

Layered double hydroxides as transesterification catalysts and nanofillers for polyester resin

Michał Kędzierski^{1), *)}, Zbigniew Bończa-Tomaszewski¹⁾, Grażyna Jaworska¹⁾, Anna Niska¹⁾

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Abstract: Saturated polyester resins were prepared by reaction of dimethyl terephthalate with alkylene glycols in the presence of layered double hydroxides (hydrotalcites, HT). The effect of HT composition (cation and anion types) on the rate and progress of transesterification was investigated. It was found that zinc-aluminum HT intercalated with anionic form of aminolauric acid [HT(ZnAl)ALA] efficiently catalyzes transesterification process, increasing the rate of reaction or lowering its temperature when compared to the reaction with use of conventional organic tin catalyst. The polyester resin obtained in this way is transparent, which along with X-ray diffraction data indicates the delamination of clay layers and formation of nanocomposite. The limitation of using ALA-intercalated HT as an additive for polyesters used in coatings is coloration of the resin with an increase of the reaction temperature above 180 °C. Colorless polyester was obtained using more thermally stable hydrotalcite intercalated with ethylenediaminetetraacetic acid, however, at the expense of significantly longer reaction time. Using HT(ZnAl)ALA catalyst a two-step synthesis of carboxyl polyester resin was performed and the obtained product was used as a component of powder coating formulation.

Keywords: layered double hydroxides, hydrotalcite, intercalation, aminolauric acid, EDTA, transesterification, catalyst, polyester resins, nanocomposites.

Warstwowe podwójne wodorotlenki jako katalizatory transestryfikacji i nanonapełniacze żywicy poliestrowej

Streszczenie: Przeprowadzono syntezę nasyconych żywic poliestrowych w reakcji tereftalanu dimetylowego z glikolami alkilenowymi, w obecności warstwowego podwójnego wodorotlenku typu hydrotalkitu (HT). Analizowano wpływ składu HT na szybkość i wydajność transestryfikacji. Najlepsze wyniki (zwiększenie szybkości reakcji lub obniżenie średniej temperatury procesu w porównaniu z szybkością i temperaturą reakcji prowadzonej w obecności tradycyjnego katalizatora organocynowego) uzyskano z zastosowaniem hydrotalkitu interkalowanego kwasem aminolaurynowym (ALA). Otrzymane w taki sposób żywice były transparentne, co w połączeniu z zanikiem refleksów hydrotalkitu w widmie XRD produktu transestryfikacji może świadczyć o utworzeniu się delaminowanego nanokompozytu. Wykorzystanie HT interkalowanego ALA w żywicach poliestrowych stosowanych do powłok jest ograniczone ze względu na zabarwienie pojawiające się w temperaturze powyżej 180 °C. W reakcji prowadzonej z udziałem bardziej stabilnego termicznie hydrotalkitu modyfikowanego kwasem etylenodiaminotetraocowym otrzymano bezbarwny poliester, jednak kosztem znacznego wydłużenia czasu reakcji. Katalizator HT(ZnAl)ALA zastosowano w dwustopniowej syntezie poliestru o łańcuchu zakończonym grupami karboksylowymi, który następnie użyto w charakterze składnika proszkowej kompozycji powłokowej.

Słowa kluczowe: warstwowe podwójne wodorotlenki, hydrotalkit, interkalacja, kwas aminolaurynowy, EDTA, transestryfikacja, katalizator, żywice poliestrowe, nanokompozyty.

Saturated polyester resins containing carboxyl or hydroxyl functional groups are widely used as binders in high solids and powder coatings. They are commonly prepared either by polyesterification of dicarboxylic

acids with diols or *via* polytransesterification between diols and esters of lower alcohols, using one of the monomers in molar excess. An example of the second method is the reaction of dimethyl terephthalate with ethylene glycol and other alkylene diols, the process extensively studied also due to its application for the synthesis of high molecular weight thermoplastic polyesters. One of the important issues is the selection of transesterification catalyst, which should have high activity and would be incorporated in the final coating without affecting its pro-

¹⁾ Industrial Chemistry Research Institute, Department of Polyesters, Epoxide Resins and Polyurethanes, Rydygiera 8 Street, 01-793 Warsaw, Poland.

