FINAL REPORT

Non-Isocyanate Polyurethane Platform for Sustainable and Advanced Rain Erosion Resistant Coatings

SERDP Project WP-2602

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14. ABSTRACT

The objective of this research was to develop a rapid curing, non-isocyanate erosion-resistant coating containing low to no volatile organic chemicals (VOCs) or hazardous air pollutants (HAPs). This coating must meet or exceed critical performance properties specified in SAE AMS-C-83231 Revision A to include peel strength, flexibility, water resistance, aromatic fuel resistance, rain erosion resistance, electrical transmission, surface resistivity, weather resistance, and strippability (Table 1 in the Appendix). In addition, resistance to lubricating oil and hydraulic fluid degradation is desirable (Table 2 in the Appendix). Proposals for use of alternative materials must include a preliminary toxicological assessment of the alternative materials.

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Executive Summary:

The overarching goal of this project was to develop Rain Erosion Resistant military coatings that are free from any isocyanate compounds, HAPs, with substantially lower VOCs, and can meet the requirements specified in SAE AMS-C83231A, as well as the additional desirable performance properties as per MIL-PRF-32239 specifications. The new generation Isocyanate-free coatings should be able to effectively replace the incumbent conventional urethane / urea coatings that are based on isocyanate compounds.

This research effort was successful in developing a platform of non-isocyanate polyurethane (NIPU) building blocks for high-performance coatings by effectively leveraging cyclic carbonate/ polyamine chemistry. One of the major intermediates – multi-functional cyclic carbonate (MFCC) – are not commercially available. A single-step, safe, energy efficient and carbon negative process for deriving MFCCs with wide range of chemical structure, MW, and functionalities has been established using commercially available epoxy compounds and carbon dioxide gas as starting materials.

A library of functional NIPU derivatives with varying functionality type and contents, MW, and chemical structures have been synthesized. These functional NIPU building blocks have been custom-designed for suitability for formulating two type of NIPU coatings – (a) two-component high-solids ambient temperature curable coatings (2K-HS-NIPU), and (b) UV-curable 100% solid coatings (UV-NIPU). This research also extended deriving functional NIPU building blocks (even though it was outside the scope of this project) for thermal-cure, moisture cure as well as water-borne NIPU coatings.

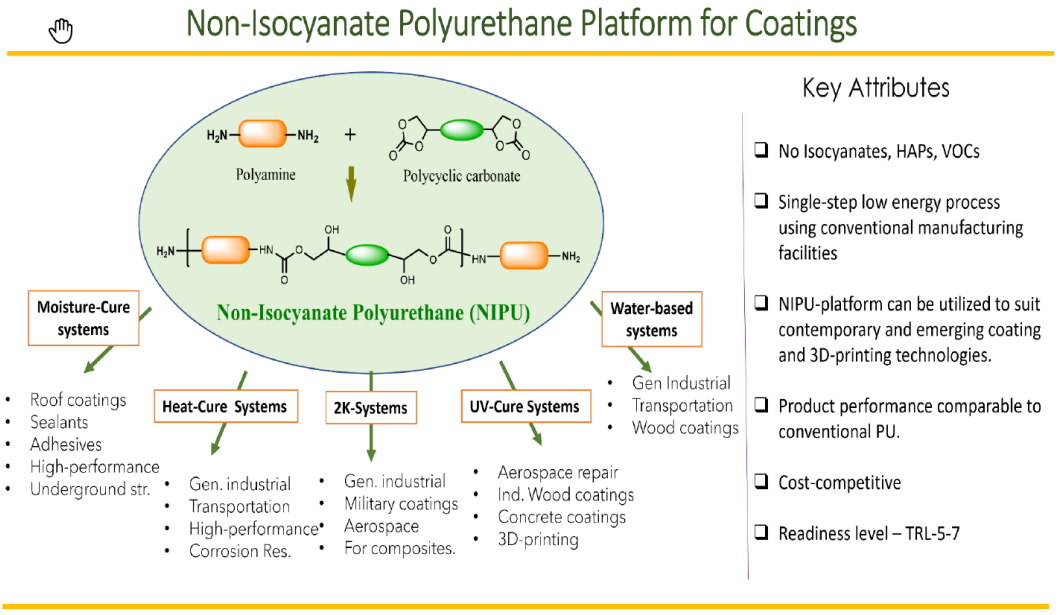
The 2K-HS-NIPU coatings were formulated using amine-terminated NIPU intermediates as one component, and aliphatic di or higher functional epoxy compounds as second component. Among various coatings developed and tested, two candidate 2K-HS-NIPUcoating candidates that passed all the tests for critical requirements were tested for rain erosion resistance. These coatings could not hold up to the rain erosion testing (failed at 10-11 seconds against the requirement of 30-60 sec).

The UV-NIPU coatings were formulated from (meth)acrylate functional NIPU oligomers an\long with other conventional components. While high viscosities of NIPU-acrylates were one of the major constraints, we could successfully formulate 100% solid compositions. None of these coatings could pass all the critical requirements, specifically balancing their % elongation, tensile strength, and low temperature flexibility was not possible. Therefore, none of UV-NIPU could make it to the Rain Erosion Test.

In this effort, the NIPU coating development was confined to a specific and unique Rain Erosion Resistant coating, as per the objective of this project. Rain Erosion Resistant coatings have very unique and stringent performance requirements that require balancing and optimizing many opposing mechanical properties, exterior durability, protective properties, ambient temperature cure within acceptable time, and above all low VOC and no usage of HAPs. Due to the nature of the NIPU chemistry adopted in this project, specifically the relatively lower reactivities of the functional groups involved (relative to isocyanate-based chemistry), these stringent requirements could not be sufficiently met. More specifically, these NIPU coatings could not pass the Rain Erosion Test that required coating to have extremely high tensile strength (~6.5 Mpa), and higher that 500% elongation, among other requirements. Due to the restrictions on VOC and HAPS, it was not possible to use very high MW

polymers, and due to the constrains of low reactivities of our NIPU functional groups, high MW could not be achieved during curing of the coatings. These factors ultimately could not make these NIPU coatings complaint to the above stated requirements.

Nevertheless, the outcome of this research project has provided with an excellent NIPU- coating platform that can be very effectively leveraged for not only a broad range of sustainable military coatings but also myriads of industrial and protective coatings with their significantly lower environmental impacts. As summarized in the graphic below, NIPU coating platform is amenable to develop advanced coating formulations on contemporary as well as emerging technologies. Moisture-cure coatings, water-borne coatings, and heat-curable coatings can be successfully formulated, besides the two-component ambient temperature cure coatings and UV-cure coatings that have been extensively studied and demonstrated in this project. Besides, NIPU platform can also be used to develop advanced and sustainable 3D-printing (Additive Manufacturing) materials. Our research group has already explored some these novel NIPU coatings spaces (outside the scope of this project) and the outcomes of this research shows tremendous potential for the next generation sustainable and high-performance coatings.



Abstract:

The objective of this research was to develop a rapid curing, non-isocyanate erosion-resistant coating containing low to no volatile organic chemicals (VOCs) or hazardous air pollutants (HAPs). This coating must meet or exceed critical performance properties specified in SAE AMS-C-83231 Revision A to include peel strength, flexibility, water resistance, aromatic fuel resistance, rain erosion resistance, electrical transmission, surface resistivity, weather resistance, and strippability (Table 1 in the Appendix). In addition, resistance to lubricating oil and hydraulic fluid degradation is desirable (Table 2 in the Appendix). Proposals for use of alternative materials must include a preliminary toxicological assessment of the alternative materials.

This report consists of three parts:

(A) Introduction and Project description.

(B) Design , Synthesis and Characterization of multi-functional Cyclic Carbonates (MFCC) Oligomers, amine-functional non-siocyanate polyurethane oligomers (NIPU-PA), and two-component high-solid coayings derived from them (@K-HS-NIPU). (Objectives 1, 2, 3 & 5)

(C) Design and development of radiation-curable NIPU coating system (UV-NIPU) , synthesis and characterization. (Objective 5)

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Chapter One

Introduction and Project Description

1.1. SERDP Relevance

This research project aimed to develop non-isocyanate polyurethane (NIPU) coatings by leveraging the potential of the cyclic carbonate/ amine chemistry and the benefits of the advanced high-solid (HS) and UV- curing coating technologies. The proposed new generation rain erosion resistant coatings, while meeting all the application/curing and performance requirements, are expected to have significantly lower or no VOC and HAPs and be completely free from isocyanate compounds, both during the manufacture of coatings or at the time of their on-site field applications, thus meeting the requirements of the SON-WPSON-16-02.

1.2. Technical Objectives

The overall objective of this proposal was to design, develop, and evaluate innovative Non-Isocyanate Polyurethane (NIPU) coating systems for environmentally sustainable rain erosion coatings that meet performance requirements specified in SAE AMS-C83231A as well as the additional desirable performance properties as per MIL-PRF-32239 specification. The objective also included a demonstration of the performance and environmental benefits of this new generation of coatings and to develop a roadmap for a strategic transition plan for implementation of this new coating technology in the field through cooperative development with the industrial partners and the end-user DOD sites.

We developed highly transformative strategies for developing these advanced coatings by leveraging cyclic carbonate/amine chemistry. We successfully developed a platform of amine-functional NIPU building blocks that are customized for high-performance rain erosion coating systems with low or no VOC or HAPs. Specifically, we have developed two distinct types of

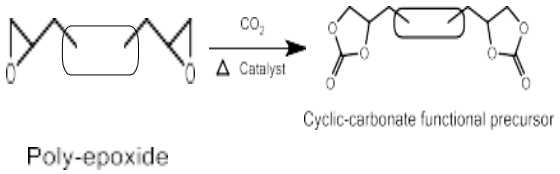
coating systems: (1) Two-component high-solid coatings (2K-HS NIPU system) and (2) 100% solid UV-curable coatings (UV-NIPU).

The specific objectives of this project and their outcomes are outlined below.

1.2.1. Objective-1: Design, synthesis, and characterization of multi-functional cyclic carbonate (MFCC) oligomers

These objective questioned the feasibility of synthesizing MFCC intermediates with varying chemistry, chemical structures, and functional group contents. MFCCs are the primary building blocks of the proposed NIPU coatings. Using sound experimental strategies, a wide range of MFCCs have been explored. Among these the direct carbonation of epoxy compounds was found to be the most effective. The synthetic route involving esterification of glycerol carbonate as well as dialkyl carbonate route nd did not yield high yield (and also found mixture of products) and hence was discontinued.

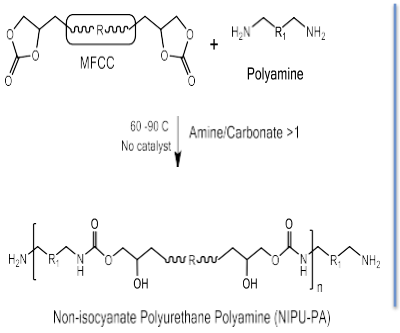
Carbonation of Epoxides route (highlights)



- Commercial -di and -tri epoxy compounds were used.
- Selection of epoxy: based on exterior durability and mechanical properties
- Aliphatic, Cycloaliphatic, silicone and hydrogenated BPA based epoxy selection
- Carbonation process is well documented in literature, leveraged to optimize conditions.
- Products characterized for: Cyclic carbonate (FT-IR)
  viscosity, Molecular weight (GPC).

1.2.2. Objective-2: Design and synthesis of amine-functional non-isocyanate polyurethane oligomers/resins (NIPU-PA)

The reaction between cyclic carbonates and primary amines to yield hydroxyl-urethanes are slower at room temperature as compared to the conventional isocyanate/hydroxyl reaction. Therefore, this chemistry is not suitable for ambient cure coatings applications. The target coatings of this SON are expected to cure rapidly under on-site ambient conditions. As per the reported literature and results of our preliminary investigations, the reaction of cyclic carbonates and primary amines can efficiently be carried out at elevated temperatures, with /without solvent, especially when the amine is used in stoichiometric excess to carbonates. Therefore, we designed and synthesized amine- terminated NIPU oligomers as "platform derivatives" that can further be used with/without subsequent modifications, for the target coatings. Thus, the benefits of the polyhydroxy urethane backbone can be exploited with alternate feasible curing chemistries to meet the critical criteria of rapid curing for the target coatings. This objective, therefore, aimed at designing amine-functional NIPU platform. We developed a range of NIPU-PA intermediates that are amenable for use in developing 2K-HS-NIPU coatings and UV-NIPU coatings. Selection of type of MFFCCs and polyamine component and theirstoichiometric proportions were experimentally determined to prepare a library of NIPU-PA intermediates.



NIPU-PAs are platform intermediates for
- 2K HS Coatings
- UV-Curable Coatings

NIPU-PA were customized for above with:
- Varying MFCC chemistry (Task #1)
- Varying amine types
- Varying Amine/Carbonate ratio (MW)

Characterized for
- Chemical structure (FT-IR, NMR)
- Viscosity, Amine equivalent wt., Color,
- Compatibility with MFCCs

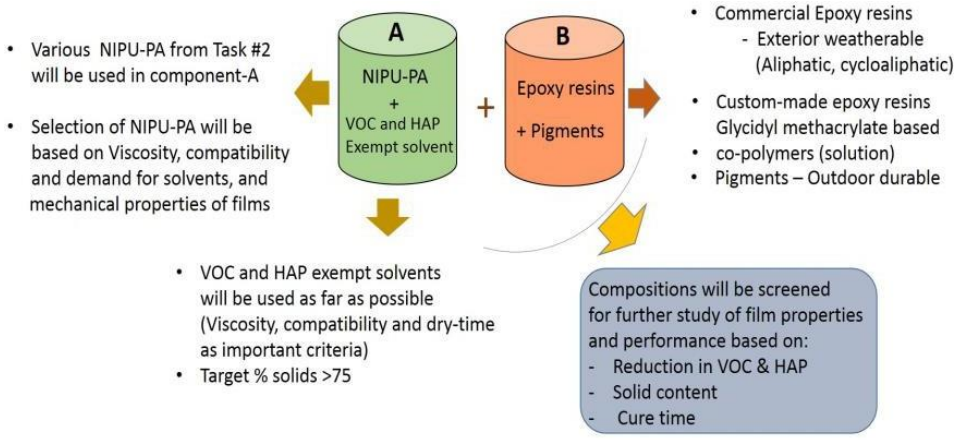
1.2.3. Objective-3: Design and development of two-component high-solid NIPU coating systems (2K-HS-NIPU)

In this task we developed 2K-HS-NIPU coating systems by careful selection of NIPU-PA platform materials that are amenable for high-solid coating systems. We used commercially available

crosslinkers (aliphatic epoxy type) that are compatible with NIPU-PA and provided desirable application and film properties.

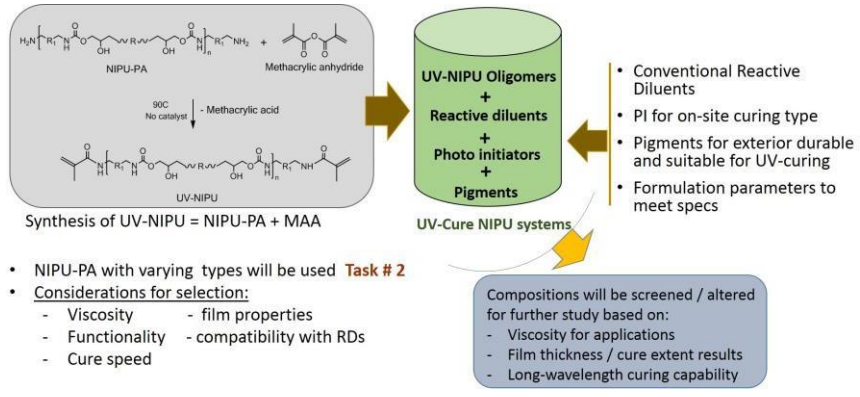
The following diagram shows design principles used in formulation of intermediates and 2K_HS-NIPU systems.

Formulation and characterization of various 2K-HS-NIPUs



1.2.4. Objective-4: Design and development of UV-curable NIPU coating systems (UV-NIPU)

In this task we explored the feasibility of the synthesis of meth(acrylate) derivatives of NIPU-PAs developed in Objective-2. Using a sound experimental strategy NIPU-PA candidates were selected (based on their equivalent weights) and meth(acrylate) oligomers ere synthesized in keeping with the requirements of the UV-cure coating systems. A range of UV-NIPU coating compositions were then be formulated by the selection of commercial reactive diluents and photo-initiators. A few UV-NIPU systems with varying compositions were selected for extensive testing and evaluation. The design principles and strategy for UV-NIPU systems is shown below.



1.2.5. Objective-5: Testing, evaluation, characterization, and demonstration of performance and environmental benefits of NIPU coatings and development of strategic transition plan

All the selected candidates - 2K-HS-NIPU and UV-NIPU coatings – were tested for their key primary properties (to establish suitability for further advanced testing). Only two selected systems were tested for rain-erosion testing as per SAE AMS-C83231A and MIL-PRF-32239.
The overall strategy for test protocols followed are summarized below.

Testing of selected (screened) 2K-HS-NIPU and UV-NIPU systems were carried out for:

- Primary film properties
- Thermal properties (TGA, DSC) EMU
- Mechanical Properties (DMA, Abrasion, Impact, adhesion on various substrates) - EMU, Sherwin Williams
- Performance properties as per SAE AMS-C 83231A (EMU, AFRL /RXSSO, UDRI)
- Rain Erosion Resistance – NSWCCD , West Bethesda, MD DoD facility
- Outdoor durability (Florida) – NSWCCD
- Resistance to lubricating and related fluids – EMU, Chemical
- - Dynamics, LLC
- Demonstration of performance and environmental benefits:
    - Analysis of results and compiled data to critically compare different systems for:
    - VOC and HAPs status - Field application issues
- Application and cure time
- Life-Cycle inventory for key materials
- Performance as per required standards
- Identify prototype candidates from both 2K-HS-NIPU and UV-NIPU for field transition plan: (in consultation with DoD and Industrial partners)
- Identify candidate systems based on a matrix consisting of the following factors:
    - Performance
    - Environmental foot print
    - Efficiency (cure time , application time)
    - Acceptance by user community (Depots, DoD sites, contractor)

1.3. Technical Approach

1.3.1. Background

The erosion-resistant protective coatings used on military aircraft and shipboard surfaces have stringent performance requirements. Polyurethanes have been, by far, the undisputed binders of choice for such coatings due to their excellent resilience, adhesion to polymer composite substrates, low-temperature flexibility, good barrier properties, and resistance to aromatic fuels, lubricating and hydraulic fluids combined with customizable thermo-mechanical properties and outstanding long-term exterior durabilityproperties. These coatings are frequently applied on-site at ambient

temperature and humidity, as multi-coat systems to build up to desired dry-film thickness. They also take a longer time to fully cure, dependingupon the ambient conditions. To meet their performance and application/curing requirements, currently, DoD uses solvent-borne two-component polyurethane coatings. The problems associated with these erosion resistance coatings, as highlighted in SON WPSON-16-02, are their much longer curing time, their

significant environmental burden due to emissions of volatiles and HAPs, and the use of hazardous isocyanate compounds.

The present commercial polyurethane coating technology is based on hazardous isocyanate compounds as primary building blocks. The use of isocyanate compounds, both at manufacturing and application sites,and their related environmental, health, and safety-related costs are enormous burdens to the DOD. Conventional PUs are synthesized by reacting di- or polyisocyanates with polymers/oligomers containing hydroxyl groups. This method has been disadvantageous because it uses toxic isocyanates, which are produced from an even more dangerous component - phosgene. Isocyanates are potent sensitizers and remain one of the most commonly reported causes of occupational asthma worldwide. Diisocyanates arewell-known dermal and inhalation sensitizers in the workplace and have been documented to cause asthma, lung damage, and in severe cases, fatal reactions. Manufacture and application of isocyanate- containing products including polyurethane materials can result in inhalation and dermal exposures to isocyanate compounds resulting in health effects, such as skin irritation and long-term asthma. Thus the "isocyanate route" for PU has been shown to constitute a threat both to the environment and to the healthof operators. Therefore, in recent decades, aggressive interest has been shown by researchers, environmental protection agencies, and industries across the world, seeking an alternative "green process"for polyurethanes that reduces or eliminates toxic substances.

VOCs and HAPs have long been recognized for their negative impacts on the environment, health, andecosystem. Reduction or elimination of VOCs and HAPs has been a major driving force that has led to thedevelopment of water-borne, high-solid, and UV-cure coating technologies. The contemporary, advanced water-borne polyurethane coatings that promise significant lowering of VOCs and HAPs are not suitable forthe rain erosion-resistant coatings of this SON since their inefficient film formation mechanism (coalescence of polymer particles), especially at lower temperatures, tends to compromise their stringentperformance properties. Also, their much longer drying times compared to solvent-based coatings, renderthem unacceptable for multi-coat on-site applications under ambient conditions.

Therefore, to effectively respond to the needs of the present SON, a sound strategic research plan has been prepared for developing non-isocyanate PU (NIPU) coatings systems that are amenable for the formulation of low or no VOC and HAPs while meeting all the stringent application, curing, and performance requirements.

1.3.2. Various approaches to non-isocyanate polyurethane

A thorough review of the literature was conducted to understand various approaches reported on non- isocyanate PU and the current state-of-the-art. Several different chemistries have been explored to synthesize PU without the use of isocyanate compounds. Among these are trans-urethanization of dimethyl carbamate and diol in presence of strong base catalyst, and the reaction of bis(2-hydroxyethyl carbamate)s with a hydroxyl group, which may be from diol or part of bis(2-hydroxyethyl carbamate) to yield liner thermoplastic PU. Another approach involves copolymerization of aziridine and super-critical CO_2 to yield cyclic urethanes and polymers containing urethanes and amine units. Ring-opening polymerization of cyclic urethanes is yet another approach, wherein five and six-membered cyclic urethanes can be prepared in a sustainable manner by reactions of alkylene diamines or amino alcohols with such reagents such as dialkyl carbonates or with pressurized CO_2 in the absence of any catalyst. In the polycarbamate route, Polymers with multiple carbamate (-$COONH_2$) functionality (polycarbamates) can be cross-linked with polyaldehyde or acetal or hemiacetal, with or without catalyst, from 0 to 140 °C to yield polyurethanes[29-31]. Most of the abovementioned approaches, however, are more suitable for preparing liner thermoplastic PU. For rain erosion resistant coatings, cross-linked films are required to provide desirable mechanical and performance properties, and hence the above approaches are not suitable.

The reaction of cyclic carbonate and amine is among the most suitable and versatile routes for the synthesis of PU for coating applications. Fundamentals for the practical application of NIPU based on five-membered cyclic carbonates (1,3-dioxolan-2-ones) in coatings, sealants, adhesives, etc., were largely developed by Figovsky during 1970 – 1980s. Recently, some reviews dedicated to the synthesis of cyclic carbonates-based NIPU have been published. When multi-functional cyclic carbonates are reacted with polyamines, polyhydroxy urethane is obtained. The reaction can yield hydroxyl urethane with either primary hydroxyl group or secondary hydroxyl group as shown in Figure 1.1. The ratio of the product obtained is largely dependent on reaction conditions such as

the type of catalyst used.

Rational investigations have also been made by some researchers to understand reaction mechanismsand the effect of reaction conditions and catalysis on the reaction of cyclic carbonates with amines. Cycliccarbonate groups interact with aliphatic and cycloaliphatic polyamines much slower than the conventional isocyanates/hydroxyl reaction at ambient temperatures. Cyclic carbonates react only with primary amino groups, in contrast to the conventional epoxy-amine systems, which react with primary as well assecondary –OH groups. This results in a decrease in crosslinking density of the polymer network formed bycyclic carbonate/amine systems.

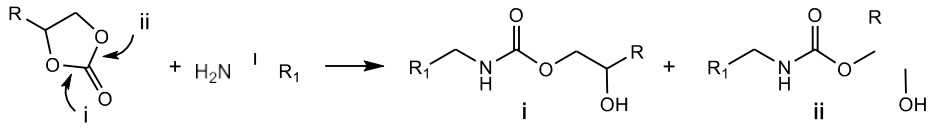


Figure 1.1. Reaction of cyclic carbonate with amine.

One important bottle-neck in this technology for NIPU is the lack of commercial availability of oligomersand polymers with multiple cyclic carbonate groups, which has led to the considerable focus towards the development of an array of such polymers with multiple cyclic carbonate groups.

Different chemistries have been explored for synthesizing polymers and oligomers with multiple cycliccarbonate functional groups. Among these, one important route includes the carbonation of oxirane compound. This reaction is highly facile and can be conducted at both atmospheric and elevated pressures with high yields in presence of catalyst. This reaction is frequently used to convert polyfunctional epoxy resins to polyfunctional cyclic carbonate resins, Figure 1.2.

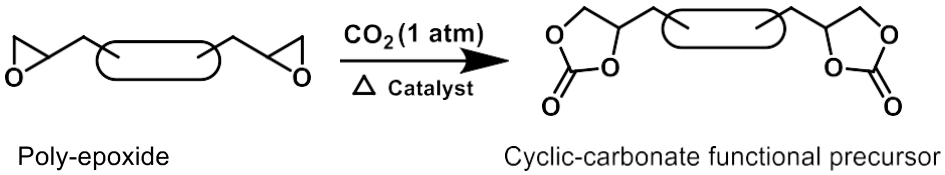


Figure 1.2. Preparation of cyclic carbonate from oxirane.

The literature presents substantial information about reaction conditions, type of catalysts, and type ofoxirane compounds used and the nature and yield of the products obtained. Another common and versatile method for preparing cyclic carbonate functional polymers is the free radical homo- or copolymerization of an unsaturated monomer containing pendant cyclic carbonate functionality. Several numbers of references of the use of unsaturated monomer types, polymerization conditions,

and product characterization are reported in the literature. More environment-friendly methods currently used for thesynthesis of cyclic carbonates are trans-esterification and trans-carbonation which led to the formation of cyclic carbonates from vicinal diols. Dialkyl carbonates, such as dimethyl carbonate, diethyl carbonate, and diphenyl carbonate are used for this type of reaction as alkylating agents and aprotic polar solvents. A bodyof literature is available that reports reaction conditions, type of catalysts, and compositions of the cyclic carbonate products formed.

1.3.3 Approach

To effectively respond to the needs of the rain erosion-resistant coatings articulated in the present SON,we adopted a sound strategic research plan for developing non-isocyanate PU (NIPU) coatings systems withlow or no VOC and HAPs while meeting all the stringent application, curing, and performance requirements. Specifically, we developed a platform of NIPU building blocks that are amenable fortwo distinct types of coating systems: 2K NIPU high-solid and NIPU UV-curable coatings. Our overall technical approach and cooperative efforts for developing a strategic plan for the implementation of this technology in the field is schematically shown in Figure 1.3.

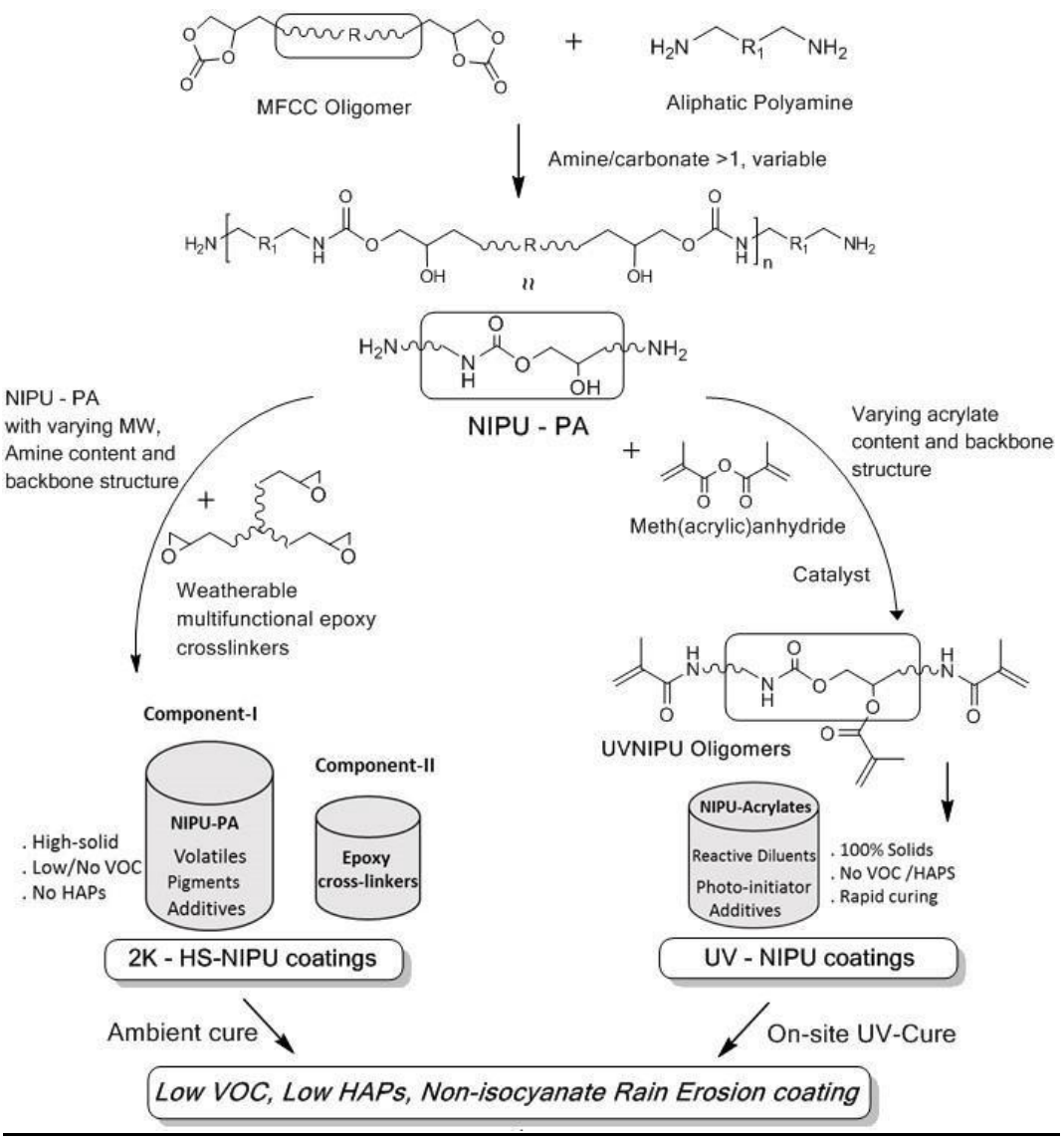


Figure 1.3. Overview of the overall technical approach and plan for implementation.

1.4. Design Strategy: NIPU-Platform

We developed NIPU pre-polymers/oligomers by step-growth polymerization of custom-designed poly-cyclic carbonate compounds and commercially available aliphatic polyamines by utilizing well established synthetic route. Our research group's preliminary work on the development of NIPU has demonstrated that by appropriate selection of these basic building blocks, their stoichiometric proportions and reaction conditions, NIPUs with tailored morphology, viscosity, and functionality can be obtained. The reasons for the versatility of this route include relatively simple chemistry with normal processing conditions, ease of functionalization for thermoset coatings, and better morphological control. Furthermore, this route produces hydroxyl urethane linkages, in contrast to urethanes by conventional isocyanate-based process, which brings some unique advantages to the system such as lower permeability, improved thermal stability, and increased chemical resistance properties. The proposed cyclic carbonate/amine route is insensitive to moisture (unlike a conventional route) and does not produce any volatiles, which eliminates the porosity problem encountered in the conventional approach, due to the formation of carbon dioxide. Another significant technical benefit offered by hydroxyl urethane structure is the formation of intra-molecular hydrogen bond through the hydroxyl group at the β-carbon atom of the polyurethane, as shown in Figures 1.4 and 1.5.

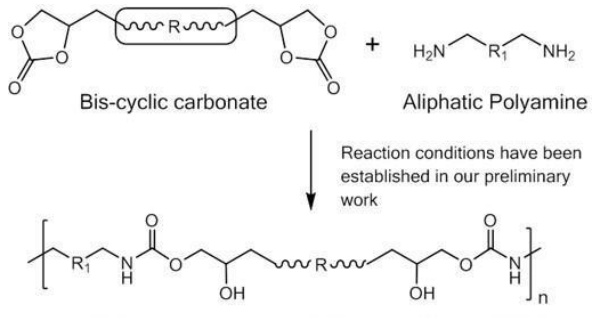


Figure 1.4. Non-isocyanate polyhydroxy urethane (NIPU)

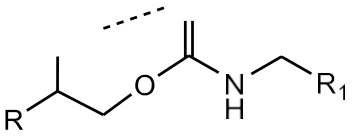


Figure 1.5. Intra-molecular H-bonding in hydroxyl polyurethane

The quantum-mechanical calculation, IR, and NMR spectroscopic investigations have confirmed the stability of such a ring. The blockage of the carbonyl oxygen considerably lowers the susceptibility of the urethane group to hydrolysis. Moreover, materials containing intra-molecular hydrogen bonds display chemical resistance 1.5 to 2 times greater compared with

materials of a similar chemical structure without such bonds. On the other hand, conventional polyurethanes are limited by their hydrolytic instability and their poor chemical resistance to aqueous solutions of acids and alkalis. The lower water absorption, higher thermal decomposition temperature, better adhesion, and abrasion resistance of hydroxyl polyurethanes are among the properties most desirable for the rain erosion coating of this SON. Therefore, we are confident that our proposed NIPU platform is well suited to strategically leverage these benefits and develop rain erosion resistant coatings of this SON. The following section outlines the specific objectives and related tasks for each objective.

