ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF SOYBEAN OIL BASED, PHOTOCURABLE, GREEN COATING MATERIALS AND THEIR APPLICATIONS IN WOOD INDUSTRY

M.Sc. THESIS

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MAY 2025

ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

SOYA FASULYESİ YAĞI ESASLI, FOTOKÜRLENEBİLEN, YEŞİL KAPLAMA MALZEMELERİNİN SENTEZİ VE AHŞAP ENDÜSTRİSİNDE UYGULAMALARI

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MAYIS 2025

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Date of Submission : 12 May 2025
Date of Defense : 26 May 2025

To my dear family,

FOREWORD

I would like to thank to my supervisors Prof. Dr. H. Ayşen ÖNEN and Assoc. Prof. Dr. Zehra YILDIZ for sharing their knowledge, colloborative efforts on my research. I present my thanks to Polymeric Materials Research and Development Laboratory (POLMAG) in Istanbul Technical University, Chemical Tests Laboratory and Textile Material Development Laboratory in Marmara University in order to provide me valuable opportunities with precious people. This research was funded by the Research Fund of Istanbul Technical University with the project number of TYL-2023-44665. I also would like to thank to USCO Endüstriyel Çözümler to supply some chemicals for the research.

I am grateful to my lovely family; my mother Hülya OKDEMİR, my father Uğur OKDEMİR, my sister Semiha OKDEMİR and my fiance Sezin HABİBOĞLU for their precious support, patience and encouragement. They provide all opportunities available in my life.

May 2025

Umur İsmail OKDEMİR
(Environmental Engineering)

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ABBREVIATIONS

AV : Acid value

DS : Degree of swelling

ESBO : Epoxidized soybean oil

FTIR : Fourier transform infrared

GF : Gel fraction

HDDA : 1,6-hexanediol diacrylate

^{1}H NMR : Proton nuclear magnetic resonance

IA : Itaconic acid

Irgacure-184 : 1-hydroxycyclohexyl phenyl ketone

NVP : N-vinyl 2-pyrrolidone

T12 : Di-n-butyltin dilaurate

TGA : Thermogravimetric analysis

TMPTMA : Trimethylolpropane trimethacrylate

NVP : N-vinyl 2-pyrrolidone

TPP : Triphenyl phosphine

UV : Ultraviolet

SYMBOLS

°C : Celcius degree
h : Hour
M : Molarity
min : Minute
mL : Mililiter
mL/min : Mililiter per minute
mm : Milimeter
MPA : Megapascal
N/cm : Newton per centimeter
ppm : Partical per million
W : Weight
s : Second
% : Percentage

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SYNTHESIS OF SOYBEAN OIL BASED, PHOTOCURABLE, GREEN COATING MATERIALS AND THEIR APPLICATIONS IN WOOD INDUSTRY

SUMMARY

Surface coatings are very important for many industries, especially in furniture coating areas. It protects the wood from external factors, enhances the durability, and provides better appearance. Due to its usage area as end product, flame resistance is economically and vitally important for wooden products. In order to provide the properties, suitable surface coatings are used.

Modern developments and research in coating technologies are on green technology and environmentally friendly coatings. That is why the UV curing technology is well-used method for coating materials. It does not contain solvents. Therefore, it eliminates the deformation of surfaces, and swelling problems. Curing processes need less time because of the technology, less energy, and low costs. Moreover, it does not waste the water, which is very important when the environmental effects are considered.

In this thesis, it was aimed that the UV-curable oligomers for wood coatings by using epoxidized soybean oil (ESBO) and itaconic acid (IA) are produced. Since ESBO is bio-based oil which is environmentally friendly, it is widely used in the market. By using ring openning reactions, 2 different oligomers (ESBO-IA and ESBO-IA-UA) were synthesized in the research. The oligomers were blended with different types of reactive diluents in different ratios in order to prepare coating formulations. The prepared formulations were applied to MDF wood surfaces after the photo-initiator was added to the formulations. By using UV light, the coatings were cured and different tests were applied to the wood surfaces in order to identify the qualities and performances of the formulations. Then, ESBO-IA and ESBO-IA-UA oligomers were characterized by fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. After, UV-cured free films of the formulations were characterized as mechanical, physicochemical and thermal properties. For mechanical properties; cross cut, water immersion, and taber abbrasion tests were applied. For physicochemical properties, degree of swelling (DS), chemical resistance and gel fraction (GF) tests were used. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were applied to the UV-cured films in order to evaluate the thermal properties.

SOYA FASULYESİ YAĞI ESASLI, FOTOKÜRLENEBİLEN, YEŞİL KAPLAMA MALZEMELERİNİN SENTEZİ VE AHŞAP ENDÜSTRİSİNDE UYGULAMALARI

ÖZET

Yüzey kaplamaları, birçok endüstri için, özellikle mobilya kaplamaları alanında çok önemlidir. Ahşap malzemeleri dış etkenlerden korur, ahşapların dayanıklılığını artırır ve mobilyalara daha iyi bir görünüm sağlar. Ahşap malzemeler dış etkilere karşı hassastır. Su, nem, UV ışınları ve mekanik darbeler gibi faktörler, ahşabın zamanla yıpranmasına neden olabilir. Yüzey kaplamaları, ahşabı koruyarak dayanıklılığını artırır ve ömrünü uzatır. Doğru bir kaplama, ahşabın rengini ve dokusunu koruyarak doğal görünümünü muhafaza etmesini sağlar.

Ahşap kaplamalar aynı zamanda hijyenik ve sürdürülebilir bir çözüm sunar. Özellikle iç mekanlarda kullanılan ahşap yüzeyler, düzenli olarak temizlenmesi gereken alanlardır. Kaplama sayesinde ahşabın gözenekleri kapanır, böylece kir ve bakteri birikimi azalır. Bunun yanı sıra çevre dostu kaplamalar kullanılarak, ahşabın ekolojik ayak izi minimize edilebilir. Ahşap endüstrisinde kullanılan su bazlı veya doğal yağ içerikli kaplamalar, hem sağlıklı bir ortam oluşturur hem de doğaya zarar vermeden ahşabın korunmasını sağlar. Ayrıca yüzey kaplamaları tasarım ve dekorasyon açısından geniş bir çeşitlilik sunar. Ahşap endüstrisinde kullanılan cilalar, vernikler ve boyalar sayesinde farklı renk ve dokular elde edilebilir. Mat, parlak ya da yarı mat bitişlerle ahşaba istenilen estetik kazandırılabilir. Böylece hem geleneksel hem de modern tasarımlara uygun yüzeyler oluşturularak mimari ve dekoratif projelerde ahşabın çok yönlü kullanımına olanak sağlanır.

Kaplama teknolojilerindeki modern gelişmeler ve araştırmalar, yeşil teknoloji ve çevre dostu kaplamalar üzerine odaklanmaktadır. Bu nedenle UV kürleme teknolojisi, kaplama malzemeleri için yaygın olarak kullanılan bir yöntemdir. UV kürleme teknolojisi için üretilen kaplama malzemeleri solvent içermez, bu nedenle uygulanan yüzeylerin deformasyonunu ve şişme problemlerini ortadan kaldırır. UV kürleme teknolojisi, kaplama malzemelerinin hızla sertleşmesini sağlayarak üretim süreçlerini daha verimli hale getirir. Geleneksel kurutma yöntemleri uzun zaman alabilir ve çevresel faktörlerden etkilenebilirken, UV kürleme sayesinde kaplama anında polimerleşerek yüzeye güçlü bir koruma sağlar. Bu yöntem, özellikle ahşap endüstrisinde cilalar, vernikler ve koruyucu kaplamalar için kullanılarak ürünlerin dayanıklılığını artırır ve uzun ömürlü bir sonuç sunar. Bu teknolojinin en büyük avantajlarından biri enerji verimliliğidir. UV kürleme, düşük enerji tüketimiyle çalışarak karbon ayak izini azaltır ve sürdürülebilir üretim süreçlerine katkı sağlar. Geleneksel termal kürleme yöntemlerinde yüksek sıcaklıklar ve uzun kurutma süreleri gerekli olabilirken, UV ışınları sayesinde kaplama saniyeler içinde sertleşir. Böylece

hem zamandan tasarruf edilir hem de üretim maliyetleri düşürülerek çevre dostu bir alternatif sunulmuş olur.

UV kürleme ile uygulanan kaplamalar, yüzeyde üstün mekanik ve kimyasal direnç kazandırır. Sertleşmiş kaplama tabakası çizilmelere, aşınmalara ve kimyasal etkilere karşı yüksek dayanıklılık gösterir. Bu özellik, özellikle mobilya ve parke gibi sık kullanıma maruz kalan ahşap ürünler için büyük bir avantaj sağlar. Aynı zamanda, UV kürlenmiş kaplamalar renk stabilitesini koruyarak uzun süre solmaya veya sararmaya karşı direnç gösterir.

Son olarak, UV kürleme teknolojisi sayesinde kaplama malzemeleri daha güvenli ve çevreye duyarlı hale gelir. Solvent bazlı kaplamalar genellikle uçucu organik bileşikler (VOC) yayarak havayı kirletebilirken, UV kürlenen kaplamalar düşük VOC içeriği sayesinde daha sağlıklı bir çalışma ortamı oluşturur. Bu özellik, hem çalışanların sağlığını koruma açısından hem de çevresel sürdürülebilirlik açısından önemli bir avantaj sağlar. Ahşap endüstrisi başta olmak üzere birçok sektörde UV kürleme teknolojisinin yaygınlaşması, hem kalite hem de çevre bilinci açısından önemli bir gelişme olarak değerlendirilmektedir.

Bu tezde, epoksitlenmiş soya fasulyesi yağı (ESBO) ve itakonik asit (IA) kullanılarak ahşap kaplamalar için UV ile kürlenebilir oligomerler üretmek amaçlanmıştır. ESBO, çevre dostu olan biyobazlı bir yağ olduğu için piyasada yaygın olarak kullanılmaktadır. Bitkisel bazlı ve çevre dostu bir bileşen olan ESBO, düşük toksisiteye sahip olması nedeniyle gıda ambalajlarında ve medikal ürünlerde güvenle kullanılabilir. Ayrıca, yüksek sıcaklıklara ve kimyasal etkilere karşı dayanıklılığı sayesinde endüstriyel kaplamalar ve yapıştırıcılarda da etkili bir katkı maddesi olarak işlev görmektedir. Sürdürülebilir üretim süreçlerine katkı sağlayan ESBO, çevre dostu alternatifler arayan sektörler için önemli bir çözüm sunmaktadır. İtakonik asit de aynı şekilde biyobazlı ve çok yönlü bir kimyasal bileşiktir ve özellikle polimer endüstrisinde önemli bir hammadde olarak kullanılır. Bitkisel kaynaklardan, özellikle şeker bazlı fermantasyonla elde edilen bu asit, çevre dostu alternatifler arayan sektörler için sürdürülebilir bir çözümdür. İtakonik asidin yapısal özellikleri, akrilik ve metakrilik türevleri ile reaksiyona girerek dayanıklı ve esnek polimerler oluşturmasını sağlar. Ayrıca, suya ve sıcaklığa karşı yüksek direnç gösterdiği için kaplamalar, yapıştırıcılar ve biyobozunur plastikler gibi birçok uygulama alanında tercih edilir.

