Influence of different environments on degradation of composites with natural fibre

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Abstract. The object of the present study was to demonstrate the behaviour of two polymer composites with natural fibre (Ramia/Ecoflex®, wood flour/PP) to exposure condition in natural environments. The environmental degradation of these composites took place in the Baltic Sea and compost. The incubation lasted for a period up to 24 months. The macro - and microscopic observations of polymer surface, weight changes and mechanical properties were tested during experiment. The characteristic parameters of both natural environments were also controlled during incubation time and their influence on the rate of degradation was discussed. The results revealed that kind of environment, where materials were landed, has significant influence on degradation rate. The environmental degradation proceeded faster in compost than in sea water. During the incubation in the Baltic Sea the conditions were favourable for the growth of bacteria while in the compost for fungi. The composition of composites with natural fibre had an influence on the rate of degradation process too. The obtained results indicate that the degradation of Ramia/Ecoflex® composite is faster than wood flour/PP composite in both natural environments.

1. Introduction
At the present time, when the large amount of litters has contaminated our planet and environmental awareness has increased, the new environmental friendly materials are in request. Natural fibres reinforced composites are very interesting alternative to synthetic oil-based fibres enhanced polymer composites, because natural fibres are derived from renewable resource. They do not have a large energy requirement to process and they have light weight, high specific modulus and are degradable. Natural fibres undergo photochemical degradation when exposed to UV radiation. They are degraded biologically because organisms recognize the chemical constituents in the cell wall and can hydrolyze them into digestible units using specific enzyme systems. Though the degradability of natural fibres can be a disadvantage in durable applications where composites are exposed to harsh environments, it can also be an advantage when degradability is desired [1].

Natural fibres may be classified in two categories: non-wood (such as flax, hemp, jute, ramie) and wood fibres (such as pine, spruce, oak, maple, aspen) [1–4]. Ramie is a perennial herbaceous plant of the nettle family (Urticaceae) native to some Asian countries. Ramie fibres have been used for centuries because of their excellent fibre properties. Fibres from Ramie are very fine and silk-like, naturally white and lustrous. Ramie is characterized by its high
length, great strength, much greater than that of cotton and silk. They are used for clothing fabrics, industrial packaging, twines, cordages, canvas, car outfits, etc. [5].

Many different species of tree are offered as wood flour and are often based on the regional availability of raw materials from wood-processing industries. The most commonly used wood flour are made from pine, oak, and maple. Wood flour itself is a complex, three-dimensional, polymer composite made up primarily of cellulose, hemicellulose and lignin [1]. Wood-plastic composites used in exterior applications have wood flour content to 50-60% by weight to prevent significant moisture sorption and the consequent negative effects.

Nowadays the important influence on the use of wood flour, particularly in Europe, have primarily the advantages of wood flour such as low density, low cost, derived from a renewable resource, reasonable processibility and biodegradability.

In composite fibres are usually coupled by natural (such as starch, cellulose, polylactic acid, soybeans) or synthetic (such as polypropylene, polyester, polyurethane) matrix. The main tasks of the embedding matrix are to hold the fibres together (giving and stabilizing the shape of the structure), to transmit the shear forces between the fibres and to work as a coating to prevent the fibres from being damaged by environmental influence [1,6].

The aim of the present study was to demonstrate the behaviour of two polymer composites with natural fibre (Ramia/Ecoflex®, wood flour/PP) to exposure condition in natural environments (Baltic Sea and compost pile).

2. Experimental

2.1. Environments

The environmental degradation of composites with natural fibre took place in the Baltic Sea and compost under natural weather depending conditions. The incubation lasted for a period up to 18 months.

2.1.1. The Baltic Sea

The incubation of polymer samples took place in the Baltic Seain Gdynia Harbour on the Norwegian Pier near the ship of the Maritime Search and Rescue Service.

The polymer samples were located in a special basket made of perforated galvanized steel, which was suspended from a rope at 2 m depth under the surface of the sea. The perforated baskets structure allowed for free movement of seawater and the access of micro-organisms and enzymes dissolved in the water to degraded material [7].

