



Study on the synthesis of new blocked polyisocyanates as crosslinking agents for hydrophobic polyurethane powder clear coatings



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ABSTRACT

Blocked polyisocyanate crosslinkers for powder coatings were synthesized using isophorone diisocyanate (IPDI), formic acid and ϵ -caprolactam. They were modified with fluorinated polyols. Two kinds of catalyst i.e. dibutyltin dilaurate and dibutyl phosphate for the synthesis were employed. The chemical structures of these compounds were confirmed by nuclear magnetic resonance (NMR) spectroscopy. The molecular mass distribution was investigated using gel permeation chromatography (GPC). During the thermal degradation of modified polyisocyanate three main stages of decomposition can be seen. The degradation of modifier occurs in the last decomposition stage at temperature range of 375–500 °C, which is confirmed by coupled TG-FTIR technique. Additionally, polyurethane powder coating systems composed of polyester resin and modified blocked polyisocyanate, were examined. The cross-linked polyurethane powder coatings resulted in improved thermal stability and surface properties i.e. lower roughness and surface free energy values as well as higher hydrophobicity, oleophobicity, gloss, scratch and abrasion resistance.

1. Introduction

Hydrophobic coatings are very important in every day live, because they can be easily cleaned. The coating surface with good hydrophobicity as well as chemical and mechanical resistance can protect substrates from moisture, organic solvents and mechanical damages, as well as prolong their lifetime. Coatings based on polyurethane systems with increased hydrophobicity were prepared in a reaction between di- or polyisocyanates (PIC) and hydroxyl terminated resins with incorporated siloxane or fluoroalkyl segments or as a result of crosslinking of specially selected resin by means of crosslinking agents containing fluoroalkyl or siloxane groups [1,2].

In our recent works the way of the modification of thermosetting polyurethane powder coatings using linear polysiloxanes containing silanol or hydroxyalkoxy groups was described [3,4]. This paper focuses on the modification of thermosetting polyurethane powder coatings using fluorine compounds. Since they have a higher bond energies C–F (485 kJ/mol) compared to the C–H (415 kJ/mol), C–C (347 kJ/mol) and C–N (335 kJ/mol) bonds present in the polyurethanes, the fluorine compounds can increase the mechanical, thermal and chemical resistance of the coatings. Due to higher hydrophobicity of C–F groups this segments can migrate to the coating surface, which leads to a significant change of the coating properties even at low fluorine content [2,5]. In addition, the incorporation of the

fluorinated chain segments into the structure of the coating should proceed without steric hindrance, because of the small radius of fluorine (0.71 Å) [6].

The previous reports were focused mainly on modification of liquid polyurethane systems containing organic solvents [7,8] or aqueous dispersions [9,10]. Blocked PIC synthesized in a reaction between a perfluorinated alcohol with *N,N*-carbonylbis caprolactam was one of the component for preparation of hydrophobic liquid polyurethane systems [11]. Hydrophobic polyurethane coatings were also obtained using polyisocyanates synthesized by the reaction of polyisocyanurates with fluorinated alcohols [12]. In order to obtain of two-component high-solid solvent-based polyurethane systems with high hydrophobicity, the perfluorinated polyoxypropylene alcohol with a molecular weight of 757 g/mol was incorporated into contained allophanate groups polyisocyanates, which were synthesized in a reaction of HDI and butan-1-ol in the presence of tin octoate [13]. Decrease in surface free energy (SFE) was also achieved for the coatings formed from polyacrylic resin and polyisocyanate contained allophanate moieties and build-in a fluorinated monoalcohol with a molecular mass of 452 g/mol [14]. Patent US discloses a process for the preparation of high-solid polyurethane coatings formed as a result of crosslinking a polyester resin with polyisocyanate with allophanate moieties and with incorporated fluorinated monoalcohol with a molecular weight of 570 g/mol [15]. There were also reports on polyurethane cationomers synthesized from

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HDI, poly(oxyethylene) glycol, *N*-methyldiethanolamine and butane-1,4-diol, which revealed a decrease in the FSE from 40 mJ/m² to 30 mJ/m² when 15% of butane-1,4-diol was replaced by 2,2,3,3-tetrafluorobutane-1,4-diol [16].

Recently, there has been considerable progress in the production of polyurethane powder coatings due to numerous advantages, such as their better properties, environment-friendly application and the variety of substrates to which they can be applied. Addition of modifier into powder coatings cannot change the consistency of powder components. All components must be extruded and pulverized. They should not hinder coating manufacturing process, adversely affect the coating curing process or decrease the stability of coating during storage. It is possible to obtain hydrophobic coatings by chemical or physical incorporation of modifier into the polyurethane matrix. For the preparation of thermoplastic hydrophobic polyurethane powder clear coatings, perfluorinated alcohols have been used [17]. Such polyurethane were obtained by the reaction of alcohol with HDI and then with hydroxyethyl acrylate, hydrogenated bisphenol A and decane-1,10-diol as a chain extender. Thermoplastic powder coatings showed worse mechanical properties than thermosetting systems, because they are not crosslinked.

The hydrophobic thermosetting powder coatings with improved reliability and durability on an epoxy polyester, epoxy, polyester or polyurethane composition may be obtained by application of the second layer containing micro- and nano-sized hydrophobic particles of PTFE and aluminium oxide on the uncured first layer of powder composition [18]. The applied coatings were then cured by heating at a temperature of 180–190 °C for 15–20 min. Hydrophobic surface layer adhered as a result of the physical interactions is abraded easily, compared to the chemically bonded surface formed by migration of the fluorine-containing chain segments.

