



Polyurea spray coatings: Tailoring material properties through chemical crosslinking

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ABSTRACT

Among the many desirable properties of polymeric coatings, the most important include ease of application, rapid cure time, adhesive properties and excellent mechanical properties. In this context, spray coated polyureas are finding increasing applications in niche areas that otherwise pose considerable challenge to the traditional coating chemistries. In this work, we demonstrate the effect of introducing chemical cross-linking on the mechanical, thermal and structural properties of spray coated polyurea. A long chain trifunctional amine was introduced as a co-reactant in the resin blend, the amount of crosslinker being varied from 0 to 3.5 mol % (crosslinking density 28–180 mol/m³, affine network model). The mechanical properties of spray coated polyurea films, both in quasi-static as well as dynamic conditions were determined. Physically crosslinked polyurea coatings (in the absence of chemical cross-linking) exhibited tensile strength $\sim 7.4 \pm 0.7$ MPa and elongation of $121 \pm 3.7\%$. Introduction of long chain amine led to an improvement in these characteristic properties till maxima at 2.2 mol%, subsequent to which both strength and elongation decreased. Chemical cross-linking led to restraining of the segmental motions reflecting in terms of increased glass transition temperature, as evidenced by dynamic mechanical analysis and differential scanning calorimetry. The chemical resistance of polyurea also improved substantially due to crosslinking, which reflected in terms of decreased swelling ratio in different organic media.

1. Introduction

Crosslinking and curing are fundamental tools for tuning the structure-property relationship in polymers [1]. Polyurea, a reaction product of diisocyanates with diamines has attracted a lot of attention by researchers and industry alike, in view of its ability to exhibit a wide range of material properties. Due to the extremely fast kinetics of the isocyanate-amine reaction, practical processing of polyurea mandates use of a reactive spray coating technique. This spray technology is growing rapidly and polyurea is being increasingly advocated for coating applications where continuous membranes devoid of seams and joints need to be applied quickly [2–4]. The inherent rapid reaction allows for uniquely short gel times that allows for their application over broad range of temperature and humidity.

Polyurea exhibits excellent mechanical properties, which in turn is attributed to the physical crosslinking due to intermolecular and intramolecular bidentate H-bonds between the urea linkages [5]. Introduction of chemical crosslinking can further alter the mechanical properties of polyurea by bestowing stiffness, ductility and chemical resistance

[6]. The consequences of chemical crosslinking on the material properties has been extensively studied in the relatively more popular class of similar polymer, i.e. polyurethanes [7,8], however such studies on polyurea are lacking. Polyurea formulations are mostly proprietary in nature where the compositional details are not disclosed. Most of the commercial formulations contain a long chain crosslinker, but the effect of its introduction on the material properties has not been systematically studied, which inspired us to undertake this study.

Polyurea exhibits a heterogeneous phase segregated microstructure, comprising of “hard” realms formed by hydrogen bonded polar urea linkages (–NH–CO–NH–) within the “soft” domains of aliphatic polyether/polyester chains [9,10]. Although physical crosslinks (H-bonding) [11,12], in the form of hard domains are dispersed throughout the polyurea matrix, the chain-extension process can be used to tune the extent and type of H-bonding [13] by increasing the vicinity of the urea linkages. Further, the ratio of aromatic: aliphatic chain extender can be suitably varied to tailor the microstructure of the polymer. The exceptional mechanical properties such as enhanced modulus, high extensibility and resiliency [14–16] of polyurea are an

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indirect manifestation of the physical crosslinks within the structure.

The deliberate introduction of chemical crosslinks can further alter the material properties of polyurea. In the context of polyurea/polyurethane, common methods of crosslinking include inclusion of a higher-functional amine (functionality > 2) [17] or maintaining a slight excess of isocyanate ($i_{NCO} > 1$) [18] and combination thereof [8]. The excess isocyanate reacts with the urethane and urea groups to form allophanate and biuret linkages respectively [19,20].

Studies on the introduction of short chain multifunctional amines like 1,3,5 triaminophenoxy benzene (TAB) [21,22], bis(4-aminophenyl) disulphide [23], 0.0 G PAMAM dendrimer [24], for crosslinking purposes has been performed. Short-chain crosslinking affects primarily the tensile properties [8,17,18,25–28], swelling behavior [28–31] and thermal degradation behavior [26,32,33]. Interestingly, most of the commercial polyurea formulations include a long chain crosslinker, the effect of introduction of which has not been explicated in the open literature. The present study focuses on the elucidation of the effect of long chain crosslinking on mechanical, thermal as well as the dynamic mechanical properties of polyurea coatings. The swelling behavior was also studied to understand the behavior of crosslinked polyurea in different media.

2. Experimental section

2.1. Materials

A commercially available isocyanate prepolymer, Suprasec 2054 (Huntsman), NCO = 15.5% was used without any further purification. Poly(propylene oxide) (PPO) based difunctional (JEFFAMINE®D-2000) and trifunctional polyether amines (JEFFAMINE®T-5000) were procured from Huntsman: the designation number referring to the approximate molecular weight of each species. An aromatic chain extender, diethyltoluenediamine (DETDA 80, Lonzacure™) which is a mixture of 3,5-diethyltoluene-2,4-diamine (2,4-DETDA) (75–81%), 3,5-diethyltoluene-2,6-diamine (2,6-DETDA) (18–20%) and dialkylated m-phenylenediamine (0.5–3%) was used without any purification. Propylene carbonate (CDH) was used for dilution of the isocyanate prepolymer. The structure and physical properties of all the reactants are presented in Table 1.

