

**INVESTIGATION OF ADHESIVE PHOTODEGRADATION
IN POLYURETHANE-BASED SINGLE-PLY ROOFING
MEMBRANE SYSTEMS**



Cameron Lawrence
2B Architectural Engineering

September 2022

July 06, 2022

Dr. Brush

Associate Chair, Undergraduate Studies
Department of Civil and Environmental Engineering
University of Waterloo
Waterloo, ON, N2L 3G1

Dear Dr. Brush,

This report, entitled "Investigation of Adhesive Photodegradation in Single-Ply Roofing Membrane Systems," was prepared as my 2B work term report. This technical report was prepared during my Co-op at FORSMITH Building Science Consultants, under the supervision of "*Sheldon Warman, Principal*". The purpose of this report is to investigate how components commonly utilized in membrane adhesive products as additives may impact their chemical and physical properties, specifically how photodegradation affects adhesion.

This report focuses on conducting a meta-analysis of multiple secondary data sources to concentrate the focus of failing membrane adhesives to the chemical properties. This was investigated by comparing the degradation of photodegradable molecules found within thermoset and thermoplastic membranes that are currently available on the market.

With the information found based on analyzing the chemical construction of these products, potential alternatives were analyzed using thermogravimetric analyses to determine the best replacement additives to solve the problem of photodegradation posing a recurring issue in the single-ply roofing industry.

This report was written entirely by me and has not received any previous academic credit at this or any other academic institution. I would like to thank Sheldon Warman and Tyler Oliveira of FORSMITH Building Science Consultants for assisting me during the reviewing of the report. I received no other help with the report.

Sincerely,

A handwritten signature in black ink, appearing to read 'Cameron Lawrence', with a stylized, flowing script.

Cameron Lawrence

**INVESTIGATION OF ADHESIVE PHOTODEGRADATION
IN POLYURETHANE-BASED SINGLE-PLY ROOFING
MEMBRANE SYSTEMS**



Cameron Lawrence
2B Architectural Engineering

September 2022

Summary

This report, titled “Investigation of Adhesive Photodegradation in Polyurethane-Based Single-Ply Roofing Membrane Systems” investigates potentially causes for a recurring issue in low-sloped roofing membranes: adhesive degradation. This exploration includes a meta-analysis of the material composition of various thermoplastic olefin (TPO), polyvinyl chloride (PVC), and ethylene propylene diene monomer (EPDM) adhesive products to discover any similarities between the failing degrading membranes. Based on the findings, thermogravimetric analyses of isocyanate, polyhydroxyurethane, and polyurea polymers were conducted to find potential alternatives to the additives currently used in TPO adhesive products to improve the resistance to photodegradation, without sacrificing the current beneficial characteristics found within the current adhesive products.

Table of Contents

Summary	iv
List of Appendices	vii
1.0 Introduction.....	1
1.1. General	1
1.2. Background	2
1.3. Scope + Objectives.....	4
2.0 Engineering Application of Photodegradation in TPO, EPDM, and PVC	5
2.1. Introduction of Secondary Sources	5
2.2. Secondary Thermogravimetric Analysis.....	6
2.3. Analysis of Thermoplastic Polyolefin.....	9
3.0 Analysis of Isocyanatic Polyurethanes Alternatives.....	14
4.0 Conclusion	18
4.1. Results	18
4.2. Recommendations	19
5.0 References.....	21

List of Figures

Figure 1 - Mechanically Fastened EPDM, Adhered EPDM, & Ballasted EPDM Details	3
Figure 2 - Plotted Thermogravimetric Analyses.....	8
Figure 3: Example of (a) TGA and (b) DTG Graph	13
Figure 4 - Isocyanate Thermogravimetric Analysis.....	28
Figure 5 - Polyurea Thermogravimetric Analysis	30
Figure 6 - Polyhydroxy urethane Thermogravimetric Analysis	32

List of Tables

Table 1 – Results of Thermogravimetric Analyses.....	7
Table 2 – Composition of OlyBond 500 Adhesive (Carlisle Syntec Systems)	10
Table 3 – Composition of Flexible FAST Adhesive (Carlisle Syntec Systems)	10
Table 4 – Composition of OlyBond500 SpotShot (GAF)	10
Table 5 – Composition of TPO LRF Adhesive M Low Temp (GAF).....	10
Table 6 – Composition of JM Roofing System Urethane Adhesive (Johns Manville)	11
Table 7 – Composition of JM TPO 1168 Membrane Adhesive (Johns Manville)	11
Table 8 – Composition of Twin Jet Adhesive (Firestone Building Products).....	11
Table 9 – Composition of I.S.O FIX TM II Adhesive (Firestone Building Products)	11
Table 10 - Rate of Degradation of Isocyanate & Alternatives.....	16
Table 11 - Rate of Degradation of PHU, Isocyanates, and Polyurea.....	17
Table 12 – Low VOC PVC Bonding Adhesive (Carlisle Syntec Systems).....	24
Table 13 – Composition of SureSeal 90-8-30A Bonding Adhesive (Carlisle Syntec Systems) ..	24
Table 14 – Composition of Everguard 2331 Bonding Adhesive (GAF)	24

Table 15 – Composition of JM PVC Membrane Adhesive Low VOC (Johns Manville)	25
Table 16 – Composition of JM Membrane Bonding Adhesive (Johns Manville).....	25
Table 17 – Composition of PVC LVOC Bonding Adhesive (Firestone B.P.)	25
Table 18 – Composition of EPDM Bonding Adhesive BA-2004(T) (Firestone B.P.)	26
Table 19 – Isocyanate Thermogravimetric Analysis Data (1)	27
Table 20 – Isocyanate Thermogravimetric Analysis Data (2)	27
Table 21 – Isocyanate Thermogravimetric Analysis Data (3)	28
Table 22 – <i>Polyurea Thermogravimetric Analysis Data (1)</i>	29
Table 23 – <i>Polyurea Thermogravimetric Analysis Data (2)</i>	29
Table 24 – <i>Polyurea Thermogravimetric Analysis Data (3)</i>	30
Table 25 - Polyhydroxy urethane Thermogravimetric Analysis Data (1)	31
Table 26 - Polyhydroxy urethane Thermogravimetric Analysis Data (2)	31
Table 27 - Polyhydroxy urethane Thermogravimetric Analysis Data (3)	32

List of Appendices

Appendix A:.....	24
APPENDIX B: Isocyanate Data	27
APPENDIX C: Polyurea Data	29
APPENDIX D: Polyhydroxy urethane Data.....	31

1.0 Introduction

1.1. General

Since the 1960s, single-ply membranes have become increasingly popular on low-slope roofing in North America (SPRI News, 2019). These membranes are extremely popular for their waterproofing properties, durability, installation process, and extended service life relative to other roofing systems. Thermoplastic polyolefin (TPO) is an innovative product to commercial roofing and has been growing in popularity rapidly for years. However, many members of the roofing and building science industries are skeptical about TPO due to many instances of the single-ply membranes separating from the substrate when using an adhesive bond. This separation can render the structure susceptible to water infiltration, causing damage to the roofing system and structural components.

Additives are substances or components that are included in products for various reasons. For example, chemical additives in food are added to increase the taste or prolong the shelf life. Similar to chemical additives in food products, additives are also used within the development of material products to improve various aspects, such as penetration resistance, UV stabilization, and longevity. However, additives within any product may come with disadvantages. In the food analogy, a negative effect of additives may be health complications or the destruction of healthy vitamins and nutrients in order to increase the shelf life. With that said, single-ply roofing membranes are constantly innovating, and companies are developing new methods to efficiently produce their products. This frequently involves altering the manufacturing process, using new chemicals and materials to enhance the product. This development often uses additives that are not well-established within the industry to maximize the performance. However, after many failures within adhered roofing membrane systems, professionals have assumed additives to be the

fundamental error. Although it is common knowledge to members of the roofing industry that these membranes systems can and do fail frequently due to the adhesive; there is limited research on the effect additives may have to the long-term performance of TPO roofs.

