Progress in Organic Coatings 125 (2018) 186–194

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Waterborne polyurethanes: A three step synthetic approach towards environmental friendly flame retardant coatings

Rasmika Patel*, Parth Kapatel

Department of Materials Science, Sardar Patel University, Vallabh Vidyanagar, 388120, Gujarat, India

ARTICLE INFO

Keywords:
Polyurethanes
Waterborne
Flame retardant
Casting
Coating

ABSTRACT

Flame retardant waterborne polyurethanes (WBPU) were synthesized by reacting a phosphorous based polyester polyol with isophorone diisocyanate (IPDI) in different mole ratios of NCO:OH in three steps. In first step, the polyester polyol was synthesized by reacting tris(bisphenol-A)mono phosphate (TBAMP), sebacic acid, polyethylene glycol which was characterised by measuring acid value and hydroxyl value. Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy and gel-permeation chromatographic techniques were used for the characterization of polyester polyol. In second step, the polyurethanes were synthesized by reacting polyester polyol with diisocyanate in different proportions. In third step, the polyurethane was neutralised using tertiaryamine. A calculated amount of water was then added at this stage followed by addition of a chain extender at controlled pH. This resulted into waterborne polyurethanes. By varying the proportion of NCO/OH, four WBPUs have been prepared. These WBPUs were subjected for coating and casting purposes. Physico-chemical properties such as particle size, dispersion stability, viscosity were measured. The flame retardency of casted films were studied by LOI (limiting oxygen index) and UL-94 test methods. Thermal properties were determined using thermogravimatric analysis (TGA) technique of casted film. Chemical resistance and Mechanical properties of the coated samples have been found out.

1. Introduction

Many coating industries over several decades largely prefer the use of polyurethanes(PUs) because of their versatile properties like hardness, chemical resistance, adhesion to wide verities of substrates like wood, metal, ceramics etc. The present trend in the course of organic coatings is to formulate and process coatings with lower levels of volatile matter which is generally a solvent. These volatile organic solvents are used in coatings to reduce the viscosity of resin for uniform application by achieving high wettability and easy processing. Once coating is applied over a substrate, it starts to lose the volatile solvents causing environment pollution. Hence there have been thrust efforts in the field of organic coating either with a minimum content of solvent or without any solvent. Waterborne coating were thought of as they have potential to replace solvent based coating without sacrificing the properties [1]. The planning for synthesis of waterborne polyurethane (WBPU) is free from evaporation of organic volatile solvent therefore atmosphere is saved from pollution [2]. The use of conventional solvent based coating are nowadays being restricted in many application over the globe due to environmental and safety issues. Therefore, PUs with aqueous-base can replace the organic solvent based coating to a vast extent. An environmental advantage of WBPUs and selective availability of expensive solvents have made WBPUs of major application in many industries like textile coatings, fiber sizings and adhesives of many polymeric and glassy surfaces [3]. Majorly all the properties of PUs can be tailor made as per the requirements and have versatile applications. The linear thermoplastic polyurethanes are synthesized by the prepolymer reaction of a diisocyanate and a polyol (mainly polyethers and polyesters) [4,5]. WBPUDs are extensively utilised as hard coatings for wood and metallic surfaces and flexible coatings for textiles industries [6]. Depending on the area of usage, polyester polyols (PEPO) or polyether polyols are usually taken as a soft segment. The PEPO is synthesized from a diol and dibasic acid and the two ends of synthesized PEPO are designed to have hydroxyl groups [7]. The PUs, which are synthesized from PEPO as soft segment, show outstanding adhesive properties, thermal stability and oliophobic surface hence oil resistance. Because the manufacturing cost is subsequently low of PEPO, the polyester-type PUs have been widely used in industrial as well as household application [8,9].

Flame retardants coatings with phosphorus-containing moieties such as phosphates, phosphazenes, phosphines, phosphites, phosphonates and phosphine oxides are extensively used to enhance flame

* Corresponding author.
E-mail address: rasmi29@yahoo.com (R. Patel).

https://doi.org/10.1016/j.porgcoat.2018.09.010
Received 6 April 2018; Received in revised form 9 August 2018; Accepted 1 September 2018

retardancy of polymers [10]. The phosphorous content in the polymer governs the flame retardency of a polymer. When exposed to fire, polyurethane releases a large amount of heat simultaneously it degrades very fast and hence the flammability of polyurethane is of prime concern. Seeing this situation, in the recent decades a lot of work is going on by the incorporation of flame retardant properties in PUs and for that, additive as well as reactive flame retardants are being used [11–13]. Although, additive flame retardants bring about certain disadvantages which includes separation of phase due to excessive concentration, loss of homogeneity, high viscosity of the formulations etc. [14]. That is why, polymer and their coating with reactive flame retardants are gaining a major interest in present days. Largely, halogenated and phosphorus based reactive flame retardants are utilised for reactive modification of polymers and hence in their coatings. Although several halogenated compounds have been banned over the time due to their toxic nature coupled with the generation of the reactive smoke during fire. These critical issues are absent in phosphorus containing compounds and they are being substituted in place of halogenated flame retardant polymer without sacrificing properties of the polymer and its coatings.

Therefore, the present work attempts to synthesise phosphorous based waterborne polyurethanes (WBPUs) by reacting phosphorous containing polyester polyol with isophorone diisocyanate. Four different types of WBPUs having different NCO/OH molar ratio have been synthesized. The resulted polyurethanes were further neutralised with triethyl amine and water then chain extended by adding diethylenetriamine (DETA) under vigorous stirring. The influence of varying NCO/OH ratios on the properties were studied. Coating was done on mild steel panels as well as glass plates and the formulations were casted into film to find out flame retardency, mechanical and chemical resistance properties.