2.1.2. The compost pile

The compost pile was prepared under natural conditions of municipal waste treatment plant in Gdynia. It consisted of the dehydrated sewage sludge, burnt lime and straw. Burnt lime (0.45 kg CaO/1 kg dry mass of compost) was added to ravage phatogenic bacterium and eggs parasites, to deacidificate sewage sludge and to convert sludge to compost. The straw was added to maintain the higher temperature of the compost pile and to loosen the structure of the compost pile. The compost pile prepared under natural conditions was not adequately aerated, so it was expected that a combination of conditions from aerobic at the upper part of pile, microaerophilic in the middle part and facultative anaerobic at the bottom of the pile could occur for microorganisms growth [7, 8].

The polymer samples were put into the special perforated basket and buried of 1 m in depth of the compost pile. The perforated structure of basket allowed for free access of macro, micro-organisms and enzymes existing in this environment to degraded material.

2.2. Materials

The two kinds of composites with the natural fibre were environmentally degraded [9, 10, 11]:
- Composite of the wood flour/polypropylene (WF/PP, 40/60%wt.) The wood flour from aspen was mixed by extrusion process with PP without any coupling agent.
- Composite of the Ramie fibre/aliphatic-aromatic polyester Ecoflex® (R/E, 43/57%wt.). Ecoflex® neat used for the composite preparation was fabricated by compression moulding of Ecoflex® granules at 120°C in Hydraulic Press for 15 minute and cooled to room temperature. The Ramie mat was sandwiched between two Ecoflex® sheets by compression moulding again at 120°C.

Ramie fibre (TOSCO Co. No.25, forty-four warps per inch and forty-six wefts per inch) used in this work was symmetrical, with good stability and reasonable porosity. Chemical composition of the Ramie was: cellulose (68.6-76.2wt. %), lignin (0.6-0.7wt.%), hemicellulose (13.1-16.7wt.%), pectin (1.9wt.%), wax (0.3wt.%), moisture content (8wt.%).

The commercial aliphatic-aromatic copolyester Ecoflex® (E, supplied by BASF) used in this work was made from 1,4-butandiol with adipic and terephthalic acids.

The pure polypropylene sample (PP) used in this work was received from PETROCHEMIA PŁOCK S.A.

2.3. Methodology

2.3.1. Characterization of compost pile [7,8,11]
- The moisture content of compost was determined by drying a sample at 105°C until constant weight was obtained.
- The activity of the dehydrogenases was measured by a spectrophotometric method using triphenyltetrazolium chloride (TTC), which is a method for the estimation of biochemical activity of microorganisms in an active sludge by the oxidation process. The method is based on the dehydrogenation of glucose added to the compost with a subsequent transfer of the hydrogen to the colourless biologically active compound of TTC, which undergoes a reduction to TTCH2 (red compound). The intensity of red colour compound TF was measured using a Specol colorimeter at 490 nm.
- The pH of the compost was determined with a Teleko N 5172 pH-meter.

2.3.2. Investigation of composites with natural fiber

After incubation the samples were taken out from both environments and washed with distilled water and dried at room temperature to a constant weight. The changes in weight, surface morphology and mechanical properties of composites were tested before and after degradation in natural environment.
- The macro and microscopic changes of polymer surface- the surface of the of polymer samples was observed in a macro (naked eyes) and micro scale (microscopic observation). Macroscopic observations of polymer surface were analysed organoleptic using of a FujiFilm S2500 HD camera, but microscopic observations were analysed with the metallographic microscope ALPHAPHOT-2YS2-H Nikon linked to the photo camera Casio QV-2900UX. The view of polymer samples surface before and after degradation was compared.
- The changes of weight- the dried polymer samples were weighed on an analytical electronic balance (Gibertini E 42s, repeatability 0.1 mg). The weight of clean and dried polymer samples after incubation in the natural environment was compared with those before incubation. The percentage weight changes of PCL samples were calculated according to the following equation:

$$\text{percentage weight change} = \frac{m_1-m_2}{m_1} \times 100$$  

(1)
where:
\[ x \] – changes of weight [%],
\[ m \] – weight of polymer sample before incubation [g],
\[ m_1 \] – weight of polymer sample after incubation [g].

