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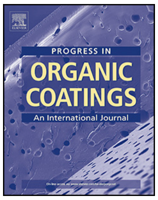

Review

UV-curable PUDs based on sustainable acrylated polyol: Study of their hydrophobic and oleophobic properties

Senthilkumar Rengasamy, Vijay Mannari*

Coating Research Institute, Eastern Michigan University, United States

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ABSTRACT

UV-curable polyurethane dispersions (UV-PUDs) are fast expanding commercial applications since they combine benefits of both water-borne as well as UV-curing technologies while addressing many technical, environmental and performance benefits. Varying the compositions and cross-link density of UV-PUD polymeric chain backbone can control the film properties of UV-PUDs. There are many design restrictions posed by availability of commercial materials. In the present research work we demonstrate synthesis and application of a multi-functional acrylate polyol derived from soybean oil, as soft-segment of UV-PUDs. A series of UV-PUDs have been designed for high performance coatings that are specifically hydrophobic and oil-resistant. To this end, UV-PUDs based on acrylated soy-polyol have been further modified by siloxane and perfluoro compounds and their films with varying cross-link density have been investigated. The UV-PUD films were characterized for their film properties, particle size, contact angle and solvent swelling ratio. The outcome of this study provides useful insights into design considerations for hydrophobic and oil-resistant UV-curable coatings.

Contents

1. Introduction

Polyurethanes are established as polymers of choice, due to their versatile structure–property relationship [1–3] in such industrial applications as coatings, sealants, adhesives textiles, foot-wear and rapidly expanding in many others [4–6]. The early development of polyurethanes for coatings was mainly limited to solvent-based or high-solid systems. Due to the environmental reasons and regulatory pressures water-borne polyurethanes (WPU) have emerged as compliant systems and have been offered both as one-component and two-component systems. Polyurethane dispersions (PUDs), a class of water-borne PUDs, are typically aqueous dispersions of high-molecular weight polyurethanes and have become very popular in recent years in coatings and related industries. While PUDs

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* Corresponding author. Tel.: +1 7344871235.
E-mail address: vijay.mannari@emich.edu (V. Mannari).

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offer many technical and environmental advantages, their predominantly thermoplastic nature and relatively slow drying, limits their applications in many industrial coatings requiring high performance.

UV-cure technology is another environmentally friendly and sustainable technology adopted by coating industry and is fast advancing and expanding in products with myriads of end-use applications. In general, most common UV-cure systems are 100% liquids comprised of acrylate functional oligomers and reactive diluents along with a suitable photo-initiators. Upon UV irradiation these systems rapidly cure through radical-initiated addition polymerization to form cross-linked film structure. A three dimensional (3D) polymeric network formed by this solvent free UV-curable coatings give excellent resistance to chemicals, scratching and weathering [7,8]. Because of these advantages, UV-cure technology can be utilized in fast drying protective coatings [9,10], printing inks, printing plates [11], microcircuits and optical disks [12–16] besides many more. Such systems have advantages of low or zero VOC, very high cure speed, low energy consumption and provides coatings with high hardness, solvent resistance and very high gloss due to their high cross-liked density. Despite these benefits, conventional UV-cure systems have some limitations, such as lack of flexibility, lower adhesion due to substantial film shrinkage, odor and skin irritation issues, and difficulties in handling after application (and before curing) due to their tacky nature [17]. One important shortcoming of such system is their applications for three-dimensional substrates that have shadow areas where the coating material has limited or no exposure to irradiation suffers from poor curing [18,19]. A dual-cure coating system having a cure mechanism in addition to UV-curing can address the aforementioned problem.

Thus, a new generation systems called UV-PUD have been introduced to address the above stated limitations of both conventional and 100% solid UV-cure systems. UV-PUDs are essentially aqueous dispersions of polyurethanes containing UV-curable acrylate functionality. In UV-PUDs, PUDs having sufficiently high molecular weight are capped with acrylic functionality [20,21] which upon cure provides excellent solvent resistance and surface and bulk properties depending on their crosslinking density. The crosslink density is controlled by the molecular weight of PUD and functionality of the capping agents. In most commercial UV-PUDs the acrylate functionality is invariably introduced at the end of the polymer chain using end-capping acrylate compound of varying functionality.