This report investigates the chemical properties of components used to develop adhesive products for common single-ply roofing membranes. The investigation was conducted through a secondary data analysis with an aim to isolate additives or components that cause photodegradation of the adhesive. The hypothesis of the investigation indicates that there will be an isolated component within thermoplastic olefin adhesive coatings that is associated with performance loss as a result of photodegradation. Therefore, the null hypothesis states that the results of the analyses conducted were inconclusive regarding isolating a component within thermoplastic olefin adhesive products that are linked to performance loss. Regardless of the outcome of the investigation, a further exploration of potential alternatives for TPO adhesives will be conducted.

1.2. Background

There are a few types of single-ply membranes used in roofing systems. The two primary types are thermoset and thermoplastic membranes. Thermoset membranes are a synthetic rubber material, that contains seams sealed using liquid adhesive or product-specific tape. Common thermoset products include ethylene propylene diene terpolymer (EPDM), chlorosulfonated polyethylene (CSPE), epichlorohydrin (ECH), neoprene (CR), and polyisobutylene (PIB). Thermoplastic membranes can be a synthetic rubber or plastic material and are heat welded at the seams. Common thermoplastic membranes are thermoplastic olefin (TPO), chlorinated polyethylene (CPE), polyvinyl chloride (PVC), copolymer alloy (CPA), ethylene interpolymer (EIP), nitrile alloys (NBP), and tripolymer alloy (TPA) (Stonewater Roofing, 2018). Although all

of these products are used in their own respective applications, the most common single-ply roofing membranes are EPDM, TPO, and PVC.

Single-ply roofing membranes can be connected to the substrate through mechanical fasteners, adhesive bonding, or ballasting. Mechanical fastening includes bolting the membrane to the substrate and reinforcing the seams with additional bolts. Adhesive bonding utilizes an adhesive or epoxy material to join the surface of the membrane and the substrate, then heat welding the seams. Lastly, ballasting involves laying loose gravel or stone on top of the membrane. The three connections are shown in Figure 1

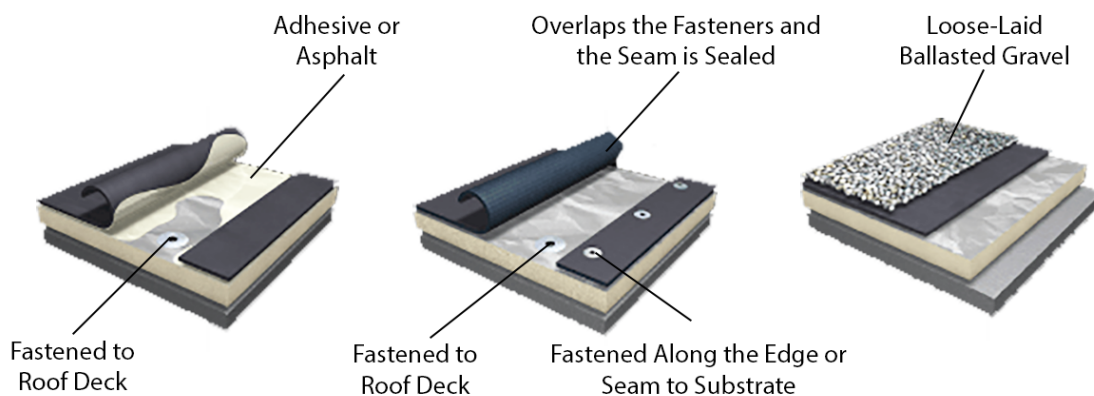


Figure 1 - Mechanically Fastened EPDM, Adhered EPDM, & Ballasted EPDM Details

*Image adapted from J. Carnes & Son Roofing (J. Carnes & Son Roofing, 2022)

Each mechanism of fastening has their own respective advantages and disadvantages. However adhesive failures of thermoplastic membranes are a novel issue not seen in other roofing systems, whereas issues such as billowing (sheet flutter) are issues with any mechanically fastened membrane and punctures from roof traffic are issues with any ballasted membrane. Adhesive degradation has been a recurring issue within TPO, a thermoplastic membrane roofing system, causing many people within the roofing industry to become skeptical of the product.

TPO manufacturers are heavily invested into the research and development phase for their products, attempting to create the best balance of cost efficiency and durability. Because of this, the products are far from level of quality and integrity of EPDM and PVC. Although PVC and EPDM adhesion has been an issue before, many assessments have determined the issues were related to faulty manufacturing or poor application. However, the chemical composition of TPO is expected to be a probable cause of its adhesive failure, causing a range of different manufacturing approaches to be implemented.

1.3. Scope + Objectives

For this study, it was of interest to investigate the composition of common adhesive products for thermoplastic olefin (TPO), ethylene propylene diene terpolymer (EPDM), and polyvinyl chloride (PVC) roofing systems and analyze recurring failures through comparisons of findings from various scholarly articles regarding photodegradation. Firstly, a secondary data analysis of heat accelerated TPO, EPDM, and PVC membranes will be conducted to test the hypothesis of TPO having the fastest rate and most severe deterioration. Secondly, the investigation will involve the analysis of product information and Safety Data Sheets (SDS) provided by Carlisle Syntec Systems, GAF, Johns Manville, and Firestone Building Products to obtain a list of chemical compounds used to develop their adhesive products. The objective of this research is to identify additives used to manufacture these membranes in an attempt to isolate compounds responsible for increasing the rate of photodegradation within the membranes and propose alternatives.

2.0 Engineering Application of Photodegradation in TPO, EPDM, and PVC

2.1. Introduction of Secondary Sources

There are many existing studies that have been conducted to test the degradation of TPO, EPDM, and PVC. However, most studies are limited to investigating the longevity of individual membranes rather than comparative analyses. Although there are no well-documented comparative analyses, many studies that have conducted for each of the three membranes followed a similar scope and objective of testing longevity. This allowed for an opportunity to analyze of the three membrane materials using reputable secondary data. To use these sources to test the outlined hypothesis, raw data collected from thermogravimetric analyses were used. Thermogravimetric analyses are a method of thermal analysis that tests the effect of mass as temperature is changed.

“Evaluation of Thermoplastic Olefin (TPO) Roofing Membranes” (Simmons, T. R.; Paroli, R. M.; Liu, K. K. Y.; Delgado, A. H.; Irwin, J. D., 1998) is an article published from National Research Council Canadian written by Simmons et al. The study included a five-year investigation of various the effect of aging TPO on various properties. This study includes an experiment that involved a thermogravimetric analysis from 23.0°C to 1000.0°C, measuring the mass in three specified intervals (25-340°C, 340-550°C, and 550-1000°C).

“Experiment Research on the Mechanical Performance of EPDM Insulation Pyrolysis Process” (Jing Jiang, Jin-sheng Xu, Xiong Chen & Zhong-shui Zhang, 2015) is an article published from the Nanjing University of Science and Technology authored by Jing Jiang, Jin-sheng Xu, Xiong Chen & Zhong-shui Zhang. The experiment involved the study of the pyrolysis process on EPDM to measure effects on mechanical and thermal behaviour. The study involved a thermogravimetric analysis of a 6.56mg sample of EPDM from 100.0°C to 800.0°C.

