MICHAŁ KĘDZIERSKI, PIOTR PENCZEK

Industrial Chemistry Research Institute
Department of Polyester and Epoxy Resins
ul. Rydygiera 8, 01-793 Warszawa
e-mail: Michal.Kedzierski@ichp.pl

# Unsaturated polyester/montmorillonite nanocomposites prepared by *in situ* intercalative copolyaddition

**Summary** — New approach to the synthesis of unsaturated polyester/clay nanocomposites is described. Various forms of organically modified montmorillonite (OMMT) were introduced *in situ* during the copolyaddition of epichlorohydrin, maleic anhydride and phthalic anhydride. The catalytic effect of OMMT containing quaternary ammonium ions was observed. The introduction of clay leads to the increase in softening temperature, as well as melt or solution viscosity of unsaturated polyester. Cured unsaturated polyester/clay compositions exhibit increased hardness and heat resistance and, in some cases, decreased flammability. The best properties, including limiting oxygen index (*LOI*) values in the range of 27—29 %, were obtained for the compositions with OMMT functionalized with hydroxyl group. In that case, covalent bonds between clay surface and unsaturated polyester are likely to be formed. The dispersion of OMMT in the polyester matrix in form of exfoliated nanocomposite was indicated by X-ray diffraction study.

**Key words**: unsaturated polyesters, organically modified montmorillonite, nanocomposites, *in situ* intercalative copolyaddition, functional properties.

Composites of polymers and nanofillers have attracted increased attention recent years. Nanosized additives, used at low loadings, can significantly affect the properties of polymeric materials. Among the most frequently investigated nanostructured fillers are layered silicates, which, being the main constituents of naturally occured smectite clays, are relatively inexpensive as compared with many synthetic nanoparticles. Many of known polymer/clay nanocomposites exhibit significantly enhanced mechanical strength, thermal stability, fire retardance or barrier properties [1—7].

Natural smectite clays consist of negatively charged aluminosilicate platelets, arranged into layered structure, and stabilized with alkaline metal cations located in the interlayer space, frequently called as „gallery". The spacing between clay layers may expand, especially when swelled by water or other polar solvents, which enable the introduction of various guest substances into the gallery, the process being known as intercalation. To enable the good miscibility of clay and organic polymers, it is usually necessary to change the nature of clay from hydrophilic to hydrophobic. The convenient method, commonly applied for this purpose, is the replacement of alkaline metal cations in clay gallery with organic cations by ion exchange.

Two main types of polymer/clay nanocomposites showing different morphology may be distinguished. In the first case, polymer chains are inserted into the clay structure and contribute to the expansion of aluminosilicate platelets, while the latter retain their stack-like arrangement. This type of morphology is called intercalated. Otherwise, when the clay layers become fully separated and well dispersed within the polymer matrix, so called exfoliated nanocomposite is obtained. Individual clay particles formed this way have thickness about one nanometer and high aspect ratio, and thus can act as very effective reinforcing fillers. The exfoliated nanocomposites show greater phase homogeneity and this kind of morphology is more desirable from the point of view of the polymer properties enhancement.

Although most attention is focused on nanoclay filled thermoplastic polymers, many attempts have been done to develop thermoset/clay nanocomposites. Unsaturated polyester (UP) resins filled with organically modified clays were described in several papers [8—11]. In order to achieve good dispersion of layered silicate in polyester matrix, clay minerals were modified using ion exchange with long chain ammonium salts or by the treatment with organofunctional silane. The resulted organoclay was then mixed with unsaturated polyester resin or introduced into unsaturated polyester by melt blending with subsequent dissolution in styrene.

