



Improving biodegradable polymer nanocomposites

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Adding silica nanoparticles to poly(3-hydroxybutyrate-co-4-hydroxybutyrate) by melt compounding makes it stronger but more brittle.

Natural source poly(3-hydroxybutyrate-co-4-hydroxybutyrate)—referred to in this article as P34HB—is a thermoplastic aliphatic polyester produced by numerous bacteria. It has good toughness and process properties when compared with poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) because of the chain of four hydroxybutyrate groups it includes. Due to its good toughness, biodegradability, and biocompatibility, it has been widely used in the fields of biomedicine and the environment. However, low mechanical strength and poor crystallizability have limited its application.

Fumed silica is an abundant, low-cost, lightweight inorganic nanofiller. It is strong, with a high modulus and good thermal stability. More important, it is environmentally benign. We have investigated the effect on the morphology and mechanical properties of incorporating fumed silica into a P34HB matrix. We found that it is a promising way to improve P34HB's performance.¹

We prepared five biodegradable P34HB/silica nanocomposites by melt compounding.¹ The nanocomposites contained varying amounts of fumed silica, and were named P34HBR, where *R* represents the percentage by weight of the silica content. For instance, P34HB5 contains 5wt% silica. We used scanning electron microscopy to examine their morphology (see Figure 1). The neat P34HB fracture surface was smooth and featureless—see Figure 1(a)—whereas silica particles were detected as white dots for the nanocomposites. When the silica content was less than 5wt%, the silica nanoparticles were homogeneously dispersed in the matrix and aggregate particle sizes were less than 100nm: see Figure 1(b) and (c). However, as silica content increased further, the number of large aggregates increased markedly: see Figure 1(d–f). Strong interactions between the nanoparticles^{2,3} resulted in some of the aggregates even exceeding 250nm in diameter.

We plotted tensile stress-strain curves of the P34HB/silica nanocomposites (see Figure 2). Corresponding data on mechanical properties is listed in Table 1. Neat P34HB showed a modulus of 497MPa, a tensile strength of 22.0MPa, and an elongation at break of 520%. Increasing the silica content resulted in increases in modulus and tensile strength

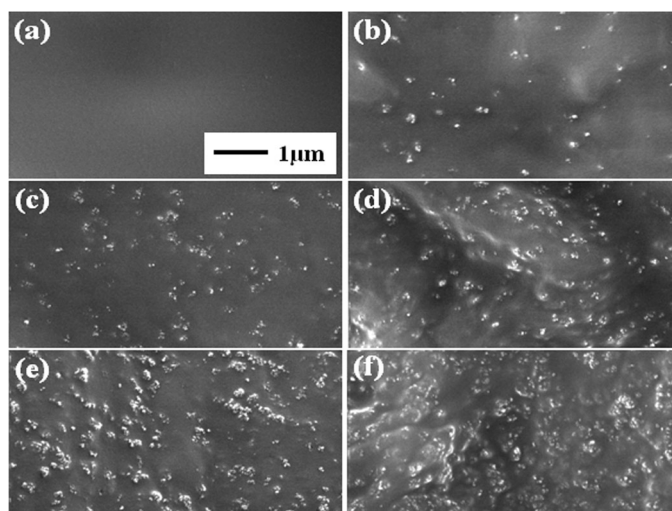


Figure 1. Scanning electron microscope images of nanocomposite fractured surfaces of (a) poly(3-hydroxybutyrate-co-4-hydroxybutyrate), referred to as P34HB, (b) P34HB1, (c) P34HB3, (d) P34HB5, (e) P34HB7, and (f) P34HB10, where in the sample name P34HBR, *R* represents the silica content percentage by weight.

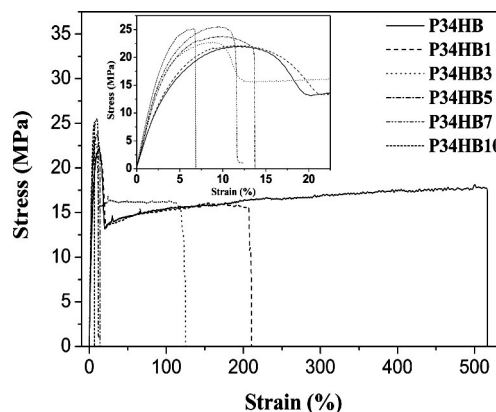


Figure 2. The tensile stress-strain curves of neat P34HB and its nanocomposites. Inset: Tensile stress at low strain.

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Table 1. Mechanical properties of P34HB and its nanocomposites.

Sample	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
P34HB	497 ± 10	22.0 ± 0.2	520 ± 39
P34HB1	501 ± 27	22.5 ± 0.2	150 ± 27
P34HB3	588 ± 36	22.9 ± 0.2	124 ± 34
P34HB5	648 ± 36	24.6 ± 0.3	12 ± 0.6
P34HB7	703 ± 12	25.5 ± 0.1	11 ± 0.3
P34HB10	729 ± 52	25.4 ± 0.5	7 ± 0.1

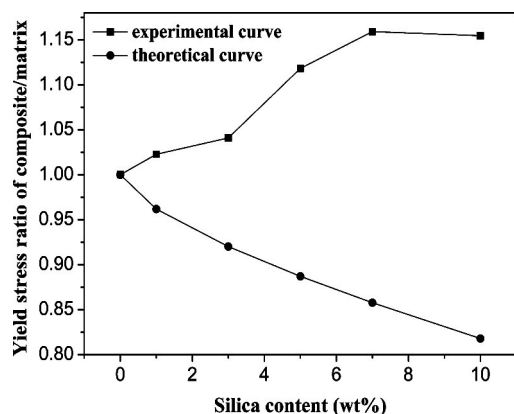


Figure 3. Effect of the silica content on the tensile yield stress ratio of the composite and matrix.

but a decrease in elongation at break. Interfacial interaction between the fillers and matrix was an important factor affecting the mechanical properties of the composites. The increased modulus and tensile yield strength of the P34HB/silica nanocomposites indicated that the nanoparticles were well wetted by the polymer matrix, with the result that a stress may be efficiently transferred from the polymer matrix to the silica nanoparticles.

To test this explanation, we used the Nicolais-Narkis model^{4,5} to predict the tensile strength of the nanocomposites in the absence of adhesion between the matrix and nanoparticles. Without adhesion, the interfacial layer would be unable to transfer stress. We plotted the experimental and theoretical (without adhesion) tensile yield stress ratio of the composite and matrix versus silica content (see Figure 3). The experimental tensile strength values were much higher than the theoretical values in all silica-containing nanocomposites. This indicates there is adhesion between P34HB and silica. Consequently, we expect an applied stress to be easily transferred from the polymer matrix to the silica nanoparticles, increasing the nanocomposites' modulus and tensile yield strength.

The elongation at break for all the nanocomposites decreased with increasing silica content, and this heightened brittleness may be caused

by silica's stress concentration effect.⁶ Generally, the addition of more fillers increases the probability of filler aggregation, which creates regions of stress concentrations that require less energy to propagate cracks. During tensile deformation, the stress cannot transfer efficiently near these flaws, resulting in failure.⁷ Furthermore, all of the nanocomposites' elongation arose from the P34HB matrix because the silica nanoparticles were more rigid than the matrix. Hence, increasing the amount of silica decreased the amount of polymer available for elongation and thus decreased the elongation to break.

In summary, we have prepared biodegradable P34HB/silica nanocomposites by melt compounding, which exhibited improved mechanical properties. We are currently studying the relationship between structure and performance in P34HB nanocomposites.

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