Research Progress on Preparation and Performance of Bio-Degradation PLA/Graphene Nanocomposites

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Abstracts. PLA (Poly(lactic acid)) as a bio-degradation and environment-friendly polyester could be used in packing, medicine, engineering, electronics and other multiple applications. However, the low strength, inherent brittleness, low heat resistance, slow crystallizations, degradation rate and other weaknesses limited PLA’s applications. Graphene as an atomically thick sheet composed of carbon atoms could be used as nanofillers to modify PLA nanocomposites’ some properties to some extent. The manufacturing processes, techniques and corresponding results were reviewed in this paper and results did prove that properties of nanocomposites could improve with the adding of an appropriate content ratio of graphene with an appropriate manufacturing technique, so as to provide references and highlights for materials researchers and multiply its great applications in packaging, medicine, engineering and electronics.

Introduction

PLA, synthesized by condensation polymerization of L-lactic acid or ring-opening polymerization of corresponding lactic directly or indirectly instilled from the fermentation of corn, potato, sugar beat, sugar cane and so on[1], is a biodegradable polyester, one kind of crystalline thermoplastic polymer with relatively high melting point and excellent mechanical properties, however, PLA and most of the biodegradable resins[2] have low strength, inherent brittleness, low heat resistance, slow crystallization and degradation rate which limits resins to be used as high strength structural components for broad practical application[3-6].

Graphene is the elementary structure of graphite with an atomically thick sheet composed of sp' carbon atoms arranged in a flat honeycomb structure which is a 2D flat sheet[7]. Graphene oxide (GO) is similar to graphene but with oxygen-containing functional groups which reduces thermal stability of nanomaterial[7,8,9-11].

The presence of oxygen-containing groups in graphene oxide other wisely reduces thermal stability of nanomaterials and the most modified way to solve this problem is to promote interaction and compatibility with some certain polymer matrix[8,9].

Owe to graphene’s remarkable mechanical strength, an extremely high surface and small-scale size effect, short-cut fibers were also used as reinforced fillers into resin matrix to improve mechanical, thermal, gas barrier and other properties of composites, few with graphene. There were several kinds of existing types of graphene, such as graphene oxide, graphene platelets. The modification methods of graphene reinforced PLA and corresponding characterization testing results were reviewed in this paper so as to provide some references and highlights for materials experiments, product design and manufacturing techniques and further multiply its great applications in packaging, medicine, engineering and electronics.

Manufacturing Processes

Introduction of Manufacturing Methods

Common methods of graphene reinforced PLA composites, such as melt-mixing process, solvent-mixing process and in-situ polymerization[14-28].
Melt-Mixing Process

Many researchers depended on melt-processing manufacturing method to improve Graphene/PLA nanocomposites’ mechanical, thermal, gas barrier and other properties. Hassouna et al.[29,30,31] prepared 3wt% expanded graphite nanofillers reinforced PLA composites through melt-processing and explored twin-screw micro-extruder to improve the dispersion and delamination of the filler. And the DSM showed that the tensile, storage modulus, as well as thermal conductivity of PLA based materials were improved.

Mortazavi et al.[32] prepared PLA/exfoliated graphite (EG) by melt-mixing in an appropriate ratio, 3wt% and 6.75wt% respectively. PLA pellets and EG were extrudes by using a twin-screw extruder and PLA/graphene composites were obtained through compression-molding.

Kim Muralu, Hassouna et al.[33-35] did some investigations and proved that the addition of expanded graphite nanofillers could to some extend improve the tensile and storage modulus as well as thermal conductivity of PLA matrix composites Hassouna et al added 3wt% expanded graphite into PLA and melt-mixed absolutely, and results achieved that expanded graphite could well improve the dispersion and the delamination of the fillers.

Chieng et al.[36] prepared PLA/EPO/xGnP environment-friendly nanocomposites successfully by melt blending method and the test results proved that the addition of xGnP into PLAS/EPO improved the tensile strength and elongation at break of nanocomposites 26.5% and 60.6% respectively. In addition, impact strength of PLA/5wt% EPO improved by 73.6% with the addition of 0.5wt% xGnP loading. In conclusion, mechanical properties of PLA were greatly improved by the addition of a small amount of graphene nanoplatelets with the content lower than 1wt%.

