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# Negative effect of clay fillers on the polyvinyl alcohol biodegradation: technical note

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**Abstract:** This work focuses on polyvinyl alcohol (PVA) biodegradation in the presence of mineral clays in an aqueous aerobic environment. PVA with a degree of hydrolysis of 88% and 72% was used for the experiments. The selected group of mineral clays (nanofillers for polymers) of montmorillonite (MMT) Cloisite® Na<sup>+</sup>; organo-modified montmorillonite (OMMT) Cloisite® 20A, Cloisite® 30B; waste kaolin; kaolin; and zeolites were prepared by synthesis of the aforementioned kaolins. The level of biodegradation was measured using a respirometer, Micro-Oxymax, and evaluated according to CO<sub>2</sub> production. Results of this test indicate a negative effect on PVA biodegradability in the presence of MMT Cloisite® Na<sup>+</sup> and Cloisite® 30B. It has been found that PVA biodegradability in the presence of no adapted inoculum was adversely affected by the biocidal effects of the organic modifier of Cloisite® 30B. In this case, PVA 88-8 biodegradation decreased by 71% and PVA 72-10 biodegradation dropped by 58%. Furthermore, the sorption of PVA on the Cloisite® Na<sup>+</sup> in the range of 40%–45% was demonstrated in the following research.

**Keywords:** adsorption; biodegradation; clay minerals; polyvinyl alcohol; synthetic zeolite.

## 1 Introduction

Clay minerals form a group of significant minerals with a multifarious structure and composition. They can be used as fillers intended for the preparation of polymeric nanocomposite films or composite films based on polymer/mineral clay. Polymer composites are defined as materials

formed by a polymer and some synthetic or natural filler, while individual components have a different structural, physical, and chemical constitution. The nanocomposite materials are defined as materials having at least one dimension of the component in the nanometer-size scale. The advantage of clay fillers is their economic modesty, availability, and safety in the environment. Dispersal of the filler particles in polymer matrix leads to the formation of a large interfacial interface between polymeric matrix and filler particles. It generally causes an improvement of process and user properties [1–3]. Most of the studies dealing with the composites used the casting method into moulds [4–6]. A processing advantage of this method may be a lower preparation temperature, where heat degradation of individual components such as glycerol or polyvinyl alcohol (PVA) is not achieved, as compared to extrusion or compression where higher temperatures are required. Thermal degradation of glycerol and PVA occurs around 250–300°C and 200–350°C, respectively [7, 8]. Among the indisputable user benefits, when compared with pure PVA films, are the resulting properties such as higher tensile strength, as reported by Sapalidis et al. [9]; barrier properties, as reported by Liu et al. [10]; and increased thermal resistance, as reported by Yu et al. [5]. Therefore, there has been an expansion of these materials in the consumer sphere. Many recent studies have focused on the properties of the composite films, especially their thermal and mechanical properties. However, only few of them have researched their biodegradability [1–3].

A positive effect on the biodegradation was observed by Ray and Okamoto [11]. The addition of montmorillonite (MMT) in PLA increased the level of biodegradation by 15%, and that of saponite, by 35%. The presented data indicated that the incorporation of different types of organic modified layered silicates (OMLS) in the PLA matrix resulted in a different mode of attack on the PLA component of the test samples, which might be due to the presence of different kinds of modified salts and pristine layered silicates. As PLA is an aliphatic polyester, it is conceivable that the incorporation of different types of OMLS resulted in a different mode of disruption of some of the ester linkages due to the presence of different kinds of surfactants and layered silicates [11].

Okamoto et al. [12] investigated the biodegradation of nanocomposites based on poly butyl succinate and

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layered silicates (MMT, saponite) and organically modified layered silicates. From microscopic pictures taken after 35 days of incubation, the positive effect on the biodegradation was demonstrated in the presence of OMLS. This observation indicated that MMT or alkylammonium cations, as well as other properties, have no effect on the biodegradability of PBS. The accelerated degradation of PBS matrix in the presence of saponite modified by hexadecyltributylphosphonium cation may be due to the presence of alkylphosphonium surfactant. This kind of behavior was also observed in the case of PLA/OMLS nanocomposite systems [12].

