



High corrosion resistant – redox active – moisture curable – conducting polyurethanes



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ARTICLE INFO

Article history:

Received 29 May 2015

Received in revised form

31 December 2015

Accepted 26 January 2016

Keywords:

Polyurethane

Conductivity

Tetraaniline

Electrochemical

Corrosion

ABSTRACT

New series of electrochemically active conducting polyurethanes (CPU) have been prepared using tetraaniline as conducting unit with IPDI-PTMG as urethane prepolymer segment. These films are robust and formed as a consequence of moisture curing of excess isocyanate. The films are novel in the sense that the conductivity is found to be in the higher side of the order of 10^{-3} S/cm and the tetraaniline segments are electrochemically oxidizable and/or reducible. The formed films have been subjected for thermal and mechanical tests such as TGA, DSC, DMTA and tensile tests to explore into the understanding of structure–property relations. The nano/microstructure of the polymers has been investigated by TEM analysis. These CPUs are found to be excellent anti-corrosion barrier coatings for mild steel.

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1. Introduction

Polyurethanes (PU) are unique commercial polymers of this century as these are useful for different applications as adhesives, elastomers, coatings for textiles/paper, foot wear, furniture/foams, packaging material, and for automotive finishes [1–3]. The bio-compatible products such as nasogastric catheters, peritoneal dialysis and infusion pumps to implanted pacemaker parts are also derived from polyurethane polymers [2]. PU elastomers are multiblock copolymers comprising of alternate “soft” polyether or polyester segments and “hard” polyurethane segments. The thermodynamic incompatibility of these segments, combined with crystallization of either or both segments, drives their microphase separation into hard and soft phases that are, respectively, below and above their glass transition temperatures. This microphase separation is responsible for the excellent elastomeric properties of polyurethanes [4].

There have been attempts found in literature for converting these insulating polymers into electrically-conducting advanced materials for application such as sensors, corrosion resistance paints, electrostatic dissipaters, EMI shielders, shape memory materials and others [5–7]. Binary composite systems, comprising

of conductive fillers such as carbon black (CB), CNTs, metal powder or conducting polymer in the polymer matrix, resulted in materials that are tough, flexible, and electrically conductive [5–8]. These unique materials, as mentioned earlier, are ideally suited for antistatic layers, electromagnetic interference shielding (EMI), chemical vapour sensors and thermal resistors [9,10].

In contrast to polyaniline, the interesting property of the oligoanilines is their ability to undergo easy processability. Oligoanilines exhibit unique molecular weight and monodispersity and also easily functionalizable. Because of these positive traits, there is a surge in synthesis of oligoaniline-based novel materials which exhibited interesting properties like pH dependent self assembly, tuneable electrochromic property and different nanoscaled morphologies [11–19]. Recently there are attempts to incorporate ‘oligoanilines’ into the back-bone of different types of processable polymers as one end attached hanging pendent group or both-ends inserted redox segment [20–23]. Electrochemical [20] and conductivity studies [21] on poly(methacrylamide) containing four and five aniline units have been reported in the literature. Apart from being electrochemical active, the polymer containing pentaniline as pendant group is electronically conducting to the tune of 10^{-4} S/cm after doping with mineral acid. Wang et al. [22] have reported polyimides from diamino capped TriAni which are electroactive with good thermal stability. Similar electroactive polyimides have been synthesized and

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studied for their electrochemical activity [23]. The polymer on GC electrode showed three oxidations and three corresponding reductions. The conductivity of the pressed polymer is 1.04×10^{-4} S/cm.

Earlier, in our previous communication [24] we incorporated/terminated polyurethane back-bone with tetraaniline or trianiline for a different series of polyurethane-prepolymers. However, the film formation was very slow and the corrosion protection was moderate. The electrochemical properties here not uniform. In the present study, we incorporated tetraaniline (TAni), one of the important oligoanilines, as terminal group in polyurethane by reacting with NCO-terminated pre-polyurethane with some fraction of –NCO leaving for moisture curing. These polyurethanes formed excellent films, in contrast to our earlier report [24]. We attempted to throw light on the mechanical, thermal, electrical, electrochemical and anti-corrosion properties of these novel conducting polymeric materials. The results are presented and discussed.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), poly(tetramethylene ether glycol) (PTMEG; $M_n = 1000$), trimethylol propane (TMP), dibutyltin dilaurate (95%), p-toluene sulphonic acid (PTSA), N-phenyl-1,4-phenylenediamine were procured from Aldrich Chemicals, USA. Ferric chloride, hydrochloric acid, acetone, n-butyl amine, toluene and sodium chloride chemicals were obtained from SD FINE Reagents Co., India. Methyl ethyl ketone (MEK), hydrochloric acid (36%), ammonium hydroxide, 1-methyl-2-pyrrolidone (NMP) chemicals were purchased from SDFINE Co., India. Tetraaniline (TAni) was prepared [25] according to a literature procedure described by Zang et al.

