



Influence of material properties on scratch-healing performance of polyacrylate-graft-polyurethane network that undergo thermally reversible crosslinking



So Young Kim^{a, b, 1}, Tae Hee Lee^{a, c, 1}, Young Il Park^a, Joon Hyun Nam^a,
Seung Man Noh^{a, **}, In Woo Cheong^{b, ***}, Jin Chul Kim^{a, *}

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

^b School of Applied Chemistry, Kyungpook National University (KNU), Daegu 41566, Republic of Korea

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

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ABSTRACT

Scratch-healing poly (methyl methacrylate)-*co*-[poly (methyl methacrylate)-*graft*-(oligo-caprolactone)] urethane networks containing a Diels Alder (DA) adduct unit (GCPNp-DAs) were successfully synthesized and shown to be capable of undergoing thermally reversible crosslinking. The synthesized polymers were coated on steel substrates to investigate the influence of their material properties on their scratch-healing performance. The reversible formation of crosslinked and de-crosslinked structures of the GCPNp-DAs at DA and retro-DA (rDA) reaction temperatures was demonstrated using FT-IR spectroscopy, differential scanning calorimetry (DSC), oscillatory rheology, and nanoindentation. The scratch-resistance and healing performances of the GCPNp-DA coatings were evaluated quantitatively using a scratch test machine equipped with an optical microscope (OM) and an atomic force microscope (AFM). These results were found to be greatly influenced by the material properties of the coatings such as the elastic modulus, indentation hardness (H_{IT}), crosslinking density (ν_c), and thermal transition temperature as well as by whether the deforming load that produced the scratches was increased in a progressive (gradual) or step-wise manner.

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1. Introduction

Polymeric coatings are employed in industrial applications such as electronics, transportation, construction and medical devices to protect substrate surfaces from physical damage, corrosion and microbial contamination [1–8]. In such systems, however, scratching of the polymeric coating quite frequently leads to corrosion or contamination of the substrate material, degrading the function or appearance of the substrate and reducing the service life of the product. Considerable research effort has therefore been devoted to eliminating or reducing the influence of scratches. The main strategies in this regard fall into two categories:

preventing scratches from forming in the first place, or healing them if they do form [9–11].

The basic principle behind preventing scratch formation is to improve the hardness and toughness of the coating by increasing the matrix crosslinking density (ν_c) and/or adding inorganic particles. While this approach is attractive in that it blocks scratch formation, it cannot be used for applications that require high elasticity, processability, compatibility, dispersion stability and/or optical transparency [12].

The techniques for healing scratches, on the other hand, use extrinsic or intrinsic healing mechanisms. In general, extrinsic scratch-healing of a polymeric coating is achieved by including microcapsules into the coating that can heal the scratches. This approach has the advantage that it provides autonomous (self) scratch healing without the need for an external stimulus [13–16]. However, it cannot be used for transparent coatings because the different reflective indices of micro-sized capsules and coating materials often cause the coating to become cloudy [17,18]. In addition, when a scratch heals in these systems, the microcapsules

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail address: jckim81@kriict.re.kr (J.C. Kim).

¹ S. Y. Kim and T. H. Lee contributed equally to this work.

collapse. Thus, scratch healing is effective the first time a region is scratched, but is increasingly ineffective if repeated scratching occurs [14]. Moreover, the inclusion of microcapsules into the coating lowers the mechanical strength and thermal stability of the coating [19,20].

Intrinsic scratch-healing of polymer coatings can occur via diverse mechanisms, including the formation of physical interactions including hydrogen bonds and charge-transfer complexes; the use of catalytic reactions; and the inclusion of dynamic crosslinking systems [21,22] such as Diels–Alder (DA) reactions [23–27] and reactions that form hindered urea bonds [28–30], alkoxyamines [31,32], boronic esters and di-thiolate bonds [33–37], with the healing process triggered by an external stimulus such as thermal energy, ultraviolet light, a change in pH, or the introduction of moisture. The advantages of this approach over the extrinsic scratch-healing technique are that it can be applied to a wide range of organic coating materials [11], it can be used with transparent coatings [38,39], it allows the repeatedly healing of scratches [40,41]. Overall, however, the durability of the coating is inversely related to its scratch-healing performance because the former requires high ν_c , while the latter relies on enhanced polymer chain mobility so that polymer chain rearrangements and hence healing can occur more easily. Therefore, striking the right balance between the material properties and the self-healing performance is a key factor in designing high-performance scratch-healing coating materials. From this point of view, the graft polymer would be a feasible candidate because its material properties can be easily tailored by varying the type, length, contents, and chemical structure of its bristles [8,42,43].

Intrinsic self-healing polymers based on the thermally reversible DA and retro-DA (rDA) reaction systems are versatile in that they provide transparent, colorless, durable, and catalyst-free coatings. When designing the system, it is necessary to quantitatively analyze two important factors: the reversible formation of the crosslinked and de-crosslinked structures, and the dependence of the scratch-healing performance on material properties such as hardness, scratch resistance, and thermal and viscoelastic properties. To date, the former has been well investigated but only a few studies to have analyzed the latter, therefore, more systematic research is needed [21,44–47].