Tetto et al. examined the effect of organic phyllosilicates on the biodegradation of polycaprolactone. This work showed also a positive effect on the biodegradation [13].

PVA98 (degree of hydrolysis, 98%) biodegradability in the presence of clay mineral MMT was researched by Chiellini et al. [14]. The results of their study demonstrated a negative effect of MMT on PVA98 biodegradation, where a decrease of about 44% was observed. The extent of mineralization was evaluated based on the amount of CO<sub>2</sub> released from the tested compounds [14]. The same result was observed by Spiridon et al. [15]. Spiridon et al. [15] investigated the biodegradability of the nanocomposite films composed of PVA/starch/clay mineral and concluded that the addition of clay nanoparticles has a negative effect on the biodegradability [15].

Chiellini et al. [14] also examined the degree and extent of adsorption and desorption of PVA on MMT. The PVA samples with degrees of hydrolysis of 72%, 88%, and 98% were used in this experiment. Their results showed that the amount of adsorbed PVA depends almost linearly on the starting PVA concentration in the suspension. Furthermore, also the preferential adsorption of PVA with a lower molecular weight was recorded. The rate of adsorption slightly increased with an increasing degree of hydrolysis. This behavior demonstrates the active role of the available hydroxyl groups of the polymer during the process of adsorption [14].

In choosing a suitable inorganic filler to mix with the polymer, the filler should not be only exposed to technological pressure, as the results of studies mentioned above have shown wherein the type of filler has a great influence on the biodegradability of the final product. In addition, other important factors include the particle size, the dispersion of the filler, and the interaction between polymer-polymer and polymer-filler [9].

The main aim of this work is to compare the influence of the filler on the PVA biodegradation. The results of this work will be a key for the preparation of

the composite materials (foils) on the base of PVA and clays. It is important to deal with this topic because PVA is, thanks to its significant properties, widely used in households, industry, and agriculture. So it could easily contaminate water and soil environment. In the water, PVA is considered to be biodegradable and non-toxic to aquatic organisms, and several degradation mechanisms have been proposed [16]. While in the terrestrial environment, it can contribute to the adsorption on soil particles of clay character and subsequently accumulate in the environment or affect the ability of biodegradation. Many studies are devoted to fillers based on natural and organically modified MMTs commercially marketed under the trademark Cloisite®. However, from the economic and ecologic points of view (decreased biodegradability in the presence of some type of the clay), it is more advantageous and cheaper to use in their preparation waste raw materials, whose undoubted advantage is their low price and availability. For this reason, natural Kaolin Sedlec 1A and waste Kaolin Strelec N were used, together with the zeolites synthesized from these kaolins.

## 2 Materials and methods

PVA materials used for the tests were the commercial products. Mowiol 88-8: the degree of hydrolysis is 88%; content of acetate groups, 12%; viscosity, 8 mPa.s; powder producer, Novácké Chemické Závody a.s., SR. The content of carbon was determined experimentally to be 52.70%. Sloviol 72-10: the degree of hydrolysis is 72%; content of acetate groups, 28%; viscosity, 10 mPa.s; powder producer, Novácké chemické závody a.s., SR. The content of carbon was determined experimentally to be 52.57%.

The water environment was simulated by aerobic activated sludge, suspended in the liquid medium. Mixed microbial culture (no adapted inoculum) from the municipal wastewater treatment plant was used as inoculum as well as laboratory-adapted inoculum on PVA. The incubation time was about 28 days. A solution of PVA without the presence of clay minerals was used as a standard.