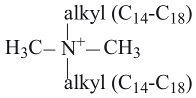
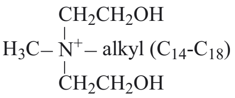
In this work, we tried another method, known as *in situ* intercalative polymerization, which consists in the intercalation of monomers in layered silicate followed by the formation of polymer within the interlayer space of clay. In our approach, organically modified clay was added *in situ* during the synthesis of unsaturated polyester. The organoclay being a nanocomposite precursor, may in addition act as acidic catalyst due to the presence of organoammonium ions. The aim was to study the effect of clay, modified different ways, on the course of reaction and the properties of unsaturated polyester compositions.

## EXPERIMENTAL

### Materials

Various forms of ion exchanged montmorillonite (MMT) were used as organically modified clays (Table 1).

**Table 1. Characteristics of clay additives**

| Symbol of clay | Interlayer cation | Interlayer distance, Å | Cation exchange capacity meq/100 g |
|---|---|---|---|
| MMT-Na | $Na^+$ | 12.3 | 145 |
| C15A |  $H_3C-\overset{\text{alkyl }(C_{14}\text{-}C_{18})}{\underset{\text{alkyl }(C_{14}\text{-}C_{18})}{N^+}}-CH_3$ | 31.5 | 125 |
| C30B |  $H_3C-\overset{CH_2CH_2OH}{\underset{CH_2CH_2OH}{N^+}}-\text{alkyl }(C_{14}\text{-}C_{18})$ | 18.5 | 90 |
| MMT-ADA | $H_3N^+(CH_2)_{12}COOH$ | 22.2 | 145 |

Commercial organoclays containing ammonium ions derived from long-chain alkylamine: Cloisite 15A and hydroxyl terminated alkylamine Cloisite 30B (C15A and C30B, respectively) were supplied by Southern Clay Products. Sodium montmorillonite (MMT-Na) Nanomer PGW was provided by Nanocor.

Organoclay montmorillonite-aminododecanoic acid (MMT-ADA) was prepared by the reaction of MMT-Na (30 g, 43.5 meq $Na^+$) with 1500 mL aqueous solution of aminododecanoic acid (14 g, 66 mmol) and 36 % hydrochloric acid (5.7 mL, 66 mmol). The resulted clay suspension was stirred at 50—60 °C for 90 minutes, then the product was filtered off and repeatedly washed until no chloride was detected in the filtrate by addition of $AgNO_3$ solution. Structural formula of the product was confirmed by elemental analysis compared with cation exchange capacity. The interlayer spacing calculated from the (001) basal reflection in the X-ray diffraction spectrum was 22.2 Å.

The substrates used to prepare the unsaturated polyester were technical grade reagents. Maleic anhydride (MA) and phthalic anhydride (PA) were supplied by Nitrogen Works Kędzierzyn SA. Epichlorohydrin (ECH) was obtained from the Chemical Works Zachem, Bydgoszcz) and 1,2-propylene glycol (PG) was provided by the Chemical Works Rokita SA. Styrene was obtained from the Chemical Company Dwory S.A.

### Preparation of unsaturated polyester compositions

The unsaturated polyesters were prepared at a molar ratio of monomers ECH:MA:PA:PG = 3:1.5:1.5:0.28 according to the procedure described in [13]. Lithium chloride (0.1 % by total weight) was used as a polyaddition catalyst. A 500 mL five-neck round bottom flask equipped with mechanical stirrer, temperature controller, nitrogen inlet, addition funnel and a reflux condenser was used. Acid anhydrides and glycol monomer, lithium chloride and clay additive were charged in the amount of 2—3 % of the initial charge weight. The mixture was heated to 120 °C, then epichlorohydrin was added dropwise over a period of 30 min. The reaction was continued at 120-130 °C until the acid number reached the minimum value. Then, the piperidine catalyst was added (0.5 % by total weight) and *cis-trans* isomerization of maleate double bonds was carried out at 155—160 °C for 1 hour.