Halka açma reaksiyonları kullanılarak, araştırmada iki farklı oligomer (ESBO-IA ve ESBO-IA-UA) sentezlenmiştir. Bu oligomerler, farklı oranlarda ve çeşitli fonksiyonel gruba sahip olan reaktif seyrelticiler ile karıştırılarak kaplama formülasyonları hazırlanmıştır. Aromatik fonksiyonel gruba sahip olduğu için NVP, bir fonksiyonel gruba sahip olduğu için MA, iki fonsiyonel gruba sahip olduğu için HDDA, ve üç fonksiyonel gruba sahip olduğu için TMPTMA kullanılmıştır. Hazırlanan formülasyonlara foto başlatıcı eklenerek karıştırılmıştır. Daha sonra MDF ahşap yüzeylerine silindir yardımıyla uygulanmıştır. Uygulama yapılırken her ahşap yüzeye eşit miktarda uygulanması için tartım yapılmıştır. UV ışığı kullanılarak kaplamalar belirli bir süre kürlenmeye bırakılmıştır. Formülasyonların kalite ve performanslarını belirlemek için kürlenmiş olan ahşap yüzeylere çeşitli testler uygulanmıştır. Daha sonra, ESBO-IA ve ESBO-IA-UA oligomerleri Fourier transfer kızılötesi (FTIR) ve proton nükleer manyetik rezonans (^{1}H NMR) spektroskopileri ile karakterize edilmiştir. Ardından, UV ile kürlenmiş serbest filmler mekanik, fizikokimyasal ve termal özellikler açısından değerlendirilmiştir. Mekanik özellikler için kesme testi, suya daldırma testi ve Taber aşınma testi uygulanmıştır. Fizikokimyasal özellikler açısından şişme derecesi (DS), kimyasal direnç ve jel fraksiyonu (GF) testleri kullanılmıştır. Termal özellikleri değerlendirmek amacıyla UV ile kürlenmiş filmlere termogravimetrik analiz (TGA) ve diferansiyel taramalı kalorimetri (DSC) analizleri uygulanmıştır.

1. INTRODUCTION

Vegetable oils, which are renewable, sustainable, and biocompatible without toxic elements, present a viable alternative to petroleum-based chemicals with various modifications. Epoxidized soybean oil, a commercially available vegetable oil, stands out as one of the key bio-based oils in the market, as discussed in the literature. Traditional coating methods using water/solvent-based coatings can cause issues like swelling or lifting of wood fibers and corrosion on metal surfaces. To overcome these challenges, a water/solvent-free formulation with the desired functionality is required.

1.1 Purpose of Thesis

Surface coatings are used extensively in different industrial areas, especially in furniture and machine coatings in order to extend the lifespan of the end product. For wood surfaces, it is important to protect the surface from external factors by maintaining the texture and colour of the surface. The conventional wood coatings require the usage of water or solvent; thus they have the risk of fiber swelling from the cellulosic wood material resulting deformation on the wood surface. Photocuring is favoured compared to the conventional solvent/water based thermal curing techniques due to the requirement of none/less water/solvent, rapid curing mechanism in just a few seconds/minutes, curing ability at lower temperatures with an effective curing rates. Soybean oil is a good candidate to be used as an alternative to the petrochemicals as being renewable, cheap, non-toxic, and abundant. It has five unsaturated groups on its backbone that is suitable to react furtherly with various chemical compounds to be used in polymer design. Itaconic acid (IA) is one of the high-value-added bio-chemicals of US Energy Department which is being manufactured by the fermentation of citric acid. The main purpose of this thesis is to design a high bio-content photocurable oligomer as an alternative to water/solvent-based traditional coating. For this purpose, different bio-based oligomers such as ESBO-IA and ESBO-IA-MDI-HEMA were obtained and tested on a MDF board.

1.2 Literature Review

Wood coatings are crucial for protecting wooden surfaces, enhancing their durability, appearance, and resistance to environmental factors. Traditional wood coatings have been largely based on petroleum-derived oligomers and resins, but as environmental concerns and sustainability goals grow, the need for bio-based alternatives has become evident. Bio-based photocurable oligomers, which can be crosslinked under ultraviolet (UV) light, are emerging as a promising solution for sustainable wood coatings. These oligomers, derived from renewable resources, offer reduced environmental impact while maintaining desirable coating properties such as hardness, scratch resistance, and durability.

Photocurable oligomers used in wood coatings generally contain acrylate or methacrylate functional groups that undergo polymerization upon UV exposure, resulting in a highly crosslinked network. One of the most widely explored sources for bio-based photocurable oligomers is vegetable oils, such as soybean, linseed, and castor oils. These oils contain unsaturated bonds that are highly reactive and can participate in photopolymerization processes. For instance, soybean oil-based acrylates have been shown to possess excellent photopolymerization properties, contributing to durable, scratch-resistant wood coatings. In a research, soybean oil-based acrylate oligomers demonstrated high curing efficiency and robust mechanical properties, indicating their potential for use in sustainable wood finishes [1]. Furthermore, the low cost and availability of vegetable oils make them an attractive feedstock for bio-based resin production [2].

In addition to vegetable oils, lignin, a natural polymer found in wood, is another promising source for bio-based photocurable oligomers. Lignin's high aromatic content imparts unique thermal and mechanical properties to coatings. Studies have shown that lignin-based oligomers can improve the resistance of wood coatings to weathering, UV degradation, and microbial attack, making them a potential candidate for high-performance wood coatings. In a work, it has been demonstrated that lignin-based photocurable resins exhibited enhanced UV stability and mechanical properties compared to traditional synthetic resins [3]. Moreover, the use of lignin not only enhances the sustainability of coatings but also valorizes this abundant byproduct of the paper and pulp industry. Similarly, the incorporation of lignin into acrylate-based resins has been found to provide a balance between biodegradability and durability, essential for eco-friendly coatings [4].

The challenges associated with bio-based photocurable oligomers primarily involve the efficiency of the curing process and achieving the required mechanical properties for long-lasting coatings. The unsaturated double bonds in vegetable oils and lignin may not fully cure under UV light, leading to coatings with suboptimal hardness or reduced mechanical strength. Therefore, researchers are focusing on improving the photopolymerization efficiency by modifying the chemical structure of these bio-based oligomers. For example, adding additional reactive functional groups, such as epoxy or isocyanate groups, can enhance the curing process and improve the performance of the coatings [5]. Additionally, the use of hybrid systems, where bio-based materials are combined with synthetic resins, has been explored to optimize the curing process and provide a balance between sustainability and performance [6].

Another significant challenge is ensuring the long-term durability of bio-based coatings when exposed to outdoor weathering. UV degradation, moisture absorption, and mechanical wear can significantly affect the performance of wood coatings. To address these issues, several strategies have been employed, such as incorporating UV stabilizers, antioxidants, and crosslinking agents into the bio-based resin formulations. A research highlighted that the addition of certain UV stabilizers to bio-based photopolymerizable oligomers improved their resistance to UV radiation, thus extending the longevity of wood coatings [7]. Furthermore, optimizing the composition of reactive diluents and photoinitiators is essential to ensure that the coatings achieve a balance between curing speed and mechanical properties [8].

2. THEORETICAL PART

2.1 Introduction to Coating

Coatings are essential materials in numerous industries, serving to protect, decorate, and enhance the functionality of surfaces. Their primary purpose is to act as a barrier against environmental factors such as corrosion, abrasion, and ultraviolet radiation, thereby prolonging the lifespan of underlying materials. A previous study highlights the versatility of coatings, which range from polymer-based systems to metallic and ceramic layers. These coatings not only safeguard substrates but also offer aesthetic qualities, such as color and texture, making them integral to applications in automotive, construction, and consumer goods sectors [9].

Modern developments in coating technologies have revolutionized their performance and environmental impact. Innovations like nanostructured coatings and smart coatings have introduced functionalities such as self-healing, anti-fouling, and conductivity. According to a previous study, nanotechnology enables the creation of coatings with improved adhesion, wear resistance, and optical properties [10]. Furthermore, sustainability has become a central focus in coating development, with water-based and bio-based formulations reducing the reliance on volatile organic compounds (VOCs). This shift reflects global efforts to meet stricter environmental regulations and adopt greener practices.

The future of coatings lies in interdisciplinary research and the integration of advanced materials. Studies in Materials Science and Engineering suggest that hybrid coatings, which combine organic and inorganic components, are paving the way for enhanced multifunctional capabilities [11]. These coatings are increasingly used in aerospace, medical devices, and renewable energy systems due to their adaptability and high performance. As researchers continue to explore novel materials and fabrication techniques, coatings are expected to play an even more pivotal role in addressing industrial challenges and contributing to sustainable development.

2.1.1 Coating Types

Coating types are diverse and cater to various industrial and functional needs, including protection, aesthetics, and enhanced performance of materials. Organic coatings, such as paints, varnishes, and polymers, are widely used due to their cost-effectiveness and versatility. These coatings often consist of polymer binders, pigments, and additives that enhance adhesion, weather resistance, and color retention. For instance, polyurethane coatings are praised for their excellent mechanical properties and UV resistance [12,13]. Additionally, bio-based organic coatings, derived from renewable resources like cellulose and plant oils, are gaining attention for their eco-friendly attributes [14]. Their ability to reduce volatile organic compound (VOC) emissions positions them as an essential alternative to traditional formulations.

Inorganic coatings, including metallic and ceramic coatings, are renowned for their superior thermal stability, corrosion resistance, and durability. Metallic coatings, such as zinc and aluminum layers, are applied through methods like galvanization and electroplating to protect against oxidation. Ceramic coatings, such as silicon carbide and titanium dioxide, exhibit exceptional heat resistance and are frequently used in aerospace and automotive industries [15]. Plasma spraying and sol-gel techniques have emerged as innovative methods to deposit inorganic coatings with precise thickness and microstructure control [16]. These advancements enable inorganic coatings to perform efficiently in extreme conditions.

Hybrid coatings are a fusion of organic and inorganic materials, combining their best properties to achieve enhanced functionalities. For example, hybrid sol-gel coatings integrate organic polymers with inorganic silica or titania, forming dense protective layers with tailored properties. These coatings are increasingly utilized in biomedical applications, renewable energy systems, and advanced electronics [17,18]. Studies highlight their versatility in providing high corrosion resistance, self-cleaning, and anti-reflective qualities [12,16]. The ongoing research and development in hybrid coatings demonstrate their potential to address complex industrial challenges while adhering to sustainability goals.

2.1.2 Coating Requirements

One of the primary requirements for coatings is to provide sufficient protection against corrosion. Corrosion resistance is a key attribute for materials exposed to moisture, salt, or harsh chemicals. Studies have highlighted the importance of advanced coatings in prolonging the lifespan of metallic structures and preventing degradation [19,20]. The application of coatings that are resistant to high temperatures and UV radiation is also critical for aerospace and automotive industries, where materials are regularly exposed to extreme conditions [21].

