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Improving self-healing performance of polyurethane coatings using PU microcapsules containing bulky-IPDI-BA and nano-clay

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ABSTRACT

In this study, polyurethane-based microcapsules filled with bulky isophorone diisocyanate, IPDI, were prepared via interfacial polymerization method in an oil-in-water emulsion. For this purpose, at first, 2,4-toluene diisocyanate, TDI, based pre-polymer was synthesized and used for the preparation of microcapsules shell compound. *n*-Butyl acetate solvent was used in the synthesis of both pre-polymer and microcapsules as a low toxic solvent. Various techniques and methods were used to characterized pre-polymer and microcapsules. Mechanical properties of microcapsule-embedded polyurethane, PU, coating was studied using tensile strength measurement under three different conditions (intact, scratched and healed). The standard salt spray test method was used to analyze the healing ability of microcapsules within the PU coatings. The crack healing properties of the PU coatings was defined using SEM micrographs. The results showed increasing healing efficiency by increasing microcapsule content. The best healing and corrosion performance was achieved for the coating with 1 wt % nanoclay and 5 or 10 wt % microcapsules as a result of barrier properties of intercalated and/or exfoliated clay platelets within the coating formulation.

1. Introduction

Self-healing coatings are smart materials which can intrinsically repair damages such as nano- and micro-sized scratches and cracks, and improving coating lifetime and efficiency. Self-healing properties are usually achieved through either intrinsic or extrinsic mechanism. In intrinsic self-healing, the polymer matrix itself contains a latent functionality that triggers repairing damage via thermally reversible reactions, hydrogen bonding, ionomeric arrangements, or molecular diffusion and entanglement [1,2]. In extrinsic mechanism, healing agent materials are introduced or pre-embedded into a polymeric matrix, through different careers such as fibers [3,4], capillaries [5–7], or microcapsules [8–11]. The healing agent is released from the careers into the damaged area and mends the crack via different mechanisms. The idea of using microcapsules containing reactive healing agent is a well-known approach to design self-healing coatings. Over the last decade, anticorrosion coatings containing microcapsules have been developed for the protection of metallic substrates from the corrosive environments (i.e. oxygen, water, acids and gases) [12,13]. An early example of this technology is the microencapsulation of endo-dicyclopentadiene (endo-DCPD) as a healing agent in poly (urea-formaldehyde) shell used along with a dispersed Grubb's catalyst [14]. In other work, hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) was used as a healing agent via phase separation method in vinyl ester matrix while the di-*n*-butyltin dilaurate (DBTL) as catalyst was encapsulated in polyurethane microcapsules and embedded in the matrix [15]. However, toxicity, high cost and sensitivity of catalysts have led researchers to work on catalyst free system, more eco-friendly and cheaper alternatives. Jin et al. [16] introduced the first dual-capsule self-healing system with appropriate thermal stability of 91% healing efficiency by separate encapsulation of epoxy in polyurethane (PU) – poly(urea-formaldehyde) (UF) double-shell wall and polyoxypropylenetriamine (POPTA) curing agent in poly(urea-formaldehyde) (UF) microcapsules. The encapsulation of air-drying healing agents such as linseed and Tung oils are among such examples reported in the literature [17]. Mirabedini et al. [18] described the preparation of linseed oil-filled ethyl cellulose microcapsules and the improvement of interfacial interaction between microcapsules and a water-based acrylic matrix via microcapsules surface treatment using three different trimethoxysilane. In this regard, Yang et al. [19] introduced the microencapsulation of

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liquid isocyanate monomers with capability of reaction with atmospheric moisture for the first time, thereafter encapsulation of solid state or blocked form of isocyanates has been reported elsewhere [20]. Encapsulation of hexamethylene diisocyanate (HDI) as healing component was reported by Huang et al. [21]. PU-based microcapsules are usually based on reaction of methylene diphenyl diisocyanate (MDI) pre-polymer and 1,4-butandiole. In Yang et al. [19] isophorone diisocyanate (IPDI) with low reactivity was microencapsulated using PU microcapsules based on the polymerization of toluene diisocyanate (TDI) pre-polymer by cyclohexanone (CH) and chlorobenzene (CLB) as solvents. Review of published articles [19,21] also shows that using the molecular weight of core materials plays an important role in the performance of self-healing coatings. Low molecular weight core materials not only need a relatively long curing time or immersion in aqueous solution, but also the mechanical properties of the healed coating layer are typically not satisfactory [22]. Haghayegh et al. [20,23] reported microencapsulation of monomeric and multi-functional IPDI using HDI-based pre-polymer shell using CLB solvent. They showed that multi-functional IPDI was able to heal the damaged coatings faster and better than IPDI monomers as a result of higher initial molecular weight of core material.

Based on the literatures, chemical composition of core and shell materials [24,25], size and size distribution of microcapsules, weight ratio of core to shell, thickness and surface morphology of shell, and healing times, have been reported to affect the efficacy of self-healing process and the final performance of the healed coatings. However, due to the use of toxic solvents such as CH and CLB, the field of research is still under consideration to replace them with less toxic solvents [26]. LD_{50} amount of *n*-butyl acetate (BA) is about 10,768 mg kg^{-1} for rat (acute oral toxicity), which are 1400 and 1110 mg/kg for CLB and CH solvents, respectively [26], indicating 10 times more toxicant of these solvents compared to BA solvent.