The obtained clay-modified polyesters were dissolved in styrene (stabilized with 75 ppm hydroquinone and 75 ppm phenotiazine inhibitors, based on the resin weight). The styrene content in resulting UP resins was adjusted to 34—36 wt. %. The final compositions were cured using methyl ethyl ketone peroxide as an initiator and cobalt naphthenate as an accelerator (2 % and 0.4 % by resin weight, respectively). Curing was performed at ambient temperature with subsequent post-curing at 80 °C for 2 hours.

For comparison, neat UP resin was synthesized at the some reaction conditions.

### Methods

The acid number (*AN*) was determined by titration with acetone-dioxane solution of potassium hydroxide according to the Polish Standard PN-87/C-89082.11.

Softening point temperature was determined using the ring-ball method according to the Polish Standard PN-73/C-04021 (ASTM D36-66).

Ball indentation hardness was determined according to ISO 2039-1:2001.

The viscosity of UP resins was determined at 21 °C using the Höppler falling-ball viscometer.

Heat deflection temperature (*HDT*) was measured according to PN-EN ISO 75-1:1998.

Limiting oxygen index (*LOI*) was measured according to the testing procedure of PN-ISO 4589-2:1999

(ASTM D 2863-97). *LOI* is defined as the minimum volume fraction of oxygen needed to sustain combustion of the specimen after ignition.

The rheological properties of clay/polyester compositions were examined using Bohlin CVO 100 rheometer using a cone-plate geometry with the diameter of 20 mm and angle of 2°. The measurements were performed at 120 °C with controlled shear-rate mode.

X-ray diffraction (XRD) patterns of powdered samples were recorded using Rigaku-Denki diffractometer equipped with Ni filtered Cu $K_\alpha$ X-ray source. 2θ angle was in the range of 2—60°.

## RESULTS AND DISCUSSION

The progress of copolyaddition was followed by the determination of *AN* value (Fig. 1). For the reactions carried out in the presence of organoclays C30B and C15A, much faster decrease in acid value was observed than in the case of neat polyester. Both these clays contain quaternary alkylammonium ions, which are known as effectively catalyzing the epoxide-anhydride reactions [14]. Otherwise, no acceleration took place when MMT-Na, as well as organoclay MMT-ADA containing primary ammonium ions, were used.

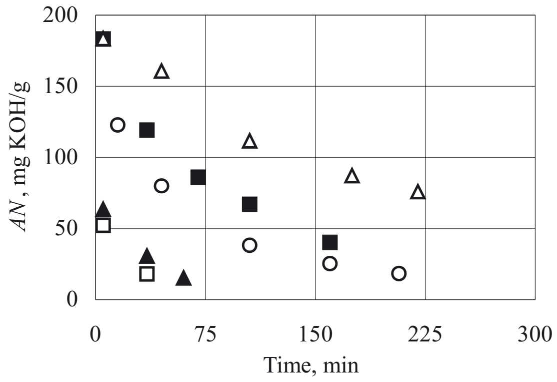


*Fig. 1. Time dependence of acid number (AN) of UP synthesized in the presence of various clays;* ■ *— unmodified resin,* △ *— MMT-ADA,* ○ *— MMT-Na,* ▲ *— C15A,* □ *— C30B*

Most of the clay/polyester compositions show increase in softening temperature by 5—10 °C as compared with unmodified UP obtained under the same reaction conditions. The addition of clay affects the rheological properties of polyesters expressed by an increase in melt and solution viscosity (Fig. 2 and Table 2). These changes in properties were most pronounced when the clays MMT-ADA (UP-5) and C30B (UP-3, UP-4), containing carboxyl and hydroxyl groups, respectively, were used.