1.4.1. Objective-1: Design, Synthesis, and Characterization of Multi-Functional Cyclic Carbonate (MFCC) Oligomers.

1.4.1.1. Task 1.1: Synthesis of MFCC using carbonation of oxirane compounds

As above discussed, one of the most widely used and feasible approaches to synthesize cyclic carbonates is the carbonation of oxirane compounds using CO_2. This synthesis involves the reaction of multi-functional epoxy compounds with CO_2 in pressurized conditions in the presence of a catalyst, with or without solvent at temperatures ranging from 80 to 140°C, followed by separation of catalyst and removal of solvent, if used, by distillation. This reaction will be carried out in a laboratory autoclave with a capacity of up to 150 bar pressure. The progress of the reaction will be determined by monitoring oxirane oxygen content (% OOC; ASTM D 1652) and FTIR spectroscopy.

As one of the important criteria for the targeted coatings of this project is exterior weather resistance, we will synthesize a series of MFCC using different multifunctional UV resistant oxirane compounds such as hydrogenated bisphenol A-based epoxy resin (ST series from Kukdo Chemicals; Eponex ® Resin 1510 from Hexion) and 1,4-Cyclohexanedimethanol diglycidyl ether (HELOXY® Modifier 107, Momentive), diglycidyl ester of hexahydrophthalic acid (CHS-EPOXY®560), etc. These basic bis-epoxides will also be modified with other linear aliphatic diols/diacids to increase their molecular weights to customize the mechanical properties of the final coatings while maintaining their durability. In Figure 1.6 the structure of durable epoxy compounds to be used to prepare MFCC are shown.

We also plan to synthesize MFCC from the tri-glycidyl ether of trimethylolpropane (TMP) (HELOXY® Modifier 48, Momentive) used along with bis-cyclic carbonates for tailoring the

functionality higher than two. This will ensure enough branching and crosslinking necessary for such desirable performance properties as oil resistance. Silicones are also important resins for exterior durable coatings. Concerning tothe weathering resistance and their flexible backbone structure, the glycidyl terminated silicone resins (SILRES® HP 1250, Wacker) will also be used to prepare their MFCCs. We are planning on developing this wide array of oligomers to have us a latitude for selection of one or a blend of multiple MFCCs to meet thestringent requirements of the mechanical properties for targeted coatings, such as high flexibility and erosion resistance. All the MFCC resins will be characterized for conversion of oxirane groups to cyclic carbonates (FTIR, %OOC), viscosity (cone and plate viscometer), molecular weight (GPC) and density.

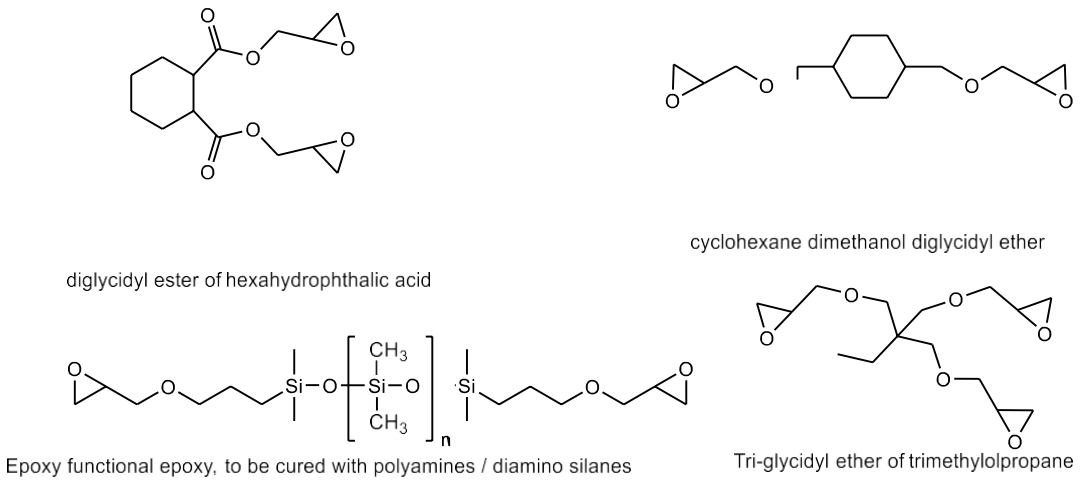


Figure 1.6. Representative examples of durable epoxy compounds to be used to prepare MFCC.

1.4.1.2. Task 1.2: synthesis of MFCC by esterification of glycerol carbonate (GC) with carboxylic acid functional polymer

As another innovative approach, we explored to utilize glycerin carbonate as a source of cyclic carbonate functionality in the polymer. Glycerol carbonate (4-hydroxymethyl-2-oxo-1,3-dioxolane) is a promising molecule bearing both a hydroxyl group and a 2-oxo-1,3-dioxolane group (5-membered cyclic carbonate) and has gained considerable interest in the last two decades because of its high reactivity and easy availability as a derivative of glycerol, a major by-product of biodiesel manufacture. Among many possible reactions of GC, one most common reaction is the esterification of the hydroxyl group of GC with the carboxylic acid group. Acid functional

polymers can be functionalized with a cyclic carbonate group upon esterification of GC with carboxylic acid group of the polymer.

We attempted to synthesize a range of polyesters by reacting a molar excess of diacids with diols to yield acid functional polyester (PE) of varying molecular weight and –COOH content, using standard esterification reaction conditions. The –COOH functional polyesters will then be esterified with 1 mole of GC per mole of carboxylic acid groups by acid-catalyzed esterification reaction at a relatively mild temperature of 110 to 120 °C with azeotropic removal of water of reaction using a suitable solvent to yield cyclic carbonate terminated polyester (PEGC), Figure 1.7. This reaction will be monitored by periodic evaluation of acid value with a target of <10 mg KOH/g. Our research group has earlier established this process that yields PEGC without appreciable loss of carbonate functionality.

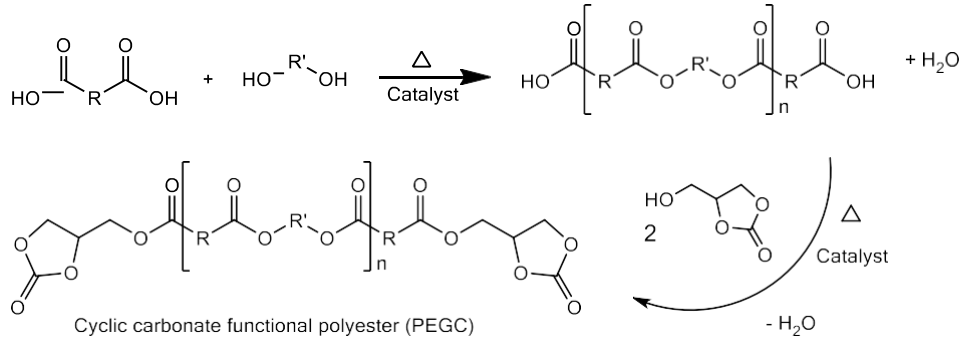


Figure 1.7. Schematic presentation of synthesis of PEGCs.

Aliphatic and cycloaliphatic monomers for these polyesters were selected to ensure the good exterior durability of the final coatings. The linear diols and diacids would impart desirable flexibility and toughness while cycloaliphatic monomers would provide the necessary stiffness to the final coatings.

Our attempts to synthesize MFCC by this task were not very successful. Since esterification , especially in the later part of the reaction, were very slow and we had products with high acid numbers. Also, we found lower yield of cyclic carbonate groups indicating some side reactions. After several attempts we decided to abandon this route for making MFCC over other more successful routes.

1.4.1.3. Task 1.3: Synthesis of MFCC from the vicinal dihydroxy compound and a dialkyl carbonate

As discussed in an earlier section, vicinal dihydroxy compounds can be trans-esterified with dialkyl carbonates such as dimethyl carbonate or diethyl carbonate, in the presence of a strong basic

catalyst to produce cyclic carbonate with the elimination of alcohol. This reaction is quite benign and "green" as compared to conventional reaction that uses toxic and hazardous phosgene.

We attempted to synthesize cyclic carbonate functional polyurethane oligomer (CCPU) using polyamine (primary amine groups), GC, and dialkyl carbonates. This is a two-step route involving two consecutive reactions, see Figure 1.8. The first reaction involves aminolysis of GC with polyamines, without any added catalyst, to give polyurethane intermediate with vicinal dihydroxy groups. In the subsequent second reaction it is converted to cyclic carbonate group upon trans-esterification with dialkyl carbonate in presence of strong / super base (such as TBD, DBU, phosphazene, sodium carbonate, potassium tert- butoxide, etc.). The trans-esterification reaction produces alcohol respective to the dialkyl carbonate used,which will be removed under vacuum. The product is anticipated to have both 5 and 6-menbered cyclic carbonate rings. These reactions will be monitored by following amine value and FTIR spectroscopy.

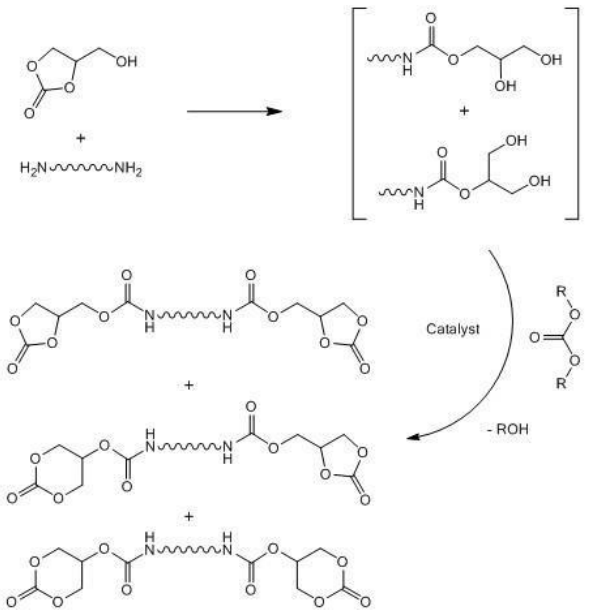


Figure 1.8. Synthetic route for MFCC from glycerol carbonate.

While this appeared promising route, the second step of this reaction scheme was difficult to produce consistent products. The product mixture (expected) were not consistent in composition with varying 5 amd 6 membered structures. We anticipated problem using these products for making NIPU-PA with good accuracy. Therefore, we did not pursue this route for deriving MFCCs.

1.4.1.4. Task 1.4: characterization of MFCCs

All the MFCCs prepared in Task 1.1, 1.2, and 1.3 will be characterized for properties such as viscosity (cone and plate viscometer), density, color, functional groups (FTIR spectroscopy), NMR, and molecular weight (GPC) using standard test methods.

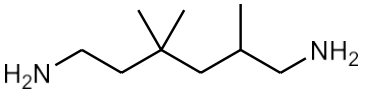
1.4.2. Objective-2: Design and Synthesis of Amine-Functional NIPU Oligomers / Resins (NIPU-PA)

In this task we strived to establish a library of NIPU-PA by reaction of a variety of MFCCs (prepared in Objective-1) with diamines compounds (MFCC/amine <1) at 50–90 °C in presence of a suitable solvent if needed. The reaction will be monitored by periodic measurement of amine value. We have successfully carried out such reactions as part of our preliminary exploratory work by reacting PEGC with aliphatic andcycloaliphatic diamines, and we do not anticipate any problems with this reaction for other types of MFCCs.

1.4.2.1. Task-2.1: Synthesis of NIPU-PA with varying backbone structure

We targeted to prepare NIPU-PAs as platform building blocks for the development of both types of coatings proposed in this project. Therefore, structural variations in its backbone will be an important design parameter to tailor the mechanical and performance properties of the targeted coatings. The important variation in the backbone structure will be as follow:

- *Type of MFCC:* A considerable component of the backbone will be MFCC. We will design different NIPU-PAs by using all the three types of MFCCs discussed in Objective-1, carbonated oxirane compounds, PEGCs, and CCPUs. As discussed above, the backbone structure of these MFCCs will be varied by the proper selection of monomers to meet the end-product requirements.
- *Type of diamines*: Besides, the second important component in the backbone of NIPU-PAs is the type of diamine used. In principle, linear aliphatic, branched aliphatic and cycloaliphatic diamines (Figure 1.9) will be used in the synthesis of NIPU-PAs to ensure good weathering properties required for the target coatings. These diamines are adequate to modify the final properties of the coatings; the cycloaliphatic diamines will contribute to the hardness of the coating while others will contribute to the flexibility. Amine terminated polydimethylsiloxanes will also be used as modifiers.



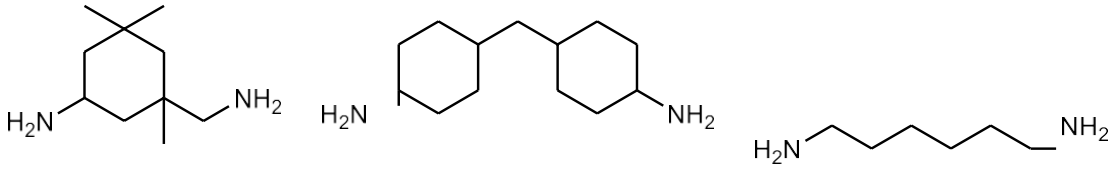


Figure 1.9. Some representative diamines for the synthesis of NIPU-PA.

1.4.2.2. Task-2.2: Synthesis of NIPU-PA with a varying molecular weight

As another important variable in the design of NIPU-PA, a series of NIPU-PAs will be synthesized with varying molecular weights. The molecular weight of NIPU-PAs is dependent on the molecular weight of MFCC used as well as on the stoichiometric ratio of amine to cyclic carbonate groups (amine index). For a given MFCC, a lower amine index will be used to synthesize higher molecular weight NIPU-PA and the other way around. While at the same amine index, higher molecular weight MFCC will yield higher molecular weight NIPU-PA but with a lower number of hydroxyl urethane groups per molecule. Lower molecular weight MFCCs are expected to give rigid structures as a result of closely spaced hydroxyl urethane groups (stiff segment) in the backbone. Keeping in mind the need for low VOC coatings, the average molecular weight of NIPU-PAs will be targeted between low to low-medium (1000 to 3000 Da).

1.4.2.3. Task-2.3: Characterization and selection of NIPU-PA variants for coating development

All the selected NIPU-PAs were characterized for properties such as average molecular weight (GPC), functional groups content (FTIR spectroscopy), viscosity (cone and plate viscometer) and viscosity profile in respective solvents/diluents to be used in coatings, compatibility with potential co-resins, Gardner color, shelf stability, and amine value. Based on the requirements of final coatings and the properties NIPU-PA, our research team, in consultation with our industry partners, will identify the most suitable NIPU-PA candidates for both 2K-HS-NIPU as well as UV-NIPU coatings. This task will be carried out concurrently with coating formulation and coating characterization as understanding the effects of structural variations on the final properties of coating is also very critical to success.

1.4.3. Objective-3: Design and Development of Two-Component High-Solid NIPU Coating Systems (2K-HS- NIPU)

The classical epoxy – amine crosslinking chemistry has been well established and popular because of the sufficiently fast reaction under ambient conditions. Building on this chemistry, as the first

approach for low VOC, non-HAPs coatings, we are proposing the development of high solid 2K NIPU coatings (2K-HS-NIPU). This two-component system will be comprised of the selected NIPU-PAs (developed in Objective-2) as onecomponent, and the second component will be the multifunctional durable polyepoxide resins/crosslinkers. We selected different commercially available durable polyepoxides such as those shown in *Task 1.1 (Figure 1.7).* The following tasks were undertaken to accomplish this objective.

1.4.3.1. Task 3.1: Synthesis and characterization of HS epoxy-functional acrylate resin (EAR)

While we attempted to prepare a range of acrylic resins with varying epoxy content, these resins had very high MW and hence viscosities. Our attempts to control MW using higher initiator concentrations as well as chain transfer agents did reduce their MW and hence viscosities, but the viscosity values were still much higher for their use in HS type coatings. Therefore, we could not pursue this route for further study.

1.4.3.2. Task 3.2: Preparation and application of 2K HS-NIPU coating compositions

The various 2K-HS NIPU coatings based on combinations of different NIPU-PAs different EARs were formulated as well as other commercially available durable polyepoxides as discussed above. All the formulations were prepared based on stoichiometric equivalents of epoxy groups and active hydrogens of NIPU-PAs with polyepoxide being one component and NIPU-PAs being the other. To accelerate the curing process, a suitable tertiary amine catalyst might be used. VOCs exempt and non-HAPssolvents was used to adjust the viscosity of the coating composition. We also used , where necessary, t-butyl acetateand diethyl or dimethyl carbonate that are VOC exempt solvents to the extent possible, along with some conventional solvents. The “pot-life” was one of the important consideration in the selection of formulation parameters. Before application, both the components were mixed thoroughly and viscosity adjusted for proper application. The coatings were applied on cleansubstrates, i.e., composite and mild steel or aluminum alloy, as specified in the prescribed test methods. The coatings were allowed to cure for one week under ambient conditions before their testing and evaluation.

The pigmented coatings were also be formulated (for a selected systems) by dispersing suitable pigments for required color suchas carbon black, titanium dioxide, etc. (exterior durable and light fastness pigments), Important additives used will be dispersing agents, gloss-control agents such

as fumed silica, anti- settling agents, flow control agents etc. The the pigments were dispersed in the NIPU-PA component, and epoxy component was used as a "hardener". We used a lab mixer equipment for pigment dispersion. Important formulation variables were the type of NIPU-PAs, type of polyepoxide compounds, pigment volume concentration (PVC), % Volume solids, VOCs, and HAPs content.

1.4.3.3. Task 3.3: Characterization of liquid coating material

The physical properties of the coating samples that were evaluated included viscosity (efflux cups), non-volatile matter (% NVM), % VOCs, density, pot-life and drying time, and coverage. The degree of dispersion will be evaluated by Hagman gauge. The shelf-stability of the systems were evaluated by an accelerated incubator test.

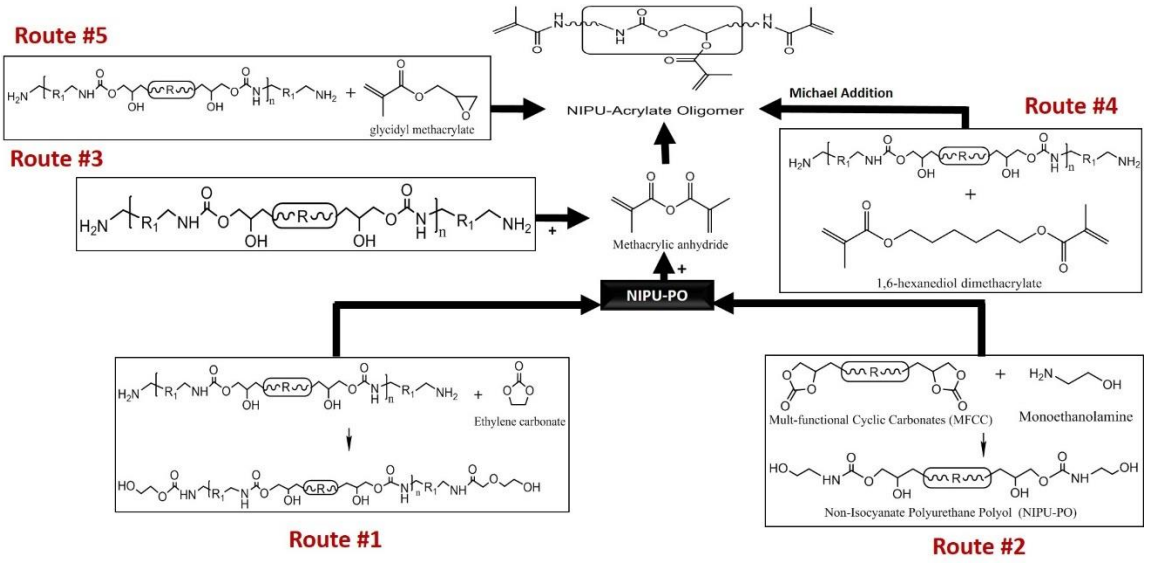
1.4.4. Objective-4: Design and development of UV-curable NIPU coating systems (UV-NIPU)

Radiation curable coatings are one of the fast-developing eco-friendly coating systems, which has 100%solid contents and exceptional rapid curing (few seconds). Since its inception, the UV-curing technology has mainly been used for flat surfaces, controlled in-factory applications, and curing systems. But recent innovations in UV curing equipment made it possible to use these systems on aircraft coatings with on-siteapplications [139-140]. Therefore, we proposed to use this crosslinking chemistry as a novel system fortargeted coatings on radome, antennas, gun shields, wing leading edges, helicopter blades, etc. We functionalized NIPU-PAs oligomers with meth(acrylate) functionality to confer UV-curable functionalityin the presence of suitable photo-initiators.

1.4.4.1. Task 4.1 Synthesis of (meth)acrylate functional oligomer from NIPU-PA

The NIPU-PAs developed in objective-2 there are essentially two types of functionalities - amine groups at chain ends and hydroxyl groups in the backbone. The NIIPU-PA oligomers we planned to introduce (meth)acrylate functionalities at both of these sites. This is generally accomplished by various reactions of NIPU-PA, such as base-catalyzed trans-esterification reaction with methyl (meth)acrylate, reaction with (meth)acryloylchloride, or with meth(acrylic) anhydride.

We successfully carried four different routes for synthesis of UV-NIPU oligomers that can meet the requirements of target coatings. The following figure summarizes these synthetic routes.



We carefully controlled and targeting the following criteria to achive useful UV-NIPU.

- Molecular weight of UV-NIPU, and hence their acrylate equivalent weights.
- The type of backbone structure of NIPU-PAs (based on the type of MFCC and polyamine), the M_W of MFCCs, and hence spacing between the hydroxyl urethane groups, and
- (Meth)acrylate equivalent weight, which we varied by varying numbers of moles of (meth)acrylicanhydride reacted per mole of NIPU-PA.

Out of all the above routes pursued, we found the direct reaction of NIPU with methacrylic anhydride as the most suitable routes. This was based on the purity of the product obtained due to extent of reactions in various routes. For instance, Michael-Addition route showed significant unreacted starting materials. This, product UV-NIPU obtained from the direct reaction of NIPU-PA and Methacrylic anhydride were only used in the subsequent studies.

1.4.4.2. Task 4.2: Characterization of UV-NIPU oligomers

The UV-NIPU oligomers (prepared from different synthetic routes) were characterized for their functional groups (FTIR spectroscopy), molecular weight (GPC), and viscosity (cone and plate viscometer). Based on these properties, some of the UV-NIPU oligomers were selected for the formulation of 100% solid UV-NIPU coatings. This selection was based on, among other factors, the viscosity of UV-NIPU oligomers, acrylate content, compatibility with conventional reactive diluents, cure response, and their anticipated properties upon UV-curing.

1.4.4.3. Task 4.3: Formulation and optimization of coating compositions

The selected UV-NIPU oligomers prepared by direct reaction of NIPU-PA and methacrylic anhydride were used to formulate UV-NIPU coatings. UV curable coatings are composed mainly of such components as (meth)acrylate functional oligomer, reactive diluents, photo-initiators, additives, and pigments. Upon curing, reactive diluents become an integral partof the cured polymer matrix, and hence they have a considerable effect on the final film properties. Therefore, we will use combinations of different reactive diluents, in varying quantities, to meet the targeted properties of the coatings as well as adequate application properties. The primary variables in using different reactive diluents will be their functionality and chemical structures.

The UV-NIPU coatings were formulated using UV-NIPU oligomers, different types of conventional reactive diluents, photo-initiators, additives, and pigments (for colored coatings). These being on-site UV-cure systems, UV-A source and appropriate photo-initiators will be tried. Clear coatings were prepared bysimple homogeneous mixing of the components while pigmented system required grinding and dispersion ofpigments in a mixture of oligomer and reactive diluents in the presence of wetting and dispersingagents. The selection of types of pigments, the dispersion process, etc. was in line with the guidelinesfor UV-curable coatings. To obtain adequate through-cure in the least exposure time and with the lowest UV intensity, the UV-NIPU resin, reactive diluent and photo initiator package were optimizedfor the intensity and spectral output of the curing lamp system.

1.4.5. Objective-5: Testing, evaluation, and characterization of NIPU coatings

All the coating samples prepared in Objectives-3 and 4, both the 2K-HS-NIPU as well as UV-NIPU types were tested for primary coating properties. These coatings were also tested for thermal (DSC, TGA) andmechanical properties (DMA). These tests helped us to understand and establish a structure–property relationship of the NIPU-based system in comparison with the conventional PU system that have been used asthe benchmark. However, as will be discussed in the subsequent section/s, none of the UV-cured coatings passed the primary test criteria (specifically low temp flexibility test and % elongation) and hence they were not evaluated for rain erosion resistance test as per SAE AMS-C83231A and MIL-PRF-32239.

1.4.5.1. Task 5.1 Testing and evaluation of primary properties, and thermo-mechanical properties.

Some of the selected coating samples prepared in Objectives-3 and 4, both the 2K-HS-NIPU as well as UV-NIPU types were tested for primary coating properties as per ASTM test methods. These properties included primary film properties such as drying time (BK Drying time recorder), dry-film thickness, hardness, flexibility, impact resistance, abrasion resistance (Taber), MEK double-rub tests, and gloss measurement. Thermal properties of coatings, glass transition temperature (clear coatings) by DSC (TA Q1000) and thermal stability using TGA (Q500) were used to determine and compared with the conventional PU counterparts. Mechanical properties of the free films were analyzed by DMA (TA Q800). Thermo- mechanical properties, combined with other film property provided useful information on the structure-property relationship of polyhydroxyl urethane and conventional PU-based coatings.

1.4.5.2. Task 5.2 Testing and evaluation of critical performance properties as per SAE AMS-C-83231A and additional properties per MIL-PRF-32239.

Based on the outcomes of Tasks 3.3 and 4.3 (for composition, VOCs, and HAPs content) and Task-5.1 (primary coating properties), a few potentially promising candidates 2K-HS-NIPU coating samples were identified for testing of critical performance properties as per SAE AMS-C-83231A and additional desirable performance properties per MIL-PRF-32239 specifications.

The Coatings Research Institute (CRI) has capabilities for conducting some tests outlined in SAE AMS-C- 83231A, such as peel strength, flexibility, water resistance, aromatic fuel resistance, electrical transmission, and surface resistivity. We used Chemical Dynamic LLC, a small business located near EMU, for carrying out tests as per MILL-PRF-32239. We collaborated with the Coating Technology Integration office (AFRL/RXSSO) at Wright-Patterson Air Force Base to carry out Rain Erosion Tests at their UDRI facility.

1.4.5.3. Task 5.3 Demonstration of performance and environmental benefits and identify potential NIPU coating candidates for further development/implementation

Our research team compiled the results and data collected from all of the above tasks and critically analyze the coating compositions, specifically for VOC and HAPs status, application and curing properties, and the desirable and critical performance properties of all the coatings evaluated. The benchmark coatings (CAPCCO) was also tested and compared. For one selected coating system we carried out Gate-To-Gate type life-cycle material and energy calculations to develop Life Cycle

Inventory data, to demonstrate the environmental andsustainability benefits. Nevertheless, the full Life-cycle assessment (LCA) was outside of the scope of this project. The technical approaches of the project are schematicallyshown in following figures.

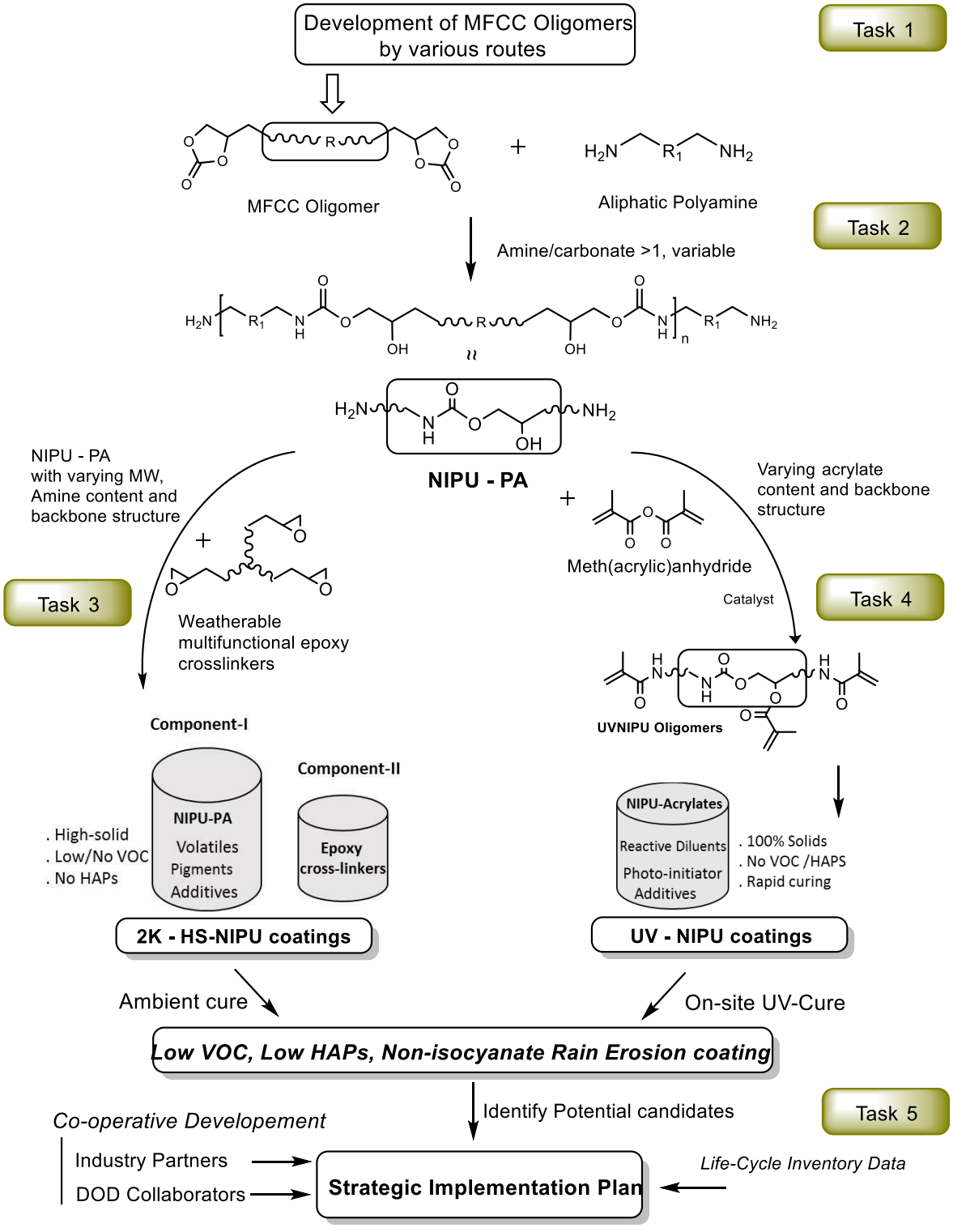
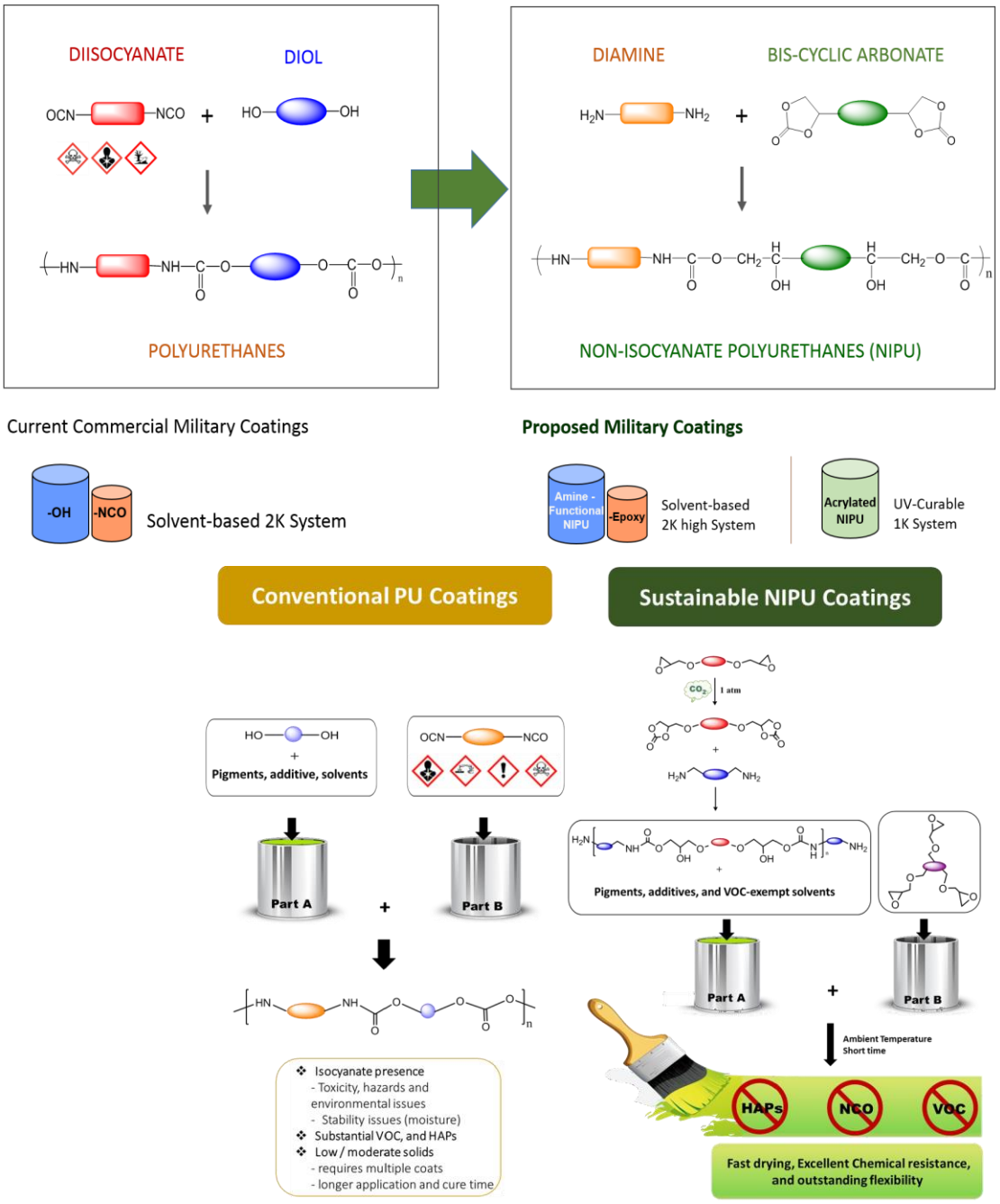


Figure 1-10. The technical approaches of the project

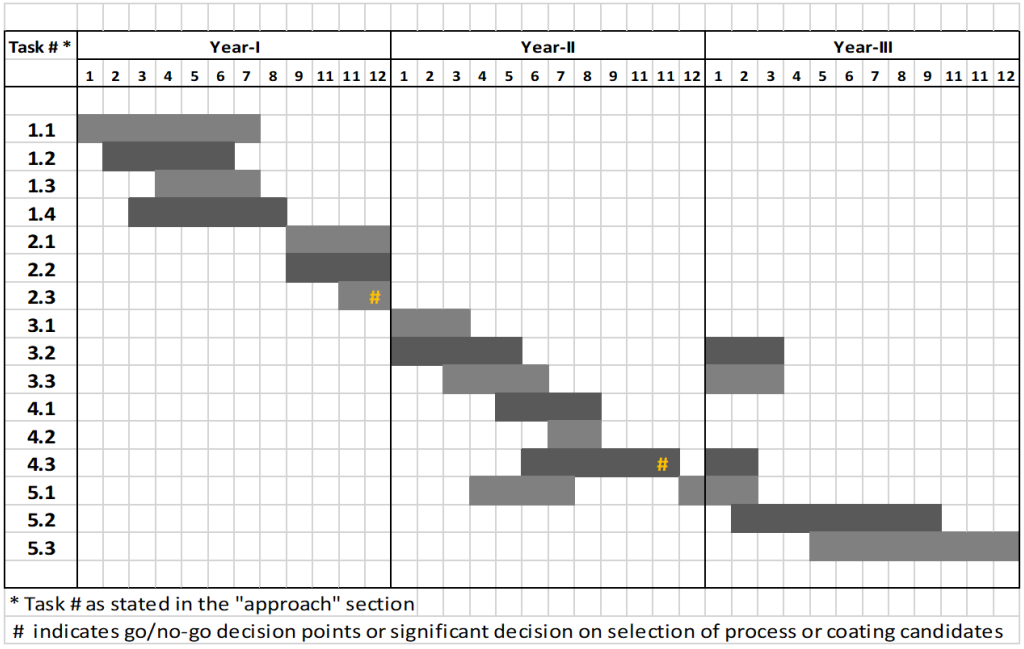


Current commercial PU-based and proposed coatings.