- The changes of mechanical properties- the maximum tensile strength (MPa) was measured at room temperature using The Tensile Testing Machine Type Fu 1000e made by VEB Thuringer Industriewerk Rauenstein, according to PN-EN ISO 527-1, 2, 3: 1998 Standard.

3. Results and discussion

3.1. The characteristics of natural environments
Taking under consideration the fact that the biotic and abiotic parameters of natural environments have a significant influence on development of living organisms, the parameters of both environments were monitored during incubation time and their influence on the degradation of composites was discussed.

The parameters of the seawater according to the State Environmental Monitoring, Inspectorate of Environmental Protection and parameters of compost are shown in Table 1.

**Table 1.** The characteristic parameters of the Baltic Sea and compost (average data from three years).

| Months     | Baltic Sea parameter’s | Compost parameter’s |
|------------|------------------------|---------------------|
|            | temperature [°C]       | pH                  | oxygen content [cm³/dm³] | salt content [ppt] | temperature [°C] | pH         | moisture content [%] | activity of dehydrogenases [mol mg⁻¹d.m.] |
| January    | 1                      | 8.2                 | 9.7                     | 6.4                  | 6                  | 5.3                 | 51             | 0.0281                   |
| February   | 3                      | 8.0                 | 10.1                    | 7.2                  | 0                  | 5.6                 | 49             | 0.0177                   |
| March      | 3                      | 8.2                 | 10.6                    | 6.3                  | 3                  | 6.0                 | 58             | 0.0331                   |
| April      | 7                      | 8.4                 | 10.0                    | 6.3                  | 11                 | 5.6                 | 55             | 0.0220                   |
| May        | 11                     | 9.0                 | 8.5                     | 6.5                  | 14                 | 6.1                 | 55             | 0.0297                   |
| June       | 13                     | 9.0                 | 8.2                     | 6.1                  | 18                 | 6.0                 | 42             | 0.0197                   |
| July       | 19                     | 8.2                 | 7.6                     | 6.4                  | 20                 | 5.8                 | 53             | 0.0387                   |
| August     | 18                     | 8.7                 | 6.8                     | 6.8                  | 25                 | 5.6                 | 59             | 0.0471                   |
| September  | 19                     | 8.4                 | 7.0                     | 6.7                  | 17                 | 6.0                 | 53             | 0.0353                   |
| October    | 12                     | 8.0                 | 6.7                     | 6.7                  | 11                 | 5.5                 | 61             | 0.0351                   |
| November   | 10                     | 8.1                 | 8.4                     | 6.8                  | 8                  | 5.9                 | 60             | 0.0318                   |
| December   | 3                      | 8.2                 | 8.0                     | 6.7                  | 1                  | 6.1                 | 55             | 0.0192                   |

Looking at the parameters presented in the Table 1 we can state, that the temperature of both natural environments was depended on the weather conditions (seasons) and had been fluctuating a lot during experiment (from 1 to 19° in sea water and 0-25° in compost). Only the temperature of natural environments during summer months was more preferable for enzymatic degradation (20-60°) [12]. The average temperature during summer months (June, July, August, September) in the Baltic Sea was 17°C and in the compost about 20°C.
Analysing characteristic parameters presented in the Table 1 we can also state that there were significant differences in the pH values of both natural environments. The average pH in the Baltic Sea was 8.4, but in compost was slightly acid - 5.8. In the Baltic Sea pH was a little above the upper limit of pH (5-8) recommended in the biodegradation process [12].

It is known that the seawater is a very specific and complicated natural environment where microorganisms, animals, salt, sunlight, fluctuation of water, rain etc. play a part in degradation in nature. The relatively low temperature and alkalinity of seawater (Table 1) could have an influence on the activity of psychrotrophic bacteria, which are able to adapt to changing conditions. During the winter months, we could observe the very low temperature and the highest oxygen content (~10 cm³/dm³). These conditions could have an influence on the activity of oxidizing enzymes, which are responsible for oxidation.

Looking at the parameters presented in the Table 1, we can state that the salinity of seawater were not change significantly. Salt content of the Baltic Sea is changed naturally and depends on tributary of rivers or heavy rains [13].