“The effect of Zn, Al layered double hydroxide on thermal decomposition of poly(vinyl chloride)” (Zhi Ping Xu, Susanta K. Saha, Paul S. Braterman, Nandika D'Souza, 2006) is an article written by members of the University of Queensland and the University of North Texas: Zhi Ping Xu, Susanta K. Saha, Paul S. Braterman, and Nandika D'Souza. It includes a systematic investigation of poly (vinyl chloride) and layered double hydroxide (LDH) in air and nitrogen investigation. The thermogravimetric portion of this study experiments the rate of degradation through mass loss, as the heating rate ($^{\circ}\text{C}/\text{min}$) is changed in air and nitrogen mediums.

A limitation with the cross-analysis of these studies is that the action taken for controlled variables may be inconsistent between the three. Because these studies were originally designed for a different reason, including some for scholarly applications and some for-company research, varying degrees of data accuracy were noted. Although each study included a thermogravimetric analysis, the methodology to collect data may vary. Potential variations could include discrepancies between equipment, procedures, or quantity of data collected. Additionally, because the purpose of each project varied slightly, the range and frequency in which data was collected also varied. Therefore, within the cross-analysis, actions were taken to minimize the variability, including reducing the range of data.

2.2. Secondary Thermogravimetric Analysis

To analyze the data from the three sources previously outlined, specific thermogravimetric data was extracted. The data included temperatures measured at various points throughout the heat accelerated aging and the mass of the sample. This data can be plotted on a thermogravimetric analysis (TGA) plot, where as the loss of mass is the dependent variable and temperature is independent.

Due to the raw data originating from three separate studies, varying control measures were taken. In this case, different sample sizes were used between the three. Therefore, to conduct an appropriate analysis of the data, the loss of mass was converted to percentage of mass loss to account for variations in the sample. The starting sample mass is assumed to be 100%, and loss of mass is measured in percent loss.

Additionally, the range of data collected varied in size, being the most limited by the EPDM study. The EPDM study stopped collecting data that exceeded 550°C, therefore, to obtain the most accurate representation of how these membranes perform relative to each other, the heat accelerated data was limited to a range with a maximum temperature of 550°C.

The data shown in Table 1 is a composition of the reproduced data from the three studies of investigation.

Table 1 – Results of Thermogravimetric Analyses

TPO		EPDM		PVC	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
23.0	100.0	100.0	100.0	400.0	100.0
250.0	100.2	150.0	99.1	430.0	97.5
340.0	95.8	260.0	97.6	450.0	87.4
375.0	95.0	360.0	80.0	470.0	70.3
400.0	80.0	510.0	53.4	490.0	58.1
550.0	26.3	550.0	51.1	510.0	51.1
				530.0	43.9
				550.0	36.9
*Reproduced from (Simmons, T. R.; Paroli, R. M.; Liu, K. K. Y.; Delgado, A. H.; Irwin, J. D., 1998)		*Reproduced from (Jing Jiang, Jin-sheng Xu, Xiong Chen & Zhong-shui Zhang, 2015)		*Reproduced from (Zhi Ping Xu, Susanta K. Saha, Paul S. Braterman, Nandika D'Souza, 2006)	

The data from Table 1 was plotted on a standard TGA plot as shown in Figure 2 for a visual representation of weight loss trends.

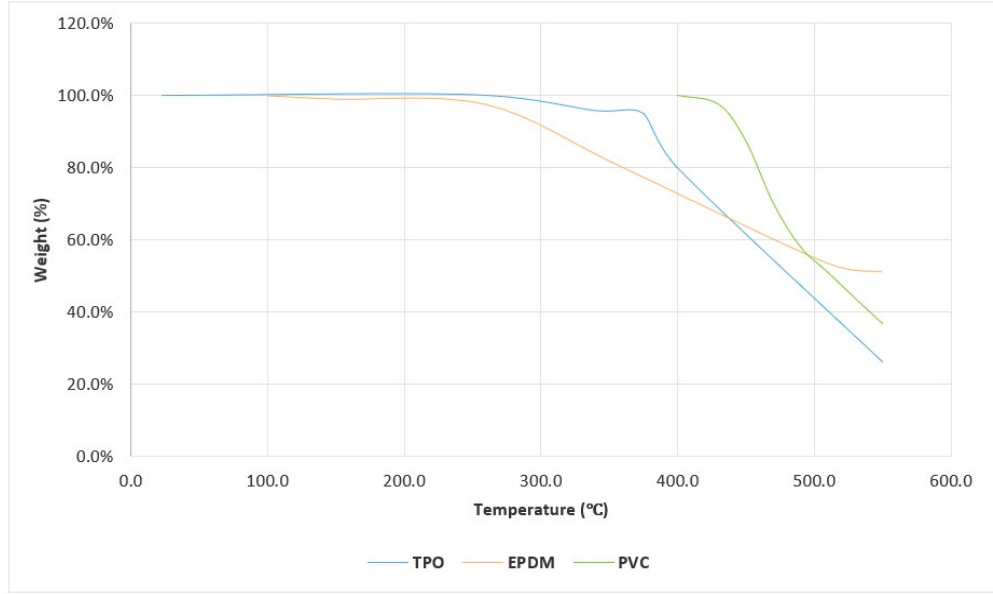


Figure 2 - Plotted Thermogravimetric Analyses

Based on the data above, it is apparent that degradation of the three products accelerates at different temperatures, starting with EPDM, followed by TPO, then PVC. However, based on visual observations, it can be seen that once the threshold temperature of degradation is reached, EPDM degrades the slowest. Although the degradation of each of the three products is not linear, a simplified rate of degradation can be modelled using start and end behaviours. To calculate the rate at which the materials degrade relative to each other, a basic slope calculation will be calculated using the following formula, where as mass at a temperature is denoted as M , temperature as T , and rate of change as m :

$$m = \frac{M_2 - M_1}{T_2 - T_1}$$

Assuming T_1 is the value at which the accelerated degradation begins and T_2 is 550°C, it was found that the rate of change for EPDM, TPO, and PVC were -0.16 (%/°C), -0.39 (%/°C), and -0.51 (%/°C), respectively. Based on these findings, it is apparent that PVC degrades at the fastest rate and EPDM degrades the slowest. However, an important observation is that although TPO reaches a mean rate of degradation that is slower than PVC, it begins degrading at lower temperatures and reaches a percentage loss of mass of 75% or more at far lower temperatures than either of the other two membranes.

In conclusion, it was found that TPO faced the most extreme impact of the three membranes analyzed in terms of loss of mass through degradation until extreme temperatures, of approximately 600°C or higher, are achieved as indicated based on their trend as modelled in Figure 2.

2.3. Analysis of Thermoplastic Polyolefin

To investigate causation for the adhesive photodegradation and overall rapid degradation observed in TPO that is not occurring as predominantly in PVC and EPDM; the chemical compounds were cross compared to determine if there were any potential common ingredients found between various TPO adhesive products that were not present in other membrane adhesives. A brief visual cross-comparison was done between eight (8) TPO adhesive products based on the available information within their Safety Data Sheets, including compound information, Chemical Abstracts Service (CAS) number, and percentage by mass to identify any correlation between their components as shown in Table 2 through Table 9. These similarities are highlighted.