1.5. Milestones

Table 1.1 shows the Gantt chart of the project schedule and delineates the timeline for each task. Thesignificant decision points (gates) for selection of a specific route (or process) or intermediate or coating candidate for subsequent efforts are shown by #. The details of the selections are discussed in the “approach” section.

Table 1.1 Gantt chart showing the project schedules and important milestones



1.6. Cooperative Development

We strongly believe that the success of such a project involving the development of a new technologyplatform, demonstration of its benefits to the stakeholders and providing a strategic roadmap for its implementation is not possible without cooperative development. We worked collaboratively with WPAFB in understanding the needs of the rain erosion tests. We also worked with AFRL, ARL and NSWCCD scientists in selections of materials, test conditions and sought technical inputs. We also sought inputs from the program manager and SAB during IPR reviews and constantly refined our work. Therefore, we have planned to involveand work cooperatively with the major stakeholders in this project.

1.7. Transition Plan

Based on the outcome of this project, we believe there is a lot of potential in transitioning this project to the next level, not necessarily for rain erosion coatings, but other military coating types. We have prepared a transition plan that highlights these area, as schematically shown below.

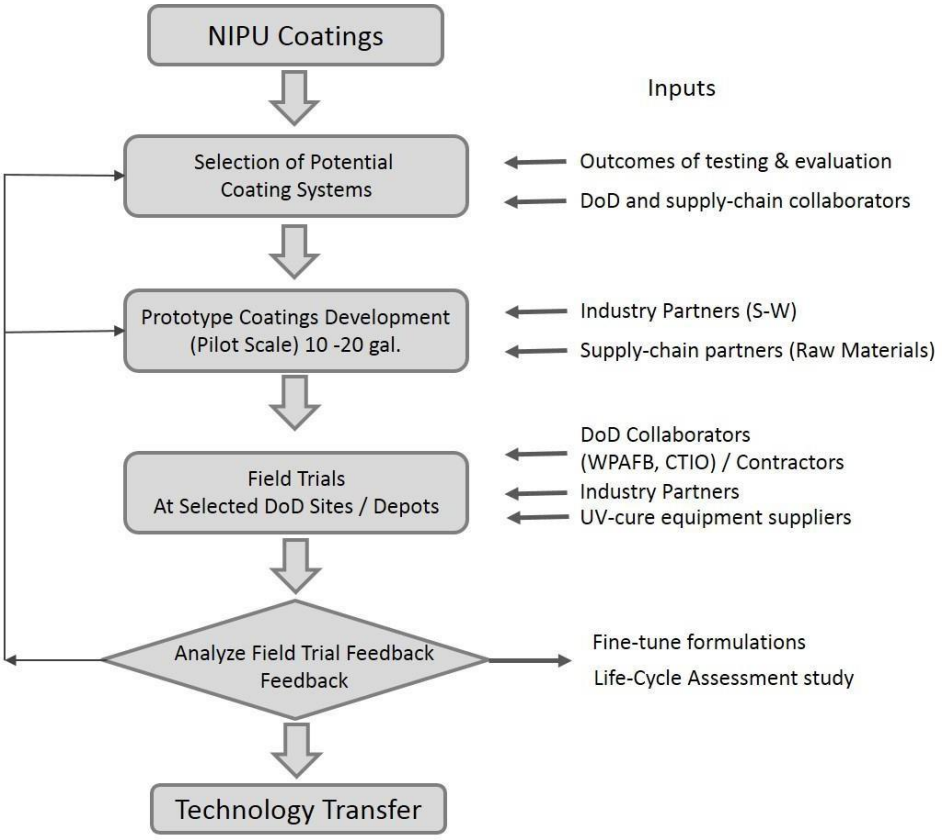


Fig. 1.12 A schematic plan for implementation of NIPU coatings in the field.

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Chapter Two

Design, synthesis, and characterization of multi-functional cyclic carbonate (MFCC) oligomers, amine-functional non-isocyanate polyurethane oligomers/resins (NIPU-PA) and two-component high-solid NIPU coating systems (2K-HS-NIPU)

(Objective-1, Objective-2, Objective-3 and Objective 5)

Abstract

The solvent-borne two-component polyurethane (PU) coatings are currently the undisputed coating systems of choice to meet the on-site application, curing, and performance requirements of manyindustrial places. Considering the constraints of usage of toxic isocyanate compounds, this project has focused on the design and development of environmentally benign two-component high solid Non- Isocyanate Polyurethane (NIPU) systems through a novel route based on cyclic carbonate/amine chemistry. Cyclic carbonates were synthesized by carbonation of epoxy compounds and reacted with an excess amount of amine to reach polyurethane polyamines (PUPA). Coatings were then prepared byusing stoichiometric proportions of PUPAs and aliphatic epoxy compounds as cross-linkers and their film properties were studied. The results revealed that by proper design of NIPU oligomers -their functional group content, backbone structure, and molecular weight- high solid 2K-coatings with outstanding performance such as low-temperature flexibility and resistance to chemicals and solvents could be obtained, and selected coating containing PUPA with Mn=1480 and 1:1.5 mol ratio of low molecular weight amine exceeds the performance of conventional isocyanate-based reference sample. Elimination of isocyanates, substantially reduced VOCs and HAPs as well as fast ambient temperature curing, make these polyurethane coatings a promising alternative for various industrial applications. The key role of molecular weight and balance between elongation and tensile strength to reach coatings with desirable mechanical properties was also demonstrated using various testing techniques.

2.1. Introduction

Conventional Polyurethanes (PUs) are products of the addition polymerization reaction between multi-functional isocyanates and polyols (Figure 2.1). PUs are among the most used polymers in many high performance applications including foams, coatings, sealants, elastomers, thermoplastics, adhesives, fibers, and so on [1]. The demand in PUs has continued to increase as thepolyurethane (PU) market today amounts to about 5% of the total polymer market and the

worldwide consumption of PU has increased steadily [2]. Currently, two-component solvent-borne polyurethanes are vastly used in many industries as the undisputed option owing to the properties they exhibit such as good adhesion to polymer composite substrates, low-temperature flexibility, good barrier properties, and resistance to various chemicals, enhanced thermo-mechanical properties, and outstanding long-term exteriordurability [3-5].

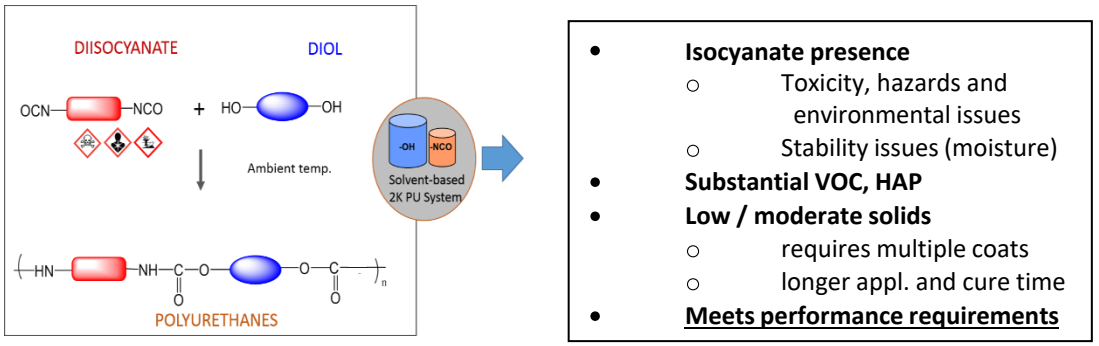


Figure 2.1. Synthesis of conventional PUs through the addition

Polymerization betweenmulti-functional isocyanates and polyols.

However, the present commercial polyurethane coating technology is based on hazardous isocyanate compounds as primary building blocks. The use of isocyanate compounds, both at manufacturing and application sites, and their related environmental, health, and safety-related costs have created serious issues in the coatings industry [6]. Therefore, increasing interest has been shown by researchers, environmental protection agencies, and industries across the world in recent decades, seeking for an alternative "green process" for polyurethanes that reduces or eliminates toxic substances. These efforts have been accelerated recently due to the implementation of strong legislation against the usage of isocyanate [7]. Non-isocyanate polyurethanes (NIPUs) have been prepared by different methods such as trans-urethanization of dimethyl carbamate and diol in presence of strong base catalyst [8-9], the reaction of bis (2-hydroxyethyl carbamate) with a hydroxyl group to form diol or part of bis (2- hydroxyethyl carbamate) to yield liner thermoplastic PU [10], copolymerization of aziridine and super- critical CO2 to yield cyclic urethanes [11] and also ring-opening polymerization of cyclic carbamates or aziridines [12-14].

Although these routes have successfully resulted in NIPUs the products have shown inferior properties compared to conventional PU without complete elimination of toxic substances such as phosgene [15]. The addition polymerization of cyclic carbonates and amine compounds has been a promising route reported by many researchers. The list of studies and publications confirms the large interest of both scientific and industrial communities in this technology [16-19]. Recently, figovski *et al.*
[20] have prepared a comprehensive list of patents and researches on the synthesis of NIPU based on this route. Cyclic carbonate/amine chemistry avoids usage of phosgene compounds and the resulting NIPU has additional hydrogen bonding which allows improved chemical resistance to non-polar solvents [8]. Among multiple possibilities to prepare cyclic carbonate monomers, carbonation of epoxy-functional compounds has attracted much attention because it will bring an extra environmentally friendly process of CO_2 consumption as well as being relatively facile and straightforward [21-23]. While many carbonation routes require supercritical conditions (temperature and CO_2 pressure), Ayogi et al. [24] have reported an efficient catalyst based on phosphonium salt that yields high conversion of epoxy to cyclic carbonate at ambient pressure.

Despite all the benefits, cyclic carbonate/amine chemistry faces a major drawback: the low reactivity between cyclic carbonates and amines, and a limited degree of advancement of reaction during the room temperature polymerization. This leads to serious problems for systems that need to be cured at ambient temperature and limits the application [25]. On the other hand, volatile organic compounds (VOC) and hazardous air pollutants (HAPs) have long been recognized for their negative impacts on the environment, health, and ecosystem, and their reduction or elimination has been a major driver that has led to the development of water-borne, high-solid, and UV-cure coating technologies [26].

Preparation and application of 2k-HS-NIPU coatings: In this part of the study, to address the challenges of NIPUs based on cyclic/carbonate amine chemistry, a three-step process was developed to reach the final coating system. As it is illustrated in Figure 2.2, cyclic carbonates were synthesized by carbonation of epoxy compounds and then reacted with amines in an excess ratio of amine/cyclic carbonate to prepare non-isocyanate polyurethane-polyamine oligomers (PUPAs). In the third step,PUPA oligomers were cured with multi-functional epoxy compounds in a 1:1 equivalent ratio to reachthe final NIPU coatings. The selection of raw materials and reaction ratios was also made based on a framework which is summarized in Figure 2.3. NIPU coatings were

designed in a way that the coatings exhibit advanced performances such as high flexibility at low temperature, high elongation, and resistance to certain chemicals specified in SAE AMS-C-83231 standard [27] together with having high solid content at the time of application and relatively short curing time at room temperature. Fourier transform infrared (FTIR) spectroscopy and titration techniques were used for the characterization of thesynthesized NIPUs, and the performance of the coatings was evaluated by various testing methods.

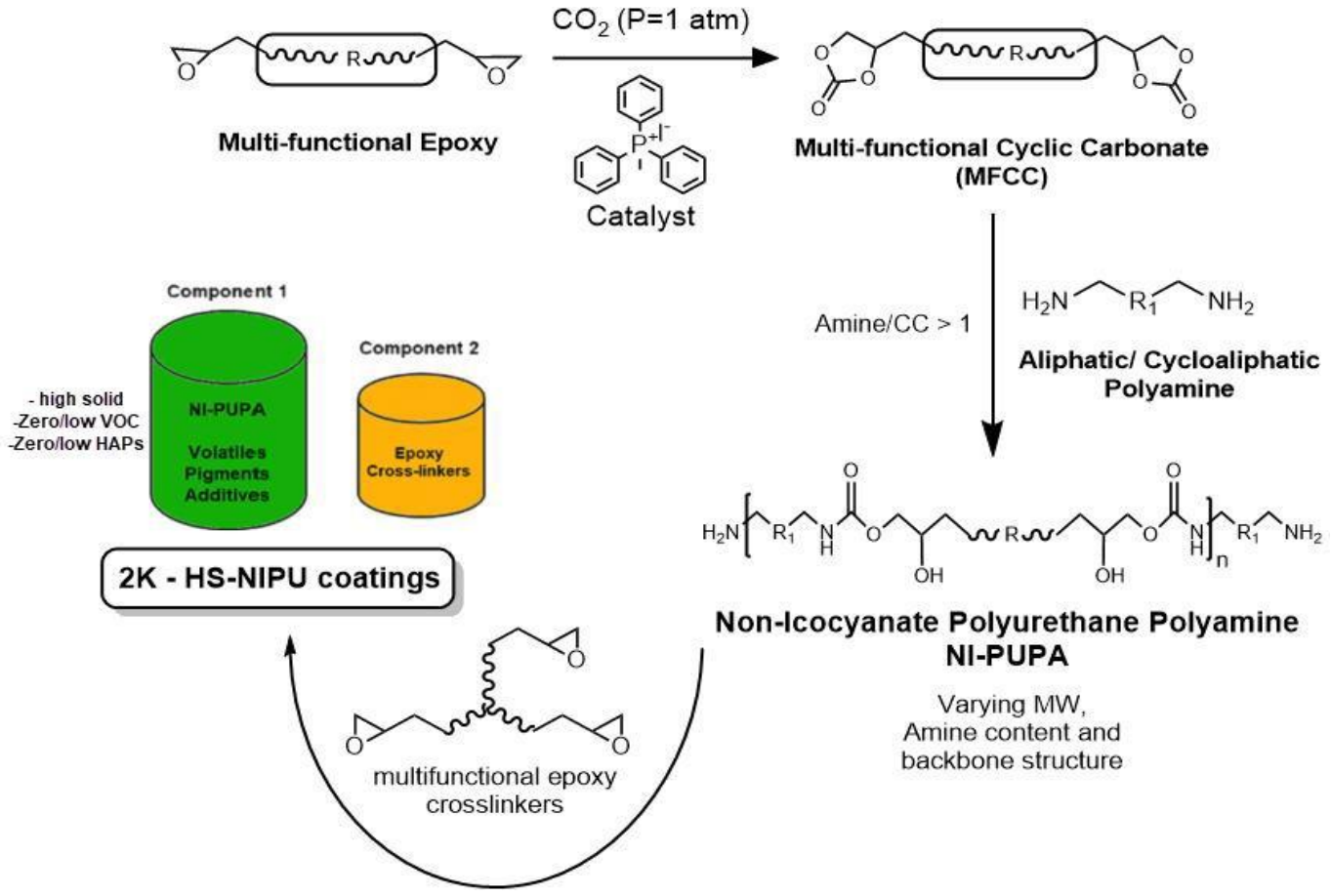


Figure 2.2. The overall strategy for the development of high-performance 2k-HS-NIPU coatings.

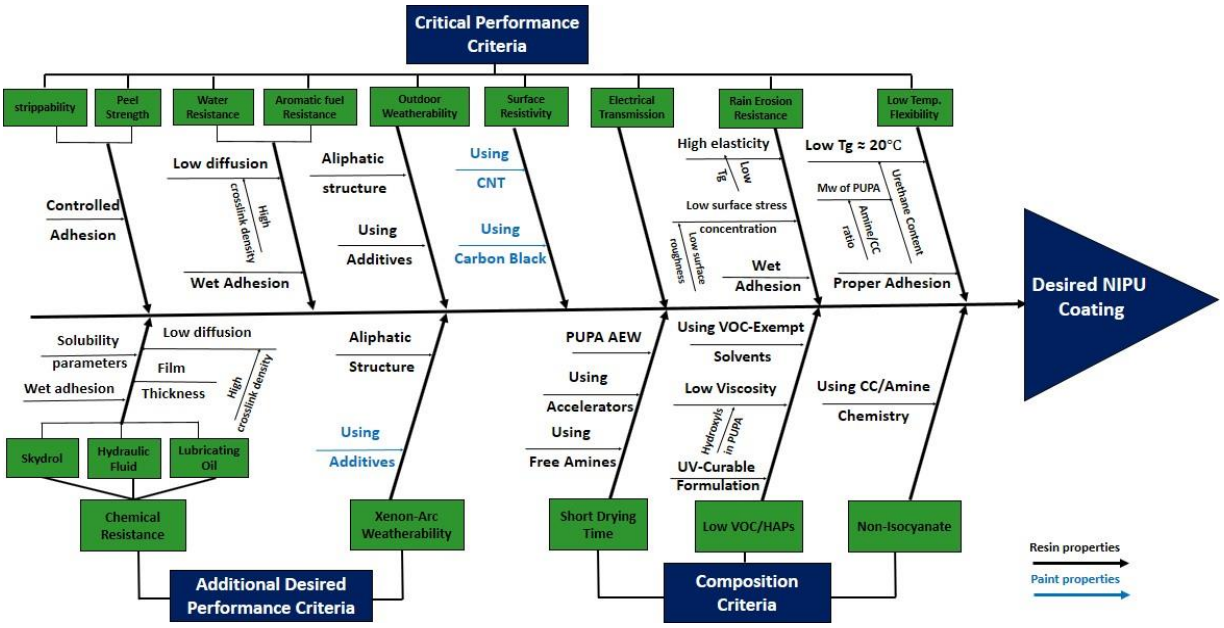


Figure 2.3. Performance Criteria and design strategy for high-performance NIPU Coatings.

2.2. Experimental

2.2.1. Materials

Different di and tri-glycidyl ether with various epoxy equivalent weights were procured from a commercial supplier to be used as the starting material and also curing agent. Isophorone diamine (IPDA) with commercial name of VESTAMIN@IPD, Trimethyl hexamethylene diamine (VESTAMIN@TMD), and 4,4'-Diaminodicyclo-hexylmethane (VESTAMIN PACM) were received from EVONIK and also Jeffamine D200 and D430 polyether amines were procured from Huntsman. Diethylenetriamine (DETA), toluene, ethyl acetate, phosphonium salt catalyst, methyl isobutyl ketone (MIBK), butanol, Parachlorobenzo- trifluoride (Oxsol 100), 1-methoxy-2-propanol, and 2,4,6-Tris(dimethyl aminomethyl)phenol (DMP-30) were all purchased from SIGMA-ALDRICH. TiO_2 pigment (Dupont Ti-Pure R960), BYK 306 surface additive, and BYK 9076 defoamer were also used for coating formulation. Figures 2.4 and 2.5 illustrate the chemical structures and names of the epoxy compounds and diamines, respectively. Iron phosphate pre-treated cold roll steel (CRS) panels with dimension of 4" × 6" (10.16 × 15.24 cm) produced by Q-panel were used as the substrate for applied coatings.

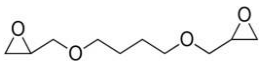
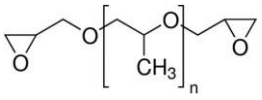
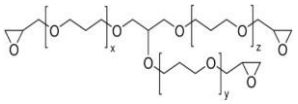
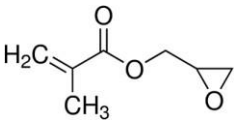
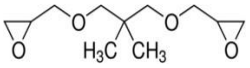
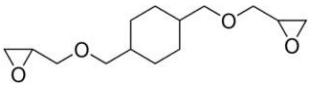
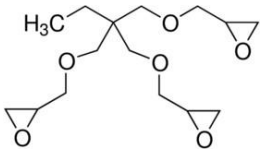
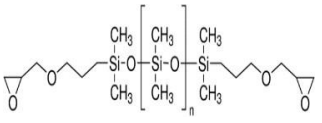
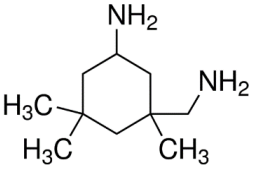
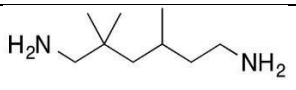
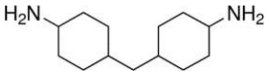
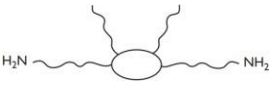
Epoxy No.	Compound Name	Structure	Epoxy No.	Compound Name	Structure
1	1,4 Butanediol Diglycidyl Ether		**2**	Polypropylene Glycol Diglycidyl Ether Mn ~640	
3	Propoxylated Glycerin Triglycidyl Ether Mn ~2000		**4**	Glycidyl Methacrylate	
5	Neopentyl Glycol Diglycidyl Ether		**6**	Cyclohexane Dimethanol Diglycidyl Ether	
7	Trimethylol Propane Triglycidyl Ether		**8**	Poly (dimethylsiloxane), Diglycidyl Ether Terminated Mn ~1250	

Figure 2.4. Chemical structure of the used epoxies.

Code	Compound Name	Structure	Code	Compound Name	Structure
IPDA	Isophorone Diamine		**TMD**	Trimethyl Hexamethylene Diamine	
PACM	4,4'-Diaminodicyclohexyl Methane		**P1074**	Dimer Diamine Mn ~540	

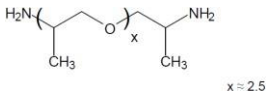
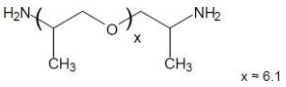
D 230	Polyoxypropylene Diamine Mn ~230		**D 400**	Polyoxypropylene Diamine Mn ~460	

Figure 2.5. Chemical structure of the used diamines.

2.2.2. Methods

2.2.2.1. Synthesis of cyclic carbonates

In the first step, three different cyclic carbonate functional materials (CC1, CC2, and CC3) were synthesized by carbonation of corresponding epoxy compounds. Phosphonium salt catalyst ((methyltriphenylphosphonium iodide (MePh.I), or tert-butyl ammonium iodide (TBAI) by 2 to 5 mol.% ofthe epoxy) was added to a solution of epoxide in 1-methoxy-2-propanol by 2 mol% of the epoxy. The atmosphere inside the flask was replaced with CO_2 (balloon at 1 atm.), and the reaction mixture was stirred at 70 C. After the reaction time, the mixture was cooled to room temperature and the productwas separated using hot water/ethyl acetate in a separatory funnel. The reaction completion was tracked using oxirane oxygen content (OOC) based on ASTM D1652 and Fourier Transform Infrared (FTIR)spectroscopy.

2.2.2.2. Synthesis of PUPAs

To reach amine functional polyurethanes cyclic carbonates were reacted with diamines in a condensation polymerization reaction in an excess ratio of amine/cyclic carbonate. This reaction was carried out in a three-neck flask with a mechanical stirrer, nitrogen inlet, temperature controller probe, and water condenser setup. The flask was filled with cyclic carbonate after distillation of ethyl acetate. The calculated amount of amine-based on equivalent weights was dissolved in solvent (Toluene, Oxsol 100, and MIBK) and added to the cyclic carbonate. The reaction temperature was raised to 90℃ and kept under stirring for the entire reaction time. The equivalent weights of cyclic carbonates were calculated from that of the corresponding epoxy compounds (which was calculated by titration method). The conversion of cyclic carbonates and urethane formation was tracked by amine value titration based on ASTM D2074 standard and FTIR spectroscopy. The target amine value after completion of the reaction was calculated based on Eq. 2.1.

$$Target\ Amine\ Value = 56100 \times \frac{(\#\ of\ amine\ equivalents\ -\ \#\ of\ CC\ equivalents)}{Total\ weight\ of\ batch\ (g)} \quad (2.1)$$

2.2.2.3. Preparation of coatings

The resulting PUPAs were further mixed with epoxies in a 1:1 equivalent ratio and applied on the acetone degreased substrate and left to cured to the form of cross-linked NIPU coatings. Since tri-glycidyl ether epoxies resulted in faster drying and less tackiness compared to two functional ones, trimethylolpropane triglycidyl ether with an epoxy equivalent weight of 140 was used as the cross-linker. DMP 30 was added to the mixture by 4 wt% of epoxy as curing accelerator as well as BYK 306 surface additive (1 wt% of total solids) and BYK 9076 defoamer (0.5 wt% of total solids). To adjust the appropriate viscosity for coating application a mixture of toluene, MIBK, and Oxsol-100 solvents were added to the coating formulation. Also, in some cases, additional amine with different equivalent ratios was added to adjust the curing time and hardness and it was named "free amine". It should be notedthat crosslinker in such cases was added in a 1:1 equivalent ratio to free amine and PUPAs combined. Moreover, a commercial fast curing isocyanate-based PU coating (Desmodur 3390 as Isocyanate compound and Joncryl 915 as polyol) was formulated according to supplier's suggestion and used as reference. Finally, a coating formulation was prepared for selected samples containing TiO_2 pigments with 8-12 % of pigment volume concentration (PVC). Pigments were dispersed in a high-speed mixeruntil the grinding of hegman gage <7 was obtained. Coatings were applied on iron phosphate pretreated panels using a film applicator. The dry film thickness was 50±5 µm and 250±20 µm for clear and pigmented coatings, respectively. Coatings were cured at room temperature and kept for 7 days before testing.

2.2.3. Characterization and testing

Carbonation reactions of epoxy compounds were carried by varying the type of solvent used and the type of catalyst under varying temperatures. The FTIR spectra were collected using KBr standard disks on Bruker Instrument at 64 scans and 2 cm^{-1} of resolution. The spectra obtained in the frequency range of 400-4000 cm^{-1} for evaluating the chemical structure of the end products. 1H (400 MHz) Nuclear Magnetic Resonance (NMR) spectroscopy measurements were performed on a JEOL 400 MHz multiple nucleus spectrometer using chloroform-d ($CDCl_3$) solvent and tetramethylsilane as internal standard. Gel Permeation Chromatography (GPC) was performed using Malvern 270 dual detector system with Phenogel 5u 10^4 A, Phenogel 5u 100 A and Phenogel

5u 50 A columns using tetrahydrofuran as the eluent at a flow rate of 1 mL/min. The sample concentration was 4 mg/mL and 100 µL of the solution was injected. Number and weight-average molecular weights (M_n and M_w, respectively) and poly dispersity index (PDI) were calibrated with standard polystyrene samples in the molecular weight range of 585 to 200,000. A Brookfield CAP1000 cone and plate viscometer with temperature range of 5 to 75 ℃ and shear rate up to 10000 sec^{-1} was used to measure the viscosity of samples. DSC analysis was performed under nitrogen atmosphere with DSC Q-500 equipment (TA Instrument) calibrated with n- octane and indium. All the samples were subjected to -80 to 180 □C in a heat/cool/heat cycle at a heating rate of 10 □C/min. Finally, Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on DSC Q-500 instrument for the temperature range of 40–580 ℃ at a heating rate of 10 □C/min. The static mechanical properties were measured with Universal Galdabini tensile testing machine and the crosshead rate was set at 50 mm/min.

The adhesion of the applied coatings was evaluated by the cross-cut tape method as per ASTM D- 3359. The hardness properties of the coatings were determined using a pencil hardness test according to ASTM D3363. The flexibility and load distribution property of the coatings were evaluated by conical mandrel and impact tester as per ASTM D522 and ASTM D2794, respectively. The flexibility test was done after keeping samples at -54 □C for 1 h to conform to the requirements of SAE AMS-C-83231A. Impact resistance was measured on the impact tester with a maximum height of 40 inches and a load of 4 lb. The resistance of samples to MEK double rubs was also evaluated by ASTM D4752 method. The curing time of the coatings (Surface tack-free time) was also measured using BYK-Gardner drying time recorder based on ASTM D5898. Moreover, the gloss of the coatings was evaluated using a BYK Gardner GmbH device according to ASTM D523. Finally, the resistance of the coatings to specific chemicals mentioned in SAE AMS-C-83231A standards for exterior aircraft polyurethanes was carried out. These tests include immersion in lubrication oil (with a specification of MIL-PRF-23699) for 24 h at 120±5 □C, immersion in hydraulic fluid (ref. MIL-PRF-83282) for 24 h at 65 □C, and exposure to Skydrol fluid as per MIL-PRF-32239. Coatings were then examined for any signs of blistering and adhesion loss. For all tests, at least three replicates were done to validate the reproducibility of generated data.

2.3. Results and discussion

2.3.1. Synthesis of cyclic carbonates and PUPAs

Carbonation reaction of epoxy compounds were carried by varying type of solvent used and type of catalyst under varying temperatures. The completion and progress of the intermediates and PUPAs were confirmed using FTIR spectroscopy. Figure 2.6 shows the FTIR spectra of the carbonation batch of 1,4- Butanediol diglycidyl ether compound at the initial stage and after the reaction time. It is clear from the results that the absorption peak at 909 cm^{-1} which is attributed to the oxirane ring was diminished after 24 h of reaction time and a sharp vibration peak at 1800 cm^{-1} was created. This peak is due to the formation of cyclic carbonate functionalities. Results were in confirmation with OOC% titration showing that the carbonation reaction had an almost complete conversion rate (99% based on titration results). The reaction times were relatively longer for larger compounds as they needed 48 h to reach conversions more than 95% as shown in Table 2.1. This can be due to the increased distance between the epoxy groups that need to be carbonated. At the interface with the solution, CO_2 will be inserted into the ring which is temporarily opened by the nucleophilic part of the catalyst assisted by interactions with OH groups of the solvent [24].

Table 2.1. Synthesis of Various cyclic carbonate (CC) compounds using phosphonium salt catalyst under ambient pressure conditions.