It is also known that a wide population of micro- and macroorganisms can exist in the compost and the most abundant are bacteria, actinomycetes and fungi [14]. The rather low temperature (below 20°C) and slightly acid pH (~6) of compost under natural weather depending conditions (Table 1) caused that psychrotrophic acidophilic microorganisms (fungi) could play the main role in the degradation of composites in that composting environment. Due to weather, as well as respiration of organisms the moisture content of the compost had been fluctuating a lot. This fluctuation of humidity of compost had an influence on the development of living organisms, which are producing enzymes involved in degradation process. Generally during degradation of composites with decreasing of moisture content the lower absolute value of activity of dehydrogenases, depending on the degree of microorganisms growth, was observed.

Considering the characteristic abiotic parameters of sea water and compost presented in Table 1 and the different microbial communities (bacteria in sea and fungi in compost), we could expect the different rate of degradation of composites with natural fibre in these two natural environments.

3.2. The evaluation of polymer changes during environmental degradation

The environmental degradation of composites with natural fibre in seawater and compost was evaluated visually at first. Figure 1 represents the surface view at macro scale of investigated composites before and after degradation in natural environments.
Generally macroscopic observations have suggested very slight vulnerability of WF/PP composite to degradation process. After 18 months of incubation in both natural environments, the surface of the samples became rough and mat. Additionally after incubation in seawater, a lot of black areas appeared on the composite surface, what was an evidence of microorganisms presence (Figure 1). According to the literature the degradation of wood-plastic composites take place primarily in the lignin component and results in a characteristic colour change [15].

At the beginning of incubation in both natural environments the surface of composite R/E was slowly microbiological attacked. The samples changed partly the colour or lost the glossiness. But after next months of incubation in natural environments the matrix of composite R/E was partially removed and the Ramie fibres were clearly visible on the top of the surface. The distinct black areas on the surfaces of composite R/E were observed at the end (12 months) of degradation in compost and seawater (Figure 1).

The results of weight changes of investigated composites with natural fibre and, for comparison, of pure polypropylene sample and aliphatic-aromatic copolyester Ecoflex® are presented in Figure 2-3.

Figure 1. Macrographs of composites with natural fibre before and after incubation in natural environments.
No significant weight loss of WF/PP composite was observed during 24 months incubation in both natural environments. The small, but stable decreases of weight (3-6%), during the whole period of experiment indicated on slowly degradation processes in material. These results suggested that on the one hand the Baltic Sea and compost pile were not sufficiently microbially active for degradation of WF/PP composite and on the other hand confirmed the good enough resistance of this composite to the environmental degradation.

According to the literature wood is degraded biologically because organisms recognized the cellulosics and hemicellulosics in the cell wall and can hydrolyze them into digestible units using specific enzyme systems [1]. Among all microorganisms involved in the degradation of cellulose fibres, the most attractive are fungi [15]. Considering the characteristic parameters of both natural environments we could statethat only during incubation WF/PP composite in compost were conditions appropriate for growth of fungi (Table 1). As a result the slightly higher weight losses of WF/PP were observed in compost (6%, Figure 3), than in seawater (3%, Figure 2) after 24 months incubation.

Comparison the weight changes WF/PP and pure polypropylene after incubation in both natural environments, the increase in weight of PP (14% in seawater and 3% in compost)was observed, as a consequence of swelling in the first period of incubation. It confirmed the bioresistance of polyolefines and their moisture stability. Till the end of experiment the swelling ratio slowly decreased.

The results presented in Figure 2 and 3 indicate that the weight losses of R/E composite had been increased with degradation time and more visible than in WF/PP case. The R/E composite had been disintegrated after 18 months incubation in both environments.

The process of degradation R/E in compost was slightly intensive, than in seawater. The observed differences between the degradation process in compost and seawater were caused by dissimilarity of environments conditions. The monitored characteristics parameters of both environments indicated that the conditions of compost were more preferable for growth of fungi, while in seawater for bacteria (Table 1).
The pure Ecoflex® was disintegrated after 12 months in compost and after 18 months in seawater. It is known that the Ecoflex® is classified as fully biodegradable (least 60% of the total organic carbon of the polymeric material has been converted into carbon dioxide during a test interval of no longer than 180 days). According to our earlier studies pure Ecoflex® samples in compost and seawater under natural weather depending conditions was degraded longer than in laboratory standard tests [11].