Table 2 – Composition of OlyBond 500 Adhesive (Carlisle Syntec Systems)

Compound	CAS Number	Percentage
Diphenylmethane Diisocyanate Mixed Isomers	26557-40-5	< 10
4,4'-Methylene Bisphenyl Isocyanate	101-68-8	37-39
Polymeric Isocyanates	9016-87-9	< 55

*Reproduced from associated Safety Data Sheet (Carlisle Syntec Systems, 2015)

Table 3 – Composition of Flexible FAST Adhesive (Carlisle Syntec Systems)

Compound	CAS Number	Percentage
Diphenylmethane-4,4'-diisocyanate (MDI)	101-68-8	25-60
4,4'-Methylenediphenyl diisocyanate, oligomers	25686-28-6	3-7
Methylenediphenyl diisocyanate	26447-40-5	10-30
Isocyanates, reaction product of polyol with methylenediphenyl diisocyanate	39420-98-9	10-30
P-MDI	9016-87-9	7-13
Diphenylmethane diisocyanate, homopolymer	39310-05-9	10-30
Diphenylmethane-2,4'- diisocyanate	5873-54-1	10-30

*Reproduced from associated Safety Data Sheet

(Carlisle Syntec Systems, 2015)

Table 4 – Composition of OlyBond500 SpotShot (GAF)

Compound	CAS Number	Percentage
Diphenylmethane Diisocyanate Mixed Isomers	26557-40-5	< 10
4,4'-Methylene Bisphenyl Isocyanate	101-68-8	37-39
Polymeric Isocyanates	9016-87-9	< 55

*Reproduced from associated Safety Data Sheet (GAF, 2016)

Table 5 – Composition of TPO LRF Adhesive M Low Temp (GAF)

Compound	CAS Number	Percentage
----------	------------	------------

Diphenylmethanediisocyanate, isomers and homologues	9016-87-9	25-50
4,4'-Methylenediphenyl diisocyanate	101-68-8	25-50
Polyol	25322-69-4	10-25
methylenediphenyl diisocyanate	26447-40-5	2.5-10

*Reproduced from associated Safety Data Sheet (GAF, 2016)

Table 6 – Composition of JM Roofing System Urethane Adhesive (Johns Manville)

Compound	CAS Number	Percentage
Isocyanic acid, polymethylenepolyphenylene ester	9016-87-9	N/A
4,4'-Methylenediphenyl diisocyanate	101-68-8	30-60
Methylenediphenyl Diisocyanate	26447-40-5	1-10

*Reproduced from associated Safety Data Sheet (Johns Manville, 2021)

Table 7 – Composition of JM TPO 1168 Membrane Adhesive (Johns Manville)

Compound	CAS Number	Percentage
Benzene, 1-chloro-4-(trifluoromethyl)-	98-56-6	60-80
Toluene	108-88-3	1-10
Methyl acetate	79-20-9	1-10

*Reproduced from associated Safety Data Sheet (Johns Manville, 2019)

Table 8 – Composition of Twin Jet Adhesive (Firestone Building Products)

Compound	CAS Number	Percentage
Polymeric Diphenylmethane Diisocyanate (pMDI)	9016-87-9	< 50
4,4'-Diphenylmethane Diisocyanate (MDI)	101-68-8	25-50
Norflurane	811-97-2	10-25
Other components below reportable levels	N/A	< 15

*Reproduced from associated Safety Data Sheet (Firestone Building Products, 2021)

Table 9 – Composition of I.S.O FIX™ II Adhesive (Firestone Building Products)

Compound	CAS Number	Percentage
Polypropylene glycol, polymethylenepolyphenylene isocyanate polymer	53862-89-8	30-60

Polymethylene polyphenyl isocyanate	9016-87- 9	10-30
1,1,1,2-Tetrafluoroethane	811-97-2	10-30
Isocyanic acid, methylene di-phenylene ester	101-68-8	7-13
Amine catalyst	6425-39- 4	1-5

*Reproduced from associated Safety Data Sheet (Firestone Building Products, 2018)

As can be seen from the tables above, there is significant similitude between components used to develop adhesives from the four manufacturers. The common factor between seven of the eight adhesives are isocyanates, which are a common compound in commercial purposes. Isocyanates are known to be one of the best chemicals for adhesives, as when used with other polymers they enhance the performance of the adhesive (Warwick Mills Inc., 2022). Isocyanates that are commonly used in commercial uses are diisocyanate (MDI), toluenediisocyanate (TDI), hexamethylene diisocyanate (HDI) and their polymeric forms (Crow, 2022). These products commonly used for the economic feasibility compared to alternatives such as aliphatic isocyanates (HDI), although MDI, TDI, and HDI are highly reactive and more “susceptible to oxidation and degradation” (Crow, 2022).

By analyzing the compounds in PVC or EPDM products by the same manufacturers (see Table 12 to Table 18 in Appendix A), the identified isocyanates are not found. This may suggest a potential cause for the discrepancy between TPO relative to PVC and EPDM. The analyzed PVC and EPDM products tended to use products such as polychloroprene, polyphenol antioxidants, phenolic resins, etc... to obtain similar properties. These additives are crucial to the integrity of the adhesive for these products, as degradation of these compounds will cause an extreme decline in performance. Isocyanates are found within polyurethane products and are highly reactive chemicals used to develop coatings (such as paint), elastomers, and building insulation materials (The National Institute for occupational Safety and Health (NIOSH), 2014). Within polyurethane

materials, these isocyanate compounds are used as additives and are intended to enhance the performance of products, such as thermal or chemical resistance.

When conducting a thermogravimetric analysis on adhesive compounds, three stages are apparent in the behaviour of the photodegradation. These three segments are differentiated by significant variation in the derivative of the rate of change as shown on a derivative thermogravimetric (DTG) graph. The first segment represents a loss of mass due to moisture; the second segment indicates the loss of mass due to degradation of volatile matter, the third segment is the decomposition of derivatives of cellulose and lignin. The TGA and DTG graphs are plotted in Figure 3.

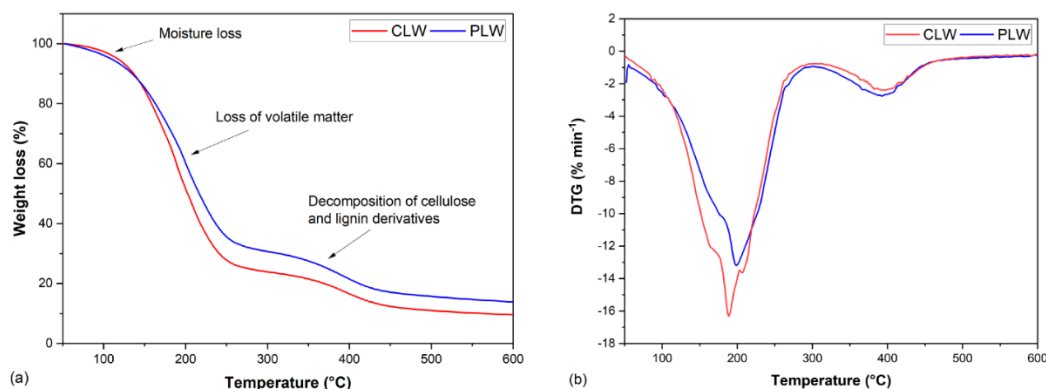


Figure 3: Example of (a) TGA and (b) DTG Graph

Typically, the loss of volatile matter is responsible for the most significant loss of weight within adhesives. All of the adhesive products analyzed include volatile organic compounds (VOCs) that degrade within this stage. These VOCs include but are not limited to benzene, toluene, and isocyanates. Because isocyanates are VOCs found in TPO adhesives and are included within the largest phase of degradation; the conclusion can be drawn that rapid degradation of polyurethane-based products will lose adhesive properties as volatile matter degrades. Contrastingly, benzene and toluene are found in both EPDM and PVC adhesives, and the

degradation of these VOCs will not affect the adhesion properties. This indicates a crucial discrepancy between the adhesive properties of TPO relative to PVC and EPDM products.

3.0 Analysis of Isocyanatic Polyurethanes Alternatives

Isocyanatic polyurethanes have been scrutinized before due to their “low thermostability” (O. Figovsky, L. Shapovalov, F. Buslov, 2005). In various applications, polyurethane materials have been found to have significantly improved mechanical properties compared to alternatives, but with such a great reduction in thermal performance, many members of the roofing industry find it difficult to justify using polyurethane based materials.