Run No.	Cyclic carbonate	Epoxy No.	Solvent	Catalyst (Mol%)	Temperature (℃)	Reaction time (h)	Conversion %
1	GCMA	4	IPA	MePh.I (5%)	25	48	88
2	GCMA	4	Toluene	MePh.I (5%)	25	----	----
3	GCMA	4	1-methoxy-2-propanol	MePh.I (5%)	25	36	99
4	GCMA	4	1-methoxy-2-propanol	TBAI (5%)	25	40	80
5	GCMA	4	1-methoxy-2-propanol	TBAI (5%)	55	48	95
6	CC7	7	1-methoxy-2-propanol	MePh.I (5%)	25	48	80
7	CC7	7	1-methoxy-2-propanol	MePh.I (5%)	55	24	97
8	CC5	5	1-methoxy-2-propanol	MePh.I (5%)	55	24	98
9	CC6	6	1-methoxy-2-propanol	MePh.I (5%)	55	24	98
10	CC1	1	1-methoxy-2-propanol	MePh.I (5%)	55	24	99
11	CC1	1	1-methoxy-2-propanol	MePh.I (2%)	55	48	98
12	CC2	2	1-methoxy-2-propanol	MePh.I (2%)	70	48	97
13	CC3	3	1-methoxy-2-propanol	MePh.I (3%)	70	48	96
14	CC8	8	1-methoxy-2-propanol	MePh.I (2%)	70	48	98

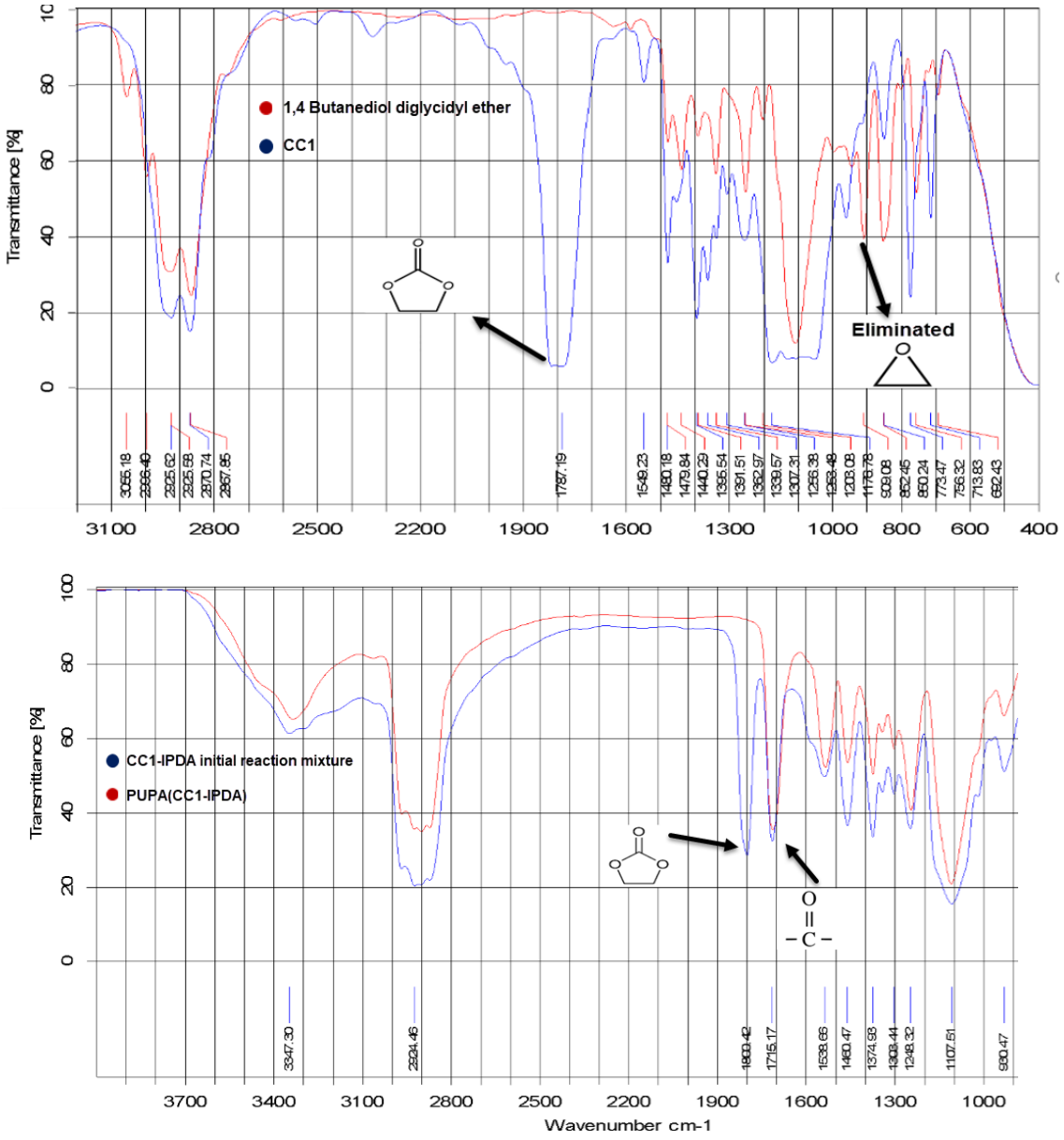


Figure 2.6. FTIR spectra of carbonation of 1,4-Butanediol diglycidyl ether and the resulting cyclic carbonate after reaction time.

According to the results of run 1 through run 3, the type of solvent plays an important role. The protic solvent such as IPA and 1-methoxy 2-propanol, appears to be activating the epoxy ring towards carbonation through hydrogen bonding between hydroxyl of solvent and epoxy oxygen. At the interface with solution, CO_2 will be inserted into the ring which is temporarily opened by the nucleophilic part of the catalyst assisted by interactions with OH groups of the solvent as shown in Figure 2.7. As regards to

the catalyst, run 4 shows that when TBAI was used as a catalyst instead of MePh.I, the reaction progress was not desirable at ambient temperature. TBAI showed lower efficiency compared to MePh.I, andhence the later was selected as catalyst for the rest of the study. Additionally, as can be seen for runs 6 through 10, with increasing epoxy functionality the reaction rates were relatively sluggish and required higher temperature to reach conversions > 95%. For the runs 11 through 14, the catalyst concentration was reduced to optimize the catalyst dose, but as shown in the Table 2.1 longer time and higher temperatures were needed to reach the target conversion, especially for the larger compounds. This can be due to more difficult accessibility of epoxy groups specially at the later stages of reaction.

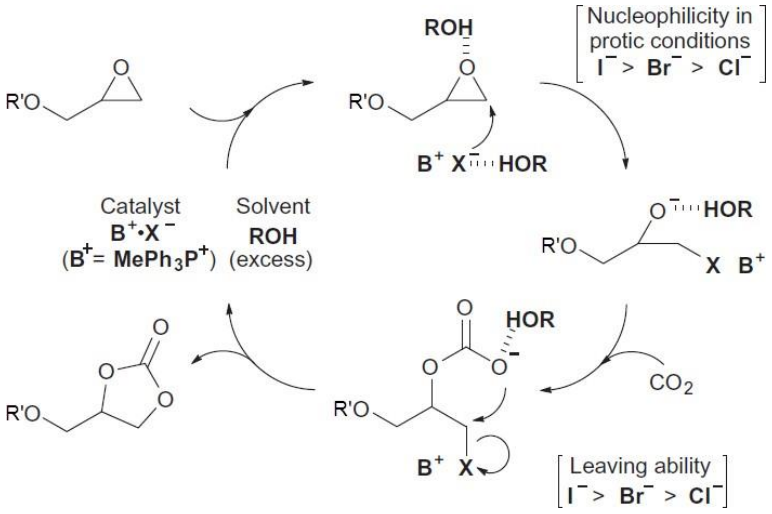


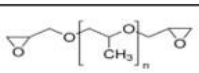
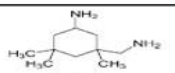
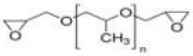
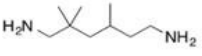
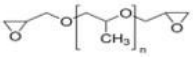
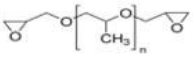
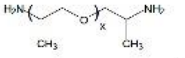
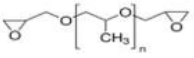
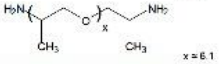
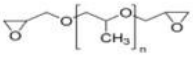
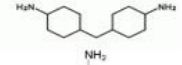
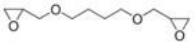
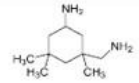
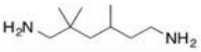
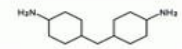
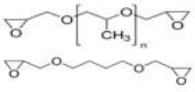
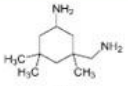
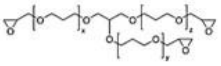
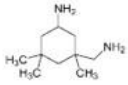
Figure 2.7. A plausible mechanism for catalyzed synthesis of MFCCs [25]

2.3.2. Synthesis and characterization of PUPA oligomers

Once the cyclic carbonates were synthesized and isolated, different ratios and types of amines were reacted with them in order to reach PUPAs. Different combinations of amines and cyclic carbonates usedin this study for the preparation of polyurethane oligomers are illustrated in Table 2.2. In the PUPA (mix- IPDA) run, CC1 and CC2 were added to the reaction mixture in a 1:1 equivalent ratio. The reaction times were considered as the time at which the amine value reached very close to the theoretically calculated target values. The completion of the reactions was also confirmed by FTIR peaks (Figure 2.8) as the peak corresponding to cyclic carbonate at 1800 cm^{-1} was diminished at that point. Also, a relative increase in the intensity of carbonyl peak at 1715 cm^{-}

[1] and broad OH peak at 3300-3500 cm^{-1} demonstrates successful opening of cyclic carbonate ring and formation of urethane functionalities as well as hydroxyl groups [19].

Table 2.2. Synthesis of various PUPA compounds using different cyclic carbonate-amine combinations.

PUPA	Cyclic carbonate	Epoxy used in Cyclic carbonate Synthesis	Amine	Reaction Time (h)	AHEW
PUPA (CC2-IPDA)	CC2			6	472
PUPA (CC2-TMD)	CC2			5	466
PUPA (CC2-1074)	CC2			8	1098
PUPA (CC2-D230)	CC2			12	526
PUPA (CC2-D400)	CC2			16	779
PUPA (CC1-PACM)	CC2			7	489
PUPA (CC1-IPDA)	CC1			4	203
PUPA (CC1-TMD)	CC1			4	255
PUPA (CC1-PACM)	CC1			5	269
PUPA (mix-IPDA)	CC1/CC2 1:1 eq.			5	322
PUPA (CC3-IPDA)	CC3			6	724

The reactions were carried out at 90℃ in toluene and Oxsol-100 as solvents

PUPA No.	PUPA (CC type-Amine)	Amine/CC ratio	Reaction Time(h)	AHEW (g/eq.)
1	(CC2-P1074)	14	8	1098
2	(CC2-D 230)	17	12	526
3	(CC2-D 400)	17	16	779
4	(CC2-IPDA-1.4)	14	12	731
5	(CC2-PACM-1.4)	14	14	764
6	(CC2-TMD)	17	4	466
7	(CC2-IPDA)	17	6	472
8	(CC2-PACM)	17	7	489
9	(CC1-IPDA)	17	4	203
10	(CC1-TMD)	17	4	255
11	(CC1-PACM)	17	5	269
12	(mix-IPDA) CC1:CC2 1:1 eq.	17	5	322
13	(mix-TMD) CC1:CC2 1:1 eq.	17	5	361
14	(mix-PACM) CC1:CC2 1:1 eq.	17	6	394
15	(CC3-IPDA)	17	6	724
16	(CC3-PACM)	17	7	746
17	(CC3-D 400)	17	15	1335
18	(CC8-IPDA)	17	-	-

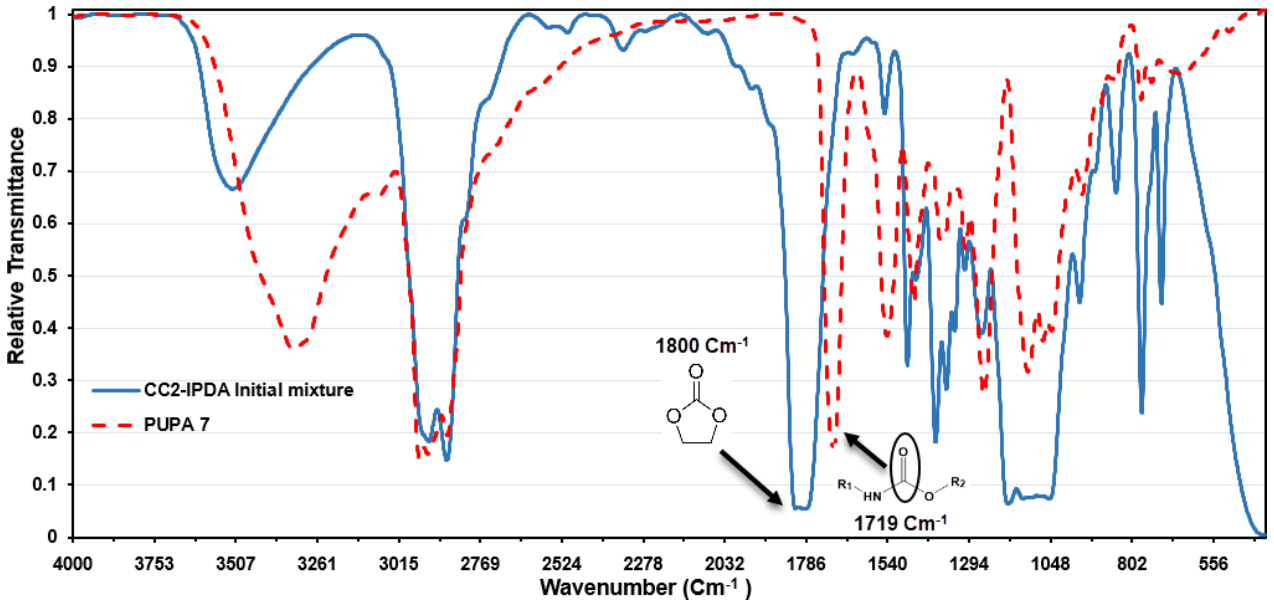


Figure 2.8. FTIR spectra of cyclic carbonate/amine mixture and the resulting PUPA after the reaction time.

H-NMR results were also recorded (Figure 2.9)nd these results are consistent with those obtained from FTIR. In Figure 2.10.a, the absence of peaks at 3.15-3.24 and 2.6-2.87 ppm can be attributed to the protons of oxirane ring (CH and CH_2, respectively) [29] as well as emergence of peaks at 4.62 and 4.8 ppm which are related to the protons in $OCHCH_2O$ of the cyclic carbonate ring [25], proved that oxirane was fully converted into cyclic carbonate. The NMR spectra of the PUPA resulting from CC2 and IPDA (Figure 2.10.b) also revealed that the peaks related to cyclic carbonate structure were diminished as a result of reaction with amines. Also, presence of peaks at 2.3-2.4 and 2.9 ppm could be related to the protons of NH_2 and its adjacent carbon [30]. This demonstrates successful termination of the PUPA oligomers with primary amines. The peak at 4.8 ppm could also be attributed to the generation of OH groups due to ring opening of cyclic carbonate [30]. Similar trend and variations in FTIR and H-NMR spectra were observed for other cyclic carbonate and PUPA samples.

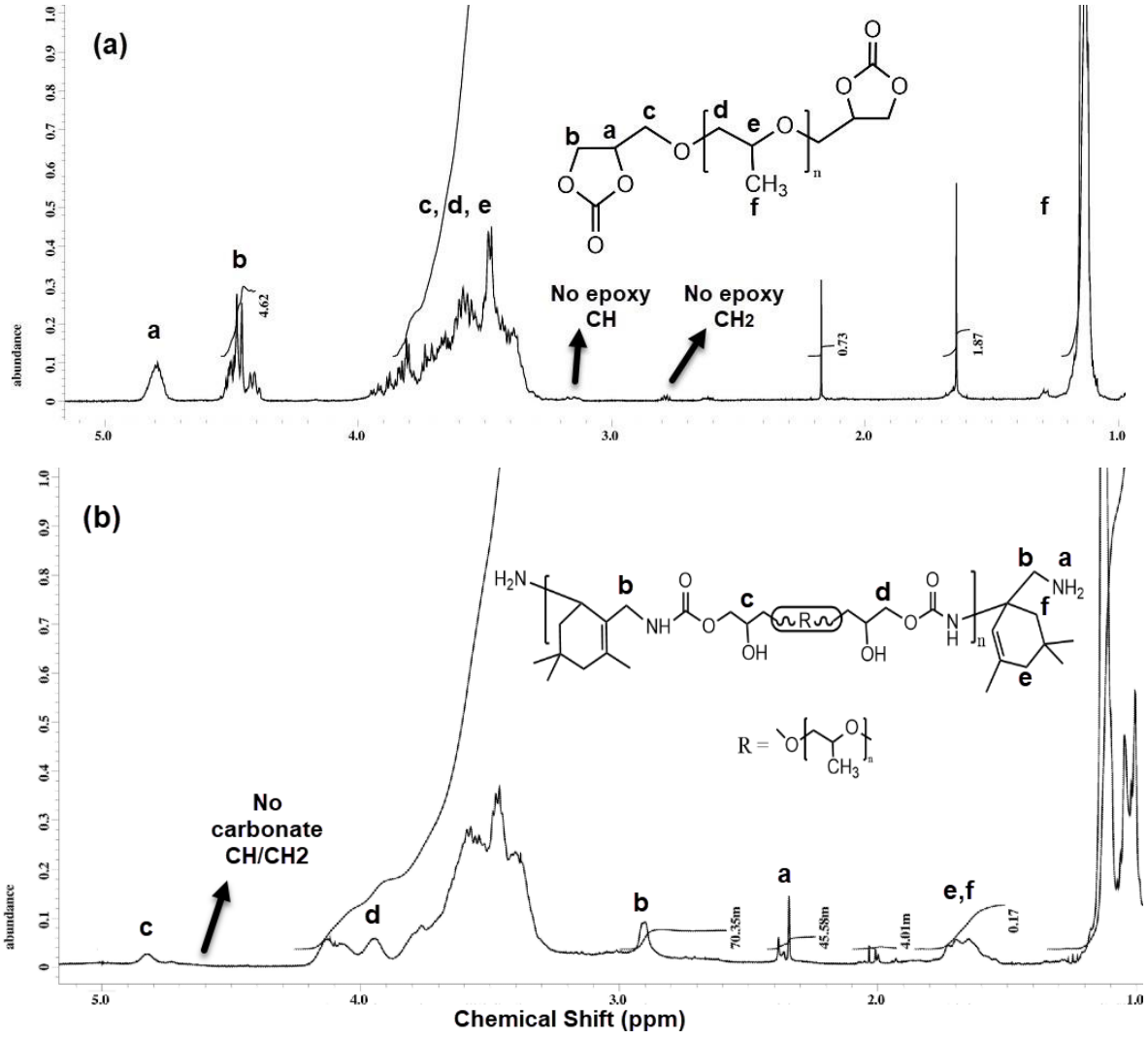


Figure 2.9. H-NMR Characterization of CC2 (a) and PUPA 7 (b) compounds in CDCl3

Depending on the structure of the reactants, various molecular weights were achieved. It should be noted that amine hydrogen equivalent weights (AHEW) have been reported since it is the effective value for further crosslinking with epoxy compounds. The reaction times were relatively higher as the molecular weight of the cyclic carbonate increased. On the other hand, it was observed that the reaction of cyclic carbonates with aliphatic polyetheramine structures (Jeffamines) was much slower compared toother amine structures. This could be attributed to less reactivity of those compounds which comes from the steric bulk hindrance of them. This hindrance reduces the nucleophilic activity of amines by aconsiderable amount which is not a desirable factor in such a

reaction [28]. The synthesis was carried outsuccessfully in both toluene and Oxsol-100 solvents. Oxsol-100 is a VOC-exempt solvent with a structure close to that of toluene. This could bring a big advantage to the final coating system as the final coating can have substantially reduced VOC.

In order to investigate the effect of the molecular weight of cyclic carbonate on that of the resultant PUPA, and to further confirm the theoretical molecular weight calculated using Carothers's equation,four NIPU oligomers were characterized using the GPC method. As shown in Table 2.3, the oligomers were prepared using the identical amine and amine/CC ratio, and they only differ in the type of cyclic carbonate used. The GPC results showed that the experimental molecular weight values were quite closeto the theoretically calculated values with PDI values close to 1. The viscosity values were higher when lower molecular weight cyclic carbonates were used, which could be due to higher urethane and hydroxyl content that increase the viscosity through hydrogen bonding interactions.

Table 2.3. Mw characterization of selected PUPAs using GPC method along with viscosity measurements.

Sample Name	M_n	M_w	PDI	Theoretical MW	Viscosity cps (75 wt.% at 25 °C)
PUPA 9	968	1025	1.060	1058	17260
PUPA 12	1008	1609	1.597	1480	15680
PUPA 7	1395	1901	1.363	1902	13502
PUPA 15	3079	3557	1.15	3736	10798

2.3.3. Properties of NIPU coatings

Based on the performance criteria required for the final properties, two-component high-solid NIPU coating (2K-HS-NIPU) coating compositions were prepared using various PUPAs (Component-I) and a di and tri-functional epoxy compounds (Component-II). Based on the performance criteria defined for the final properties of the NIPU coatings (Figure 2.3), the synthesized PUPAs were further cured with a tri- functional epoxy compound and subjected to different coating tests. Three main types of properties were considered as the initial scale for screening: Flexibility of the coatings at low temperature, having enough cross-linking to pass the

resistance tests against different chemicals, and also fast curing at room temperature. 100 double rubs of MEK, less than 10 h of tack-free time as well as passing the flexibility test were considered as the basic requirement for different coatings. Also in some cases, in order to decrease the tack-free time and increasing the crosslinking density, different amines were added to the mixture as free amines which were separately cured with an epoxy cross-linker. Table 2.4 shows the screening criteria used for screening the 2K-HS-NIPU coatings. Table 2.5 shows a summary of different coating systems subjected to screening tests.

Table 2.4. Screening of the NIPU coatings according to the initial performance criteria

Initial Performance Criteria	**Low Temperature Flexibility @ -54 ℃**	**MEK Double Rub**	**Curing Time at 25 ℃ (tack free, h)**
Required Value	Pass	100	10
NIPU System* **PUPA + Epoxy Crosslinker**	**Urethane Content**	**-54 ℃ Flexibility**	**MEK Double-Rubs**	**Tack-free Time (h)**
PUPA 3 + Epoxy 1	1.36	Tacky film	-	-
PUPA 2 + Epoxy 1	1.86	Tacky film	-	-
PUPA 16 + Epoxy 1	1.65	Tacky film	-	-
PUPA 7 + Epoxy 1	2.24	Pass	40	48
PUPA 3 + Epoxy 7	1.73	Pass	25	72
PUPA 1 + Epoxy 7	1.69	pass	31	48
PUPA 6 + Epoxy 7	2.08	pass	51	24
PUPA 7 + Epoxy 7	2.19	Pass	55	18
PUPA 8 + Epoxy 7	2.09	Pass	45	20
PUPA 9 + Epoxy 7	3.33	Fail	200	5
PUPA 11 + Epoxy 7	3.11	Fail	200	6
PUPA 15 + Epoxy 7	1.56	Pass	44	>48
PUPA 16 + Epoxy 7	1.43	Pass	42	>48

* All the films were applied with 50±5 µm DFT.

The results in Table 2.4 indicated that when high molecular weight amines (lower amine

hydrogen concentration) were used along with a di-functional epoxy crosslinker, the films remained tacky. Insufficient curing of such samples could be due to low glass transition temperature Tg of starting materials as well as insufficient crosslinking caused by higher AHEW of the PUPAs. However, when the same PUPAs were cured with three-functional epoxies, the films did cure but showed very long tack-free times and low MEK double rub resistance due to insufficient crosslink density. As expected, the PUPAs of lower molecular weight lead to higher crosslink density, and showed enhancement in the MEK double- rub and curing rate at the expense of failure in flexibility tests. In contrast, using of high molecularweight PUPAs resulted in high flexibility, longer curing times, and low chemical resistance.

Table 2.5. Coating properties obtained from different NIPU samples *modified by blending or free amine addition* in the initial screening

Sample No.	Coating System NIPU + 1:1 eq. Free Amine	-54 ℃ Flexibility	MEK Double-Rubs	Tack-free time (h)
1	NIPU 13 (mix-TMD)	pass	90	6
2	NIPU 12 (mix-IPDI)	Pass	100	8
3	NIPU 1 (CC2-1074) + DETA	Pass	34	10
4	NIPU 6 (CC2-TMD) + DETA	Fail	65	6
5	NIPU 8 (mix-DMP) + DETA adduct	Fail	>200	3.5
6	NIPU 13 (mix-TMD) + 5 wt% DETA adduct	Fail	>200	3
7	NIPU 12 (mix-IPDI) + DETA	Fail	180	3
8	NIPU 12 (mix-IPDI) + DETA adduct	Fail	190	3
9	NIPU 7 (CC2-IPDI) + DETA	Pass	100	5
10	NIPU 7 (CC2-IPDI) + DETA adduct	Pass	90	6
11	NIPU 9 (CC1-IPDI) + IPDA	Fail	>200	5.5
12	NIPU 11 (CC1-PACM) + IPDA	Fail	>200	7
13	NIPU 12 (mix-IPDI) + IPDA	Pass	130	6
14	NIPU 14 (mix-PACM) + IPDA	Pass	170	10
15	NIPU 7 (CC2-IPDI) + IPDA	Pass	70	8
16	NIPU 8 (CC2-PACM) + IPDA	Pass	120	12
17	NIPU (CC1-PACM) + DETA	Fail	>200	2.5
18	NIPU (CC1-PACM) + DETA adduct	Fail	>200	3.57

* All the films were applied with 50±5 µm DFT.
* In all the systems the free amine was added in 1:1 equivalents ratio with respect to PUPA.
* NIPU samples cured with epoxy 7 as crosslinker.

The results revealed that the NIPUs made from CC2 and CC3 did not have a desirable curing rate, however, by the addition of free amine the number could be achieved within the target range. Coatings taken from CC1 also failed in flexibility while having very good chemical resistance and curing time. The point indicated that the closer the crosslinking points are (lower molecular weight PUPAs), it is harder to achieve flexibility at low temperature despite good chemical resistance. NIPUs made with a mixture of CC1 and CC2 were found to be able to show the desired balance between different needed properties as for NIPU (mix-IPDA) coating, more than 100 MEK double rubs, and 8 h of curing time was achieved when applied with 2 mils of DFT. Regarding the amines used to achieve PUPAs, it was observed that samples prepared with IPDA had a more balanced property compared to other amine structures used in coatings. The cycloaliphatic structure of IPDA could be the reason for enhanced MEK resistance compared to aliphatic structures of compounds like TMD and also its relatively high reactivity (lower molecular weight) compared to PACM, can lead to faster curing times.

In summary, none of the coating systems met all the required performance criteria. We attributed thepoor solvent resistance and longer tack-free times to lower average functionality of the system. The lower functional group concentration of reacting species leads to longer tack-free time (chemical kinetics) while at the same time that would produce network with lower crosslink density, resulting in poor solvent and chemical resistance.

In order to address this problem, two approaches were identified: first, addition of different amines/amine adducts as free amines to the system, and second optimizing functionality of PUPAs by suitable choice of cyclic carbonate compounds or their blends. The new systems based on these approaches were formulated and studied. Table 2.7 shows the results of various 2K-HS-NIPU coating compositions and their performance properties. It should be noted that each NIPU sample is coded by the number of its corresponding PUPA when cured with epoxy 7 as cross-linker.

The results in Table 2.5 revealed that although the NIPUs made from CC2 and CC3 did not have desirable curing rates, addition of free amine compound significantly speeded up cure reaction and achieved the targeted tack-free time. It should be noted that addition of much higher amount of free amine could lead to undesirable increase in the crosslink density and subsequent short pot life and inferior flexibility. In fact, usage of CCs with higher molecular weight (~640 Da and ~2000 Da for CC2 and CC3, respectively) results into amines with much higher AHEW. This can further result in lower reactivity and crosslinking ability of PUPAs since the reaction sites are much less

concentrated. Furthermore, NIPUs made with mixture of CC1 and CC2 were found to have a good balance between the required properties, as for NIPU 12 coating (Sample 2), more than 100 MEK double rubs and 8h of curing time were achieved. Regarding the amines used in synthesis of PUPAs, it was observed that samples prepared with IPDA had more balanced properties compared to other amines. The cycloaliphatic structure of IPDA could be the reason for enhanced MEK resistance compared to aliphatic structures of compounds like TMD. Also, its relatively higher reactivity compared to PACM, could haveled to the faster curing rates.

Based on initial screenings, four different NIPU coatings were subjected to extended tests including resistance to different chemicals as well as water resistance while still being applied with 2 mils of DFT without pigmentation. The results for selected coating systems are illustrated in Figure 2.10. As expected, samples containing IPDA, showed better performance in terms of chemical resistance. One of the hardest tests to pass was resistance against Skydrol fluid. It is utilized in aerospace installations as hydraulic fluid and degrades the organic structures very rapidly. When it mixes with the moisture in the environment, two chemical phases are created one of which is very acidic and aggressive [29]. Among coating samples, NIPU (mix-IPDA) showed better resistance against Skydrol when 1:1 eq. amount of IPDAwas added as free amine Therefore, it was selected as the system that can provide fast curing as well as appropriate flexibility and resistance to chemicals.

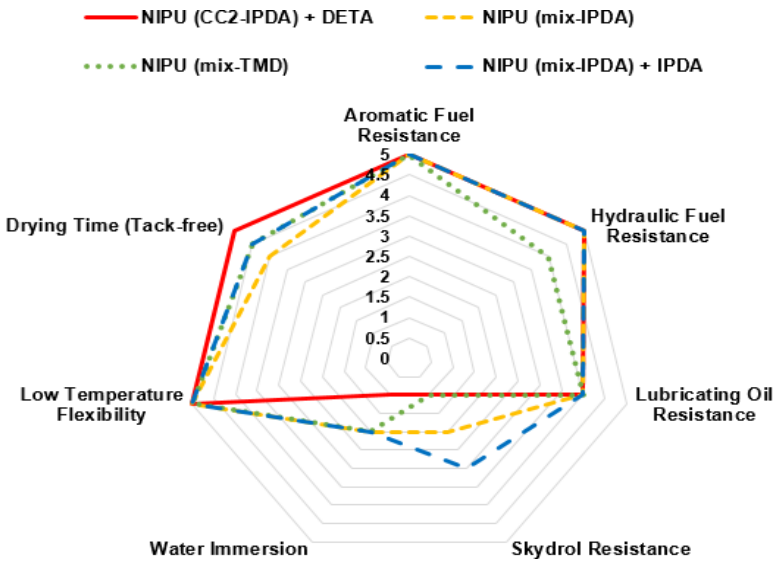


Figure 2.10. Extended evaluation of selected NIPU samples.

2.3.4. Effect of free amine addition and VOC exempt solvent

Based on the outcomes of the tests for 2K-HS-NIPU coatings, four of the NIPU coatings that outperformed the others were subjected to extended tests including resistance to different chemicals as well as water resistance and the results were compared to the reference sample. Table 2.6 shows the performance of NIPU (mix-IPDA) (NIPU 12) coatings with different dosages of IPDA as free amine. In general, all the 2K-HS-NIPU coatings passed the desirable tests. Furthermore, all the formulated coating systems had higher solid content, and consequently lower VOC compared to the reference. This was because of the proper designing and development of the NIPU structures with controlled molecular weights, and hence viscosities, which reduced the need for solvents. The reference sample did not pass the flexibility test, most probably due to its high Tg. As expected, samples containing IPDA, showed better performance in terms of chemical resistance. One of the most stringent tests to pass was resistance against Skydrol fluid, which is utilized in aerospace installations as hydraulic fluid. When it mixes with the moisture in the environment, two chemical phases are created one of which is very acidic and aggressive [32]. Among coating samples, NIPU 12 showed better resistance against Skydrol when 1:1 eq. amount of IPDA was added as free amine. Therefore, it was selected as the system that can provide fast curing and resistance to chemicals, which outperforms the reference in flexibility. Based on its good overall performance, coating system based on NIPU 12 containing IPDA as free amine was selected for further exploring of the effect of IPDA as free amine on the performance properties.

Table 2.6: Properties of the four selected coating systems in comparison with the reference

sample and effect offree amine addition to the flexibility and chemical resistance of NIPU (mix-IPDA) coating.

