

# Degradability of organic-inorganic cellulose acetate butyrate hybrids in sea water

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Environmental degradability of novel organic-inorganic cellulose acetate butyrate hybrids obtained via sol-gel process was investigated. The degradation of hybrids was studied under marine exposure conditions in the Baltic Sea for a period of 25 weeks. The influence of characteristic parameters of sea water on the degree of degradation monitored by changes of weight and optical microscopy was discussed. The degraded samples were also examined by FT-IR spectroscopy. It has been established that the CAB/silica hybrids are more susceptible to biodegradation in sea water environment than pure cellulose acetate butyrate.

**Keywords:** degradation, cellulose acetate butyrate, organic-inorganic hybrids, sea water.

## INTRODUCTION

Rapid changes in public legislation caused by growing environmental pollution problem brought about considerable research interest in the design and development of new environmentally friendly materials which are one of the available options for the plastic waste disposal problem. Recent trends towards biodegradable materials have been focusing on the use of natural biopolymers like cellulose and starch. These materials offer several advantages: they are low cost, abundant and available from renewable resources. However, they have also some limitations like poor processability or high water absorbency. Therefore, cellulose esters seem to be an interesting alternative for the production of environmentally friendly materials<sup>1</sup>. Cellulose acetate butyrate (CAB) is a thermoplastic polymer that has good mechanical properties, can be readily processed and is also susceptible to biodegradation<sup>2</sup>. There are numerous reports in the literature associated with polymer blends based on cellulose derivatives, however, there are only few which describe materials based on CAB and their susceptibility to biodegradation<sup>2-6</sup>. So far, no information about the effect of silica incorporation into CAB matrix on the degradation of the material has previously been available. In this work, for the first time, we discuss the susceptibility to biodegradation of cellulose acetate butyrate organic-inorganic hybrids in comparison with pure CAB.

In our study we used a novel hybrid material, obtained via sol-gel processing, which combines two components: organic polymer (CAB) and inorganic solid (silica particles). Hybrid materials, due to their unique properties, are promising systems with potential application in coatings, membranes, biomaterials, sensors and catalysis<sup>7-10</sup>. They open new possibilities of tailoring materials with improved mechanical and chemical properties, desirable toughness as well as elasticity comparing to pure organic polymers<sup>11-15</sup>. Sol-gel processing is one of the most ef-

ficient methods for preparation of hybrid materials. This technique comprises an initial hydrolysis of metal alkoxides and subsequent condensation reactions, resulting in metal oxides. The most commonly used precursor, which yields a silica network, is tetraethoxysilane (TEOS). The main advantages of sol-gel processing are mild conditions, i.e. low reaction temperature, and ease of control<sup>11, 16</sup>.

The aim of this work was to investigate the susceptibility to biodegradation of cellulose acetate butyrate organic-inorganic hybrids in the Baltic Sea water environment. We have examined the effect on degradation of two plasticizers: conventional diethyl phthalate (DEP) and biodegradable tributyl citrate (TBC). The degradation process was studied by determination of weight changes, chemical changes (ATR-FTIR) as well as by macro- and microscopic observation of samples surface.

## EXPERIMENTAL

### Materials

Cellulose acetate butyrate (Mn = 70000, containing 12–15 wt.% acetyl, 1.2–2.2 wt.% hydroxyl, 35–39 wt.% butyryl) and TEOS (98%) were supplied by Sigma Aldrich. Diethyl phthalate (DEP) and tributyl citrate (TBC) used as plasticizers were purchased from POCH and Fluka, respectively. Hydrochloric acid (HCl 35–38%) and acetone were supplied by POCH and used as received.

### Hybrid preparation

Organic-inorganic hybrids based on cellulose acetate butyrate (CAB) were synthesized according to the procedure we described in detail in Patent Pending (Polish Patent Office)<sup>17</sup>. The samples compositions and codes are presented in Table 1. In the typical preparation of hybrids polymer (CAB) was dissolved in acetone at room temperature, followed by plasticizer and TEOS addition and mixed vigorously using magnetic stirrer. Afterwards, cata-

lytic amount of hydrochloric acid solution was added to initiate the sol-gel process. The homogenous solution was cast on a PTFE dish and left exposed to atmospheric conditions at room temperature followed by drying in a vacuum drier to ensure complete evaporation of acetone<sup>18</sup>. Samples of pure CAB and polymer with 25% of plasticizer: diethyl phthalate (DEP) and tributyl citrate (TBC) were also prepared as a reference material.