Clay minerals used for the tests were commercial products or laboratory-prepared products. Kaolin Sedlec 1A: the particle sizes are as follows: 63%, <2 μm; 24%, 2–5 μm; 10%, 5–10 μm; 3.5%, 10–20 μm; 0.2%, >20 μm; 0.005%, >60 μm. Strength is 2.5 MPa. Producer is Sedlečský Kaolin a.s., ČR. Waste kaolin: Kaoline-Strelec is the source of quartz sand used to in foundry and glass industry. Particle size for ~90% is <45 μm. Producer

is Sklopísek Strelec a.s., ČR. Synthetic zeolites: the samples of zeolites were prepared by a synthesis of the above kaolins. Cloisite® Na<sup>+</sup>: the main component is MMT. Particle size is 16–22 µm. It is hydrophilic. The producer is Southern Clay Products, USA [17]. Cloisite® 20A: the main component is OMMT. The organic modifier was dimethyl dihydrogenated, tallow, quaternary ammonium chloride. Particle size is 14–18 µm. It is strongly hydrophobic. The producer is Southern Clay Products, USA [17]. Cloisite® 30B: the main component is OMMT. Particle size is 14–18 µm. It is strongly hydrophobic. The organic modifier was methyl, tallou, bis-2-hydroxyethyl, quaternary ammonium chloride. Producer is Southern Clay Products, USA [17].

All other chemicals employed were of analytical purity, produced or delivered by Pliva Lachema Brno, Czech Republic.

## 2.1 Aerobic biodegradation experiment

Aerobic biodegradability was determined by using a respirometer MicroOxymax. The tested PVA sample was the sole source of organic carbon and energy in the environment. The experiment ran for approximately 28 days. The conditions of the test were as follows: suspension volume was 50 ml; dried sludge, 500 mg dm<sup>-3</sup>; concentration of PVA, 200 mg dm<sup>-3</sup>; concentration of the mineral clay, 200 mg dm<sup>-3</sup>; temperature, 25 ± 1°C; and pH = 7 ± 0.5. A mixed microbial culture and PVA adapted microbial culture in the form of activated sludge from a municipal wastewater treatment plant were applied as the inoculum. At the beginning of the experiment, the aerobic activated sludge was centrifuged at 3000 RPM<sup>-1</sup> for 10 min at 25°C. Then the biomass was removed and suspended in the biomedium. The biomedium for aerobic experiments had the following composition: 800 ml aerated distilled water was put into a 1-l bottle and also 1-ml quantities of stock solutions, CaCl<sub>2</sub> (27.5 g dm<sup>-3</sup>), FeCl<sub>3</sub> · 6H<sub>2</sub>O (0.25 g dm<sup>-3</sup>), MgSO<sub>4</sub> · 7H<sub>2</sub>O (22.5 g dm<sup>-3</sup>), and solutions of trace elements, H<sub>3</sub>BO<sub>3</sub> (0.75 g dm<sup>-3</sup>), (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O (0.05 g dm<sup>-3</sup>), CoSO<sub>4</sub> · 7H<sub>2</sub>O (0.18 g dm<sup>-3</sup>), CuSO<sub>4</sub> · 5H<sub>2</sub>O (0.5 g dm<sup>-3</sup>), ZnSO<sub>4</sub> · 7H<sub>2</sub>O (0.1 g dm<sup>-3</sup>), FeSO<sub>4</sub> · 7H<sub>2</sub>O (3 g dm<sup>-3</sup>). Twenty milliliters of phosphate buffered solution was also added (8.2 g dm<sup>-3</sup> KH<sub>2</sub>PO<sub>4</sub>, 21.75 g dm<sup>-3</sup> K<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O, 44.7 g dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O) and 5 ml of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (10 g dm<sup>-3</sup>). All were mixed and filled into 1-l aerated distilled water within 24 h.