Coating System	Solid Content wt.%	Aromatic Fuel	Hydraulic Fluid	Lubricating Oil	Skydrol (1-5)	-54 ℃ Flexibility	T_g (℃)	Tack-free (h)	Pot-life (h)
NIPU (mix-IPDA)	70	Pass	Pass	Pass	2	Pass	53	8	10
NIPU (mix-IPDA) + 1:1 IPDA	73	Pass	Pass	Pass	3	Pass	42	6	6
NIPU (mix-IPDA) + 1:1.25 IPDA	75	Pass	Pass	Pass	3	Pass	42	6	5
NIPU (mix-IPDA) + 1:1.5 IPDA	78	Pass	Pass	Pass	4	Pass	40	5.5	5
NIPU (mix-IPDA) + 1:2 IPDA	80	Pass	Pass	Pass	4	Fail	37	4.5	4

It could be observed from the results that the addition of free amine improved the resistance of coatings against Skydrol as an aggressive chemical as well as decreasing the tack-free time. This could be due to increased crosslinking introduced into the coating system which helps to resists degradation of the film and increases the rate of crosslinking reactions. However, by increasing the level of free IPDA to 1:2 equivalents concerning to PUPA, the flexibility of the coating was failed which can be as a result of an increase in the glass transition temperature (Tg). Therefore, the coating system of NIPU (mix-IPDA) + 1:1.5 IPDA was considered as the sample for achieving fast curing together with high flexibility and sufficient crosslinking.

The reduction of the amount of VOC in the coating formulation was another goal perused by the authors. First, it was observed that due to the selection of raw materials with lower viscosities and controlling the molecular weight of the PUPAs, the total solid content of the coating (as shown in Table 2.5) is more than 70 wt%. By trying various VOC exempt solvents, parachlorobenzotrifluoride (known as Oxsol-100) was able to efficiently dissolve the synthesized PUPAs and was used in the coating formulation. Table 2.7 shows the difference in coating pot-life and tack-free time between the samples thinned with toluene and Oxsol-100. The coatings that were thinned in pure Oxsol-100 showed increasedpot-life as well as tack-free time. This can be due to the slower evaporation rate of Oxsol-100 which is
0.9 (n-BuAc=1) compared to 2.24 for toluene. For this study, a mixture of toluene and Oxsol-100 was observed to maintain the tack-free time in an acceptable range without a significant increase in VOC content.

Table 2.7. Effect of usage of Oxsol-100 as VOC exempt solvent on

curing time and pot-lifeof NIPU (mix-IPDA) coating.

Coating System	Pot-life (h)	Tack-free Time (h)
NIPU (mix-IPDA) in toluene	10	8
NIPU (mix-IPDA) in Oxsol-100	>24	16
NIPU (mix-IPDA) in Toluene/Oxsol-100	20	13

2.3.5. Properties of pigmented NIPU coatings

Another performance criterion of the studied coatings was to exhibit prolonged mechanical strength and elasticity in severe conditions such as erosion caused by rain droplets once they hit the surface with high velocity. According to the specifications, formulations containing TiO_2 pigments at PVC=8% were prepared and applied on the substrate to obtain coatings with 250±20 µm of DFT. The comprehensive coating properties of different NIPU coatings are summarized in Table 2.8. Results revealed that NIPU coating made from a mixture of CC1 and CC2 did not pass the cold flexibility test while they had passed the same test with lower film thickness. In such coatings with an epoxy/amine curing mechanism, the additional internal stress associated with excessive coating thickness could result in cracking of the material while improving the chemical resistance due to increased total crosslinking [30]. This complies with the findings where coatings made from higher molecular weight exhibited better MEK resistance compared to the same system with lower thickness. Therefore, it could be concluded that coatings witha higher molecular weight of PUPA provide a better possibility to maintain cold flexibility with higher thicknesses [31].

Table 2.8. Coating properties obtained from NIPU samples formulated with 8% of PVC and 250 µm of DFT.

Sample No.	Coating System	MEK Double-Rubs (25% loss)	Aromatic Fuel	Lubricating Oil	Hydraulic fluid	Flexibility 1/8" at -56 ℃	Adhesion (2-3 mils thickness)	Water Immersion	Pencil Hardness	Impact resistance		Gloss	
										Direct	Indirect	20˚	60˚
1	NIPU (mix,IPDA)	180±5	Pass	Pass	Pass	Fail	5B	Pass	3H	160	140	80	91
2	NIPU (CC2,IPDA)	155±5	Pass	Pass	Pass	Fail	5B	Pass	2B	160	160	77	88
3	NIPU (CC3,IPDA)	140±5	Pass	Pass	Pass	Pass	4B	Pass (Adhesion loss)	5B	160	160	27	72
4	NIPU (CC3,IPDA) + IPDA	150±5	Pass	Pass	Pass	Pass	4B	Pass	HB	160	160	80	90
V	Reference 1	170±5	Pass	Pass	Pass	Fail	5B	Pass	H	160	160	70	83
VI	Reference 2	180±5	Pass	Pass	Pass	Fail	4B	Pass (Adhesion loss)	2B	160	160	77	87

While NIPU (CC3-IPDA) coating showed required chemical resistance and flexibility, it had significantlylower hardness values with 5B while by addition of free amine the pencil hardness was recovered up to HB for this sample. To better understand the mechanical properties of the coatings, tensile strength and DSC were carried out on NIPU samples and the reference. Figure 2.10 displays the stress-strain behavior of the coating samples. The data derived from the tensile strength test are provided in Table 2.9together with the data derived from DSC and TGA analyses.

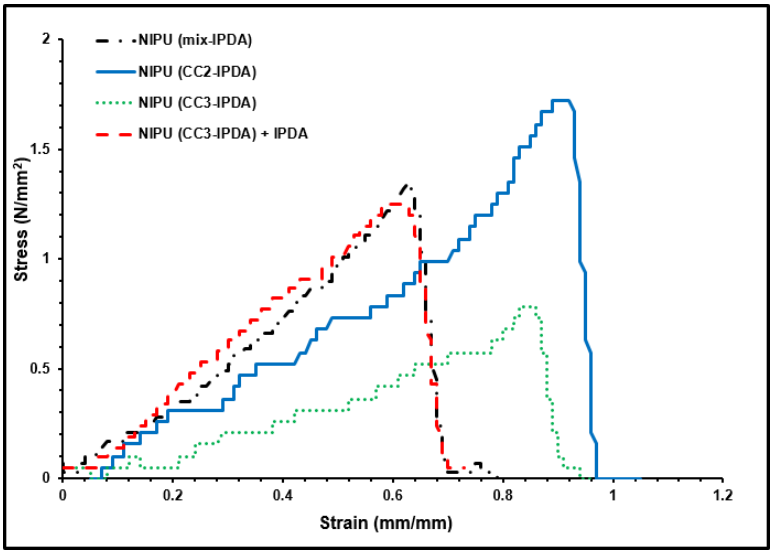


Figure 2.10. Stress-strain plots of NIPU coatings derived from tensile strength test.

Table 2.9. Thermal and mechanical properties of NIPU coatings. Tg: Glass transition temperature, Td 50%: Thetemperature of 50% decomposition.

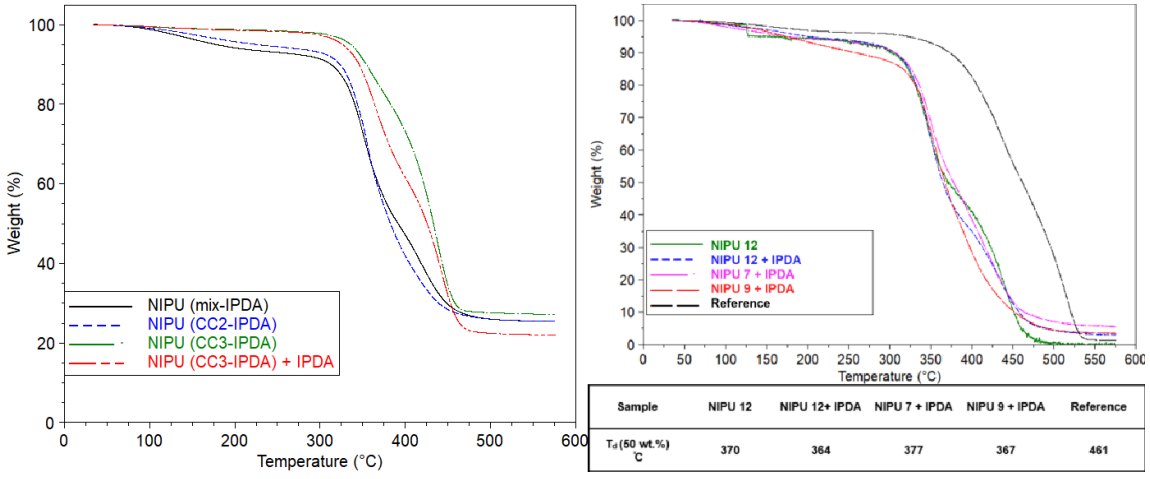
Coating System	T_g (℃)	T_d 50% (℃)	Elongation at Break (%)	Tensile Strength (MPa)	Young's Modulus (MPa)
NIPU (mix,IPDA)	45	391	123	1.35	0.97
NIPU (CC2,IPDA)	16	382	195	1.71	0.73
NIPU (CC3,IPDA)	-31	433	164	0.78	0.31
NIPU (CC3,IPDA) + IPDA	-11	425	107	1.25	1.01
Reference 1	20	473	135	1.04	0.81
Reference 2	36	443	136	0.98	0.83

It is clear from the graph that NIPU samples 1,3 and 4 failed to resist the deformation and high-stresslevels while the sample from CC2 showed superior performance in terms of tensile strength. The young modulus of NIPU coatings decreased by increasing the molecular weight of the PUPA which is a sign of reduced stiffness in the chains of the polymer due to a decrease in density of urethane functionalities in the backbone [32]. On the other hand, the elongation of the coatings increased by an increase in the molecular weight of the PUPA. The results suggest that an increase in molecular weight of the PUPA can increase the elongation and flexibility of the coatings as the glass transition temperature is significantly lower for NIPUs made with bigger PUPAs. At the same time presence of more functional groups like urethane is needed to increase the elasticity and toughness of the structure through interactions between such functional groups.

2.3.6. Thermal stability of the NIPU coatings

Resulting NIPU systems which are hydroxyurethanes contain more functional groups compared to conventional polyurethanes. Therefore, it is important to test how such systems behave in heating condition. Thermal stability of the selected coating samples was analyzed by the TGA method. Figure 2.11 shows a thermogram of selected NIPU samples and a reference PU sample showing 50% decomposition temperatures. The results showed that all the NIPU samples studied showed comparable results of 50% decomposition temperature of ~ 370℃. A two-step weight loss for NIPU 12 could be attributed to difference between CC1 and CC2 behavior as for CC1 containing coatings,

presence of more urethane groups in smaller chains could trigger the degradation of urethane linkages at relatively lower temperatures forming CO, CO_2, and ammonia [33] whereas the higher thermal decomposition temperature of NIPU 7 coating can be attributed to the lower urethane group content (due to higher molecular weight of the soft segments) [34]. However, the 50% decomposition temperature for reference sample was observed to be about 100 ℃ higher compared to NIPU coatings due to the presence of beta-hydroxyl groups in NIPU that are believed to participate in the thermal decomposition. As it is shown in Figure 2.13, the NIPU samples had comparable thermal stability to the reference one as for all samples the 50% decomposition temperature was above 390 ℃. A small weight loss for NIPU (mix-IPDA) and NIPU (CC2- IPDA) at lower temperatures can be attributed to the presence of more urethane groups in smaller chains which triggers the degradation of urethane linkages forming CO, CO_2, and ammonia [33].



Sample	NIPU 12	NIPU 12+ IPDA	NIPU 7 + IPDA	NIPU 9 + IPDA	Reference
T_d (50 wt.%) ℃	370	364	377	367	461

Figure 2.11. TGA thermograms and 50% decomposition temperature of different NIPU coatings compared to reference.

2.3.7. Coating properties: Formulated samples at 12 mils (300 ± 10 µm) DFT (Sample preparation for rain erosion test per SAE AMS-C83231A and MIL-PRF-32239

Several hybrid urea/urethane systems were prepared using a synthesized NCO terminated pre-polymer. The ratio of amine crosslinker to polyol crosslinker was varied from 100/0 to 25/75 and measured the properties summarized as below: The goal was to make something similar to CAAPCOAT's expected structure with much reduced NCO levels.

#1: NCO/OH : 1.22/1

CAAPCO PART A							
CALCULATIONS							
RAW MATERIAL	Weight in gm	Eq. Wt.	Equivalents	-NCO Eqvnts	-OH Eqvnts	% By weight	Solids %
diethyleneglycol	0.00	106.12	0.00	0.00	0.00	0.00	
Terathan T-250	45.00	172.85	0.26		0.26	35.48	
caprolactone	0.00	114.00	0.00		0.00	0.00	
H12MDI	41.73	131.15	0.32	0.32		32.91	
DBTL	0.09						
MIBK	20.00						
xylene	20.00	-	-	-	-	15.77	
TOTAL	126.82		0.58	0.32	0.26	84.16	
NCO/-OH Ratio	1.22	86.73					
Excess NCO equivelants	0.06						
initial %NCO (theoretical)	10.54						
final %NCO (theoretical)	1.92						
final %NCO (practical)	1.33						
number of repeating units	5.00						
NCO/OH ratio needed	1.22						
OH/NCO ratio needed (using what if)	0.82						
NVM%	68.39						
NCO terminated prepolymer Mw	2675.46						
NCO terminated prepolymer Eq. wt. (theoretical/solid)	1337.73						
NCO terminated prepolymer Eq. wt. (theoretical/solution)	1956.02						
NCO terminated prepolymer Eq. wt. (practical/solid)	2159.69						
NCO terminated prepolymer Eq. wt. (practical/solution)	3157.89						
total MIBK needed 52.50							
toal xylene needed 52.50							

clear-coat formulation				
	eq. wt. (solution)	weight	NVM%	
part A	4799.30	20.00	0.45	
vestamin A-139 in MIBK	215.38	0.90	0.65	
DBTL (1% in MIBK nad MEK, 39:60 by weight)		1.25		
Pigmented coating				
	wt.	Eq. wt. (solution)	NVM%	density
Part A	16.00	3157.89	0.68	1.00
TiO2	4.50			4.20
Tinuvin 5151	0.48			
BYK 306 (1% of total solids)	0.16		0.13	
BYK 054 (.5% of total solids)	0.08			
BYK 9076 (5% of pig)	0.23		0.25	
DBTL (1% in MIBK nad MEK, 39:60 by weight)	1.03			
vestamin A-139 in MIBK	1.09	215.38	0.65	0.86
solvent	14.00			
total	37.57			
total weight in the dispersion cup	23.57			
NVM% of part A	0.46			
Pig wt.%	0.12			
PVC	8.07			
CPVC	56.18			

Gel time (viscosity doubled) ~ 6 h

#2: NCO/OH : 1.5/1

CAAPCO PART A							
CALCULATIONS							
RAW MATERIAL	Weight in gm	Eq. Wt.	Equivalen	-NCO Eqvnts	-OH Eqvnts	% By weight	Solids %
diethyleneglycol	0	106.12	0	0	0	0	
Terathan T-250	45	172.85	0.2603		0.2603	33.0125	
caprolactone	0	114	0		0	0	
H12MDI	51.2156	131.15	0.3905	0.3905		37.5724	
DBTL	0.0962						
MIBK	20						
xylene	20	-	-	-	-	14.6722	
TOTAL	136.31		0.6509	0.3905	0.2603	85.26	
NCO/-OH Ratio	1.5	96.22					
Excess NCO equivelants	0.1302						
initial %NCO (theoretical)	12.03						
final %NCO (theoretical)	4.01						
final %NCO (practical)	2.82						
number of repeating units	2.5						
NCO/OH ratio needed	1.5						
OH/NCO ratio needed	0.666667						
NVM%	70.5849						
NCO terminated prepolymer Mw	1468.9	1478.3					
NCO terminated prepolymer Eq. wt. (theoretical/solid)	734.45						
NCO terminated prepolymer Eq. wt. (theoretical/solution)	1040.52						
NCO terminated prepolymer Eq. wt. (practical/solid)	1051.27						
NCO terminated prepolymer Eq. wt. (practical/solution)	1489.362						
total MIBK needed	52.5						
toal xylene needed	52.5						

clear-coat formulation				
	eq. wt. (solution)	weight	NVM%	
part A	2335.98109	20	45%	
vestamin A-139 in MIBK	215.384615	1.84406129	65%	
DBTL (1% in MIBK nad MEK, 39:60 by weight)		0.61191839		
Pigmented coating				
	wt. Eq. wt. (solution)		NVM%	density
Part A	12	1489.3617	71%	1
TiO2	3.85			4.2
Tinuvin 5151	0.40			
BYK 306 (1% of total solids)	0.13		12.50%	
BYK 054 (.5% of total solids)	0.07			
BYK 9076 (5% of pig)	0.19		25%	
DBTL (1% in MIBK nad MEK, 39:60 by	0.74			
vestamin A-139 in MIBK	1.74	215.38	65%	0.86
solvent	10.50			
total	29.62			
total weight in the dispersion cup	19.12			
NVM% of part A	0.47			
Pig wt.%	0.13			
PVC	8.04			
CPVC	56.18			

#3: NCO/OH : 1.36/1 (50:50 by wt. mixture of #1 and #2)

clear-coat formulation				
	eq. wt. (solution)	weight	NVM%	
part A #1	4799.30	10.00	0.45	
part A #2	2335.98	10.00	0.45	
vestamin A-139 in MIBK	215.38	1.37	0.65	
DBTL (1% in MIBK nad MEK, 39:60 by weight)		0.59		

Pigmented coating	wt.	Eq. wt. (solution)	NVM%	density
part A #1	7.00	3157.89	0.68	1.00
part A #2	7.00	1489.36	0.71	1.00
TiO2	2.40			4.20
Tinuvin 5151	0.24			
BYK 306 (1% of total solids)	0.08		0.13	
BYK 054 (.5% of total solids)	0.04			
BYK 9076 (5% of pig)	0.12		0.25	
DBTL (1% in MIBK nad MEK, 39:60 by weight)	0.73			
vestamin A-139 in MIBK	1.49	215.38	0.65	0.86
solvent	9.50			
total	28.60			
total weight in the dispersion cup	19.10			
NVM% of part A	0.47			
Pig wt.%	0.08			
PVC	8.06			
CPVC	56.18			

After application of NIPU coatings, samples were tested for critical performance criteria mentioned in statement of need and thermo-mechanical properties. At this stage, a rain erosion resistant reference sample was obtained and applied in order to study the developed coatings. Screening results of the reference sample (CAPCOAT) revealed that, coating samples need to have very high elongation % (approx. 500%) and high tensile strength values (9.5 MPa) in order to be comparable in terms of elastic properties and erosion resistant. Although initial samples which were applied at lower film thickness, had shown good flexibility at low temperature, the results for thicker (up to 12 mils DFT) coatings revealed a failure in cold flexibility for such samples. Therefore, PUPAs with higher molecular weight and more flexible moieties in the backbone were targeted, formulated, and tested. Table 2.12 summarizes various coating and mechanical properties of selected NIPU coatings in comparison with CAPCOATreference sample. As shown in the Table 2-10 and also Figure 2-12, it was observed that there was a huge gap between them and the reference sample in terms of both elongation and tensile strength. Hence, we had to go back to our initial design of components and manipulate the starting materials/compositions accordingly.

Table 2.12. Properties of selected NIPU coating samples in comparison with CAAPCOAT.

NIPU Coating System	MEK Double Rub (25%	Aromatic Fuel	Lubricating Oil	Hydraulic fluid	Flexibility (1/8" at -56 ℃)	Water Immersion	Pencil Hardness	Impact resistance		Elongation (%)	Tensile Strength (MPa)
								Direct	Indirect		
(mix,IPDA)	180±5	Pass	Pass	Pass	Fail	Pass	3H	160	140	123	1.35
CC2,IPDA)	155±5	Pass	Pass	Pass	Fail	Pass	2B	160	160	195	1.71
(CC3,IPDA)	140±5	Pass	Pass	Pass	Pass	Pass (Adhesion loss)	5B	160	160	164	0.78
CC3,IPDA) + IPDA	150±5	Pass	Pass	Pass	Pass	Pass	HB	160	160	`107	1.25
Reference	165±5	Pass	Pass	Pass	Pass	Pass	7H	160	160	548	9.42

* DFT = 12 mils

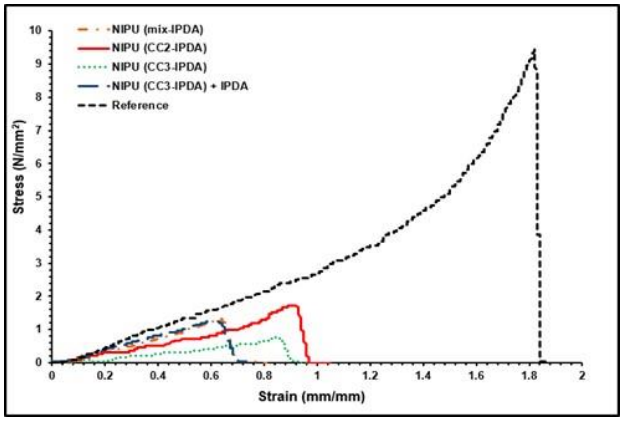


Figure 2.12. Stress-strain plots of NIPU coatings derived from tensile strength test.

At this stage, it was concluded that further manipulation of PUPA structure and type of the epoxy crosslinker needs to be carried out. This was because the tested systems were highly deficient in terms of both elongation and tensile strength properties compared to the reference sample. A factorial design of experiment was started using various starting CCs, different amines, varying amine/CC ratios and crosslinkers with different structures and functionalities. Figure 2.13,

represents the chemical structure of starting epoxies (to obtain MFCCs), amines, and epoxy crosslinkers used in this part of research.

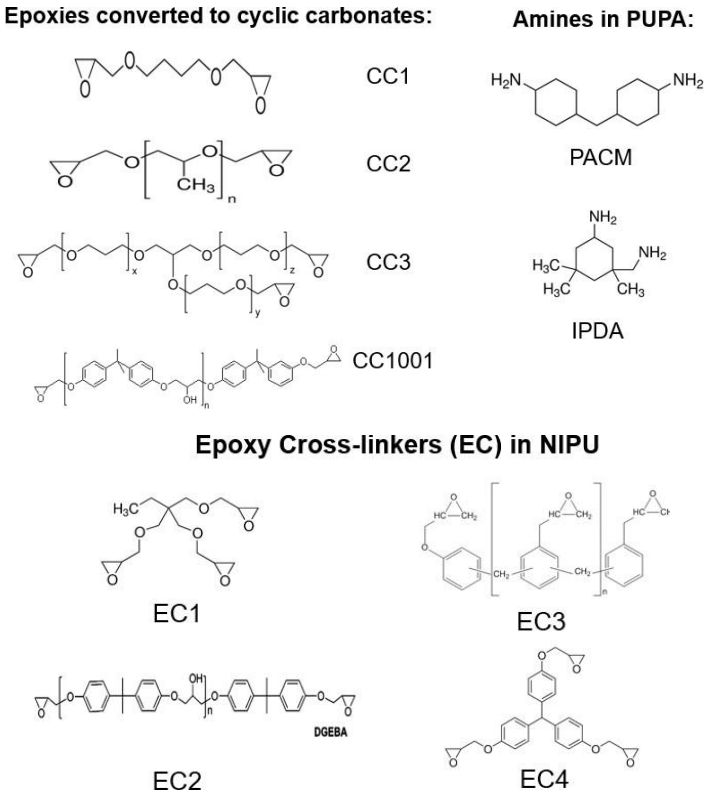


Figure 2.13. Chemical structure of different compounds used to obtain formulated 2k-HS-NIPU coatings.

The rationale for selecting this approach was to investigate the effect of parameters such as aromaticity in the backbone, increased urethane repeating units, increase molecular weight and crosslinker functionality on the final properties of the coatings. Results of elongation and tensile strength (Figures 2.14 and 2.15) revealed that, by incorporation of certain aromaticity levels, samples with enhanced mechanical properties could be obtained. Moreover, usage of linear crosslinker (EC2) in coating formulation, lead to increased elongation/tensile strength combination. Also, it was observed that incorporation of a different amine with cycloaliphatic structure significantly improved the mechanical properties. Majority of the coating compositions could successfully pass the chemical resistance requirements of the project, however, low temperature flexibility and drying time were the criteria that limited the selection of the samples. Among all samples tested, 5 systems (shown in Table 2.13) were identified as the ones with the promise to be subjected to further studies and testing. It was generally observed that very high

elongation or very high tensile strength values could be achieved separately by different systems, but only selected samples had a suitable combination of both properties and even those samples were still not comparable with the benchmark sample.

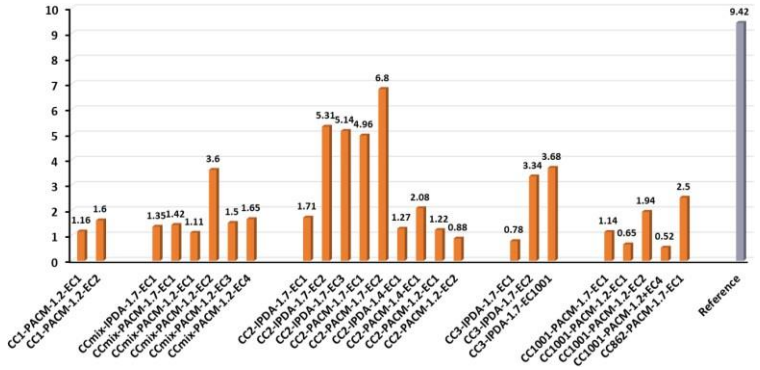


Figure 2.14. Tensile strength values of 2k-HS-NIPU coatings

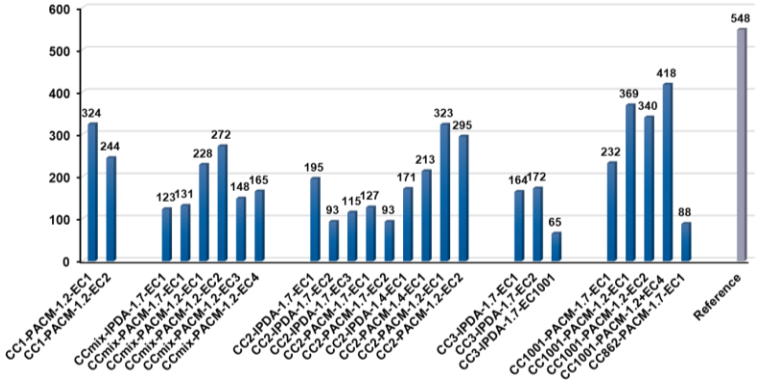


Figure 2.15. Elongation% values of 2k-HS-NIPU coatings

Table 2.13. Coating properties of final selected 2k-HS-NIPU coatings.

Coating Composition	Water resistance	Flexibility @ -54	Hydraulic fluid resistance	Lubricantoil resistance	Fluid B	% Elongation	Tensile strength (Mpa)	Young Modulus
CAAPCOAT Equivalent #1 (NCO/OH : 1.22/1)	PASS	PASS	PASS	Fail	PASS	830	.41	.36
CAAPCOAT Equivalent #2 (NCO/OH : 1.5/1)	PASS (adhesion loss)	PASS	PASS	PASS	PASS	263	1.12	6.36
CAAPCOAT Equivalent #3 (NCO/OH : 1.36/1)	PASS	PASS	PASS	PASS	PASS	480	.845	1.92
CAAPCOAT	PASS	PASS	PASS	PASS	PASS	548	9.42	6.95

Coating properties of final selected 2K-HS-NIPU coatings.

NIPU sample	CC1-PACM-1.2/EC2	CCmix-PACM-1.2/EC2	CC2-PACM-1.2/EC1	CCAr1001-PACM-1.2/EC2	CC3-IPDA-1.7/EC2	Reference (CAAPCO)
Flexibility (1/8 in at -56 °C)	Fail	Pass	Pass	Pass	Pass	Pass
Impact Resistance (in.Ib)	160	160	160	160	160	160
Wet Adhesion (24 h in DI water)	5B	5B	3B	5B	2B	5B
MEK Double-rub (Cycle)	150	125±5	150	150	80±10	150
Fuel B (1 h at R.T.)	Pass	Pass	Pass	Pass	Pass	Pass
Hydraulic Fluid (24 h at 65 °C)	Pass	Pass	Pass	Pass	Pass	Pass
Lubricant Oil (24 h at 120 °C)	Pass	Pass	Pass	Pass	Fail	Pass
Tensile Strength (MPa)	1.60	3.6	1.22	1.94	3.34	9.42
% Elongation	244	272	323	340	172	548

Figure 2.16 shows the AirFoil sample appearance coated with either CCmix-PACM or CCAr1001-PACM before and after rain erosion test as per SAE AMS-C83231A and MIL-PRF-32239. The coated samples werefailed after about 11 min exposure to the test conditions.

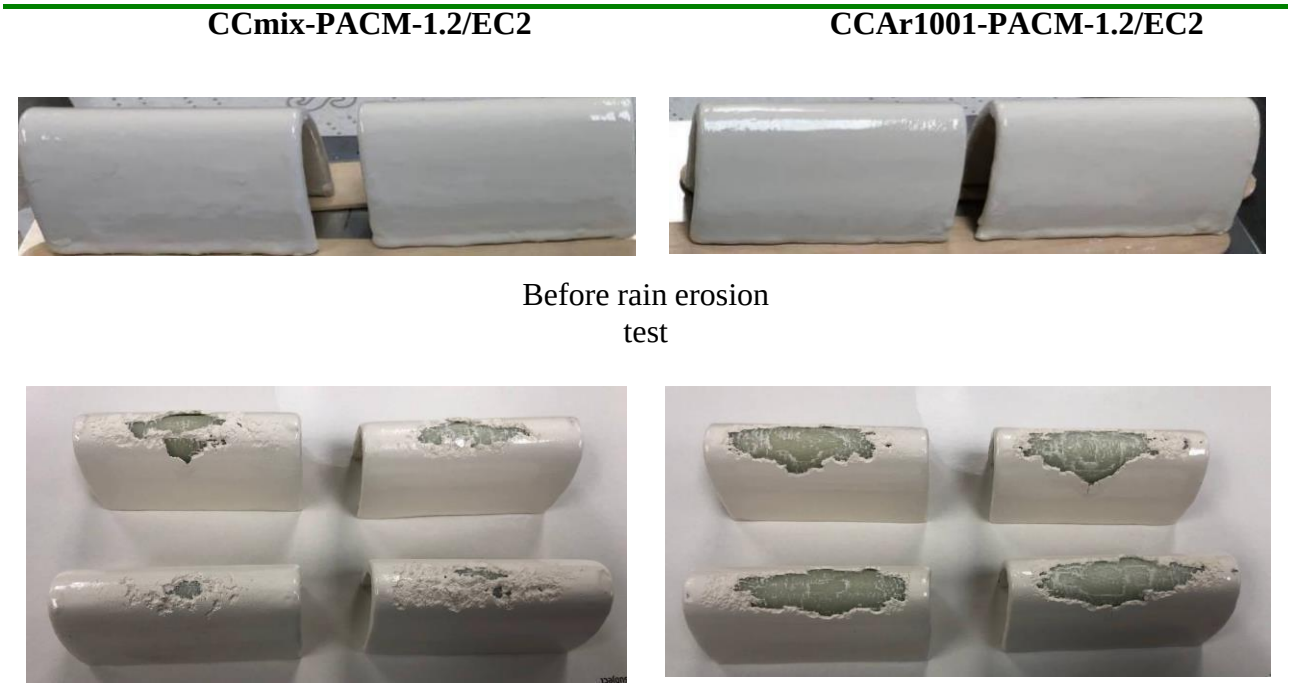


Figure 2.16. AirFoil sample appearance coated with either CCmix-PACM or CCAr1001-PACM before and after rain erosion

A detailed report from UDRI for Rain Erosion Test is appended as Appendix-II to this report.

2.4. Supplementary tests on PIPU systems

Moreover, effect of addition of carbon nano tube (CNT) (Table 2.14) and graphene oxide (GO) (Table 2.15) on the mechanical properties of NIPU coatings were studied. Different amounts of CNT and GO were incorporated into the coating formulations. It was found that such addition could enhance the tensile strength of the samples but will reduce the elongation and cause the flexibility of the systems to fail (if added in high amount). An optimum level of CNT could improve the properties and also adjust the surface resistivity of the coatings in the required range of the SON. Addition of CNT and graphene oxide, although could adjust the surface resistivity and tensile

strength, but significantly reduced the flexibility and elongation properties of the coating systems. Effect of usage of amino siloxanes as additional amine reagent (Table 2.16) was also studied. It was found that such silanes could improve tensile strength with the precaution that only a minor percentage should be used to avoid loss of flexibility. Usage of aminosiloxanes in the structure of PUPA was tried initially. However, such siloxanes had a major problemof incompatibility with other building blocks. Therefore, making PUPAs based on siloxanes could not be successful. One approach to take benefit of those systems was to physically blend a compatible amine functional poly phenylmethyl siloxane (PPMS) as "free amine" with the synthesized PUPA and curing both with the same epoxy crosslinker. It led to enhanced film properties, adhesion, and tensile strength at the expense of reduction in elongation.

Table 2.14. Effect of CNT incorporation on NIPU properties.

