

## Biodegradation Paths of Mater-Bi<sup>®</sup>/Kenaf Biodegradable Composites

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**ABSTRACT:** Composites obtained from biodegradable polymers and natural–organic fillers are attracting increasing interest, thanks to the environmental advantages they promise. On the other hand, the real biodegradation performance of a biodegradable polymer/natural organic filler composite should be assessed by performing specific biodegradation tests. These are often carried out under laboratory conditions, but more realistic conditions should be taken into account. In this work, a systematic study on the biodegradation of kenaf fiber-filled Mater-Bi<sup>®</sup> composites in different environments is presented, and some interesting parameters for the understanding of the optimum way to obtain a fast degradation of the composites can be extrapolated. In particular, it was found that the presence of the fibers, the environmental conditions, and the manufacturing procedures of the composites can significantly affect the biodegradation behavior. The results can be used to determine the most suitable disposal environments for biodegradation of Mater-Bi<sup>®</sup>-based wastes. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3198–3208, 2013

**KEYWORDS:** biodegradable; composites; degradation; morphology

Received 5 September 2012; accepted 14 January 2013; published online 20 February 2013

**DOI:** 10.1002/app.39027

### INTRODUCTION

Over the last years, there is a growing interest toward raw materials obtained from renewable sources and/or biodegradable, mainly owing to the rising concern about the preservation of natural resources and recycling. The production and the use of plastic materials increase the problems regarding waste disposal because of their environmental stability. Use and eventual disposal of traditional composite structures, typically made of non-biodegradable plastics reinforced with inorganic fibers, are considered critically because of the increasing environmental consciousness and the requirements from legislative authorities to abide by.

Industrial and research efforts, therefore, have been devoted to the development of polymers that can degrade rapidly after disposal. These materials can be an interesting alternative to the traditional nonbiodegradable polymers, especially when their recycling is difficult or not economical.

According to the literature, biodegradable polymers (either synthetic or natural) such as polyesters, poly(ester amide)s, poly(vinyl alcohol), poly(lactic acid), polyhydroxyalkanoates, starch and starch derivatives, and cellulose have been investigated for the production of composites containing natural–organic fillers.<sup>1–4</sup>

Novamont's Mater-Bi<sup>®</sup>, for instance, is a class of biodegradable polymers usually based on the modified starch and synthetic polymers (such as aliphatic polyesters).<sup>4–6</sup> Mater-Bi<sup>®</sup> and its related composites can find important commercial application as they show interesting mechanical properties, thermal stability, processability, and biodegradability, as reported in many articles from the literature.<sup>6–15</sup>

Several advantages are associated with the use of natural fibers, including low cost, relative abundance, low density, high specific properties, and lack of hazardous residues upon incineration.<sup>16–20</sup> Bast fibers, such as hemp, jute, flax, kenaf, and sisal, are most commonly used as reinforcement in polymer matrix composites and for industrial applications.<sup>21</sup>

Kenaf (*Hibiscus cannabinus* L., family Malvaceae) is an annual, productive source for cellulosic fibers: in 3 months (after sowing the seeds) it can grow (up to 10 cm/day under optimum ambient conditions),<sup>22</sup> reaching a height of more than 3 m and a base diameter of 3–5 cm, under a wide range of weather conditions.<sup>23,24</sup> Furthermore, it takes 15 MJ of energy to produce 1 kg of kenaf, whereas it takes 54 MJ to produce 1 kg of glass fiber,<sup>22</sup> and thus giving a significant environmental advantage in terms of energy consumption. The bark of this plant shows a

rather dense structure and it constitutes approximately 30–40% of the stem dry weight, showing an orientated high crystalline fiber pattern. The core is wood-like and makes up the remaining 60–70% of the stem,<sup>25</sup> revealing an isotropic and almost amorphous pattern. On average, natural fibers, including kenaf fibers, contain 60–80% cellulose, 5–20% lignin (pectin), and up to 20% moisture.<sup>26–29</sup>

Kenaf absorbs nitrogen and phosphorus from the soil (average absorption rate for kenaf is 0.81 g/m<sup>2</sup>/day for nitrogen and 0.11 g/m<sup>2</sup>/day for phosphorus) and accumulates carbon dioxide at a significantly high rate as the photosynthesis rate of kenaf is much higher than those of conventional trees.<sup>22,30</sup> For these reasons, kenaf has been actively cultivated in recent years.<sup>31</sup> Recently, kenaf has been used as an alternative raw material in place of wood to provide an alternative to limit the continuous destruction of forests. It has also been used to make nonwoven mats for the automotive industry, as well as textiles.<sup>32</sup> A single fiber of kenaf can show a tensile strength as high as 11.9 GPa, and an elastic modulus of approximately 60 GPa.<sup>33</sup> Because of its superior toughness and high aspect ratio in comparison to other fibers, kenaf bast fiber is known to have a good potential as a reinforcing fiber for thermoplastic composites.<sup>34–37</sup>

Thus, the combination of natural fibers with biodegradable polymers offers an answer to the search for sustainable development and cost-effective solutions for several applications.

The effect of starch in promoting the biodegradation of Mater-Bi<sup>®</sup> during composting was reported by Bastioli.<sup>6</sup> Degradation of Mater-Bi<sup>®</sup> in different environments, such as natural sea and active sewage sludge, was investigated by Rutkowska et al.,<sup>38,39</sup> finding a complete destruction of the samples after 4 weeks of direct exposure to the natural environment. Di Franco et al.<sup>4</sup> studied the biodegradation of Mater-Bi<sup>®</sup> Z/sisal composites buried in soil and in biotic aqueous medium. Alvarez et al.<sup>40</sup> found that Mater-Bi<sup>®</sup> Y/sisal fiber composites showed a reduced water sorption in comparison with the pure polymer after indoor burial tests. The less hydrophilic tendency of fibers (if compared to starch) and their interactions with the matrix could explain this behavior.

However, as regards the biodegradation of Mater-Bi<sup>®</sup>/natural organic filler composites in different environments from those listed above, just a few data are available in the scientific literature.

In a previous study, we investigated the influence of processing method, filler presence, matrix pretreatment, and actual environment conditions (winter and summer) on the biodegradation of Mater-Bi<sup>®</sup>/wood flour composites in a specific environment (wastewater treatment plant).<sup>41</sup>

The aim of this study was to investigate and compare the biodegradability of kenaf/Mater-Bi<sup>®</sup> composites after disposal in different environments, such as wastewater treatment plants and landfill, as well as laboratory conditions.

