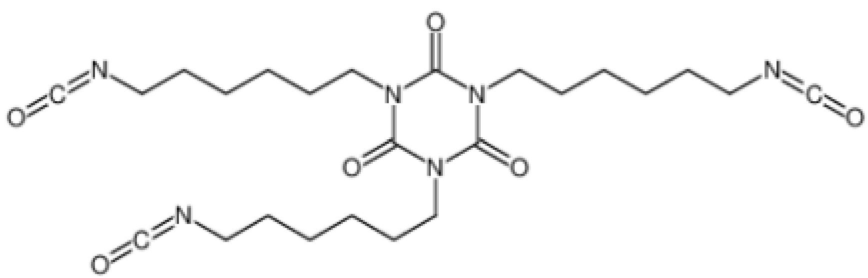


Figure A2 – The chemical structure for 3HDI

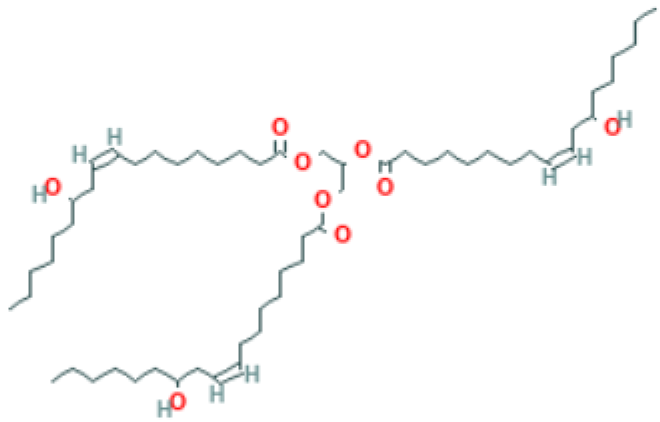


Figure A3 – The chemical structure for castor oil

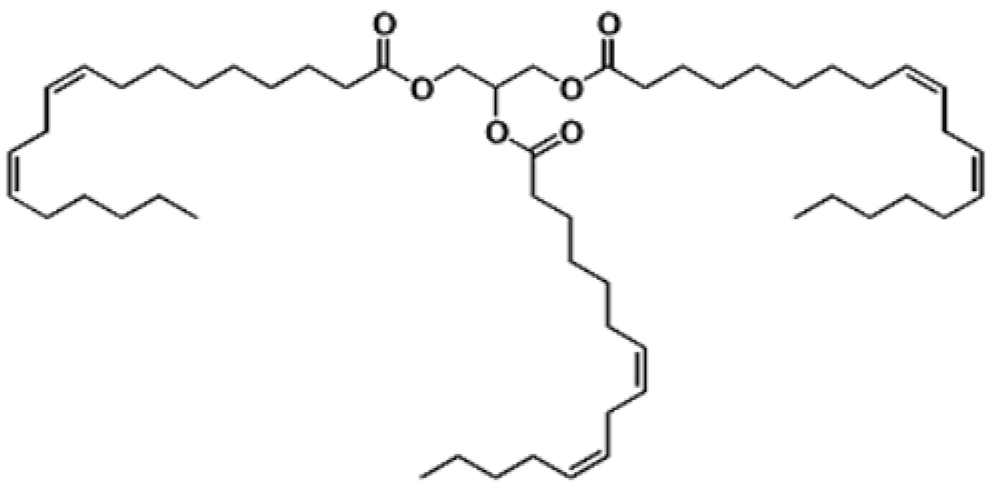


Figure A4 – The chemical structure for linseed oil