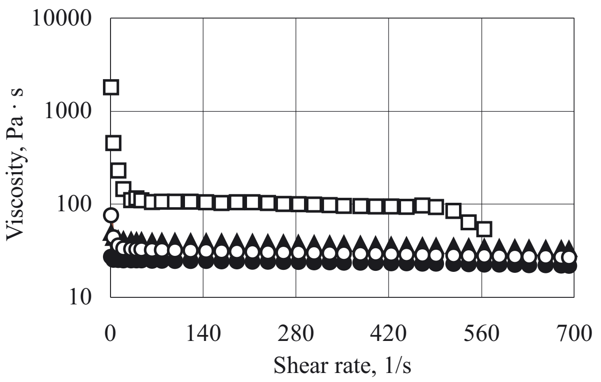


*Fig. 2. Melt viscosity (at 120 °C) versus shear rate of UP modified with various clay additives;* ● *— unmodified,* □ *— C30B,* ▲ *— C15A,* ○ *— MMT-Na*

**Table 2. Properties of clay/unsaturated polyester compositions**

| Symbol of UP composition | Clay, kind/ amount in wt. % | UP | | UP resin | |
|---|---|---|---|---|---|
| | | *AN*, mg KOH/g | softening temperature, °C | styrene content wt. % | viscosity at 21 °C mPa · s |
| UP-0 | unmodified | 40 | 78 | 35 | 919 |
| UP-1 | MMT-Na/2 | 18 | 78 | 36 | 1107 |
| UP-2 | C15A/2 | 15 | 83 | 35 | 1181 |
| UP-3 | C30B/2 | 18 | 87 | 36 | 1993 |
| UP-4 | C30B/3 | 24 | 90 | 33 | 2583 |
| UP-5 | MMT-ADA/2 | 63 | 88 | 34 | 6715 |
| | | | | 42 | 1697 |

The clay-modified polyesters were dissolved in styrene to obtain unsaturated polyester resins. As it was mentioned in Experimental part, curing of the resins was performed at ambient temperature using conventional redox system, followed with post-cure at 80 °C. The presence of organically modified clay show a noticeable effect on the properties of cured polyester compositions, that exhibit increase in hardness and *HDT* as compared with unmodified polyester (Table 3). No significant change in hardness and slight decrease in heat stability were found for the polyester containing MMT-Na (UP-1).

**Table 3. Properties of cured clay/unsaturated polyester compositions**

| Symbol of UP composition | Styrene content wt. % | Hardness MPa | *HDT*, °C | *LOI*, % |
|---|---|---|---|---|
| UP-0 | 35 | 116 | 63.5 | 24.1 |
| UP-1 | 36 | 119.6 | 60.3 | 22.7 |
| UP-2 | 35 | 123.5 | 64.7 | 22.3 |
| UP-3 | 36 | 127.6 | 65.6 | 27.4 |
| UP-4 | 33 | 139.7 | 67.6 | 28.7 |
| UP-5 | 42 | 134.1 | 68.7 | 21.0 |

The *LOI* values of maleic-phthalic-epichlorohydrin polyester resins are in the range 23—25 [15]. The materials showing *LOI* of 26 % or higher are rated among flame retardant ones. To attain self-extinguishing properties of halogen containing resins, the addition of synergist, *e.g.* antimony trioxide, is usually employed. The flame retardance of clay/polyester compositions is affected by styrene content in the resin and the type of clay used (Table 3). The polyesters modified by MMT-Na (UP-1) and long alkylammonium clay C15A (UP-2) show decreased *LOI* values in comparison with neat polyester, as well as polyester containing organoclay MMT-ADA (UP-5). The latter case may be explained by high styrene content (42 wt. %) in the resin, that excess styrene has been added to lower the viscosity of composition and to improve its casting properties. The highest *LOI* values, in the range of 27—29 %, were determined for the polyesters modified with hydroxyl terminated organoclay C30B. The observed increase in flame retardance is comparable to the effect of antimony trioxide, used as a fire-retardant synergist in the commercial epichlorohydrin-based polyester resin, Polimal 160.