## EXPERIMENTAL

### Materials

The material used in this study is a Mater-Bi “TF” grade, kindly supplied by Novamont (Italy). Its actual composition is proprie-

tary; however, it is known that it belongs to the recent family of vegetable-oil-based Mater-Bi biodegradable polymers. Its measured melt flow index is 46 g/10 min (at  $T = 150^{\circ}\text{C}$  and under 5 kg load).

The polymer matrix was used in humid (“PT1,” i.e., as received) or dry state (“PT2,” pretreated for 10 h in vacuum oven at  $T = 60^{\circ}\text{C}$ ).

Kenaf fibers were supplied by K.E.F.I. (Italy) and cut at approximately 5-cm length before processing. The average  $L/D$  ratio was approximately 710.<sup>15</sup> The fibers were basically used under “as-received” conditions, with no specific, previous chemical treatment to assess their behavior under these processing conditions (more likely to be adopted in the industrial manufacturing processes). Physical treatments prior to processing included drying the fibers in a ventilated oven at  $70^{\circ}\text{C}$  for 10 h.

### Preparation and Processing

The preparation of composite materials filled with kenaf fibers was performed using a Brabender (Germany) PLE 300 batch mixer, fitted with two counter-rotating cams and a chamber of 50 cm<sup>3</sup>, operating at  $T = 140^{\circ}\text{C}$  and  $v = 30$  rpm (up to reaching a constant value of the torque). These conditions were chosen on the basis of the previous studies.<sup>5</sup> The composites were prepared at 15 wt % filler content. Mixing was performed up to reaching constant torque, after which the mixer shafts were stopped and the material was taken.

The specimens for the following characterizations were obtained by compression molding, using a Carver (USA) laboratory press ( $T = 140^{\circ}\text{C}$ , residence time = 4 min) and by cutting them off the compression-molded plates (thickness, 0.5–1.3 mm, width 10 mm, and length 90 mm). To estimate the influence of surface roughness, same samples were prepared either with Teflon or with paper sheets as antisticking medium between the materials and the molding plates.

### Biodegradation

#### Degradation in Active Sewage Sludge Reactor

Biodegradation tests were based on the weight loss measurements, performed on the above-described samples, after immersion in an active sewage sludge reactor (part of an urban wastewater treatment plant, and classifiable as a plug-flow reactor), choosing a time scale up to 16 weeks.<sup>39</sup>

The main processing parameters of the water treatment plant are reported in the previous study.<sup>41</sup>

In particular, it can be stated that the pH is almost the same during both summer and winter, but the other parameters show some difference upon changing the season. Nevertheless, inside each testing period, the overall biodegradation conditions can be considered sufficiently homogeneous. These test conditions are interesting as active sewage sludge typically contains a heterogeneous population of bacteria which are responsible for the consumption of organic matter for their metabolism.<sup>40</sup>

Prior to immersion, all the samples were subjected to a mild drying in vacuum oven at  $60^{\circ}\text{C}$  for 20 h and then immediately weighed and their average surface roughness ( $R_a$ ) was measured using a Zeiss (Germany) Handysurf E-35A surface measuring

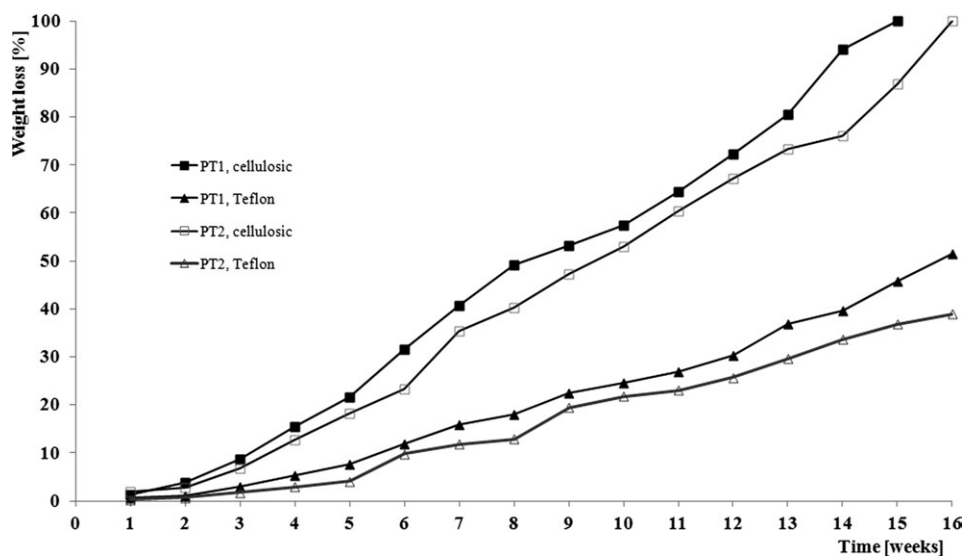


Figure 1. Weight loss as a function of immersion time, summer conditions (kenaf composites).

station, according to the methods described elsewhere.<sup>41,42</sup> In particular, every 7 days, selected samples of each preparation were removed from their supports, washed with tap water, and then with distilled water. After sterilization, using a CaMi (Italy) Violet germicide UV lamp (18 W, radiation wavelength 253.7 nm, exposure time about 20 min), the samples were stored in

vacuum oven at 60°C for 20 h, and finally weighed, calculating the percent weight variation, WL, according to the formula:

$$WL(\%) = 100(W_t - W_0)/W_0$$

where  $W_t$  is the weight at time  $t$  and  $W_0$  is the initial weight.