^{*)} Author for correspondence; e-mail: Michal.Kedzierski@ichp.pl

properties and appearance. Many studies concerning the DMT transesterification with the use of various catalysts, including salts of bivalent metals such as zinc, manganese, cobalt, cadmium and magnesium [1, 2] as well as compounds of tetravalent titanium [3], have been reported. In other works heterogeneous basic catalysts including basic zeolites [4], alumina, magnesia [5] and alumina-supported alkali metals and hydroxides (so called superbases) [6] were investigated. Homogeneous acid catalyst are less active and corrosive, while highly active alkaline catalysts require the absence of moisture. Another problem are undesirable side reactions resulting in the coloured by-products. In practice, tin organic compounds such as butylstannic acid are commonly used in the synthesis of polyester resins for powder coatings. They are hydrolytically stable and can be incorporated into the final coating without affecting its properties. On the other hand, organotin catalysts require relatively high transesterification temperatures (near 200 °C) and, due to their toxicity, they are the subject of increasingly stringent regulations concerning the use in commercial products [7, 8].

Saturated polyester resins account for over half of worldwide production of the binders for powder coating systems, a class of quickly developing finishing materials, which in contrary to solvent-based paints do not emit volatile organic compounds during the coating process.

Research efforts in this field comprise the development of low temperature cured coatings, combining the suitable processing performance (like storage stability, flow and film forming properties) with good mechanical properties (like hardness and elasticity) as well as weather and UV resistance. One of the methods to improve the coatings performance is the use of nanofillers, which, added even in a small amount, can distinctly improve the material properties. For example, Holzmann and coworkers introduced two kinds of nanoparticles: surface modified titania and hydroxyapatite during the synthesis of polyester resin, subsequently used for the preparation of powder coating. The weathering experiments showed a

significantly improved UV resistance of the resulting coating materials [9, 10]. The group of Piazza introduced organically modified nanoclay into epoxy-based powder coatings by extrusion method, resulting in an enhancement of the coating thermal stability [11]. In our laboratory, we studied the effect of clay nanofillers on the properties of thermosetting and UV-curable polyesters for powder coatings [12].

In this work, we used various inorganic and organically modified layered double hydroxide (hydrotalcite) compounds as additives in the synthesis of polyester resin. Due to the layered structure and possibility of delamination in the polymer matrix hydrotalcite can play a role of functional nanofiller [13–16]. On the other hand, basic sites in the HT structure may be catalytically active in transesterification processes, as it was shown in several studies [17, 18].

EXPERIMENTAL PART

Materials

Ethylene glycol (POCh), neopentyl glycol (Perstorp), dimethyl terephthalate (Helm AG), hexanediol (BASF), phthalic anhydride (Nitrogen Works Kędzierzyn) and trimellitic anhydride (Polynt S.p.A) were used for the synthesis of hydroxyl and carboxyl functional polyesters. Fascat 4100 (butylstannic acid, Arkema) and ethyltriphenylphosphonium bromide (ICR) were used as transesterification and crosslinking catalysts, respectively.

Preparation of modified hydrotalcites

The organically modified hydrotalcites were prepared using co-precipitation method by mixing aluminum nitrate and magnesium nitrate aqueous solutions (at molar ratio Al to Mg of 1:2) with a solution of organic acid salt at pH adjusted to 10. The process was carried out under nitrogen atmosphere to prevent the undesired reaction of mixed hydroxide with carbon dioxide. In two cases (tyrosine and *p*-aminobenzoic acid) another synthetic

Table 1. Characteristics of HT compounds used as additives in polytransesterification of DMT with alkylene glycols

