



Assessment of adhesion and surface properties of polyurethane coatings based on non-polar and hydrophobic soft segment



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ABSTRACT

Polyurethane (PU)-based coatings attract much more attention in various applications due to their unique and versatile properties. Non-polar hydrophobic PU coatings are being extensively explored as advanced coatings. Here, a novel hydrophobic PU coating is synthesized based on combination of non-polar polyols, polypropylene glycol (PPG) and hydroxyl terminated polybutadiene (HTPB). The adhesion properties, micro-hardness and water uptake behavior of samples are characterized. The effect of composition (HTPB/PPG molar ratio) on the surface properties of synthesized PU coatings are analyzed by Fourier-transformed infrared spectrometry (FTIR-ATR), contact angle measurement and atomic force microscopy (AFM). Results show sample with 0.25% molar ratio HTPB has maximum lap shear strength and negligible water absorption. So, the synthesized PU coating with optimized composition could support enough adhesion to substrate and provide hydrophobic surface properties.

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1. Introduction

Nowadays, polymeric coatings made from polymeric materials are commonly applied on a variety of substrates in order to protect the substrate from corrosion, wear, chemical invasion or providing new properties on the surface. Polymeric coatings are required to adhere well to the substrate [1,2].

One of the main challenges in designing polymeric coatings is to manufacture a material with different and even conflicting properties such as easy handling, flexibility, elastic behavior, low hardness, enough attachment as well as resistance against corrosive and abrasive environments which should be taken into account in the material selection process [3–5].

Among different types of polymeric coatings, non-polar hydrophobic ones are being extensively explored as advanced coatings. Such these coatings are commonly utilized in marine and biomedical applications as well as self-cleaning surfaces [6–9]. The mechanism of action of such surfaces is based on reducing the interactions between the surface and bio-masses (e.g. algae, proteins, bacteria, cells). However, designing an inert non-polar polymeric coating that can be properly attached to its substrate is a problematic issue from the engineering point of view [10,11].

In order to achieve the unique surface properties of non-polar hydrophobic coatings, three following strategies were suggested:

- Increasing surface crystallinity followed by freezing surface functional groups. However, it could be limited because to semi crystalline polymers and also results in reducing elasticity as well as flexibility [12,13].
- Chemical crosslinking in surface is caused freezing surface functional groups so. However, it could be limited because to thermoset polymers [14].
- Selecting low surface free energy (SFE) materials (non-polar polymers, e.g. polyolefin, Poly (dimethylsiloxane), Poly (tetrafluoroethylene) (PTFE), etc.), although some of them, e.g. PTFE and PDMS exhibit low mechanical strengths [15–17].

To improve the mechanical and adhesion properties of the non-polar coatings, some studies have utilized chemical modifications of polymeric chains such as making polyurethane and polyurea linkage in structure [18–22], preparation of a blending system by mixing with semi-crystalline polymers or addition of fillers [23,24].

Polyurethane-based coatings are common and useful coating materials which have entered a stage of stable progress and advanced technological exploitation. The wide applicability of PU coatings is due to versatility in selection of monomeric materials from a huge list of macrodiol, diisocyanate and chain extender that could provide a wide range of physical, mechanical and adhesion properties [25–27].

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Furthermore, from adhesion point of view, higher molar cohesive energy (360 kJ/mol) of urethane bonds in PU structure compared to other bonds provides sufficient adhesion of the coating to various substrates [25]. Besides, flexible polymeric chains which were used as the soft segment result in lower hardness, higher flexibility as well as prevention of crack propagation due to increase in the loss of energy. Using non-polar polymeric chains such as hydroxyl terminated Polybutadiene (HTPB), Poly(isobutylene) (PIB), PTHF, Poly(propylene oxide) (PPO) and PDMS as the soft segment reduces the molecular adhesion of media to the surface. However, utilizing these kinds of materials can decrease physical and mechanical properties due to the limited physical and chemical interactions in PU structure [16,28].

Hydroxyl terminated polybutadiene (HTPB)-a low viscosity colorless liquid with number average molecular weight of 1500–10,000 g/gmol is used in production of adhesives, foams, and unsaturated polyesters as well as a polymer additive. Although non-polar and hydrophobic characteristic as well as the weak physical and mechanical properties, limits the selection of HTPB for such application, it exhibits excellent properties such as low glass transition temperature, high flexibility, high abrasion resistance, hydrolytic stability and resistance to solvents [29–32].

HTPB based polyurethanes are widely used in various applications due to two important characteristics including low surface energy and low temperature flexibility [33]. For instance, they have been extensively utilized as composite solid propellants [34], adhesives [35], toughened polymer [36], gas separation membranes [37], membrane for biomedical applications [38], separators [39,40] and coatings [41].