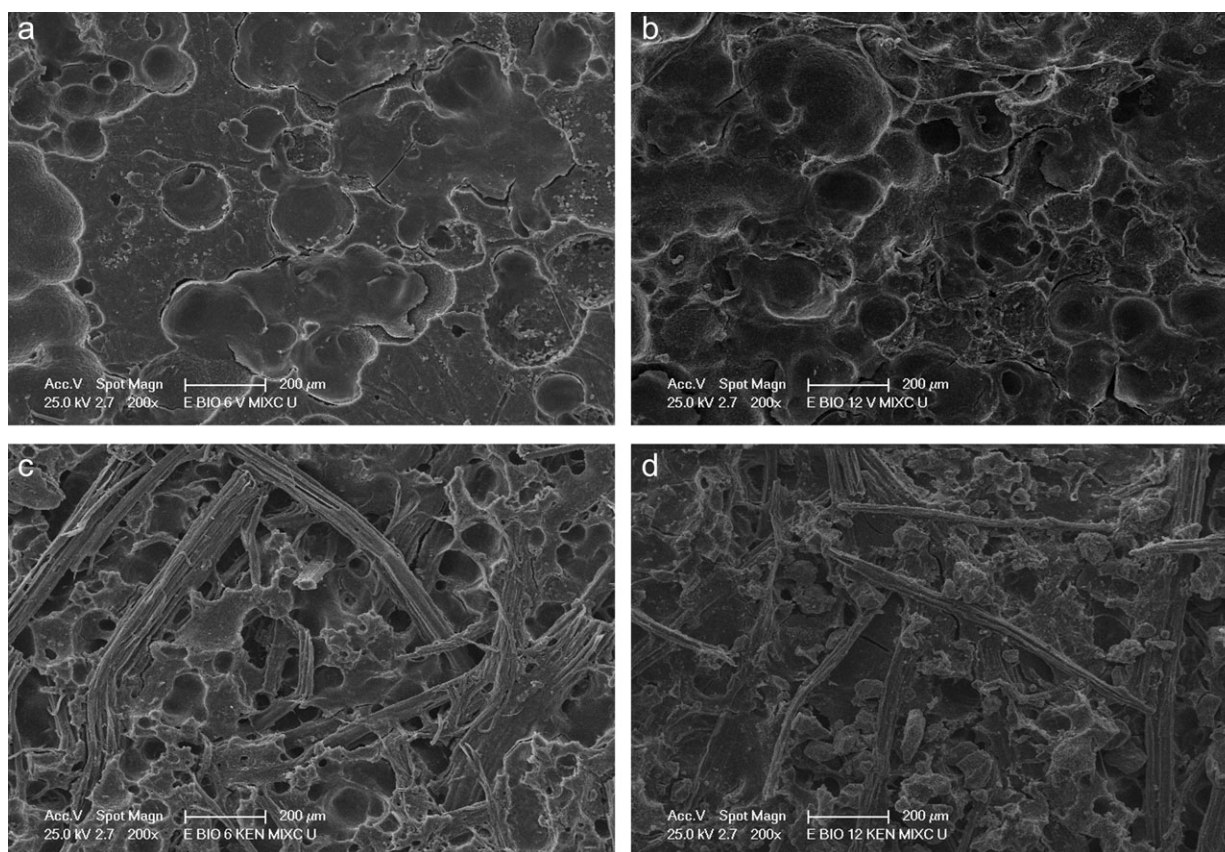


Figure 2. Neat polymer (a, b) and composite (c, d) after 6- and 12-week immersion, respectively.



**Table I.** Surface Roughness of Samples Before Immersion

	Neat polymer	15 wt % Kenaf composite
Surface roughness ( $\mu\text{m}$ ), paper sheet	2.6	2.8
Surface roughness ( $\mu\text{m}$ ), Teflon sheet	0.1	0.3

After weighing, the samples were stored in a refrigerator at 20°C to freeze any bacterial activity before subjecting them to morphological analysis, performed with a Philips (The Netherlands) ESEM XL30 apparatus. Meanwhile, a sample of each system was immersed in distilled water for the same duration of the investigated samples. Their weight variations were measured weekly and taken as calibration values to properly evaluate the weight losses of the materials immersed in active sludge. It was found that the weight loss of these calibration samples was always below 1%, and therefore the weight loss observed for the materials immersed in activated sludge can be attributed to the bacterial activity only.

All the tests were performed twice, both during summer and winter, to assess the influence of the environmental conditions. According to the meteorological observations of the period,<sup>41</sup> the estimated average temperature in the summer conditions was 25°C, whereas during the winter it was 12°C, with average relative humidity ranging from 69% (summer) to 73% (winter).

Single deviations were not reported in the figures for the sake of clarity and easier readability of the results. Each data point was the average of seven samples. The data reproducibility was fair, ranging from 5% (winter conditions) to 9% (summer conditions).

#### Degradation in Compost

Biodegradation in compost was performed on compression-molded samples, prepared as described previously by putting them into contact with compost supplied by AMAP S.p.A. (Italy), made of sludge from wastewater treatment plants, wood chips, green clippings, dried leaves, and straw, keeping a relative humidity of approximately 50–70%. About 35–40 samples of each material were vertically buried at 4–6 cm depth to guarantee aerobic degradation conditions at a horizontal distance of 5–6 cm between samples. At selected times, three to four samples of each material were washed with water and dried in vacuum oven at 60°C for 20 h till a constant weight was achieved. Based on the sample weight before and after degradation, the average percent weight loss was calculated. As in the previous characterization, each data point was the average of seven samples, whereas the estimated experimental error was  $\pm 5\%$ .

**Table II.** Surface Roughness of Composite Samples Before Immersion

	PT1 composite	PT2 composite
Surface roughness ( $\mu\text{m}$ )	2.8	2.7

**Table III.** Comparison Between Surface Roughness Upon Using Different Antiadherent Media During Compression Molding

	PT1 composite, cellulosic	PT1 composite, Teflon
Surface roughness ( $\mu\text{m}$ )	2.8	0.3

#### *In Vitro* Microbial Degradation

To evaluate the difference between plug-flow sewage treatment reactor, compost and *in vitro* conditions, a sample of the bacterial microflora of the real plant, was taken and inoculated in M9 medium according to the procedures described elsewhere.<sup>43,44</sup>

In particular, 10 mL of inoculated M9 medium was dissolved in 90 mL of sterile physiological solution (NaCl, 0.9%). Serial dilutions were made with sterile solution and aliquots of all samples were plated for microbial growth by using the spread plate method, distributing 0.1 mL of dilutions directly over the plate's surfaces.

The samples of Mater-Bi and its composites were sterilized under UV light (as described previously), put in the middle of Petri dishes, and contaminated with the pure cultures.

For the contamination, each pure culture was previously grown in 10 mL of liquid medium (Nutrient Broth); then, 20 mL of the same medium, with an agar concentration of 30 g/L, was added to obtain an agar final concentration of 20 g/L and finally poured into Petri dishes. Samples were taken to 37°C to favor the growth of microorganisms and verify whether polymer biodegradation occurred. A sterile control was performed to verify if the degradation was owing only to microorganism activity. The polymer samples were sterilized under UV light, put in the middle of Petri dishes without any inoculum, and incubated in the same conditions as above. After predetermined period of microbial degradation, the samples were washed with distilled water and dried in vacuum oven at 60°C for 20 h to constant weight, to quantitatively evaluate the level of sample degradation by weight loss measurements and scanning electron microscopy (SEM) analysis. The same procedure was carried out for each selected period of degradation. As in the previous characterization, each data point was the average of seven samples, whereas the estimated experimental error was  $\pm 4\%$ .