The specific benefits of UV-PUDs are low or zero VOC, no need for reactive diluents, much lower shrinkage, reduced oxygen inhibition and ready to handle before UV cure due to their tendency to form dry-to-touch films even before UV-curing, due to their sufficiently high molecular weight [22]. Since water is used as continuous phase, viscosity is not an issue. Absence of reactive diluents makes UV-PUD technology more environmental friendly and free from odor and skin irritation issues. Due to the aforementioned distinct advantages, the UV-PUD technology steadily extended its branches to many sectors of industrial applications [23,17,24]. The UV-PUDs exhibits excellent resistant to chemicals [23,25], water [23,26], mar [27,28] and weathering [23,29,30]. The conventional UV-cure systems where reactive diluents are used generally suffer from volume shrinkage upon curing. As Mequanint and Sanderson [31] explained, the shrinkage is caused by conversion of nonbonding distances between the monomers are converted to shorter bonding distances in polymers. The shrinkage develops internal stresses responsible for delamination of films from underlying substrate over a period of time or even with minimal external forces. Unlike conventional UV-cured system, UV-PUD provides films with better flexibility due to low crosslink density of their films. Since crosslink density is low, the average MW between crosslinks is higher, and due to presence of urethane groups that results in tack-free film before irradiation [22,32]. These characteristics make UV-PUD more suitable for furniture and floor applications where handling of tack-free film become more useful during irradiation process.

In the present work we have designed and developed UV-PUDs with unique set of attributes. We have attempted to prepare “green” UV-PUDs that have high bio-based content (sustainability) and exhibit superior hydrophobicity and oil (hydrocarbon) resistance. In order to accomplish this goal, we have used a soy-based acrylated polyol developed earlier by our research group [33] and used that as a primary soft-segment of UV-PUD. It should be noted that unlike conventional UV-PUDs, these UV-PUDs have acrylate functionality on the soft-segment and thus is evenly distributed along the entire polymer chain. In order to make them hydrophobic and oil resistant, we have also incorporated polysiloxane diol as a component of soft segment. While soy-polyols are known to provide hydrophobicity to the film [34–37], in order to enhance this property as well as to confer oil resistance of their films, PUDs were modified with perfluoro moiety in varying degree. Further, to study the effect of cross-link density of their UV-cured film on various properties, polymer chains were end-capped with acrylate groups in varying degree. UV-cured film properties of these PUDs have been studied as function of their composition and cross-link density.

2. Experimental

2.1. Raw materials

Acrylic polyol (AESO) was derived from epoxidized soybean oil (ESO) (Arkema, USA, Vikoflex 7170) and polydimethylsiloxane diol (PDMS diol, Silmer OH-Di-10) was procured from Siltech Corporation, Canada. Isophorone diisocyanate (IPDI, Desmodur-I) was received from Bayer Material Science, USA, and dimethylolpropionic acid (DMPA) from Geo Specialty Chemicals, USA, were used as procured. Darocur^{TM} 1173, a radical type photo-initiator was obtained from BASF, USA. All other raw materials such as triethylamine (TEA), N-methyl-2-pyrrolidone (NMP), acetone, dibutyltin dilaurate (DBTDL), 1,4-butanediol, tetrafluoroboric acid (HBF_4) 48% in water, 2-hydroxyethyl acrylate (HEA), monomethylether of hydroquinone (MEHQ), diethyl ether, anhydrous magnesium sulfate, 4,4′,5,5′,5″-pentafluoro-1-pentanol (PFP) and 1-heptanol (Hept) were purchased from Sigma–Aldrich, USA, and used as received.

2.2. Methods of characterization

Acrylated soy-oligomers have been characterized for oxirane oxygen content (ASTM D – 1652-97), acid number (ASTM D – 1639-96), iodine value (ASTM D – 5768-02) and hydroxyl number (ASTM D – 4274-05). Viscosity of the epoxidized vegetable oils and their derivatives were determined at 25 °C using the Brookfield viscometer. Gel permeation chromatography (GPC) was used to determine the molecular weight of oligomers. Various UV-PUDs were mixed with 3% of free-radical type photo-initiator Daracure^{TM} 1173 and applied on cold rolled steel panels (6″ × 4″ × 0.032″) to ~50 μm wet film thickness and cured under UV-irradiation. A UV-cure system (Fusion UV) with a D-bulb was used with the conveyor belt speed set to 40 feet/min. Using a compact radiometer (UVPS), the energy density measured was ~2100 mJ/cm^2. Properties of cured films were tested and compared after 7 days. The UV-cured film properties were characterized for pencil hardness (ASTM D – 3363), impact resistance (ASTM D – 2794-99), Adhesion (cross-cut) test (ASTM D – 3359-02), MEK double-rub test (ASTM D – 4752-98). BYK