In addition to corrosion resistance, coatings need to maintain their integrity over extended periods of exposure to environmental factors. A critical property of coatings is their ability to adhere firmly to substrates without peeling or cracking. For instance, epoxy and polyurethane coatings are commonly used for their superior adhesion properties in applications such as pipelines and marine vessels [20]. Furthermore, scientists studied the influence of surface preparation on coating adhesion, emphasizing that roughening or cleaning the surface enhances the bonding strength between the substrate and the coating [22]. Another requirement is the maintenance of aesthetic qualities, where coatings also provide resistance to fading, scratching, and staining. This is particularly important in consumer goods and construction materials, where visual appearance affects both functional and market value.

Finally, coating requirements must also account for environmental sustainability. The development of eco-friendly coatings that minimize harmful emissions or hazardous components is a growing concern. A research has explored the use of water-based coatings and bio-based polymers as alternatives to solvent-based systems, which have detrimental effects on air quality and human health [23]. These green technologies not only ensure compliance with environmental regulations but also meet consumer demands for safer and more sustainable products. Additionally, advances in nanotechnology have led to the development of coatings with enhanced properties such as self-healing and anti-fouling characteristics, further expanding the range of applications [19,21]. The continuous research in coating technology is crucial for meeting the growing need for high-performance and environmentally responsible materials.

2.2 UV Light Curing Technology

UV curing is a photochemical method that utilizes intense ultraviolet light to rapidly "cure" or "dry" materials like inks, coatings, and adhesives. Ultraviolet radiation, which is invisible to the human eye, is the most powerful form of radiation and is classified into three categories based on wavelength: UVA (320-400 nm), UVB (280-320 nm), and UVC (180-280 nm). The rate of polymerization in UV-curing processes is influenced by factors such as the activity and concentration of functional groups, the intensity of the UV light, and the viscosity of the resin. To regulate radical formation and manage the polymerization rate during the photochemical treatment of EA systems, impurities and air must be removed. Numerous studies in the literature have addressed adhesion issues in EA coatings by investigating double bond conversion and variations in surface energy between the bonding components [24].

UV-curing processes can be categorized into two main types based on the polymerization mechanism: free radical and cationic. While ultraviolet (UV) light initiates both types of polymerization, it does not interfere with the subsequent propagation or termination stages. Free radical polymerization, which commonly involves acrylate-functional resins, is more prevalent compared to cationic polymerization. In the free radical process, unsaturated molecules such as those containing alkene groups—like vinyl ether and acrylates—play a role. Conversely, cationic polymerization uses photoinitiators that generate cations, leading to the formation of Bronsted or Lewis acids during the initiation phase. These acids then facilitate the polymerization of compounds like epoxides or vinyl ethers. Although initiation and propagation occur in a manner similar to radical polymerization, cationic polymerization does not terminate through neutralization but rather via nucleophilic impurities.

Oxygen presence has differing effects on these two polymerization types: it inhibits radical formation in free radical polymerization, while cationic polymerization remains unaffected. Furthermore, the resulting polymers from both mechanisms are insoluble. Cationic polymerization also stands out due to its unique termination method, which relies on reactions with nucleophilic impurities rather than neutralization. Diagrams such as Figures 2.1 and 2.2 typically illustrate the detailed reaction pathways involved in UV-induced free radical and cationic polymerization processes [25,26].

Accordingly, R• radical is generated by the photo decomposition of the initiator. M and M• represent the monomer and monomeric radical, respectively.

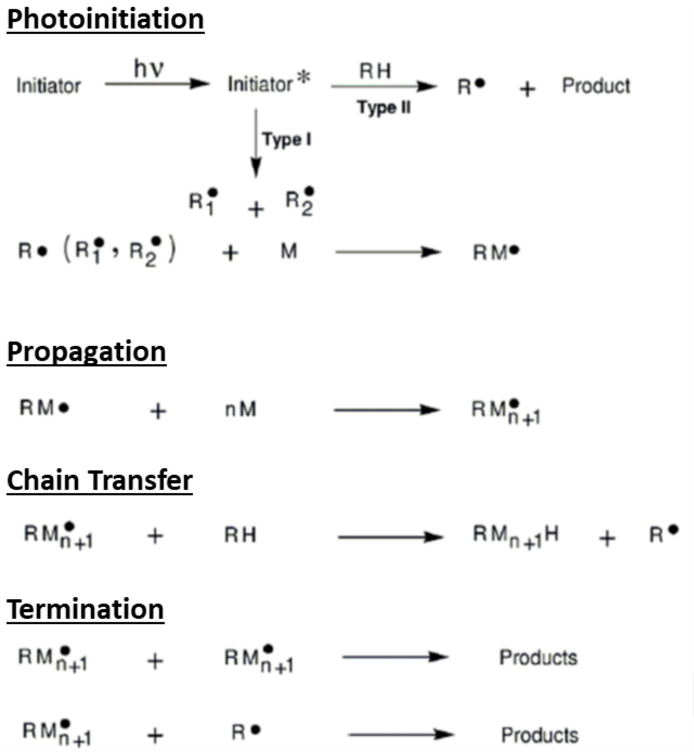


Figure 2.1 : Reaction scheme of free radical photopolymerization [27].

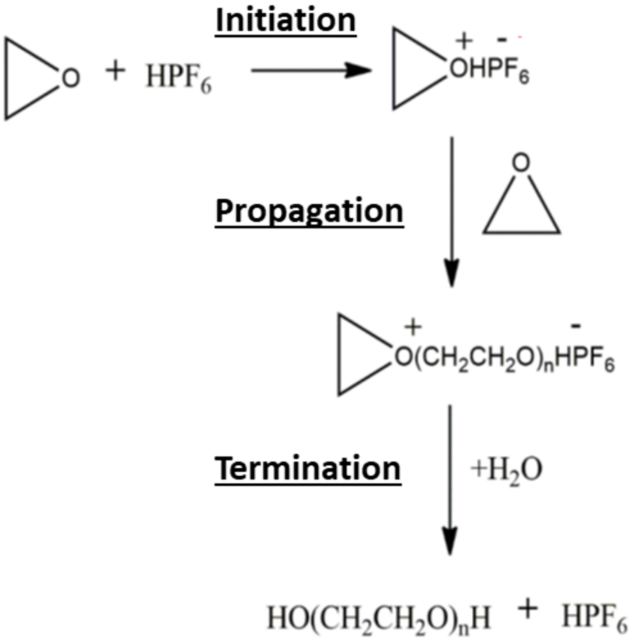


Figure 2.2 : Reaction scheme of cationic ring-openning photopolymerization [27].

A UV curing system consists of reactive oligomers, diluents, and photoinitiators, which work together to achieve rapid hardening of materials. Commonly used oligomers include acrylic acid esters such as epoxy acrylates, polyester acrylates, urethane acrylates, and silicone acrylates. To initiate the curing process, liquid monomers and oligomers are mixed with a small proportion of photoinitiators and exposed to UV energy. Within seconds, products like inks, coatings, and adhesives solidify instantly. This process eliminates the need for solvents, minimizes environmental pollutants, and preserves both coating thickness and material volume. As a result, UV curing is highly efficient, offering faster production, reduced waste, energy savings, and minimal emissions even at low temperatures. Additional benefits include strong adhesion to diverse substrates, high curing rates, adjustable elasticity, long-term storage stability, exceptional scratch resistance, and excellent optical clarity, resulting in superior surface quality [28-32]. Furthermore, it can be applied across a wide temperature range, making it suitable for heat-sensitive materials.

Despite its many advantages, UV curing technology does have some limitations. Challenges include difficulty in applying it to complex shapes, significant shrinkage after curing, and reduced durability due to continuous UV light absorption, which impacts weatherability. Additionally, the process can only cure areas directly exposed to UV light, requiring at least one of the adherent materials to be transparent. These constraints highlight the need for further advancements to address such issues and enhance the versatility of UV curing systems [24,33].

2.2.1 Photoinitiators

Photoinitiators play a crucial role in UV curing by absorbing light and initiating photochemical reactions between oligomers and monomers, leading to polymerization and crosslinking to form the final product. During the curing process, photoinitiators absorb ultraviolet and visible light within the wavelength range of 250-550 nm, as indicated in Figure 2.3 [34]. This absorption converts light energy into chemical energy, triggering polymerization through mechanisms involving free radicals and reactive cations. The presence of photoinitiators in the formulation enables UV light to cure films by reacting with double bonds, ensuring a successful curing process.

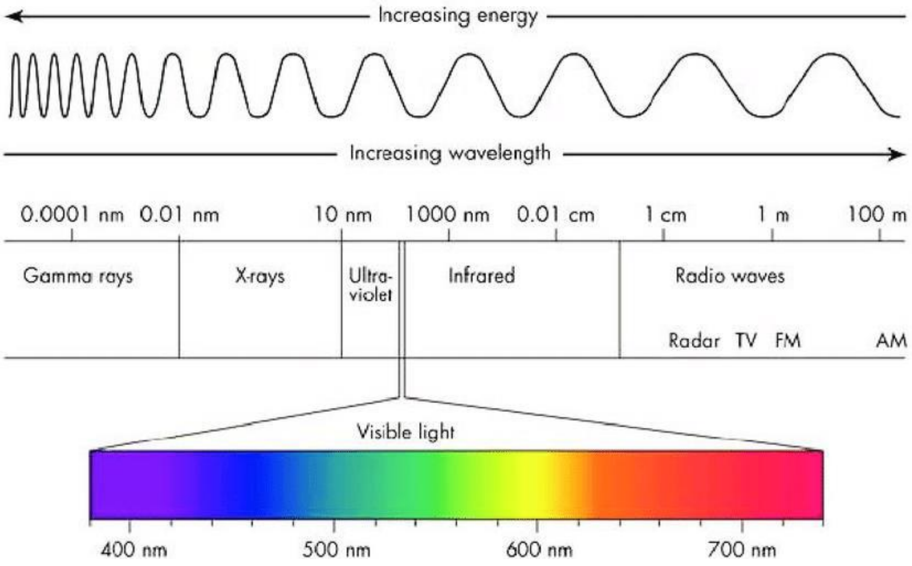


Figure 2.3 : The electromagnetic spectrum [34].

Photoinitiators function by generating free radicals or strong acids when exposed to light, triggering polymerization processes. Commonly used photoinitiators include benzoin derivatives, benzil ketals, acetophenone derivatives, aromatic ketone/amine combinations, and onium salts. While organic photoinitiators dominate the market, inorganic and organometallic variants are becoming increasingly popular. To excite electrons to a higher energy level and activate the curing process, photoinitiators require high-intensity light emission. For thicker films, using lower amounts of photoinitiators helps to reduce coating-related issues. Moreover, homogeneous cross-linked structures can be achieved by combining a minimal amount of photoinitiators with a highly intensive UV light source. However, excessive photoinitiator concentrations may compromise adhesion and mechanical properties by limiting light exposure during UV polymerization.

Different photoinitiators are utilized depending on the type of polymerization. In free radical polymerization, initiators are derived from aryl alkyl ketones, and hydrogen donors can be obtained from diaryl ketones in combination with tertiary amines. For cationic polymerization, photoinitiators such as vinyl ethers, diaryliodonium, triarylsulfonium hexafluoroantimonates, and hexafluorophosphates are employed. These formulations are tailored to meet specific requirements and challenges in UV curing processes [35,36].