## RESULTS AND DISCUSSION

### Active Sewage Sludge

It is important to analyze the results separately for winter and summer conditions. This is owing to the bacterial metabolism and species distribution being dependent on the surrounding temperature,<sup>41,45</sup> which is significantly different from the summer to the winter conditions, as better described in the EXPERIMENTAL section.

### Summer

Figure 1 shows the curves of percent weight loss of the composites as a function of the immersion time in the active sewage sludge, for PT1 and PT2 samples. The curves directly compare the samples which were prepared by compression molding using

**Table IV.** Comparison of Weight Losses and Induction Times

	PT1 composite, cellulosic	PT1 composite, Teflon	PT2 composite, cellulosic	PT2 composite, Teflon
Weight loss (%)	100 <sup>a</sup>	52	97	39
Induction time (weeks)	3.1	5.6	3.5	6

<sup>a</sup>After 15 weeks.

cellulosic (paper) or Teflon-made sheets, and thus the effects of their surface smoothness.

In our previous study,<sup>41</sup> we had already determined the weight loss of the neat, unfilled polymer as a function of the immersion time. In particular, the weight losses for the PT1 samples were approximately 10, 25, 55, and 70% after 4, 8, 12, and 16 weeks of immersion time, respectively; for the PT2 samples, they were approximately 5, 30, 50, and 70%, respectively. These results can be directly compared with the weight loss curves of PT1-cellulosic and PT2-cellulosic as shown in Figures 1 and 2, respectively. It can be clearly observed that the biodegradation rates of the composites are significantly higher than those of the neat polymer, in agreement with the results found for wood flour-filled composites<sup>41</sup> and by other researchers on similar systems.<sup>4,40</sup> This can be attributed to several factors.

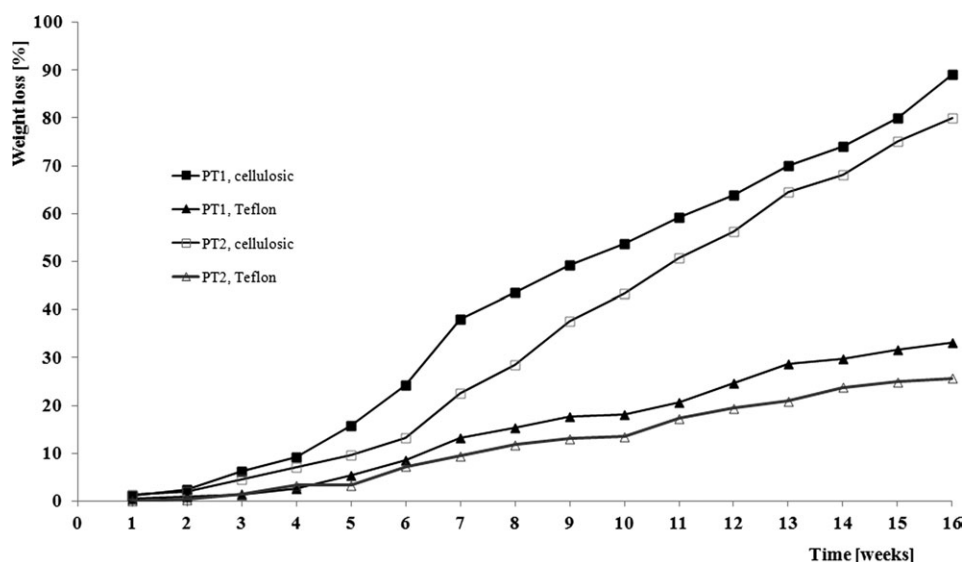
The first factor to be taken into account is the surface roughness of the samples. The measured surface roughness for the neat polymer was lower than that of the composite as summarized in Table I: the higher surface roughness of the composite is able to provide more sites where the bacterial colonies can settle and proliferate.

Another factor which can explain the significantly higher degradation rates in the composites is related to the action that the fibers themselves can provide as support for the bacterial

growth.<sup>4,40</sup> Other factors which can account for this behavior are the presence of defects and voids at the interface between the polymer matrix and the fiber.

Furthermore, this aspect gains increasing importance upon increasing the immersion time, as the progressive leaching of the biodegradable components of the polymer and the cellulose chain breakdown in the fibers gradually increase the number of paths and physical support the bacteria can rely on while performing their degradation action. All of this was confirmed by SEM analysis, as clearly observable by comparing Figure 2(a,b) (showing neat Mater-Bi after 6 and 12 weeks, respectively) with Figure 2(c,d) (showing 15 wt % composite after 6 and 12 weeks).

Another important result is that the PT2 treatment (i.e., the thermal pretreatment of the polymer matrix prior to processing) significantly slows down the overall biodegradation kinetics. In particular, it was found that the PT1 composites achieve complete biodegradation after 15 weeks, whereas PT2 ones showed about 97% after 16 weeks. This is further proved by the increase of the induction time (defined as the immersion time corresponding to a 10% weight decrease), which was about 3.1 weeks for the PT1 samples and 3.5 weeks for the PT2 ones. Also in this case, an explanation can be found considering the surface roughness of PT1 and PT2 samples as summarized in Table II.

**Figure 3.** Weight loss as a function of immersion time, winter conditions (kenaf composites).

**Table V.** Comparison Between Weight Losses, Summer and Winter Conditions

	4 Weeks	8 Weeks	12 Weeks
PT1 (cellulosic) summer (%)	16	49	72
PT1 (cellulosic) winter (%)	9	44	64
PT2 (cellulosic) summer (%)	13	40	67
PT2 (cellulosic) winter (%)	7	28	56

The experimental data point out a slightly reduced surface roughness of the PT2 samples in comparison to the PT1 ones. This can, at least partially, account for the higher resistance of the PT2 samples to biodegradation. In addition, it can be observed that the higher humidity can favor the bacteria attachment and penetration inside the sample.

The role of surface morphology is also fundamental to explain the different results found for the samples prepared by using cellulosic or Teflon sheets during compression molding. The average surface roughness measured for PT1 samples compressed with the aid of cellulosic or Teflon sheets, respectively, as summarized in Table III.