Hydrotalcite type	Interlayer anion	Preparation method (C – coprecipitation, R – rehydration of calcined HT)	Interlayer distance, Å	pK_b of amino group
HT(ZnAl)ALA	aminolaurate	C	17.2 (28.7)	3.4
HT(ZnAl)	carbonate	C	7.6	–
HT(ZnAl)Tyr	tyrosine (carboxylate form)	R	17.1	4.9
HT(ZnAl)PAB	<i>p</i> -aminobenzoate	R	15.9	9.4
HT(ZnAl)EDTA	ethylenediamine – tetraacetate	C	14.2 (26.2)	3.6
HT(MgAl)	carbonate	commercial (Aldrich)	7.6	–
HT(MgAl)ALA	aminolaurate	C	17.1 (29.1)	3.4
HT(MgAl)OPPA	octylphenylphosphate	C	28.1	–
HT(MgAl)TPA	terephthalate	C	14.3 (24.4)	–

method was employed, *i.e.* a stoichiometric mixture of aluminum and magnesium oxides obtained by calcination of commercial Mg-Al-hydroxalite at 500 °C, was rehydrated by a solution of amino acid salt. This method, based on the known „memory effect”, enables the reconstruction of mixed hydroxide crystalline structure with an inclusion of the anions from aqueous solution. The resulting suspension of MHT precipitate was then aged by heating at 75 °C (Table 1).

Preparation of hydroxyl polyester resin by transesterification method

The synthesis of polyester resin was carried out in 500 cm³ glass reactor equipped with a stainless steel stirrer, distillation column and inert gas inlet. A mixture of 9.8 g ethylene glycol, 148.3 g neopentyl glycol and 283.5 g dimethyl terephthalate and a catalyst (1.8 wt part per 100 wt. parts of the resin) was placed in the reactor and heated under nitrogen atmosphere until methanol begins to distill. The heating was continued with gradually increasing reaction temperature and the progress of reaction was monitored by the amount of methanol condensed at the outlet of the reactor. The obtained polyester re-

sins were characterized by the determination of softening point temperature, hydroxyl number and GPC analysis (Table 2).

Preparation of carboxyl polyester resin in two-step process

The synthesis was performed in 2000 cm³ glass reactor with a stainless steel stirrer, distillation column and inert gas inlet, equipped with dynamic temperature control system Unistat 410 (Huber). In the first stage a mixture of 687 g (6.6 mol) neopentyl glycol, 62.4 g (0.53 mol) hexanediol, 1286 g (6.6 mol) dimethyl terephthalate and HT(ZnAl)ALA catalyst (0.2 wt part per 100 wt parts of the resin) were placed in the reactor and heated under argon atmosphere until methanol had distilled off. 390 cm³ methanol (73 % yield) was collected. The process was continued under vacuum at 180 °C. In the second stage of the reaction, 228 g (1.19 mol) trimellitic anhydride was added and the reaction mixture was heated for 3 hours at 200–210 °C. The resin with an acid number of 56.1 mg KOH/g and softening temperature of 95 °C was obtained. The same procedure was performed using butylstannic acid as catalyst (Table 3).

Table 2. Synthesis of polyester resins by transesterification of DMT with alkylene glycols in the presence of HT catalysts

Catalyst (1.8 phr)	Average reaction temperature, °C ^{*)}	Reaction time, min	Methanol yield, %	Softening temperature °C	OH number mg KOH/g	GPC, $M_n(DP)$	Resin appearance (Gardner colour)
Fascat 4100 (BSA)	184	90	83.8	78	59.0	1527 (2.17)	transparent (1)
HT(ZnAl)ALA	180	30	82	66	81.4	1035 (1.97)	semi transparent (6)
HT(ZnAl)ALA	159	180	75	59	102.4	854 (1.83)	transparent (4)
HT(ZnAl)	185	100	76	78	82.5	1222 (2.04)	opaque (2)
HT(ZnAl)Tyr	180	180	73	67	88.0	1031 (1.87)	opaque (2)
HT(ZnAl)EDTA	185	395	69.2	68	74.9	1086 (1.96)	transparent (1)
HT(MgAl)	186	260	66.7	71	96.9	992 (1.89)	opaque (0)
calcined HT (MgO + Al ₂ O ₃)	185	225	46.1	50	137.0	—	opaque (0)
HT(ZnAl)PAB	185	170	76.5	63	92.2	—	opaque (2)
HT(MgAl)ALA	168, 190	400, 115	53, 76.9	liquid 63	154.0, 127.0	—	opaque (2)
HT(MgAl)OPPA	190	270	54.7	38	91.1	—	opaque (0)
HT(MgAl)TPA	190	400	54.7	67	110.1	—	opaque (0)

^{*)} Average of the starting temperature and the final temperature at which methanol was formed.

