The crystal morphology and mechanical properties based on poly(l-lactic acid)/silica nanocomposites

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Abstract. Nano silica (SiO2) was introduced into Poly(L-lactic acid) (PLLA) matrix to prepare PLLA/SiO2 nanocomposites, and the crystal morphology, crystallization behavior and mechanical performance were investigated. The XRD experimental data indicated that nano SiO2 could improve the crystallization of PLLA, and PLLA/SiO2 nanocomposites exhibited sharp diffraction peak after isothermal crystallization. In addition, through the POM analysis, PLLA/SiO2 sample had the typical spherulite structure, and the size of the spherulite became larger with the increase of crystallization temperature. The tensile testing showed that a small amount of SiO2 could improve and retain the mechanical performance of PLLA

1. Introduction
Silica (SiO2) widely exists in the earth's crust, and also was widely employed in many fields such as ceramics materials[1], glass materials[2], polymer filler[3], etc. Pei et al.[4] reported that a core-shell SiO2@MgO with flower structure was synthesized, and the synthesized core-shell SiO2@MgO sample showed excellent performance for the removal of crystal violet, and the maximum adsorption capacity was 2244.85 mg/g, exhibiting a promising environmental remediation material. Meng and coauthor[5] synthesized a magnetic sonophotocatalyst Fe3O4@SiO2@TiO2 nanocomposites to enhance biodegradability of organophosphate pesticide. The experimental results showed that the Fe3O4@SiO2@TiO2 nanocomposites had good photocatalytic performance and stability. That is, the Fe3O4@SiO2@TiO2 nanocomposites were used for the fifth time, the CODcr removal efficiency was still very high (about 62.38%).

Poly(L-lactic acid) (PLLA), as very promising biodegradable materials[6], has achieved excellent development for application[7]. The hydroxyapatite and the bone morphogenetic protein-2 were introduced into PLLA to prepare the bioactive scaffold material, the animal experiments indicated that PLLA/hydroxyapatite/bone morphogenetic protein-2 can significantly induce and promote bone tissue formation [8]. The poly (L-lactic acid)/ZrO2 nanofibrous membranes were fabricated using electrospinning technique, and the antimicrobial activity and release behavior showed that poly(L-lactic acid)/ZrO2 nanofibrous exhibited well controlled release and better antimicrobial activity against Staphylococcus aureus[9]. In addition, PLLA was used in nanocomposites[10-11], biomaterials[12], etc. However, there exist some critical defects including slow crystallization rate and low heat resistance to reflect the application of PLLA. Adding SiO2 into PLLA matrix is a value technology method for improving the performance of PLLA. Wu et al[13] reported that modified SiO2 through ring-opening of L-lactide or nucleophilic addition reaction was added into PLA matrix to solve the low melt strength of PLLA. Results showed that long grafted chains modified on the surface of SiO2...
through nucleophilic addition reaction were contributed to a significant enhancement in the melt strength of PLA.

In this work, we fabricated PLLA/ SiO₂ nanocomposites using traditional melt blending technology, and their crystal morphology; crystallization and mechanical properties of PLLA/SiO₂ nanocomposites were investigated using polarized optical microscopy (POM), X-ray diffraction (XRD), and tensile testing.

2. PLLA/SiO₂ nanocomposites
Dry nano-SiO₂ and PLLA was blended in a counter-rotating mixer, and the detailed operating procedure is similar to that used for other PLLA based materials[14].

3. Results and Discussion

3.1. Crystallization and morphology
The crystallization behavior is very important research topics for semi-crystalline polymer. Figure 1 shows the XRD curves of SiO₂, PLLA and PLLA with different SiO₂ content without heat treatment. It is very clear that the diffraction peaks of PLLA and PLLA/ SiO₂ are very wide, showing that the crystallization degree is very low. However, the diffraction peaks of PLLA/ SiO₂ nanocomposites after isothermal crystallization at 105°C for 20 min become very sharp (See Figure 2), but the diffraction peak of the neat PLLA still is very wide, these discrepancy indicated that SiO₂ play an important role in improving the crystallization of PLLA, this also further confirmed by literature reports about the nucleating effect of SiO₂ for PLLA [15]. In addition, the strongest diffraction peak of PLLA at 2θ =16.7° belong to diffraction from (110) planes, and the others peaks at 2θ =14.9° , 19.0° , 22.3° occur from the (010) planes, (203) planes and (205) planes, respectively [16].

![Figure 1. XRD curves of SiO₂, PLLA and PLLA/ SiO₂ with heat treatment.](image-url)
The crystal morphology is also very crucial for application, because the morphology of PLLA is related to its performance. Figure 3 shows the POM of PLLA/3% SiO$_2$ at different crystallization temperature. It can be seen that the PLLA/3% SiO$_2$ exhibits typical spherulite, and the spherulites become bigger with an increase of crystallization temperature, the reason is that the PLLA crystals become more perfect at higher crystallization temperature through the ordered arrangement of molecular chain with stronger motility.

3.2. Mechanical Properties
Mechanical performance directly affects the application of PLLA. The mechanical performance of PLLA/SiO$_2$ nanocomposites was investigated using the electronic tensile tester. Table 1 shows the tensile strength and elongation at break of PLLA and PLLA/SiO$_2$ nanocomposites. Apart from 1.5% SiO$_2$, the tensile strength and elongation at break of PLLA decreases with the increasing of SiO$_2$ content, and the different result of PLLA/1.5%SiO$_2$ may result from the dispersibility of SiO$_2$ in PLLA matrix and testing error. Upon the addition of 0.3% SiO$_2$, the tensile strength and elongation at break have the maximum value, they are 49.7MPa and 7.58%, respectively. This result indicates that a small
The amount of SiO2 can improve and retain the mechanical performance. In contrast, a large amount of SiO2 reduces the mechanical properties.

Table 1. Mechanical properties of PLLA and PLLA/SiO2 nanocomposites.

| Sample           | tensile strength (MPa) | elongation at break (%) |
|------------------|------------------------|-------------------------|
| PLLA             | 47.6±2.4               | 5.2±0.6                 |
| PLLA/0.3%SiO2    | 49.7±1.7               | 7.6±0.5                 |
| PLLA/0.7%SiO2    | 46.9±2.1               | 5.9±0.3                 |
| PLLA/1.5%SiO2    | 48.1±1.3               | 6.3±0.4                 |
| PLLA/3%SiO2      | 45.7±1.7               | 5.5±0.4                 |
| PLLA/5%SiO2      | 44.5±0.9               | 2.7±0.3                 |

4. Conclusion
The crystallization behavior, morphology and mechanical properties of PLLA/SiO2 nanocomposites were studied, and the XRD and POM measure indicated that SiO2 could accelerate the crystallization of PLLA. The addition of SiO2 could also increase the nuclear density of PLLA matrix, but the crystal morphology still was typical spherulite structure. In addition, 0.3% SiO2 made the tensile strength and elongation at break of PLLA exhibits the maximum value.

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