The extent of mineralization was evaluated from the amount of carbon dioxide evolved from the tested compounds minus the amount of carbon dioxide produced by

the blanks. It was expressed as a percentage of theoretical amount of carbon dioxide calculated from the carbon content of tested compounds. According to equation 1:

$$D_{\text{CO}_2} = [n_{\text{SAMPLE}} - n_{\text{BLANK}} / \text{Th}] \times 100 \quad (1)$$

where  $n_{\text{SAMPLE}}$  is the amount of CO<sub>2</sub> generated by decomposition of the samples (mol),  $n_{\text{BLANK}}$  is the amount of CO<sub>2</sub> produced by endogenous respiration (mol), Th is the theoretical amount of produced CO<sub>2</sub> (mmol), according to equation 2:

$$\text{Th} = [m_{\text{vz.}} \times (\text{DOC}/100)] / M_{\text{c}} \quad (2)$$

where  $m_{\text{vz.}}$  is the sample weight (mg), DOC is the amount of dissolved organic carbon in the tested sample (%),  $M_{\text{c}}$  is the molar mass of carbon (g mol<sup>-1</sup>).

At the beginning and end of the experiment, sludge solids, pH, and reference DOC were determined for all samples. All measurements were performed three times in parallel.

## 2.2 Sorption experiment – screening test

Conditions of the test were as follows: suspension volume was 50 ml; concentration of PVA, 200 mg dm<sup>-3</sup>; and concentration of mineral clay, 200 mg dm<sup>-3</sup>. Ten milligrams of the mineral clay was mixed with 45 ml of distilled water. After clay was steeped, 5 ml of PVA solution was added, PVA concentration was 200 mg dm<sup>-3</sup>. From this moment, the time ( $t_0$ ) was measured. The suspensions of mineral clay and PVA were kept on electromagnetic stirrer – 370 RPM<sup>-1</sup>. At various intervals, 5 ml aliquots of the suspensions were removed, filtered, and analyzed for PVA content.

Two types of sorption experiments were conducted; the short-term experiments were measured for 45 min, and the long-term experiment was observed for 28 days due to possible resorption of PVA back into the environment. All measurements were performed three times in parallel.

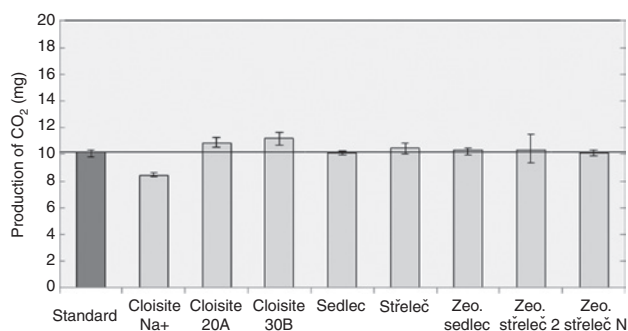
## 3 Results and discussion

In the first part of this work, the influence of clay minerals on respiration of microbial inoculum was monitored. The experiment ran for approximately 31 days. As a comparison, the substance used was sodium benzoate, which is defined as a biodegradable substance. The biodegradation of sodium benzoate peaked at 84.1%. After that, the level of biodegradation remained steady. Relatively high rate of biodegradation shows the sufficient microbial revival of activated sludge. Achieved results

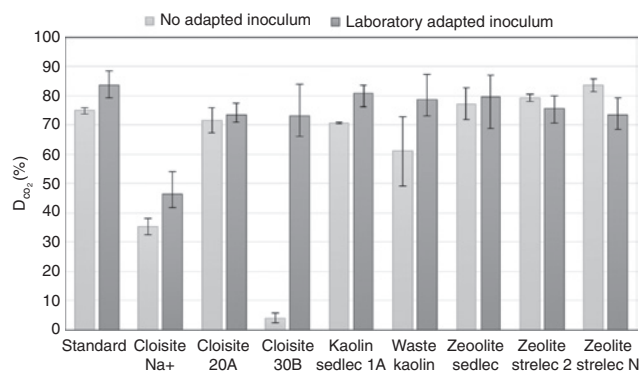
are consistent with study of Zheng et al. [18], as there was no evidence of acute and chronic toxicity of silicate nanoparticles to the viability of activated sludge microorganisms. As can be seen from Figure 1, the negative effect on the respiration of the activated sludge in the presence of Cloisite® Na<sup>+</sup> was detected. The respiration decreased by 17%. On the other hand, a slightly positive effect was observed in nanoclay Cloisite® 20A and Cloisite® 30B, where the respiration increased by 7.1% and 10.5%, respectively, despite the fact that, according to available literature, they exhibited biocidal effect [10, 19]. It could be caused by an organic modifier of Cloisite® 20A and Cloisite® 30B, which may result in its decomposition and in the subsequent increase in respiration.

