



Designing an elastomeric polyurethane coating with enhanced mechanical and self-healing properties: The influence of disulfide chain extender

Masoud Yarmohammadi^a, Mansour Shahidzadeh^{a,*}, Bahram Ramezanzadeh^{b,*}

^a Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Malek-Ashtar University of Technology (MUT), PO Box: 16765-3454, Lavizan, Tehran, Iran

^b Department of Surface Coatings and Corrosion, Institute for Color Science and Technology, No. 59, Vafamanesh St., Hossain Abad Sq., Lavizan, Tehran, Iran

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ABSTRACT

Polyurethane has been widely used in various coating industries due to its good weathering resistance, promising appearance, excellent elasticity and good mechanical properties. However, most of the polyurethanes are elastomeric and show poor resistance to mechanical damages. Efforts have been made to design polyurethanes with proper self-healing properties. In this study the self-healable polyurethanes and polyurethane-ureas coatings were prepared using hydroxyl-terminated polybutadiene, three functional amino alcohols as cross-linker and disulfide containing compounds as a chain extender and healing agents. The mechanical and healing properties of the coatings were optimized to achieve the highest recovery properties. For this purpose, dynamic mechanical thermal analysis (DMTA) and tensile test were employed. The results revealed that using 0.8 equivalent of 2-hydroxyethyl disulfide as chain extender besides of using 0.15 equivalent of the triethanol amine as cross-linker in the polymer matrix led to the maximum recovery ability. Maintaining to about 41% of fresh polymer strength and healing of the scratch were established as a result of using the optimized contents of components. Also, tensile test results revealed that the tensile strength increased by performing the thiol-ene side reactions in PU matrix which increased the cross-linking density and decreased the healing ability due to the elimination of the metathesis reaction source.

1. Introduction

Nowadays, smart polymers are one the most desirable field of materials with the approach of mimicking the natural systems that are depended to stimuli to perform an action [1]. Smart polymeric coating, as one the most desirable materials, has been considered as self-healing materials due to their ability in inhibition of corrosion process [2]. Among various categories of smart materials, the self-healable polymeric coatings have been employed to solve many disadvantages of the polymers like aging, cost of repairing and losing properties during the time [3]. In this category of smart materials, any damage or scratch created in the coating could be healed by carrying out a chemical reaction or physical interaction in polymer matrix induced by stimuli [4]. Using thermo reversible Diels-Alder reactions for preparing green and sustainable coating with healing ability [5,6], preparing self-healable polymeric nanocomposite as an excellent coating for steel [7] and capsulation of natural oils as extrinsic healing agent in poly(urea-formaldehyde) matrix [8] can be mentioned as of the most important smart materials in making self-healable coatings. Self-healing ability in a polymer matrix could be originated by intrinsic and extrinsic

methods, where everyone has some advantages and disadvantages [9]. Among these various methods, dynamic covalent reaction category is one of the most desirable methods for insertion of self-healing properties in the polymer materials due to its advantages like requiring a mild condition for initiation of the healing process, the dependence of any extrinsic stimulator and non-weakening of mechanical properties. Many types of dynamic covalent reactions have been studied as a healing agent in self-healable polymers including Diels-Alder reactions [10,11], dynamic-covalent boronic esters [12] and metathesis reaction of carbon-carbon [13] or sulfur-sulfur bonds [14]. Presenting metathesis reaction of olefins with its specialized Grubs catalyst could be mentioned as one of the most important inventions in chemistry, especially green chemistry, which has been interested in material science due to its unique advantages such as high yield, stereoselectivity, regioselectivity, no by-product, no side reaction, etc. [15]. In recent years the researches on disulfide metathesis reaction have been developed in preparation of self-healable smart materials. The high cost of Grubs catalyst or other derivation of olefin metathesis catalysts faced many difficulties to this reaction in using in all materials. The sulfur-sulfur metathesis reaction could be considered as the solution for this problem

* Corresponding authors.

E-mail addresses: shahidzadeh@mut.ac.ir (M. Shahidzadeh), ramezanzadeh-bh@icrc.ac.ir (B. Ramezanzadeh).

due to its independence of catalyst and low required activation energy for performing metathesis reaction [16]. Therefore, researches on the preparation of the self-healable smart materials via this category of metathesis reactions have been developed in recent years. Using disulfide metathesis reaction in preparation of the photoirradiation-sensitive self-healable polymer [17] and room-temperature self-healing polyurethane elastomers [18], inducing reforming ability in the natural rubbers [19], inverse vulcanization of dynamic covalent polymers [20] and many other researches in recent years [21–23] established the importance of this reaction in preparation of the smart materials. It should be noted that the nature of the disulfide bond-containing compound is the most affected parameter on the required activation energy of the metathesis reaction [24]. Therefore, the proper disulfide containing compound is chosen regarding the application of the product and the simulation method for metathesis reaction.