Kim, Murariu et al.[37,38] blended EG nanofillers and PLA to manufacture nanofillers reinforced PLA nanocomposites. The results proved that nanocomposite exhibited very excellent rigidity and the Young’s modulus and storage modulus increased with EG content.

Above were reviews on melt-processing of graphene reinforced PLA nanocomposites. This manufacturing method was extremely simple and sample easy to be produced industrially.

Solvent-Mixing Process

Zhang et al.[39] incorporated 0.4 wt% exfoliated octadecylamine-functionalized graphene (ODAG) into PLA and prepared PLA/ODAG nanocomposites. The results showed that the tensile strength, Young’s modulus and the elongation at break of the nanocomposite were significantly increased by 34%, 44% and 160%, respectively, as compared to unfilled PLA.

Chen et al.[40] prepared PLA/graphene nanocomposites by direct solution-blending of PLA with graphene. The results showed that graphene nanosheets were well dispersed in the PLA matrix and no obvious aggregations were found in the PLA/graphene nanocomposites.

Wang et al.[41] prepared PLA/GO nanocomposites via solution blending. The results showed that when the content of fillers was lower than 0.5wt%, they exhibit heterogeneous nucleation effect for PLA, improving the crystallization behavior of PLA greatly.

Wang[42] prepared a series of PLA/GO-ODA nanocomposites by solution blending technique and investigated how GO-ODA contents influence their morphology, structure, thermal properties, crystallization properties, mechanical properties and gas barrier property. The TGA results showed that the thermal stability of PLA was significantly improved.

Chen et al.[43] prepared graphene/PLA composite film by physical blending and ultrasonic method. The resistance, mechanical properties, thermal stability and gas barrier properties of composite membrane were explored. By adding 1% graphene, the tensile strength increased by 33.3% and When adding graphene to 5%, thermal resistance reduced by 46.3%.

Shi[44] prepared Pristine exfoliated graphene(p-EG) / PLLA and silanized exfoliated(s-EG) / PLLA nanocomposites by graphene solution mixing-coagulation melt pressed processing techniques and solution casting method using laboratory made exfoliated graphene as fillers. DMA tests showed that the increase of storage modulus and glass transition temperature of s-EG/PLLA. DSC analysis showed that s-EG/PLLA composite exhibit lower cold crystallization.
PLL A / GOs nanocomposite was prepared by Wang et al.[45] via direct solution casting in this work. It is found that the presence of 0.02% GOs had enhanced significantly the crystallization rate of PLLA, but not changed the crystallization mechanism.

Ma et al.[46] prepared PLA/HA/GO nanocomposite membranes by electrospinning method. HA, GO and PLA can integrated into 3D framework which could create a potential scaffold so as to promote cell adhesion and growth.

Widsanusan et al.[47] compared neat PLA and PLA-(GO:SA) with content ratio of 1:1 and the result proved that the adding of GO and SA could improve the tensile strength of nanocomposites by 32%. It was proved that the effect of GO and the compatibility effect of SA could to some extend improve mechanical properties of GO reinforced nanocomposites.

Yang et al.[48] prepared PLA/GO/MCNTs nanocomposite with solution-blending method and then nanofiber composites were manufactured by electro-spinning method, cut into pieces for property tests. And the results proved that the adding of GP could improve thermal property and stability of nanocomposites and delay the degradation rate of PLA.

Chieng et al.[49] prepared PLA/epoxidized palm oil and the results showed that the addition of 0.3wt% graphene nanoplatelets could improve the tensile strength by 26.5% and elongation at break up to 60.6%.

Pinto et al.[50] showed that incorporation of small amounts (0.4 wt.%) of GO and GNP in PLA significantly increases tensile strength and Young’s modulus. Then Pinto et al.[51] incorporated graphene oxide and graphene nanoplatelets (GNP) into PLA. And results proved that graphene oxide and graphene nanoplatelets could change films surface topography, roughness and wettability, with surface free energy increased by 59%.