Table 3. Synthesis of carboxyl polyester resins by transesterification of DMT with alkylene glycols followed by reaction with trimellitic anhydride

Catalyst, 0.2 phr	Monomers, mol				1st stage			Hydroxyl polyester		Carboxyl polyester (CPE)		
	GNP	HD	DMT	BTM (2nd stage)	average reaction temp., °C	reaction time, h	methanol yield, %	softening temp., °C	GPC $M_n(DP)$	softening temp., °C	acid number mg KOH/g	viscosity cone-plate mPa · s at 200 °C
Fascat 4100 (BSA)	5.5	0.44	5.5	0.99	186	8	89.0	74.5	1329 (2.69)	94.6	66.5	825
HT(ZnAl)ALA	6.6	0.53	6.6	1.19	168	7,5	73.2	67	985 (2.19)	95	56.1	788

Preparation of powder coating formulations

Powder coating formulations (Table 4) were prepared by mixing the carboxyl polyester resin with epoxy hardener, crosslinking catalyst, degassing agent and flow aid. All the ingredients were milled together in an analytical mill (IKA), heated to melt at 100 °C, cooled and milled into powder form.

Table 4. Formulations of powder coatings based on carboxyl polyesters synthesized with the use of BSA and HT(ZnAl)ALA catalysts (parts by weight)

Ingredient	CPE-BSA	CPE-HT(ZnAl)ALA
Carboxyl polyester (CPE)	10	8.4
Epidian 012 hardener	10	10
BTFEF crosslinking catalyst	0.050	0.042
Byk 361	0.07	0.064
Benzoine	0.01	0.092

Methods of testing

– Elemental analysis was performed using a Series II CHNS/O Perkin-Elmer analyser.

– Powder X-ray diffraction (XRD) patterns were recorded using Bruker-AXS D8 D8 Advance Series 2 powder diffractometer working with Co-K α radiation ($k = 1.79 \text{ \AA}$).

– BET surface area was determined by nitrogen sorption experiments conducting at 150 °C using a Micromeritics TriStar II 3020 automated gas adsorption analyzer.

– Hydroxyl number of polyesters was determined by esterification of the hydroxyl groups with pyromellitic anhydride in acetone in the presence of 1-methylimidazole. The excess anhydride reagent was hydrolyzed and the resulting acid was titrated with potassium hydroxide ethanolic solution using *m*-cresol purple as indicator. Titration with ethanolic KOH was also used to measure the acid number (AN) values for polyester resins.

– Softening point temperature was determined using the ring-and-ball apparatus Petrotest RKA5 according to ASTM D36.

– The average molecular weights of polyester resins were determined by Gel Permeation Chromatography using Shimadzu LC-10 AVp system with two Phenogel 5 μ Linear 50 \AA columns (300 \times 7,8 mm) equipped with refractive index and UV-VIS detectors. THF was used as eluent at a flow rate of 1 cm³/min at 40 °C. Polystyrene standards were used to obtain a calibration curve.

– Gardner Colour of 25 wt % polyester solutions in acetone–dioxane (1:1) was evaluated by comparison with colour standards (ASTM D1544).

– Differential scanning calorimetry (DSC) thermograms of powder coating compositions were recorded using a Mettler Toledo DSC 822e instrument. Samples of

about 5 mg weight were heated at the rate of 20 °C/min from 30 to 250 °C, cooled down to 30 °C, and reheated again to 250 °C. The glass transition temperature T_g was determined as the midpoint of the transition in the thermogram from the second heating.

