Design, formulation and synthesis of UV/Thermal dual cure, bio-based polyurethane coatings

Ozlem Kubra Akdogan

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Design, Formulation, and Synthesis of UV/Thermal Dual Cure, Bio-Based Polyurethane Coatings

by

Ozlem Kubra AKDOGAN

Thesis
Submitted to the Department of Polymers & Coatings Technology
Eastern Michigan University
in partial fulfilment of the requirements for the degree of
MASTER OF SCIENCE
in
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Vijay Mannari, Ph.D, Chair
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Ypsilanti, Michigan
Abstract

In the present work, polyurethane resins have been synthesized using soybean oil based polyols (> 80% bio-renewable content) as a primary component. To overcome some of the limitations associated with soft and flexible structure of soy-based polyols, the resin has been designed with two unique set of functional groups –OH and acrylate, as a means of crosslinking sites. Such resin system can be cured by two independent cure mechanisms – (a) thermal (or ambient) curing of –OH groups by use of isocyanate cross-linkers, and (b) by UV-curing of acrylate functional groups using appropriate photoinitiators. Thus, this dual-curable system can provide a means to control the degree of curing and hence the thermo-mechanical properties and performance of these coatings. The study shows that dual-cure coatings with high bio-based content can be successfully formulated and that their properties can be varied by controlling the degree of cure reactions.
# Table of Contents

Abstract .................................................................................................................................................. ii

List of Tables ......................................................................................................................................... v

List of Figures ......................................................................................................................................... vi

Chapter 1: Introduction ......................................................................................................................... 1

Background ........................................................................................................................................... 1

Problem Statement ................................................................................................................................. 1

Nature and Significance of the Problem ............................................................................................... 1

Purpose and Objectives of the Study ..................................................................................................... 3

Research Questions ............................................................................................................................... 3

Review of the Literature ......................................................................................................................... 4

  Bio-based & green coatings .................................................................................................................. 8

  Sustainable cure process ..................................................................................................................... 10

Chapter 2: Methods ............................................................................................................................... 12

Methods ................................................................................................................................................ 12

  Design and development of the dual-curing coatings ........................................................................ 12

  Raw material selection ....................................................................................................................... 13

  Determination of molecular weight and molecular weight distribution (GPC) ......................... 15

  Differential scanning analysis (DSC) ................................................................................................. 15
Fourier transform infrared spectroscopy (FT-IR) ................................................................. 15

Coatings film characterization ........................................................................................... 16

Chapter 3: Experimental .................................................................................................... 18

Raw Materials .................................................................................................................... 18

Research Design ................................................................................................................. 18

Synthesis of Polyester Acrylate Oligomer (PEA) and Epoxy Resin-Itaconic Acid Polyester
Oligomer (EIP) .................................................................................................................. 19

Preparation of Two Component Dual Cure Coatings Compositions ..................................... 21

Curing Conditions .............................................................................................................. 22

Chapter 4: Results and Discussion ..................................................................................... 24

Design and Synthesis of Oligomers .................................................................................. 24

Cure Sequence and Characterization ................................................................................ 25

Chapter 5: Conclusion ...................................................................................................... 31
List of Tables

Table 1: Composition of the dual-cure bio-renewable based coatings .................................................. 22
Table 2: Viscosity of each coating composition .................................................................................. 22
Table 3: Characterization of the PEA-based coatings cured with single and sequential methods ............................................................................................................. 27
Table 4: Characterization of the EIP-based coatings cured with single and sequential methods ............................................................................................................. 28
Table 5: The extent of cure of the PEA-based coatings cured with single & sequential method ............................................................................................................. 28
Table 6: The extent of the cure of the EIP-based coatings cured with single & sequential method ............................................................................................................. 29
List of Figures

Figure 1: Chemical structure of some representative chain extenders ........................................ 5
Figure 2: Schematic representation of polyol preparation a) polyether polyol (PETP)
          b) polyester polyol (PESP).............................................................................................. 6
Figure 3: Schematic representation of isocyanate group ............................................................. 6
Figure 4: Some representative aliphatic and aromatic isocyanates ............................................. 7
Figure 5: Schematic representation of isocyanate reactions with: a) water, b) amine, c) alcohol,
          d) self-addition polymerization-1 and e) self- addition polymerization-2......................... 8
Figure 6: Representation of dual cure mechanisms ..................................................................... 13
Figure 7: Synthesis of polyester acrylate Oligomer (PEA) ......................................................... 20
Figure 8: Synthesis of epoxy resin-Itaconic acid polyester oligomer (EIP) ................................. 21
Chapter 1: Introduction

Background

While bio-based renewable resources can be excellent alternatives to non-renewable counterparts considering climate change and governmental regulations, there are still some inherent drawbacks of using bio-based materials in coatings. Agro-based materials have inconsistent compositions based on season, weather, irrigation, etc., and that poses a significant challenge. Among other challenges are the cost of collection, purification, finding markets for by-products. Another major consideration is supply chain issues of availability of such bio-based materials in large quantities for large scale usages. These challenges and their appropriate solutions will shape the future growth of these sustainable materials. Value addition of these bio-based materials via chemical modifications is a very promising route to overcome many aforementioned challenges and making them competitive vis-a-vis petro-based raw materials.

