



Development of tri-functional biobased reactive diluent from ricinoleic acid for UV curable coating application



Ganesh Phalak^a, Deepak Patil^a, Vishal Vignesh^b, Shashank Mhaske^{a,*}

^a Department of Polymer and Surface Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga (E), Mumbai 400019, India

^b Department of Materials Science and Engineering, University of Florida, Gainesville, FL, USA

ARTICLE INFO

Keywords:

Ricinoleic acid
Ricinamide triol
Ricinamide triacrylate
Biobased reactive diluent
UV curable

ABSTRACT

Renewable based materials have come out as an environmentally friendly alternative to petrochemical based materials due to their sustainability, lower carbon footprints and often lesser price. A tri-functional acrylate monomer was synthesized from Ricinoleic acid (RA) and used as biobased reactive diluent along with an oligomer for a UV curable coating application. The ricinoleic acid was modified by using sodium methoxide catalyzed amidation with diethanolamine and converted into fatty amide based triol. This synthesized ricinamide triol (RTO) was further reacted with glycidyl methacrylate in presence of triphenylphosphine. The synthesized products were fully characterized by FTIR, GPC and end group analysis. The chemical structure of RTO and ricinamide triacrylate (RTA) was elucidated from ¹H NMR, ¹³C NMR spectroscopy. In comparison, the commercial triacrylate was examined. The influence of addition of reactive diluents on the viscosity of oligomer with varying concentrations up to 10–30 wt% was studied using rheometer. The UV curing behavior of coatings was estimated by FTIR. The UV cured coatings were further characterized by DSC, XRD, and TGA analysis. The UV curing coatings were evaluated to determine the mechanical, physical and solvent resistance properties. The Biobased content, gel content and water absorption property of UV cured coatings was also examined.

1. Introduction

In coating industries generally, solvent borne coatings are based on reactive oligomers or polymers which are cross linked through baking process. Consequently, usage of solvent borne coatings is responsible for the emission of volatile organic components (VOCs) in environment. It contributes to global warming, degradation of ozone layer, and also related with human health issues (Johansson and Johansson, 2008). The coating industries have been required to develop environmentally friendly coatings with low VOCs emission. Therefore, ultra-violet curing (UV) technology have received large attention in coating industry due to their low energy consumption, low capital investment, very fast curing at ambient temperature, zero emission of VOCs and hazardous air pollutants (HAPs).

The most common formulations for UV curable coating contain three important components: unsaturated acrylic oligomer, photoinitiator and reactive diluent (Wang and Soucek, 2013; He et al., 2007). The oligomers used for formulations such as urethane acrylate, epoxy acrylate, polyester acrylate and silicon acrylate etc. Usually, reactive diluents are incorporated into UV curing system to reduce the viscosity of oligomers (Glockner et al., 2008). Reactive diluent is a low viscosity

and compatible material act as a solvent in UV curing systems, is chemically copolymerizes with oligomer in presence of photoinitiator and converted into the cross linked film during photo-polymerization (Fouassier et al., 2010). The mono functional reactive diluents have lead to reduced modulus and improved ductility of cross linked film, where as di- and multi-functional reactive diluents gives reverse effect. It was accepted that, higher the functionality of reactive diluent increases rapid curing rate and high degree of crosslink density of coating (Kaewpirom and Kunwong, 2012). Commercially, the majority of raw materials for UV curing system are derived from fast depleting non renewable resources.

The petroleum based reactive diluents have excellent properties but several of their restrictions are skin irritancy, poor pigment wetting and film shrinkage often in poor adhesion. Therefore, biobased derived reactive diluent would be promising alternative for petroleum based reactive diluent (Rengasamy and Mannari, 2013). The biobased reactive diluent should also differentiate themselves with low toxicity and low volatility (Chen et al., 2015). In modern era, synthesis of monomers and polymers from renewable materials has received increasing attention to the researchers and industrial sectors for replacement of petroleum-derived materials (Ma et al., 2014). The reasons behind that, there is

* Corresponding author.

E-mail address: st.mhaske@ictmumbai.edu.in (S. Mhaske).

rapid dwindling of petroleum resources, global warming, economical, and other environmental problems (Choi et al., 2014). The incorporation of photo curable functionalities into renewable resources can offer a green + green approach to recent coating industry (Fertier et al., 2013). A number of publications have explained the photo polymerization of renewable materials with chemically modified structures. Jingcheng Liu et al. synthesized a series of multi-arms cardanol based acrylate by using cardanol and biobased polyols as precursors to produce UV curable coatings. The results elucidated that the coatings with high biomass content reveal good properties such as adhesion, gloss and acid resistance (Liu et al., 2016). The biobased antibacterial methacrylate in UV curable coatings synthesized from tannic acid and varied amount of glycidyl methacrylate. Tannic acid methacrylate UV curable coatings were shown good antimicrobial and physical properties (Liu et al., 2014). Muller et al. reported radiation curable binder based on acrylated castor oil glycerides (Müller and Wilke, 2014). The developed soybean oil based UV curable acrylate oligomers are used as environment friendly and sustainable uv-cured coatings with control mechanical properties for various applications (Rengasamy and Mannari, 2013). The two different types of UV curable monomers from eugenol via thiol-ene reaction and further copolymerized with acrylated epoxidised soybean oil. The eugenol based monomers were incorporated into acrylated epoxidised soybean oil enhances properties of UV curable coatings (Dai et al., 2016b). Liu et al. developed UV curable hyperbranched methacrylates from natural tannic acid. The results shows that the hyperbranched methacrylates combined with acrylated soybean oil could produce UV curable coatings of balanced coating performance with high biorenewable content (Liu et al., 2013). Thus, development of UV curable coating from renewable materials is attractive approach in coating industry.