A process for the preparation of polyester resins which contain carboxyl groups and fluorinated substituents for hydrophobic polyester powder clear coatings was described in a paper by Xiong and co-workers [19]. This resin was synthesized by a polycondensation of butane-1,4-diol, isophthalic anhydride and with the product resulting from an addition of 1H,1H,7H-dodecafluoro-1-heptanol to epichlorohydrin.

The method for the modification of thermosetting polyurethane powder systems using monofunctional fluorinated alcohols has been described in our earlier reports [20,21]. Fluorinated alcohols were built into biuret or allophanate polyisocyanate crosslinkers. The SFE of obtained coatings was reduced from 46.2 mJ/m² for unmodified coatings only to 38.5 mJ/m² for coatings contained fluorinated alcohols. Moreover, no increase in the thermal stability of the modified coatings was observed.

The aim of this work was to develop a way of synthesis of new blocked polyisocyanate crosslinkers for hydrophobic thermosetting polyurethane powder clear coatings. In this work, linear hydroxyl terminated fluorinated polyols were built into the biuretpolyisocyanates and blocked. The use of bifunctional polyols results in higher functionality and higher molecular weight of polyisocyanates than modification by means of fluorinated alcohols. Higher functionality of polyisocyanate leads to higher crosslinking density of powder coatings and better application properties. Spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (¹H-NMR and ¹³C NMR) were used in order to determine the chemical structure of these polyisocyanates. The simultaneous thermal analysis and Fourier transform infrared spectroscopy (TG/FTIR) was used for investigate the mechanism of decomposition of these polyisocyanates. In order to examine the effect of employed modifier on the properties of polyurethane powder coatings, the studies of the thermal stability, roughness, gloss, contact angle, cupping, abrasion as well as scratch resistance, hardness and adhesion to steel surface were also performed. The relationship between coating properties as well as modifier type and content was discussed.

2. Experimental

2.1. Raw materials and reagents

Desmodur I - isophorone diisocyanate (IPDI) from Evonik Industries A.G. (Essen, Germany). ϵ -caprolactam (CAP) from Grupa Azoty S. A. (Tarnów, Poland). *PolyFox PF-636*, Mn = 1200 g/mol, fluorine content: 38,57% (PF-636), *PolyFox PF-6520*, Mn = 9450 g/mol, fluorine content: 40,15% (PF-6520) from Omnova Solution Inc. (Great Britain). *Sirales PE 6110* – polyester resin based on isophthalic acid and neopentyl glycol, acid value: 4–6 mg KOH/g, hydroxyl value: 30–45 mg KOH/g, T_g: 60 °C (SIR), from Sir Industriale SpA (Macherio Monza e della Brianza, Italy). *Benzoin* from Aldrich (Buchs, Switzerland), *WorleeAdd 902* (acrylate resin) and *Resiflow PH-240* (polyacrylic resin adsorbed on silica) from Worlée – Chemie G.m.b.H (Lauenburg, Germany).

2.2. Synthesis of modified blocked polyisocyanates

The synthesis involved four stages: synthesis of ureaisocyanate, synthesis of biuretpolyisocyanate, modifier addition and blocking reaction.

2.2.1. Synthesis of ureaisocyanate

IPDI and *dibutyltin dilaurate* as well as *dibutyl phosphate* as a catalysts (both at 0.1 wt% with respect to diisocyanate) were placed in a three-necked flask equipped with a reflux condenser, thermometer, glass stirrer, nitrogen inlet and dropping funnel. A calculated amount of *formic acid* (to keep the molar ratio of IPDI to formic acid at 4:1) was introduced drop-wise to diisocyanate. The time of introduction was adjusted to 30 min. After introduction of *formic acid*, the reaction mixture was then maintained at the temperature of 75 °C, stirred and refluxed for 3 h. The end point of the reaction was controlled by the content of –NCO groups. The typical dibutylamine method was employed. Excess of unreacted dibutylamine was titrated with aqueous HCl against bromophenol blue [18].

2.2.2. Biuretpolyisocyanate synthesis

The reaction mixture was heated up to 140 °C, stirred and refluxed for 6 h.

2.2.3. Modifier addition

A calculated amount of modifier was added to reaction mixture in each case (the amount of modifier was selected in such a way as to make sure that its content in the coating was within the range of 0,5–10%). Addition of modifier to polyisocyanate took place at the temperature of 65–75 °C for 2 h. In order to decrease the viscosity of the reaction mixture, THF (20 wt%) was added. After that time the content of –NCO groups decreased to the value which had been calculated theoretically.

2.2.4. Blocking reaction

A calculated amount of the blocking agent (ϵ -caprolactam, CAP) was added to the reaction mixture in each case (the molar ratio of –NCO group to blocking agent at 1:1). The reaction was carried out at the temperature of 65 °C for 4 h. The products were evaporated under vacuum and dried at the temperature of 80 ± 1 °C to remove the solvent. The reaction scheme characterizing all steps of the synthesis was presented in Fig. 1.

2.3. Preparation of lacquer compositions and coatings

The blocked polyisocyanate was mixed with polyester resin *Sirales 6110* (NCO:OH molar ratio = 1:1) as well as flow control agent *Resiflow PH – 240* (3 wt%) and degassing agents: *WorleeAdd 902* (1.5 wt%) and *benzoin* (1 wt%). The mixture was milled and extruded in

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