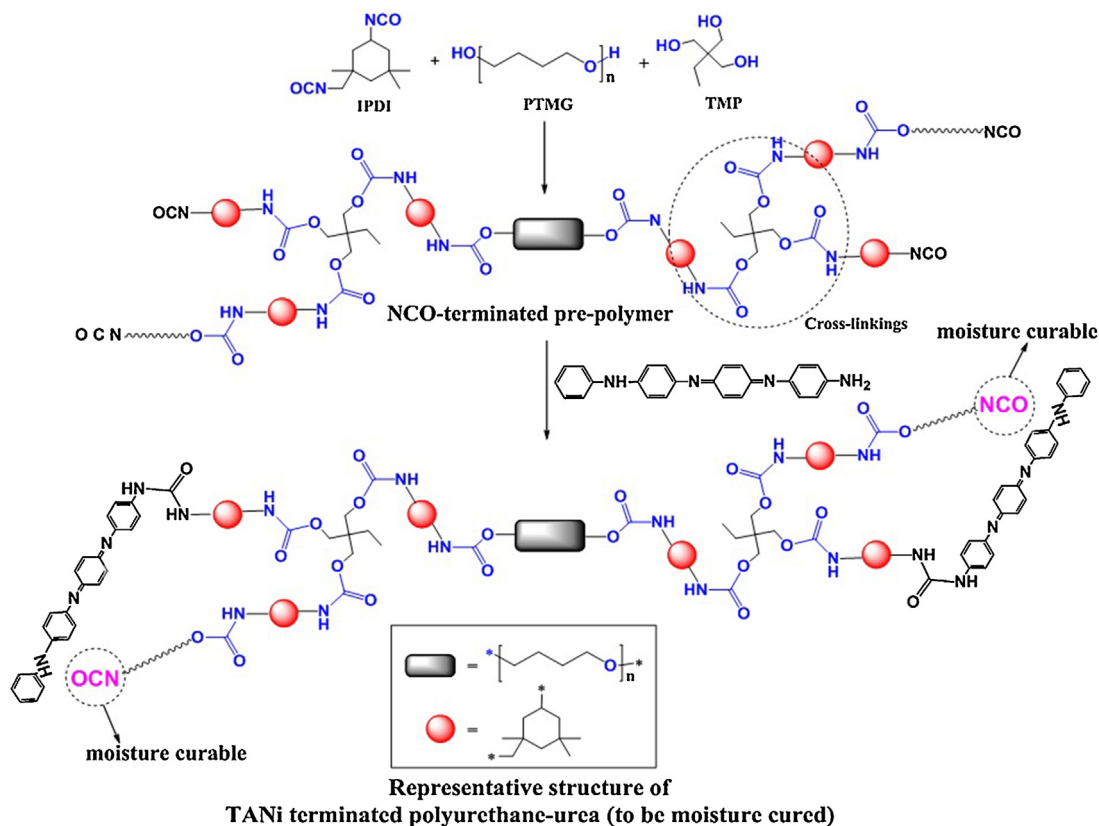
2.2. Synthesis of conducting polyurethanes (CPUs)

The preparations of TAni containing conducting polyurethanes (CPU-10%, CPU-12.5% and CPU-15%) were carried out in two step reaction sequence. First a three-necked, moisture-free round bottomed flask was flushed with dry nitrogen and charged with calculated amount of IPDI (0.027 eq.), PTMEG-1000 (0.008 eq.), TMP (0.0133 eq.) and a drop of dibutyltin dilaurate was added as catalyst. The flask was heated at 70–75 °C for nearly 2–3 h with vigorous overhead stirring. During this time NCO values were checked at constant time intervals by standard n-butyl amine titration method. When appropriate NCO% value was reached, the pre-polymer was reacted with various amounts of TAni (10 wt%, 12.5 wt% or 15 wt% based on PTMG weight or 0.0011 eq., 0.00137 eq. or 0.00165 eq.) after dissolving in small amount of MEK and 1-methyl-2-pyrrolidone (NMP) solvent (10 ml). The reaction mixture was heated with stirring for period of 4 h after which time heating was stopped and stirring continued for further period of 12 h. The tetraaniline containing polyurethane was formed. Pure polyurethane was also synthesized as describe above with 0.0257 eq. of IPDI, 0.008 eq. and 0.0133 eq. of TMP without TAni.

The obtained CPUs were casted in Teflon dishes for free standing films. For doped films, 10 g of polyurethane solution from above reaction mixture was stirred with 0.9 g of PTSA for 2 h and casted in Teflon Petri dish for free standing doped films.

2.3. Characterization methods

FT-IR spectra were recorded on a Perkin Elmer Spectrum-100 spectrometer using KBr pellet technique. UV–vis spectral measurements were carried out on a Spectro UV-Vis Double Beam PC-8 Scanning Auto cell, LABOMED INC. Thermo gravimetric analyses of polymer samples were carried out using TA Instruments (TGA Q500 V20.8, USA) from ambient to 600 °C under nitrogen



Scheme 1. Scheme showing general structure of CPUs and steps involved in its synthesis.

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