Coating Composition	Water resistance	Cold Flexibility	Hydraulic fluid resistance	Lubricant oil resistance	B Fluid	MEK Double-rub	Pencil Hardness	Impact Resistance
NIPU (CC2-PACM-1.2-EC1) + 0.5 wt.% CNT	Pass	Pass	Pass	Pass	Pass	>200	2B	160
NIPU (CC2-PACM-1.2-EC1)	Adhesion Loss	Pass	Pass	Pass	Pass	140 ±10	4B	160
Reference	Pass	Pass	Pass	Pass	Pass	170 ±10	7H	160

Coating Composition	Tensile strength MPa	Elongation %	Surface Resistivity ohm/sq.
NIPU (CC2-PACM-1.2-EC1)	1.22	323	1.3 E +5
NIPU (CC2-PACM-1.2-EC1) + 0.5 wt.% CNT	1.83	273	5.5 E +11

Table 2.15. Effect of GO incorporation on NIPU properties.

Coating Composition	Water resistance	Cold Flexibility	Lubricant oil resistance	MEK Double-rub	Pencil Hardness	Impact Resistance	Tensile strength (MPa)	Elongation %
NIPU (CC2-PACM-1.2-EC1) + 15 wt.% GO	Pass	Fail	Pass	>200	3H	160	2.01	244
NIPU (CC2-PACM-1.2-EC1) + 10 wt.% GO	Pass	Fail	Pass	>200	3H	160	1.37	266
NIPU (CC2-PACM-1.2-EC1) + 5 wt.% GO	Pass	Fail	Pass	180 ±10	2H	160	1.26	335
NIPU (CC2-PACM-1.2 EC1)	Adhesion Loss	Pass	Pass	140 ±10	4B	160	1.22	323
Reference	Pass	Pass	Pass	170 ±10	7H	160	548	9.42

Table 2.16. Effect of amine functional PPMS addition on mechanical properties.

Coating Composition	Elongation %	Tensile strength MPa
PPMS 30%	91	3.33
PPMS 15%	121	3.20
NIPU (CC2-PACM-1.4-EC1)	213	2.08
Reference	548	9.42

2.5. Conclusions

In this study, non-isocyanate polyurethanes were synthesized using a novel method. Polyurethane Polyamines were first achieved utilizing cyclic carbonate/amine chemistry and subsequently cured with multi-functional epoxy compound to form a crosslinked coating. The coatings were subjected to various types of characterization and performance testing based on the required criteria.

Results indicated that cyclic carbonates can efficiently be synthesized by carbonation of epoxy compounds under ambient conditions thanks to the efficient catalytic behavior of phosphonium saltsand the alcoholic solvent. FTIR analyses and amine value titration also proved that different

PUPAs witha wide range of molecular weights can further be achieved by using different combinations of cyclic carbonates and amines. By appropriate selection of starting materials and controlling the molecular weight of PUPAs, fast curing coatings with appropriate chemical resistance and flexibility can be achievedat lower thicknesses. The performance of coatings can be tuned by the addition of certain amounts of free amine to the formulation. The high solid content of the final coatings as well as the possibility of usage of a VOC exempt solvent for thinning makes this coating system a very promising option for environmentally compliant usages especially when curing time is not a priority. Last but not least important, the comparison of the thermal and mechanical properties of NIPU coatings revealed that in order to reach high flexibility and tensile strength at the same time, higher molecular weights and high toughness in the structures are the key requirements.

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Chapter Three

Design and development of radiation-curable NIPU coating systems (UV-NIPU) forhigh-performance applications: synthesis and characterization

Objective-4

Abstract

In this part of study, UV-curing crosslinking chemistry is implemented as a novel approach for designing green non-isocyanate polyurethane (UV-NIPU) coatings for various military applications. Synthesis of novel UV-curable non-isocyanate urethane acrylate (NIPU-AC) oligomers was carried out in three steps: First, multi-functional cyclic carbonates (MFCC) were prepared by carbonation of aliphatic epoxy compounds under mild temperature and pressure conditions in the presence of a catalyst. In the next step, amine-terminated polyurethane oligomers (PUPAs) were synthesized by the reaction of MFCCs with stoichiometric excess amount of aliphatic and cycloaliphatic amines. The progress of reactions were monitored by different titrimetric methods as per ASTM standards and Fourier Transform Infrared (FTIR) spectroscopy by following the peaks associated with cyclic carbonates and NH groups (~1800 and ~1715 cm-1, respectively) of urethanes. Finally, various synthetic routes were explored to synthesize (meth)acrylate functional UV-curable oligomers. In the optimum route, (meth)acrylate functionality was introduced by direct reaction of amine groups at the chain ends of PUPAs with methacrylic anhydride (MAAH). The amine value titration and FTIR confirmed successful synthesis of NIPU-AC oligomers with >95% yield. Evaluation of formulated UV-curable NIPU coatings for military- critical performance properties, such as low temperature flexibility and resistance to aromatic fuels and lubricating and hydraulic fluids, showed that high-performance UV-curable NIPU coatings can be successfully developed by the proper design of NIPU-AC oligomers, selection of appropriate reactive diluents, and UV-cure conditions.

3.1. Introduction

Ultraviolet (UV) curing has attracted much attention in recent decades thanks to its remarkable advantages, such as rapid polymer network formation, low energy and space requirements, and most importantly low VOC emissions. Although UV-curing technology has mainly been used for flat surfaces and controlled, in-factory applications for many years, recent innovations in UV-curing equipment have set the stage for using these systems in on-site coating applications to cure

coatings on non-flat and heat-sensitive substrates. Free-radical initiated UV-curable formulations typically contain three main components: a radical photoinitiator to produce free radicals, a functionalized oligomer as the major film forming component, and reactive diluent(s) for adjusting the viscosity, reactivity and thermomechanical properties of cured films [1,2].

Urethane acrylates are among the widely used oligomers in radiation-cure formulations because they provide exceptional balance of mechanical and chemical properties [2–7]. Urethane acrylates are conventionally synthesized by reacting a hydroxyalkyl acrylate monomer with an isocyanate-terminated prepolymer, prepared from the reaction of polyols and polyisocyantes [3,8–10]. While urethane acrylates have expanding applications, the use of toxic isocyanates in their preparation presents serious health and environmental hazards both in production [11] and application [12–16]. Therefore, the Occupational Safety and Health Administration (OSHA) has set regulations that establish exposure limits of common isocyanates, such as toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), and hexamethylene diisocyanate (HDI) [17]. This presents opportunities to develop non-isocyanate polyurethane oligomers that can cater to the needs of UV-cure coating formulations for various end-use applications.

Recently, urethane acrylate has been synthesized via isocyanate-free routes. One of the common routes for non-isocyanate polyurethane acrylates (NIPU-ACs) is the reaction of non-isocyanate polyurethane polyols (NIPU-POs) with MAAH, while NIPU-POs are synthesized through the reaction of alkylene carbonates with primary diamines (DA) or amino alcohols. Figovsky et al. [18], for instance, synthesized various urethane diols from commercially available cyclic carbonates and diamines, using an excess molar amount of alkylene carbonate over DA, followed by reaction with MAAH at 105-110°C to yield urethane diacrylates in relatively short times. In another study, Assumpsion and Mathias [19] first synthesized three urethane diols by reacting alkylene carbonates with DA or amino alcohols and then methacrylated them with MAAH. They used DMF as the solvent, which is known to be hazardous [20], and 1-(dimethylamino) pyridine (DMAP) as the catalyst to produce urethane dimethacrylates at room temperature and relatively long reaction times. Using a similar method, Wang and Soucek [21] synthesized three different non-isocyanate urethane dimethacrylate reactive diluents by reacting alkylene carbonate with the amino alcohol in dimethyl chloride, followed by reacting with MAAH. The first step was conducted at room temperature, and the methacrylation step was performed at 0 °C for 24 hours, in the presence of DMAP as the catalyst. Although the yield in the first step was high, the methacrylation step had a low yield. Moreover, the separation of the sample was relatively time- consuming

because it included several steps, including acid-base extraction, multiple washes, drying process, and solvent removal.

Despite various applications of urethane acrylates, including coatings, adhesives and sealants, medicals, packaging, printing inks, and elastomers, which are thoroughly covered in a recent review paper 22, utilization of non-isocyanate polyurethane acrylates in high-performance military coatings has been rarely, if ever, reported. Some of the currently used specialized military protective coatings are two-component isocyanate-based polyurethanes, which contain up to 800 grams per liter of volatile organic compounds (VOCs) and high levels of hazardous air pollutants (HAPs) mainly due to the presenceof high amounts of organic solvents in the coating's formulation. In addition to the safety, health, and environmental concerns associated with these coatings, their use presents a significant production backlog due to their long cure times. Therefore, there is a need to offer an environmentally-sustainable and efficient coating system for these specific military applications.

The goal of this part of study was to design, develop, and evaluate UV-NIPU coatings for specified military applications. To accomplish this objective, first, a series of polyurethane polyamines (PUPAs), as the main building blocks of UV-curable coatings, was synthesized through the reaction of multi- functional cyclic carbonates (MFCCs) and primary diamines, as described in our previous studies and shown in Figure 3.1 [23,24]. PUPAs and MFCCs were then reacted with ethylene carbonate and monoethanolamine, respectively, to obtain polyurethane polyols (PUPOs). Besides reaction of PUPOs with MAAH (route #1), other possible chemical routes were tried and evaluated for their efficiency and potential for scale-up. These routes included: (#2) direct reaction of polyurethane polyamines (PUPAs), which could be synthesized through the efficient and well-reviewed reaction of multifunctional cyclic carbonates (CCs) with primary diamines [25–30] with MAAH to save time and effort by removing one synthesis step, (#3) reaction of PUPAs with the epoxy group of glycidyl methacrylate that occurs via the nucleophilic attack of the amine nitrogen on the terminal carbon of the epoxy functionality [31], and (#4) via Michael addition reaction [32] between PUPAs and hexanediol diacrylate in a 1:2 equivalent ratio. Figure 3.2 summarizes the schemes of chemical routes used in this study.

Finally, a range of UV-NIPU compositions (both clear and pigmented) was formulated by selection of proper reactive diluents and photo-initiators, and their UV-cured coatings were characterized as per military specifications, i.e. SAE AMS-C-83231 standard33 for polyurethane military coating systems.

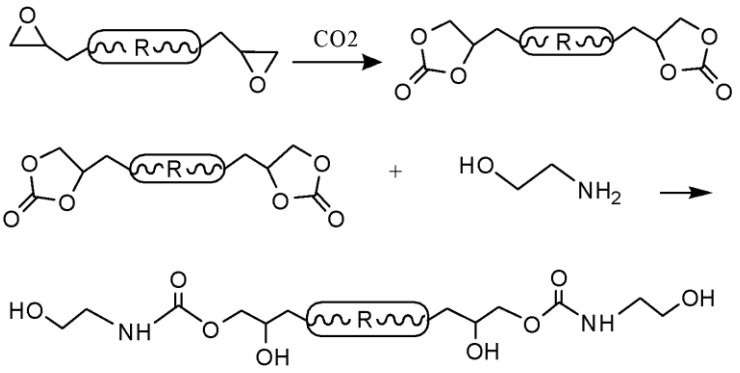


Figure 3.1. Synthesis of CCs and PUPAs

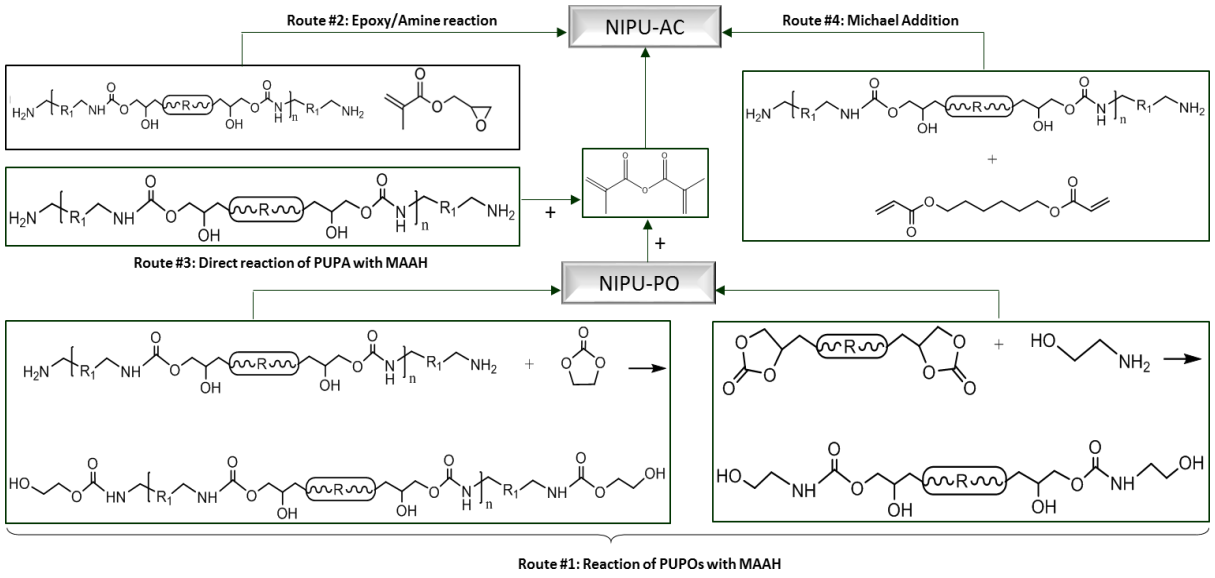


Figure 3.2. Different routes to achieve NIPU-acrylates.

3.2. Experimental

3.2.1. Materials

The following materials were procured from commercial suppliers, with their names shown in the parenthesis, and used as received.

Poly(propylene glycol) diglycidyl and propoxylated glycerin triglycidyl (Emerald Performance Materials, USA), Isophorene diamine (Vestamine IPD), bis (para-aminocyclohexyl) methane (Vestamin PACM), and methacrylic anhydride (Evonik, USA), Dimer fatty diamine (Priamine

1074, Croda, USA), Ethylene carbonate (EC, Huntsman, USA). 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (darocur 1173), 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184), and bis(2,4,6-trimethylbenzoyl)-phenylphosphine- oxide) (Irgacure 819) (Ciba Specialty Chemicals); Hexanediol diacrylate (HDDA) and OCTYL/DECYL ACRYLATE (ODA-N) (Allnex); Silmer ACR D-208 (Siltech);Titanium dioxide pigment (T-Pure R-960, DuPont). Methyltriphenylphosphonium iodide (Me.Ph.I), Glycidol, glycidyl methacrylate, isopropylthioxanthane (ITX), Toluenesulfonic acid (PTSA), butylated hydroxytoluene (BHT) and all the solvents (Sigma Aldrich, USA).

3.2.2. Instrumentation

Structural characterization of the NIPU-ACs was performed by Fourier Transformation Infrared (FTIR) spectroscopy using a Bruker Tensor 27 FTIR analyzer with 8 scans recorded in the range of 400-4000 cm^{-1} and Nuclear Magnetic Resonance (NMR) spectroscopy measurements using a JEOL 400 MHz multiple nucleus spectrometer using deuterated chloroform as solvent and tetramethylsilane (TMS) as an internal standard.

Confocal micro-Raman spectroscopy was used to track the Raman peak signatures in uncured and cured clear-coats, as well as the pigmented coatings. A 60 mW, 532 nm HeNe laser was focused to a spot with a diameter of 3.3 μm using a 10× objective (numerical aperture of 0.2). Raman spectra with a resolution of 1.5 cm^{-1} (1800 lines per millimeter grating) were collected via single point measurements over different areas of the sample, as well as different focusing depths, to track the homogeneity of the UV-curing process. The area of the C=C band at 1636 cm^{-1} (AC=C) was followed as function of depth, and the area of the CH_2 (ACH2) at 1456 cm^{-1}, which was not affected by curing, was chosen to normalize the C=C band to avoid data misinterpretation due to the loss in intensity with increasing depth, fluctuations of the laser intensity, or other external perturbations. The conversion in each depth was then calculated according to Eq. 3.1:

$$\textbf{Conversion (\%)} = 100 * (1 - Az/Am) \qquad (3.1)$$

which Az = (AC=C/ACH2)z and the initial ratio Am = (AC=C/ACH2)m determined from the liquid formulations scanned in the same conditions as the cured samples [34].

Differential scanning calorimetry (DSC, Mechanical analyzer Q-2000 TA equipment calibrated with n- octane and indium) was performed to investigate the Tg of the cured samples. About 5-7 mg of each cross-linked film was encapsulated in a T zero aluminum pan, using T zero standard aluminum lid (TA Instruments).The samples were scanned under a nitrogen atmosphere on a Heat/Cool/Heat cycle, in which each sample was initially heated to 170°C and held isothermally for 30 min. The samples were then cooled to -70°C and held isothermally for 5 min before heating again to 170°C. Heating and cooling rates were 10°C/min. Finally, thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere on DSC Q-500 instrument for the temperature range of 40–580°C at a heating rate of 10°C/min. The static mechanical properties were measured according to ASTM D882-02 using a Universal Galdabini tensile testing machine, setting the crosshead speed at 300 mm/min and the initial grip separation at 50 mm.

3.2.3. Synthesis of Polyurethane Polyamines (PUPAs)

Following an optimized method reported in our previous study [chapter 2, 35], MFCCs were synthesized via the carbonation reaction of epoxy compounds in the presence of Me.Ph.I as a catalyst. In a single-neck flask, methyltriphenylphosphonium iodide was dissolved in a mixture of epoxy compounds and 1-methoxy-2-propanol solvent. After flushing with a jet of dry CO_2 gas to replace air with CO_2, a rubber balloon filled with dry CO_2 gas, at slightly higher than atmospheric pressure, was attached to the reaction flask. The reaction mixture was stirred at 70 °C, with intermittent refilling of CO_2 balloon. The completion of the reaction was tracked by oxirane oxygen content (OOC%) titration according to ASTM D1652 and observing the disappearance peak at 907 cm^{-1} associated with C-O-C of the oxirane ring. After
>95% of conversion, the mixture was cooled to room temperature, and the solvent and catalyst were removed using hot water/ethyl acetate in a separatory funnel. The ethyl acetate phase containing cyclic carbonates was dried using anhydrous sodium sulfate, and the product was isolated by vacuum distillation of the solvent.

Non-isocyanate PUPAs were then obtained by the reaction between cyclic carbonates and stoichiometric excess primary diamines (amine/CC equivalent ratio: 1.7:1) without using any catalyst.The cyclic carbonate, together with toluene as solvent, was charged into a three-neck flask equipped with a mechanical stirrer, condenser, and a means for N2 inlet. The calculated amount of amine wasthen added to the mixture, and the temperature was raised to 90°C. The completion of reaction was tracked using amine value titration as per ASTM D2024 standard and FTIR

(disappearance of the peak at 1800 cm-1 corresponding to cyclic carbonate). The resulted PUPAs were identified by "the name of CC compound used in their synthesis" followed by "the name of diamine used in their preparation." For example, PUPA prepared from CC1 and IPDA was names as PUPA (1-IPDA).

3.2.4. Synthesis of non-isocyanate urethane acrylates (NIPU-ACs)

As summarized in Figure 3.2, NIPU-ACs were synthesized through four synthetic approaches. The NIPU-POs as intermediates for route #1 were prepared using two methods, including the reaction of PUPA with ethylene carbonate and the direct reaction of cyclic carbonates with monoethanolamine. Each of these approaches had advantages and disadvantages. The criteria used for selection of the best were the reaction time, ease of tracking the progress of reaction, product color, and other reaction conditions, such as temperature and necessity of using a catalyst.

2.3.5. Synthesis of PUPO

PUPOs were synthesized by a ring-opening reaction of monoethanolamine with cyclic carbonates. In athree-neck flask using a mechanical stirrer, nitrogen inlet, temperature controller probe, and water condenser setup, monoethanolamine was dissolved in n-butanol and added to the CC compound in a 1:1 equivalent ratio at room temperature. The equivalents of CCs were calculated from the epoxy equivalent weights of the corresponding epoxy compound. The temperature was raised to 90°C, and stirring was continued until more than 95% of conversion was achieved, and the residual ethanolamine was removedusing vacuum distillation. The near-zero amine values after distillation indicated the removal of unreacted ethanolamine. The progress of the reaction was tracked using amine value titration as per ASTM D2074 and FTIR spectroscopy (disappearance of 1800 cm-1 peak corresponding to cyclic carbonates).

In another method, after the completion of the PUPA synthesis reaction, ethylene carbonate was added to the mixture of PUPA and solvent in 1:1 equivalent ratio to amines. The addition was done to the same reaction setup used for PUPA synthesis. The temperature was increased to 100°C, and the mixture was kept under stirring. The reaction was tracked by the amine value titration as per ASTM D2074 and also the FTIR peak at 1800 cm-1 corresponding to cyclic carbonates.

3.2.5.1. Route #1: Synthesis of NIPU-ACs through PUPOs and MAAH reaction

Once the PUPOs were prepared, MAAH was dissolved in additional toluene and added in 2:1

molar ratio to the PUPO in the same reaction flask. The addition of MAAH was carried out at room temperature, and p-TSA (2.5 wt. % of MAAH) was added as the catalyst. BHT (0.25 wt. % of total solids) was added to the mixture as the free-radical inhibitor to avoid polymerization of acrylate groups. The reaction temperature was then increased to 65°C and maintained for 3h, and raised to 100°C after that. The progress of the reaction was tracked by evaluation of the FTIR peak at 1780 cm-1 associated with theanhydride group of MAAH. Acid value was determined according to ASTM D974. Once the target acid value (due to the production of methacrylic acid as the byproduct) was reached, the mixture wasvacuum distilled at 110°C until the acid value of the mixture dropped to less than 5. In order to assist the removal of the methacrylic acid, a small amount of methanol was added to the mixture before application of vacuum.

3.2.5.2. Route #2: Synthesis of NIPU-ACs through PUPAs and GMA reaction

In this route, calculated amount of PUPA was placed into a three-neck flask attached with a mechanical stirrer, means for nitrogen inlet, temperature controller probe, and water condenser setup. GMA was then dissolved in acrylonitrile solvent and added in a 1:1 equivalent ratio of amine hydrogen equivalent weight (AHEW) of the PUPA. Addition was done at room temperature, in the presence of BHT inhibitor (0.25 wt. % of solids). Reaction temperature was raised to 60°C, and stirring was continued.FTIR spectroscopy was used to track the disappearance of peak at 907 cm-1 corresponding to C-O-C stretching of epoxide groups. Determination of oxirane oxygen content (OOC%) was also carried out to follow the extent of reaction. Since the presence of amines interferes with the OOC% titrimetric method, the value was adjusted by subtracting the contribution of amine, as per Eq. 3.2.

OOC%= Total measured OOC%-OOC% Measured due to presence of amines (3.2)

3.2.5.3. Route #3: Synthesis of NIPU-ACs through direct reaction of MAAH with PUPAs

In order to prepare the urethane acrylate oligomer through route #3, PUPA, toluene, and BHT (0.25wt % of total solid) were placed into a three-neck flask equipped with a temperature controller, a condenser, and a means for nitrogen inlet. MAAH (1:1 equivalent ratio to amine) was the added drop- wise, while the flask was kept in an ice bath. After the complete addition, the temperature was raised to 60°C. The progress in the reaction was monitored by amine value titration and FTIR spectroscopy to trace the changes in the anhydride peak (1780-1790 cm-1). The reaction was continued until the amine value reached close to zero, and the anhydride peak was disappeared. After the completion of the reaction, methacrylic acid, which was produced as a byproduct, was

removed by vacuum distillation using a mechanical vacuum pump. Since the viscosity of the resulted NIPU-AC was too high, it was diluted with toluene to a solid content of 75-80%.

3.2.5.4. Route #4: Synthesis of NIPU-ACs through Michael-Addition reaction of HDDA and PUPAs

In another trial route to obtain NIPU-ACs, PUPAs were charged in a three-neck flask equipped with a mechanical stirrer, condenser, and a means for nitrogen inlet. Toluene was added as solvent and 1:2 equivalent ratio of HDDA (with respect to amine eq. weight) was added at room temperature. After the addition of BHT (0.25 wt. %) as inhibitor, the reaction temperature was raised to 80°C and kept under stirring. Reduction of FTIR peak at 1640 cm^{-1} corresponding to C=C stretch as well as determination of primary amine value (as per ASTM 2074) was utilized to track the progress of reaction. In order to obtain the primary amine value, the sum of secondary and tertiary amines was subtracted from the total amine value.

3.2.6. Preparation and evaluation of UV-NIPU coatings

Aluminum alloy (2024-T3 grade) and cold rolled steel (CRS) test panels (Q-Panels, USA) were used for the application of films. The substrates were cleaned with acetone and dried before use. The UV-NIPU formulations were prepared by thorough mixing of NIPU-AC oligomers with varying amounts of reactive diluents (HDDA, ODA, and Silmer D-208) and photoinitiator, at room temperature for 15 min. Darocur 1173 (3 wt % of total solids) was used as photoionitiator for the clear-coats. Pigmented coatings were prepared by dispersing titanium dioxide with a pigment volume concentration (PVC) of 8%, using a Flacktech high speed mixer machine. A 80:20 by wt. mixture of Irgacure 184 / Irgacure 819 (dose of 2 wt. %), together with of 0.6 wt. % of isopropylthioxanthane (ITX), were used as the photoinitiator package. The films were casted on the substrate using a square film applicator. Due to high viscosities of the UV- NIPU samples (even after the addition of reactive diluents), a small amount of toluene (up to 10 wt % of NIPU-AC oligomers) was added to the final mixture to adjust viscosity for coating application. All coatings were applied using an additive layer-by- layer approach, to reach a total dry film thickness (DFT) of 10 mils. The clear-coats were applied with a DFT of 5 mils per coat, while the pigmented coatings were applied with DFT of 1 mil. Each coat was fully UV-cured before application of the subsequent layer. UV-curing was done by 3 passes under a Fusion UV system with a H-bulb with the conveyor belt speed set to 12 feet/min and energy density of ~0.70 J/cm^2. At least three replicate test panels were prepared for each test.

Coating properties were evaluated according to SAE AMS-C-83231A military standards, including a flexibility test after conditioning the samples at -54°C for 1 hour, water immersion test for 24 hours, and resistance to aromatic fuel B after 1 hour of immersion (ASTM D471). Moreover, resistance to other chemicals, such as lubricating oil (immersion for 24 hours at 120°C) and hydraulic fluid (immersion for 24 hours at 65°C), was investigated according to MIL-PRF-32239.

3.3. Result and Discussion

The objective of this research was to design and develop rapidly curing coatings with significantly reduced health, safety, and environmental burden that can efficiently replace incumbent systems for military applications. In this regard, we aimed to design and prepare a series of UV-curable non- isocyanate urethane systems with low levels of VOC and HAPs, which could meet the military requirements that were mentioned in previous sections. To meet these goals, we identified two key requirements as the most critical screening tests to help us guide the development of these novel coatings and screen through them. These screening criteria include:

Pass the flexibility test at 1/8" after being kept at -54°C for one hour, according to SAE AMS-C-83231A. And could show MEK double rub resistance of at least 90-100, according to ASTM D4752-06.

In order to achieve this goal, it was important that we meticulously design NIPU-AC oligomers with optimum molecular weight, functionality, and urethane content. Besides, other components in the formulation also needed to be judiciously selected.

NIPU-AC oligomer is a major component controlling performance of these UV-cure coatings and hence a number of NIPU-ACs were synthesized with varying composition and synthetic routes, to select the best oligomers. Then, UV-curable coatings containing different reactive diluents and concentration were prepared and evaluated.

3.3.1. Preparation of polyurethane polyamines

Figure 3.3 shows the probable chemical structures of the two multi-functional cyclic carbonate compounds synthesized in high yields (~ 97%) under mild conditions by carbonation of the corresponding epoxy compounds. Figure 3.4 shows a series of PUPAs with varying chemical structures and molecular weights, which were successfully prepared by reaction of primary aliphatic and cyclo- aliphatic diamines with the prepared MFCCs.

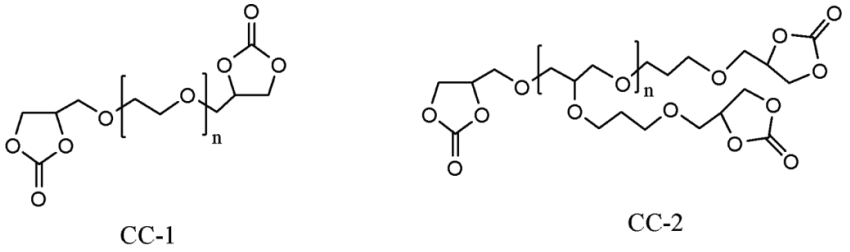


Figure 3.3. Chemical structure of the prepared cyclic carbonates

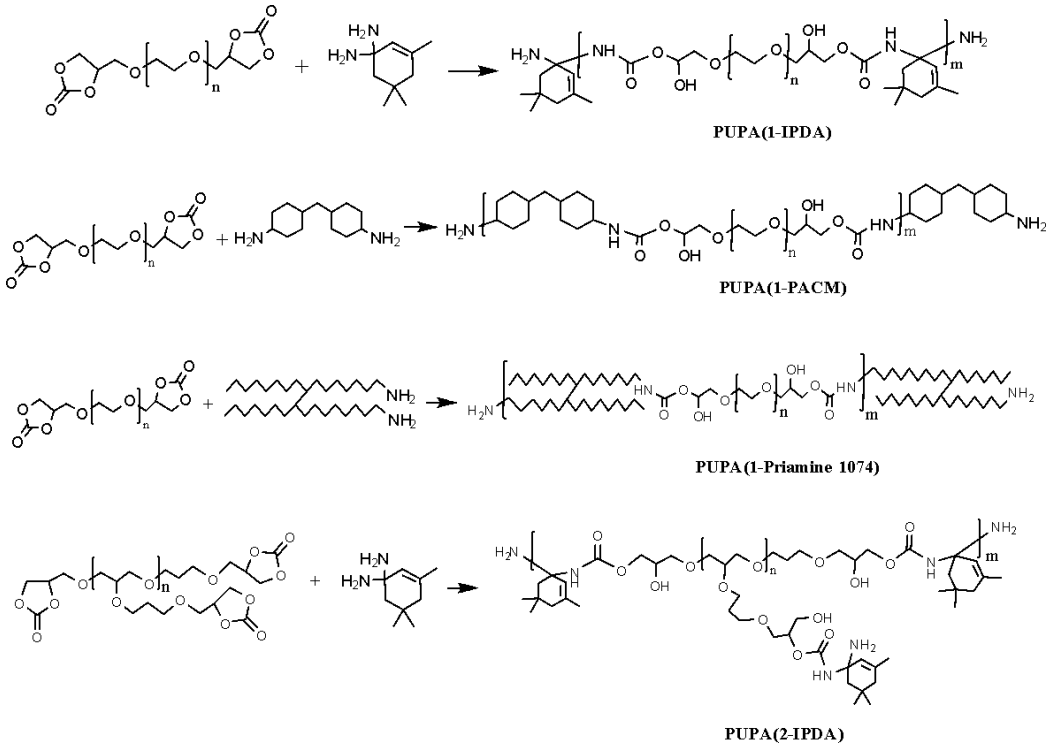


Figure 3.4. Synthesis of a series of PUPAs

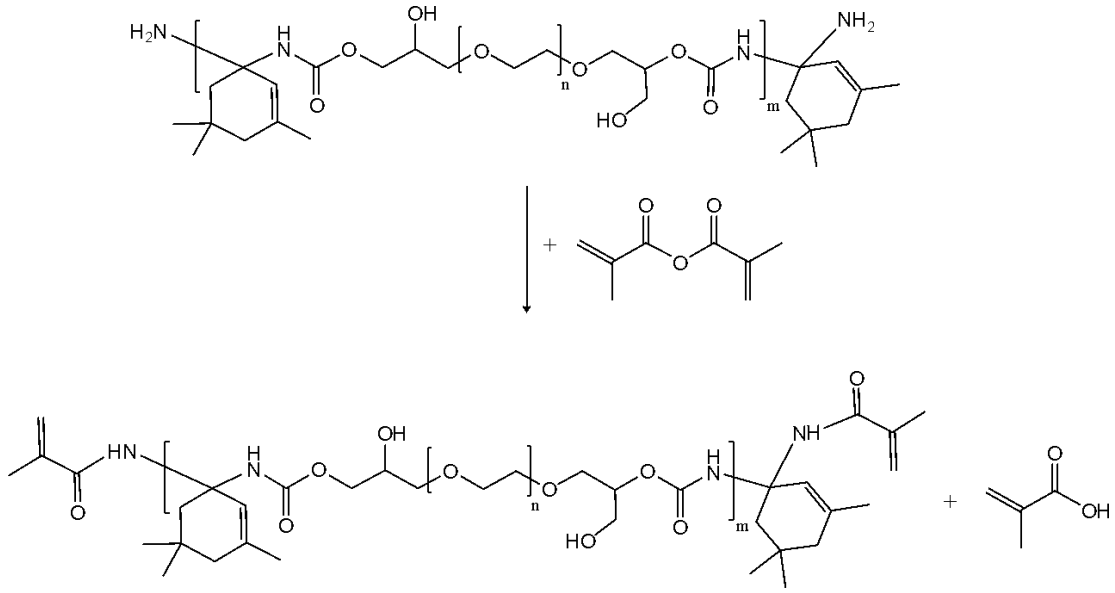
3.3.2. Preparation of urethane acrylate oligomers

Table 3.1 summarizes several NIPU-ACs synthesized for this study using the routes mentioned in section 2.5. Urethane acrylates were named using "NIPU-ACs" as an abbreviation for non-isocyanate urethane acrylate, followed by "number for the synthetic route", "type of MFCC", "type of amine" and,in some cases, "abbreviated name of the fourth compound" such as GMA.