After studying the effect of clay minerals on the respiration of microorganisms of the activated sludge, the measurement of the biodegradation of PVA 88-08 and PVA 72-10 was initiated in the presence of selected clay minerals.

Mixed microbial culture was used as inoculum in the biodegradation experiment of PVA 88-08. The maximal biodegradation of the standard was reached at 75%. Similar results were achieved during the decomposition in the presence of Cloisite® 20A where the biodegradation peaked at 71%, whereas, as can be seen from Figure 2, the biodegradation of PVA 88-08 in the presence of the Cloisite® 30B reached only 4% and, in the presence of Cloisite® Na<sup>+</sup>, rose to 35%. Nanoclay Cloisite® 30B has biocidal effects on organic modifier, which include quaternary ammonium salts in its structure. Thus, Na<sup>+</sup> sorption at nanoclay Cloisite® has been demonstrated to be at 40%. The sorption course is seen in Figure 3. The chart shows that the sorption is almost instantaneous. The biodegradation of 61% of PVA 88-08 was recorded in the presence of the Waste kaolin Strelec. Decreasing the biodegradation can be caused by the presence of impurities and other inhibitory substances. From Figure 2, it is also evident that



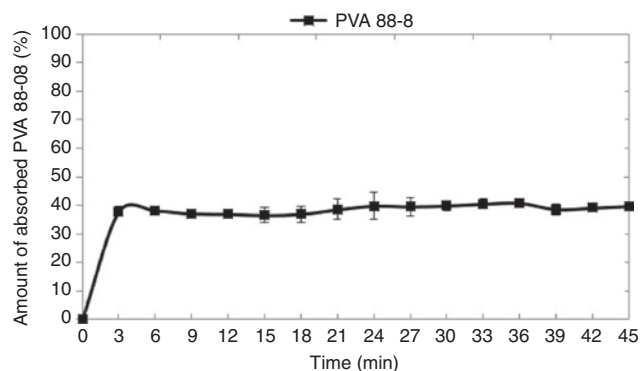
**Figure 1:** The respiration of microorganisms of the activated sludge in the presence of clay minerals ( $\pm$ standard deviation); standard – endogenous respiration.



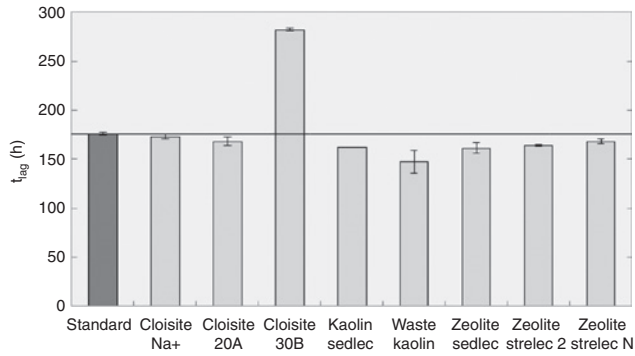
**Figure 2:** The level of PVA 88-8 biodegradation with no adapted inoculum and laboratory-adapted inoculum in the presence of a selected group of clay minerals ( $\pm$ standard deviation).

the presence of zeolites has a slightly positive effect on the biodegradation of PVA 88-08. The decomposition of PVA 88-08 in the presence of the zeolites was observed in the range of 77%–84%. The presence of clay minerals has not affected the lag phase during PVA 88-08 decomposition. As can be seen from Figure 4, the process of PVA 88-8 biodegradation begins after 160–180 h. The only exception is the presence of clay Cloisite® 30B, where the process of biodegradation began after 282 h due to the influence of inhibition caused by the organic modifier of nanoclay Cloisite® 30B.