In the current study, we conducted a detailed investigation of the relationship between the material properties and scratch-healing performance of poly (methyl methacrylate)-*co*-[poly (methyl methacrylate)-*graft*-(oligo-caprolactone)] urethane networks containing a DA adduct unit (GCPNp-DAs). In the first part of the paper we demonstrate the reversible formation of the cross-linked and de-crosslinked structures of the GCPNp-DAs at DA and rDA reaction temperatures. In addition, the difference between the viscoelastic properties of GCPNp-DAs and those of conventional crosslinked poly (urethane acrylate)s (GCPNp-Hs), which otherwise have similar chemical structures and ν_c levels, was also investigated when both polymers were subjected to DA and rDA temperatures. The second part of the paper describes the quantitative analysis of the scratch-resistance and healing performances of the coatings as a function of material properties such as elastic modulus, indentation hardness (H_{IT}), ν_c , glass transition temperature (T_g) and thermal stability.

2. Experimental section

2.1. Materials

Maleic anhydride, furan, ethanol amine, furfuryl alcohol, isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), 2,2'-azobis (2-methylpropionitrile) (AIBN), ethyl acetate, ethanol,

toluene and 2-butanone were purchased from Sigma-Aldrich and were used as received. Methyl methacrylate (MMA) obtained from Sigma-Aldrich and hydroxyl-terminated caprolactone methacrylate monomers provided from Mirae Chemicals were passed through a basic alumina column to remove inhibitors before polymerization.

2.2. Synthesis

2.2.1. 4,10-Dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (1)

Maleic anhydride (10 g, 102 mmol) and furan (9.24 g, 136 mmol) were mixed and stirred in ethyl acetate (20 mL) at room temperature for 24 h. After completion of the reaction, precipitated white powder was filtered, washed with toluene, and dried in vacuo. No further purification step was needed (yield: 85.6%). ¹H NMR (300 Hz, DMSO-*d*₆) peak δ values: 6.59 (s, 2H), 5.36 (s, 2H), and 3.32 (s, 2H) ppm.

2.2.2. 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2)

To a 250 mL two-neck round-bottom flask in an ice bath, the product 1 (30 g, 120 mmol) and ethanol (40 mL) were added and stirred for 15 min. Afterwards, a solution of ethanolamine (7.58 g, 124 mmol) in ethanol (10 mL) was slowly dropped over the course of 30 min into the flask in the ice bath under stirring and the reaction mixture was then kept at room temperature for an additional 30 min until 1 completely dissolved. Then, the solution was refluxed for 24 h. After the reaction completed, the solution was cooled down. The obtained yellowish solid powder was filtered and dried in vacuo (yield 46.6%). ¹H NMR (300 Hz, DMSO-*d*₆) peak δ values: 6.53 (s, 2H), 5.10 (s, 2H), 4.74 (br, 1H), 3.40 (br, 4H), and 2.90 (s, 2H) ppm.

2.2.3. N-(2-Hydroxyethyl)-maleimide (3)

To a 250 mL two-neck round-bottom flask equipped with a reflux condenser, the product 2 (10 g, 47.8 mmol) was added and refluxed in toluene (100 mL) for over 24 h. The degree of conversion of 2 to HEM was monitored by tracking the decrease in the intensities of the ¹H NMR peaks at 6.520 ppm and 5.104 ppm, which are characteristic peaks of the furan moiety. After the completion of the reaction, the solution was cooled down. The white powders crystallized from the solution were filtered and dried in vacuo (yield 83.02%). ¹H NMR (300 Hz, DMSO-*d*₆) peak δ values: 6.97 (s, 2H), 4.80 (br, 1H), and 3.44 (br, 4H) ppm.

2.2.4. DA adducts (DAA)

To a one-neck round-bottom flask, HEM and furfuryl alcohol in a 1:1 M ratio were added into toluene and then the resulting mixture was heated at 75 °C under stirring for 12 h. Light-yellowish precipitate formed and this product was filtered, washed twice with ether, and dried in vacuo. ¹H NMR (300 MHz, CDCl₃) peak δ values (ppm): 6.52 (br, 2H), 5.07 (s, 1H), 4.92 (br, 1H), 4.75 (br, 1H), 4.01 (d, 1H), 3.71 (d, 1H), 3.41 (s, 4H), 3.03 (d, 1H), and 2.89 (d, 1H).

2.2.5. DA diisocyanate crosslinker (DADI)

For DAA and IPDI, each monomer was added into 2-butanone with a 1:2 M ratio and then the mixtures were heated at 35 °C in the presence of DBTDL under stirring for 6 h. After the reaction completed, the reaction solvent was evaporated under reduced pressure and the product was stored under a nitrogen atmosphere. FT-IR bands (cm⁻¹): 3354 (-NH), 2950–2850 (-C-H₂), 2270 (-NCO), 1720 (C=O), and 1540 (C-N).

2.2.6. Diisocyanate crosslinker (DI)

For 1,6-hexanediol and IPDI, each monomer was added into 2-

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