In addition to thermostability, there has been concern regarding the safety of isocyanatic compounds, prompting research into prospective alternatives. Isocyanates are volatile organic compounds (VOCs) and are known to be potential human carcinogens. Exposure to polyurethane products through application or manufacturing can directly have negative health implications such as skin irritation, difficulty breathing, or long-term lung issues (United States Department of Labor, 2022). Although measures have been taken in the workplace to require a National Institute for Occupational Safety & Health (NIOSH) certified supplied-air respirator when working with isocyanates (Employment and Social Development Canada, 2021), there is still a large push for manufacturers to develop products without the use of isocyanates.

Because of safety and thermal performance concerns, two products have been commonly proposed as potential alternatives to polyurethane-based products that use isocyanates to reduce the use of the VOC additive. Firstly, a method to prepare compounds with increased thermostability is by “using **polyhydroxy urethane** instead of block diisocyanates” (O. Figovsky, L. Shapovalov, F. Buslov, 2005). A second alternative is **polyurea**. Polyurea shares many

advantageous properties to polyurethane, however “some of these properties are enhanced in the new polyurea structural adhesive, and a range of other benefits is brought along” (Adhesive Platform, 2022). To compare the performance of polyurethanes, polyhydroxy urethanes (PHU), and polyureas, a TGA was done for multiple polymers of each compound. This meta-analysis of six (6) independent studies, including two isocyanate (see appendix B), two polyurea (see appendix C), and two polyhydroxurethane (see appendix D) studies. For consistency, the same controls were implemented for each TGA as previously mentioned, including using a starting weight of 100%.

The intention of the cross-analysis is to identify if either of the two commonly proposed alternatives (polyureas and PHUs) would improve the thermal performance of thermoplastic olefin adhesives while using alternatives that are known to have similar adhesion properties.

To calculate the rate at which the three compounds degrade relative to each other, an average rate of degradation will be calculated. Because the loss of moisture will vary between adhesives, the average rate of degradation was taken starting from the beginning of the loss of volatile matter. The rate of degradation will be calculated using the following formula whereas mass at a temperature is denoted as M , temperature as T , and rate of change as m :

$$m = \frac{M_2 - M_1}{T_2 - T_1}$$

Assuming T_1 is the temperature at which the volatile compound degradation begins and T_2 is temperature at which the volatile compound degradation ends. The results of these calculations are shown in Table 10.

Table 10 - Rate of Degradation of Isocyanate & Alternatives

Isocyanates		Polyurea		Polyhydroxy urethane	
Polymer	Rate of Deg. (%/100°C)	Polymer	Rate of Deg. (%/100°C)	Polymer	Rate of Deg. (%/100°C)
TDI Elastomer	-0.397	PA4N-Urea	-0.247	PHU(0)	-0.293
TDI Foam	-0.328	PA5N-Urea	-0.237	PHU(30)	-0.287
MDI Foam	-0.266	PA6N-1-Urea	-0.270	PHU(50)	-0.293
EPPU	-0.488	PA6N-2-Urea	-0.280	PHU(70)	-0.293
EPPU-2	-0.573	PA7N-Urea	-0.247	PHU(100)	-0.290
		ATPUa	-0.247	1,6-Hexanediamine	-0.285
		ATPUa-Zn(II)	-0.237	1,8-Diaminooctane	-0.370
		ATPUa-Mn(II)	-0.270	Isophorondiamine	-0.333
		ATPUa-Co(II)	-0.280		
		ATPUa-Ni(II)	-0.247		

The results of Table 10 were ordered from in order of decreasing magnitude of the rate of degradation, whereas isocyanates are labelled red, polyureas are green, and polyhydroxy urethanes are blue. This is shown in Table 11.

Table 11 - Rate of Degradation of PHU, Isocyanates, and Polyurea

Rank	Polymer	Rate of Degradation (%/100°C)
23	EPPU-2	-0.573
22	EPPU	-0.488
21	TDI Elastomer	-0.397
20	1,8-Diaminooctane	-0.370
19	Isophorondiamine	-0.333
18	TDI Foam	-0.328
17	PHU(0)	-0.293
16	PHU(50)	-0.293
15	PHU(70)	-0.293
14	PHU(100)	-0.290
13	PHU(30)	-0.287
12	1,6-Hexanediamine	-0.285
11	PA6N-2-Urea	-0.280
10	PA6N-1-Urea	-0.270
9	MDI Foam	-0.266
8	PA4N-Urea	-0.247
7	PA7N-Urea	-0.247
6	PA5N-Urea	-0.237
5	ATPUa	-0.198
4	ATPUa-Ni(II)	-0.175
3	ATPUa-Mn(II)	-0.144
2	ATPUa-Co(II)	-0.138
1	ATPUa-Zn(II)	-0.110

Based on the results of ordering the polymers in decreasing rate of degradation, it can be observed ten of the eleven polymers with the lowest rate of degradation were polyureas while the three polymers with the highest rate of degradation were isocyanates. Based on observation of the

list, it is notable that on average polyureas had the best performance in terms of rate of degradation, followed by polyhydroxy urethanes, and then isocyanates, maintaining averages of -2.04, -0.306, -0.410 (%/100°C), respectively. Based on this information it is evident that isocyanates are the worst of the analyzed isomers apart from an outlier, MDI Foam. Although MDI Foam obtained the 9th lowest rate of degradation; a general conclusion was isocyanates performed poorly.

4.0 Conclusion

4.1. Results

Although polyurethane based adhesives are commonly found in thermoplastic olefin products, the analyses within the report demonstrate an extremely insufficient performance in regard to photodegradation. Based on a meta-analysis of many studies published from various reputable institutions, the skepticism regarding the long-term viability of TPO is warranted. The findings indicate the deficiencies can be correlated to the chemical compounds used to formulate the adhesives, based on the isolation of isocyanates as a common factor between many failing TPO adhesives. By comparing isocyanates to well-studied isomers with properties known to be similar to isocyanates, polyhydroxy urethanes and polyureas, isocyanates were found to have significantly higher rates of photodegradation based on thermogravimetric analyses. Isocyanates were found to have a rate of degradation 134% higher than polyhydroxy urethanes and 201% higher than polyureas.

With the information founded in the analyses of this report, it is highly recommended that companies that manufacture adhesive products for thermoplastic olefin roofing membrane systems transfer from the usage of isocyanates to polyhydroxy urethanes or preferably polyureas. Multiple sources cited in this investigation claim that both products have equivalent if not improved

adhesive properties relative to isocyanates and have now been established as better in resisting degradation in high temperatures.

If manufacturers could transition to the usage of polyureas, there could be significant improvement and reduced skepticism towards TPO products. As mentioned, the largest concern within TPO systems is the viability of the product in the long term. Changing the formula of TPO adhesives by switching isocyanates to a proven alternative, such as polyurea, will improve a failing characteristic of existing products. This will directly correlate to improved longevity within the thermoplastic olefin adhesives and allow for further innovation within the single-ply roofing membrane industry.

4.2. Recommendations

This report includes a meta-analysis of many studies discussing single-ply roofing membranes and improves upon the cohesion between them by comparing three products that are not currently well-studied relative to one another. Outside of the building science community, much of the information regarding characteristics of TPO, PVC, and EPDM is not common knowledge, therefore by bringing it together in an analysis of a common failure, photodegradation, the knowledge can reach a wider, yet relevant, audience.

To further the research of single-ply roofing membranes, specifically the photodegradation of thermoplastic olefin adhesives, controlled studies would be recommended for future research. The primary limitation of the analyses conducted within this report include the lack of experimental controls between the various studies, requiring controlled decisions to be made after the data was collected. This caused a loss of a significant amount of data that may have been relevant in an attempt to standardize the studies to conform to a set of controlled variables. For future experimentation, it would be extremely beneficial to conduct a set of thermogravimetric

analyses on an increased sample size of TPO, EPDM, and PVC systems (including polyurethane-based and non-polyurethane-based adhesives) to test the durability of the products through heat accelerated aging. By increasing the control on the experiment, more definitive conclusions can be drawn to ensure that no external variables were overlooked within the analyses.