The reported results unquestionably show that the surface smoothness of the Teflon-prepared samples is much higher than that of the cellulosic-prepared ones. The reduced presence of surface irregularities where the bacteria can adhere, settle, and proliferate has thus significantly affected the biodegradability of the obtained composites, both in terms of weight loss after 16 weeks and in terms of induction time as summarized in Table IV.

### Winter

Figure 3 shows the curves of percent weight loss of the composites as a function of the immersion time in active sewage sludge, for PT1 and PT2 samples, either prepared with Teflon-based or with cellulosic-based antiadherent sheets.

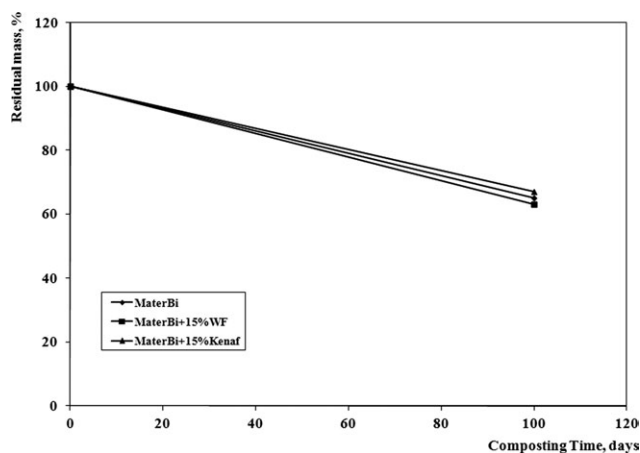
First, the results must be discussed with comparison to those of the neat polymer in the same season.

In our previous study,<sup>41</sup> the weight losses for the PT1 samples were found to be approximately 5, 17, 34, and 47% after 4, 8, 12, and 16 weeks of immersion time, respectively; for the PT2 samples, it was approximately 4, 17, 28, and 39%, respectively. The comparison with the trend observed for the composites (Figures 1 and 3) shows, once more, a considerably increased weight loss.

Of course, similar considerations as in the summer conditions can be done, with concern to the effects that the average surface roughness has on the overall biodegradation kinetics. This regards, once more, the direct comparison between composites and neat polymer, PT1, and PT2 treatment, Teflon, or cellu-

**Table VI.** Comparison Between Induction Times, Summer and Winter Conditions

	PT1 composite (cellulosic) summer	PT1 composite (cellulosic) winter	PT2 composite (cellulosic) summer	PT2 composite (cellulosic) winter
Induction time (weeks)	3.1	4.1	3.5	5.1



**Figure 4.** Residual mass of different samples as a function of the composting time.

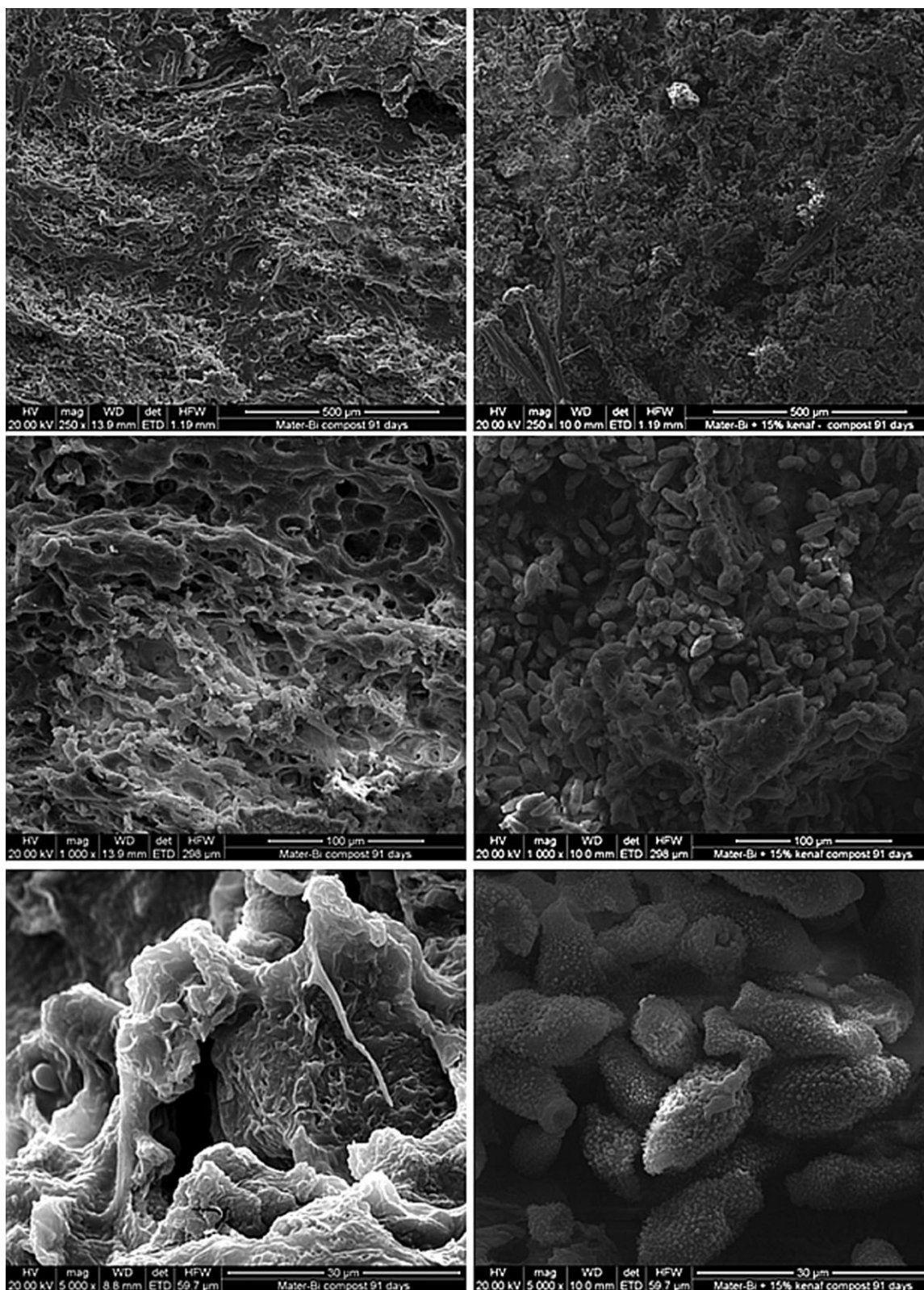
losic-sheet-compressed samples. The conclusions which can be drawn are absolutely analogous to those previously done as the comparison between the surface roughness of the various samples is obviously independent on the season.

