Progress in Organic Coatings 89 (2015) 271–276

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Preparation of polyurethane microcapsules with different polyols component for encapsulation of isophorone diisocyanate healing agent

Pooneh Kardar

Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 May 2015
Received in revised form 19 August 2015
Accepted 10 September 2015

Keywords:
Self-healing
Microcapsules
Isophorone diisocyanate
Polyurethane
Polyol

ABSTRACT

Microcapsules containing isophorone diisocyanate (IPDI) as healing agents for using in self-healing polymers have been successfully prepared via interfacial polymerization of polyurethane (PU). Microcapsules were manufactured using different polyols including 1,4-butandiol, 1,6-hexanediol and glycerol. The fabrication of PU prepolymer and microencapsulation of IPDI were proved by Fourier transform infrared (FTIR) and thermo-gravimetric analysis (TGA). High yields of IPDI/PU microcapsules were obtained using 1,4-butandiol and 1,6-hexanediol as polyol monomers as determined by TGA. Scanning electron microscopy (SEM) showed synthesis of smooth spherical microcapsules of 1.7 and 3 μm in diameter using 1,4-butandiol and 1,6-hexanediol as polyol, respectively.

1. Introduction

Self-healing materials represent a new class of smart and responsive materials [1,2]. Self-healing materials have the ability to repair damages automatically. In polymeric coating materials, polymer degradation may appear in the formation of small cracks that would decrease materials mechanical properties and its lifetime. In these cases, self-healing materials are significantly important and beneficial to avoid mechanical properties degradation and further damage.

Incorporating of self-healing properties in polymeric materials is classified in two categories: (i) intrinsic (non-autonomous) self-healing materials, that are endowed with the intrinsic ability of healing cracks by the polymers themselves but require an external trigger, and (ii) extrinsic (autonomous) that involves healing agents encapsulated and embedded into the polymer's matrix in advance [3–5]. When crack occurs, mechanical forces destroy the capsule or pipeline and trigger the release of self-healing agent [6,7].

In microencapsulation, particles of solids, liquids or gases are embedded in an inert shell and this shell avoids the external environments to damage inside [8–15]. To date, the encapsulation of dicyclopentadiene (DCPD) monomer and other microcapsules such as microcapsule containing dibutyltin dilaurate (DBTL) catalyst dispersed in polydimethylsiloxane (PDMS) matrix have been extensively studied [16–19]. On the other hand, Sondari et al. studied the possibility of glycerol as polyol component for encapsulated self-healing agent containing different materials as healing agent [20]. Another example of monomer encapsulated to give self-healing property is isophorone diisocyanate (IPDI) encapsulated in polyurethane shell which is a free catalyst healing agent since it is reactive with environmental moisture [21].

In this paper, the encapsulation isophorone diisocyanate monomer as a healing agent via interfacial polymerization in a stabilized aqueous emulsion has been investigated. Here the possibility of 1,4-butandiol, 1,6-hexanediol, and glycerol as polyol monomers for polyurethane microcapsule shell was studied.

The encapsulated material in this study is IPDI, a monomeric aliphatic diisocyanate which is reactive with water and this brings the possibility of single-part, catalyst-free self-healing system which is functional in the presence of an aqueous or moisture-laden environment.

2. Experimental

2.1. Preparation of prepolymer and microcapsules

Toluene diisocyanate (TDI) prepolymer was prepared for the microcapsule shells. A representative synthesis route is shown

