

Biodegradation properties of poly(butylene succinate) and chitosan nanocomposites

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Soil burial tests, conducted under natural conditions, were used to investigate the biodegradability of bio-nanocomposites containing silica, silicate, and graphene reinforcements.

The high cost and poor mechanical properties of biodegradable polymers are major drawbacks that have hindered their widespread application compared with conventional thermoplastics.^{1,2} In recent years, the inclusion of nanoparticles into biodegradable polymer matrices has attracted a substantial research effort in the development of polymeric materials with improved or desired properties. The effect of fillers on the biodegradability of the polymers in such composites, however, has largely been ignored.³

The biopolymer chitosan (CS) is derived from deacetylation of chitin and is the second most abundant natural biopolymer after cellulose. There have been many studies in which blends and composites based on CS, as well as on biodegradable aliphatic polyesters such as poly(butylene succinate)—PBS—have been reported.^{4–6} No insights into the biodegradability of such composite systems, however, have yet been provided.

In this work we have conducted biodegradation investigations on bio-nanocomposites.⁷ For these studies, we performed soil burial tests under natural conditions on blends of biodegradable polymers. These samples included PBS and chitosan blended with different amounts of silica, silicate, and graphene reinforcements. The PBS:CS nanocomposite, with 10% silicate is shown in Figure 1. These cross-sectional images illustrate that the CS flakes were uniformly incorporated in the PBS matrix before burial. We observed initiation of degradation after 15 days of embedding, at which point the interfacial areas between the PBS and CS were affected. After 30 days of embedding, extensive degradation had taken place. This was confirmed by the loss of structure and because the CS platelets were largely absent from the sample cross section.

We found that the mass of the samples decreased with the soil embedding time, which confirmed the initiation of degradation. The

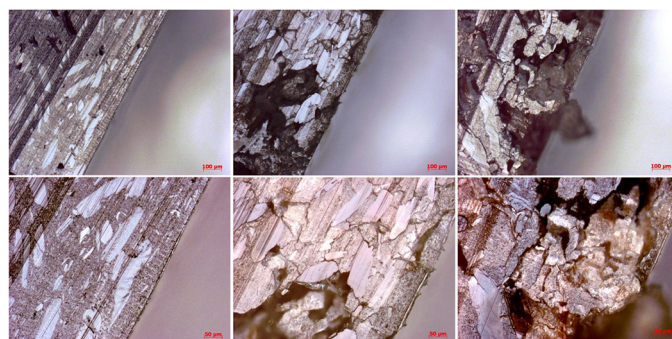


Figure 1. Cross sections through the poly(butylene succinate):chitosan (PBS:CS) nanocomposite sample that also contained 10% silicate. These images were obtained after embedding periods of 0 (left), 15 (middle), and 30 (right) days. Scale bars indicate 100 and 50 μm in the top and bottom rows, respectively.

PBS:CS blend (i.e., containing no reinforcements) exhibited the maximum extent of biodegradation (4% after 60 days), but biodegradation was also appreciable in the other samples. This was particularly surprising for the silica and silicate nanocomposites, considering that those experiments were conducted in natural conditions at room temperature. In addition, our results showed that by increasing the amount of filler in the composites, the amount of weight loss also increased. This was caused by a decrease in the overall strength of the polymer upon addition of a large amount of filler particles. Moreover, before burial, all the samples had relatively smooth and crack-free surfaces. We subsequently observed that the surfaces of the samples became rough with increasing embedding period and that more prominent surface cracks appeared. This result supports the loss of mass of the samples because of appreciable biodegradation.

Our measurements also revealed that the peak melting point (T_m) of the nanocomposites was shifted to higher values for those samples that were embedded for 15 and 30 days (see Figure 2). With even higher embedding times (45 or 60 days), however, there was no further increase