2.2.2 Reactive Diluents

Reactive diluents play a pivotal role in UV-curable formulations, serving functions such as reducing viscosity, managing crosslinking density, and enhancing mechanical and chemical resistance properties. Acrylic-based reactive diluents are particularly popular due to their excellent clarity, optical transparency, and resistance to yellowing. Numerous studies in the literature have investigated how the type and concentration of reactive diluents affect the end product's properties. For example, urethane acrylate oligomer has been synthesized and combined with 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) to examine the impact of diluent functionality on coating characteristics. Findings indicate that formulations containing TMPTA, which exhibit higher crosslinking density, result in improved glass transition temperature and enhanced thermal stability of the coating material [37]. Another study investigated the impact of reactive diluent concentration on the thermal degradation properties of N-(4-hydroxy phenyl) maleimide derivatives, selecting N-vinylpyrrolidone (NVP) as the reactive diluent. The findings revealed that the composition with 80% maleimide derivative and 20% NVP exhibited the highest thermal stability, achieving a char yield of 30% [38]. Additionally, research has also explored how dipropylene glycol diglycidyl ether, as a reactive diluent, influences the mechanical properties of multi-walled carbon nanotube (MWCNT) composites [39].

2.2.3 Additives

Additives are chemical components designed to improve formulation characteristics, provide additional functions to the resin, and enhance specific qualities of the final product. In UV-curing systems, plasticizers are commonly used additives that help regulate viscosity and rheology in adhesive formulations. Other frequently employed additives include antioxidants, antistatic and antifogging agents, thermal and UV stabilizers, flame retardants, color pigments, and tackifiers. These additives collectively contribute to optimizing the formulation and tailoring it for various applications [40,41].

2.2.4 Application Areas of UV-Curable Coating

UV-curable coatings are versatile and can be applied across a variety of areas, including printing technology, plastics, wood, metals, and other surfaces that benefit from UV curing methods. These coatings enhance hardness and wear resistance, particularly on plastic surfaces, while also providing brightness and scratch resistance. In the wood industry, polyester, acrylic, and urethane-acrylic resin blends are frequently used. Polyester resins are more affordable, but they lack the durability of other options, whereas acrylic resins offer superior wear resistance and flexibility but at a higher cost. UV curing is especially suitable for heat-sensitive wooden materials like furniture, as well as kitchen and bathroom cabinets.

In the metal coating industry, UV-curable coatings are highly favored due to their energy efficiency and time-saving nature. This technology is commonly used for metal boxes, energy generators, and cables. These coatings deliver excellent performance attributes, including wear resistance, durability, flexibility, and heat resistance. By offering these advantages, UV-curable coatings have become an optimal choice for enhancing surface quality and functional properties across various industries [36,42].

2.3 Epoxidized Vegetable Oils

Epoxidized vegetable oils (EVOs) are altered oils containing an epoxide group (-O-), which is usually incorporated through reactions with peracetic or performic acids. In recent years, they have attracted significant interest due to their potential use in creating biodegradable polymers, coatings, and as sustainable substitutes for petroleum-based chemicals. The process of epoxidation improves the chemical characteristics of vegetable oils, enhancing their reactivity, stability, and compatibility with various materials [43]. The synthesis of EVO’s generally involves reacting unsaturated vegetable oils, such as soybean, linseed, or palm oil, with an oxidizing agent commonly peracetic or performic acid under catalytic conditions. In Figure 2.4 [44], epoxidation of double bonds with this performic acid is illustrated.

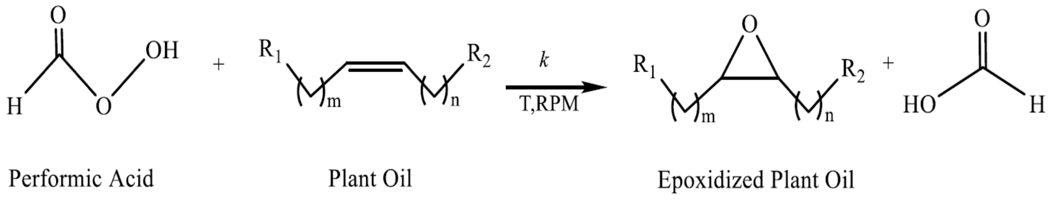


Figure 2.4 : Epoxidation of double bonds with this performic acid.

This process introduces an epoxide group, which is highly reactive and suitable for further functionalization, making EVO’s adaptable intermediates for a wide range of industrial purposes [45]. Numerous studies have focused on optimizing reaction parameters, including temperature, reactant concentrations, and solvent selection, to enhance the efficiency of the epoxidation process and maximize product yield.

One of the most promising applications of EVO’s is their use in the production of environmentally friendly polymers and coatings. As renewable resources, EVO’s can replace petroleum-derived materials in the manufacturing of plastics, coatings, and adhesives, which are traditionally associated with environmental pollution and high carbon footprints. The introduction of the epoxide group into vegetable oils significantly improves their mechanical properties, such as tensile strength and elasticity, making them suitable for applications in the automotive and packaging industries [46]. Furthermore, EVO’s are being explored as raw materials for the production of bioplastics. The high reactivity of the epoxide group enables the formation of crosslinked networks that provide the desired rigidity and stability in the final product. Various studies have demonstrated that EVO’s, when combined with curing agents or other bio-based monomers, can produce polymers with properties comparable to traditional petroleum-based plastics [43,47]. In addition to their use in plastics, EVOs are employed in the formulation of coatings and adhesives due to their excellent adhesion properties, flexibility, and resistance to environmental factors. They are increasingly used in the automotive and aerospace industries, where high-performance coatings are required for protection against wear, corrosion, and UV degradation [45,48].

A significant benefit of EVO’s is their renewable and biodegradable nature. With the increasing emphasis on sustainability, there has been a growing demand for environmentally friendly alternatives to petroleum-based products. EVOs present a viable solution, being sourced from natural, renewable resources and offering superior biodegradability compared to synthetic polymers [46]. Furthermore, the production of EVOs typically involves milder reaction conditions and consumes less energy than the synthesis of conventional synthetic polymers, thereby minimizing their overall environmental footprint [49].

2.3.1 Epoxidized Soybean Oil (ESBO)

Epoxidized soybean oil (ESBO) is a renewable material derived from the epoxidation of soybean oil, a process that adds reactive epoxide groups to the fatty acid chains within the oil. This chemical modification enhances the reactivity of the oil, making it versatile for industrial applications such as bio-based polymers, coatings, and adhesives. As a sustainable alternative to petroleum-based products, ESBO stands out for its biodegradability and lower environmental impact, offering a path to reduce dependence on fossil fuels [45]. This discussion examines the synthesis techniques, potential uses, and ecological benefits of ESBO, with an emphasis on recent advancements in the field. The epoxidation of soybean oil generally involves reacting the oil with oxidizing agents like peracetic acid or performic acid under precisely controlled conditions. This process targets the double bonds in the fatty acid chains, converting them into reactive epoxide groups. A key obstacle in the synthesis of ESBO is the need to fine tune reaction parameters including temperature, catalyst choice, and solvent usage to achieve a high yield while reducing the formation of unwanted by-products [49]. In figure 2.5 [50], the general chemical equation for the epoxidation of soybean oil is represented, where R represents the alkyl chains of fatty acids in soybean oil, and R'CO3H is the oxidizing agent.

$$\mathrm{R\text{-}CH{=}CH\text{-}R + R'CO_3H \rightarrow R\text{-}CH(O)\text{-}CH(R')\text{-}R}$$

Figure 2.5 : General chemical equation of soybean oil epoxidation.

2.3.2 Itaconic Acid (IA)

Itaconic acid (IA) is a dicarboxylic acid with the molecular formula $C_5H_6O_4$. It has emerged as a valuable bio-based compound, offering great potential as a renewable feedstock for diverse applications, including polymers, biofuels, and specialty chemicals. Derived from renewable resources like glucose, IA's broad chemical reactivity has attracted significant interest within materials science, chemical engineering, and sustainable manufacturing [51]. IA is a water-soluble, crystalline solid characterized by its colorless appearance. Its two carboxyl groups (-COOH) contribute to its high reactivity, enabling it to participate in various chemical processes such as esterification, amidation, and polymerization. With a melting point of 165 °C and a pKa value of approximately 4.5, itaconic acid demonstrates pronounced acidic properties [52]. Commonly utilized as a monomer, itaconic acid plays a key role in the synthesis of polyitaconic acid (PIA), a biopolymer with applications in superabsorbent materials, drug delivery systems, and water treatment technologies. Moreover, IA-based polymers are being explored for use in biodegradable plastics, which provide an eco-friendly alternative to traditional petroleum-based plastics [53]. In addition, IA is utilized in the production of numerous chemical derivatives, including itaconate esters, which serve as crosslinking agents in coatings and adhesives. These esters enhance mechanical properties, making them particularly well-suited for applications such as industrial coatings and water-based paints. Their inclusion contributes to improved durability and performance, aligning with the demands of modern industrial and commercial uses.

The incorporation of itaconic acid, especially in polymer production, plays a crucial role in promoting sustainability. Unlike traditional petrochemical-derived monomers, itaconic acid is sourced from renewable resources, thereby minimizing the ecological footprint of its manufacturing process. Moreover, itaconic acid and its derivatives exhibit biodegradability, presenting a notable advantage over synthetic polymers, which are non-biodegradable and contribute significantly to persistent environmental pollution. This highlights the potential of itaconic acid in advancing environmentally friendly material solutions [54]. The production of itaconic acid through microbial fermentation provides a more sustainable and energy-efficient approach compared to conventional chemical synthesis methods. This process significantly lowers the environmental impact by reducing the carbon footprint associated with itaconic acid production. As a result, fermentation-based production positions itaconic acid as an eco-friendly alternative to many synthetic monomers, aligning with the growing emphasis on sustainable and green manufacturing practices [55].

3. EXPERIMENTAL PARTS

3.1 Materials and Chemicals

3.1.1 Monomers and Resins

Trimethylolpropane trimethacrylate (TMPTMA):

It was used as received. It is a three functional reactive diluent with high chemical/heat/weather/abrasion resistance, high crosslink density, and impact strength. It can be used in wire/cable coating formulations, paints, hard rubber objects etc.

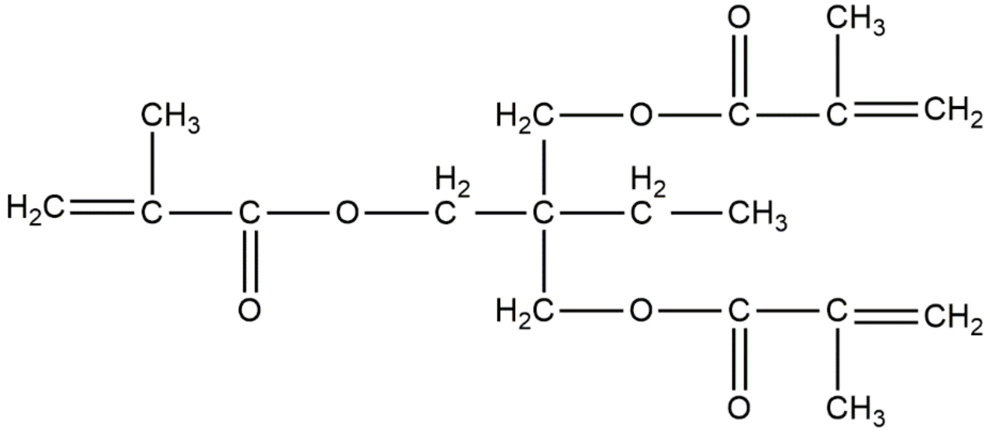


Figure 3.1 : Trimethylolpropane trimethacrylate.