Huang et al.[52] solution coagulated and prepared GO reinforced PLA nanocomposite and the results suggested that the GONS/PLA nanocomposite films have excellent gas-barrier property which degarated from O2 or high-energy light.

Above were solvent-mixing processes of grapheme/PLA reinforced nanocomposites. The advantage of this method can be make graphene dispersing uniformly in PLA under the condition of stirring or untra-sonic.

Other Manufacturing Methods

Lei prepared[53] Poly(methyl methacrylate) functionalized graphene(PFG) via admicellar polymerization. All the results proved that PFG could to some extend improve the electrical, thermal, mechanical properties.

Gong et al.[54] prepared MWNTs / HA composites through in situ method by wet method with the help of ultrasonic, and PLA/MWNTs/HA composite membranes were prepared by solution casting method. And tensile modulus and storage modulus first increased then decreased, and the glass transition temperature increased.

Graphene/PLA and GO/PLA were prepared through the solution intercalation by Dong et al.[55]. The dispersion, thermal and mechanical properties were also analyzed and compared. The characterization results of graphene and GO oxide indicated that hydrazine hydrate could reduce GO and the graphene prepared is of high purity. By adding 0.5% graphene, the tensile strength and impact strength reached the maximum.

Results and Discussion

By concluding and analyzing above reviews, some tips were obtained as follows.

The Appropriate Content Ratio of Graphene in PLA Nanocomposites

Hassouna, Mortazavi, Kim, Hassouna[29-35,37,38] all added 3wt% exfoliated graphene nanofillers into PLA and manufactured graphene reinforced nanocomposites. The characterization results proved that properties of tensile strength, storage modulus, thermal property, elastic modulus and so on could to some extend be improved.
Chieng[36], Zhang[39], Wang[42], Chen[43] added the content of graphene nanoplatelets 0.3wt%, 0.4wt%, 0.2wt%, 1wt%, respectively into PLA, and its tensile strength was improved by 26.5%, 34%, 46.5% and 33.3% correspondingly. Wang[41] prepared nanocomposites and their crystallization behavior was modified with the content of graphene lower than 0.5wt%, but Wang[45] proved that the crystallization mechanism were not changed with 0.02wt% graphene nanofillers.

From above, several existing types of graphene such as graphene oxide and graphene nanoplatelets could be added into PLA. Generally speaking, the adding content ratio of graphene was about 3wt% and graphene nanoplatelet 0~0.5wt%.

The Adding of Modifiers Played an Important Role in Manufacturing Graphene/PLA Nanocomposites

Some modifiers were also added into PLA/graphene nanocomposites to modify their properties, such as Chieng[49] added epoxidized palm oil, Chen et al[40] used chloroform as mutual solvent. The adding of modifiers could make the connection and inner-connection between graphene and PLA much easier, and for further mechanical properties such as tensile strength and elastic modulus could be improved.

The Manufacturing Methods and Corresponding Improved Properties Were Important during Manufacturing Graphene/PLA Nanocomposites

The adding of graphene into PLA could indeed improve mechanical, thermal, electric, gas barrier and other properties of PLA. Therefore, the choosing of an appropriate manufacturing method was important.

Conclusions and Suggestions

The significant researches on bio-degradation graphene/PLA nanocomposites have been summarized in this review article. Several conclusions and suggestions were obtained as follows.

The Effecting Elements during Manufacturing Procedure

Most researchers took advantage of solution-mixing, melt-mixing and few with admicellar polymerization, in-situ polymerization and solution intercalation. The experiments proved that the mixing sequence and melt-mixing parameters, such as aspect ratio and size all made to some extend effects on different states of dispersion and different filler localizations.

Some Problems to Be Solved

Some problems such as the interconnection between graphene and PLA, dispersion of graphene into PLA, alignment and anti-agglomeration of grapheme into PLA, the ranging and its control of graphene in PLA, the intra-surface between graphene, PLA and fibers in further manufacturing graphene/PLA/fiber reinforced composites were needed to be solved.

References