Vegetables oils are interesting alternative to non-renewable resources that have been used for coating applications. They are inexpensive and widely available from different resources. As known previously, the internal double bonds of vegetable oils have a low reactivity; hence, a wise option is chemical modification to make them more reactive under UV irradiation (Fertier et al., 2013). Vegetables oils are triglycerides and contain at least one unsaturated long chain fatty acid in their chemical structure. Therefore, the suitable structure of vegetables oils are easily used to produced valuable monomers and polymers by chemical modification. Dean Webster et. al., designed glucose modified soybean oil based monomers for high performance coatings. A carboxylic acid functional trimer made from modified isosorbide and its cross linking with epoxidised sucrose soyate, resulting biobased thermoset with good hardness and flexibility (Ma et al., 2016b). The biobased highly epoxy functional thermoset was prepared by epoxidised sucrose soyate cross linked with natural carboxylic acids without used any catalyst and toxic compounds. The biobased thermoset possessed excellent thermal and mechanical properties (Ma and Webster, 2015; Ma et al., 2016a). On hydrolysis, triglyceride of vegetable oil gives different fatty acids and glycerol. Fatty acids from vegetable oils may serve as starting materials for synthesis of biobased polymer (Palaskar et al., 2010; Petrovic, 2008). Among vegetable oils, castor oil has attracted more interest for preparation of different biodegradable polymer (Mutlu and Meier, 2010; Ogunniyi, 2006). It contains about 85–90% of ricinoleic acid, hydroxylated unsaturated fatty acids (Lebarbé et al., 2013). Ricinoleic acid obtained from the hydrolysis of castor oil and has secondary hydroxyl groups in the 12th position, a double bond in the 9th position and a carboxyl group (Slivniak and Domb, 2005; Billault et al., 2004). In previous literatures, the synthesized oligomeric di and tri-acrylate based on ricinoleic acid amide derived from esterification of castor oil by acryloyl chloride. UV curable compositions were prepared by photo polymerization of di and tri-acrylate with varying amount of commercial reactive diluents i.e. tripropylene glycol diacrylate and trimethylol propane triacrylate respectively (Palanisamy and Rao, 2007). The overall results revealed that the crosslink density of coating increased with varying amount of

reactive diluents. Therefore castor oil based di and tri-acrylate demonstrated good properties and dilution with commercial acrylate improved conversions as well as viscoelastic properties (Rao and Palanisamy, 2008; Rao and Palanisamy, 2010). Li et al., prepared uv-curable waterborne polyurethane acrylate based on castor oil/pentaerythritol triacrylate. The coating shows improved water resistance, and glass transition temperature with increasing castor oil content (Li et al., 2014).

The objective of the present work is to prepare a biobased reactive diluent for uv-curable systems. The ricinamide triacrylate is synthesis via two step route using ricinoleic acid, diethanolamine and glycidyl methacrylate as raw materials. For comparison, the commercial triacrylate, Trimethylolpropane ethoxylate triacrylate (TMPEOTA) was also examined. The viscosity behavior of UV cured mixtures was studied by rheometer with increasing content of reactive diluent. The investigation on the UV curing behavior of coating was conducted via FTIR. The mechanical physical and solvent resistance property of the UV cured coatings also estimated. The functionality and chemical structure of RTA was evaluated from the ^1H NMR. In UV curing system, the addition of reactive diluent with additional cross-linking sites improved the flexibility and toughness of urethane acrylate oligomer. The thermal, mechanical and physical properties of UV cured coatings were estimated with an increased content of reactive diluent.

2. Material and methods

2.1. Materials

Ricinoleic Acid (RA) was obtained from Jayant Agro, Mumbai, India. Diethanol amine, sodium methoxide, anhydrous sodium sulphate, sodium chloride, toluene, triphenylphosphine (TPP) and hydroquinone were procured from S.D Fine Chemicals limited (India) and used as received. The glycidyl methacrylate was obtained from Sigma Aldrich Mumbai, India. The urethane di-acrylate oligomer and Trimethylolpropane ethoxylate triacrylate was purchased from Allnex Resins India Private Limited, Mumbai. The photo-initiator IRGACURE 184 was received from CIBA, Mumbai.

2.2. Synthesis of ricinamide triol (RTO)

Ricinamide triol was synthesized by reacting ricinoleic acid with diethanolamine as shown in Fig. 1. Diethanolamine (0.012 mol, 1.263 g), and sodium methoxide catalyst (0.021 g, 0.5 wt%) were placed into a four-necked, round-bottom flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a reflux condenser. The resultant mixture was dissolved in toluene as an azeotropic solvent. Ricinoleic acid (0.01 mol, 2.985 g) was added drop wise in reaction mixture under continuous stirring and heated at 120–130 °C with continuous stirring under a steady flow of nitrogen gas. The reaction was refluxed for 3–4 h, until the considered quantify of water is collected in reflux condenser. The progress of reaction was studied by calculating the acid value at regular intervals of time. After the completion of reaction, the product was washed with 15% NaCl solution several times to remove unreacted traces from product. The product was dried with anhydrous sodium sulphate and toluene was evaporated by using rotary evaporator. The final product obtained was viscous and yellowish in color.

2.3. Synthesis of ricinamide triacrylate (RTA)

As shown in Fig. 2, Ricinamide triacrylate was prepared from RTO (0.01 mol, 3.852 g), TPP (1.5 wt%, 0.250 g) as catalyst for epoxy ring opening, and hydroquinone (0.1 wt%, 0.016 g) were added into four-necked, round-bottom flask equipped with a mechanical stirrer, a dropping funnel, a thermometer, a condenser, and a nitrogen inlet. The resultant mixture was diluted with toluene and heated at 70 °C for 1 h.

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