2. Experimental

2.1. Materials

The reagents bisphenol-A, phosphorous oxycloride ($POCl_3$), N, *N*-dimethyl aniline, sebacic acid. polyethylene-glycol (PEG- M.W. 600), xylene, methyl-ethyl keton(MEK), para-toluene sulphonic acid, isophorone diisocyanate(IPDI), dibutyl tin dilaurate(DBTDL) were procured from Sigma Aldrich. Triethyleamine(TEA), diethylenetriamine (DETA) were obtain from Himedia laboratories, Mumbai. These reagents were used as such without purification. For the synthesis of dispersions, deionised water was used. Mild steel panels and glass panels were used for coating purpose and for casting purpose glass mould was used.

2.2. Characterization

Number average molecular weight, weight average molecular weight and molecular weight distribution of polymers were determined using Gel Permeation Chromatography (GPC) of Perkin Elmer USA (Model Turbo matrix – 40).

Elemental analysis of monomer was found out using PERKIN ELMER USA (Model 2400 SERIES II).

The infra-red spectra of the monomer, polyester-polyol and waterborne polyurethanes were recorded in KBr pallet using Perkin Elmer USA (Model SPECTRUM GX, FT-IR spectrophotometer).

The structure of polyester polyol was confirmed by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra with the help of Bruker, Switzerland Model AVANCE 400. Final product was dissolved in acetone and TMS (Tetramethyl Silane) was used as internal reference.

Particle size and viscosity are two important parameters. Particle size was measured using Microtrac, Particle Size Analyzer USA. For this study, samples were first diluted in deionized water and then were exposed to ultrasonication followed by particle size analysis. The viscosities of WBPU dispersions (WBPUDs) were measured in a Brookfield Digital Viscometer (Model DV-II + PRO) at 25 °C using the spindle (No.61) at 60 rpm.

The colloidal stability of waterborne dispersion is a very important characteristic which determines the safety period for storage. This study was performed in sealed clean containers having freshly synthesized WBPUDs at room temperature and monitoring any kind of phase separation up to a period of 12 months.

The decompositions of WBPU films were analyzed using Diamond Perkin Elmer Thermogravimetry analyzer. 4 to 6 mg samples were heated from 30 °C to 450 °C in platinum crucible in nitrogen atmosphere at a heating rate of 10 °C min^{-1} and the weight loss and temperature difference were recorded as a function of temperature.

Flame retardancy of the films was determined by limiting oxygen index (LOI) value (ASTM D2863) and vertical burning test method UL-94 (ASTM D3801). LOI is measured in terms of volume percentage. In UL-94, sample which is under experiment gets V_0 rating if it extinguish itself in 10 s. In other case if there is a dripping of polymer or continuous burning is seen, V_1 or V_2 ratings are assigned.

Tensile test of films was done using INSTRON 5500R Universal Testing Machine. Micro-tensile specimens of dumbbell shaped specimens of 25 mm (length) × 5 mm (width) × 1 mm (thickness) were used. The specimens were elongated at 500 mm/min of cross head speed.

Physical properties like drying time (surface drying, tack free drying and hard drying) of all the WBPUDs films were examined as per the standards.

Chemical resistance tests of coated panels were performed according to ASTM D 1647–89 by immersing the panels (dry film thickness of 40 μm) into water, methanol, acid, and alkali solutions. Wax was used to seal all the edges of glass panel. This was done to ensure no leakage or transfer of material from edges of glass panel. The panels were then dipped in water, methanol, 3% (w/w) sulfuric acid solution, and 3% (w/w) sodium hydroxide solution. Further the samples were examined for visual appearance after 10 days.

2.3. Synthesis of phosphorous based monomer, polyester polyol and waterborne polyurethanes

2.3.1. Synthesis of tris - bisphenol-A mono phosphate (TBAMP) monomer

The monomer tris(bisphenol-A) mono phosphate(TBAMP) was synthesized [16] by reacting bisphenol-A (3.0 mol, 6.84 gm) and phosphorous oxychloride (1.0 mol, 0.91 ml) at the temperature of 130 °C for 10 h in presence of a catalyst N, N, dimethyl aniline (0.0133 mol) in an inert atmosphere of nitrogen. Final product was obtained by dissolving crude product in minimum amount of acetone followed by neutralization with sodium bicarbonate (5% solution). The re-precipitation of the neutral product was carried out by the addition of cold water. The product was filtered, dried and crystallized from methanol.

2.3.2. Synthesis of polyester-polyol based on tris (bisphenol-A) monophosphate

The polyester polyol was synthesized in a one step process as shown in reaction Scheme 1. TBAMP(1.0 mol, 22.8gm), sebacic acid (3.0 mol, 60.6 gm) and PEG 600(polyethylene-glycol) (2.0 mol, 107.1 ml) were charged in a three-necked round bottom flask equipped with dean and stark apparatus and condenser. Xylene was used as reaction medium and para toluene sulphonic acid (0.003% by weight) was used as catalyst. The charge was initially heated to 120 °C and further reaction was carried out between 190 °C–200 °C temperature. The conversation of polyester-polyol was monitored by determining an acid number with respect to time. When an acid value of 25 mg KOH/gm of resin was reached, the reaction was stopped. In the reaction, water was produced as byproduct and pure viscous liquid product was obtained by vacuum distillation. Finally, polyester polyol was discharged into glass