The 3rd International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/3/20230556

Recent Advances of Polylactic Acid (PLA) Toughening Methods

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Abstract. Nowadays, polylactic acid (PLA) has been one of the most important packaging materials in daily life. PLA is eco-friendly because it can be made from renewable resources and is degradable, but it also has a drawback that is lack of toughening. In this review, papers about 3 main methods that could help improve the toughening of the PLA have been collected. They are blending, copolymerization and composition. Blending is a physical method to make the materials uniformly to improve the properties of the material. Copolymerization is the reaction of polymerizing various compounds into one substance under certain conditions. Composition is the termination of reaction by combining two growing free radicals to form a saturated macromolecule. This work will give some exact examples to improve the toughening of the PLA. It is expected that there will be better research methods and materials that are able to improve the toughness of PLA in the future.

Keywords: PLA, Toughening, Blending, Copolymerization, Composition.

1. Introduction

Polylactic acid or polyactide (PLA) could be a perishable and bioactive polyester created of carboxylic acid building blocks. Artificial chemical compound PLA could be a non-toxic and non-irritating substance. Lactic acid is its primary raw material and is produced mostly by the fermentation of starch (such as corn and rice). Additionally, cellulose, kitchen trash, and fish waste can be used to obtain it. The product created from PLA are often directly composted or burned once use, and may finally entirely scale back dioxide and water, meeting the requirements of property development. PLA raw ingredients area unit accessible from a range of sources. The primary factors influencing PLA's widespread utilization are its high degree of transparency, durability, biocompatibility, and heat resistance. PLA can be produced through ring-opening polymerization (ROP) of lactide in two steps. The core technology of dehydration of lactic acid to oligomer, depolymerization to lactide, and ring-opening polymerization to arrange PLA is the synthesis and purification of lactide.

The purification of lactide is incredibly necessary within the whole ROP chemical process. Solely high purity lactide is often wont to synthesize PLA with high relative molecular weight and smart physical properties. If the purity of lactide is not high, it will have an effect on the standard of the ultimate product PLA.

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DOI: 10.54254/2755-2721/3/20230556

The two-step method involves the purification step of lactide, so the process is complex and the cost is high. However, the PLA with controllable high molecular weight and chemical structure and good mechanical properties can be produced by controlling the purity and reaction conditions of lactide, so it is the most widely used method in industry at present. In addition, PLA is thermoplastic and might be employed in several fields. The merchandise ready with PLA, like packaging materials, fibers, etc., area unit chiefly employed in disposable merchandise, like disposable ware and packages, car doors, clothes, electrical devices, medical and healthcare products and different fields. In the past decades, PLA has been widely used as a packaging material for consumer goods. PLA reduces dependence on petroleum raw materials because it is made from renewable resources and compostable, which solves the problem of solid waste treatment. PLA is currently the second largest production and consumption of bioplastics in the world. However, PLA has a fatal disadvantage: poor toughness. This paper will collect the toughening methods of PLA through different ways.

2. Blending

Blending refers to co-mixing, which is a physical method to make several materials uniformly mixed to improve material properties, Therefore, the scientists use blending to enhance the toughness of PLA. The blending of PLA and rubber such as polybutadiene (PB) and polyisoprene (PIB) has successfully improved the fracture elongation, tensile toughness and impact toughness. This method makes the area of the low-modulus material dispersed in the polylactic acid matrix. The rubber domains are used as stress concentration bodies. Once the crack expands, it will interact with the rubber domain, resulting in cavitation and/or cracking of the rubber material. Both of these mechanisms will consume energy to prevent crack growth, and may cause material failure to change from brittle state to ductile state. However, rubber-like blends need to be dispersed in PLA as small particles (usually 0.1 ~ 1.0 μ m) The interface adhesion with PLA shall be such that the glass transition temperature (Tg) of rubber shall be at least 20 ℃ lower than the test or service temperature; The molecular weight should not be too low; It is thermally stable at the processing temperature of PLA. However, most of the rubbers used for modification are incompatible with PLA, resulting in phase separation: that is, weak interfacial adhesion and poor dispersion between the two phases. Another blending method refers to use biodegradable materials, which cannot only improve the mechanical properties, hydrophilicity and degradability of PLA, but also fundamentally solve the problem of material pollution.

In Chen et al.' research, their experiment's goal is to form toughened and high-strength PLA/poly (butylene adipate-co-terephthalate) (PBAT) blends that may be with success ready through surface compatibilization and dynamic vulcanisation throughout reactive soften mixing, with atiny low quantity of epoxy-functional styrene–acrylic acid (ESA) oligomer By branching some PLA and PBAT onto the most chain of ESA, the experiment intends to attain the compatibilization target. At constant time, powerfully crosslinked PBAT with a particular network distribution were cured by ESA within the PLA matrix. The lacy PBAT particles and also the strengthened interface each encourage the large-scale matrix plastic deformation necessary for economical energy consumption, that significantly will increase the toughening result. The balance between toughness and strength was discovered. The toughness and elongation at break were determined to be 62.4 kJ/m2 and 232%. The foremost vital finding from analysis is that the molecular structures of ESA are crucial in terms of enhancing surface adhesion and morphology and come through high toughening potency [1]. As a result, blending's outcome can assist PLA become more durable.