Problem Statement

To the best of our knowledge, dual-cure, bio-based coatings have not been sufficiently explored by the researchers. In consideration of synergist effect of using dual-cure and bio-based materials, there is a need to study these systems.

Nature and Significance of the Problem

The evaluation of risk assessment analysis of raw materials needs attention due to social, environmental, and economic reasons. Throughout the evaluation, the primary issue that the
researchers studying raw materials are facing resource limitations and ecological concerns. For that reason, the demand of “green” work model is increased.

Devoted researchers have come up with different “green” approaches for sustainable innovations. Several attempts have been made to patent ideas that describe concept of dual-cure or bio-based coatings. Unfortunately, providing both features in patented applications are very few.

Chinese researchers patented a biological paint consisting of vegetable oil, turpentine, pine oil, and tangerine oil for architectural applications. They prepared vegetable oil by stillingia, linoleic oil, and tung oil. They claimed the biological paint of the invention is completely made of natural material and that the manufacturing process has no pollution, thereby completely solving the pollution problem of use and production process of the current paint. However, the curing process contains heat to preserve certain temperature for curing that brings an environmental disadvantage to the system (Chinese Patent No. 10201524A, 2010).

Changchun Institute of Applied Chemistry Chinese Academy of Sciences patented ultraviolet thermal, dual-cure, anticorrosive paint based on polyaniline. The formulation mainly consisted of polyurethane polyol component, polyurethane curing agent, and polyaniline. Although they have claimed that the coating formulation does not contain Pb, Cr, Zn, and other heavy metals, or any organic solvent, since the raw materials are not derived from bio-based resources, the system is not sustainable and fully environmentally friendly as they proposed (Chinese Patent No. 10051576A, 2008).

Researchers have used different weight ranges of renewable materials selected from various bio-based components. Armstrong World Inc. blended bio-based components with coatings formulation used for flooring applications (U.S. Patent No. 125918P, 2008). They have
claimed that the novelty of the invention diminishes dependence of limited resources such as fossil fuels while enhancing durability of the flooring application.

**Purpose and Objectives of the Study**

In this study, we have designed and developed a dual curable, high bio-based content (soybean oil content) polymeric binder that promises to meet the performance requirements of industrial coating. Our design strategy for this binder system combines hard and durable epoxy backbone with soft and flexible soy-based structure to obtain good mechanical properties and bio-based balanced content. This oligomeric binder containing two distinct sets of reactive functionalities has been used to cure by two independent mechanisms. The oligomer system contains acrylate and hydroxyl groups capable of a photon-induced cure as well as condensation cure (henceforth mentioned as thermal cure) by using an external cross-linker. These two cross-linking mechanism provide a means for controlling the thermo-mechanical properties of coatings. The study investigates how each cure type contributes to the final cured film’s properties. The study further tries to explore the extent of cross-linking for each type of curing, as well as for the dual-curing, and also in different sequences to understand the underlying mechanism. The study provides a practical insight into the dual-cure process and about its optimization, which will be very useful for further extending such studies to other dual-cure system.

**Research Questions**

This study aims to respond the following questions:

1) What is the extent of cure in each type of cure (i.e., UV-Curing, thermal curing, and dual curing)?
2) How does the bio-renewable, soybean-oil-based materials affect the curing extent of the coatings?

3) How does the cure sequence in dual curing affect the final film properties?

**Review of the Literature**

**Polyurethanes.** Otto Bayer and his colleagues prepared the polyurethane (PU) for the first time by polyaddition of hexane-1,6-diisocyanate (HDI) and 1,4-butanediol (BDO), the 1930s. Their goal was to substitute expensive and scarce natural rubber with an alternative that was cheaper and more abundant.\(^5\) However, the commercialization and acceptance of PU as a binder system for coatings took a long time, mainly due to the very high reactivity and toxic and hazardous nature of isocyanates, one of the important components for making PU. \(^6\)–\(^9\) The challenge therefore, was to develop safe and efficient methods for handling and making isocyanate compounds amenable for their use in coatings. Within the following years, the use of PU became widespread in various applications from protective coatings to industrial finishes. The reason for success was mainly driven by some remarkable properties of the PU such as flexibility, light fastness, softness, and toughness, combined with excellent long durability of their films. \(^5\),\(^10\)–\(^12\) As an illustration of the widespread applications of polyurethanes, consider the paper industry adopted the attractive characteristics of PU to diminish the number of paper slices without compromising the papers durability, resistant to oil, and grease control.\(^13\) Another example in this regard could be contribution of PU coatings to the production of sulfur mustard (SM) gas-resistant garments that are widely used in military applications.\(^14\)

Advancements in technology of synthesizing PU with various mechanical and physical properties brought significant advantages that allowed to produce high-performing materials. The ability to modify the final physical and mechanical properties by varying the ratio of hard
and soft segments, as well as the chemical composition of their building blocks allows for a myriad of applications.\textsuperscript{15-17} Chain extenders and isocyanates are categorized as hard segment, while polyols are soft segment category in PU formulation. Hybrid compositions containing sequences of such segments would enhance the overall performance.\textsuperscript{18-20}