In the experiment with inoculum adapted to PVA88-8, 84% of the standard was biodegraded. The final values of PVA biodegradation in the presence of OMMT Cloisite® 20A and Cloisite® 30B are 73% for both. In the case of the suspension containing nanoclay Cloisite® 30B, it has been shown that the adapted inoculum is less susceptible to biocidal effects of organic modifier of the nanoclay Cloisite® 30B. As can be seen from Figure 2, the maximum of PVA biodegradation in the presence Cloisite® Na<sup>+</sup> has reached 40%. This behavior has been caused by the



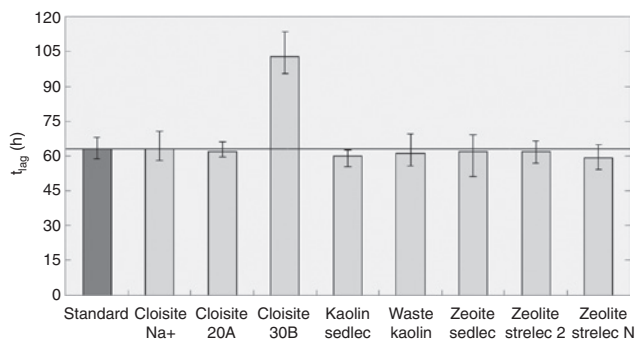
**Figure 3:** Kinetic trend of PVA 88-08 adsorption on Cloisite® Na<sup>+</sup> ( $\pm$ standard deviation).



**Figure 4:** The lag phase during the PVA 88-8 biodegradation with no adapted inoculum in the presence of the selected group of clay minerals ( $\pm$ standard deviation).

mentioned PVA sorption on the clay mineral with the sorption of 40%. The experiment has shown that in the presence of clay minerals, the biodegradability of PVA 88-08 declined. However, it has been observed that the laboratory-adapted inoculum is less susceptible to biocidal effects of organic modifier Cloisite® 30B. The maximum PVA biodegradation soared to 75%. As can be seen from Figure 5, the presence of clay minerals had no effects on the lag phase during the PVA 88-08 decomposition. The process of PVA 88-8 biodegradation began after 60th h. The only exception is the presence of clay Cloisite® 30B, where the process of biodegradation began after the 100th h (Figure 5).

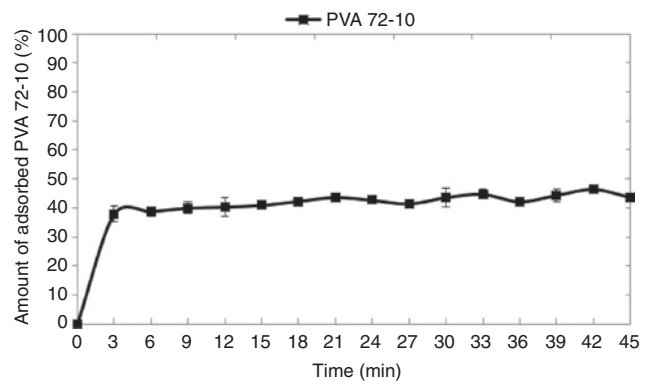
In another experiment, the biodegradation of PVA 72-10 was observed. Mixed microbial culture was used as inoculum. During the experiment, which ran for approximately 36 days, the standard decomposition was 76%. The lowest level of PVA 72-10 biodegradation was observed in the presence of nanoclay Cloisite® 30B, where the biodegradation peaked at 18% of PVA. This low level of degradation has been caused by biocidal effects of organic



