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Mechanical and crystal enhancements to polylactide with silver-nanoparticle filler

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Processing poly(lactic acid) with low concentrations of silver using a twin-screw extruder leads to nanocomposites with enhanced crystallinity and improved mechanical properties.

Biopolymers represent a particularly promising solution for overcoming the issue of plastic waste.[1] Among biopolymers, poly(lactic acid) (i.e., PLA), which is synthesized using biomass-based renewable feedstock and a compostable aliphatic polyester, is one of the most cost-competitive substitutes for petroleum-based polymers.[2–5] PLA finds application in a number of industrial sectors, including packaging, automotive, biomedical fields, and tissue engineering.[2,4–6] In particular, PLA is widely employed in the packaging industry because of its high transparency, stiffness, strength, and excellent printability.[7] The thermal stability, toughness, and permeability of PLA are low compared to those of petroleum-based polymers, however.[4–6,8]

One strategy to enhance the mechanical properties of polylactide is by combining it with reinforcing fillers. Fillers strongly influence the crystalline phase parameters of PLA.[4,5,8] In particular, the addition of nanoparticles has been shown to increase its toughness. Among this class of materials, silver nanoparticles (AgNPs) have attracted attention in recent years as a result of their conductivity, biocide spectrum,[8–11] low volatility, and low toxicity to human cells.[12–14] It is noteworthy that relatively high concentrations of AgNPs (i.e., 1wt%) have not been shown to significantly modify the mechanical properties of PLA.[8,15,16]

In our work, we have evaluated the effect of low concentrations of AgNPs on the mechanical properties of PLA. We prepared PLA/AgNP nanocomposites by melt compounding in a twin-screw extruder at 180°C with a screw speed of 100rpm.

We characterized our PLA/AgNP nanocomposites using temperature-modulated differential scanning calorimetry (TMDSC). In this process, we reheated the samples from 30 to 190°C (at 3°C/min) and used a modulation amplitude and period of ±0.5 and 60s, respectively.

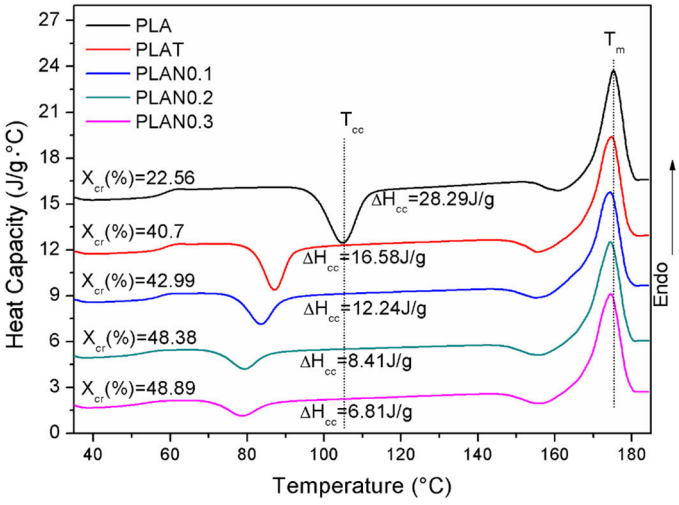

Figure 1. *The total heat capacity of the nanocomposite samples, obtained via temperature-modulated differential scanning calorimetry. PLA: Poly(lactic acid). PLAT: PLA processed in a twin-screw extruder under the same conditions as the nanocomposites. PLAN0.1, PLAN0.2, PLAN0.3: PLA/silver nanoparticle (AgNP) composites with varying concentrations of AgNPs (i.e., 0.1, 0.2, and 0.3wt%). ΔH_{cc}: Cold-crystallization enthalpy. T_{cc}: Cold-crystallization temperature. X_{cr}: Crystallinity percentage.*

Table 1. *Mechanical properties of the nanocomposites, obtained via tensile test.*[19]

Samples	Young's modulus (GPa)	Stress at break (MPa)	Strain at break (%)	Toughness MJ/m^3
PLA	3.79±0.25	61.03±1.81	4.35±1.64	2.14±1.00
PLAT	4.02±0.12	59.42±2.31	5.49±0.55	2.99±0.33
PLAN0.1	3.66±0.16	48.99±1.13	14.86±2.14	7.32±1.27
PLAN0.2	3.74±0.07	51.14±1.05	10.05±2.19	5.15±1.26
PLAN0.3	3.54±0.14	48.33±1.86	9.12±1.01	4.33±0.47

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Additionally, we used wide-angle x-ray diffraction (WAXD) to obtain information about the crystalline structure and crystal lattices of the samples. Finally, we measured the stress-strain curves, from which we estimated the strain and stress at break, toughness, and Young's modulus. We then correlated the mechanical responses with the silver content to determine its influence on the sample properties.

Our thermal analysis results indicate that AgNPs act as a nucleating agent of PLA during cold and melt crystallization. The nanocomposites exhibited cold crystallization temperatures (T_{cc}) lower than neat PLA and PLAT (i.e., PLA processed by a twin-screw extruder under the same conditions as the nanocomposites), and the T_{cc} decreased with the AgNP content (see Figure 1). The T_{cc} and cold-crystallization enthalpy (i.e., ΔH_{cc}) diminished from 104.8 to a minimum of 78.7°C and from 28.3 to 6.8J/g, respectively, and the overall enthalpy of the samples remained constant (approximately 52J/g). Remarkably, the effect of AgNPs upon crystallinity is observed when ΔH_{cc} is decreasing—see Figure 1—which suggests that the crystallization of the nanocomposites increases with the AgNP concentration.