In general, PU resins are prepared by a step-growth polymerization process using polyol and isocyanate as primary ingredients. Catalysts are frequently added to accelerate the polymerization reactions. Polyols or macro glycols\textsuperscript{21} are reactive species in the PU synthesis. They are categorized by their molecular weight (MW). Low molecular weight (LMW) polyols such as neopentyl glycol and glycerol (Fig. 1) are called monomeric polyols and are used as chain extenders, while high molecular weight (HMW) counterparts are called polymeric polyols and are utilized as primary building blocks in PU synthesis. MW and functionality of the polyol determine rigidity and elasticity of the PU, so polyol has noticeable impact on the characteristics of the final PU properties.\textsuperscript{22} Consequently, choosing polyol for PU synthesis is very critical to reach the desired properties. Polyols used for coating applications are typically liquids consisting of at least two functional groups. Polyester polyol (PESP) and polyether polyol (PETP) are considered as the most prominent examples of the polyols.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{Chemical structure of some representative chain extenders}
\end{figure}

\textbf{PESP synthesis is performed by polyaddition reaction of acids and alcohols. However, synthesis of PETP requires organic oxides as well as initiators that contains active hydrogen}
atoms (Fig. 2). Consumption of PETP is higher than PESP worldwide due to the higher thermal stability and solvent resistance, however, it is much more expensive than PETP.  

![Chemical structure of polyether polyol (PETP) and polyester polyol (PESP)](image)

Polyisocyanates represent another important group of PU building blocks. They are electrophilic compounds containing reactive isocyanate group, where carbon atom attached to two electronegative atoms-nitrogen and oxygen---making carbon atom especially electrophilic, as shown in Fig. 3.

![Chemical structure of isocyanate group](image)

This reactive species are classified by the number of isocyanate groups in the backbone such as -mono, -di and -poly isocyanates. In addition, the classification for morphological structure is made with the position of -NCO group to an aromatic ring. Compounds containing direct attachment of -NCO group to an aromatic ring are called aromatic isocyanates, but when attached to a carbon atom of an aliphatic system, they are called aliphatic isocyanates. The most prominent differences between isocyanates are their reactivity and outdoor durability. Aromatic isocyanates are more reactive than aliphatic ones; however, they are more sensitive to photo-
degradation when exposed to sunlight (UV irradiation). Consequently, characteristic properties of isocyanates guide their selection for a specific end-use application. Aromatic isocyanates are preferred for indoor and primer applications, while aliphatic isocyanates are mostly used for the applications that require UV stabilization as well as good color retention and film clarity. Some typical monomeric isocyanate compounds used in coatings are shown in Fig 4.

![Diagram of isocyanate compounds](image)

**Figure 4:** Some representative aliphatic and aromatic isocyanates.

As demonstrated in Fig. 5, isocyanates can react with nucleophilic substances such as water, amine, and alcohols, among many others. Carbon dioxide, urethane and urea are produced in these reactions, respectively. In addition, isocyanates can also react with themselves through a so-called self-addition polymerization to form cyclic compounds (Fig. 5, e).
Figure 5: Schematic representation of isocyanate reactions with: (a) water, (b) amine, (c) alcohol, (d) self-edition polymerization-1 and (e) self-addition polymerization-2

Consequently, advancements in science and technology allowed researchers to control the chemistry of PU using versatile raw materials. Unlimited number of backbone designs are offered by a wide selection of hard and soft segments to achieve the desired properties for a broad spectrum of applications. Longitudinal studies have proven that the properties of the segmented PU strongly depend on the chemistry of hard and soft segments and their ratios. As a result, chemical structures and the ratio between hard and soft segments play a vital role in preparation of tailor-made PU. To optimize the final performance, it is important to examine the raw materials very carefully and design functional coatings with controlled properties and performance.

Bio-based & green coatings. In the recent years, there has been tremendous awareness, understanding and efforts to use materials and processes that are sustainable over the long term.
If we look at the value chain of synthetic polymer-based products, such as coatings, most of our raw materials are dependent on fossil petroleum resources that are finite and hence they are unsustainable. In the past few decades, significant effort has been successfully made to reduce volatile organic compound (VOC) contents. While the priority of the coatings industry has shifted based on regulations, formulators and business owners started to think about how to meet requirements with lowering volatile organic compounds (VOC) and hazardous air pollutant (HAPS) in formulation so as to reduce ozone production. Despite substantial progress and implementation of many compliant technologies, our contemporary coating materials still heavily depend on petro-based feedstock, which contribute to much higher carbon foot prints of the products compared to if they are made from “green” materials.

Bio-based, specifically agro-based annually renewable materials, present a very interesting class of materials with potential for replacing petro-based resources in polymer based industries. Soybean is an important source of oil and US is the largest producer. Total production of soybean oil reached to 338.004 thousand metric tons in December 2016 worldwide according to United States Department of Agriculture report. A substantial quantity of soybean oil, after human consumption, is available for industrial use. Being a triglyceride with desirable unsaturation, a number of chemical modifications are possible for its modification. Soybean oil is very promising and has already being used as a bio-based material in coatings, with significantly lower carbon footprint. While soybean and similar agro-based oils have been in use for many decades, the performance of such materials are frequently sub-par, mainly due to their inherent soft structure.