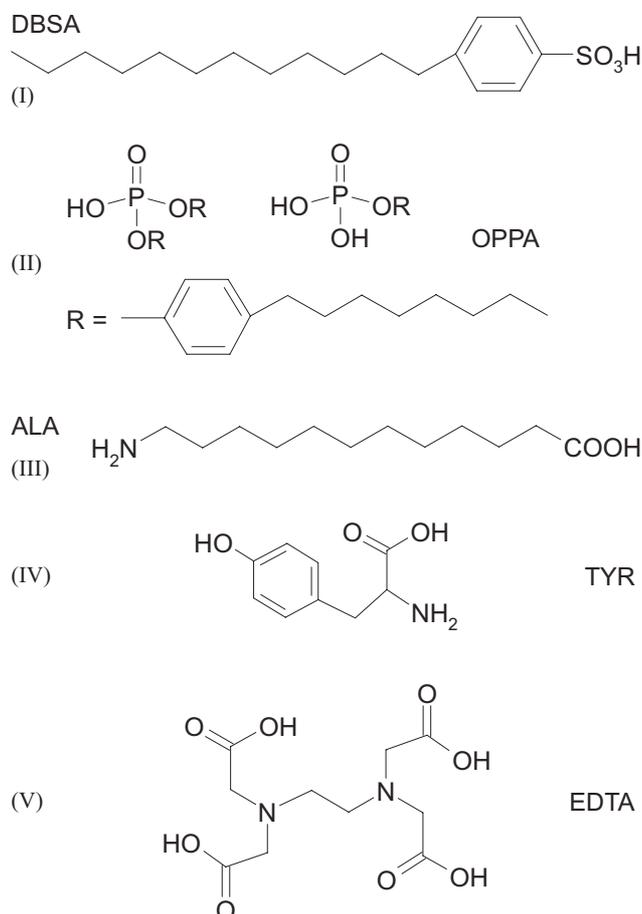
RESULTS AND DISCUSSION

Layered double hydroxides, also known as anionic clays or hydrotalcite-like (HT) compounds were originally found in natural deposits, however, they are commonly synthesized in large amounts for various applications like basic catalysts, adsorbents, acid scavengers (*e.g.* PVC stabilizers), anion exchangers or antacid drugs. The general formula of HT compounds can be expressed as:



HT particles are composed of positively charged layers formed by edge-sharing divalent (Me_I) and trivalent (Me_{II}) metal hydroxides octahedra separated by an inter-layer space containing water and anionic compounds compensating the layer charge generated by the presence of trivalent cations.

Several organic acids [Formulas (I)–(V)] were introduced in their anionic forms into magnesium-aluminum and zinc-aluminum hydrotalcite using coprecipitation or calcination-rehydration procedures. Schematic structures of Mg-Al hydrotalcite in form of carbonate and inter-



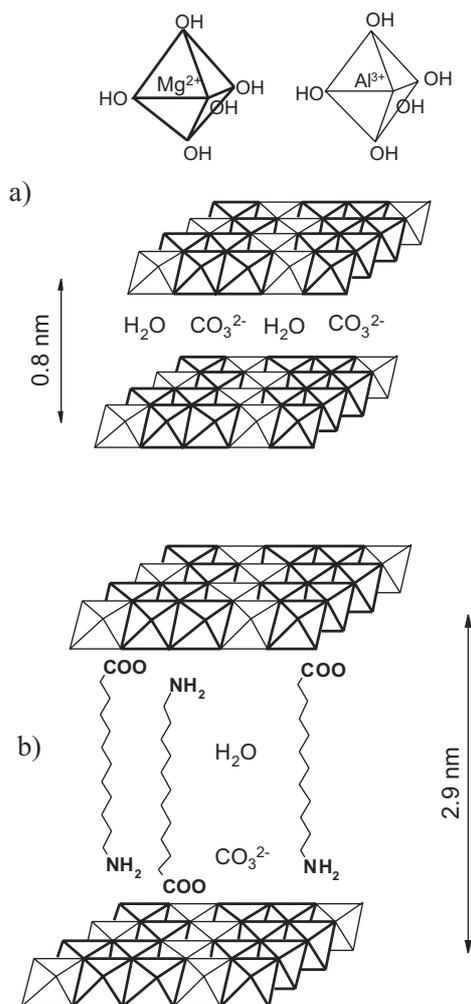


Fig. 1. Schematic structure of: a) magnesium-aluminum hydrotalcite in carbonate form, b) product of its intercalation with aminolauric acid

calated with aminolauric acid anions are shown in Fig. 1. The obtained HT compounds were added to the reaction of dimethyl terephthalate (DMT) with alkylene glycols leading to the formation of hydroxyl functional polyester resin. For comparison purposes the same reaction was carried out in the presence of a conventional catalyst (butylstannic acid, BSA).