1,6-Hexanediol diacrylate (HDDA, tech. 90 % Sigma-Aldrich):

It was used as received. It is suitable to use in UV/EB curable systems. It has two functional end groups, so it can be used as difunctional reactive diluent to decrease viscosity and to obtain better moisture resistance.

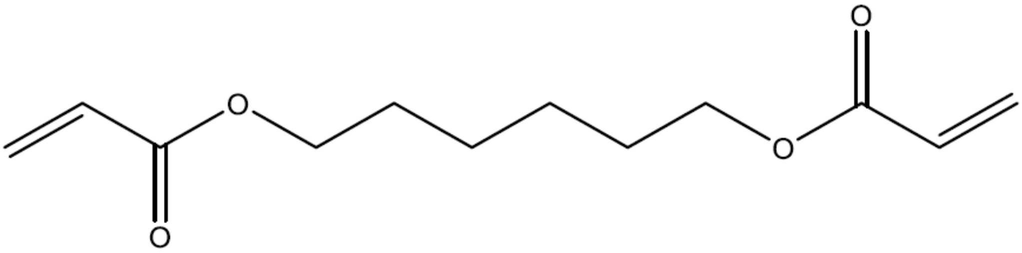


Figure 3.2 : 1,6-Hexanediol diacrylate.

Methyl acrylate (MA):

It was used as received. It has one functional end group, so it can be used as monofunctional reactive diluent.

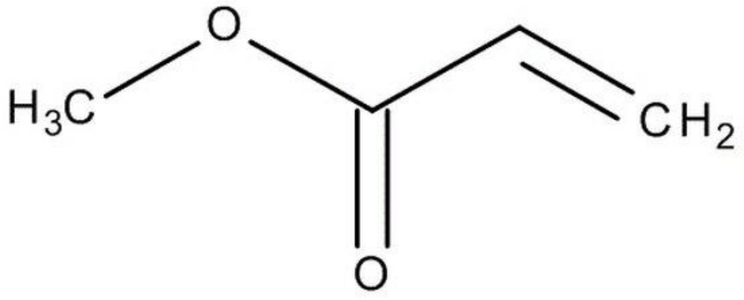


Figure 3.3 : Methyl acrylate.

Epoxidized soybean oil (ESBO) :

It was used as received. It has good stabilizing ability; threfore, it is possible to add it in formulations as secondary plasticizer, stabilizer for polymer systems.

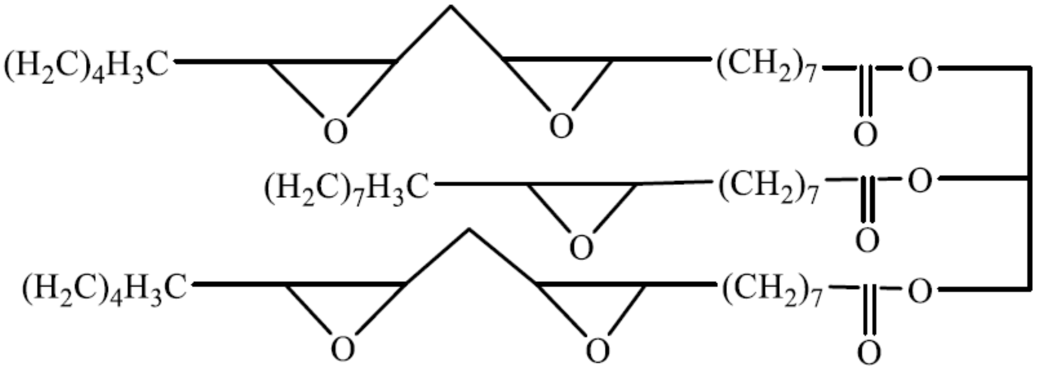


Figure 3.4 : Epoxidized soybean oil structure.

N-vinyl pyrrolidone (NVP, ≥ 99 %, Sigma-Aldrich):

It was used as received. It is a reactive diluent that can be used in UV/EB curable inks, coatings, adhesives, etc.

3.1.2 Solvents

Ethanol (≥ 99.8 %, Sigma-Aldrich):

It was used as received.

Methanol(≥ 99.8%, Merck):

It was used as received.

3.1.3 Other Materials and Chemicals

Triphenyl phosphine (TPP, 99 %, Sigma-Aldrich):

It was used as received.

2-methylhydroquinone (HQ, 99 %, Abcr):

It was used as received.

Phenolphthalein (Indicator, Sigma-Aldrich):
It was used as received.

2-Hydroxyethyl methacrylate (HEMA, ≥ 99 %, TCl Co.):

It was used as received. It contains ≤ 50 ppm monomethyl ether hydroquinone as inhibitor.

Methyene diphenyl diisocyanate (MDI):

It was used as received.

Di-n-butyltin dilaurate (T12, 95 %, Alfa Aesar):

It was used as received. It is used as catalyst.

1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba Specialty Chemicals):

It was used as received. It is generally used for UV photopolymerization of acrylates, mono/multi-functional vinyl monomers without having yellowing color changing on the coating.

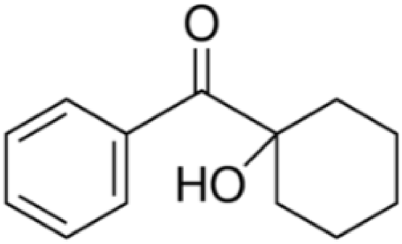


Figure 3.5 : Irgacure-184.

3.2 Characterization, Aanalysis, and Testing Equipment

3.2.1 Acid Value (AV)

The acid value is determined by the amount (in milligrams) of potassium hydroxide required to neutralize one gram of the prepared resin. To measure this, a specific amount of the sample is dissolved in a suitable solvent, and six drops of phenolphthalein are added. The mixture is then titrated with potassium hydroxide until it develops a stable pink or red color. The acid value is calculated using equation 1, where V indicates the volume of potassium hydroxide used during titration, M is the molarity of the potassium hydroxide solution, and W represents the weight (in grams) of the undiluted sample [56].

$$\mathbf{AV=\frac{V\times M\times 56,1}{W}} \tag{1}$$

3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyzes were carried out in Perkin Elmer Spectrum 100 FTIR spectroptometer in mid-infrared range (600-4000 cm-1), that uses a ZnSe ATR-crystal with a variable angle accessory. Omnic software was used to record the spectral data at a resolution of 8 cm-1 and 64 co-added scans.

3.2.3 Proton Nuclear Magnetic Resonance (1H NMR) Spectroscopy

1H NMR spectroscopy was carried out on Agilent VNMRS 500 MHz NMR instrument, by using deuterated chloroform (CDCl3) and deuterated dimethylsulfoxide (DMSO-d6) as solvents and tetramethylsilane (TMS) as an internal standard. The measurement was performed with 3 s acquisition time, 20 ppm spectral width, 125 transients of 65k data points obtained over a 15 min data accumulation time.

3.2.4 Thermogravimetric Analysis (TGA)

TGA analysis was performed with a TA TGA Q50 instrument under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C. Nitrogen flow rate was 30 mL/min.

3.2.5 Differential Scanning Calorimetry (DSC)

Thermal transition temperatures were measured by DSC, TA DSC Q10, at a heating rate of 10°C/min, from −80°C to 400°C under 50 mL/min nitrogen flow rate.

3.2.6 Gel Content

The gel fraction (GF %) of the UV-cured free films was measured by dipping the films into THF for one week at room temperature. After that the films were dried on a filter paper at 30 °C for 24 h. The GF (%) values were calculated by using the equation 2 where *W1* and *W2* show the weights of the films before and after swelling [57].

$$\mathbf{GF(\%)=\left[\frac{W_1}{W_2}\right]\times 100} \tag{2}$$

3.2.7 Swelling Test

To determine the degree of swelling (DS %) of UV-cured free films, the samples were immersed in 10 mL of solvent (ethanol, toluene, or distilled water) at room temperature for a week. After swelling, the films were dried on filter paper until their weight stabilized. The DS % was calculated using equation 3, where W1 represents the weight of the films before swelling and W2 represents their weight after swelling [57].

$$\mathbf{DS(\%)=\left[\frac{W_2-W_1}{W_1}\right]\times 100} \tag{3}$$

3.2.8 Chemical Resistance

The chemical resistance of UV-cured free films was assessed by measuring the percentage of weight loss after two weeks of exposure to chemical solvents at room temperature. The solvents used were 10% NaOH and 10% HCl solutions. Following the exposure, the films were rinsed with distilled water and dried on filter paper at 55

°C. The weight loss (%) was calculated using equation 4, where W1 represents the weight of the films before exposure, and W2 represents the weight after exposure [58].

$$\textbf{Weight Loss (\%)}=\left[\frac{W_1-W_2}{W_1}\right]\times 100 \qquad (4)$$

3.2.9 Shore Hardness

The Shore D hardness of the UV-cured free films was determined by Zwick Shore D Durometer by using 5 kg loading according to ASTM D2240 standard.

3.2.10 Tensile Testing

The mechanical properties of UV-cured free films were analyzed using the Instron 4411 tensile testing machine. Tests were conducted at room temperature with an extension rate of 5 mm/min. Measurements included tensile strength (MPa), elongation at break (%), and modulus (MPa), all of which were documented during the testing process.

3.2.11 Cross-cut Adhesion Test

UV-cured films on plates were left at room temperature for 24 hours before performing the cross-cut test on the coated surfaces. Using the BYK Gardner apparatus, cuts were made on the coated surface, followed by the application of pressure-sensitive tape, which was then swiftly removed. The extent of coating removal was assessed on a scale from 0B to 5B. In this scale, 0 indicates over 65% removal, 1 corresponds to 35–65% removal, 2 represents 15–35% removal, 3 indicates 5–15% removal, 4 corresponds to less than 5% removal, and 5 indicates no removal of the coating from the surface [59].

3.2.12 Taber Abrasion Test

The abrasion resistance of the UV-cured coated surface was evaluated using a Taber Type Abrasion Tester GT-7012-T (Gotech Testing Machine). The resin-coated plates were conditioned for 24 hours at 23 °C ± 2 °C and 50% ± 5% relative humidity, and the tests were conducted under the same conditions. The initial weight of the coated plates was recorded, and the weight of each sample was measured every 100 cycles. Testing continued until visible wear appeared on the coated surface.

The wear index of the coated plates was calculated using equation 5, where I represents the average mass loss (mg) per thousand abrasion cycles, A is the sample's weight (mg) before cycling, B is the weight (mg) after cycling, and C denotes the total number of abrasion cycles [60].

$$\mathbf{I=\frac{(A\text{-}B)\times 1000}{C}} \tag{5}$$

3.2.13 Water Immersion Test

UV-cured films on plates were left at room temperature for 24 hours before undergoing the water immersion test. To assess the water resistance of the coatings, the samples were submerged in a tank of distilled water at 38 °C for 24 hours. Once removed from the tank and dried, the samples were evaluated within 5–10 minutes. Any changes in the coating were observed and rated on a scale from 0 to 10. Additionally, changes in gloss and color were re-evaluated after 24 hours of conditioning to examine the lasting effects of the water exposure [61].