5.0 References

- Adhesive Platform. (2022). *POLYUREA ADHESIVE – A FAST CURING STRUCTURAL ADHESIVE*. Retrieved from Adhesive Platform: <https://www.adhesiveplatform.com/>
- Anitha Sukumaran Nair, s. C. (2019). *Hybrid Poly(hydroxy urethane)s: Folded-Sheet Morphology and Thermoreversible Adhesion*. American Chemical Society.
- Carlisle Syntec Systems. (2015). *Safety Data Sheet: Flexible FAST Part A*.
- Carlisle Syntec Systems. (2015). *Safety Data Sheet: OlyBond 500 BA Part A*.
- Carlisle Syntec Systems. (2020). *Safety Data Sheet: Low VOC PVC Bonding Adhesive*.
- Carlisle Syntec Systems. (2022). *Safety Data Sheet: SureSeal 90-8-30A Bonding Adhesive*.
- Crow. (2022, August). *Addition Reactions of Isocyanates*. Retrieved from polymerdatabase.com: <http://polymerdatabase.com/polymer%20chemistry/Urethanes.html>
- Employment and Social Development Canada. (2021). *Isocyanates: Control Measures Guideline*. Retrieved from Government of Canada: <https://www.canada.ca/en/employment-social-development/services/health-safety/reports/control-measures.html>
- Fiona Magliozzi, A. S. (2020). *Hydrolysable bio-based polyhydroxyurethane networks with shape memory behavior at body temperature*. HAL Open Science.
- Firestone Building Products. (2018). *Safety Data Sheet: EPDM Bonding Adhesive BA-2004(T)*.
- Firestone Building Products. (2018). *Safety Data Sheet: I.S.O FIX II Adhesive*.
- Firestone Building Products. (2021). *Safety Data Sheet: Twin Jet Adhesive Part 1*.
- Firestone Building Products. (n.d.). *Safety Data Sheet: PVC LVOC Bonding Adhesive*.

GAF. (2016). *Safety Data Sheet: OlyBond500 SpotShot (GAF)*.

GAF. (2016). *Safety Data Sheet: TPO LRF Adhesive M Low Temp Part 1*.

GAF. (2018). *Safety Data Sheet: EverGuard 2331 Bonding Adhesive*.

Hongxing Yang, Q. D. (2021). *Superstrong Adhesive of Isocyanate-Free Polyurea with a Branched Structure*. American Chemical Society: Applied Polymer Materials.

J. Carnes & Son Roofing. (2022). *Low Slope & Flat Roofing Solutions*. New Hampshire: Flat Roofing Contractors in New Hampshire.

Jin Hong Kim, W. L.-G.-S. (2018). *Synthesis of Thermally Stable Recative Polyurethane and Its Physical Effects in Epoxy Composites*. Applied Sciences.

Jing Jiang, Jin-sheng Xu, Xiong Chen & Zhong-shui Zhang. (2015). *Experiment Research on the Mechanical Performance of EPDM Insulation Pyrolysis Process*. 201: Nanjing University of Science and Technology.

Johns Manville. (2019). *JM Membrane Bonding Adhesive*.

Johns Manville. (2019). *Safety Data Sheet: JM TPO 1168 Membrane Adhesive*.

Johns Manville. (2020). *Safety Data Sheet: JM PVC Membrane Adhesive (Low VOC)*.

Johns Manville. (2021). *Safety Data Sheet: JM Roofing System Urethane Adhesive - Part 1*.

Joseph G. Cordaro, K. W. (2017). *Thermal Decomposition and Characterization of TDI polymers using TGA coupled GC-MS*. Retrieved from U.S. Department of Energy: Office of Scientific and Technical Information: <https://www.osti.gov/servlets/purl/1465005>

- Laxmi, S. K. (2019). *Development of coordination polyureas derived from amine terminated polyurea and metal ions have 'd5','d7','d8' and 'd10' orbitals: From synthesis to applications*. Elsevier.
- O. Figovsky, L. Shapovalov, F. Buslov. (2005). *Ultraviolet and thermostable non-isocyanate polyurethane coatings*. OCCA.
- Simmons, T. R.; Paroli, R. M.; Liu, K. K. Y.; Delgado, A. H.; Irwin, J. D. (1998). *Evaluation of Thermoplastic Olefin (TPO) Roofing Membranes*. National Research Council Canada.
- SPRI News. (2019, January 9). *Single-Ply Roofing 101*. (Single Ply Roofing Industry) Retrieved July 6, 2022, from <https://www.spri.org/2019/01/single-ply-roofing-101/>
- Stonewater Roofing. (2018, March 26). *Comparing The Diggerent Single-Ply Roofing Membranes*. (Stonewater Roofing) Retrieved July 06, 2022, from <https://stonewaterroofing.com/comparing-single-ply-roofing-membranes/>
- The National Institute for occupational Safety and Health (NIOSH). (2014, April). *Workplace Safety and Health Topics: Isocyanates*. (Centers for Disease Control and Prevention) Retrieved July 2022, from <https://www.cdc.gov/niosh/topics/isocyanates/default.html>
- United States Department of Labor. (2022). *Safety and Health Topics: Isocyanates*. Retrieved from Occupational Safety and Health Administration: <https://www.osha.gov/isocyanates>
- Warwick Mills Inc. (2022). *Isocyanate Adhesion*. Retrieved from Warwickmills.com: <http://www.warwickmills.com/Isocyanate-Adhesion.aspx>
- Zhi Ping Xu, Susanta K. Saha, Paul S. Braterman, Nandika D'Souza. (2006). *The effect of Zn, Al layered double hydroxide on thermaldecomposition of poly(vinyl chloride)*. Elsevier.

Appendix A: EPDM and PVC Safety Data Sheet Information

Table 12 – Low VOC PVC Bonding Adhesive (Carlisle Syntec Systems)

Compound	CAS Number	Percentage
Polyphenol antioxidant	N/A	0.1-1
Zinc Oxide	1314-13-2	0.1-1
Toluene	108-88-3	1-5
Acetone	67-64-1	40-70
Parachlorobenzotrifluoride	98-56-6	5-10

*Reproduced from associated Safety Data Sheet (Carlisle Syntec Systems, 2020)

Table 13 – Composition of SureSeal 90-8-30A Bonding Adhesive (Carlisle Syntec Systems)

Compound	CAS Number	Percentage
Polychloroprene	N/A	10-30
Phenolic Resin	N/A	1-5
Magnesium oxide (MgO)	1309-48-4	0.5-1.5
Toluene	108-88-3	30-60
Solvent naphtha, petroleum, light aliphatic	64742-89-8	15-40
Acetone	67-64-1	5-10
Xylenes (o-, m-, p- isomers)	1330-20-7	1-5

*Reproduced from associated Safety Data Sheet (Carlisle Syntec Systems, 2022)

Table 14 – Composition of Everguard 2331 Bonding Adhesive (GAF)

Compound	CAS Number	Percentage
Acetone	67-64-1	55-75
Methyl Ethyl Ketone	78-93-3	3-10
Toluene	108-88-3	1-5
Parachlorobenzotrifluoride (PCBTF)	98-56-6	< 1

*Reproduced from associated Safety Data Sheet (GAF, 2018)

Table 15 – Composition of JM PVC Membrane Adhesive Low VOC (Johns Manville)

Compound	CAS Number	Percentage
Acetone	67-64-1	60-80
2-Butanone	78-93-3	3-10
Toluene	108-88-3	1-5

*Reproduced from associated Safety Data Sheet (Johns Manville, 2020)

Table 16 – Composition of JM Membrane Bonding Adhesive (Johns Manville)

Compound	CAS Number	Percentage
Toluene	108-88-3	30-60
n-Hexane	110-54-3	10-30
Acetone	67-64-1	10-30

*Reproduced from associated Safety Data Sheet (Johns Manville, 2019)

Table 17 – Composition of PVC LVOC Bonding Adhesive (Firestone B.P.)

