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BIOSTABILITY OF POLYVINYLCHLORIDE-BASED NANOCOMPOSITES UNDER ANAEROBIC CONDITIONS

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ABSTRACT
Research was conducted into biostability of PVC films filled with clay in an anaerobic environment. Nanocomposites based on PVC containing 10% with nanofiller CLOISTE Na+ (natural montmorillonite) or organically modified nanofiller montmorillonite CLOISTE 30B (organic fraction – methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride) exhibited a reduced migration of plasticiser – dioctyl phthalate (DEHP) by approx. 10% in 24 hours. The stability was more obvious in long-term investigation, migration 15% lower that of plasticised PVC occurred. The question thus was whether improvement would also be evident in environmental conditions. Therefore, films in test were prepared from PVC and from nanocomposite based on PVC/clay. Biodegradability testing was performed in an aqueous environment under anaerobic conditions with digested activated sludge from municipal wastewater treatment plant. Evalution of biodegradation was based on methane and carbon dioxide produced in the gas phase.
Keywords: polyvinylchloride, nanocomposite, DEHP, anaerobic

1. INTRODUCTION
Phthalic acid esters are a class of refractory organic compounds widely used as plasticizers in polyvinyl chloride (PVC) plastics. They are among the most common industrial chemicals and have become widespread in the environment as they have been found in sediments, natural waters, soils, plants and aquatic organisms [1]. As a result of both the large quantities produced and their widespread distribution, the phthalic acid esters have become ubiquitous environmental pollutants. Some of them di-(2-ethylhexyl) phthalate are suspected to be mutagents and carcinogents and have been listed as priority pollutants [2]. Metabolic breakdown of phthalic acid esters by microorganisms is considered to be one of the major routes of environmental degradation for these widespread pollutants. Numerous studies have been demonstrated the biodegradation of several phthalic acid esters under aerobic conditions in soil, natural waters and wastewater [3-5]. Wang [4] investigated the kinetics of phthalic acid esters degradation by acclimated activated sludge.
Some organisms selectively hydrolyze only one ester bond to give the monoalkyl phthalate plus an alcohol; the alcohol is then used for growth. Other organisms are capable of the complete mineralization of either the monoalkyl or dialkyl phthalate. The pathway of degradation is as follows:

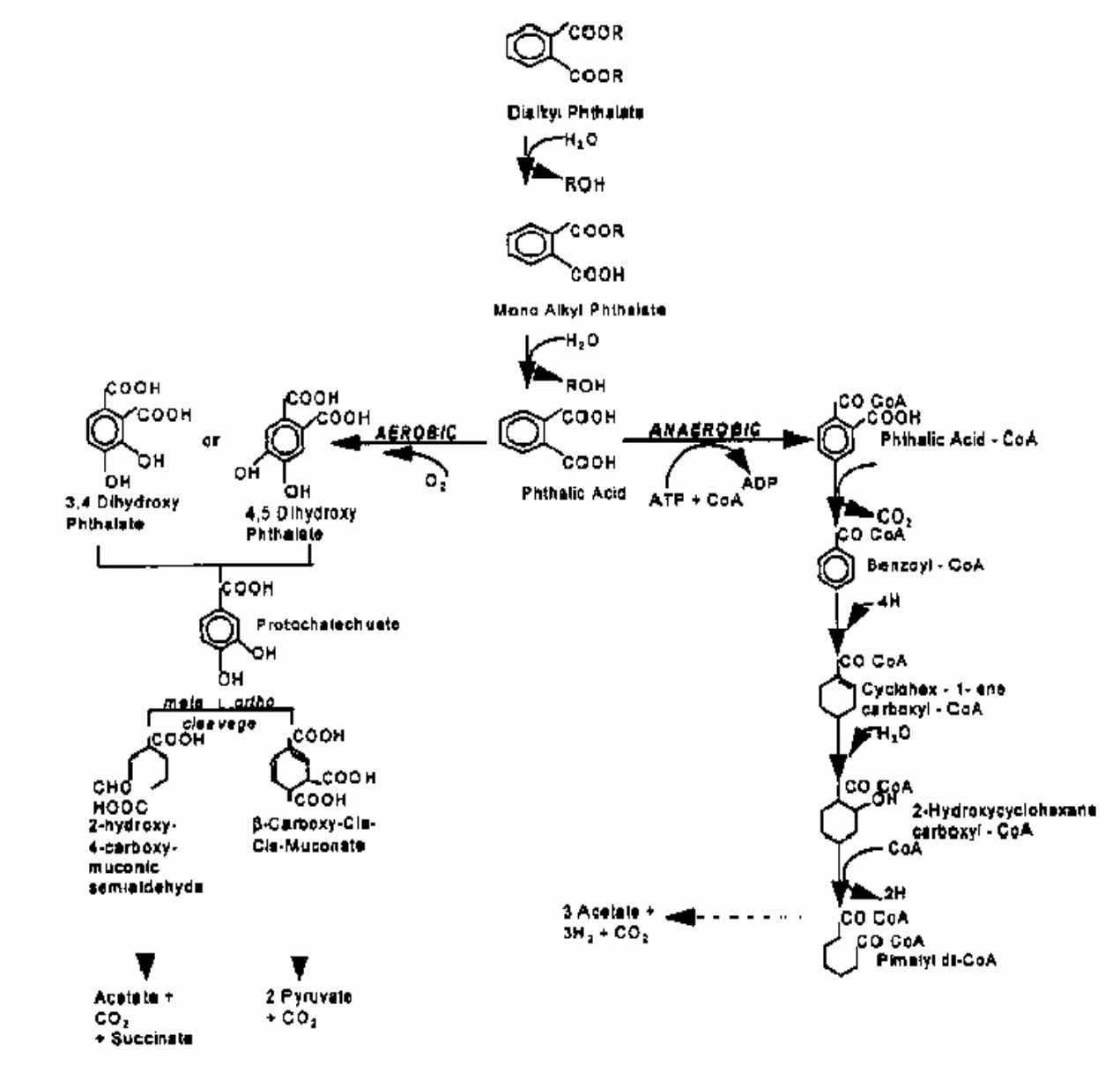

Figure 1. Pathway of degradation of phthalic acid esters

The objective of the present study is to investigate the susceptibility to anaerobic degradation of PVC plasticised films and dioctyl phthalate (DEHP) in digested sludge and to determine relative rates of anaerobic biodegradation.The degree and rate of degradation of a given compound are usually evaluated indirectly according to specific methane and carbon dioxide production.

2. EXPERIMENTAL

Biostability of tested samples (nanocomposites based on PVC containing 10% nanofiller CLOISTE Na+ (natural), organically modified nanofiller montmorillonite CLOISTE 30B (organic fraction – methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride) was observed in an anaerobic aqueous environment employing: laboratory equipment (capacity the apparatus is 20 positions) – biodegradability procedure was assessed the basis of methane and carbon dioxide production .

Experimental conditions:

Samples (testet PVC films) was inserted into 300ml flask and 100 ml liquid phase (mineral medium and anerobic sludge) was added. Mixed microbial culture was used as a source of microorganisms –

activated sludge from municipal wastewater treatment. The content of bottles was bubbled with nitrogen 10 min. to eliminate oxygen and then hermetic covered and inserted in thermostat at 37 °C. Gas chromatography was used for determining the total gas production.
Gas chromatography - Chrom -5, column filled with Porapack QS, length 3.6meter, diameter 3 mm
Detector: Termal conductivity detector - TCD, temperature 100°C
Carrier gas : helium 99,999%, flow rate30 ml / min
Termostat: 50°C, injector: 100°C
Calibration: mixed gas 4,05% CH4, 0,798% CO2, 95,152% N2 –Linde Technoplyn a.s., CR

Description of tested materials [6] :
Sample 38 – polyvinylchloride, DEHP, 38,49 % total organic carbon
Sample 39 – polyvinylchloride, DEHP, 10 % clay Cloisite® 30B, 38,10 % total organic carbon
Sample 45 – polyvinylchloride, DEHP, 10 % clay Cloisite® Na+, 38,20 % total organic carbon
Cloisite® Na+ is a natural montmorillonite. Cloisite® Na+ is an additive for plastics to improve various plastic physical properties, such as reinforcement, HDT, CLTE and barrier.
Cloisite® 30B is an additive for plastics to improve various plastic physical properties, such as reinforcement, HDT, CLTE and barrier.
di-(2-ethylhexyl) phthalate (DEHP*)*

3. RESULTS AND DISCUSSION

Evalution of biodegradation was based on methane and carbon dioxide produced in the gas phase. Biodegradation of di-(2-ethylhexyl) phthalate during 1100 hours. was 16 % (Fig. 2). Biodegradation (D_c) PVC films 38 without nanoclay according to methane and carbon dioxide produced in the gas phase was only 1 % during 1800 hours (Fig. 3).