**Table 1.** Sample compositions and codes

Sample code	Polymer/TEOS (wt. ratio)	DEP content (%)	TBC content (%)
CAB	–	–	–
CAB DEP	–	25	–
CAB6 DEP	93.75/6.25	25	–
CAB12 DEP	87.5/12.5	25	–
CAB TBC	–	–	25
CAB6 TBC	93.75/6.25	–	25
CAB12 TBC	87.5/12.5	–	25

## Environment

The incubation of cellulose acetate butyrate hybrids took place in the Baltic Sea water in Gdynia Harbour. The samples were cut into 15 x 20 mm rectangles and located in a special galvanized sheet basket at 2 m depth under the sea surface, near the ship of the Polish Ship Salvage Company. The incubation of polymer samples in sea water lasted 25 weeks. After incubation the samples were taken out from the environment, washed thoroughly with distilled water and dried at room temperature to a constant weight.

## Methods

### Macroscopic observation

Macroscopic observation of hybrids surface changes during degradation was done using digital photo camera Casio QV2900UX.

### Optical microscopy

Microscopic observation was performed in transmission light with an optical microscope Nikon Alphaphot-2YS2 connected with digital photo camera Casio QV2900UX, at magnification 1:350.

### Changes in weight

The weight changes of the degraded samples (%) were determined using an electronic balance Gibertini E 42s, comparing with mass of undegraded samples before incubation. In a typical experiment, at least 3–5 samples were taken out from the sea environment and the average weight was used.

### Mechanical properties

Mechanical properties (tensile strength and elongation at break) of the samples before incubation were investigated using a universal tensile machine (Instron 5565) with sample films 150 mm in length and 10 mm in width and at a crosshead speed of 100 mm/min at room temperature (according to the test method described in International Standards PN-EN ISO 527-1:1998, PN-EN ISO-3:1998). At least five tests were performed for each type of the sample, to ensure the reliability of the test results, and the average was used.

## The FT-IR spectra

The FT-IR spectra were recorded on PerkinElmer, Spectrum 100 FT-IR spectrometer using ATR (attenuated total reflection) technique, over a range of 400–4000 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Degradation environment

The characteristic parameters of sea water according to the Institute of Meteorology and Water Management in Gdynia, Poland are presented in Table 2.

