



ELSEVIER

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Characteristics of dual-curable blocked isocyanate with thermal radical initiator for low-temperature curing of automotive coatings



Kevin Injoe Jung^{a,1}, Beomjin Kim^{b,1}, Dong Geun Lee^a, Tae-Hee Lee^{b,c}, Seo Yeon Choi^b, Jin Chul Kim^b, Seung Man Noh^{b,*}, Young Il Park^{b,*}, Hyun Wook Jung^{a,*}

^a Department of Chemical and Biological Engineering, Korea University, Seoul 02841, Republic of Korea

^b Research Center for Green Fine Chemicals, Korea Research Institute of Chemical Technology, Ulsan 44412, Republic of Korea

^c Department of Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

ARTICLE INFO

Keywords:

Dual-curable blocked isocyanate

TRI

Low-temperature curing

Automotive coatings

Radical reaction

Urethane reaction

ABSTRACT

Dual-curable blocked isocyanate with a thermal radical initiator (BL-Tri-cHD) was designed and synthesized to perform low-temperature curing of automotive coatings. BL-Tri-cHD can simultaneously react with both unsaturated C=C double bonds for free-radical polymerization and hydroxyl groups for the urethane reaction in hydroxyl-functionalized urethane methacrylate oligomers (HFUMO) under mild thermal curing conditions. The dual crosslinking behavior and mechanical properties of HFUMO-based coatings using BL-Tri-cHD were compared with those of a commercial blocked isocyanate thermal crosslinker (Desmodur® BL-PL350). The onset temperature for initiating cured by BL-Tri-cHD was about 68 °C, confirming faster crosslinking at relatively lower temperature than BL-PL350, which initiated curing at 140 °C. To quantitatively evaluate the properties of cured coatings, a nano-indentation was made in the surfaces of clearcoat films cured at 150 °C, 130 °C, and 120 °C. Films cured using BL-Tri-cHD and BL-PL350 at 150 °C exhibited similar indentation patterns. The indentation curves for the films with BL-Tri-cHD cured at lower curing temperatures such as 130 °C and 120 °C showed favorable penetration depth profiles similar to the sample cured at 150 °C, whereas the films with BL-PL350 cured below 150 °C had a less dense network structure, resulting in a deeper penetration depth than the sample cured at 150 °C. Therefore, we report that dual-curable BL-Tri-cHD demonstrates promising performance in automotive coating applications and possesses the ability to form highly crosslinked networks, even at low curing temperatures.

1. Introduction

Current thermally cured coatings in automotive applications are generally applied in the in-line processes at high curing temperatures of around 150 °C during the process time of 30 min. These curing conditions should guarantee a crosslinking reaction in the main resin, which contains functional groups of crosslinkable moieties, and crosslinkers. Considering the unfavorable nature of high-temperature curing and its inefficient energy consumption, low-temperature curing technology in the field of automotive coatings has been steadily developed as an eco-friendly and economical alternative. This technique has many advantages, such as reduced CO₂ production, energy saving, and lower facility costs due to faster and more efficient production. Furthermore, the use of high-performance engineering polymers to realize light-weight vehicles is gradually increasing [1–4]. However, coating

technology involving car bodies composed of engineering plastics is restricted at current curing temperatures, as plastics can be distorted or deformed from their intrinsic glassy transition states, when exposed to high temperatures. Therefore, it is necessary to develop novel coating materials and crosslinking technologies at lower curing temperatures, in order to encourage practical use of plastic substrates in car bodies.

Many attempts to achieve low-temperature curing technologies for automotive coating systems have been made [5–8]. Photo-curing methods applicable to automotive coatings could be a viable option, but require a very high investment cost for the installation of specialized photo-curing equipment and ventilation. There are few technical reports on crosslinkers such as thermal radical initiators (TRI) for low-temperature curing applications. The blocked isocyanate system has been used in a wide variety of one-pack (1K) coating materials as a representative low-temperature curing method [9,10]. However, in

* Corresponding authors.

E-mail addresses: smnoh@kRICT.re.kr (S.M. Noh), ypark@kRICT.re.kr (Y.I. Park), hwjung@grtrkr.korea.ac.kr (H.W. Jung).

¹ These authors contributed equally to this work.

spite of many efforts to lower the deblocking temperature of blocked isocyanate agents, it has proven difficult to effectively reduce the deblocking temperature of many agents such as phenol, oxime, and pyrazole [11–13]. Furthermore, coatings cured at low temperatures are prone to display unfavorable physical properties compared to those cured under normal thermal conditions.

Some thermal radical initiators, such as benzoyl peroxide (BPO), have caused explosions while stored under unexpectedly high temperatures due to their highly exothermic reactivity upon heating [14]. To overcome such drawbacks, TRI based on *O*-imino-isourea was developed to endow free-radical polymerization upon unsaturated polymeric resins [15–17], thereby confirming that radical polymerization by TRI could be achieved below 100 °C. Polymers produced via free-radical polymerization play a leading role in forming rigid and dense crosslinked network in the curing or polymerization stages, and necessarily affect various physical and rheological properties of the outermost coating. For these reasons, new low-temperature curing technology should be developed so that coatings cured at lower temperatures satisfy existing qualification requirements and are safely storable. Our strategy in this study was to design a thermally dual-curable system that can provide coatings with good film properties at lower temperatures than conventional curing systems.