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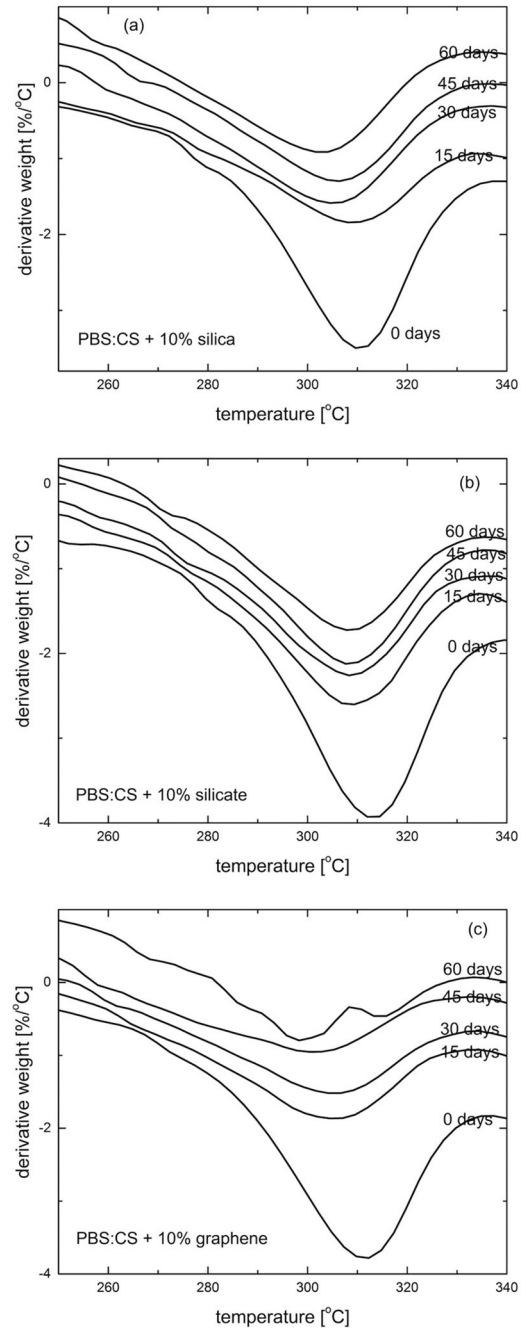
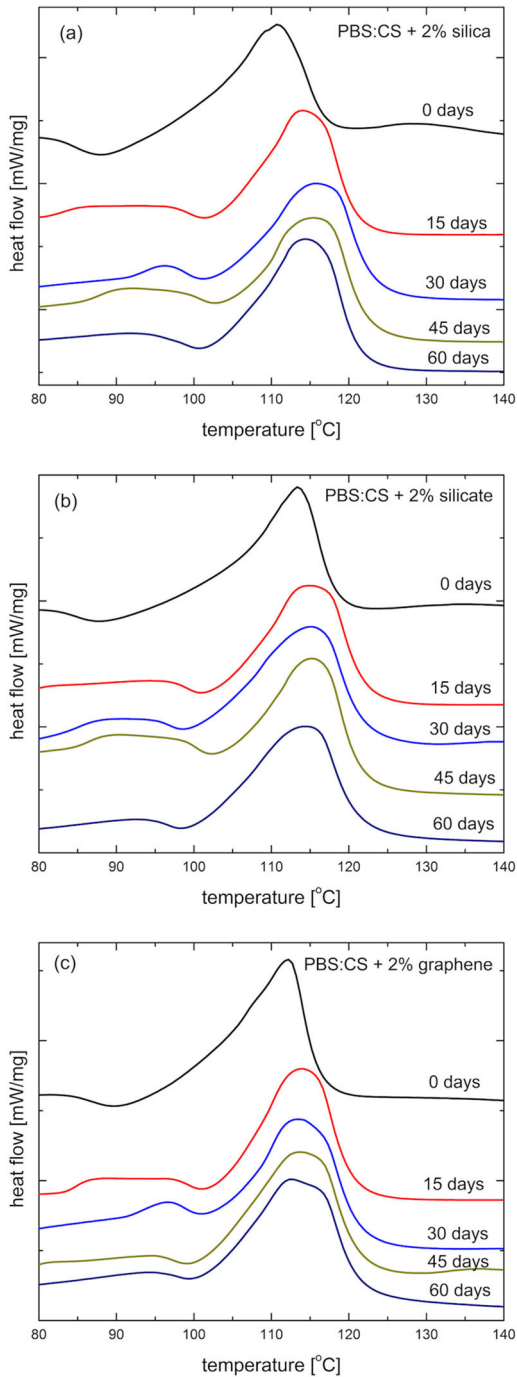


Figure 2. Differential scanning calorimetry melting thermograms of PBS:CS composites containing 2% (a) silica, (b) silicate, and (c) graphene as the filler material. The results are shown as a function of embedding time in soil.

Figure 3. Thermogravimetric analysis thermograms that demonstrate changes in the degradation temperature of chitosan, as a function of embedding time for PBS:CS samples with (a) silica, (b) silicate, and (c) graphene nanocomposites at a filler content of 10%.

in T_m (or even a minor decrease). The PBS melting transitions in the composites also became broader after the soil embedding, indicating that the composites went through some structural change. The increase in T_m during the initial degradation phase suggests that there may have been an increase in the overall crystallinity of the samples. We believe that this increased crystallinity was caused by microbes preferentially degrading the random amorphous component of the polymers. Presumably, after 30–45 days, the easily accessible amorphous portions of the composites had been degraded by the microbes. The microbes then attacked the ordered or crystalline regions, which caused the decrease in T_m and crystallinity. We also observed that the rate of weight loss decreased during the 45–60 day period of embedding. This loss of material can be correlated with the preferential degradation of CS in the composites, but we would also expect the amorphous content of the PBS phase to have been degraded in the process.

Thermogravimetric analysis (TGA) thermograms for our blend and composite samples (conducted in a nitrogen atmosphere) exhibit two mass loss regions. The first of these regions (see Figure 3) has a peak degradation temperature of 310°C—corresponding to CS degradation—and the second has a peak degradation temperature of about 390°C, which is caused by PBS. After embedding, the degradation temperature of the lower peak shifted to lower values as the biodegradation time increased. This result indicates that the changes occurring during the biodegradation process specifically reduced the thermal resistance of CS. It is also consistent with our findings of increased PBS crystallinity and the preferential degradation of CS in the nanocomposites. From our TGA-mass spectrometry measurements (conducted in an air atmosphere), we observed that the evolution of various components occurred at lower temperatures with increasing embedding time. We can explain this because the aerobic oxidation produces functional groups—such as carboxylic acid (COOH)—during the early stages of biodegradation. Such groups usually have lower thermal stabilities and thus give rise to an overall lower degradation temperature. After 30 days of embedding, we find that the evolution of the components (caused by degradation) occurred at the same temperatures as the samples before burial.

In summary, we have conducted biodegradation studies on nanocomposite samples that consist of PBS and CS blended with different levels of silica, silicate, and graphene reinforcements. Overall, our results indicate that the fillers hindered the biodegradation of the polymers in the nanocomposites and that varying degrees of biodegradation were achieved, depending on the type and amount of filler. Furthermore, the degradation mechanisms were unaffected by the type of reinforcement used in the nanocomposite samples. Our future work will involve long-term biodegradation studies. We also aim to further correlate the physicochemical performance of our samples with the degradation behavior, which will provide more insights for practical applications.

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