In this research, we have successfully attempted to develop a high bio-based content coating system that can be cured to achieve very good (comparable to petro-based counterparts)
thermo-mechanical properties. We have tried to achieve this by designing polymeric resin with two distinct set of reactive functionalities---acrylate and hydroxyl. Using dual-cure chemistry, the coatings based on these binders are cured under two completely independent cure mechanism. The –OH groups are cured using isocyanate-type cross-linkers by condensation or step-growth type curing (referred to as thermal curing hereinafter), while acrylate groups are polymerized by UV-initiated radical type cross-linking. The coatings are characterized for their extent of cure and for their properties and performance.

**Sustainable cure process.** In addition to using bio-renewable materials, another route to address the sustainability is to develop and implement a sustainable and efficient cure processes. Through reducing environmental hazardous components as well as providing fast and efficient curing with no or low emissions, radiation curing enables a sustainable curing process, which brings “green” ideology to the coatings system.

Radiation cure technology has been very attractive to synthetic polymer chemistry researchers mainly due to fast reactions and absence of volatiles. The two important extant technologies are: electron beam (EB) and ultraviolet (UV) curing techniques. The UV curing technology typically relies on using photon-induced generation of free-radicals that initiates chain polymerization of reactive components whereas EB employs ionized irradiation of high energy electrons to initiate chain polymerization reaction. Due to high voltage, vacuum, operation and capital cost requirements in EB cure technology, UV cure technology has more market share in coatings application. EB and UV technologies have low energy consumption (compared to conventional thermal curing process), low overall costs, rapid curing, and suitable for heat sensitive substrates. However, UV cure process has many inherent challenges including limited penetration depth that limits applied film thickness, difficulty in curing three-dimensional
products, restrictions on use of certain pigments or additives (UV-absorbing type). The free-radical type curing is also significantly affected by oxygen inhibition at and near the surface. Also, in general, UV-curing process invariably produces cured films with volume shrinkage leading to poor adhesion. Coating composition and cure process must be optimized to achieve high functional group (typically acrylic) conversion so as to get optimum film performance.⁵⁰,⁵³–⁵⁵

One of the important limitation is the issues of inadequate curing on three-dimensional substrates, where the recessed areas (where UV light cannot reach) are under cured or not cured at all. To address this issue without compromising the desired performance and production efficiency features of UV cure technology, the dual-cure systems have been introduced. In dual-cure systems, the coatings after applications are cured, in addition to the cure initiated by UV-exposure, by another independent-cure mechanism that does not require UV-source.⁵⁶–⁶¹ This cure mechanism (that does not need UV source) is often referred to as “dark cure.” Thus, dual-cure systems enables successful application of such coatings onto three-dimensional substrates. The dual-cure systems may have a variety of dark-cure mechanisms. These include thermal curing, oxidative curing (air-drying), moisture curing, and/or condensation-curing under ambient temperature of UV-curing process. Depending upon the dark-cure mechanism, the two cure-processes can be carried out successively (in different order) or in some cases, as in case of ambient temperature cure, simultaneously. The sequence of curing (UV-curing first followed by dark-curing or vice-a-versa), may have substantial differences in the extent of cure and hence the properties of the cured coatings. Therefore, detailed study of these variables is required to optimize the dual-cure process.
Chapter 2: Methods

Methods

**Design and development of the dual-curing coatings.** In the present research, we have aimed to design and develop sustainable dual-cure coating system based on bio-based raw materials. The two curing mechanisms of this system are (a) UV-initiated free-radical type chain-growth polymerization acrylate functional groups, and (b) ambient temperature cure step-growth polymerization of isocyanate and hydroxyl functional groups. Specifically, the oligomer synthesized for dual-cure system is comprised of acrylate and hydroxyl functional groups. The coating compositions are prepared by mixing the dual cure oligomers with polyisocyanate cross-linker. The compositions with varying oligomer types have been applied and dual cured in different sequence to form acrylic/polyurethane hybrid films. The following study has focused on the effect of cure sequence on the extent of cure and film properties (Fig. 6). The results of this study has provided very useful insight into the understanding of the mechanism of curing. The outcome of this research will help coating formulators not only with understanding of the cure mechanism but in optimization of the cure process.
Figure 6: Representation of dual cure mechanisms

**Raw material selection.** A 2,2-Dimethyl-1,3-Propanediol (Neopentyl glycol, NPG) has been used as a building block in the synthesis of polyester polyols used for deriving polyurethane coatings. Although Phthalic anhydride (PA) is widely used for making a variety of resins in coatings industry, it has significant odor and could cause serious hazards to human health. Itaconic acid, on the other hand, is a bio-based compound derived from sugar nominated as one of the thirty top value-added chemicals by the United States Department of Energy in 2004. Itaconic acid could be used as a primary di-acid component in synthesis of polyester polyols. An old example of this reaction was reported by Kopecek research group, who reacted itaconic acid polyethylene glycol (PEG) using one of the strongest acids---tosylic acid---as a catalyst to produce polyester for pharmaceutical applications. Itaconic acid has also
been highly utilized in polymers and coatings field, and the resulted polymers are reported to have have impressive tensile properties.\textsuperscript{30-32}

Epoxy resins of diglycidyl ether Bis-phenol-A (DGEBA) are widely employed in coatings, adhesives, and composite industries.\textsuperscript{2} These resins are typically prepared by condensation of Bisphenol-A (BPA) and epichlorohydrin, followed by dehydrochlorination, and provide desirable mechanical strength and adhesion properties. Significant environmental advantages can be gained using bio-based epichlorohydrin derived from glycerin that is now commercially available. BPA is a white crystalline compound used in making epoxy resins for coatings and adhesives where good thermal and mechanical properties, and chemical resistance is required. However, BPA is reported to cause severe negative impacts both on the human health and environment.\textsuperscript{33–37} Due to excellent properties of BPA, researchers are working to find safer processes of production through utilization of alternative compounds, which may eliminate the harmful effects of BPA.