The effects of hydrotalcite composition (cation and anion types) on the rate of transesterification process and the properties of obtained polyester components were investigated. To this aim we employed Mg-Al and Zn-Al hydrotalcites in carbonate forms, the mixed oxides prepared by calcination of HT at 500 °C as well as a range of HT intercalated with anions of organic acids. Table 1 presents the denotations of HT-based additives as well as the information on their interlayer distances and basicity of amino group for amino acid-intercalated clays. The reaction parameters (average temperature, time and yield of methanol by-product) as well as the properties of the resulting polyesters (average molecular weight by GPC, softening temperature and appearance) are shown in Table 2.

In the presence of carbonate-Zn-Al hydrotalcite the transesterification reaction can be conducted at an average temperature 185 °C in a time period similar to that of BSA-catalyzed process, resulting in polyester resin with softening temperature $T_g = 76$ °C. The same process carried out with addition of Mg-Al-hydrotalcite or its calcination product gives distinctly lower methanol yield and softening point value despite more than twofold longer reaction time. The higher activity of carbonate-Zn-Al hydrotalcite in relation to its Mg-Al counterpart was also observed for organically modified double hydroxides. It can be seen on the example of Zn-Al hydrotalcite modified with aminolauric acid, denoted in Tables 1 and 2 as HT(ZnAl)ALA. It enables transesterification of DMT with glycols to proceed at a relatively low average temperature 159 °C in 3 hours. With an increase of reaction temperature to 180 °C, the time needed to exceed 80 % yield (as indicated by the volume of produced methanol) is shortened to 30 minutes compared to 90 minutes in the case of BSA-catalyzed process. A lower catalytic activity was observed using ALA-modified Mg-Al-hydrotalcite, which gave good reaction yield only at higher temperature (average 190 °C).

However, a disadvantage of ALA-containing catalyst is brown discoloration of the resin, progressing with an increase in the reaction temperature. This may be connected with a limited thermal stability of ALA-intercalated clay and its possible decomposition in the temperatures close to 200 °C reached at the end of process. Aminolauric acid itself begins to decompose above 200 °C starting from dehydration and intermolecular condensation, additionally clays may decrease the degradation temperature of ALA [19]. We tried to overcome this limitation using more thermally stable HT modified with ethylenediaminetetraacetic acid (EDTA). Thermogravimetric profiles of ALA- and EDTA-intercalated hydrotalcites are shown in Fig. 2.

The reaction catalyzed with EDTA-modified Zn-Al-HT gives a transparent, almost colorless product,

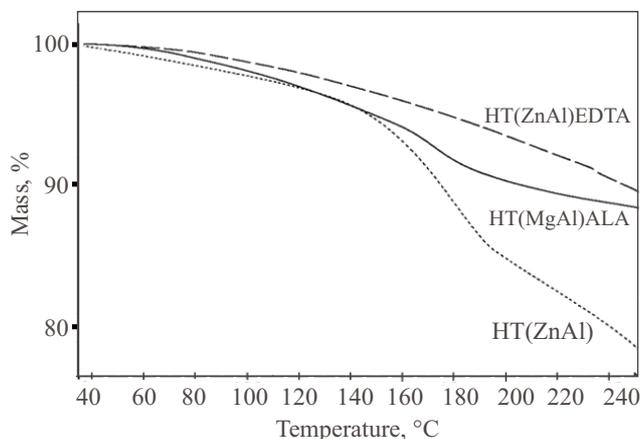


Fig. 2. Thermogravimetry profiles of three types of hydrotalcites: carbonate Zn-Al, aminolauric-intercalated Mg-Al and EDTA-intercalated Zn-Al

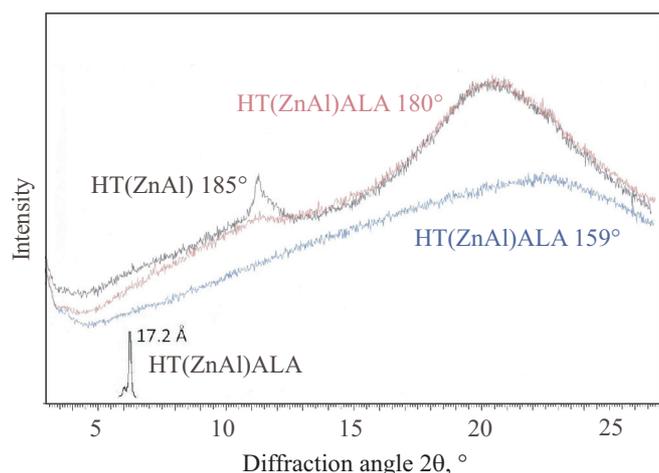


Fig. 3. XRD patterns of polyester resins prepared in the presence of zinc-aluminum hydrotalcite: with carbonate anion (reaction at 185 °C) and intercalated with aminolauroic acid ALA (polytransesterification at 159 and 180 °C); for comparison the location of basal reflection for HT(ZnAl)ALA is shown

