



# Structure and properties of polyurethane-based powder clear coatings systems modified with hydrotalcites



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## ABSTRACT

In this study, polyurethane powder clear coating systems consisting of polyester resin, blocked polyisocyanate and hydrotalcites (HT) intercalated with carbonate, aminododecanate, and ethylenediaminetetraacetate were examined. The blocked polyisocyanate crosslinkers for powder coatings were synthesized using trimethylhexamethylene diisocyanate (TMDI), formic acid,  $\epsilon$ -caprolactam, dibutyltin dilaurate and triethylamine as catalysts. The powder coatings were investigated by atomic force microscopy (AFM) and X-ray diffraction analysis (XRD). The surface structure was correlated with the chemical structure of the coatings and macroscopic surface behavior: contact angle, surface free energy, gloss, elasticity, cupping, impact and scratch resistance, hardness as well as adhesion to steel surface.

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## 1. Introduction

In recent years, the development of organic coatings frequently involves the dispersion of inorganic nanoscale materials in a polymer matrix to improve the mechanical, physical and thermal properties at very low filler content [1]. Although cationic clays are the most often investigated layered nanofillers, their anionic analogs, namely layered double hydroxides (LDHs, hydrotalcites) are also a subject of increasing interest.

LDHs are compounds with the general formula:  $[\text{Me}_I^{2+}_{1-x}\text{Me}_{II}^{3+}_x(\text{OH})_2][\text{A}^{y-}_{x/y}(\text{nH}_2\text{O})]$ , where  $\text{Me}_I$  and  $\text{Me}_{II}$  denote divalent and trivalent metal cations, respectively. A typical example of this class is naturally occurring magnesium-aluminium hydroxycarbonate  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}[\text{CO}_3] \cdot 4\text{H}_2\text{O}$ , firstly reported by Hochstetter in 1842 and named as hydrotalcite (HT) due to its talc-like appearance and high water content [2]. Its chemical synthesis was accomplished a century later by coprecipitation from a mixture of Mg and Al chlorides under basic conditions [3]. HT was first manufactured on an industrial scale in 1966 by Kyowa Chemical Industry Co., Ltd. and it found many applications as basic catalyst, adsorbent

and acid scavenger (e.g. heavy metal-free PVC stabilizer) or antacid drug [4].

LDH particles are composed of positively charged layers formed by edge-sharing octahedra of divalent and trivalent metal hydroxides. The space between the layers contains water and anionic compounds compensating the electrostatic charge (Fig. 1). The layered structure of LDH and possibility of making them hydrophobic by intercalation of organic anions has inspired many researchers to investigate hydrotalcite as nanofiller in polymeric matrices [5–9]. It was reported that the incorporation of few percent HT additive can give an improvement in the mechanical properties, thermal stability and fire retardancy of polymers [1,10–13]. Akzo Nobel company introduced into the market a range of HT modified with fatty acids (Perkalite<sup>TM</sup>) as additives for polymeric materials [14]. The high surface area and anion-exchange ability of LDH make them interesting for corrosion protection coating applications. To this aim, various corrosion inhibiting anions were inserted into LDH interlayer and the resulting compounds were used for modification of coatings [15].

Powder coatings are high quality finishing materials, which in contrary to solvent-based paints do not emit volatile organic compounds during the coating process. Despite over a half century of research and development in this field, there is still need to combine the suitable processing performance (low-temperature cure, storage stability, flow and film forming properties) with good

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mechanical properties as well as weather and UV resistance of the final coatings. One of the methods to improve the powder coating performance is the use of nanofillers, which added even in a small amount can distinctly improve the material properties. Various nanosized additives have been used for this purpose, including titania and hydroxyapatite [16,17], montmorillonite clay [18] or graphene [19]. There are several examples of using hydrotalcites as nanofillers in coating materials. Epoxy coating containing HT intercalated with tungstate or (2-benzothiazolylthio) succinic acid showed improved corrosion protection for metallic substrates [20,21]. In the work of Fina et al. HT intercalated with lactate, gluconate, fatty acid and rosin were used as components of nanostructured intumescent coatings resulting in an improved thermal shielding performance [22]. Hydrotalcite-based composites applied as a primer layer provided an excellent stone chip resistance to an automotive coating system [23]. Also, the thermal and mechanical properties of acrylic-urethane UV curing coatings were improved by using HT intercalated with long alkyl sulfate anions [24]. Recently, it was reported that organically modified HT can be delaminated in the polyester resin used as powder coating component [25]. However, there is a lack of research papers on the effect of layered double hydroxide nanofillers on the properties of powder coatings.

In this work, a series of hydrotalcite-type compounds intercalated with various organic anions was used to modify the properties of polyurethane powder coatings. The dispersion of LDH in the polymer matrix was investigated by X-Ray diffraction analysis (XRD). Atomic force microscopy (AFM) was employed for visualizing the surface topography, adhesion and deformation of the cured coatings. In order to examine the influence of LDH additive on the properties of polyurethane powder coatings, the measurements of the contact angle, surface free energy, gloss, roughness, scratch and impact resistance, hardness, elasticity, cupping and adhesion to steel were carried out. The relationship between coating properties and LDHs content and type is discussed.