Acrylated epoxidized soybean oil (AESO) is a commercial product derived from soybean oil, which is considered to be a proper alternative for fuel-based raw materials used in coatings composition. Because of its soft segment structure, as well as long and unsaturated polymer chains, AESO can bring significant advantages to the coating system. Improving flexibility, elongation, and impact and scratch resistances, soybean derivatives were studied by many research groups worldwide.\textsuperscript{38–49} Unfortunately, using only AESO in formulation brought insufficient physical and mechanical properties such as low modulus, and poor adhesion to the substrate, which has forced the scientists to develop new systems to promote better adhesion and flexibility using AESO.
**Determination of molecular weight and molecular weight distribution (GPC).**

Malvern Viscotek 270 Gel Permission Chromatography (GPC) equipped with refractometer, right angle light scattering and viscometer detectors on a set of four columns were used to analyze molecular weight and molecular weight distribution. Filtered (0.1 μl) samples (0.1-0.2 mg in 10 mL THF) were manually injected into the system. THF was used as the eluent and permeated through the columns at the flow rate of 1 mL/min. The data collected were processed and analyzed using OmniSEC 4.7.0 software.

**Differential scanning analysis (DSC).** Mechanical Analyzer Q 2000 TA Instrument (DSC) with LNCS (liquid nitrogen cooling system) was used to analyze dual-cured films of coatings. To calculate sample heat flow, an empty aluminum T zero pan sealed with a T zero aluminum lid was used as reference. The sample mass for these measurements was about 5-7 mg. Each cross-linked film was encapsulated in a T zero aluminum pan, using T zero standard aluminum lid (TA Instruments). Tg of the films were determined from analysis of DSC thermogram. The samples were scanned on a Heat/Cool/Heat cycle in which each sample was initially heated to 100 °C and held isothermally for 5 min. The samples were then cooled to 0 °C and held isothermally for 5 min before heating again to 100 °C. Heating and cooling rates were 10 °C/min. Crystallization point was obtained from the cooling portion of the cycle while the Tg, and melting point was obtained from the second heating portion of the cycle.

**Fourier transform infrared spectroscopy (FT-IR).** Cure characterization of samples was carried out by FT-IR spectroscopy in the operating range between 400 and 4000 cm⁻¹ using Tensor 27 FTIR analyzer (Bruker). The representative spectra for wave number versus transmission were obtained using Opus 4.5 software. Percent conversion measurements were made by calculating the peak area ratio of the specific peak (analyte) to an internal standard.
peak. The reduction in the intensity of the peak is used to determine the amount of the functional group that is converted to cross-links in the sample during the curing process. The extent of cure has been calculated as followings:

$$\% C = \left( \frac{Ab(\text{analyte}_0/\text{standard}_0) - Ab(\text{analyte}_t/\text{analyte}_t)}{Ab(\text{analyte}_0/\text{standard}_0)} \right) \times 100$$

where Ab is the area of absorption band or height, “0” indicates before cure while “t” corresponds after cure.

Carbonyl peak has been used as the internal reference peak in calculation of % cure extent for both acrylate and isocyanate groups. For determination of extent of thermal cure (NCO/OH reaction), absorption peak corresponding to -NCO at 2260-2675 cm$^{-1}$, and for UV-cure of acrylate peak corresponding to stretching vibration of CH$_2$=CH- at 1630-1650 cm$^{-1}$ was used.

**Coatings film characterization.** The cured coatings were evaluated for adhesion (ASTM D-3359), pencil hardness (ASTM D-3363), pendulum hardness (ASTM D4366), impact resistance (ASTM D2794 – 93), and chemical resistance (MEK double-rub test, ASTM D4752), as per standard test methods.
**Mechanical properties.** Adhesion test of applied coated surfaces was examined by cross-cut (crosshatch) test method to measure resistance of paints to separation from the substrate.

An impact resistance test was carried out by using BYK Gardner impact tester, using 2 lb weight from maximum height of 80 cm and weight dropped onto the coated surface (direct impact) and on the opposite side of the panel with reference to the coated surface (reverse impact).

A pendulum hardness test was carried out by using Koenig type of pendulum, (Sheen Instruments). The moment when needle made contact with the surface and it stopped was read from rocker counter.

A pencil hardness test was used to study the hardness of coated panels. Pencils ranging from 6B to 6H were used for the test.