**Table 2.** The characteristic parameters of the Baltic Sea water

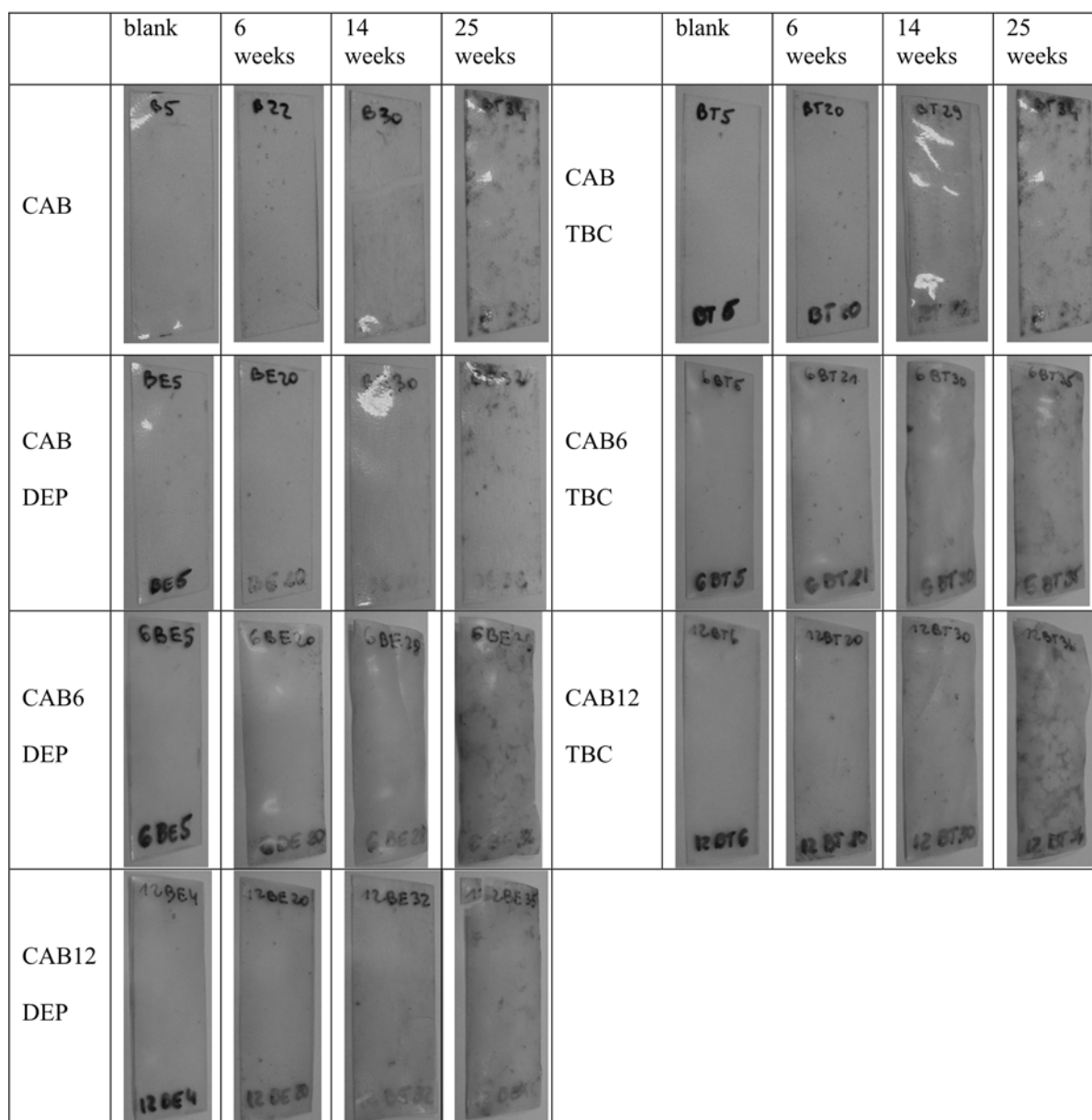
Parameter	Period: April – September
Temperature (°C)	7.2 – 20.1
pH	8.2 – 8.5
O <sub>2</sub> content (cm <sup>3</sup> /dm <sup>3</sup> )	6.5 – 10.0
Cl <sup>-</sup> content (g/kg)	3.3 – 3.6
Salinity (ppt)	6.1 – 6.5

It is known that the abiotic parameters of sea water (temperature, pH, salinity and oxygen content) have a significant influence on the development of living microorganisms in natural environment. Taking into consideration the characteristic parameters of the Baltic Sea water (Table 2) we can state that the temperature of sea water during the experiment (7.2–20.1°C) was lower than preferred for enzymatic degradation which is in the range of 20–60°C<sup>19</sup>. The value of pH in sea water was alkaline (8.2–8.5) on the stable level during the whole time of incubation, while the preferred pH for enzymatic degradation is in the range of 5–8<sup>19</sup>. We assume that low temperature of the Baltic Sea and slight alkalinity of the sea water could have had an influence on the development of psychrotrophic bacteria. In the first period of incubation, (April) we could observe lower temperatures (7.2°C) and the highest oxygen content (10 cm<sup>3</sup>/dm<sup>3</sup>). These conditions have an influence on the activity of oxidizing enzymes. The situation was also favourable for development of aerobic epilithic bacteria. The metabolism of these microorganisms probably caused the decrease of oxygen content (6.5 cm<sup>3</sup>/dm<sup>3</sup> in September) and the changing concentration of carbon dioxide in sea water<sup>20</sup>.