2.2. Spraying of polyurea

A formulation comprising of long chain amine (D-2000), crosslinker (T-5000) and chain extender (DETDA) was used as the resin blend, i.e. Part B for polyurea preparation. Isocyanate precursor was diluted with requisite amount of propylene carbonate and used as the isocyanate source, i.e. Part A. The amount of each component was calculated as follows:

$$m_{iso} \cdot n_{eq,iso} = [m_{a \min e, 1} \cdot n_{eq,a \min e, 1} + m_{a \min e, 2} \cdot n_{eq,a \min e, 2}] i_{NCO} \quad (1)$$

where, m_{iso} and $m_{a \min e}$ refer to the mass of isocyanate and amine respectively and $n_{eq,iso}$ and $n_{eq,a \min e}$ are the equivalent number of isocyanate and amine respectively. In all the formulations, an NCO index (i_{NCO}) of 1.1 was maintained. A dilution of 10% (v/v) for the prepolymer was found to be mandatory to effect spraying of polyurea. The details of the formulation are presented in Table 2. It is to be noted that the amount of suprasec 2054 and propylene carbonate was 90.8 and 9.2 respectively for all the formulation. The hard segment content was determined as per established procedure (Eq. (2)) [34].

$$HS (\%) = \frac{(m_{iso} + m_{chain \ extender}) \times 100}{m_{iso} + m_{chain \ extender} + m_{amine}} \quad (2)$$

The amount of isocyanate (m_{iso}) used for calculating %HS refer to the mass of prepolymer, which also include significant contribution of the long polyether chains used for preparation of the prepolymer. Hence, this figure of hard segment is much higher than the actual hard

segment content in the polymer. The samples have been designated as PUX- followed by the contribution (mol % x10) of the crosslinker in the polymer. The individual contributions of amine, crosslinker and the chain extender to the total urea content in the sample is presented in the supplementary section, and have been tabulated and depicted pictorially in Table S1 and Figure S1 respectively.

A spray-coater (Graco E 10 HP equipped with fusion air-purge spray gun (AW2222, Graco) was used to prepare polyurea films of uniform thickness (3 mm). Both the block and hose heaters were maintained at 70°C during the spraying operation and performed at a pressure of 2000 ± 100 psi. The mixing ratio of A and B components was 1:1(v/v).

2.3. Characterization

The quasi-static mechanical properties of fully cured polyurea specimens (post 15 days of spraying) were measured in tensile mode using Universal Testing Machine (International Equipments) according to ASTM D 412C standard. At least five identical specimens were tested for each composition and the average results along with the standard deviation values have been reported. Dynamic mechanical analysis was performed on rectangular specimens (50 mm × 8 mm × 3 mm) using DMA (Artemis 242E, Netzsch). A dual-cantilever bending mode was used, which permitted controlled movement of the sample during testing. The nominal sample size for the DMA test is 50 mm × 8 mm × 3 mm (l × b × h). The experiments were conducted at frequency of 1 Hz over a broad temperature range (-80 to 150 °C @ 2 °C/min).

Swelling studies on polyurea samples were performed by placing disc shaped samples (50 mm dia, thickness ~3 mm) in different solvents for extended periods. The extent of swelling was quantified in terms of their swelling ratio.

$$Swelling \ Ratio (\%) = \frac{(M_{swollen} - M_{dry}) \times 100}{M_{dry}} \quad (3)$$

where, M_{dry} and $M_{swollen}$ refer to the initially dry specimen and post-equilibrium (7 days) of immersion in solvent.

Thermal degradation behavior of polyurea samples was studied using Perkin Elmer Diamond STG-DTA under a constant N₂ flow rate (20 ml/min). For all experimentations ~ 5.0 ± 0.5 mg of sample was used and a heating rate of 10 °C/min was maintained for heating of sample from 50 to 800 °C. Thermal transitions in the sample were determined using Differential Scanning Calorimetry (TA instruments, Q 20) under inert atmosphere. ~5 mg of the sample was placed in an aluminum pan (capacity 40 µL), which was sealed with a lid. Samples were heated under a nitrogen gas flow of 50 ml min⁻¹ from -80 °C to 150 °C at a constant heating rate (10 °C min⁻¹) to prevent oxidative degradation of the sample during analysis. The T_g was estimated from the midpoint of the glass transition phenomenon. FTIR spectra of samples were recorded in the wavelength range 4000-600 cm⁻¹ using Fourier Transform Infrared (FTIR) spectroscopy on a Thermo Fisher FTIR (NICOLET 8700) with an attenuated total reflectance (ATR) crystal accessory.

3. Results and discussion

3.1. Effect of crosslinking on mechanical properties

There are primarily two major constraints for preparation of polyurea films through spray coating technique; the most important being the maintenance of a stoichiometric balance of amine and isocyanate. In addition, there exist an operational constraint of maintaining 1:1 v/v ratio of isocyanate and amine. For the latter, the isocyanate prepolymer needs to be diluted with a reactive diluent (10%v/v) to ensure similar viscosities of resin blend and isocyanates [35]. The dependence of

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