Further discussion can be done with concern to the comparison between winter and summer conditions. The differences between the weight losses at specified time are more clearly summarized in Table V.

The results point out that, as expectable, there is a reduction of the weight losses at fixed time, and thus of the biodegradation kinetics, from summer to winter conditions. This is a direct consequence of the environmental temperature, which is estimated to be approximately 25°C in summer and 12°C in winter (average values)<sup>41</sup> and, in turn, exerts a significant influence on the bacterial activity. However, it is needful to take into account that the bacterial population change by changing the environmental conditions, especially after temperature variations. However, it is worth noting that this influence shows to be a main inhibition of the bacterial metabolism during the first stages of immersion, as demonstrated by the weight loss values after 4 weeks which are, in summer conditions, almost twice as much as in winter. On the other hand, once that the bacterial population has gone beyond these first stages and got into more steady conditions, the differences between summer and winter are considerably reduced, being not higher than 10% at 12 weeks. This is even clearer by comparing the induction times (Table VI). The inhibiting effect of the winter environmental temperatures leads to induction times which are higher from 32 to 46%.

Finally, some considerations may be done regarding the different behaviors of kenaf-filled and wood-filled composites (investigated in our previous study). It can be stated that, on average, the biodegradation rates (under comparable conditions) are



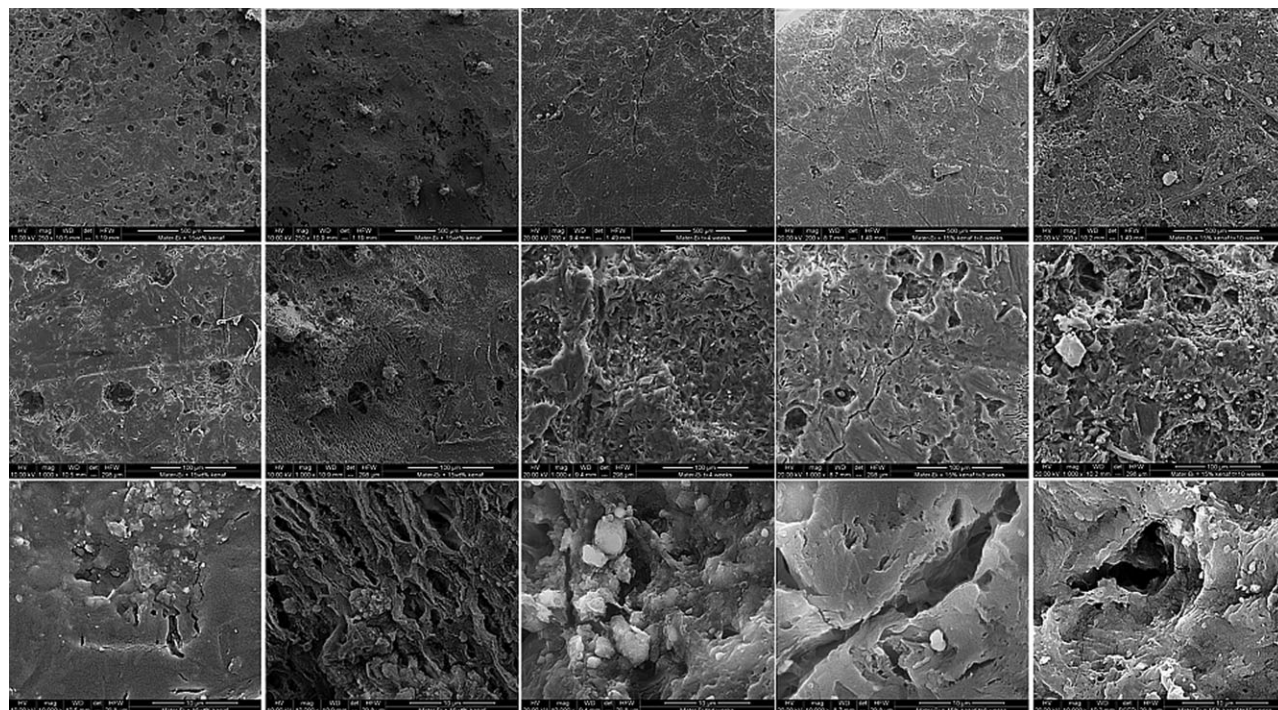


**Figure 5.** Neat Mater-Bi (left) and composite (right), after 91 days under compost conditions (different magnifications).

significantly higher in the kenaf-filled rather than in the wood-filled ones. Explanations for this result might be found in the higher *L/D* ratio of the kenaf fibers<sup>15</sup> and especially to the dif-

ferent cellulose, hemicellulose, and lignin content. Literature reports, in fact, indicate that lignin content in kenaf bast fibers is significantly lower than in wood fibers from European beech



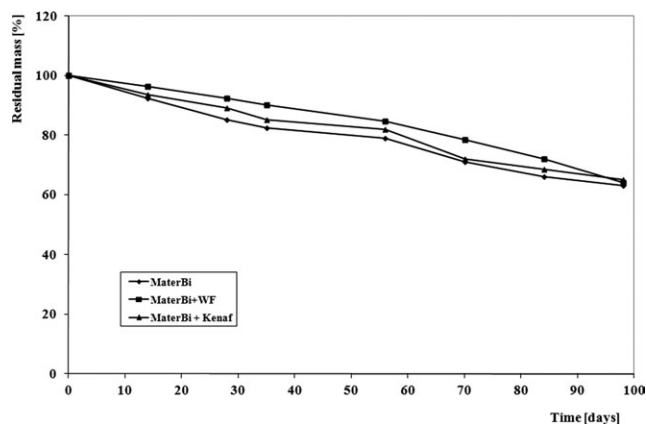


**Figure 6.** Evolution of the morphology of the composites, at increasing composting time (from left to right), at different magnifications.

(as those used in our study).<sup>33,46</sup> It is also known from the literature that lignin degradation is very difficult owing to its structural complexity, high molecular weight, and its insolubility<sup>47</sup>; therefore, it can be concluded that the higher lignin content of beech wood fibers in comparison to kenaf bast fibers can account for the different biodegradation rates observed.