### Evaluation of the changes in samples during incubation in sea water

The macroscopic observations of CAB samples surface are presented in Fig. 1. The changes of the surface of CAB samples obtained with DEP were more visible than for hybrids with TBC plasticizer. The brown areas on the surface of polymer samples are connected with living organisms in sea water, especially with the development of psychrotrophic bacteria<sup>21</sup>. The longer incubation time in sea water resulted in the bigger amount of brown areas on the samples surface.

The changes of surface morphology of the examined samples are shown in Fig. 2. The slight changes of the surface morphology were observed for the cellulose acetate butyrate. In contrast, CAB/silica hybrids showed the more distinct changes of surface morphology. We observed the correlation between the degree of degradation and the



**Figure 1.** Macroscopic observations of CAB samples surface

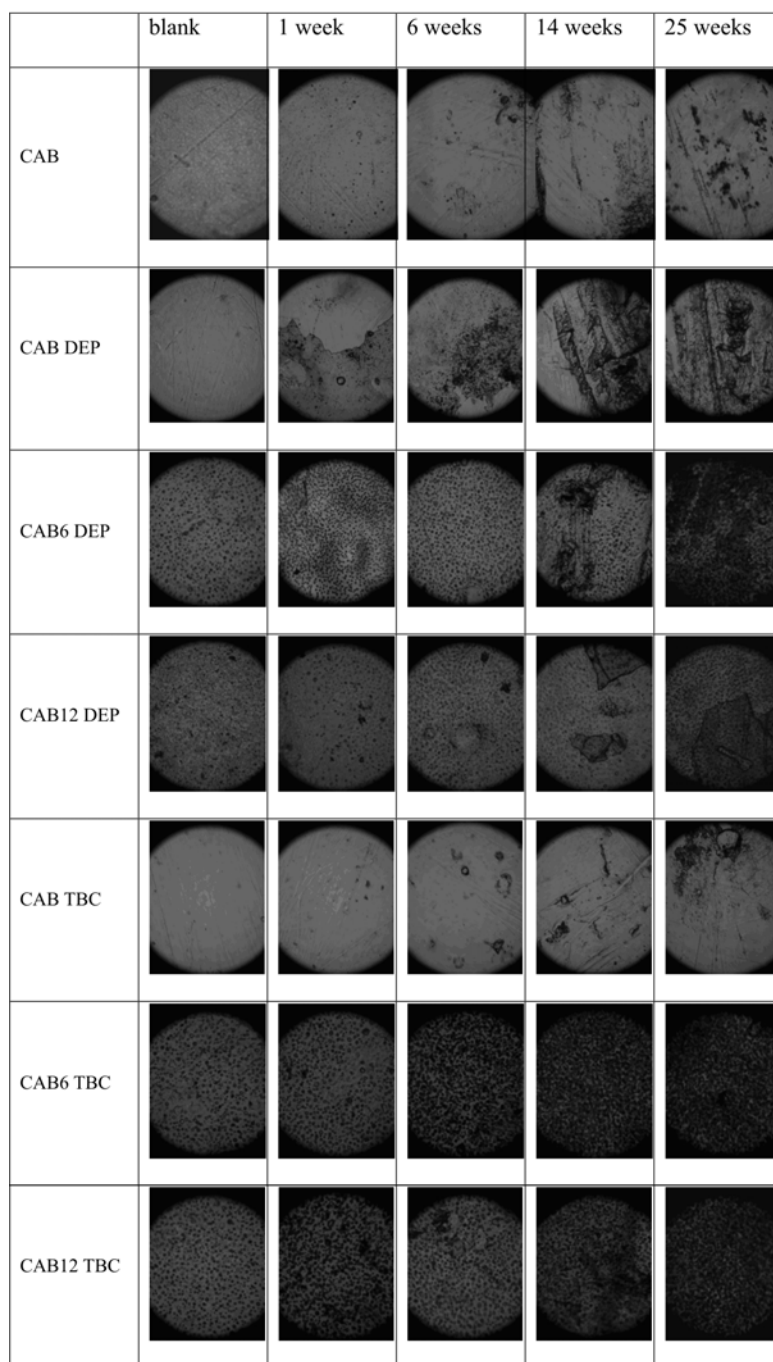
amount of inorganic phase introduced into CAB matrix. The changes of surface morphology of CAB samples obtained with DEP were also more visible than for the samples with TBC. The dark places observed on the micrographs of the samples after the incubation in the Baltic Sea are connected with the presence of microorganisms from the microbiological active environment of the sea water<sup>22</sup>.