The extent of changes in physicochemical and application properties of clay-modified polyesters is largely dependent on the type of cation present in the interlayer gallery of clay. By using sodium montmorillonite, compositions with similar or slightly decreased properties than those of unmodified polyester were obtained. The miscibility of hydrophilic clay and hydrophobic polyester is poor and the formation of conventional composite is likely in that case. On the other hand, the organo-modified clays, being more compatible with organic polymer, affect the properties of polyester compositions more significantly, especially in the case of clays with attached hydroxyl or carboxyl group. The presence of functional groups may facilitate the interaction between inorganic and organic phase due to the formation of covalent bond between clay and the polyester matrix.

The ability of UP to bond covalently with the surface of organoclay was supported by the experiment, when the copolyaddition of maleic anhydride, phthalic anhydride and epichlorohydrin was carried out in toluene suspension of the clay MMT-ADA, containing amino acid. After the reaction, the clay was separated and washed out from acetone-soluble substances using Soxhlet extraction. The elemental analysis of such modified clay shows an increase in carbon content (from initial 19.3 to 33.6 wt. %) accompanied with the decrease in nitrogen content (from initial 1.8 down to 0.7 wt. %). Additionally the product contains 5.9 wt. % of chlorine.

FT-IR spectrum of the modified clay shows the presence of absorption peaks at 1283 cm$^{-1}$ and 1727 cm$^{-1}$, which may be assigned respectively to asymmetric C-O and C=O stretching vibrations of ester bond (Fig. 3). The bands at 1640 cm$^{-1}$ and 1587 cm$^{-1}$ correspond to C=C stretching vibrations of maleic and phthalic units, while the peak at 1702 cm$^{-1}$ may be assigned to free carboxyl group. From these analytical data, it may be concluded that the organic fraction being strongly bound to the clay surface contains the oligomeric ester compounds formed in epoxide-anhydride reaction. The interlayer spacing of polyester-modified clay, calculated from (001) reflection at XRD spectrum as 19.6 Å, is slightly decreased when compared with 22.2 Å of initial MMT-ADA. This indicates that the clay preserves its stack-like organization and the polyester is intercalated into the interlayer space.

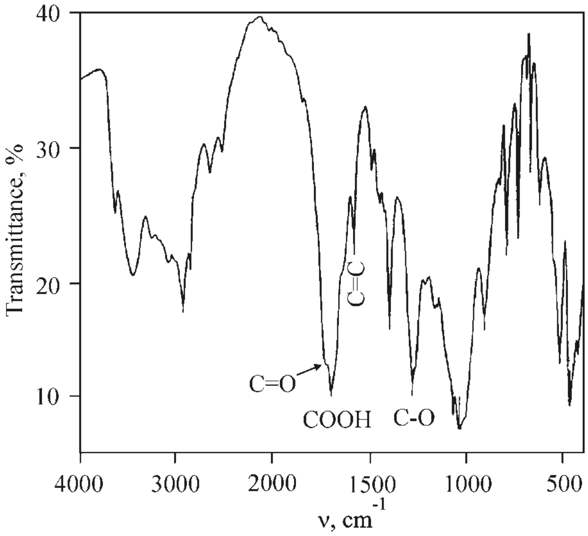


*Fig. 3. FT-IR spectrum of clay MMT-ADA modified by the reaction with epichlorohydrine, maleic anhydride and phthalic anhydride*

The cured polyester composition UP-4, prepared in the presence of 3 wt. % of organoclay C30B, was pow-