### Composting

Figure 4 shows the residual mass of the investigated materials upon performing 98 days of composting. The neat Mater-Bi was compared with the composite at 15 wt % kenaf content and the results were compared with a reference composite containing 15 wt % of wood flour. After 98 days of composting, the reduction of weight owing to biodegradation is almost the same in all of the three materials, and therefore the important result is that the



**Figure 7.** Residual mass of different samples upon increasing the *in vitro* conditioning time.

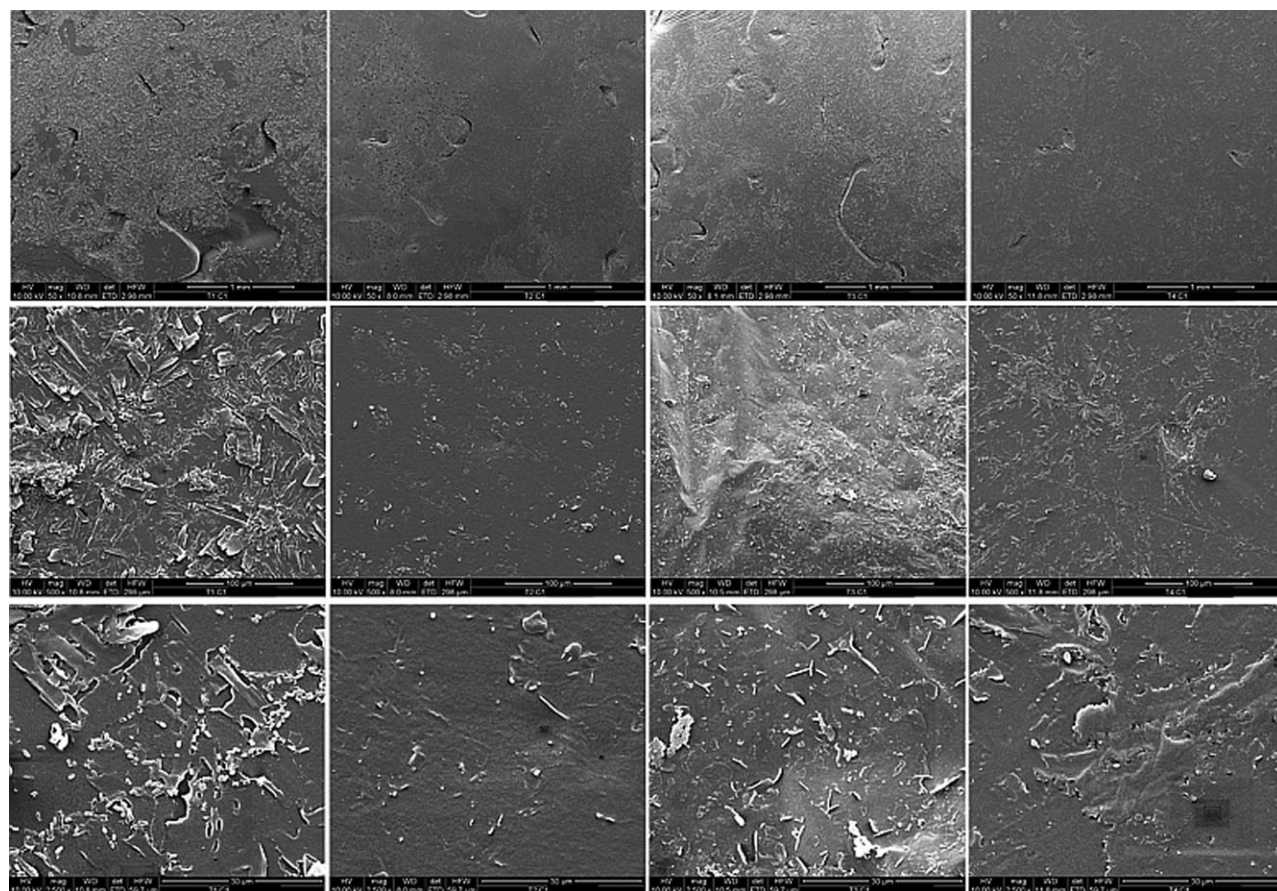
presence of natural fibers (wood or kenaf, regardless of their different lignin contents) does not significantly affect the biodegradability of the neat polymer under composting conditions (within the time frame of the investigation), in contrast with the behavior observed under active sewage sludge immersion conditions. Therefore, the well-known compostability of Mater-Bi is not significantly altered by the presence of natural–organic fibers. This may be owing to the fact that, under composting conditions, the bacterial rooting onto the natural fibers is hampered in comparison to active sewage sludge conditions, where the intense turbulence could foster it.

Figure 5 shows the direct comparison between neat Mater-Bi and kenaf composites after 91 days in compost conditions. In particular, each row shows the Mater-Bi sample (left) and the Mater-Bi/kenaf composite (right), at increasing magnification from the upper to the lower row. It can be observed that, although the morphology is basically different, the overall degree of bacterial attack (see upper row) is comparable, in agreement with the weight loss measurements. However, composite morphologies show evidence of bacteria on the surface, clearly visible at higher magnification (micrograph on the bottom corner), providing a further proof that natural fibers can promote bacterial adhesion on the composite sample.

Furthermore, aggregates on the surface sample can be identified with a bacterial morphology typical of Staphylococci. The high extracellular lignocellulolytic activity showed by this kind of bacteria has been already reported by other authors, supported by exoglucanase enzymes activity essay.<sup>48</sup>

Figure 6 shows how the morphology in the composites evolves, upon increasing the composting time (from 2 to 10 weeks, from the left to the right), at different magnifications (increasing





**Figure 8.** Evolution of the morphology of the neat polymer, at increasing *in vitro* degradation time (from left to right), at increasing magnifications (from top to bottom).

magnification from the upper to the lower row). Morphological analysis shows that the degradation increases as the composting time increases, in agreement with the previous analysis. This further shows that the bacterial attack involves both the matrix and the kenaf fibers. This can be better seen in the lower row, which shows the morphology at higher magnification.