Compound	CAS Number	Percentage
Acetone	67-64-1	65-70
Methyl ethyl ketone	78-93-3	1-5
Toluene	108-88-3	1-5
Di(benzothiazool-2-yl)disulfide	120-78-5	0.1
Other components below reportable levels		< 25

*Reproduced from associated Safety Data Sheet (Firestone Building Products)

Table 18 – Composition of EPDM Bonding Adhesive BA-2004(T) (Firestone B.P.)

Compound	CAS Number	Percentage
Toluene	108-88-3	34-44
Naphtha, petroleum, solventrefinedlight (Primarily Hexane)	64741-84-0	25-35
Polymers	N/A	11-36
Polychlorophene	9010-98-4	< 12
Acetone	67-64-1	5-10
Xylene	1330-20-7	< 1
Magnesium oxide	1309-48-4	< 1
Zinc oxide	1314-13-2	< 0.3

*Reproduced from associated Safety Data Sheet (Firestone Building Products, 2018)

APPENDIX B: Isocyanate Data

Table 19 – Isocyanate Thermogravimetric Analysis Data (1)

TDI Elastomer		TDI Foam		MDI Foam	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
236	100%	168	100%	237	100%
270	95%	202	100%	271	96%
296	86%	237	95%	305	88%
304	79%	271	85%	322	81%
321	75%	305	80%	339	68%
347	72%	339	60%	356	50%
372	70%	373	35%	373	45%
394	68%	406	25%	406	35%
414	61%	440	13%	440	30%
435	58%	473	10%	473	27%
454	50%	506	8%	507	24%
464	30%			540	23%
474	12%				
484	3%				
498	2%				

*Reproduced from (Joseph G. Cordaro, 2017)

Table 20 – Isocyanate Thermogravimetric Analysis Data (2)

EPPU		EPPU-2	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
50	100%	50	100%
100	100%	100	100%
150	100%	150	100%
168	95%	207	95%
200	90%	250	93%
250	82%	300	89%
288	80%	341	80%
300	78%	350	71%
350	60%	400	22%
400	15%	450	3%
450	1%	500	3%
500	1%		

*Reproduced from (Joseph G. Cordaro, 2017)

Table 21 – Isocyanate Thermogravimetric Analysis Data (3)

PA4N-Urea		PA5N-Urea		PA6N-1-Urea	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
50	100%	50	100%	50	100%
100	95%	100	96%	100	100%
150	90%	150	90%	150	98%
200	87%	200	85%	200	90%
250	70%	250	80%	250	82%
300	55%	300	65%	300	70%
350	35%	350	37%	350	41%
400	20%	400	20%	400	24%
450	15%	450	15%	450	11%
500	13%	500	14%	500	9%

*Reproduced from (Jin Hong Kim, 2018)

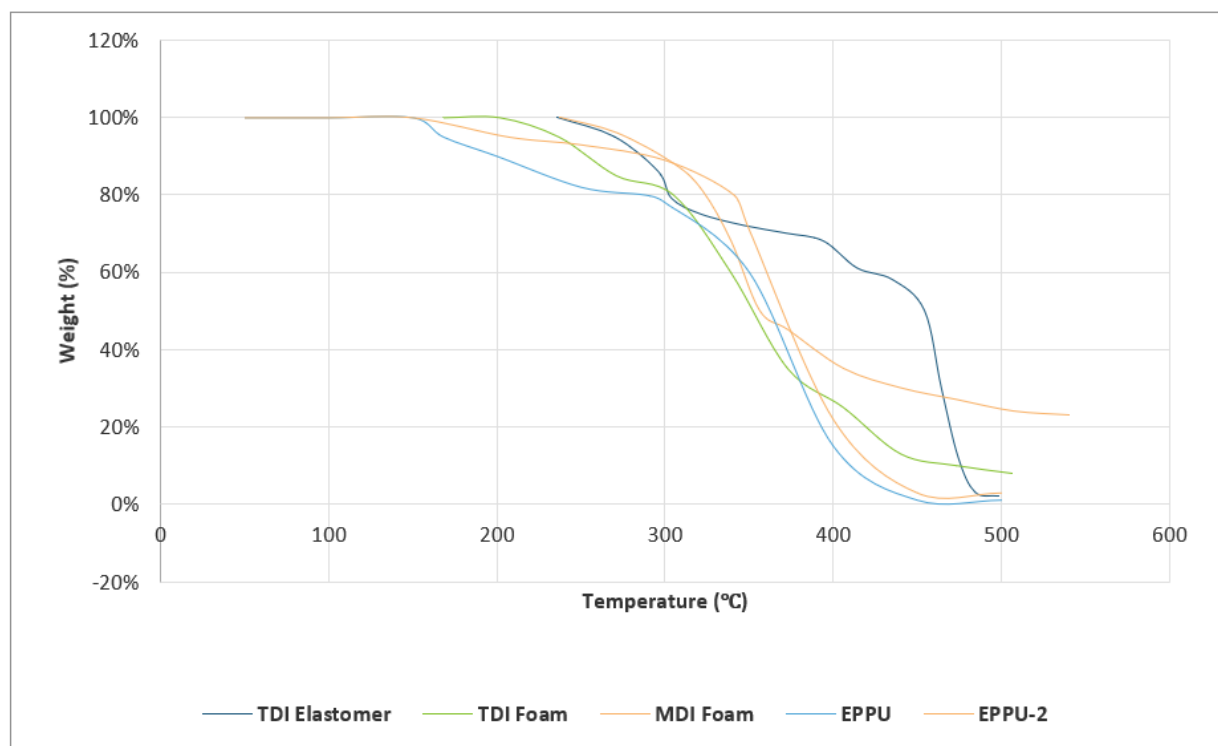


Figure 4 - Isocyanate Thermogravimetric Analysis

APPENDIX C: Polyurea Data

Table 22 – Polyurea Thermogravimetric Analysis Data (1)

PA6N-2-Urea		PA7N-Urea	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
50	100%	50	100%
100	100%	100	95%
150	97%	150	88%
200	92%	200	82%
250	85%	250	69%
300	65%	300	47%
350	45%	350	40%
400	18%	400	20%
450	10%	450	10%
500	8%	500	8%

*Reproduced from (Hongxing Yang, 2021)

Table 23 – Polyurea Thermogravimetric Analysis Data (2)

ATPUa		ATPUa-Zn(II)		ATPUa-Mn(II)	
Temperature	Weight %	Temperature	Weight %	Temperature	Weight %
0	100%	0	100%	0	100%
100	100%	100	92%	100	98%
200	95%	200	87%	200	92%
300	90%	300	70%	300	72%
400	40%	400	38%	400	38%
500	20%	500	30%	500	28%
600	13%	600	28%	600	22%
700	11%	700	25%	700	20%
800	10%	800	21%	800	17%

*Reproduced from (Laxmi, 2019)

Table 24 – Polyurea Thermogravimetric Analysis Data (3)

ATPUa-Co(II)		ATPUa-Ni(II)	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
0	100%	0	100%
100	99%	100	97%
200	88%	200	90%
300	72%	300	62%
400	38%	400	25%
500	28%	500	23%
600	22%	600	20%
700	19%	700	18%
800	17%	800	15%

*Reproduced from (Laxmi, 2019)