In our previous work [26], polyurethane-based microcapsules containing IPDI monomers were synthesized using TDI-based pre-polymer and IPDI as the shell and core materials, respectively, using either CH or BA as solvent. Here, we examine the synthesis of microcapsules filled with bulky-IPDI using BA as a low toxicity solvent. Moreover, effect of addition of organoclay nanoparticles on the mechanical and anti-corrosion performance of microcapsule-embedded PU coatings has been studied.

2. Experimental

2.1. Materials

Cycloaliphatic polyisocyanate based on isophorone diisocyanate (VESTANAT T 1890 E), IPDI with NCO content of 12 ± 0.3%, molar mass of 793.4 g/mol, and 70 ± 1 wt % solid content in BA solvent was supplied by Evonik industries AG (Germany). Gum Arabic (GA), 1,4-butanediol (BD), 2,4-toluene diisocyanate (TDI) and BA were purchased from Merck industrial group. Nano-clay (Cloisite 30B) was purchased from Southern Clay Products-USA. Hydroxyl acrylic resin, Tacryl 352N, and its hardener, Desmodur® N 75 MPA/X were supplied from TAAK Resin Co, Iran and Covestro AG, Germany, respectively. All substances were analytical grade and used as-received without additional purification.

2.2. Microcapsules preparation

2.2.1. Synthesis of pre-polymer

TDI monomer (21.9 g) was dissolved in BA (141.7 g) at 80 °C under magnetic stirring in a 2-necked glass vessel under N_2 gas purging. BD (4.2 g) was gradually added to the solution under mechanical agitation. N_2 was purged to the reaction vessel for about 20 min and it was sealed with cork and the reaction was continued for 36 h under magnetic stirring [19,26]. NCO content of the prepared pre-polymer was determined as 19.3 ± 0.7% using titration method according to ASTM D2572 test practice. The number average ($\bar{M}_n$) and weight average ($\bar{M}_w$) molecular weight of the synthesized pre-polymer were defined via gel permeation chromatography (GPC Agilent 1100 series with refractive index detector) as 700 and 816 g mol^{-1}, respectively. The solid content of pre-polymer was measured as 15.5 wt %. The pre-polymer solution was kept in a fridge until further usage. The details for pre-polymer characterization were reported elsewhere [26].

Bulky-IPDI-filled PU microcapsules were prepared using TDI-based pre-polymer via interfacial polymerization [26]. To this end, GA (6.5 g) was added to deionized water (45 mL) and mixed for 3 h at ambient temperature. The solution was then transferred to a 100 mL beaker placed in a programmable water bath. Bulky-IPDI solution (6.0 g IPDI and defined BA for preparing a 60 wt % solution) was decanted to (7.25 g) pre-polymer solution. The resultant suspension was gently poured into the GA solution. The temperature of water bath was elevated to 70 ± 1 °C at a rate of 7 °C min^{-1} under various mixing speeds of 500, 700, 900 and 1100 rpm. At 50 °C, BD (3.2 g), as a chain extender, was gently added to the emulsion and mixing was continued for further 1 h. When the microcapsule suspension reached the room temperature, it was rinsed several times with deionized water. Finally, the prepared microcapsules were freeze-dried at 45 ± 5 °C and low pressure of 10 ± 2 m.Pa using a freeze dryer device (Dena Vacuum Industry Co. Iran). A graphical mechanism of PU microcapsule preparation is depicted in Fig. 1.

2.3. Characterization of prepared microcapsules

2.3.1. Morphology of microcapsules

The morphology, shape and size of prepared microcapsules were evaluated using a scanning electron microscope (SEM((Tescan Vega 2, 20 kV voltage) and an optical microscope (OM) (Olympus CX21FS1) equipped with a Canon Power shot SX40 digital camera.

2.3.2. Particle size distribution of microcapsules

Average microcapsules size prepared at different mixing speeds was determined using a particle size analyzer instrument, AZM 110 CILAS (PSA).

2.3.3. Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy was used to characterize pre-polymer, microcapsules and microcapsules shell. Microcapsule shell was separated from the core content by extraction method. About (0.5 g) of microcapsules was added into (20 mL) BA and sonicated using an ultrasonic bath (Model HD3200, KE-76 probe, Bandelin) for 15 min. The shell component was then separated from the suspension through filter

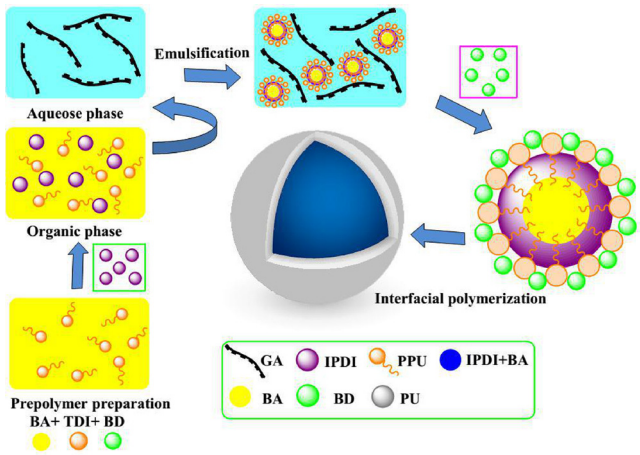

Fig. 1. Graphical synthesis mechanism of PU microcapsules.