3.3 Synthesis of the Bio-Derived Oligomers

3.3.1 Synthesis of the Itaconic Acid Modified Epoxidized Soybean Oil Oligomer (ESBO-IA)

ESBO-IA oligomers were synthesized by the following method; certain amount of ESBO was put in a three-necked round bottom flask equipped with a magnetic stirrer, and heated up. At 70 °C, certain amount of IA, 300 ppm HQ, and 1000 ppm TPP were added to the flask. After the flask reached 120 °C, the mixture was stirred for 2 hours. Then, the mixture was cooled down. The mixture is used in the formulations with different type of reactive diluents and different ratios.

3.3.2 Synthesis of the Bio-Derived Urethane Methacrylates

In the reaction, there are three different types of reactive diluents were used. As monofunctional reactive diluent, methyl acrylate was used. Because of its two functional end groups, HDDA was used as difunctional reactive diluent. TMPTMA was used as three functional reactive diluent since it has three functional end groups. A known amount of HEMA and a reactive diluent were mixed in the three-necked round bottom flask. The flask was heated up to 65 °C, and certain amount of MDI was added into the flask at 65 °C. Then, the flask kept heated up to 80 °C, stirred for 1 hour. At the end of 1 hour, 4 droplets of T12 was added. After 10 minutes of stirring, ESBO-IA oligomer was mixed in the flask. The flask was stirred 20 minutes more, then it was cooled down.

3.3.3 Preparation and Application of Wood Coating Formulations

In Figure 11, application process of resins to wood plate and curing steps were illustrated. The formulations of the resins were prepared by changing amount of different reactive diluents. 5 % wt photoinitiator were mixed into the resin formulation and stirred until it was mixed homogeneously. After preparation, the resin applied to the surface and a transparent PE film was put on top of the surface. In order to distribute the resin to all surface, a hand roller was used. Then, the wood plate covered with resin and PE film was put under the UV light in order to cure the resin. Each resin was cured during 3 minutes. After the curing process, PE film removed from the surface and the wood plate covered with resin was prepared.

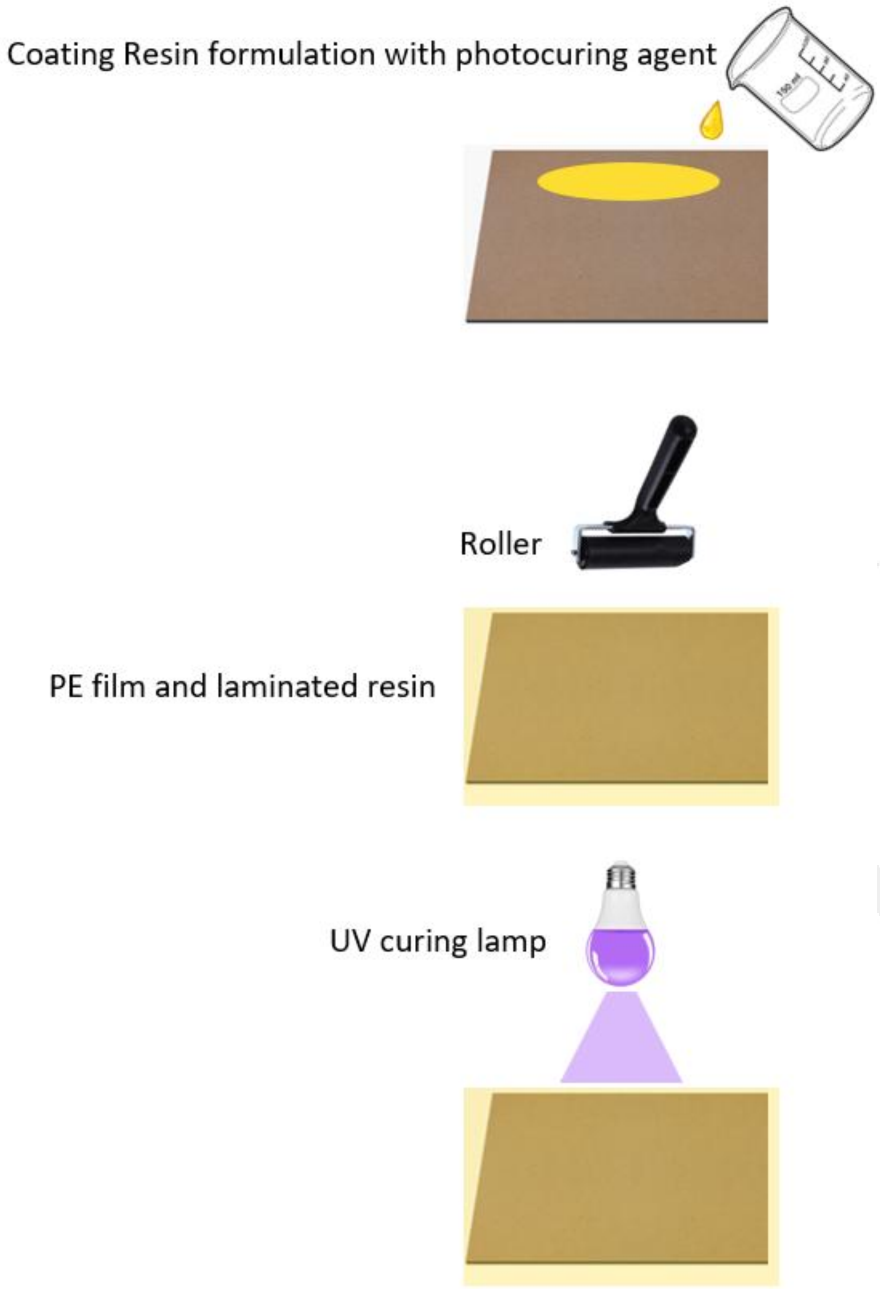


Figure 3.6 : Schematic representation of coating and UV-curing set-up.

4. RESULTS AND DISCUSSION

4.1 Synthesis of the ESBO-IA Oligomer

In this section, analysis of ESBO-IA oligomer were given, which was polymerized with ring opening polymerization method as it was shown in Figure 4.1. Firstly, ^{1}H-NMR analysis was evaluated. In Figure 4.2, the chemical structure of ESBO-IA was shown. With the red numbers, diferent types of bondings were indicated. The same numbers also were used in the Figure 4.3, which gives the result of ^{1}H-NMR. The peaks in the 1.1-1.4 ppm region indicate saturated triglyceride group protons. In the range of 1.4-1.7 ppm, the methylene group protons adjacent to the epoxide groups was formed. The peak at 2.4 ppm indicates protons in the allylic position. Methylene protons formed as a result of the epoxide ring opening reaction were formed in the region of 4.1-4.4 ppm [62,63].

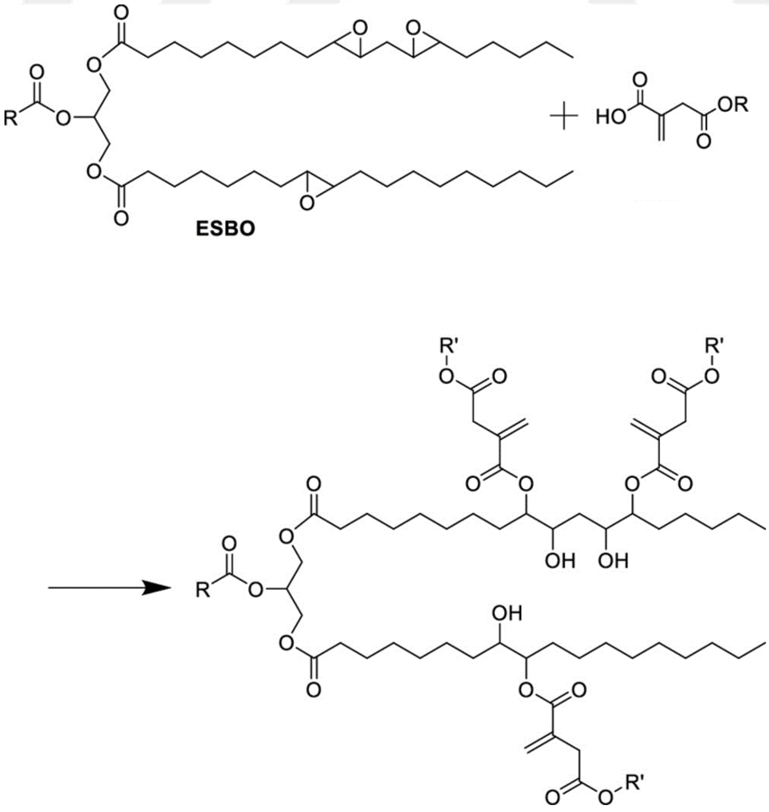


Figure 4.1 : Ring opening polymerization of ESBO-IA Oligomer.

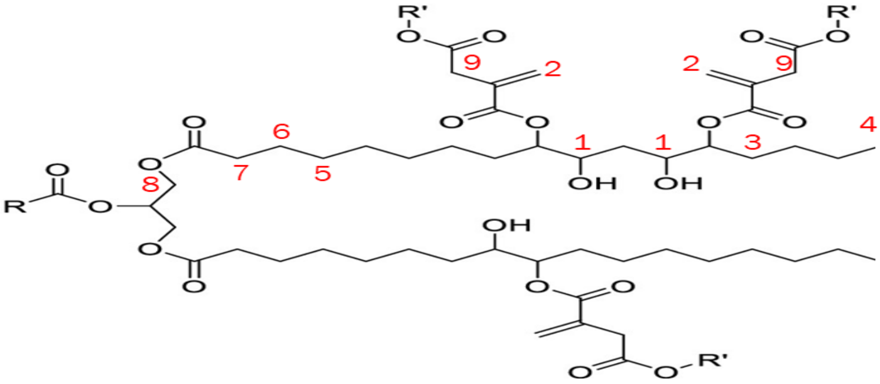


Figure 4.2 : Structure of ESBO-IA Oligomer.

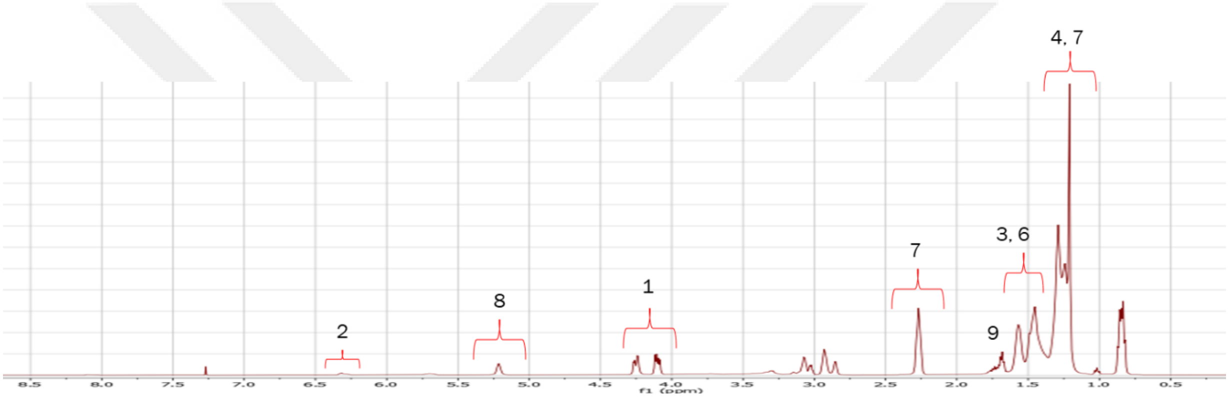


Figure 4.3 : H-NMR spectra of the ESBO-IA Oligomer.