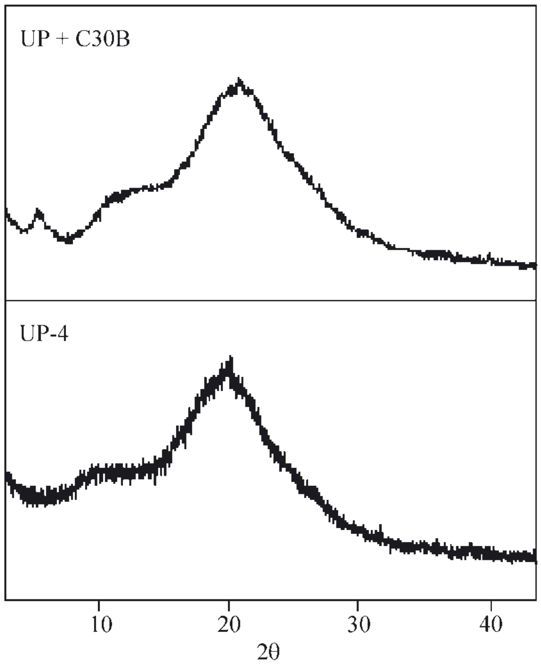


*Fig. 4. XRD difractograms of physical blend of unsaturated polyester with organoclay (UP + C30B) and unsaturated polyester synthesized in the presence of organoclay (UP-4) composition*

dered and analyzed using XRD method (Fig. 4). For comparison, a diffractogram for physical blend of the same organoclay and unmodified polyester was recorded. XRD pattern of the blended composition shows the presence of intense diffraction peak at the low angle region, corresponding to (001) basal reflection of the organoclay. The presence of that peak is not observed in the diffractogram of composition UP-4, which may indicate the delamination of organoclay added during the polyester synthesis. Then exfoliated nanocomposite is possible to be formed, which corresponds well to the observed changes in polyester properties. Further XRD analyses are in progress to examine the morphology of various clay-polyester composition.

## CONCLUSIONS

Unsaturated polyester/clay hybrids were prepared by *in situ* intercalative copolyaddition of epichlorohydrine, maleic anhydride and phthalic anhydride. The reaction rate and the properties of clay-modified unsaturated polyesters depend on the type of cation present in the clay gallery. The clays containing quaternary alkylammonium ions increase the rate of copolyaddition, expressed as change in acid value with time. The presence of clay involves the increase in softening temperature as well as melt and solution viscosity of unsaturated polyester. Cured UP resins containing organoammonium clays show improved heat resistance, increased hardness and, in some cases, decreased flammability when compared with UP synthesized without the addition of clay. The most significant changes in polyester properties were observed in the case of organoclay functionalized with hydroxyl groups that are capable of forming covalent bonds between clay and unsaturated polyester. The possibility of exfoliated nanocomposite formation was indicated by XRD measurements.

## REFERENCES

1. Le Baron P. C., Wang Z., Pinnavaia T. J.: *Appl. Clay Sci.* 1999, **15**, 11.
2. Alexandre M., Dubois P.: *Mater. Sci. Eng.* 2000, **28**, 1.
3. Biswas M., Ray S. S.: *Adv. Polym. Sci.* 2001, **15**, 170.
4. Ray S. S., Okamoto M.: *Prog. Polym. Sci.* 2003, **28,** 1539.
5. Nour M. A.: *Polimery* 2002, **47**, 326.
6. Kacperski M.: *Polimery* 2002, **47**, 801.
7. Kacperski M.: *Polimery* 2003, **48**, 85.
8. Kornmann X., Berglund L. A., Skerte J., Giannelis E. P.: *Polym. Eng. Sci.* 1998, **38**, 1351.
9. Oleksy M., Galina H.: *Polimery* 1999, **34**, 430; *ibid.* 2000, **45**, 541.
10. Suh D. J., Lim Y. T., Park O. O.: *Polymer* 2000, **41**, 8557.
11. Bharadwaj R. K., Mehrabi A. R., Hamilton C., Trujillo C., Murga M., Fan R., Chavira A., Thompson A. K.: *Polymer* 2002, **43**, 3699.
12. Kim H. G., Oh D. H., Lee H. B., Min K. E.: *J. Appl. Polym. Sci.* 2004, **92**, 238.
13. Kicko-Walczak E., Kłosowska-Wołkowicz Z., Szilke B.: *Polimery* 1975, **20**, 421.
14. Fischer R. F.: *J. Polym. Sci.* 1960, **44**, 155.
15. Kłosowska-Wołkowicz Z., Kicko-Walczak E.: *Polimery* 1982, **27**, 18.