#### ***In Vitro* Biodegradation**

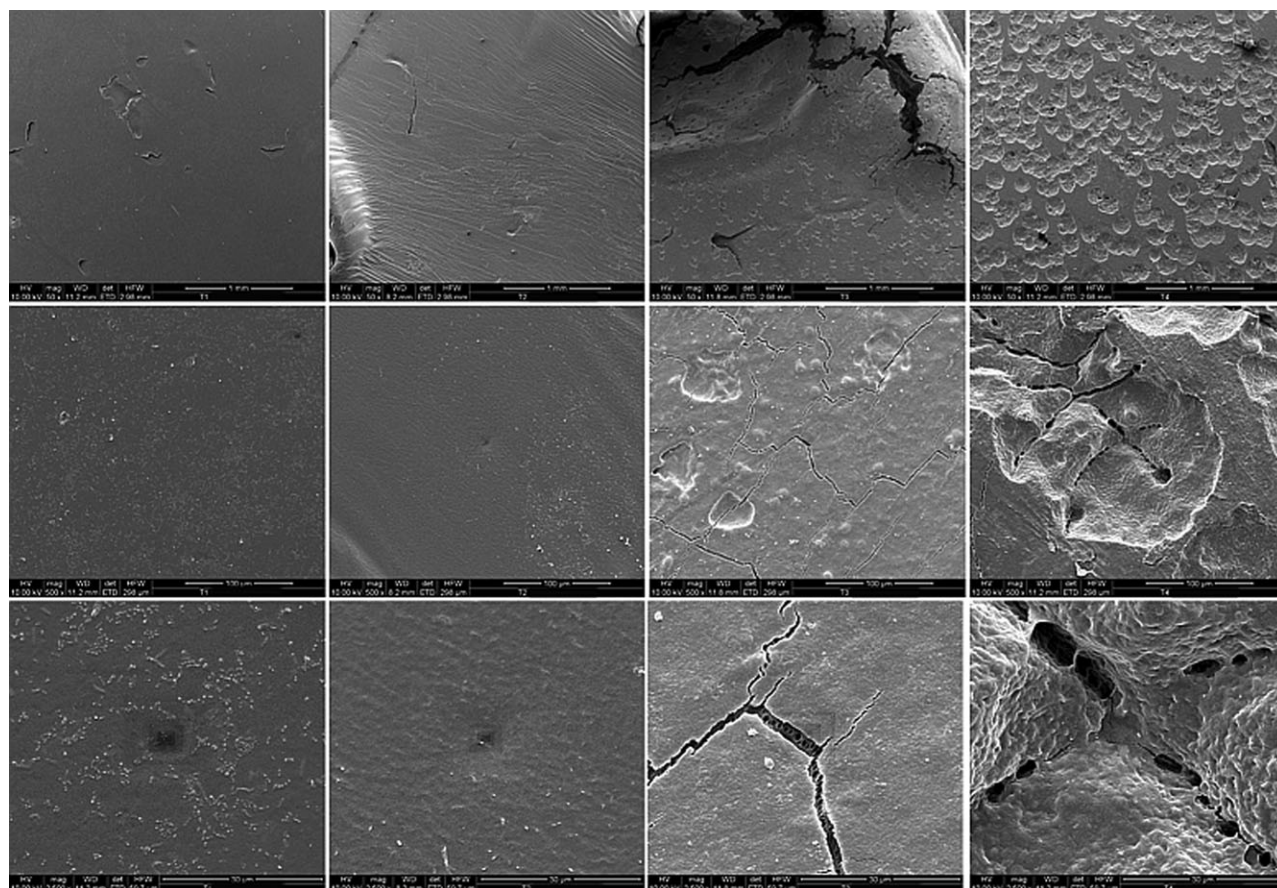
Figure 7 shows the trend of the residual mass upon increasing the *in vitro* conditioning time, for the same systems as in the previous paragraphs.

The main observation to be drawn is that, on average, there are no remarkable differences between the neat MaterBi and the composite filled with 15 wt % of kenaf. This result is of interest as it is in contrast with those found in the samples immersed in the active sewage sludge reactor, while it is in agreement with the behavior under composting conditions. This could provide a further confirmation to the explanation proposed in the previous paragraph: it is likely that this different behavior is owing to the hampering for bacterial rooting onto the fibers under zero-turbulence conditions, in comparison to the high turbulence available in the active sewage sludge reactor.

Figure 8 shows the morphologies of neat Mater-Bi upon increasing the *in vitro* degradation time (from left to right)

and the magnification (from top to bottom). Some comments may be drawn by observing the evolution (from left to right). First, the samples appear as being covered by bacteria and these can be better observed at the highest magnification. This first step, therefore, involves mainly bacterial adhesion onto the sample surfaces. The second step does not show significant differences, probably because of the induction time needed for the metabolic activity of the bacteria, as previously discussed with regard to the weight loss. The third step shows significant traces of bacterial degradation of the substrate. Finally, the fourth step shows an enlargement of the degradation zones, with a pitting effect which confirms how the degradation process, although slow, is going on. These observations and results are in agreement with those concerning the weight loss measurements.

Figure 9 shows the morphology evolution of the composites. The considerations which can be done are similar to those concerning the neat polymer, but a significant difference can be observed: the degradation proceeds much more quickly, and the pits owing to the bacterial activity are much clearly visible in the last column on the right. This provides a further confirmation of the increased degradation rate involving the composites, as already observed upon performing the weight-loss measurements.



**Figure 9.** Evolution of the morphology of the kenaf composites, at increasing *in vitro* degradation time (from left to right), and increasing magnifications (from top to bottom).

## CONCLUSIONS

In this work, a systematic study on the biodegradability of Mater-Bi®/kenaf eco-composites after disposal in several different environments such as wastewater treatment plant and landfill, as well as laboratory conditions, was carried out.

The results pointed out that the biodegradation rates are strongly dependent on the manufacturing procedure of the materials. Higher surface roughness and/or the presence of humidity in the polymer matrix before processing can definitely increase the biodegradation rates of the obtained samples. Furthermore, the influence of environmental temperature is strong as well, leading to significant decreases in the biodegradation rate during the winter season, in comparison to summer. As regards the role of kenaf fibers, they proved to significantly increase the biodegradation rates in active sewage sludge environment while, under composting or laboratory conditions, the differences between the neat Mater-Bi and the composite samples were only marginal. These results were attributed to the support action that the natural–organic fibers can provide to bacterial colonies and, on the other hand, the relatively high turbulence conditions which are typically present inside an active sewage sludge tank.

The overall results, therefore, provide an overview on some interesting parameters to understand the optimum way to obtain a fast degradation of the composites, and can be used to

determine the most suitable disposal environments for biodegradation of Mater-Bi®-based wastes.

## ACKNOWLEDGMENTS

Thanks are owing to Prof. M. Gennari and Dr. C. Abbate (DISPA—University of Catania) for the support provided for *in vitro* tests.

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