Figure 3 shows the periodical changes in the weight loss of the CAB sample films after the incubation in the sea water as a function of the incubation time.

The observation of the samples was confirmed by the results of their weight changes. The results of the degradation experiment showed that the organic-inorganic hybrids are more susceptible to environment conditions of the Baltic Sea than the pure cellulose acetate butyrate. The weight loss of pure CAB during the whole incubation time was not very significant (1.9%) which is due to the chemical structure of this polymer. The degradation rate of CAB is slow because the substituents on the CAB (acetyl and butyryl groups) and steric hindrance prevent the microorganisms from destroying macrochains of cel-

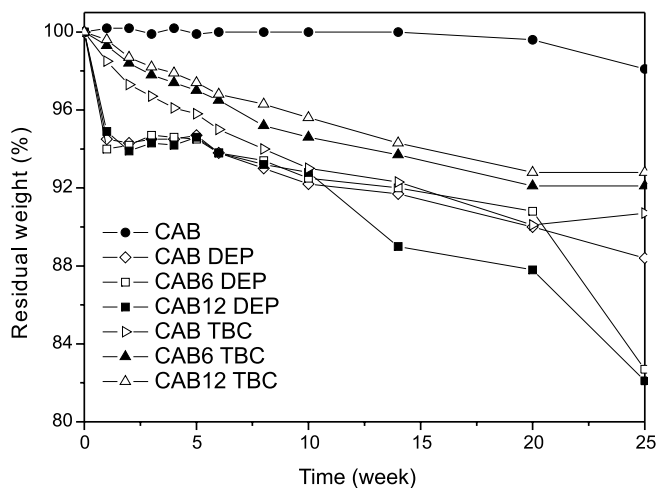
lulose. The same behaviour was also observed by Wang and co-workers<sup>6</sup>.

In our experiment the CAB samples behaved in a particular mode, depending on the amount of the inorganic phase incorporated into polymer matrix and on the type and amount of the plasticizer. In the hybrids with DEP plasticizer, the degradation process was proportional to the silica content (after 20 weeks of incubation CAB6 DEP= 9.2%; CAB12 DEP=12.2%), but in the hybrids with TBC plasticizer we do not observe the same tendency (CAB6 TBC=7.9%; CAB12 TBC=7.2%). The degradation dynamics and weight changes of samples with DEP plasticizer (CAB DEP, CAB6 DEP, CAB12 DEP) were more visible than for the samples with TBC plasticizer (CAB TBC, CAB6 TBC, CAB 12TBC). In the beginning, after 1 week of incubation in seawater, the decrease of weight for all CAB samples with DEP was very fast (CAB6 DEP=6%; CAB12 DEP=5.1%), followed by almost constant value (CAB6 DEP=5.4%; CAB12 DEP=5.8%) for the next 4 weeks. After 25 weeks of incubation in sea water organic-inorganic hybrids CAB6 DEP and CAB12 DEP lost respectively 17.3% and 17.9%