As can be seen in Table 3.1, the direct reaction of PUPA with MAAH was the most feasible reaction considering the highest % conversion in the shortest reaction time. Besides, this reaction was easily monitored using amine value titration and FTIR spectroscopy as mentioned before. Figure 3.5 represents the synthesis of NIPU-AC (3-2-IPDA) oligomer via this route. As shown in Figure 3.6, the FT-IR peak associated with the anhydride group at 1800 cm^{-1} disappeared after the methacrylation was completed. Figure 3.7 illustrates the HNMR characterization of this oligomer, which validates the proposed structure of NIPU-AC.

Table 1. NIPU-AC oligomers prepared for the study

Urethane acrylate		Reactants			Characteristics			
Synthetic routes	Identity	Corresponding compounds			Reaction time (h)	% (meth)acrylation	Final color	Acrylate EW
		1	2	3				
Route #1	NIPU-AC (1-1-1074)	PUPA (1-1074)	EC	MAAH	20	90	Dark brown	2352.06
	NIPU-AC (1-1-PACM)	PUPA (1-PACM)	EC	MAAH	20	90	Dark brown	1135.8
	NIPU-AC(1-2-EA)	CC-2	Ethanol amine	MAAH	15	90	Orange	812.7
Route #2	NIPU-AC (2-1-PACM-GMA)	PUPA (1-PACM)	GMA	-	20	55	Pale brown	1264
	NIPU-AC (2-2-IPDA- GMA)	PUPA (2-IPDA)	GMA	-	48	25	Pale brown	1733.9
Route #3	NIPU-AC	PUPA	MAAH	-	5	95	brown	923.7
	(3-1-IPDA)	(1-IPDA)						
	NIPU-AC (3-2-IPDA)	PUPA (2-IPDA)	MAAH	-	5	95	brown	1518.6
Route #4	NIPU-AC (4-1-IPDA)	PUPA (1-IPDA)	HDDA	glycidol	25	53	yellow	1306.7



NIPU-AC (3-1-IPDA)

Figure 3.5. Synthesis of NIPU-AC (3-1-IPDA) oligomer

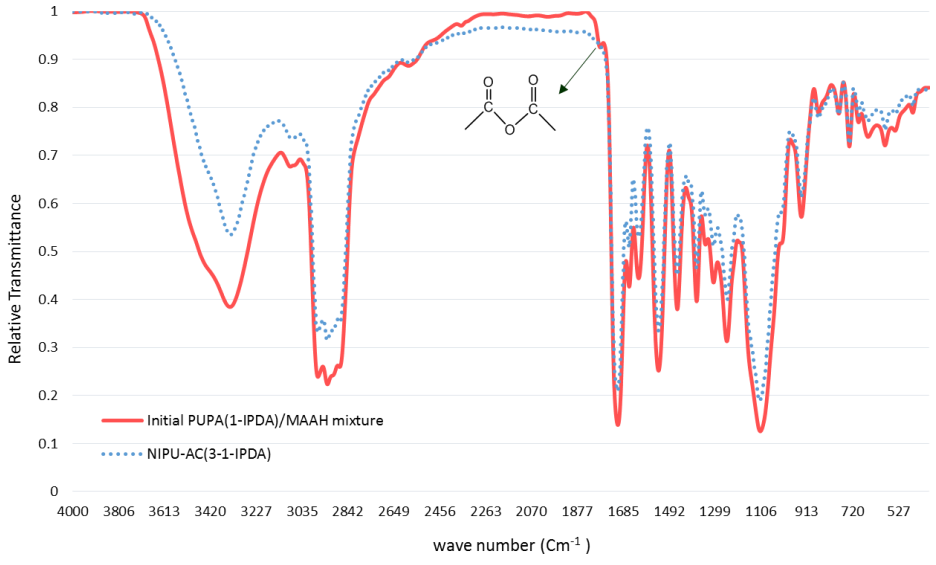


Figure 3.6. Tracking the methacrylation reaction in route #3 using FTIR spectroscopy

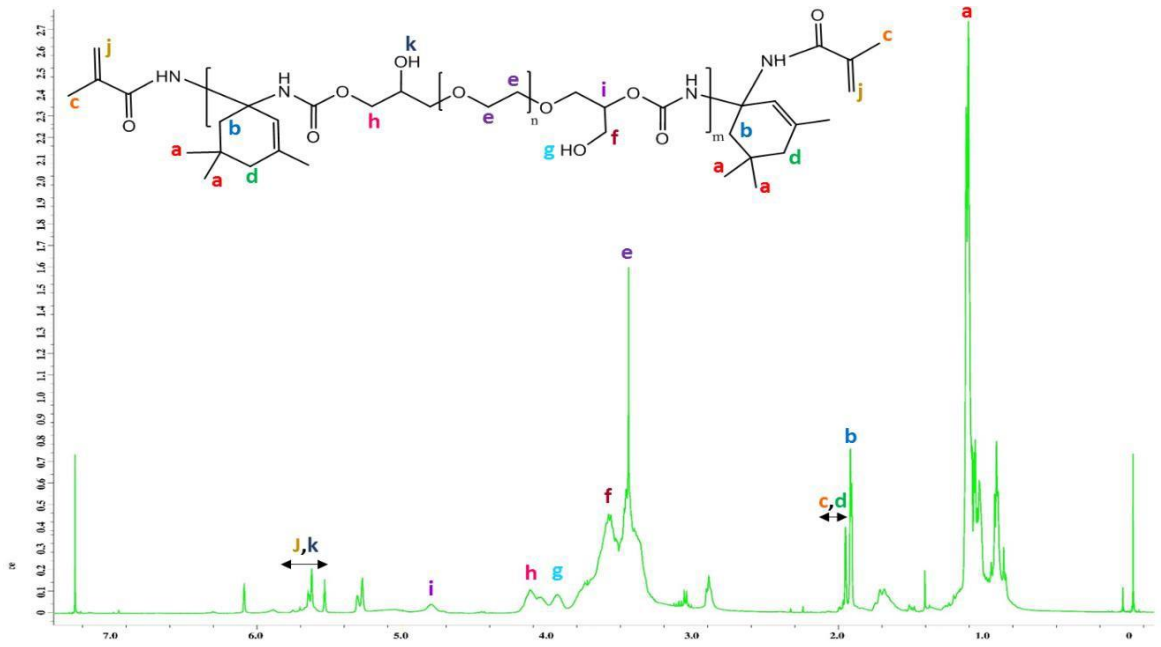


Figure 3.7. H-NMR spectrum of NIPU-AC (3-1-IPDA) oligomer

3.3.3. Coating formulation, UV-curing, and evaluation

3.3.3.1. Selection of the proper UV-curable clear-coat compositions

As a preliminary study, clear-coat compositions containing only urethane acrylate oligomers and 3 wt% of Darocur 1173 as the photoinitiator, without the addition of any reactive diluents, were prepared (coating systems #1 to #5, #13, #14, and #26). The clear coats were applied on clean aluminum panels and UV-cured. They were then subjected to the two most critical screening tests, i.e. low-temperature flexibility and MEK-double rub test. The results for coatings containing urethane acrylates, which were synthesized through routes #1, #2, and #4, are summarized in Table 2, and the results for those synthesized through route #3, the most feasible route, are included in Table 3. Some of the films remained tacky after UV-curing, probably due to oxygen inhibition on the surface, which could beimproved by increasing the acrylate concentration1 (e.g., by addition of reactive diluents to the system). It should be mentioned that systems that failed the flexibility test in this step were excluded from furtherinvestigation.

In the next step, a series of clear-coat compositions containing various reactive diluents in different concentrations were prepared (systems #6 to #12, #15 to #25, #27, and #28), and the UV-cured films were subjected to the above mentioned critical tests. According to the results demonstrated in Tables
3.2 and 3.3, systems with higher equivalent weight were usually more flexible, as expected. For example, NIPU-AC (3-1-IPDA), which has a lower acrylate equivalent weight than NIPU-AC (3-2-IPDA), failed the flexibility test. Moreover, by increasing the weight percent of reactive diluents and consequently increasing the crosslink density, MEK-double Rub numbers increased while flexibility decreased. On the other hand, although the addition of 5 wt. % silicone acrylate enhanced the flexibility in some cases, it slightly decreased the MEK resistance of the coatings, which might be due to the high permeability of silicon owing to its low Tg and high free volume [36]. Since chemical properties are essential for military applications, silicone acrylate was excluded from further study in this research. Considering the screening criteria, system #18 and system #27 were selected as the best systems for further evaluation of military critical performance properties.

3.3.3.2. Evaluation of the clear-coat systems for military applications

A series of aluminum test panels, primed with Aeroglaze 9947 wash primer, were coated with 10 ± 2 mils dry film thickness of the two selected coating compositions (#18 and #27), cured under

UV- radiation, and evaluated as per military test specifications SAE AMS-C-83231A and MIL-PRF-32239. Both systems passed the water immersion test with no visible change in their appearance (no swelling,blistering, delamination, or other defects), or loss of adhesion after 24 h of immersion. Also, both samples passed the hydraulic fluid resistance test, since they only showed slight staining without any blistering, softening, or other defects. Regarding resistance to Aromatic Fuel B, system #27 performed better than system #18. We attribute this to more urethane content in system #27, which brings more chemical resistance thanks to greater H-bonding among urethane groups. Furthermore, both the coatings were delaminated after immersion in lubricating oil, probably due to their lower adhesion due to the internal stresses in the film induced by shrinkage during UV-curing, which is a typical issue associated with most UV-cure coatings [37]. Figure 3.8 summarizes the characteristics of these two paint systems.

Table 3.2. Testing of the UVNIPU coating systems:

Coating Composition					Testing	
System #	**Urethane acrylate oligomer(s)**	**HDDA Wt. %**	**ODA Wt. %**	**Silmer D208 Wt. %**	**Flexibility @ -54 °C**	**MEK Double rubs**
1	NIPU-AC (1-1-1074)	0	0	0	Tacky film	
2	NIPU-AC (1-1-PACM)	0	0	0	Tacky film	
3	NIPU-AC (1-2-EA)	0	0	0	Pass	65± 5
4	NIPU-AC (2-2-IPDA-GMA)	0	0	0	Fail	150± 5
5	NIPU-AC (4-1-1074)	0	0	0	Fail	100± 5
6	NIPU-AC (1-1-1074)	20	0	0	Pass	80 ± 5
7	NIPU-AC (1-1-1074)	0	20	0	Tacky film	
8	NIPU-AC (1-1-PACM)	20	0	0	Fail	>200
9	NIPU-AC (1-1-PACM)	0	20	0	Tacky film	
10	NIPU-AC (2-1-IPDA-GMA)	0	20	0	Tacky film	
11	NIPU-AC (1-2-EA)	0	20	0	Pass	65 ± 5
12	NIPU-AC (1-2-EA)	20	0	0	Fail	85 ± 5

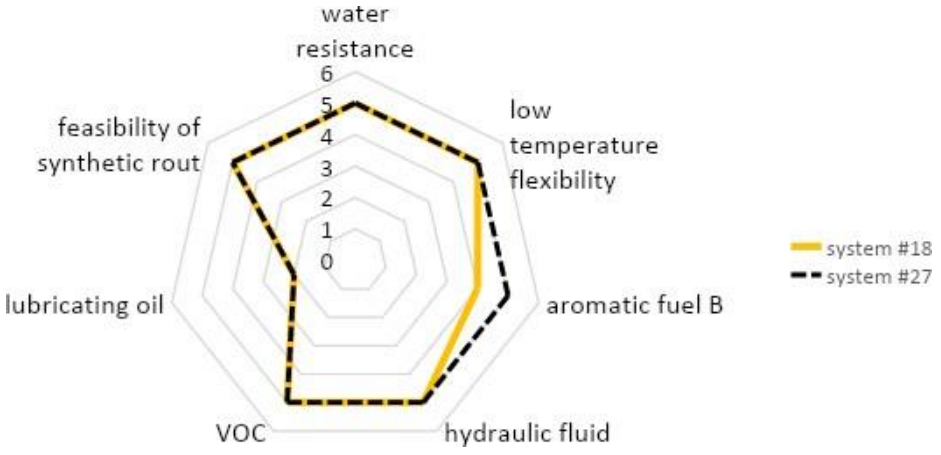
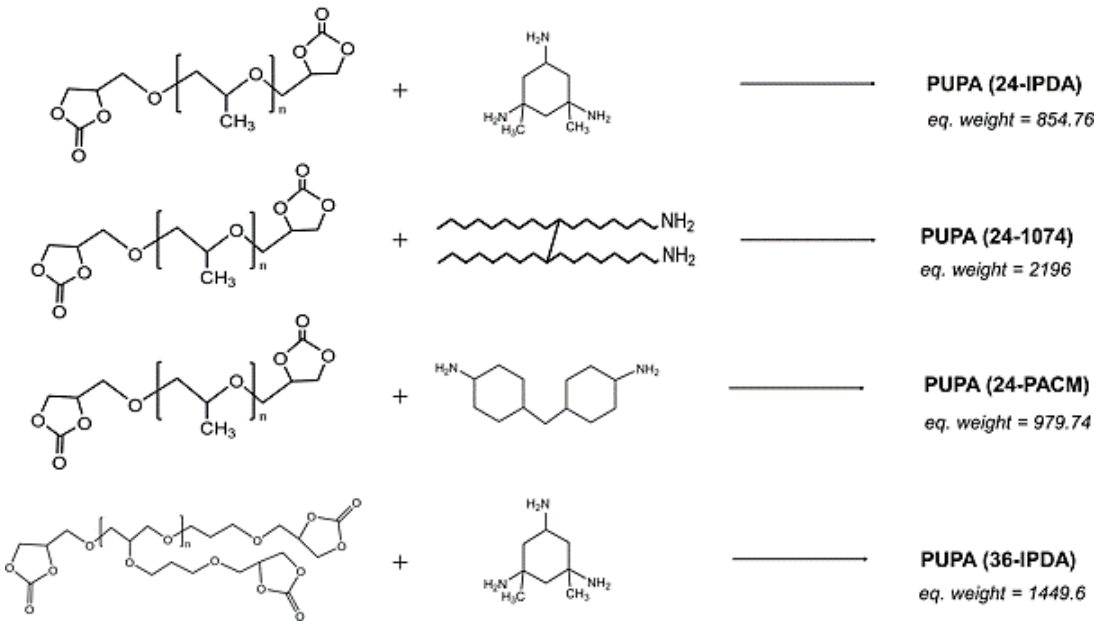


Figure 3.8. Characteristics of UV-NIPU clear-coats

Table 3.3. Testing of the UVNIPU coating systems containing UA oligomers prepared through routes #3 anddifferent concentrations of reactive diluents

Coating Composition					Testing	
System #	**Urethane acrylate oligomer(s)**	**HDDA wt %**	**ODA wt %**	**Silmer D208 wt%**	**Flexibility @ -54 °C**	**MEK Double rubs**
13	NIPU-AC (3-1-IPDA)	0	0	0	Fail	75± 5
14	NIPU-AC (3-2-IPDA)	0	0	0	Tacky film	
15	NIPU-AC (3-1-IPDA)	10	10	0	Fail	100 ± 5
16	NIPU-AC (3-1-IPDA)	0	0	10	Pass	40 ± 5
17	NIPU-AC (3-1-IPDA)	20	0	5	Fail	125 ± 5
18	NIPU-AC (3-2-IPDA)	20	0	0	Pass	90 ± 5
19	NIPU-AC (3-2-IPDA)	0	20	0	Tacky film	
20	NIPU-AC (3-2-IPDA)	10	10	0	Pass	60 ± 5
21	NIPU-AC (3-2-IPDA)	20	0	5	Pass	85 ± 5
23	NIPU-AC (3-2-IPDA)	0	0	10	Pass	35 ± 5
24	NIPU-AC (3-2-IPDA)	30	0	0	Fail	105 ± 5
25	NIPU-AC (3-2-IPDA)	30	0	5	Fail	100 ± 5
26*	NIPU-AC (3-2-IPDA)+ NIPU-AC (3-1-IPDA)	0	0	0	Pass	85± 5
27*	NIPU-AC (3-2-IPDA)+ NIPU-AC (3-1-IPDA)	20	0	0	Pass	95 ± 5
28*	NIPU-AC (3-2-IPDA)+ NIPU-AC (3-1-IPDA)	20	0	5	Pass	85 ± 5

* The NIPU-AC oligomers were mixed in 1:1 equivalent ratio.



3.3.3.3. Evaluation of the pigmented coating systems for military applications

According to the results reported in section 3.3.3.2, systems #18 and #27 were selected to be used as the binder in the final pigmented coatings designed for military applications. The evaluation results are summarized in Table 3.4 and Figure 3.9. The coating properties obtained from pigmented samples were similar to those of unpigmented samples, indicating that pigmentation did not cause any issue in the radiation-curing of UVNIPU samples. Moreover, coatings were still flexible at very low temperatures. However, formulation of coatings with pigments could not improve the coating properties in terms of resistance to specific fluids, such as lubricating oil and aromatic fuel B.

Table 4. Evaluation of the pigmented UVNIPU coating systems as per military specifications [SAE AMS-C-83231A and MIL-PRF-32239]

UVNIPU system	Composition			Evaluation				
	Binder System#	TiO2 (PVC)	HDDA Wt%	Flexibility @ -54 °C	Water Immersion	Hydraulic Fluid	Aromatic Fuel B	Lubricating oil
1	18	8	20	Pass	Pass	Pass	Delamination	Delamination
2	27	8	20	Pass	Pass	Pass	Delamination	Delamination

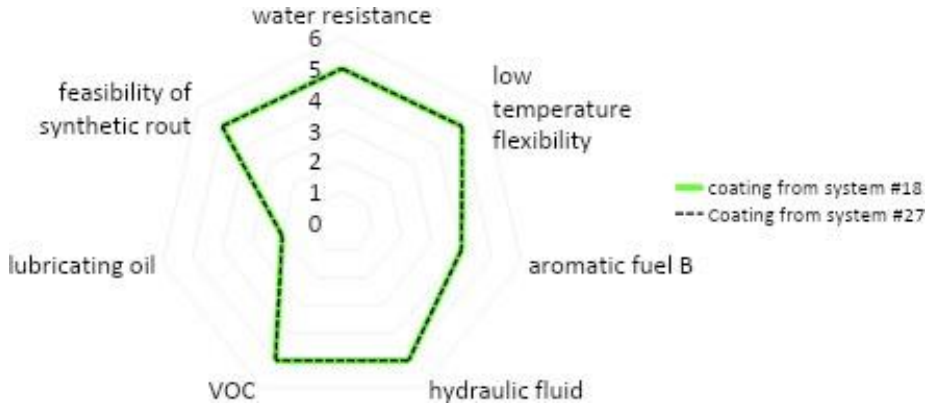


Figure 3.9. Characteristic of UV-NIPU pigmented coatings

3.3.4. Thermo-mechanical properties

The two selected UVNIPU coating formulations (#1 and #2) were also evaluated for their thermo- mechanical properties. As represented in Figure 3.10, According to the TGA thermograms, UVNIPU 1 and UVNIPU 2 coatings showed a similar trend of heat stability with 50% decomposition temperatures of 441 and 433°C, respectively. Since the resulting NIPU systems are ß-hydroxyurethanes and contain hydroxyl groups unlike conventional polyurethanes, it is important to test how such systems behave in heating conditions. Higher thermal stability of the UVNIPU 1 and 2 coatings could be due to the presence of a relatively large and stable structure of CC2 and

CC3, which reduces the concentration of hydroxyurethanes [23]. Thermal decomposition started at lower temperatures for the UVNIPU 2 sample. This could be due to the higher urethane content of UVNIPU 2 compared to UVNIPU, and the lower decomposition temperature of urethane linkage.

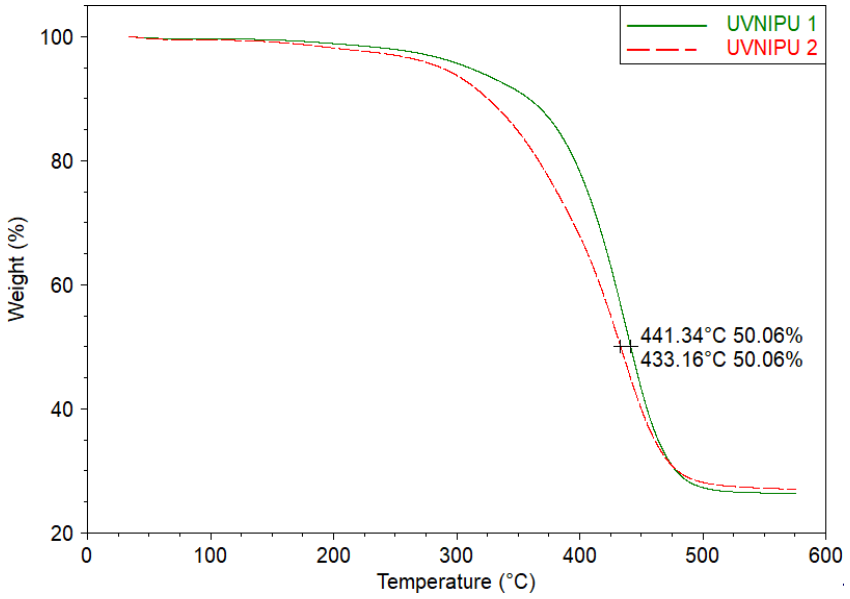


Figure 3.10. TGA thermogram of selected UVNIPU formulations

The quantitative results of TGA and DSC are summarized in Table 3.5, together with the tensile test results. No Tg was detected for the UVNIPU 1 sample in the temperature range of the DSC test. This could be due to the flexible backbone of such compositions. However, since this sample passed the low- temperature flexibility test, its Tg should be less than 25°C. The coating sample based on the mixture of CC2 and CC3 (UVNIPU-2) showed superior mechanical properties as the tensile strength and elongation at break were higher compared to the other sample. This could be due to higher crosslinking in such coatings, which reinforces the integrity of the polymer network. Overall, UVNIPU coatings #18 and #27 showed satisfying thermal and mechanical properties and could be promising options for military applications.

Table 3.5. Thermo-mechanical properties of UVNIPU coating systems

UVNIPU system	Evaluation				
	Tg (°C)	Tensile strength (MPa)	Elongation % @break	Modulus (MPa)	50% decomposition Temperature (°C)
1	N/A	1.28	42	7	441
2	14.8	2.07	63	24	433

3.3.5. Depth profiling to investigate curing conversion

Raman spectroscopy was used to explore the curing conversion of the selected UVNIPU coating formulations (both clear and pigmented). As demonstrated in Figure 3.11, for clear-coats, the C=C peak disappeared after the curing, while for the pigmented coatings, its intensity was considerably reduced. This might be due to the negative effect of pigments on UV penetration and, therefore, lower acrylic conversion. This trend was constant in all the depths for both clear and pigmented coatings. In other words, all samples showed homogeneous curing; that is, no statistical differences were found between the Raman spectra at different focusing depths (Figure 3.12).

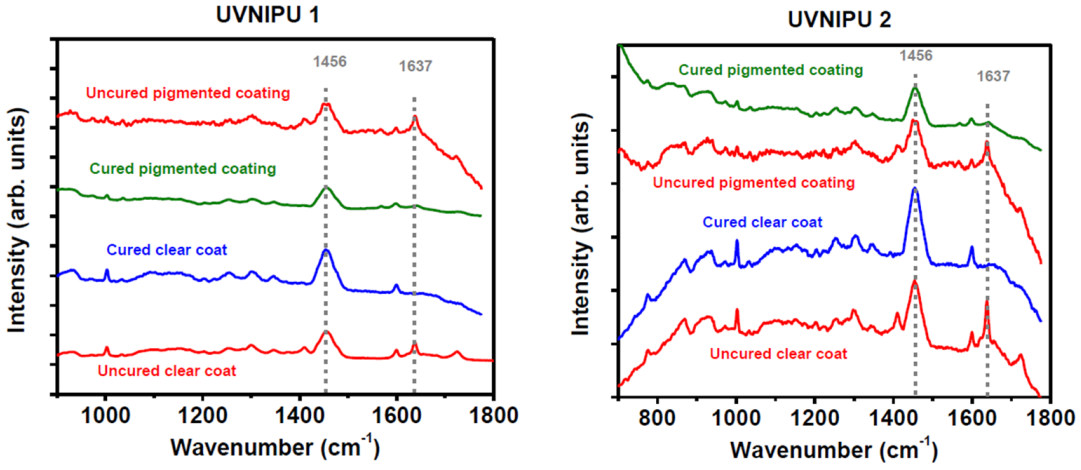


Figure 3.11. Raman spectra of clear and pigmented UVNIPU coatings

3.3.6. Before/after UV-curing

The areas of the characteristic Raman peaks (1456 and 1637 cm^{-1}) were compared after subtracting the background and fitting to Gaussian curves. The %conversion of acrylic groups, which was calculated according to Eq. 3.1, was 59.33% and 81.25% for the pigmented UVNIPU 1 and

UVNIPU 2, respectively. This difference might be due to the higher acrylate content in the latter. Higher conversion and, therefore, improved crosslink density further support our previous results (i.e., better properties of UVNIPU 2 compared to UVNIPU 1).

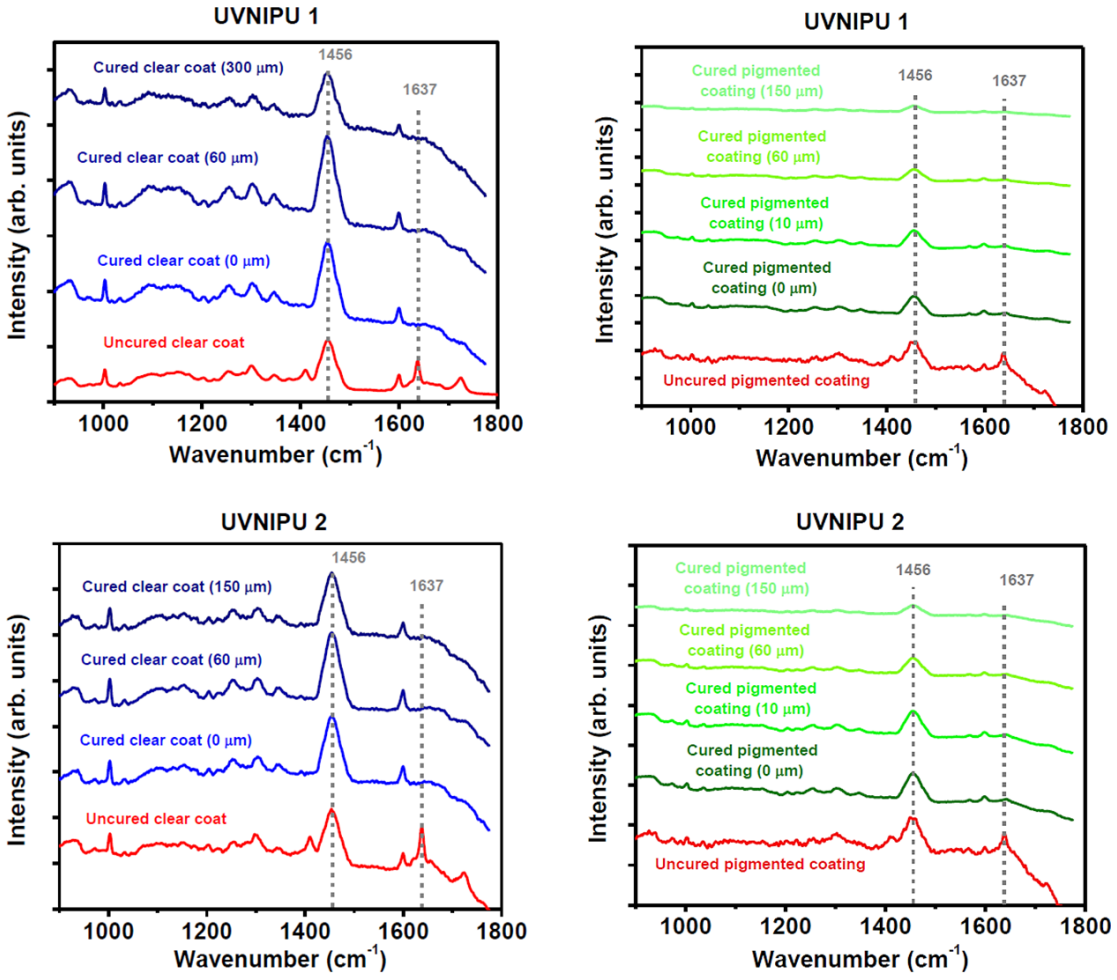


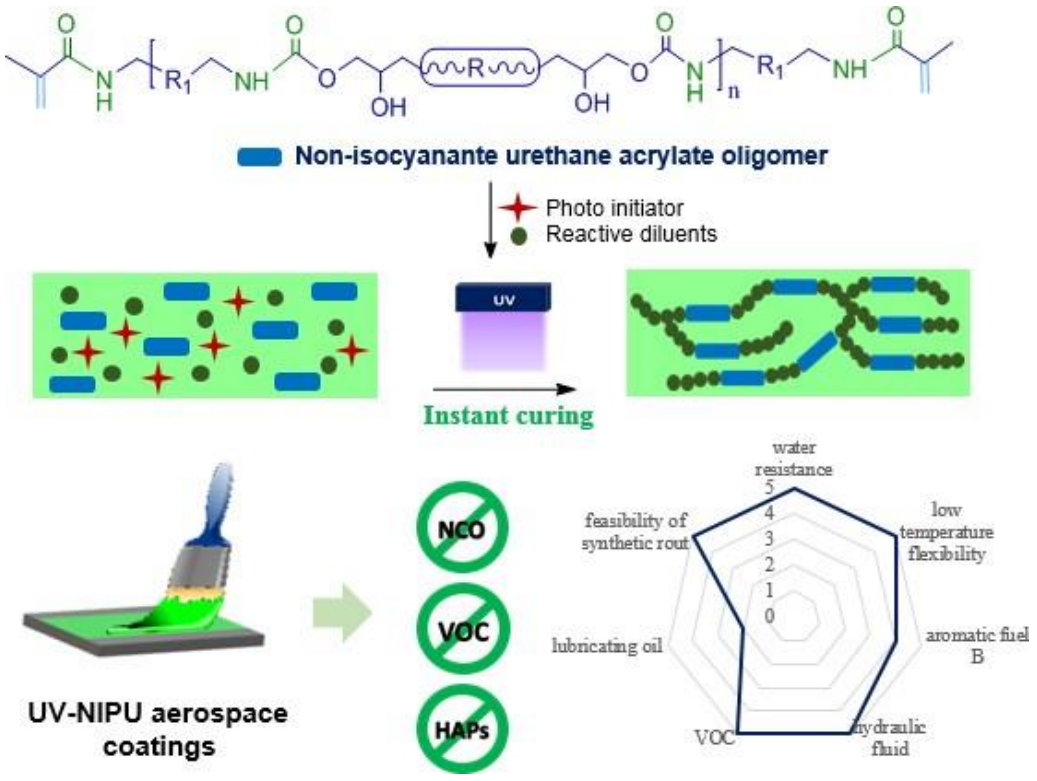
Figure 3.12. Depth profile of clear and pigmented UVNIPU coatings

3.4. Conclusion

In this study, a novel series of urethane acrylate oligomers was successfully prepared via non-isocyanate routes and characterized. Different chemical routes were examined to reach an optimum wayto obtain urethane acrylates. Sustainable UV-curable NIPU coatings were formulated using these urethane acrylates as primary compounds, along with the conventional reactive diluents and photo- initiators, and evaluated for critical performance properties per military specifications (MIL-PRF-32239). Compared to traditionally-used military coatings, these new generations of NIPU coatings showed significant improvements in decreasing curing time and the levels of VOCs and

HAPs. Overall, the UVNIPU coatings showed satisfying thermal and mechanical properties and could be promising options for military applications. Moreover, Raman spectroscopy and coating properties results revealed that sufficient curing of UVNIPU coatings could be achieved even with the presence of TiO2 pigment.

Graphical summary:



As a final conclusion on UV-NIPU coatings, while we could successfully synthesize and demonstrated use of non-isocyanate PU in UV-cure coatings, for the purpose of our current target coatings – Rain Erosion Coatings – these systems were not suitable. It was not possible to manipulate and customize properties, specifically the mechanical properties like % elongation and low temperature flexibility, within the constraints of specifications of rain erosion resistant coatings. Nevertheless, the UV-NIPU has great potential for other military coatings or industrial coating applications, which will need an additional work for their exploitation in military or other types of industrial and protective coatings.

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4.0 Life-Cycle Assessment / Life-Cycle Inventory

Life-cycle assessment is a useful tool to quantify the environmental impact of the product /process on various impact categories. In this project, a full Cradle-to-Cradle or even Gate-to-Gate assessment was not possible due to non-availability of all required data on the Life-Cycle Inventory (LCI) on commercial scale manufacturing. Also, the LCI for the incumbent (isocyanate-based) PU Rain erosion coatings are also not available for comparison.