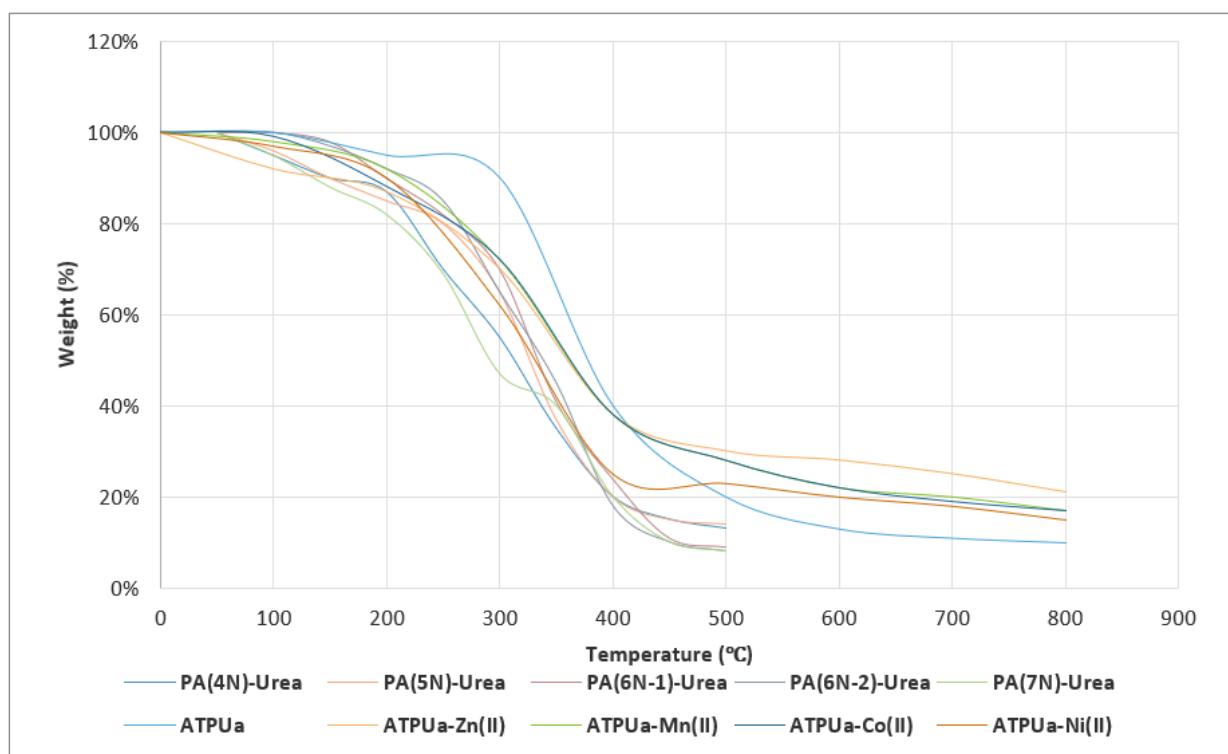


Figure 5 - Polyurea Thermogravimetric Analysis

APPENDIX D: Polyhydroxy urethane Data

Table 25 - Polyhydroxy urethane Thermogravimetric Analysis Data (1)

PHU(0)		PHU(30)		PHU(50)	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
50	100%	50	100%	50	100%
100	100%	100	100%	100	100%
150	98%	150	97%	150	99%
200	95%	200	94%	200	95%
250	67%	250	68%	250	70%
300	50%	300	49%	300	52%
350	32%	350	30%	350	31%
400	11%	400	11%	400	11%
450	8%	450	9%	450	9%
500	7%	500	8%	500	7%

*Reproduced from (Fiona Magliozzi, 2020)

Table 26 - Polyhydroxy urethane Thermogravimetric Analysis Data (2)

PHU(70)		PHU(100)	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
50	100%	50	100%
100	99%	100	98%
150	97%	150	96%
200	95%	200	95%
250	80%	250	78%
300	56%	300	55%
350	34%	350	42%
400	10%	400	11%
450	8%	450	9%
500	7%	500	8%

*Reproduced from (Fiona Magliozzi, 2020)

Table 27 - Polyhydroxy urethane Thermogravimetric Analysis Data (3)

1,6-Hexanediamine		1,8-Diaminooctane		Isophorondiamine	
Temp (°C)	Mass (%)	Temp (°C)	Mass (%)	Temp (°C)	Mass (%)
180	100%	180	100%	180	100%
251	95%	269	95%	251	95%
275	90%	313	80%	275	89%
320	71%	350	65%	311	77%
380	57%	400	48%	416	25%
443	35%	455	26%	500	14%
475	27%	475	20%		
500	24%	500	17%		

*Reproduced from (Anitha Sukumaran Nair, 2019)

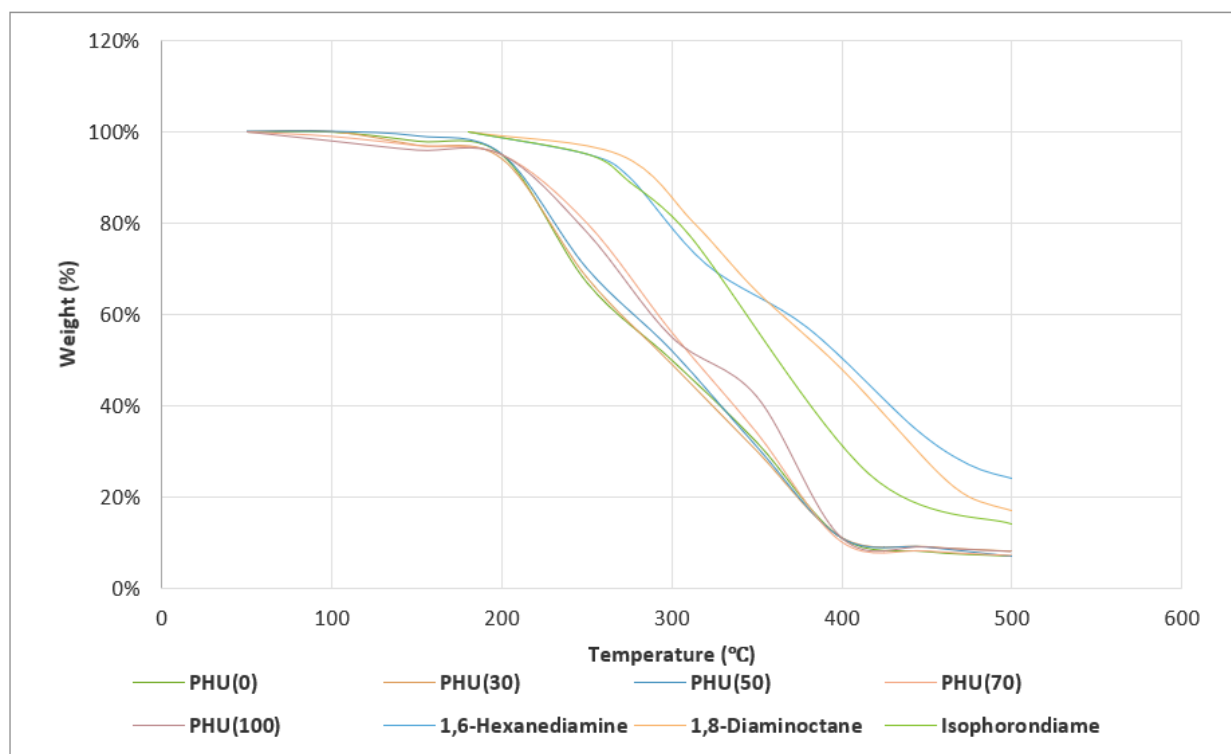


Figure 6 - Polyhydroxy urethane Thermogravimetric Analysis