**Chemical properties.** Solvent resistance of coating was evaluated by using methyl ethyl ketone (MEK) as a solvent. The test was carried out by rubbing the coating with a cheese cloth saturated with the MEK solvent, attached onto a 2 lbs hammer head. One back-and-forth scrubbing the surface was considered as a cycle. Actual failure point assigned where the pinholes could be observed at every end of the 20 cycles. The maximum cycle that applied for a panel was 200.
Chapter 3: Experimental

**Raw Materials**

A liquid epoxy resin (DER 331) was procured from Dow Chemical Company. Itaconic acid (IA), glycidyl methacrylate (GMA), triphenylphosphine (TPP), hydroquinone (HQ), dibutyltin dilaurate (DBTL), tetrahydrofuran (THF) neopentyl glycol (NPG) and phthalic anhydride (PhA) were purchased from Sigma-Aldrich, USA. Dipropylene glycol diacrylate (DPGDA) and epoxidized soybean oil (AESO, EBECRYL 860) were supplied by Allnex. Photoinitiators- Irgacure 819 and 187 were kindly received from BASF. Isocyanate cross-linker Desomdur 3900 was supplied by Covestro. All the materials were used as received. TRU cold rolled steel test panels (6” × 4” × 0.032”) were received from ACT test panel technologies, USA.

**Research Design**

Polyester-based pre-polymer was prepared via a two-step procedure: the esterification reaction between neopentyl glycol (NPG) and phthalic anhydride (PA) to produce acid functional prepolymer, followed by reaction with glycidyl methacrylic acid (GMA) to form acrylated polyester oligomer (PEA) as demonstrated in Fig. 7. Fig. 8 represents the other esterification reaction between epoxy resin (ER) and itaconic acid (IA), followed by the acrylate functionalization reaction of acid-functional epoxy polyester (using GMA) to form acrylated epoxidized polyester oligomer (EIP).
Synthesis of Polyester Acrylate Oligomer (PEA) and Epoxy Resin-Itaconic Acid Polyester Oligomer (EIP)

The reactions were conducted in 500 mL three-neck flasks equipped with a mechanical stirrer, nitrogen inlet, and thermocouple. For PEA, 111.08 g (1.5 equivalents) of PA and 52.08 g (0.75 equivalents) of NPG were added to the flask. After a nitrogen purge, 0.2% HQ was added along with 1% TPP and dissolved in epoxy resin into the flask and the temperature was raised to 150 °C. Reaction was monitored every 30 minutes. Heating was stopped when expected acid (164.32) and was reached. For EIP, 168.30 g (0.90 equivalents) of epoxy resin was added to the flask. After a nitrogen purge, 0.2% HQ, added along with 1% TPP and dissolved in epoxy resin into the flask. Furthermore, 117.09 g (1.80 equivalents) of itaconic acid was added and the temperature raised to 120 °C. The reaction was monitored every 30 minutes. Heating was stopped when expected acid (147.57) and epoxy (0.14) value were reached.

For PEA, 67.93 g (0.48 equivalents) of glycidyl methacrylate (GMA) was added in the same flask, and the reaction temperature was dropped to 120 °C. The reaction was stirred at 120 °C and monitored every 30 minutes until an acid value of below 9 was reached. The light-yellow color mixture was collected and stored in glass bottle. For EIP, 106.72 g (0.75 equivalents) of glycidyl methacrylate (GMA) was added to receive EIP. The reaction was stirred at 105 °C and monitored every 30 minutes until acid value of below 9 was reached. The pale-yellow color mixture was collected and stored in glass bottle.
Figure 7: Synthesis of polyester acrylate oligomer (PEA).
**Preparation of Two Component Dual Cure Coatings Compositions**

Two component coating compositions for dual cure were prepared by proper mixing of the components (EIP, PEA, AESO, and Desmodur 3900) as per the mixing ratio under a mechanical stirrer for 10 minutes. The compositions are summarized in Tables 1 and 2.
Table 1: Composition of the dual-cure bio-renewable based coatings

<table>
<thead>
<tr>
<th>Coating system</th>
<th>Composition</th>
<th>RRM%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PEA</td>
<td>EIP</td>
</tr>
<tr>
<td>PEA</td>
<td>48.57</td>
<td>-</td>
</tr>
<tr>
<td>PEA-AESO</td>
<td>16.67</td>
<td>-</td>
</tr>
<tr>
<td>EIP</td>
<td>-</td>
<td>41.23</td>
</tr>
<tr>
<td>EIP-AESO</td>
<td>-</td>
<td>13.54</td>
</tr>
</tbody>
</table>

As summarized in Table 2, all the coating compositions demonstrated relatively low viscosities, which facilitated the application of the coatings.

Table 2: Viscosity of each coating composition

<table>
<thead>
<tr>
<th>Coating System</th>
<th>Viscosity (Pa. s @ 25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEA-AESO</td>
<td>15.28</td>
</tr>
<tr>
<td>PEA</td>
<td>11.27</td>
</tr>
<tr>
<td>EIP-AESO</td>
<td>13.62</td>
</tr>
<tr>
<td>EIP</td>
<td>9.34</td>
</tr>
</tbody>
</table>

Curing Conditions

The two component coatings formulations were applied onto test panels using a BYK automatic drawdown application instrument, with bar #22. All the coatings were applied with a wet film thickness (WFT) of 2 mils and were cured by one of the following methods:
1. Only condensation: The condensation curing (via NCO: OH react.) was carried out by application of coatings and placing them in a dark place for 7 days. The coatings were then characterized after seven days period.

2. Only UV curing: UV curing was carried out by exposing panels to a UV source (Fusion UV, United States, F300S) with a H bulb (13 mm) at (~2600 mJ/cm²) intensity (measured by Janoptik UV radiometer). The films were evaluated within half an hour.

