

Fabrication of poly(lactic acid) composites with improved tensile strength

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Functionalizing graphene oxide with steric acid increases its compatibility with poly(lactic acid), leading to improved tensile strength composites.

Bioplastics, or biodegradable plastics, have received much attention because of their environmental friendliness. Poly(lactic acid)—PLA—is the most popular biopolymer currently in use. However, bioplastics also have a number of drawbacks, including limited shelf-life and lower mechanical strength compared to regular non-biodegradable plastics.

Our aim is to improve the mechanical strength of PLA by using graphene as a reinforcing filler due to its outstanding properties such as large surface area and high Young's modulus.^{1,2} Especially compared to carbon nanotubes, graphene has a high surface-to-volume ratio, giving it the potential to be used as a nanofiller to improve polymer properties. However, owing to the insufficient surface wettability of graphene, using it as a nanofiller in PLA/graphene composites often leads to heterogeneous mixing, poor dispersion, and cracking, which results in lower mechanical strength.

Recently, we developed a procedure for the surface modification of graphene oxide (GO) sheets using stearic acid (SA) as a surface wetting agent (see Figure 1). This surface modification increases the lipophilicity and compatibility of GO with PLA, resulting in enhancement of the tensile strength of the PLA-GO composite.³

We prepared GO-SA nanocomposites with mass ratios of GO to SA of 1:1, 1:3, and 1:5. X-ray photoelectron spectroscopy results indicated that the surface coverage of GO with SA increases with the amount of SA in the composite. This can be explained by the substitution of the long alkyl chain groups from SA to the epoxy groups on the GO sheets.

Composite films of PLA-(GO:SA) were subjected to mechanical property testing (see Table 1). The tests included measuring tensile strength, secant modulus, and elongation at break. The secant modulus is related to the ratio of stress versus strain, and is determined by the slope of a line from the origin to any point on a stress-strain curve. Both the secant modulus and the elongation at break provide a measure

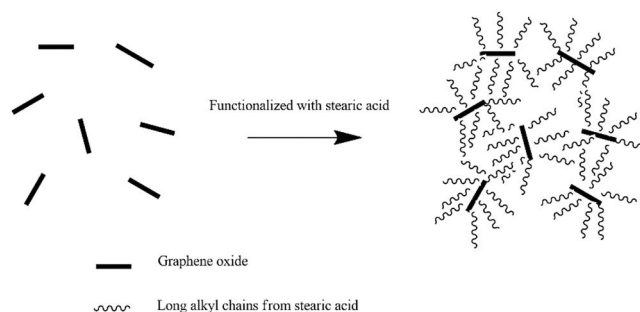


Figure 1. Graphene oxide (GO) sheets are functionalized with long alkyl fatty chains from stearic acid (SA) to increase their compatibility with poly(lactic acid) (PLA).

of the brittleness and stiffness of materials. It was found that the PLA-(GO:SA) 1:1 composite showed the highest tensile strength. Compared to PLA alone, the tensile strength of the PLA-(GO:SA) 1:1 composite was 32% higher. This increase was partly due to the enhanced compatibility of the PLA with surface-modified GO, which in turn improved the interfacial adhesion between the GO:SA sheets and the PLA matrix. However, the elongation at break was still low (< 4%) in all samples due to the inherent stiffness of PLA and PLA-(GO:SA).

Transesterification reactions offer further improvements in the tensile strength of the PLA-(GO:SA) composite films.⁴ Using 1 wt% titanium (IV) butoxide—Ti(OBu)₄—as a transesterification catalyst during fabrication of the PLA-(GO:SA) 1:1 films aids compatibilization. A schematic representation of the transesterification mechanism of PLA-(GO:SA) 1:1 in the presence of Ti(OBu)₄ is shown in Figure 2.

The PLA-(GO:SA) 1:1-Ti(OBu)₄ exhibited film tensile strength of 51.9(±3.7)MPa, which is significantly higher than that of the PLA-(GO:SA) 1:1 film. This indicates that transesterification reactions can be beneficial to PLA-GO film fabrication. The structures of the PLA-(GO:SA) matrix before and after transesterification show

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Table 1. Tensile properties of PLA, PLA-(GO:SA) 1:1, PLA-(GO:SA) 1:3, and PLA-(GO:SA) 1:5 films. $Ti(OBu)_4$: Titanium (IV) butoxide.

Film sample	Tensile strength (MPa)	Elongation at break (%)	Secant modulus at 2% strain (GPa)
PLA	37.5 ± 3.2	3.1 ± 0.2	0.190 ± 0.010
PLA-(GO:SA) 1:1	49.4 ± 0.3	2.5 ± 0.3	0.289 ± 0.003
PLA-(GO:SA) 1:3	45.7 ± 2.3	2.6 ± 0.3	0.325 ± 0.018
PLA-(GO:SA) 1:5	44.4 ± 1.9	2.7 ± 0.4	0.325 ± 0.019
PLA-(GO:SA) 1:1- $Ti(OBu)_4$ (1wt%)	51.9 ± 3.7	3.2 ± 0.3	0.275 ± 0.019