The diffraction patterns that we obtained exhibited two intense peaks, at 16.4°—with a reflection at (200)/(110)—and 18.7° (203). These peaks shifted toward higher values as the silver content increased. As shown in Figure 2, the AgNP content provoked a more ordered lateral chain in the crystalline lattices, from less perfect crystals (α') to more perfect crystals (α). We found that these results were corroborated by the lattice spacing obtained from the Bragg equation.[17]

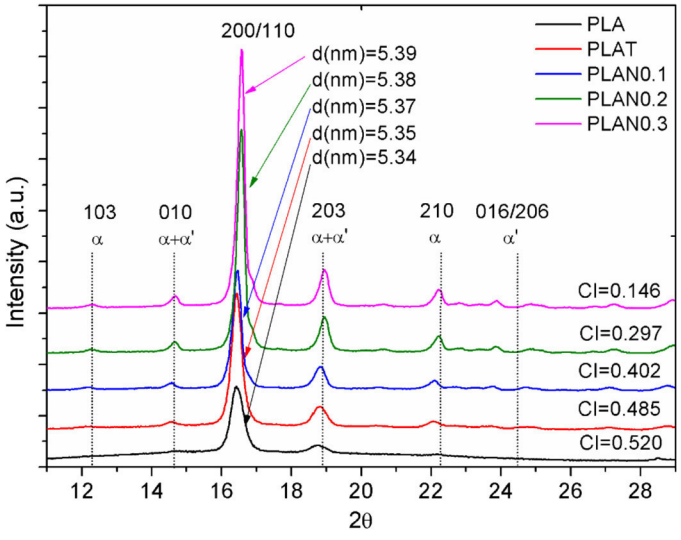

Figure 2. *Diffraction patterns of PLA, PLAT, and nanocomposite samples. d: The spacing between adjacent lattice planes. a.u.: Arbitrary units. 2θ: Diffraction angle. α: Ordered crystals. α′: Disordered crystals. CI: Crystallinity index. Numbered peaks represent Miller indices.*

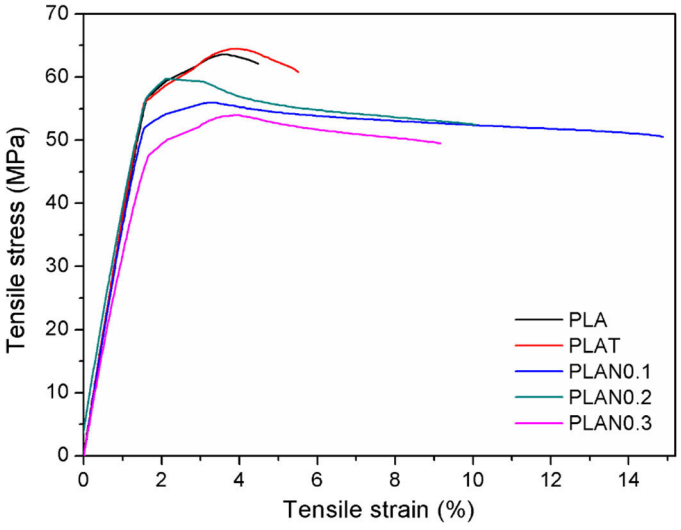

Figure 3. *Representative stress-strain curves.*

In fact, two polymorphic forms (i.e., α and α' crystals) exist within the nanocomposites. Their presence is shown by the (203) reflection, which lies away from the 19.2° peak that would represent the α form. Although the crystallinity index (CI) shows raw PLA to have a low crystallinity, processing influenced both the CI and the crystallinity. As previously mentioned, AgNPs act as a heterogeneous nucleating agent, further increasing the crystallinity of PLA (observed by the CI).

We found that lower AgNP content promoted an enhancement to the strain at break of the nanocomposites compared to those with no significant modifications (i.e., PLA and PLAT).[9,18] Indeed, the nanocomposites achieved enhancements of two to three times compared with raw PLA (i.e., from 4.3 to 14.8%): see Table 1.[19] Some research has shown that low nanoparticle loading impacts the biodegradation of PLA by modifying the generation of enzymes. As a result of this, the capacity of crystallization is preserved, which ultimately enhances the mechanical behavior.[20–22] Figure 3[19] shows the sample behavior of stress-strain curves that we obtained via tensile tests. We found that the nanocomposites exhibit a higher toughness (see Table 1[19]) compared to the raw and processed polymer samples. However, with an increasing silver content, toughness decreased slightly. Irrespective of their silver content and crystallinity, however, all samples exhibited Young's moduli of over 3.5GPa.

In summary, we have found that AgNPs affect the crystal structure and morphology of the polymer matrix, as well as its ability to organize. Indeed, the addition of AgNPs leads to crystallization, enhanced crystallinity, and lower crystallization temperature. Furthermore, we found

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that AgNP modified the lattice space—i.e., (200)/(110) peak—thereby providing further proof of structure reorganization, from disordered to more ordered crystals. The nanofiller also improved toughness and elongation at break of the nanocomposites. At low concentrations, AgNPs promoted more disordered crystals, making them less resistant to deformation. Because of this, the addition of another component (such as an elastomer, coupling agent, or plastizicer) is unnecessary. Finally, mechanical and thermal properties were improved for all nanoparticle concentrations, with the best results achieved at concentrations of 0.1wt%. In the next stage of our research, we will analyze the viscoelastic behavior of nanocomposites to obtain detailed information about the influence of AgNPs on the storage and loss moduli, viscosity, and molecular weight distribution.

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