3. UV curing followed by condensation: Condensation cure was continued according to Method 1 right after the completion of UV curing according to Method 2.

4. Condensation followed by UV curing: Method 2 was performed right after the completion of condensation curing (7 days).
Chapter 4: Results and Discussion

Design and Synthesis of Oligomers

Our goal in this study was understanding the effect of the combination of hard acrylated oligomers with soft bio-based materials (containing high acrylate content) on the film properties as well as cure extent. EIP was synthesized via the reaction of itaconic acid with DGEBA, followed by introducing acrylate functionalities using GMA. PEA was prepared through reaction of neopentyl glycol and phthalic anhydride, followed by reaction with GMA to achieve relatively low molecular weight oligomers (~800 g/mol). Therefore, EIP and PEA oligomers contain both acrylic and -OH groups, which allow UV curing and condensation polymerization, respectively. The number average molecular weight of PEA was 711, while EIP was 825 g/mole. The molecular weights of the prepolymer have been kept low to make a high acrylate content.

PA was used to take advantage of its properties such as hardness, abrasion resistance, and proper adhesion to plastic and metal surfaces, which can compensate the shortcomings of vegetable oil based soft segment. IA was used for two main reasons: its bio-based nature and double bonds that could undergo UV curing. An inhibitor was utilized to prevent premature polymerization of acrylate during synthesis.

AESO is an acrylated triglyceride with very flexible structure owing to presence of fatty acid chains. The presence of hydroxyl and acrylate functional groups in its structure, combined with its good compatibility with a wide range of oligomers and cross-linkers, make it a good candidate as the soft segment for this dual cure study. Thus, it is expected that addition of AESO to our systems will result in crosslinked film with balanced distribution of soft and hard segment after dual-curing. In this study, AESO was combined in a 05:1 equivalent ratio either to EIP or PEA based systems.
Cure Sequence and Characterization

Another important goal of this study was to formulate dual curable systems and study the effect of the cure sequence on extent of cure and final film properties. The designed systems had two distinct cure mechanisms: (a) free radical polymerization of acrylate groups (b) condensation polymerization of hydroxyls with isocyanates. These two mechanisms were distinct and independent. However, it should be noted that while the acrylate curing can be triggered only by exposure to UV source, hydroxyl and isocyanate condensation reaction could occur as soon as the components are mixed at ambient temperature. Therefore, we studied two different sequences of UV/Thermal and thermal/UV. In the UV/thermal process, the compositions were mixed, immediately applied and cured by exposure to UV source. The primary coating’s properties and functional group characterizations were carried out within 30 minutes of application and curing. It should be noted that some condensation reaction (NCO/OH) may have occurred during this period; we attempted to minimize this reactions by characterization of the film within 30 minutes time. Figure 9 represents FT-IR spectrum for EIP, AESO + EIP, PEA, and AESO + EIP compositions.
FT-IR/ATR and transmissions of the characteristic peak corresponding to acrylate groups could be clearly observed from the absorption peaks corresponding to stretching vibration of CH$_2$=CH- at 1630 -1650 cm$^{-1}$. The disappearance of the isocyanate peaks at 2260-2675 cm$^{-1}$ proved that curing took place. The peak area ratio method was used to calculate the extent of cure while carbonyl peak was chosen as a reference peak.

These films where then allowed to cure 7 days at room temperature and were again characterized for film properties and cure extent. Thermal-only cure process was carried out for 7 days at room temperature. For thermal/UV cure process, the coatings were applied and left in a dark place for 7 days at ambient temperature, followed by UV curing. The panels were
characterized once after the seven-day period before UV curing and once after it. The results are summarized in Tables 3 and 4. Cure characterization was conducted using FT-IR spectroscopic method. The extent of functional group conversion was calculated by peak area ratio method. The results are demonstrated in Tables 5 and 6.

Table 3: Characterization of the PEA-based coatings cured with single and sequential methods

<table>
<thead>
<tr>
<th>System</th>
<th>EIP composition</th>
<th>EIP+AESO composition</th>
<th>EIP composition</th>
<th>EIP+AESO composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EIP composition</td>
<td>EIP+AESO composition</td>
<td>EIP composition</td>
<td>EIP+AESO composition</td>
</tr>
<tr>
<td>Curing method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pendulum Hardness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEK Rub</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adhesion (Cross-Cut)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Impact Resistance (D/R)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>66</td>
<td>29</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
<td>F</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>75</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>0B</td>
<td>0B</td>
<td>0B</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>40/40</td>
<td>160/100</td>
<td>80/40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60/40</td>
<td>20/20</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2H</td>
<td>3H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>125</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
<td>2B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100/40</td>
<td>40/0</td>
</tr>
</tbody>
</table>
Table 4: Characterization of the EIP-based coatings cured with single and sequential methods