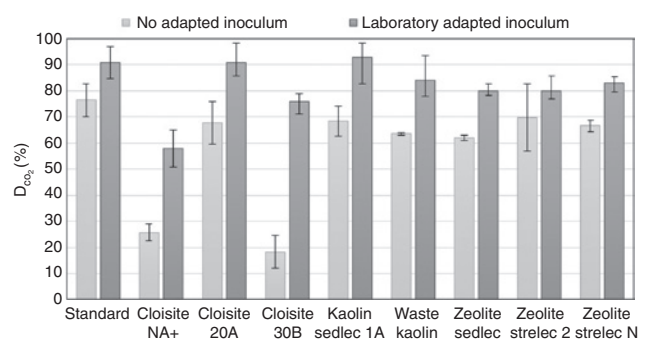
**Figure 5:** The lag phase during the PVA 88-8 biodegradation with laboratory adapted inoculum in the presence of the selected group of clay minerals ( $\pm$ standard deviation).

modifier because the sorption has not been demonstrated. In contrast, the sorption of PVA 72-10 on the surface of natural MMT – Cloisite® Na<sup>+</sup> has been observed. As can be seen from Figure 6, the extent of sorption was determined at 44% and PVA biodegradation peaked at 26%. The final values of biodegradation of PVA 72-10 in the presence of selected species of clay minerals and no adapted inoculum are shown in Figure 7. As can be seen from the chart, the presence of clay minerals had a negative effect on PVA 72-10 biodegradation. The lag phases were shorter with PVA in the presence of clay minerals than the lag phase with PVA without the presence of clay minerals. As can be seen from Figure 8, the process of PVA 72-10 biodegradation in the presence of mineral clays began after around 190–210 h. The lag phase of standard ran for approximately 237 h. The same time was needed for the beginning of the process of PVA 72-10 biodegradation in the presence of Cloisite® 30B.

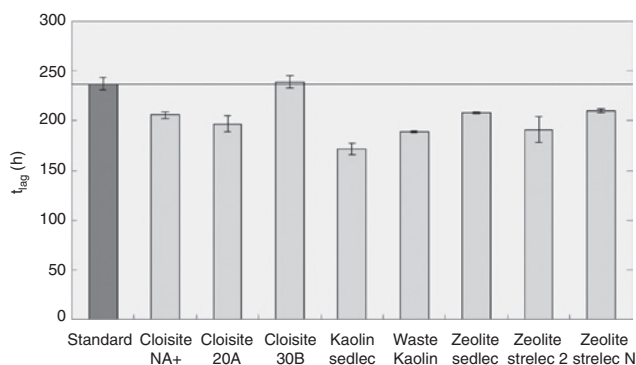
In the last biodegradation experiment, PVA 72-10 was used and the laboratory-adapted activated sludge as inoculum. In this experiment, the highest level of PVA



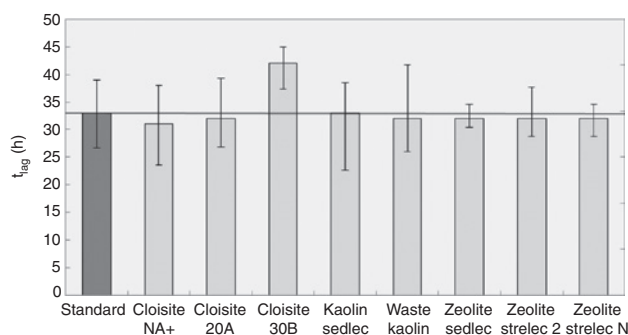
**Figure 6:** Kinetic trend of PVA 72-10 adsorption on Cloisite® Na<sup>+</sup> ( $\pm$ standard deviation).



**Figure 7:** The level of PVA 72-10 biodegradation with no adapted inoculum and laboratory-adapted inoculum in the presence of selected group of clay minerals ( $\pm$ standard deviation).



**Figure 8:** The lag phase during the PVA 72-10 biodegradation with no adapted inoculum in the presence of the selected group of clay minerals ( $\pm$ standard deviation).