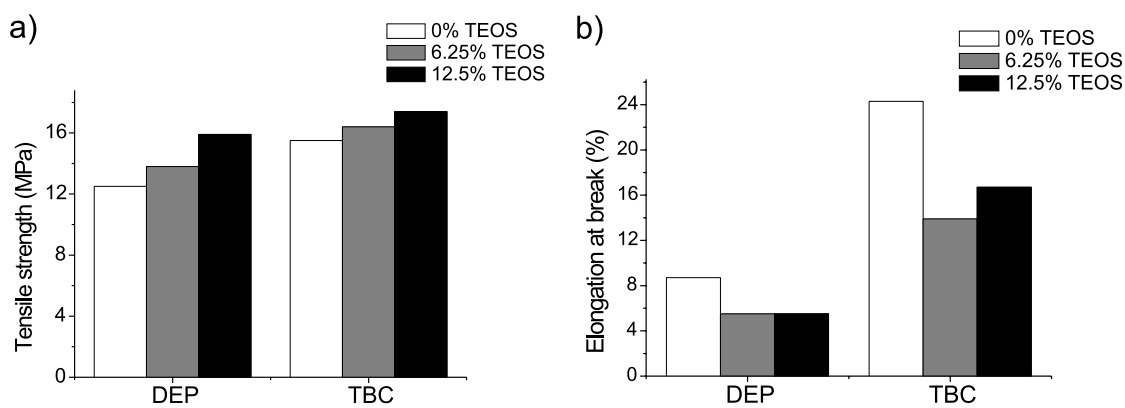


**Figure 2.** Microscopic observations of the CAB samples surface

of its weight, while CAB DEP sample (without silica) only 11.6%. Investigation of the degradability of the CAB samples with TBC revealed slow, almost with the constant rate weight changes during the whole time of the experiment. The highest weight loss was observed for CAB TBC hybrid (9.3%), while CAB6 TBC and CAB12 TBC were degraded in 7.9% and 7.2%, respectively. The obtained results showed that both silica and the plasticizer play important roles in the degradation process of the samples. The addition of plasticizers to the pure CAB induces bigger changes in weight loss. This effect is amplified by the introduction of the inorganic phase into polymer matrix. Interestingly, the weight loss of the samples with DEP was more significant than of the samples with biodegradable TBC. We assume that this is due to the better plasticizing effectiveness of TBC (Fig. 4). The samples with DEP are more brittle and have higher tendency to



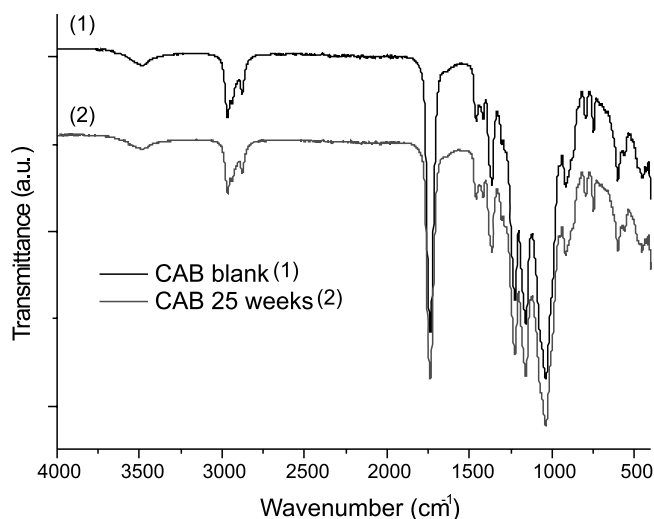
**Figure 3.** Weight losses of CAB, CAB DEP, CAB TBC and CAB/silica hybrids during the degradation process in the sea water



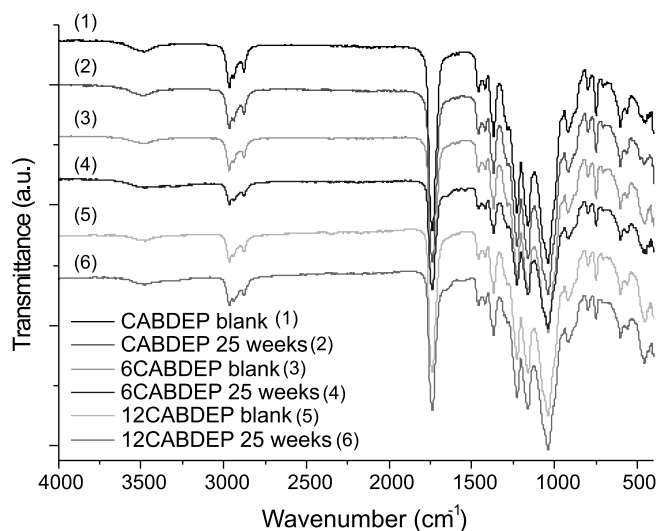
**Figure 4.** Comparison of mechanical properties of CAB and CAB/silica hybrids with DEP and TBC plasticizers