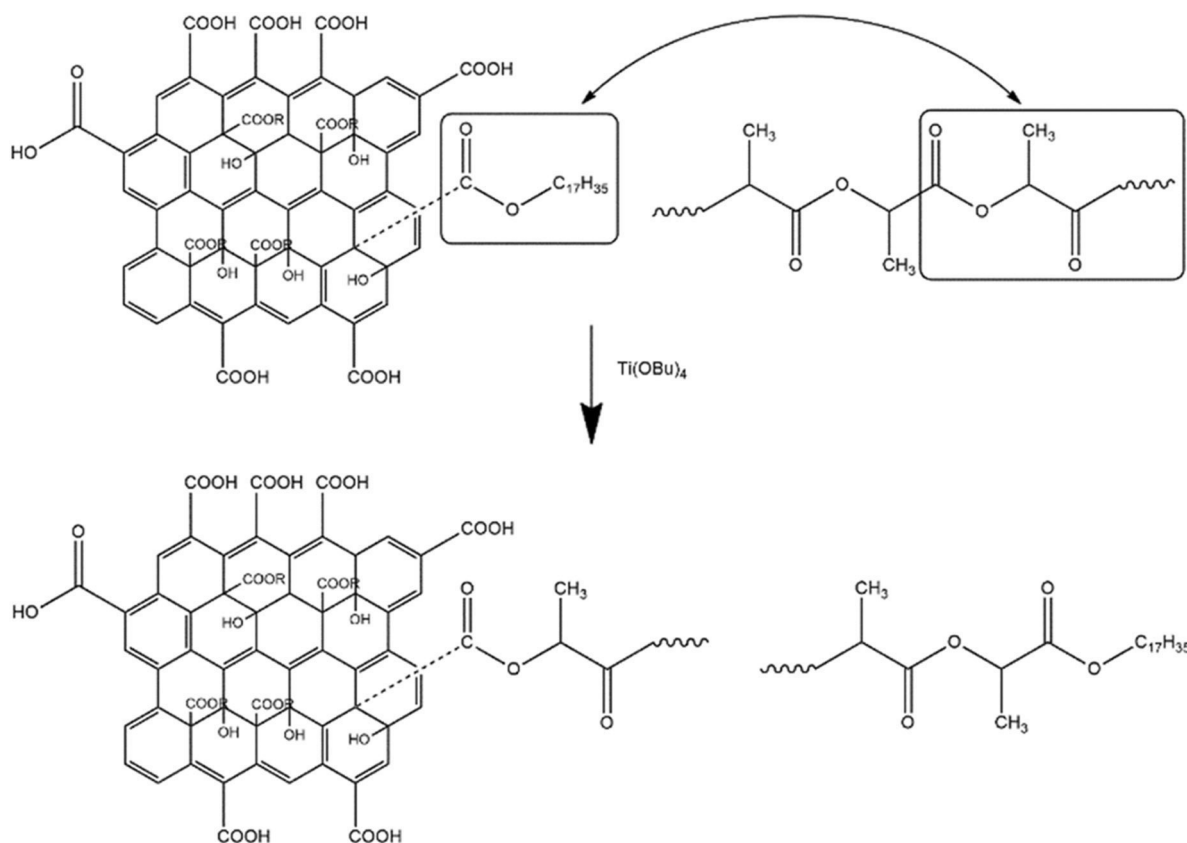


Figure 2. Mechanism of transesterification in PLA-(GO:SA) 1:1 catalyzed by $Ti(OBu)_4$.

GO components chemically bonded to the PLA via the SA units (see Figure 3). This results in enhanced interfacial adhesion.

In summary, we have successfully fabricated PLA-(GO:SA) composite films with improved tensile strength compared to PLA alone. The results show that the tensile strengths of the PLA-(GO:SA) 1:1 and PLA-(GO:SA) 1:1- $Ti(OBu)_4$ films are 32 and 38% higher, respectively, than PLA, due to a combination of the reinforcing effect of the GO and

the compatibilizing effect of the SA. Transesterification of these composites using $Ti(OBu)_4$ as a catalyst can further enhance compatibility. Our next step will be to prepare PLA-(GO:SA) composites with improved elongation at break that also show high tensile strength.

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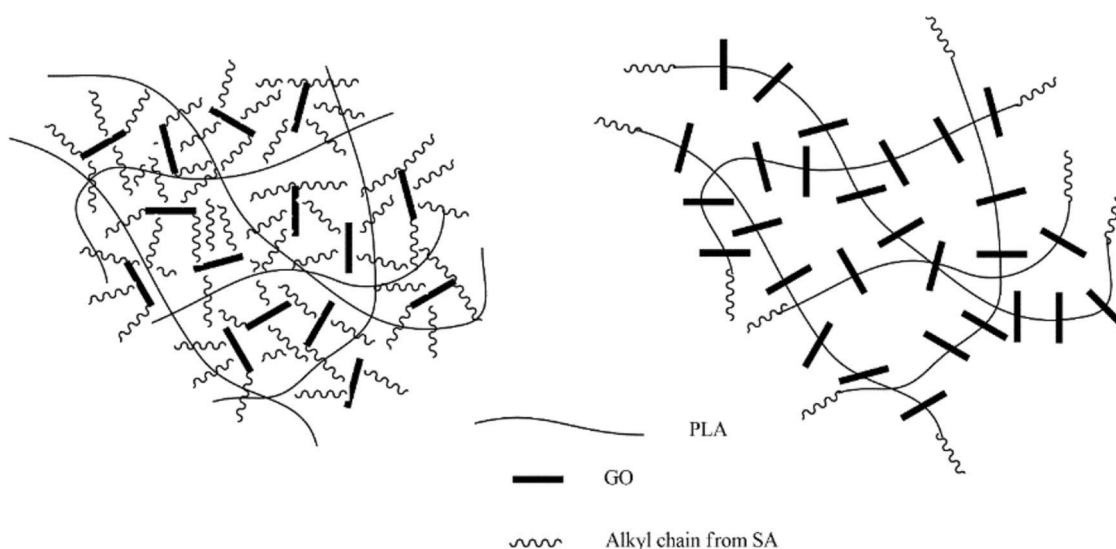


Figure 3. Visualized structures of PLA-(GO:SA) (left) before and (right) after transesterification. The SA units attached to the GO react with the PLA, enhancing interfacial adhesion.

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