however the transesterification proceeds very slow (above 6 hours at 185 °C). This can be explained by a very low specific surface area of EDTA-intercalated hydrotalcite (0.01 m²/g) compared to those of carbonate-Zn-Al-HT (16.8 m²/g) and ALA-intercalated Zn-Al-HT (7.62 m²/g). Also using *p*-aminobenzoic acid-intercalated HT a lower extent of resin discoloration was observed, although the reaction time at 185 °C was several times longer than for ALA-containing clay, probably due to much lower basicity of aromatic amine group. Hydrotalcites intercalated with anionic forms of organic acid not containing amine substituents (octylphenyl phosphate, terephthalate) exhibit significantly lower catalytic activities than their ALA-intercalated counterpart. The transparency of polyester resins containing about 2 wt % of HT(ZnAl)ALA indicates the possible delamination of HT layers and formation of nanocomposite. This can be supported by XRD spectrum of the polyester resin obtained at 159 °C, which does not contain reflections of HT crystalline phase (Fig. 3). On the contrary, XRD pattern of polyester synthesized in the presence of carbonate-Zn-Al hydrotalcite includes a diffraction peak corresponding to the interlayer distance of 9 Å, showing a preservation of non-intercalated structure of HT layers. XRD spectrum of the polyester formed in the reaction conducted at higher average temperature (180 °C) using HT(ZnAl)ALA additive contains no distinct reflections but a broad peak near 9 Å appears, which may be due to a partial rearrangement of inorganic HT layers as a result of thermal decomposition of HT-amino acid compound.

The progress of transesterification, estimated from the quantity of methanol distilled from the reaction mixture, was in the range 67–84 %, exceeding 80 % for the process catalyzed by BSA and HT(ZnAl)ALA and falling below 70 % for less active HT(MgAl) and HT(ZnAl)EDTA catalysts. The hydroxyl number values for the prepared poly-

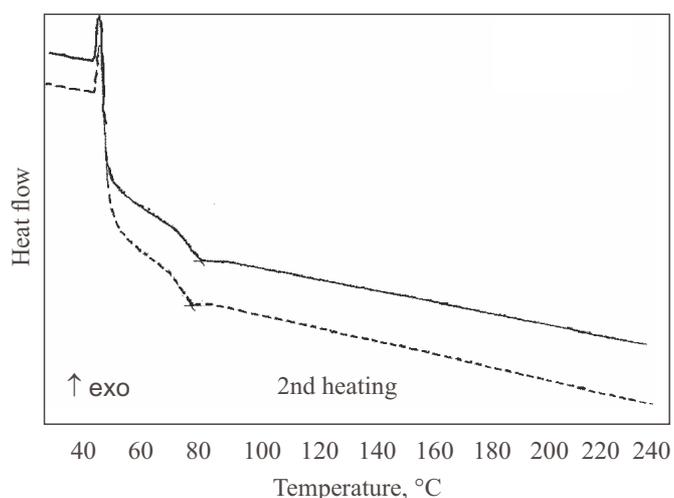
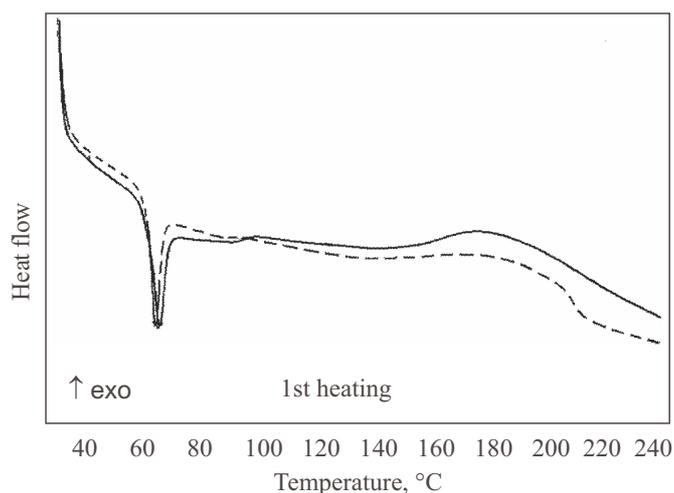