In Figure 4.4, FTIR spectra of ESBO and ESBO-IA oligomers were shown. C-H bending peaks are around 990-820 (number 1, 2, 3). Since the itaconic acid reacted to epoxide groups, the peaks disappeared after polymerization.

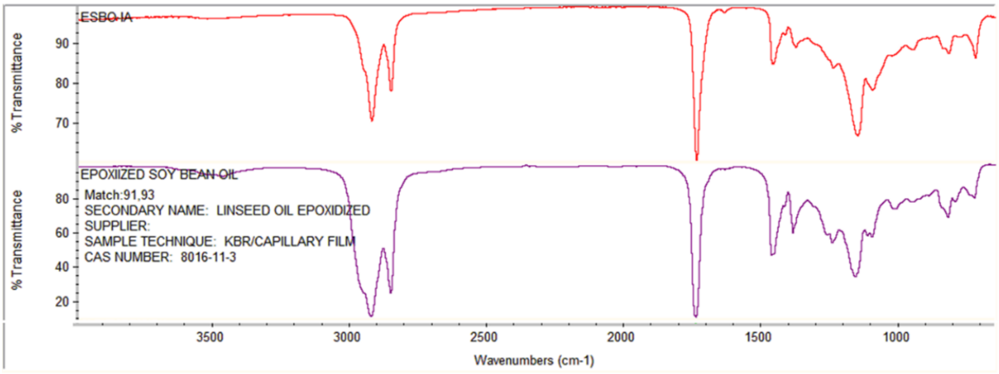


Figure 4.4 : FTIR spectra of ESBO and ESBO-IA oligomers.

In Figure 4.5, weight loss and cycle diagram of taber test was shown. Depending on the crosslinking and end groups, weight loss of the oligomers was changing. Without reactive diluents, oligomer has a rigid film structure. So, it has the most weight loss comparing with the other versions containing reactive diluents. NVP as reactive diluent has rigid aromatic groups. That is why the oligomer with NVP is not flexible. It causes weight loss too. MA has less functional groups then HDDA, and also has less crosslinking density [64].

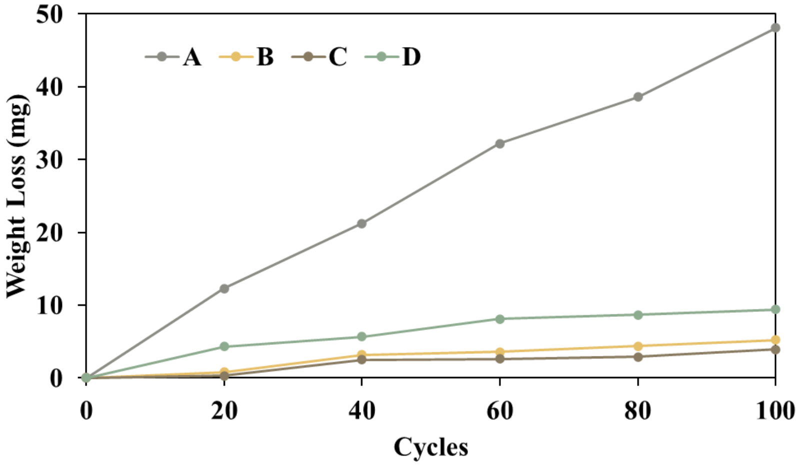


Figure 4.5 : Taber abrasion test results of samples by means of reactive diluent type.

The results of water immersion test is similar with taber test, because both tests are depending on the physical structure of oligomer. In Figure 4.6, it could be observed that the film of the oligomer without reactive diluent was solved in water mostly due to its film structure. The oligomer with HDDA has the least surface deformation upon water exposure beacuse of its crosslinking density and its flexibility. Since it has rigid aromatic end groups, NVP was also solved in the water and could not resist.

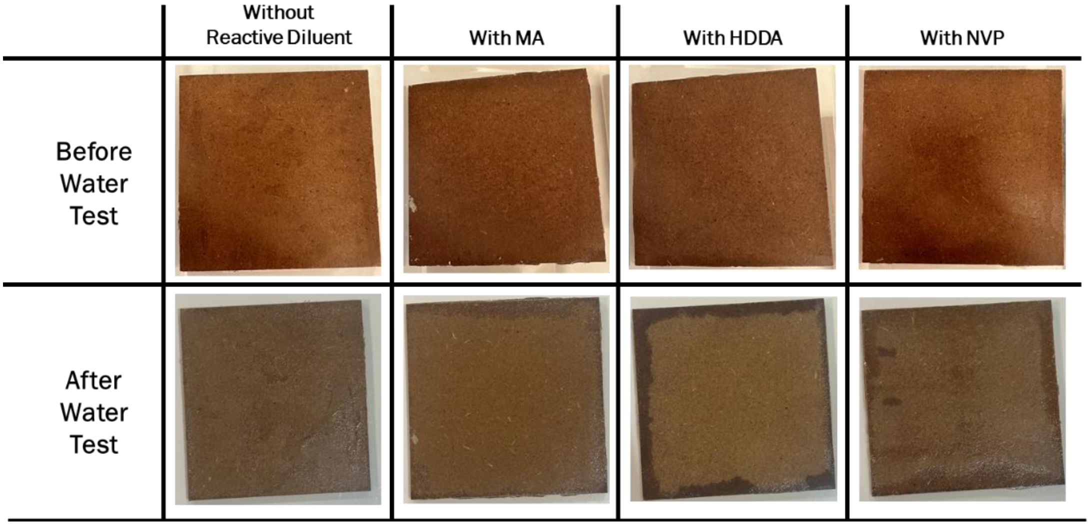


Figure 4.6 : Water immersion test results of oligomers with and without reactive diluents.

4.2 Synthesis of the ESBO-IA-UA Oligomer

In this section, chemical and physical analysis of ESBO-IA-UA oligomer were given. In Figure 4.7, FTIR spectra of the synthesized oligomers along with the formation/disappearance of various functional peaks was shown. The spectral analysis confirmed the integration of IA into the ESBO backbone, as indicated by the C=C peak at 1636 cm^{-1}. The presence of HEMA was identified through the =CH peak at 810 cm^{-1}. A peak at 1695 cm^{-1} signified the formation of carbamate ester (NHCO-) units in both the MDI-HEMA adduct and the UA-IA-ESBO oligomer spectra. The depletion of isocyanates led to the disappearance of the peak at 2270 cm^{-1} in the UA-IA-ESBO oligomer spectra. Additionally, C-H (methyl and methylene) stretching vibrations were consistently observed across all spectra in the 2800–3000 cm^{-1} range [65-67].

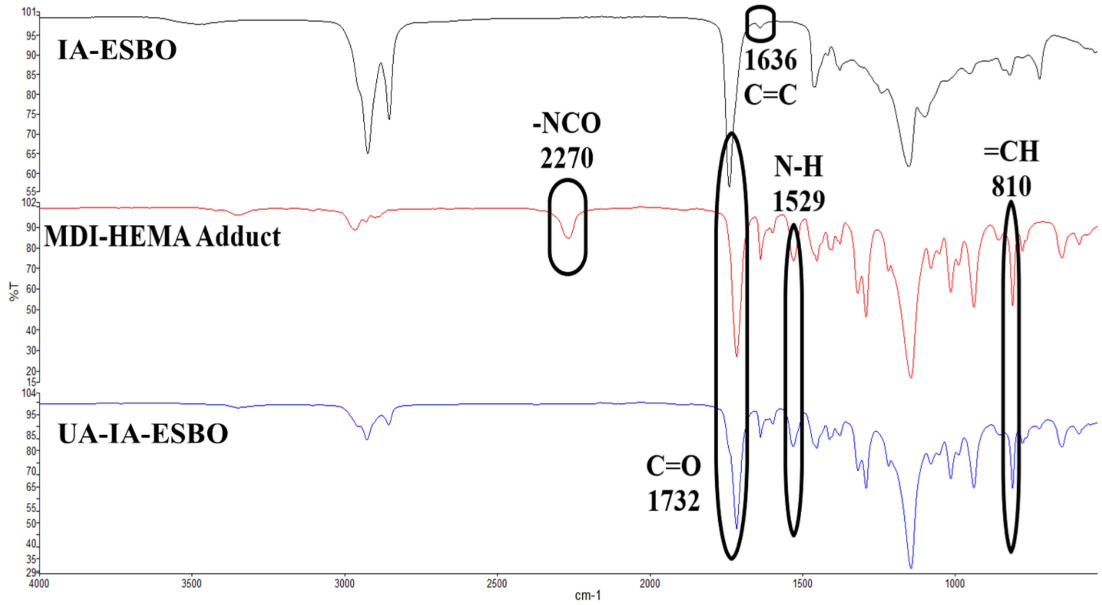


Figure 4.7 : FTIR spectra of the synthesized oligomers.

The ^{1}H NMR spectra of the synthesized oligomers are presented in Figure 4.8. A peak at 3.44 ppm, appearing in all spectra, corresponds to the characteristic IA CH_2 protons. In both the MDI-HEMA and UA-IA-ESBO spectra, peaks at 5.59–5.60 ppm and 6.10–6.18 ppm indicate the characteristic HEMA signals for $C(CH_3)=CH_2$ trans and $C(CH_3)=CH_2$ cis configurations, respectively. Additionally, the peak at 4.23 ppm is associated with the $–O–CH_2–CH_2–O–$ structure of HEMA. Further supporting the presence of HEMA in the oligomer structure are peaks at 1.95 ppm (CH_3), 1.52 ppm, and 0.98 ppm ($-CH_3$ in the allylic position). The protons of the aromatic structure of MDI are observed at 3.87 ppm. Moreover, the reaction between the MDI-HEMA adduct and IA-ESBO oligomer is confirmed by the newly formed peak at 4.48 ppm, which corresponds to the –NH– groups of urethane methacrylate [68-70].