Polyurethanes (PUs) and their derivatives including polyurethane-ureas (PUUs) are one of the most important classes of polymeric coatings [25] with incredible properties such as excellent elasticity [26], toughness [27], and good chemical resistance [28,29]. Wide range of PUs can be obtained from changing the ingredients like polyol, isocyanate, chain extender and cross-linker [30]. Changing the chain extender compound, as a very effective substance on PUs properties, seems to be a facile and common way to achieve various categories of PUs with a broad range of properties [31,32]. Applying chain extender with amine functional groups leads to preparation of PUs with improved mechanical properties [25]. The chain extender with amine functional groups increases the non-covalent bonds, intensifying the internal three-dimensional urea bonding [33–35]. Moreover, among various categories of polyurethanes, the hydroxyl terminated polybutadiene (HTPB) based PUs have been considered in many researches [36] and industries [37] due to some unique properties of HTPB such as low glass transition temperature ($-75\text{ }^{\circ}\text{C}$), hydrolytic stability, low moisture permeation, resistance to acidic solutions and bases, high loading capacity for solid particles, significant hydrophobicity and long age in low temperatures. On the other hand, these properties make the HTPB based polyurethanes as one of the best candidates in coating application for aluminum, steel, etc. which have been considered in many studies [38–40]. Therefore, it seemed that inducing the self-healing ability in HTPB based polyurethanes could be led to applicable PU coatings with incredible healing properties.

In continuous of our previous studies on modification of HTPB based PUs properties [41–43], preparing self-healable coatings by the HTPB has been carried out to achieve polyurethane coating for the pipeline with proper mechanical and healing ability. In this regard, HTPB based PUs and PUUs have been prepared one shot using disulfide containing chain extenders as a self-healing agent, three functional hydroxyl amines as cross-linker and isophorone diisocyanate as the curing agent (Fig. 1). Noticeably, disulfide-containing compounds have been used as chain extenders to improve the PUs mechanical properties via intensifying the non-covalent hard segments interactions and inducing the self-healing ability, simultaneously. Also, the constant amount of cross-linker in the polymer matrix has been used to reinforce the mechanical properties of PUs via formation of chemical cross-linking bonds. It could be assumed that insertion of disulfide bonds in polymer matrix led to performing ability of disulfide metathesis reaction in prepared elastomers to provide self-healing ability. Optimizing the chain extender content has been investigated by dynamical mechanical thermal. Moreover, the effect of chain extender structure and content besides of cross-linker structure effect on the mechanical properties and morphology of the coating were studied by a tensile test. The healing ability of HTPB based PUs has been investigated by various macro and micro scratch tests.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), Triethanol amine (TEA) and Bis(4-aminophenyl)methane (BAM) were purchased from Merck Co. 2-Hydroxyethyl disulfide (HES) was from Sigma. Hydroxyl terminated polybutadiene (HTPB) ($\bar{M}_w = 3420$, Hydroxyl number = 0.64 and functionality = 2.2) was supplied from Zibo Elim. Boron trifluoride triethanolamine complex (T_{313}) was purchased from Shenzhen Hongyuan. 4-Aminophenyl disulfide (ADS) was synthesized according to the procedure reported in literature [44]. All of the materials and reagents were used without further purification.

2.2. General procedure for samples preparation

The calculated amount of chain extender (Table 1) was dissolved in 10 mL dichloromethane and then added to a one-necked round bottom flask containing HTPB (7.00 g, 2.04 mmol, 4.48 meq.) and cross-linker (7.90×10^{-1} meq.). The flask was placed in a $60\text{ }^{\circ}\text{C}$ oil bath under vacuum to remove the solvent and solution degassing for 2 h. Then, the stoichiometric ratio of IPDI as a curing agent was added to the solution, and the solution agitated for 15 min in the same conditions. After that, the solution was cast in a mold and placed in an oven to complete the curing step at $60\text{ }^{\circ}\text{C}$ for 48 h.

2.3. Instruments and analysis techniques

2.3.1. Swelling test

Swelling test was carried out according to the method reported in the literature [45] using toluene as solvent and at room temperature for 50 h. Elastomer densities, cross-linking density, and molecular weights were calculated according to the literature [46,47].

2.3.2. Tensile test

The tensile test was performed by Hiwa 200 instrument. All gages size and shape were compatible with standard D638-02a (type IV) [48]. All tensile tests were carried out in 500 mm min^{-1} rate at room temperature. The PUs molecular weight between the cross-linking points (M_c) was calculated according to the following equation (Eq. (1)) [49–51].

$$\bar{M}_c = \frac{\rho RT}{\delta} (\alpha - \alpha^{-2}) \quad (1)$$

Where ρ is referred to the density of the elastomer, T is the absolute temperature, δ shows the tensile stress, and α is equal to $L_f L_o^{-1}$, where L_o and L_f are the lengths of the specimen before and after applying of stress.

2.3.3. Dynamical mechanical thermal analysis

Dynamical mechanical thermal analysis (DMTA) test was performed by a Perkin 800 instrument. This analysis was carried out in the temperature range of -100 to $100\text{ }^{\circ}\text{C}$, at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ under an N_2 atmosphere at 1 Hz to obtain elastomers storage modulus and $\tan \delta$ curves.

2.3.4. Healing ability studies

The healing ability of the PUs was investigated through tensile test results. The strength at yield point for the virgin and healed samples was obtained. To this end, the two pieces of the sample were moved into the mold to place the shear point gages in the vicinity. The healing process started by placing the mold into the oven at $70\text{ }^{\circ}\text{C}$. The samples strength was tested again after 2 and 4 h. The healing percentage in this step was calculated by following equation (Eq. (2)):

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