In this study, a dual-curable blocked isocyanate with a thermal radical initiator named BL-Tri-cHD as the crosslinker for the low-temperature curing process was designed and tested. We found that BL-Tri-cHD was able to react with both unsaturated double (C=C) bonds for free-radical polymerization and hydroxyl (–OH) groups for urethane reaction in hydroxyl-functionalized urethane methacrylate oligomers (HFUMO) during thermal curing. BL-Tri-cHD was blocked with a recently developed cycle TRI derivative based on *O*-imino-isourea (see Fig. 1(a)) [16]. The schematic reaction mechanism of HFUMO and BL-Tri-cHD is shown in Fig. 2. The isocyanate group and radicals of TRI separate in BL-Tri-cHD above a specific temperature and respectively react with hydroxyl and acryl groups in the HFUMO resin.

Furthermore, the crosslinking behavior and mechanical properties of HFUMO-based coatings with BL-Tri-cHD were compared with those of a commercial blocked isocyanate thermal crosslinker (Desmodur® BL-

PL350 MPA/SN, Coverstro). During the thermal curing process, the real-time crosslinking properties of HFUMO-based samples were rheologically investigated using a rotational rheometer equipped with a heating chamber [16–20]. In particular, the pendulum periods and logarithmic damping ratios of samples were measured using a rigid-body pendulum tester (RPT), which is a suitable instrument to examine the curing dynamics of thin film coatings [17,21–25]. The structure and curing reaction of BL-Tri-cHD were confirmed by FT-IR [26,27]. The surface mechanical properties of fully cured thin free films were evaluated using a nano-indentation tester (NHT) [28–34].

2. Experimental

2.1. Design and synthesis of BL-Tri-cHD

(*Z*)-cyclohexanone *O*-(*N,N'*-dicyclohexylcarbamimidoyl) oxime (cHDCC) was synthesized according to the method reported in the literature [16], and exhibited good performance as a TRI. Desmodur® N-3300 (HDIt) was added to a solution of cHDCC dispersed in *n*-butylacetate (BAC). After being stirred for 12 h at room temperature under an argon atmosphere, the reactive isocyanate group of HDIt was easily blocked with a secondary amine group of cHDCC, as depicted in Fig. 1(a), and was deblocked at moderate temperatures [35,36]. The synthesized chemical structure of BL-Tri-cHD was characterized using FT-IR (Nicolet 6700/Nicolet Continuum, Thermo Fisher Scientific Inc., USA) in attenuated transmittance reflectance (ATR) mode. The blocking of isocyanate was checked by monitoring the disappearance of isocyanate peak at 2260 cm⁻¹ (Fig. 1(b)): Its peak (2260 cm⁻¹) fell to below 5% of the initial value when three TRIs per one single HDIt (3 equivalent amount of isocyanate) were present in the mixture. Note that the reaction was undertaken without any purification.

This newly designed BL-Tri-cHD was expected to react by the mechanism shown in Fig. 2. Three dissociated TRIs pursue acryl groups in HFUMO and initiate the radical reaction, while the NCO sites of the deblocked isocyanate bond react with hydroxyl groups and expedite the urethane reaction.

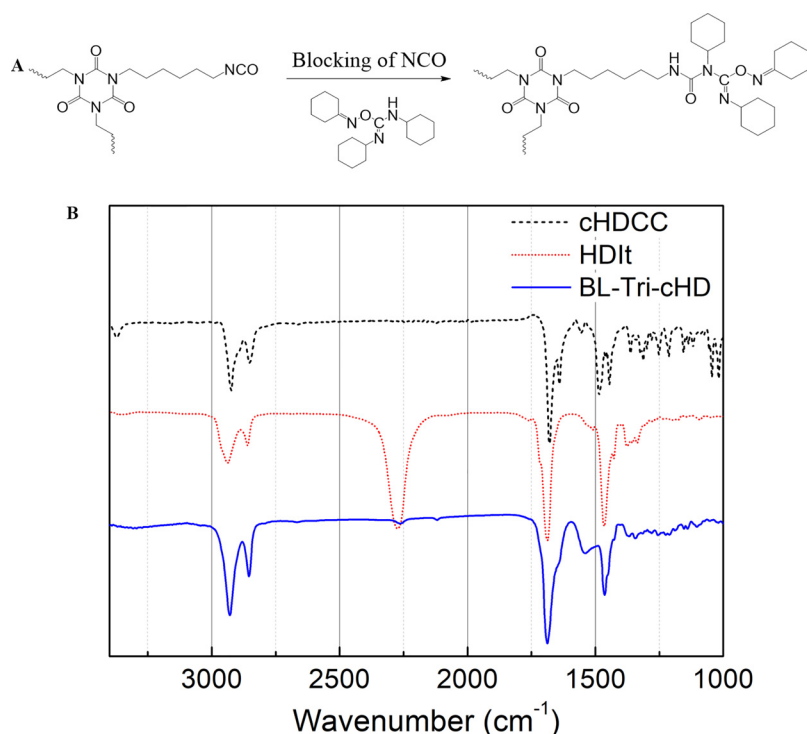


Fig. 1. (a) Synthetic scheme of BL-Tri-cHD and (b) FT-IR results of synthesized BL-Tri-cHD.

Download English Version:

<https://daneshyari.com/en/article/10140023>

Download Persian Version:

<https://daneshyari.com/article/10140023>

[Daneshyari.com](https://daneshyari.com)