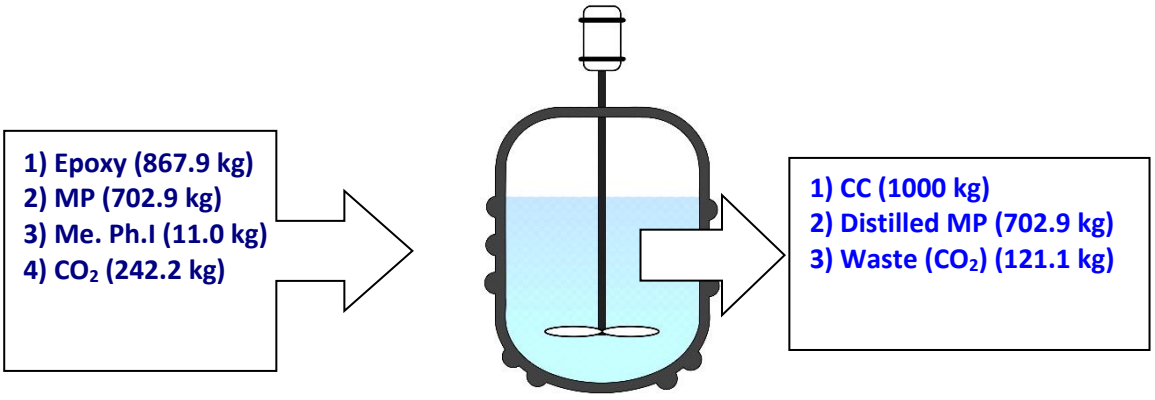
In view of this, we have attempted to develop some LCI data - material / energy consumption data – for a Gate-to-Gate system boundaries (manufacturing) for a representative intermediate product for NIPU coatings, NIPU-PA.

Energy Balance for production of 1000 kg NIPU-PA

Basis: 1000 kg of NIPU-PA (75.5 % solid)

Synthesis was done in single reactor in two steps

STEP 1: Cyclic carbonation (multi-functional cyclic carbonate, CC) RUN No. 12



First Step: 1000 kg Cyclic Carbonated product

Compound	Intended amount (g)	wt%	Specific heat capacity at 20 °C	Raw Materials consumed for producing of 1000 kg product (kg)
Erysis GE24 (Epoxy)	55.20	47.90	1110 J/(kg °C)	(878.90 - 11.0) = 867.9
Methoxy Propanol (MP)	44.10	38.30	2.426 J/g °K (2426 J/Kg °C)	702.90
Me. Ph.I (2 mol% of the epoxy)	0.70	0.60	Assumed similar to Epoxy resin 1110 J/(kg °C)	11.00
CO2 gas (100% excess) Pursing CO_2 gas during the reaction time (1 atm.	15.20	13.20	36.61 J/(mol K) at 15 °C 38.01 J/(mol K) at 100 °C (isobaric) 37.35 kJ/mol K *1 moles CO2* = 44.0095 *gram* 0.849 (kJ/kg °K)	242.20
Total	115.20	100.00		1834.90
Reaction Time	48 h			
Temperature	70 °C			
Agitation speed	200 rpm			
After distillation and washing	Yield: 54.5 %			

Energy Balance for Producing 1000 kg CC Product

Mass Input = 1834.90 kg

Mass output = 1834.90 kg (1000 kg CC product + 702.80 kg MP + 121.10 kg CO_2)

Step 1 (48 h)

1. Electrical Energy for stirring via 5 HP Motor for 48 h
2. Energy (heat loss) requires maintaining temperature at 70 °C for 48 h
3. Energy requires elevating temperature from 25 to 70 °C
4. Energy requires for distillation of MP after terminating of the reaction

1. Electrical Energy: 5 HP equals 223.71 kJ/min $\Rightarrow$ in 48 h is 644.28×10^3 kJ,
2. Heat loss through reaction wall $\approx$ 100 kJ (in 10 min) therefore in 48 h is 28.8×10^3 kJ,

Total Energy consumption from 1 and 2 (Q_{EL}) = 644.28×10^3 kJ + 28.8×10^3 kJ = 673.08×10^3 kJ.

3. Q= m.Cp.ΔT (Heat consumed for raising temperature from 25 to 70 °C)

Q_{1Ep}= 867.90 kg $\times$ 1110 J/(kg °C) $\times$ 45 C = 43.352×10^3 kJ

Q_{2MP}= 702.90 $\times$ 2426 J/(Kg °C) $\times$ 45 C = 76.736×10^3 kJ

$Q_{2Mi.Ph.I}$ = 11.0 $\times$ 1110 J/(Kg °C) $\times$ 45 C = 0.549×10^3 kJ

Q_{2CO2} = 242.20 $\times$ 849 J/(Kg °C) $\times$ 45 C = 9.253×10^3 kJ

Q = 129.890×10^3 kJ

4. Required energy for distillation of MP (702.90 kg)

Latent Heat of Vaporization for MP: (est.) 166 Btu/lb = 92.3 cal/g = 3.86×10^5 J/kg,

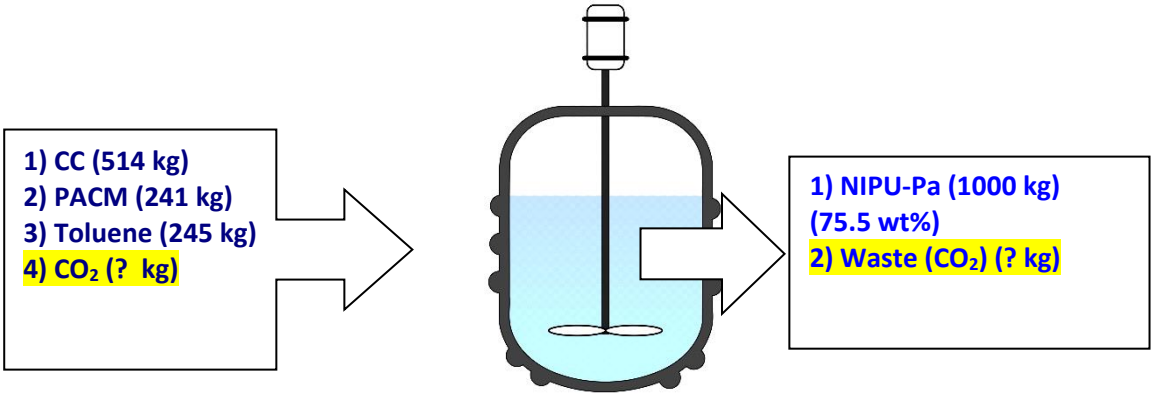
- Boiling Point of MP at 1 atm: 121°C ($\Delta T = 121\text{-}70 = 51$)
- Q_{d1} (Energy requires to increase temperature from 70 to 121 °C) = 702.90 kg × 2426 J/(Kg °C) × 51 = 86.967×10^3 kJ
- Q_{LHV} = 702.90 kg × 3.86 X 10^5 J/kg = 271.3194×10^3 kJ

MP Distillation Energy (Q_d) = $Q_{d1} + Q_{LHV}$ = $86.967 \times 10^3 + 271.319 \times 10^3 = 358.286 \times 10^3$ kJ

Total Energy consumed in the first step of the reaction = $Q + Q_d + Q_{EL} = 129.890 \times 10^3 + 673.08 \times 10^3 + 358.286 \times 10^3 = 1161.256 \times 10^3$ kJ

STEP 2: Basis: 1000 kg of NIPU-PA (75.5 % solid)

STEP 1: Cyclic carbonation (multi-functional cyclic carbonate, CC) RUN No. 12



Second Step: 1000 kg NIPUPa product

STEP 2: Synthesis of PUPAs (Run No. 8: CC2-PACM)

Compound	Intended amount (g)	wt%	*Heat Capacity (Cp)*	Raw Materials consumed for producing of 1000 kg product (kg) (75.5 solid content)
CC2		51.40		514
Diaminodicyclohexyl Methane (PACM) Amine		24.10	Cp: 596.67 J/mol.K Molar mass: 210.365 $g{\cdot}mol^{-1}$ Cp= 2.836 J/°K	241
Toluene		24.50	At 0 °C: 1.61 KJ/Kg °C At 50 °C: 1.8 KJ/Kg °C At 100 °C: 1.968 KJ/Kg °C	245
Total		100		1000
Amine/CC ratio: 1.7				
NIPU- PA	75.5 % solution			
Solid Content	75.5			
Reaction Time	7 h			
Temperature	90 °C			
Agitation speed	200 rpm			
Pursing CO_2 gas during the reaction time (1 atm.)				

Energy Balance for Producing 1000 kg NIPU-Pa Product (75.5 % solid content)

Mass Input = 1000 kg = (514 kg CC + 241 kg PACM + 245 kg Toluene)

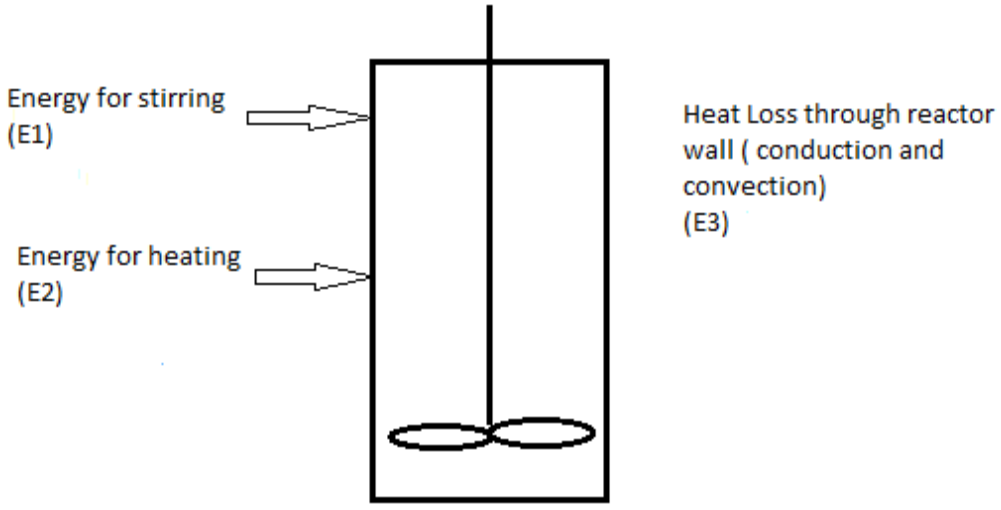
Mass output = 1000 kg (NIPU-Pa)

Step 2 (7 h)

E1: Electrical Energy for stirring via 5 HP Motor for 7 h

Energy requires elevating temperature from 25 to 90 °C

Energy (heat loss) requires maintaining temperature at 90 °C for 7 h



E1: Electrical Energy: 5 HP equals 223.71 kJ/min $\Rightarrow$ in 7 h is 93.958×10^3 kJ

E3: Heat loss through reaction wall $\approx$ 120 kJ (in 10 min) therefore in 7 h is 5.04×10^3 kJ

Total Energy Lost (Q_{EL}) = 93.958×10^3 kJ +5.04×10^3 kJ = $\underline{98.998 \times 10^3 \text{ kJ}}$

E2: Q= m.Cp.ΔT (Heat consumed for raising temperature from 25 to 90 °C)

Q_{1CC}= 514 kg $\times$ 1110 J/(kg °C) $\times$ 65 C = 37.085×10^3 kJ

Q_{2PAMC}= 241 kg $\times$ 2.836 J/(kg °C) $\times$ 65 C = 44.431 kJ

$Q_{3Toluene}$ = 245 $\times$ 1900 J/kG °C) $\times$ 65 C = 30.257×10^3 kJ

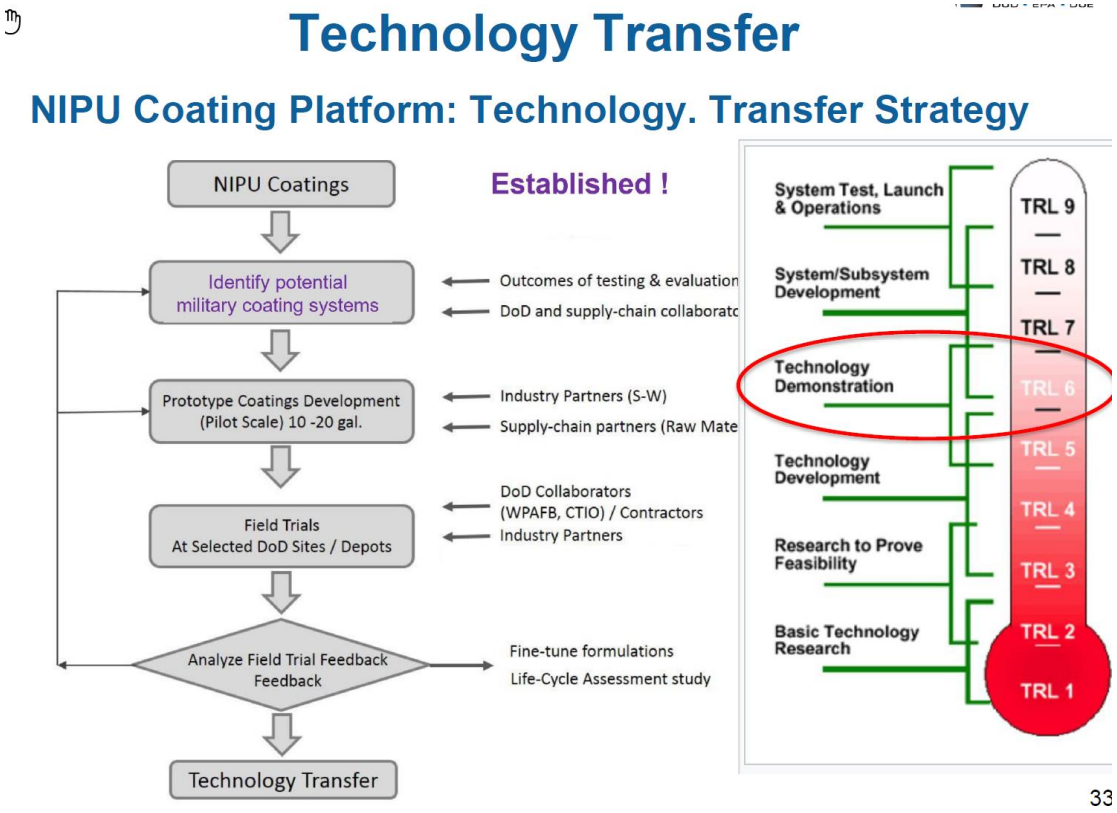
Q = 67.386×10^3 kJ

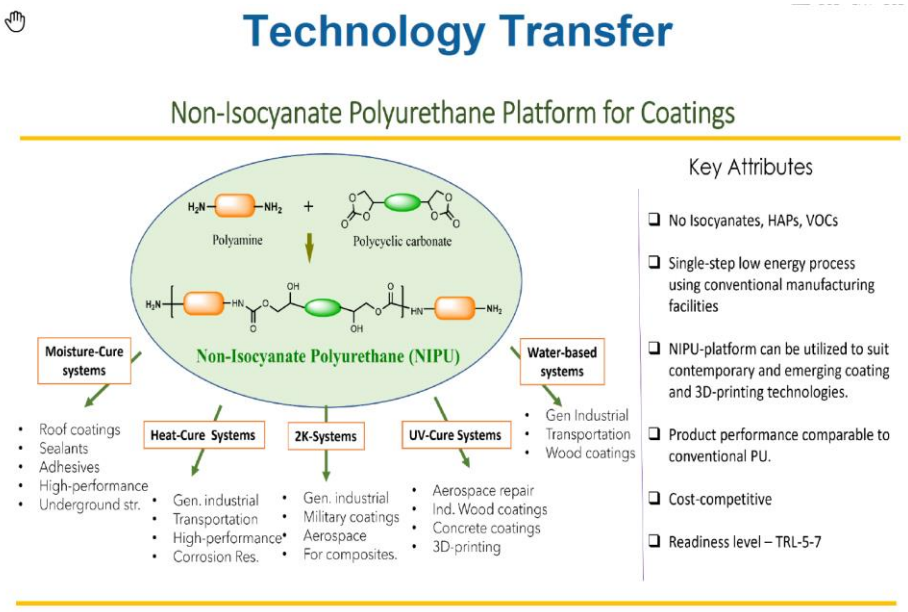
$\underline{\text{Total Energy consumed in the second step of the reaction} = Q + Q_{EL} = 67.386 \times 10^3 \text{ kJ} + 98.998 \times 10^3 = 166.384 \times 10^3 \text{ kJ}}$

$\underline{\text{TOTAL NEEDED ENERGY} = ((1161.256 \times 10^3 \text{ kJ}) \times 0.514) + (166.384 \times 10^3 \text{ kJ}) = 596.886 \times 10^3 + 166.384 \times 10^3 = 763.270 \times 10^3 \text{ kJ}}$

5.0 Transition plan.

The following schematic graphic summarizes our transition plan of this NIPU-Technology





Appendix-1

Specifications for NIPU-Coatings for intended Rain Erosion Resistant Coatings

Appendix

Table 1 Critical Performance Properties (ref: SAE AMS-C-83231A)

Material Property	Test Method	Target Criteria	Substrate
Peel Strength	Following complete cure, 2-1" wide strips shall be cut lengthwise through the coating. The material will be peeled back at a 180 degree pull at 2 in/minute	7 pounds per inch	Composite
Flexibility	Conditioned at -54 deg C (-65 deg F) for 1 hour then bent over 1/8" mandrel per Fed Std 141 Method 6223	No cracking or loss of adhesion	2024-O anodized
Water Resistance	Immersion in distilled water for 24 hours at standard conditions. The exposed coupons will be tested for visual appearance and peel.	No evidence of blistering, swelling, checking or visible color change. Peel strength shall not be below 7 pounds/in	Composite
Aromatic Fuel Resistance	Immersion in ASTM D471 Fuel B for 1 hour. The exposed coupons will be tested for visual appearance and peel	No evidence of blistering, swelling, checking or visible color change. Peel strength shall not be below 7 pounds/in	Composite
Rain Erosion Resistance	Placed on propeller blade and spun at 500MPH in specialized rain erosion test rig.	No Erosion through a 0.012 to 0.014" coating after 150 minute (minimum) and 180 minute (goal)	Composite Air Foils
Electrical Transmission	Transmission efficiency of microwave power tested between several points on coated substrate.	Min electrical transmission of 85, 90 or 95 %	Composite
Surface Resistivity	500-volt megohmmeter used to measure resistivity between several points on coated substrate.	No less than 0.5 megohms nor more than 15 megohms per square	Composite
Weather Resistance	Continuous outdoor weathering for 6 months	No signs of film deterioration such as: chalking, checking, cracking, embrittlement, loss of adhesion or loss of resiliency	Composite
Strippability	Strippable using laser, Flashjet or approved chemical stripper.	Strippable	Composite

Table 2 Additional Desired Performance Properties (ref: MIL-PRF-32239)

Material Property	Test Method	Target Criteria	Substrate
Weather Resistance	Exposure for 3000hrs in a Xenon-Arc chamber that is cycling between 102 minutes of light only and 18 minutes of light and DI water spray	Color change $\Delta E \leq 1$ Adhesion $\geq 4B$ GE Impact Flexibility $\geq 10\%$	Composite Composite 2024-O anodized
Lubricating Oil Resistance	MIL-PRF-23699: Immersion in lube oil for 24 hours at 250±5°F	The coating shall not exhibit any blistering, softening, or other coating defects. Slight staining of the coating is acceptable	Composite
Hydraulic Fluid Resistance (MIL-PRF-83282 & Skydrol)	MIL-PRF-83282: Immersion in hydraulic fluid for 24 hours at 150±5°F; Skydrol: Ref. MIL-PRF-32239 (AF Coating System Specification)	The coating shall not exhibit any blistering, softening, or other coating defects. Slight staining of the coating is acceptable	Composite

Appendix-II

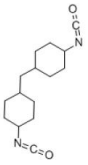
Evaluation of benchmark (isocyanate-based) incumbent Rain Erosion Resistant Commercial Product

ע

Benchmark Product

- We identified with the help of ARL, a benchmark product CAAPCO Cw-4, and evaluated. 2K-PU system

Part A	NCO functional polyester
Solvents	MIBK (12-14%) Xylenes (36-42%) Ethylbenzene (7-12%)
Solid content	45.75%
Free Isocyanate	Bis(4cyclohexylisocyanate) 0.5%
NCO% (total mixture)	1.27
Pigment wt.% (TGA)	17.9% of solids 8.1 % total
Pigment wt.% (Muffle furnace)	16.2% of solids 7.4% total
Approx. PVC	6%
Total NCO eq. wt.	3308
Resin solid NCO eq. wt. (resin=37.41% of total)	1237
Part B	Curing agent Aliphatic amine
Solvent	MIBK (45-90%)
Solid content	54→40→10 (Amine seems to be volatile)
Amine Value (total mixture)	338
Amine eq. Weight	165
Mixing ratio (A/B)	100/4.5
NCO/Amine eq. ratio	1.12
Amine value (amine solid)	??



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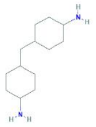

Present in Base

As per, product datasheet

42

Benchmark analysis

CAAPCO Cw-4 : Film Properties

Pot-life	4 h
Curing time (tack-free)	2-3 h
Solid content	45 wt.%
MEK Double Rubs	165±5
Flexibility (1/8" at -56°C)	Pass
Adhesion	5B
Water resistance	Pass
Pencil Hardness	7H
Impact Resistance	Direct: >160 (lb. in) Indirect: >160 (lb. in)
T_g	-23 °C
T_d (50%)	401 °C
Elongation at Break	548%
Tensile Strength	9.42 MPa
Young's modulus	

Appendix-III

UDRI Report on Rain Erosion Testing.

University of Dayton Research Institute

EASTERN MICHIGAN UNIVERSITY
RAIN EROSION TESTING
FINAL REPORT

CRADA Number: 18-061-RX-01
Purchase Order: P0047643
UDRI Report Number: UDR-TR-2021-36
UDRI Project Number: J8V7V2

Prepared by:
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ANAB ACCREDITED ISO/IEC 17025 TESTING LABORATORY

Certificate Number: L1189-1

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March 2021

Approved:

Matthew Rothgeb
Group Leader, UDRI

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1.0 INTRODUCTION

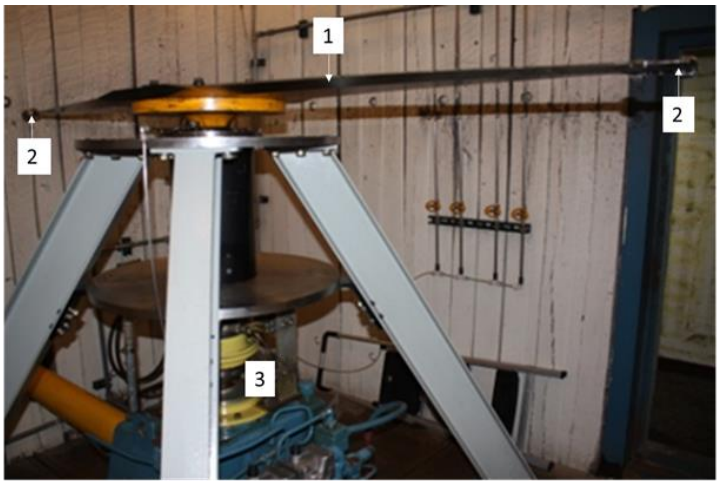
The University of Dayton Research Institute (UDRI), Coatings, Corrosion and Erosion Group (CCEG) performed rain erosion tests at the Air Force Research Laboratory (AFRL) Erosion Test Facility, Building 20A located at Wright-Patterson AFB, Ohio, for Eastern Michigan University on March 2, 2021. The rain erosion testing performed is within the scope of UDRI's ISO/IEC 17025:2017 accreditation.

The objective was to evaluate rain erosion durability of aerospace coating material. This was determined by evaluating the material at simulated rain conditions prescribed by Eastern Michigan University. There were no witnesses to the rain erosion testing due to current Covid-19 restrictions. Ms. LaNay Barley of UDRI was the chief operator for the rain erosion testing.

2.0 RAIN EROSION TEST APPARATUS

The AFRL Rain Erosion Test Facility provides the best laboratory simulation of rain environment for evaluating materials and investigating rain erosion mechanisms. The Rain Erosion Test Facility investigations have been correlated with actual flight test results, taking into consideration the relative ranking of the erosion resistance of materials and the mode of failure of these materials under the influence of raindrop impingement.

The rain erosion test apparatus consists of an eight-foot diameter, double arm blade designed to produce high tip velocities with zero lift and low drag coefficient in **Figure 1**. Duplicate test specimens are mounted at the leading edge tip sections of the double rotating arm. The specimen can be rotated at variable velocities between 100 and 650 mph.



1. Double-Arm Blade 2. Mated Specimen Location 3. Vertical Drive Gear Box

Figure 1: Rain Erosion Test Apparatus

The simulated rainfall is produced by four curved manifold quadrants in **Figure 2**. Each manifold has 24 equally-spaced capillaries. De-ionized water is delivered to the four manifold quadrants simultaneously from a constant-volume water storage tank. Temperature-controlled water then fills the capillaries to produce raindrops.

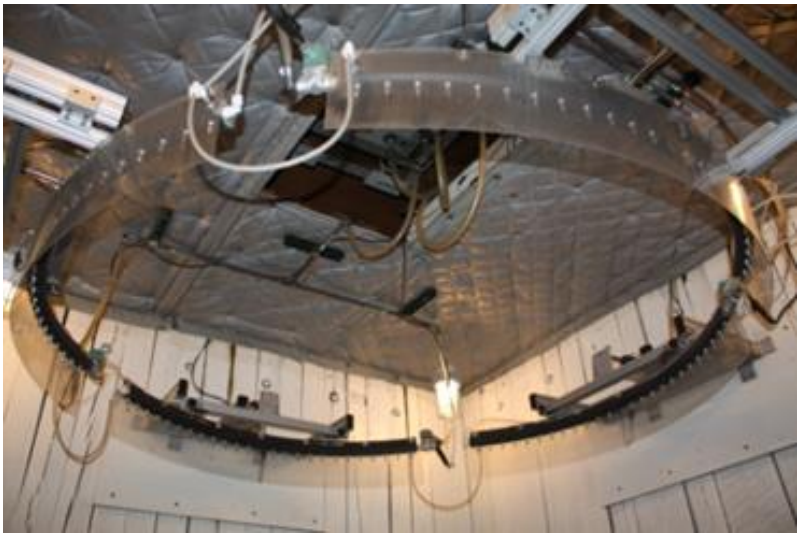


Figure 2: Curved Manifold Quadrants to Simulate Rainfall

Drop size and drop rate are controlled by the water temperature, capillary orifice diameter, and head pressure of the water storage tank. Raindrops from the simulation apparatus impact the test specimens throughout their entire circular path. Drop size and drop rate are approximately 1.8 to 2.2 mm, and 6 to 7 drops per second, respectively.

All functions of the apparatus are controlled and monitored from the control room. Variable speed operation is possible through the operator's manual control. Magnetic pickups and LED strobe lights provide stop motion viewing of the test specimens under actual test conditions. Closed-circuit color cameras and monitors allow the operator to visually observe the test specimens undergoing rain field exposure. Test are digitally recorded and made available to the customer for later study.

2.1 Test Plan

Eastern Michigan University test plan is in **Table 1**. A total of eight (8) coated specimens were tested. All tests were performed at a rain drop size of approximately 2 mm diameter at one-inch

per hour rain rate. The test specimens were tested at 440 mph at impact angle of 90 degrees. The exposure time was until failure or maximum 60 minutes.

Table 1: Eastern Michigan University Test Plan

Number of Specimens	8
Geometry	Airfoil
Speed (s)	440 mph
Impingement Angle	90°
Composition	Aeroglaze 4977 wash primer, non-isocyanate polyurethane topcoat
Run-time	Maximum 60 minutes

2.1.1 Specimen Configuration/Set-up

Figure 3 shows the specimen configuration on the double blade tip at the angle of impact.

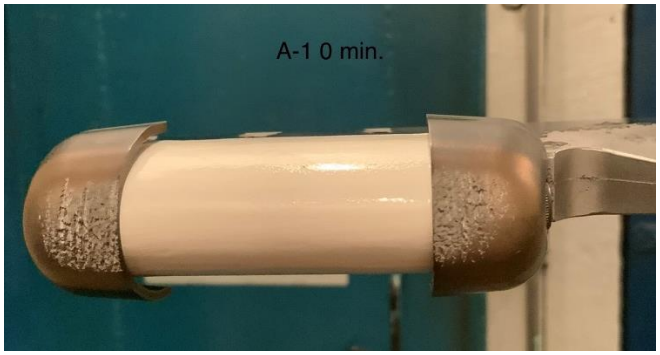


Figure 3: Test Specimen Fixed to Blade Tip at 90° Impact Angle

2.2 Failure Analysis

Specimens were inspected for damage after exposure conditions outlined in the test plan were achieved and characterized by using terms such as pitting, cratering, cracking, material loss or fracture, core-crushing, and delamination. The evaluations were reported as a function of time during the test run(s). The failure mode was defined as eroded to substrate or substrate exposed. Failures near the specimen holder edges are usually taken as anomalies. A video of testing was provided for detailed analysis.

3.0 RESULTS

Table 2 presents a summary of results. The results apply to the samples as received and only to those tested. All the samples experienced erosion failure within 11 minutes of exposure. A representative photo of Sample ID 1-2 is shown in **Figure 4.** For more details, the generated AFRL/UDRI Rain Erosion Test Data Report is in the Appendix.

Table 2: Summary of Rain Erosion Results

Sample ID	Speed (mph)	Exposure (min)	Impact Angle (90°)	Results
1-1	440	11	Airfoil	Erosion Failure
1-2	440	11	Airfoil	Erosion Failure
2-1	440	9	Airfoil	Erosion Failure
2-2	440	9	Airfoil	Erosion Failure
1-3	440	10	Airfoil	Erosion Failure
2-3	440	10	Airfoil	Erosion Failure
1-4	440	9	Airfoil	Erosion Failure
2-4	440	9	Airfoil	Erosion Failure

Figure 4: Specimen ID 1-2 after Rain Exposure at 440 MPH

4.0 APPENDIX

The AFRL/UDRI Rain Erosion Test Report shows a separate entry for each sample. The first entry line contains the AFRL ID assigned for sample tracking; the User ID was assigned by Eastern Michigan University to each sample; specimen configuration provides the sample shape and angle mounted; the date the sample was tested; the velocity at which sample travelled through simulated rain field and duration in minutes. The second line of each entry is a description of the sample. At the bottom of each entry is a comment section for the operator observations of the test.

AFRL/UDRI Rain Erosion Test Report

Tech Initials: LB **Facility User: Eastern Michigan universit** **Account #: J8V7V2**

Test Witnessed by: N/A

AFRL ID	User ID	Specimen Configuration	Test Date	Velocity (MPH)	Exposure (min.)
R11962	1-1	AF	02-Mar-21	440	11

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

1 min. center leading edge coating penetration / 3 min. center leading edge multiple coating penetration sites / 10 min. center leading edge additional coating penetration, substrate exposed / 11 min. inboard, outboard leading edge additional (add'l) coating penetration, add'l substrate exposed / erosion failure

R11963	1-2	AF	02-Mar-21	440	11

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

2 min. center outboard coating penetration / 4 min. center coating penetration / 11 min. upper and lower center leading edge coating delamination substrate exposed / erosion failure

R11964	2-1	AF	02-Mar-21	440	9

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

6 min. lower center leading edge coating penetration / 7.5 min. add'l coating penetration center leading edge, substrate exposed / 9 min. inboard, outboard leading edge add'l coating penetration, add'l substrate exposed / erosion failure

R11965	2-2	AF	02-Mar-21	440	9

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

5 min. lower outboard, center leading edge coating penetration / 5 min. center inboard leading edge coating penetration / 9 min. add'l coating penetration, center leading edge, substrate exposed / erosion failure

R11966	1-3	AF	02-Mar-21	440	10

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

1 min. center leading edge coating penetration / 4 min. upper center leading edge multiple coating penetration sites / 10 min. outboard leading edge coating penetration, center leading edge additional coating penetration, substrate exposed / erosion failure

R11967	2-3	AF	02-Mar-21	440	10

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

1 min. center leading edge coating penetration / 2 min. coating penetration across leading edge / 4 min. add'l coating penetration across leading edge / 7 min. add'l coating penetration across leading edge substrate exposed / 10 min. add'l coating penetration across leading edge add'l substrate exposed / erosion failure

AFRL/UDRI Rain Erosion Test Report

Tech Initials: LB **Facility User: Eastern Michigan universit** **Account #: J8V7V2**

Test Witnessed by: N/A

AFRL ID	User ID	Specimen Configuration	Test Date	Velocity (MPH)	Exposure (min.)
R11968	1-4	AF	02-Mar-21	440	9

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

6 min. center leading edge coating penetration / 7 min. add'l coating penetration center leading edge / 8 min. central inboard leading edge coating penetration / 9 min. center leading edge add'l coating penetration, substrate exposed / erosion failure

R11969	2-4	AF	02-Mar-21	440	9

No pretreatment, Aeroglaze 4977 wash primer, Non-isocyanate polyurethane topcoat

Comments

1 min. center leading edge coating penetration / 2 min. center inboard, center outboard leading edge coating penetration / 4 min. add'l coating penetration across leading edge / 5 min. add'l coating penetration along leading edge, substrate exposed / 9 min. add'l coating penetration along leading edge, add'l substrate exposed / erosion failure