crack than the samples with TBC. Therefore, the higher weight losses of the DEP samples during the experiment in the dynamic sea water might also be induced by mechanical stress due to the natural movement of water. Hybrids with TBC show similar tensile strength to the samples with DEP, however the elongation at break is significantly higher in the case of TBC plasticized hybrids. Figure 4 shows the mechanical properties (tensile strength and elongation at break) of CAB and CAB/silica hybrids obtained with various amount of TEOS and two kinds of plasticizers: DEP and TBC. Taking into consideration these results and the observed weight changes we can conclude that the bigger stiffness and brittleness of the hybrids the higher weight loss during experiment. The results revealed also a synergistic effect of the silica phase which hinder the plastic flow and causes hardening and reinforcing of the polymer.

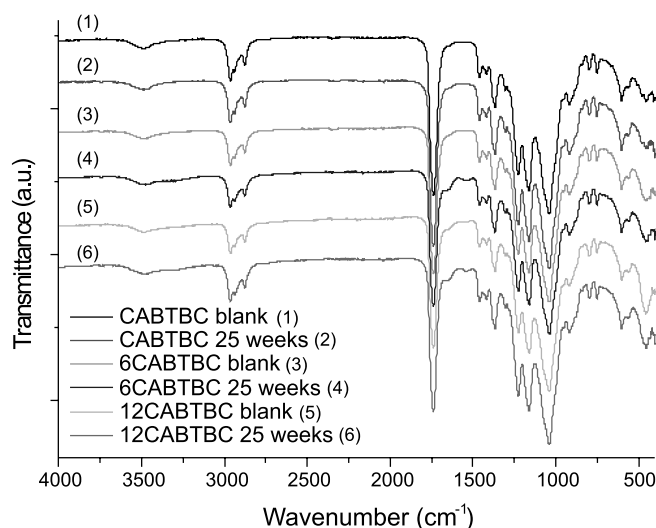
The analysis of ATR-FTIR spectra of the samples (Fig. 5–7) revealed practically no changes of the main bands ( $1750\text{ cm}^{-1}$  (C=O),  $1230\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$  (C-O-C),  $3500\text{ cm}^{-1}$  (OH) and  $1050\text{ cm}^{-1}$  (stretching mode from the polymer backbone)) during the incubation period for pure CAB, as well for all the organic-inorganic hybrids. This is due to the unchanged chemical structure of polymer, a major component of all CAB-hybrids, whose degradation is slow. These results indicate that enzymatic processes predominantly take place in the environmental degradation. The enzymatic degradation is only related to



**Figure 5.** The ATR-FTIR spectra of CAB samples before and after the incubation in the sea water



**Figure 6.** The ATR-FTIR spectra of CABDEP samples before and after the incubation in the sea water



**Figure 7.** The ATR-FTIR spectra of CABTBC samples before and after the incubation in the sea water

the changes of polymer surface and weight losses. The FT-IR data are in agreement with other results and confirmed that for the incubation period of 25 weeks the main role in environment degradation of CAB-hybrids play the amount of inorganic phase and type of the plasticizer introduced in the polymer matrix.

## CONCLUSIONS

The results of this study indicate that the organic-inorganic hybrids based on cellulose acetate butyrate are more susceptible to degradation in natural sea water environment than the pure polymer. The higher the amount of silica incorporated into the CAB with the DEP plasticizer, the higher degradability of the samples. The experiment also showed a synergistic effect of the applied plasticizer on the degradation rate of the CAB/silica hybrids. The CAB/silica hybrids with diethyl phthalate were degraded faster than the hybrids with tributyl citrate due to the higher brittleness of those samples.

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