To the best knowledge of the authors, PPG-TDI based polyurethanes has lower physical and mechanical properties such as tensile strength, tear strength, hardness and usually elastic modulus [25,42]. Besides these limitations, they benefit from hydrolytic stability and chain flexibility compared to traditional ester and ether based polyols. Also, PPG serves as an available low cost polyol. Utilizing a short chain polyol serves as a common strategy for improving polyurethane mechanical properties. Moreover, obtaining synergistic effects in polyurethane system suggest mixing of long chain polyol (HTPB) and short chain (PPG) together. There are a few studies about polyurethanes based on HTPB/PPG mixture in the literatures. Coutinho et al. studied HTPB/PPG polyurethane systems as an adhesive [43] and gas separation membrane [44]. They synthesized anionic waterborne polyurethanes using dimethylolpropionic acid (DMPA) in main backbone chain. Adhesion strength, thermal stability and gas separation of samples were completely evaluated [43–46]. They observed improving of mechanical and thermal properties with addition of HTPB to PPG.

According to our previous study, optimization of the soft segment composition as well as the formation of three dimensional (3D) chemical and physical networks make it possible to achieve polyurethanes with unique mechanical and physical properties [42].

Therefore, the aim of the present study was to synthesize and investigate the polyurethane coating composition with unique properties, including easy handling, sufficient adhesion to substrate, high flexibility and less hardness and controllable hydrophilicity/hydrophobicity. To optimize the synthesized PU structure and properties, five different molar composition of soft segment component was evaluated.

2. Materials and methods

2.1. Materials

Materials which were used to synthesize polyurethane coatings were hydroxyl terminated polybutadiene (HTPB) with average

functionality of 2.18 and number-average molecular weight of 3452 (gr/gmol) which was locally synthesized and characterized [47–50], Polypropylene glycol (PPG) with functionality of 2 and number-average molecular weight of 1968 (gr/gmol) which was supplied by a local company (Iran Polyurethane Co.), 2,4-toluene diisocyanate (TDI), Formamid, Tetrahydrofuran (THF) and N,N-Dimethylacetamide (DMAC) purchased from Merck and 1,4-butanediol (BDO) which was supplied by Aldrich. Distilled water was obtained in the laboratory. These materials were used without further purification.

2.2. Synthesis of polyurethane-based coatings

Polyurethane coatings were prepared without using any additives such as Pigments, Fillers, etc. based on the method described in our pervious paper [33]. Briefly, prepolymer were synthesized using blends of (HTPB/PPG) and TDI (80 °C and N₂ atmosphere for 2 h). Then, BDO solution (50/50, v/v% in THF/DMAC mixture) was added drop wise to the prepolymer mixture (80 °C, 4 h). At the end of reaction, the viscous liquid was transferred to a pre-heated mold (Teflon® coated – 125 mm × 75 mm × 2 mm) followed by incubation on a hot plate (at 100 °C for 12 h). Synthesized PU samples were kept in a desiccator before use. Polyurethane samples with different mole fractions of HTPB/PPG are listed in Table 1. In the rest of the paper, Polyurethane coatings will be referred to as PCH_x, where x represents the mole fraction (multiplied by 100) of HTPB component in soft segment prepolymer.

2.3. Characterization techniques

2.3.1. Adhesion strength

The Lap-shear strength was measured according to ASTM D 1002, using a Cesare Galdabini test machine at a tensile speed of 2.0 mm min⁻¹. First, Glass substrates (100 mm × 20 mm × 2 mm) with smooth surfaces were cleaned using detergent and hot water to remove surface contaminations. Then, surfaces of glass plates (with areas of 20 mm × 20 mm) were completely wetted with polyurethane viscose liquid. Two of such glass plates were then gripped and placed in an oven at 80 °C for 12 h.

2.3.2. Water uptake

Bulk hydrophobicity/hydrophilicity of polyurethanes was quantified by measuring the amount of water absorbed by each polymer at room temperature. Samples were punched as a circular sheet with a diameter of 5 mm and immersed in water to determine the swelling ratio at room temperature. Weight Change percentages of samples due to water uptake were calculated using the following formula:

$$\text{Water uptake(\%)} = \frac{m_t - m_o}{m_o} \times 100 \quad (1)$$

where m_t and m_o are the weight of wet sample over time and that of the dry samples, respectively.

Table 1
The formulation of synthesized polyurethane coating samples.

Sample code	Molar composition of samples (HTPB/PPG/TDI/BDO)	\bar{M}_n of soft segment mixture	Hard segment content (% wt)
PCH000	1/0/10/9	3452	56
PCH025	0.25/0.75/10/9	3081	52
PCH050	0.5/0.5/10/9	2710	48
PCH075	0.75/0.25/10/9	2339	45
PCH100	0/1/10/9	1968	42

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