Susceptibility of composites with natural fibre to environmental degradation was also evaluated based on mechanical properties. Changes of mechanical properties of investigated composites after degradation in seawater and compost were checked up by measurement of tensile strength at break. The results are presented in Figure 4 and 5.

At the beginning of incubation in seawater and compost the tensile strength of WF/PP composite slightly decreased, but after that the tensile strength in both environments was increased (to 20MPa in seawater and to 17MPa in compost). The increasing in tensile strength was caused by hydrophilic property of wood fibre. The absorbed water facilitated an orientation of stress transferring macrochains of polypropylene matrix. This resulted in the higher mechanical properties (Figure 4 and 5). But the further growing up of the microorganisms caused the deterioration and the breaking of microchains in polypropylene matrix resulting in the decrease of tensile strength (to 7 MPa in seawater and to 9MPa in compost after 24 months of incubation).

According to the literature if the moisture content of wood flour in the composite exceeds the fibre saturation point, decay fungi can begin to attack the wood component leading to both weight loss and significant reduction in mechanical properties of composite too [16].

The addition of Ramie fibre to Ecoflex® caused the significant increase of tensile strength of the samples. The maximum tensile strength of Ecoflex® was 10 MPa while of R/E composite - was 87 MPa. During the incubation of R/E composite in both environments the tensile strength had been decreasing distinctly with the degradation time and at the end of experiment microorganisms caused the breaking of polymer chains in matrix resulting in the fragmentation of composites.

Figure 4. Tensile strength [MPa] of polymer samples after incubation in seawater.

Figure 5. Tensile strength [MPa] of polymer samples after incubation in compost.
After 9 months of degradation of R/E composite in compost the samples of composite were torn up already into the pieces whereas in seawater the mechanical properties could be still estimated. The microscopic observations of investigated composites surface presented in Figure 6 confirms our previous results of weight changes and mechanical properties. After incubation in both natural environments, the composites were not homogeneously destroyed over the whole polymer surface and there were different images depending on the place. The micrographs the most repeated images observed under the metallographic microscope were done.

**Figure 6.** Micrographs of composites with natural fibre before and after incubation in natural environments.
The reference surface of WF/PP sample was not homogenous and consisted of visible natural wood fibre (dark places) and PP matrix (bright places). During the all incubation time in both natural environments we could observed the increase of bright elements on the surface, what was connected with wood fibre degradation. Additionally at the end of degradation (24 months) the attachment of microorganisms was visible on the surface of WF/PP.

The surface of R/E composite before degradation was fully rough. After incubation in both environments there was clearly visible erosion of the composite surface. The microscopic observations of investigated composites indicated on different degradation behaviour of composites in the Baltic Sea and compost (Figure 6). Generally, R/E samples were degraded in compost faster than in seawater, because the condition of compost were more favourable for growth of fungi. After 15 months of incubation in compost the agglomeration of fungi was distinctly observed on the surface of R/E. The changes of R/E surface during the environmental degradation (after 18 months) lead to the erosion (damage) in the form of the observed a lot of cracks (Figure 6).

Summarizing the microscopic observations after incubation in seawater and compost have shown vulnerability of both composites with natural fibre to the microbiological attack.

4. Conclusions

The results of the study revealed that the composites with natural fibre were susceptible to degradation in natural environments. Generally composites with natural fibre were degraded in compost faster than in seawater, because the conditions of compost were more favourable for growth of fungi.

The composition of composites had an influence on the rate of degradation process in both natural environments. The Ramie/Ecoflex \textsuperscript{®} composite was degraded more distinctly in both environments than the wood flour/polypropylene.

The macro and microscopic observations and weight changes indicate that the natural fibres coupled by non-degradable matrix accelerated their degradation in compost and seawater. In contrast, the addition of natural fibres to biodegradable polymer improved mechanical properties, but delay their disintegration in natural environments.

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