E-mail address: kardar@icrc.ac.ir

http://dx.doi.org/10.1016/j.porgcoat.2015.09.009
0300-9440/

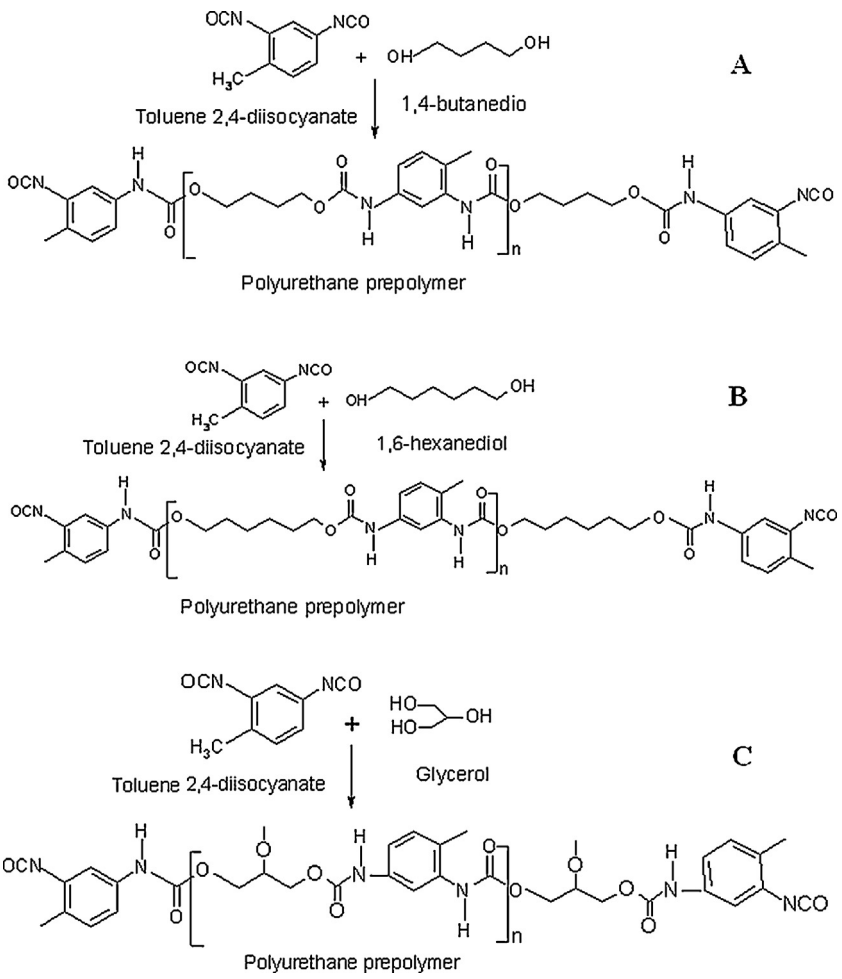

Fig. 1. Reaction of polyurethane prepolymer synthesized using (A) 1,4-butanediol, (B) 1,6-hexanediol and (C) glycerol.

in Fig. 1. Toluene 2,4-diisocyanate (TDI, Sigma–Aldrich) was dissolved into cyclohexanone (Sigma–Aldrich) in a 250 mL flask. The mixture was then kept in an 80 °C oil bath and stirred up using a magnetic stirrer. 1,4-butanediol (BD, Sigma–Aldrich), 1,6-hexanediol (HD, Sigma–Aldrich) or glycerol (Sigma–Aldrich) was slowly added. The synthesis of prepolymer was performed in TDI to polyol molar ratio of 3:1 [20,21]. The reaction continued for 24 h with N_2 purging. The mixture was then distilled at 100 °C under vacuum for 4–5 h and excess materials were removed and a yellowish, viscous prepolymer remained in the flask.

At room temperature, 30 mL of deionized water and Arabic gum as surfactant (4.5 g, Sigma Aldrich) were mixed. The solution was stirred for 3 h before beginning encapsulation.

To prepare the microencapsuls, 2.9 g prepolymer was dissolved into 4 g chlorobenzene (ClB, Sigma Aldrich) at 68 °C. Once the prepolymer was completely dissolved, 9.5 g isophorone diisocyanate (IPDI, Sigma Aldrich) was added and mixed well. The mixture was then slowly poured into the Arabic gum solution at room temperature. The water bath was heated to 70 °C at a rate of 7 °C/min. At 50 °C, 0.03 mol of 1,4-butanediol, 1,6-hexanediol or glycerol was added to the mixture as chain extender since the reaction of isocyanate group in prepolymer with chain extender accrues above 50 °C. After 45 min the polyurethane shell was formed as schematically shown in Fig. 2. The suspension of microcapsules was cooled, rinsed with deionized water and filtered, then air-dried for 48 h before further analysis.

2.2. Characterization of prepolymer and microcapsules

2.2.1. Titration of NCO content in prepolymer

0.15 g synthesized prepolymer was dissolved in 25 mL dry toluene with a mechanical agitator. 25 mL di-n-butylamine solution was added and mixed for 15 min. Then, 100 mL isopropyl alcohol and 5 drops of bromophenol blue indicator solution were added. The NCO content is calculated as follows:

$$\text{NCO}\ \ (\text{wt.\%}) = \frac{[(B - V) \times N \times 0.0420]}{W} \times 100$$

where B and V (both in mL) represent the volumes of HCl for titration of the blank (sample without prepolymer) and the prepolymer, respectively, N is normality of HCl, and W is grams of prepolymer.

2.2.2. Fourier transform infrared (FTIR)

The prepolymer reaction was confirmed by FTIR. FTIR analysis was conducted using a Perkin Elmer 1600 FTIR.

2.2.3. Thermo gravimetric analysis (TGA)

Thermal stability of the synthesized microcapsules was studied using a thermogravimetric analysis (Perkin Elmer – Pyric Diamond). Small amounts of microcapsules (1–2 mg) were heated from 25 to 650 °C at a rate of 10 °C/min in a N_2 environment.

2.2.4. Scanning electron microscopy (SEM)

Surface morphology and size of capsules were examined by SEM (FEI Quanta 600 FEG-SEM). Microcapsules were put on a conductive