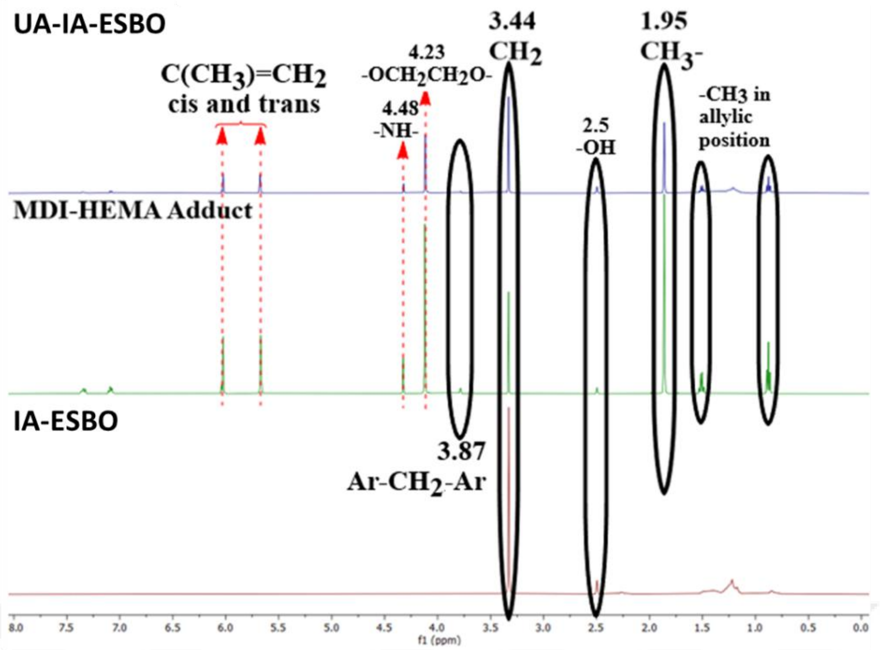


Figure 4.8 : ^{1}H NMR spectra of the synthesized oligomer.

The physicochemical characteristics of films are influenced by their crosslinking density, which is also affected by the type and functionality of reactive diluents. Table 4.1 presents the degree of swelling (DS, %), gel fraction (GF, %), and weight loss values of UV-cured free films when exposed to acidic and basic chemical conditions. As the crosslinking density increases, both DS (%) and weight loss (%) decrease, whereas GF (%) reflects a higher crosslinking density. According to Table 4.1, multifunctional reactive diluents enhance chemical resistance and reinforce the film structure, preventing deformation by increasing crosslinking density. The presence of strong intermolecular bonds in carbamate esters, along with additional interactions such as hydrogen bonding and stiff aromatic groups from MDI, contributes to outstanding chemical resistance across all films. Since water interacts minimally with polymer chains and serves as a neutral medium, it exhibits the lowest swelling ratio. Sample C demonstrated the most favorable physicochemical properties in terms of swelling behavior, GF, and chemical resistance due to incorporating the three-functional reactive diluent (TMPTMA) in its composition [70-72].

Table 4.1 : Physicochemical test results of the UV-cured free films.

Samples	DS (%)			GF (%)	Chemical Resistance (weight loss) (%)	
	Toluene	Ethanol	Distilled Water		NaOH (10%)	HCl (10%)
(A) with TMPTMA	5.18	0.64	0.75	0.93	0.20	0.15
(B) with HDDA	7.06	4.18	0.91	0.89	0.51	0.28
(C) with MA	30.40	9.34	2.53	0.83	1.25	0.93

The thermal characteristics of UV-cured free films were analyzed using TGA and DSC techniques. As illustrated in Figure 20 and Table 4.2, weight loss during thermal degradation and overall thermal stability are influenced by the number of functional groups, which define the crosslinking density. A higher crosslinking density improves thermal stability. According to Figure 4.9(b), the mass loss curve indicates that all samples remained stable up to 206°C, beyond which rapid ester decomposition of soybean oil occurred in all cases [73]. Based on the TGA curves, significant thermal degradation of polymeric urethane methacrylate units was observed above 390°C. TGA results also show that the sample containing TMPTMA as a reactive diluent exhibits superior thermal stability due to the presence of three-functional groups. These functional groups promote hydrogen bonding, which requires additional energy for thermal breakdown [74-77]. Examining Figure 4.9(a) and Table 4.2, the primary decomposition temperature of UV-cured free films, associated with the degradation of urethane groups and the formation of primary amines, is within the 390–430°C range. Due to variations in the number of functional groups in reactive diluents, this decomposition temperature gradually increases from MA to TMPTMA [78].

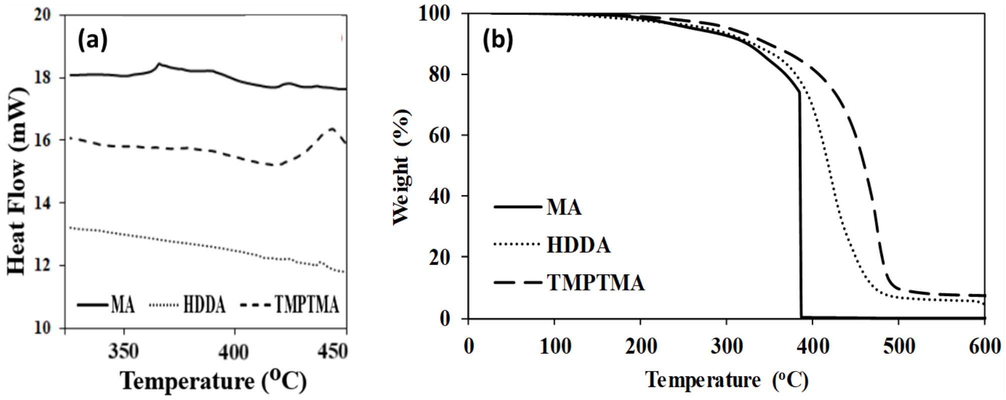


Figure 4.9 : DSC (a) and TGA (b) curves of UV-cured films.

Table 4.2 : Thermogravimetric behaviour and decomposition data of UV-cured free films.

Sample Codes	Temperature at 5% Weight Loss	Temperature at 50% Weight Loss	Residue at 400 °C (%)	Char Yield at 600 °C (%)	Decompositon Temperature (T_d)(°C)
TMPTMA	302	460	82	7.45	430
HDDA	276	418	69	4.58	412
MA	259	385	0.3	0.09	390

For the mechanical properties of the oligomer film, Taber abrasion test, cross-cut tape adhesion test, and water immersion test were applied to the coated surface. Taber abrasion test was applied to the surface without any additional load in order to evaluate the characteristics. In Figure 4.10, the results of Taber abrasion test were given with up to 100 cycles abrasion values. The samples with multifunctional reactive diluents (B and C) has better resistance against abrasion compared to sample A with monofunctional reactive diluent. Hydrogen bonds between the carbamate esters of urethane methacrylates and TMPTMA increased the oligomer's resistance to the abrasion [79,80]. Thus, it is examined that the sample A with monofunctional reactive diluent has the highest weight loss.

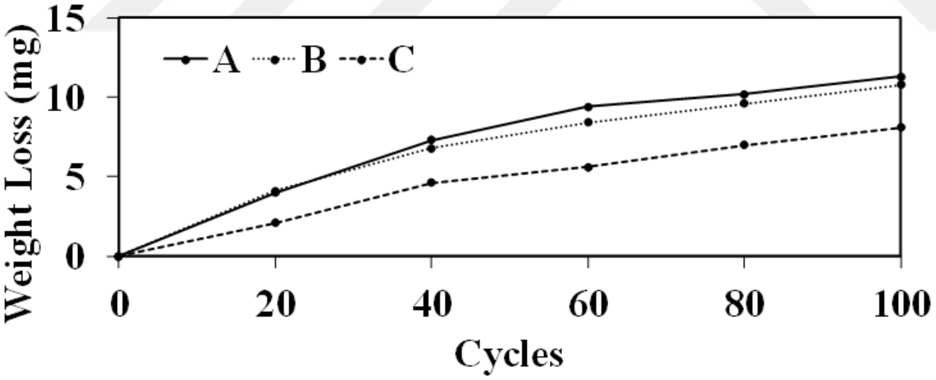
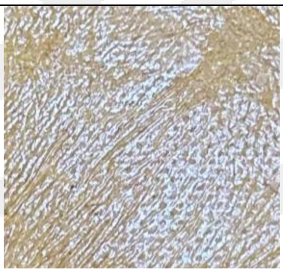
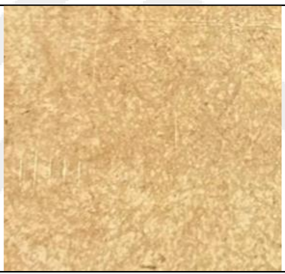
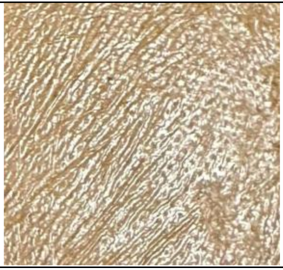


Figure 4.10 : Taber abrasion test result of coated wood plates.

By using ASTM D3359 method, cross-cut tape test applied to the samples. In Table 4.3, results of water immersion test and cross-cut tape test were given. Based on the results, mono-functional reactive diluents tend to lower the crosslink density, leading to a more flexible polymer structure that enhances surface cohesion. In contrast, an increase in crosslinking density results in a stiffer, more rigid coating. Examining the cross-cut adhesion results, it is evident that as the number of functional groups increases, the adhesion performance declines due to reduced flexibility in the polymer structure. Consequently, sample C exhibited the poorest adhesion properties because it contained a three-functional reactive diluent [81,82].

For water immersion test, ASTM D714-25 method was used, and the samples evaluated regarding the images, the blister types and densities. According to the results, blisters were depending on the crosslinking density of the samples. Sample A has the most visible blisters because of its less crosslinking density caused by mono-functional reactive diluent. Same result was observed in water immersion test which demonstrated that the sample with TMPTMA has better water resistance, and also its blister size is medium no 8. The results could be supported that the multifunctional reactive diluents enhances the water resistance [83].

Table 4.3 : Test results of Cross-cut Adhesion and Water Immersion tests.

Samples		**A**	**B**	**C**
Cross-Cut Adhesion		**4B**	**4B**	**3B**
Water Immersion Test	**Before Test**			
	After 24 h Water Immersion			
	Blister Type/Size	**Medium No 4**	**Medium Dense No 8**	**Medium No 8**

5. CONCLUSIONS

The presented thesis work includes synthesis, characterization, and application of 2 different UV-curable oligomers which are ESBO-IA and ESBO-IA-UA. By using blending method, the oligomers were blended with different types of reactive diluents in order to obtain specific properties. Prepared formulations were characterized by fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopies. Then, the oligomers were applied to MDF wood surfaces and the properties were tested. Taber test, water immersion test, and cross cut test were applied in order to understand the mechanical properties of the oligomers. According to the mechanical test results, increasing crosslinking ratio of reactive diluents provided better mechanical properties. For physicochemical properties, the same result was obtained. Degree of swelling was decreased; chemical resistance and gel fraction were increased.

When all results were evaluated, the proposed ESBO-IA based oligomers were successfully synthesized and included in coating formulations for MDF wood surfaces.

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- **U. İ. Okdemir, Z. Yildiz, H. A. Onen**, (2024) “Synthesis And Application Of Bio-based Photocurable Oligomers For Wood Coatings”, Polymat 2024, Mexican.

- **U. İ. Okdemir, Z. Yildiz, H. A. Onen**, (2024) “High Bio-Content Photocurable Coatings for Wood Surfaces Derived from Itaconic Acid”, 19th Asian Chemical Congress 2024, Turkey.

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