<table>
<thead>
<tr>
<th>System</th>
<th>PEA composition</th>
<th>PEA+AESO composition</th>
<th>PEA composition</th>
<th>PEA+AESO composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV-only + thermal</td>
<td>UV-only + thermal</td>
<td>Thermal only + UV</td>
<td>Thermal only + UV</td>
</tr>
<tr>
<td>Pendulum Hardness</td>
<td>77</td>
<td>100</td>
<td>146</td>
<td>186</td>
</tr>
<tr>
<td>Pencil Hardness</td>
<td>B</td>
<td>2B</td>
<td>3H</td>
<td>3H</td>
</tr>
<tr>
<td>MEK Rub</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>125</td>
</tr>
<tr>
<td>Adhesion (Cross-Cut)</td>
<td>0B</td>
<td>0B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Impact Resistance (D/R)</td>
<td>40/20</td>
<td>90/60</td>
<td>100/60</td>
<td>80/80</td>
</tr>
<tr>
<td>&amp; 60/60</td>
<td>&amp; 60/40</td>
<td>&amp; 120/6</td>
<td>&amp; 120/10</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: The extent of cure of the PEA-based coatings cured with single & sequential method

<table>
<thead>
<tr>
<th>System</th>
<th>PEA composition</th>
<th>PEA+AESO composition</th>
<th>PEA composition</th>
<th>PEA+AESO composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV-only + thermal</td>
<td>UV-only + thermal</td>
<td>Thermal only + UV</td>
<td>Thermal only + UV</td>
</tr>
<tr>
<td>% Acrylate Conversion</td>
<td>65.3</td>
<td>78.37</td>
<td>1.9</td>
<td>6.3</td>
</tr>
<tr>
<td>% NCO Conversion</td>
<td>9.02</td>
<td>9.32</td>
<td>82.37</td>
<td>90.12</td>
</tr>
<tr>
<td>Conversion</td>
<td>92.27</td>
<td>95.82</td>
<td>92.75</td>
<td>95.12</td>
</tr>
</tbody>
</table>
Table 6: The extent of the cure of the EIP-based coatings cured with single & sequential method

<table>
<thead>
<tr>
<th>System</th>
<th>EIP composition</th>
<th>EIP+AESO composition</th>
<th>EIP composition</th>
<th>EIP+AESO composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV-only</td>
<td>UV</td>
<td>UV</td>
<td>Thermal only</td>
<td>Thermal + UV</td>
</tr>
<tr>
<td>UV + thermal</td>
<td>UV-only</td>
<td>UV + thermal</td>
<td>Thermal + UV</td>
<td>Thermal + UV</td>
</tr>
<tr>
<td>% Acrylate conversion</td>
<td>78.70</td>
<td>89.73</td>
<td>2.9</td>
<td>98.14</td>
</tr>
<tr>
<td>% Isocyanate Conversion</td>
<td>8.17</td>
<td>89.27</td>
<td>89.02</td>
<td>96.23</td>
</tr>
</tbody>
</table>

The results demonstrate that, acrylate conversion of the EIP-based composition was higher than PEA-based coatings, while isocyanate conversion showed opposite trends. Regarding PEA system, UV-only method resulted in 65.3% acrylate conversion. This amount was increased by 18.6% and 24.33% in UV/thermal and thermal/UV, respectively. For EIP-based, while UV-only method induced 78.70% acrylate conversion, UV/thermal and thermal/UV resulted in 14.01% and 24.45% more acrylate conversion, respectively. It can be concluded from the results that, in general, thermal cure has a positive effect on acrylate conversion. However, it should be noted that the sequence of the curing significantly affects the final conversion. This might be due the fact that when UV curing is employed first, it partially immobilizes the polymer chains by blocking the radicals inside the matrix due to vitrification, which prevents further condensation polymerization of hydroxyl/isocyanates. On the contrary, when thermal cure is employed first, the chains are still enable to move.

Regarding the NCO conversion, thermal-only cure resulted in 82.17% conversion in PEA system while thermal/UV cure showed 12.6% more. Similarly, EIP system showed 8.09% more isocyanate conversion in thermal/UV cure compared to thermal-only cure.
Moreover, almost in all the cases, both acrylate and NCO conversion increased when AESO added to the systems regardless of the method of curing. This can be explained by increasing the improved mobility of the reactive species due to the high free volume in the AESO structure.
Chapter 5: Conclusion

While coatings based on bio-based raw materials are environmentally friendly alternatives for the petro-based ones, many of them demonstrate poor performances compared to the conventional coatings, which poses a greater challenge in acceptance of such materials by end-users.

The overall objective of the project was to develop an environmentally friendly coating system using “green” approach from raw materials to process. This study has addressed the above-mentioned problem through designing bio-based systems with suitable additional functionalities. In the present work, polyurethane resins have been synthesized with soybean-oil-based polyols as the main building block. Then, in order to overcome the limitations associated with soft and flexible structure of soy-based polyols, the resin systems has been successfully designed and developed with two different functional groups including hydroxyls and acrylates, which could undergo crosslinking using two independent and distinct curing methods: (a) thermal curing of –OH groups with of isocyanate cross-linkers, and (b) UV-curing of acrylate functional groups using appropriate photoinitiators.

Another objective of this study was to understand the effect of each individual cure-type, and specially their sequence on the final film properties. In this regards, the coatings cured by each individual mechanism as well as dual-cure mechanism have been characterized for their performance properties and their extent of cure. NCO and acrylate conversion differences between the UV/thermal curing sequences proved that cure sequence has a significant effect on the final conversion and therefore properties of the coatings. Although UV curing does have its own benefits, a further challenge came to our attention that molecular oxygen inhibits radical polymerization due to open-air conditions. When UV curing was performed first, condensation
polymerization was decreased due to vitrification, while performing thermal curing first had a positive effect on acrylate conversion.
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