**Figure 9:** The lag phase during the PVA 72-10 biodegradation with laboratory-adapted inoculum in the presence of the selected group of clay minerals ( $\pm$ standard deviation).

biodegradation was recorded during the shortest time of incubation. After 21 days of incubation, the biodegradation of standard soared up to 91%, which is a value 16% higher than in the experiment with no adapted inoculum. By using the laboratory-adapted inoculum in the presence of clay minerals, the biodegradation occurred at 80%–90% of PVA 72-10 contained in the individual suspensions, while the presence of kaolin Sedlec and Cloisite® 20A PVA 72-10 decomposition reached values over 90%. It has been also confirmed that the laboratory-adapted inoculum is less susceptible to the biocidal effects of organic modifier nanoclay Cloisite® 30B, where PVA biodegradation reached 76%. Again, the sorption in the extent of 44% has been proven. During the biodegradation in the presence of nanoclay Cloisite® Na<sup>+</sup>, 58% of PVA 72-10 contained in a reaction flask was decomposed. The presence of clay minerals has not affected the lag phase during PVA 72-10 decomposition. As can be seen from Figure 9, the process of PVA 72-10 biodegradation begins after 31–33 h. The only exception is the presence of clay Cloisite® 30B, where the process of biodegradation began after the 42nd h.

The sorption of PVA on clay minerals has been observed only in one of the studied clay minerals, namely, within natural MMT-Cloisite® Na<sup>+</sup>. As already mentioned, the adsorption of PVA 72-10 peaked at 44% after 45 min, and in the case of PVA 88-08, approximately 40% of PVA contained in the solution was adsorbed. In a hydrated form, it led to weakening of the forces and delaying of individual layers, intercalation or exfoliation, leading to the separation of individual layers of clay mineral, which could be a reason of the observed sorption.

In the long-term experiment, the sorption has been demonstrated only on nanoclay Cloisite® Na<sup>+</sup>, and during the experiment, the resorption back into the environment has not been recorded. The experiment was running for 28 days.

## 4 Conclusion

Based on the results of studied samples, it can be argued that a significantly negative effect on PVA biodegradability has been observed in the presence of natural MMT Cloisite® Na<sup>+</sup> in both environments, in the environment with no adapted inoculum and in the environment with adapted inoculum. During the experiment, sorption of PVA on the Cloisite® Na<sup>+</sup> occurred. In the short-term experiments, the sorption has been recorded in the range of 45% for PVA72 and 40% for PVA88. After 28 days of monitoring in the long-term experiment, the resorption of PVA back to the environment has not occurred. It is the evidence supporting the hypothesis that the sorption of PVA on Cloisite® Na<sup>+</sup> in the aqueous environment is the irreversible process, while a percentage of the sorbed PVA corresponds to the percentage of decreased PVA biodegradation. It should also be mentioned that the possible negative effect on the microbial population caused by intercalated sodium cation release from the interlayer space of MMT in the aqueous medium. The negative impact on biodegradation has been also determined in the presence of OMMT Cloisite® 30B in the environment with no adapted inoculum. There has been a biodegradation of 4% for PVA88 and 18% for PVA72. Low level of PVA decomposition has been caused by biocidal effects of the organic modifier of the clay mineral. Conversely, the laboratory-adapted inoculum was less susceptible to biocidal effect when the decomposition has been about 75% of PVA. These results also show that the lag phase has been shorter during the biological degradation of PVA in the presence of kaolin, especially in the presence of kaolin Sedlec 1A. Also a positive effect of zeolites on PVA88 biodegradation has been observed in no adapted environment, where the biodegradation peaked at 80%. The results can be summarized as follows:

- PVA adsorbed on the natural MMT Cloisite® Na<sup>+</sup> is not biodegradable.
- Organic modifiers of the MMT (quarternary ammonium salts) have no inhibition effect on the biodegradation of PVA.
- MMT and OMMT in the concentration, which are used in the materials, do not have stabilization effect or antimicrobial effect on the PVA materials.
- Kaolines and synthetic zeolites prepared from waste materials have a positive effect on the biodegradation of PVA and can be used as filler.

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