## 2. Experimental

### 2.1. Starting materials

Vestanat TMDI – a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diisocyanate (TMDI) was purchased from Evonik Industries A.G. (Marl, Germany). Rucote 102–polyester resin based on isophthalic acid and neopentyl glycol, acid value: 11–14 mg KOH/g, hydroxyl value: 35–45 mg KOH/g,  $T_g$ : 59 °C (RU), was supplied by Bayer A.G. (Leverkusen, Germany). Formic acid 100% from POCH (Gliwice, Poland),  $\epsilon$ -caprolactam (C) from Zakłady Azotowe w Tarnowie – Mościcach S.A. (Tarnów, Poland) and aminolauric acid from TCI were used. WorleeAdd 902 (acrylate resin), Resiflow PH-240 (polyacrylic resin adsorbed on silica) and WorleeAdd ST-70 (stannous octoate (II)) were provided by Worlée – Chemie G.m.b.H (Lauenburg, Germany). Benzoin and magnesium-aluminium hydrotalcite in carbonate form ( $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$ ) were purchased from Aldrich (Buchs, Switzerland). Magnesium nitrate hexahydrate, aluminium nitrate nonahydrate, zinc nitrate hexahydrate and ethylenediaminetetraacetic acid were provided by POCh S.A. (Gliwice, Poland).

### 2.2. Preparation of hydrotalcite-type LDH compounds

Organically modified hydrotalcite compounds were prepared using coprecipitation method. In a typical procedure 0.14 mol amino acid and 0.14 mol sodium hydroxide were dissolved in 300 ml water, then solution of 0.28 mol aluminium nitrate (or zinc

nitrate) and 0.14 mol magnesium nitrate in 200 ml water was added at 1 ml/min. The pH of the reaction mixture was maintained at 10 by addition of 1 M sodium hydroxide. The process was carried out under nitrogen atmosphere to prevent the undesired reaction of mixed hydroxide with carbon dioxide. The resulting suspension of HT precipitate was then aged by heating at 75 °C.

### 2.3. Synthesis of curing agent for powder coatings

Polyisocyanate was synthesized according to the procedure described in details in earlier reports [26,27]. The synthesis consisted of three stages: preparation of urea polyisocyanate, synthesis of biuret polyisocyanate, and blocking reaction. Urea polyisocyanate was obtained in the reaction of diisocyanate and formic acid at the molar ratio of 4:1 in the presence of dibutyltin dilaurate and triethylamine as catalysts (both at 0.1 wt% with respect to diisocyanate) at  $60 \pm 1$  °C. In order to form biuret moieties, the reaction mixture was heated up to  $140 \pm 1$  °C, stirred and refluxed during 10 h. Free NCO groups were blocked by use of  $\epsilon$ -caprolactam (C) at the final stage.

### 2.4. Preparation of powder compositions and coatings

Hydrotalcites were added to the polyisocyanate during the final stage after completion of the –NCO group blocking. The amount of hydrotalcite was selected in such a way as to make sure that its content in the coating was 1 and 3%. The mixture of HT and PIC was heating to 80 °C and sonicated during 30 min. The hot mixture of HT and PIC was cast onto a PTFE film, cooled and crushed into fine pieces.

The lacquer compositions consisted of: blocked polyisocyanates, polyester resin Rucote 102 (the NCO:OH molecular ratio = 1:1), degassing agents WorléeAdd 902 (1,5%) and benzoin (1%), PU catalyst WorléeAdd ST-70 (0,5%) and levelling agent Resiflow PH-240 (3%).

The mixture was milled and extruded in a co-rotating twin screw miniextruder EHP 2  $\times$  12 Sline from Zamak (Kraków, Poland) and then pulverized to the average particle size of 60  $\mu$ m. Temperature distribution in the extruder was as follows: zone I–95 °C, zone II–110 °C, zone III–120 °C, adapter–125 °C. Screw rotational speed: was 250 r.p.m. The final powder coating was applied by electrostatic gun PEM X–1 controlled by EPG Sprint X (CORONA) from Wagner (Alstatten, Switzerland) to steel panels and cured at 170 °C for 30 min. The obtained coatings were named according to the hydrotalcite type and content e.g., PU/1%Mg,Al-ALA stands for polyurethane (PU) containing 1 wt.% hydrotalcite Mg,Al-Ala.

### 2.5. Measurements

#### 2.5.1. Elemental analysis and BET measurements of HT

Elemental analysis of LDHs was performed using a Series II CHNS/O Perkin-Elmer analyser. BET surface area and average particle size were determined by nitrogen sorption experiments conducted at ambient temperature using a Micromeritics TriStar II 3020 automated gas adsorption analyzer.

#### 2.5.2. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns of LDHs were recorded using Bruker-AXS D8 Advance Series 2 powder diffractometer working with Co-K $\alpha$  radiation ( $k = 1.79 \text{ \AA}$ ). Interlayer distance was calculated from Bragg's Law using the  $d_{003}$  peak from the diffraction pattern. XRD patterns of powder coatings were recorded on a Philips PW 1040 diffractometer equipped with an X-Celerator detector using Cu-K $\alpha$ 1/ $\alpha$ 2 radiation. Data were collected between

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