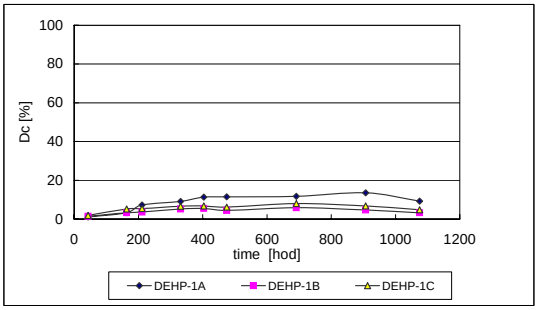

Figure 2. Biodegradability of di-(2-ethylhexyl) phthalate

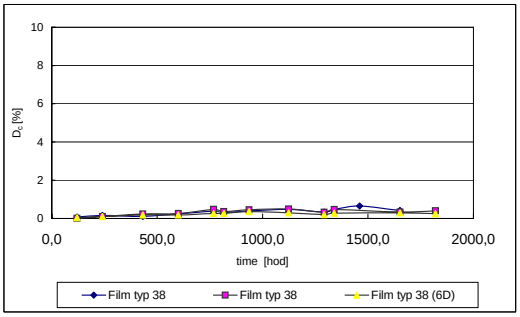

Figure 3 Biodegradability of PVC film typ 38

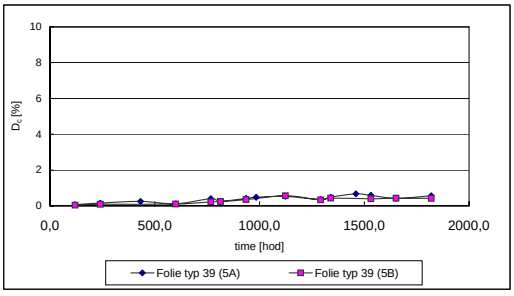

Figure 4. Biodegradability of PVC film typ 39

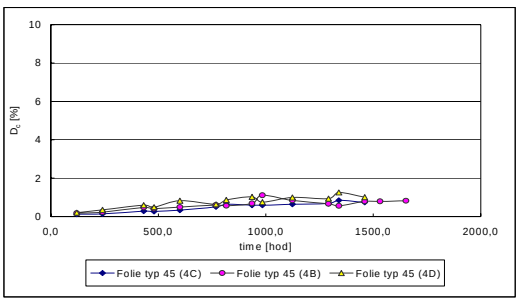

Figure5 Biodegradability of PVC film typ 45

Biodegradation (D_c) PVC films 39 with 10 % clay Cloisite® 30B according to methane and carbon dioxide produced in the gas phase was only 0,8 % during 1800 hours (Fig. 4) and biodegradation (D_c) PVC films 45 with 10 % clay Cloisite® Na+, according to methane and carbon dioxide produced in the gas phase was only 0,8 % during 1800 hours (Fig. 5).

Table 1 Anaerobic biodegradation of PVC films - percentage of removal according to CH_4 production (D_C), according to CH_4 production and production of CO_2 in liquid phase (D_{tC}) and weight loss

Tested material	D_c [%]	D_{tc} [%]	Weight loss [%]
Film typ 38 polyvinylchloride, DEHP	0,7-1,0	3	1,40
Film typ 39 polyvinylchloride , DEHP , 10 % clay Cloisite® 30B	0,6-0,8	7	1,16
Film typ 45 polyvinylchloride, DEHP, 10 % clay Cloisite® Na+,	0,9-1,2	5	6,76

Total biodegradation of PVC films 38, 38 and 45 is demonstrated in the Tab. 1. Percentage of removal according to CH_4 production ($\mathbf{D_C}$), biodegradation based on CH_4 production and production of CO_2 in liquid phase ($\mathbf{D_{tC}}$) and according to weight loss during biotic test. There is showed that biodegradability of this PVC foils reach max. 7%. Biostability of PVC after addition of nanofillers Cloisite 30B and Cloisite Na + little degreased in anaerobic aquatic environment.

4. CONCLUSION

Stability of the nanocomposite materials – foils PVC/clay was being studied in an anaerobic environment. As nanofillers were used clays Cloisite 30B and Cloisite Na +. The biostability was aimed on determination of production methane an carbon dioxide by analysing with gas chromatography (Hewlett-Packard model 5890 II with TCD detector). PVC foils without clay were degraded, with more than 3 % removed in 76 days. PVC foils with 10% nanofiller Cloisite 30B were also degraded, with 7% removed in 76 days. And finally PVC foils with 10% nanofiller Cloisite Na+ were also degraded, with 5% removed in 76 days under anerobic environment.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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