Fig. 4. DSC thermogram of the curing process of powder coating compositions based on polyester resins prepared using HT(ZnAl)ALA (dashed line) and BSA (solid line) catalysts

ester resins, between 59 and 102 mg KOH/g, correspond to almost twofold difference in average molecular weights determined by GPC. In general, the resins with higher molecular weights were obtained when the reaction was carried out at higher temperatures (about 185 °C). The softening temperatures of polyesters synthesized in the presence of inorganic hydrotalcites were increased in comparison to the resins with similar molecular weights, but containing organically modified HT's. This can be explained by plasticizing effect of the intercalated molecules, known *e.g.* from the studies on epoxy/organoclay systems [20].

HT(ZnAl)ALA catalyst was used in the preparation of carboxyl polyester resin for powder coating using a two-step process. In the first step, hydroxyl polyester was synthesized by reaction of dimethyl terephthalate with neopentyl glycol and hexanediol. The obtained prepolymer was reacted with trimellitic anhydride to produce carboxyl functional polyester. For comparison, the same synthetic procedure was carried out with the use of conventional BSA catalyst in the transesterification step. The

properties of hydroxy functional prepolymers and final carboxyl polyesters are shown in Table 3. The reaction temperature was maintained not to exceed 180 °C and the resin prepared with HT(ZnAl)ALA catalyst was only slightly colored (Gardner scale 2).

Powder coating formulations were prepared by mixing the as-prepared polyester resins with epoxy hardener (in an equimolar ratio of carboxyl and epoxy groups), ethyl triphenylphosphonium bromide as crosslinking catalyst and standard additives (benzoin as degassing agent and Byk 361 flow aid). The curing was studied with differential scanning calorimetry (DSC) and the resulting thermograms are illustrated in Fig. 4. The first heating curves show endothermic melting peaks about 65 °C followed by exothermic curing reaction, which begins at about 140 °C. DSC traces from the second heating show endothermic shift corresponding to glass transition of the cured resin with T_g values near 80 °C (taken as the inflection midpoint). No appreciable difference between the curing profiles and T_g of the crosslinked polyesters was observed irrespective of using BSA and HT(ZnAl)ALA catalysts in polyester synthesis. Zn-Al hydrotalcite intercalated with aminolauric acid can therefore be used as an efficient tin-free polytransesterification catalyst in the preparation of polyester resins for powder coatings, however the reaction temperature should be controlled to avoid the formation of colored product.

CONCLUSIONS

The polytransesterification of dimethyl terephthalate with alkylene glycols carried out in the presence of carbonate-Zn-Al hydrotalcite gives hydroxyl functional polyester with a softening temperature of 78 °C at a reaction rate comparable to that catalyzed by butylstannic acid. Using Zn-Al hydrotalcite intercalated with aminolauric acid a decrease in the average reaction temperature (to 159 °C) or a threefold increase in the reaction rate at 185 °C was achieved when compared to conventional BSA-catalyzed process. The polyester resins obtained in this way are transparent, which along with X-ray diffraction data indicates the delamination of HT layers and formation of nanocomposite. Using a two step procedure, involving transesterification of DMT with alkylene glycols catalyzed by ALA-intercalated HT and reaction with trimellitic anhydride, carboxyl functional polyester was obtained and used as a component of powder coating formulation.

At higher reaction temperatures exceeding 180 °C a brown discoloration of the resin prepared using ALA-containing catalyst was observed due to thermal instability of amino acid. Hydrotalcites intercalated with other organic acids exhibit significantly lower catalytic activities in transesterification reaction, however EDTA-modified HT shows good thermal stability and compatibility with polyester resulting in a colorless transparent product.

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