3. Copolymerization

Copolymerization is the reaction of polymerizing various compounds into one substance under certain conditions. Plasticizing modification refers to mixing 0.5%-30% plasticizers with high boiling point, low volatility and non-toxic into PLA matrix to significantly improve the flexibility of PLA, improve low-temperature brittleness and improve overall processing performance. Specifically, chemical plasticizer refers to the grafting reaction between plasticizer and PLA molecular chain segment, and the use of its own steric hindrance to expand the PLA molecular chain spacing to play a toughening

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effect. The advantages of single-molecular and low-molecular plasticizers are that compared with macromolecules, they are easier to mix with PLA evenly, effectively improving the toughness of PLA and reducing Tg. However, the migration or volatilization over time will make PLA lose its toughness and pollute food and drugs. While the toughening effect of oligomer plasticizer is not as good as that of low molecular plasticizer, it can better achieve the balance between strength and toughness of PLA materials and reduce the migration rate.

Greco and colleagues investigated the employment of PLA plasticized by different cardanol and epoxidized cardanol acetate, within the motility molding of hollow objects. After melting and mixing, rotational molding machinery used in a lab was used to prepare the plasticized PLA samples. Poly (ethylene glycol) (PEG) and plasticized PLA were made for comparison, too. Even though rotational molding had a very slow cooling rate, samples made entirely of amorphous PLA and PLA plasticized with cashew phenol compounds were obtained. PLA plasticized with PEG, in contrast, displayed extremely high crystallinity. Plasticized PLA was produced through melting, mixture, and processed through motion molding instrumentation. This made it impossible to extract the rotogrammed box-shaped sample. The plasticizing effect of cashew phenol derivatives has been confirmed by the tensile test of the rotational molding prototype, which highlights the reduced modulus and strength as well as the improved fracture strain compared with pure PLA. Therefore, the effective toughening of PLA is achieved by exploitation of cashew phenol-derivatives as plasticizers, which involved reduction within the glass transition of the chemical compound and a discount within the crystallization mechanics. As the addition of plasticizer leads to the reduction of Tg, even during the aging at room temperature, there will be a significant crystallization effect, which will lead to significant embrittlement of the material. Compared with pure PLA, this highlights the reduced modulus and strength as well as the improved fracture strain. In their work, it was assessed whether cardanol and epoxidized cardanol acetate might be used to plasticize PLA during rotational molding. The addition of two hundredth cardanol to PLA resulted in a decrease in Tg, but no increase in crystallinity was found. That made the structure entirely amorphous. The creation of a semi-crystalline structure, which was distinguished by a significantly lower crystallinity than that attained using PEG, was facilitated by the addition of epoxidized cardanol acetate. Compared with pure PLA, the obtained PLA project is characterised by a lot of lower modulus and strength, and multiplied fracture strain and toughness. specifically, compared with epoxidized cardanol acetate, the modulus and strength of cardanol were lower, highlight the upper plasticizing result of cardanol. However, the obtained terribly robust plasticized PLA was characterised by vital recrystallization result for a protracted time even at cold [2]. In their experiment, an ionomer based on imidazolium and a poly (ionic liquid) - b-PLA polymer (ILA) were created because the PLA's toughening agents. utilizing a multi-step method that comes with activity, continuous compound feed copolymerization, quaternization reaction, and mixing amongst ionomers. By combining PLA with ILA and ionomer, PLA materials with wonderful transparency, high toughness, and medication characteristics were with success created. The blends' part morphology, mechanical characteristics, and transparency were all fastidiously examined in relevance the composition of the ionomer and therefore the ILA compatibilizer. The best formula (PLA/E12/ILA 60/40/5) exhibits excellent 89-93% light transmittance, 45 kJ/m^2 high impact strength, and 170% elongation at break. More curiously, the mixture has appealing antibacterial capabilities due to imidazolium cations as well as anion groups. In addition to producing impact of compatibilization and high efficiency toughening synergistically, the ion exchange between the imidazole-containing ionomer system and the ILA copolymer also provided a new approach for the creation of high-performance PLA materials [3]. This project developed a green modification technique that significantly increased the PLA's toughness. Here, lactide is grafted onto alkaline lignin (LG) after it has been first alkylated with dodecane (LA). By exploitating ring-opening chemical process, alkylated lignin-lactide graft polymer (GLG-g-LA) was created. It may be utilised as useful fillers to strengthen packaging films manufactured from polylactic acid (PLA). ^{31}P-NMR analysis discovered that the relative signal of the -COOH and -OH radical dramatically attenuated whereas the phenoplast radical peak wholly nonexistent. The graft magnitude relation of GLG-g-LA polymer was quite double that of

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LG graft polymer (LG-g-LA). Following that, PLA could be combined with both two copolymers, and various PLA composite films were created via tape casting. In particular, the PLA/GLG-g-LA's elongation at break was improved to 41.98%. Generally, it is a high-performance and biodegradable material that may be utilized in packaging because of its toughness, superior ultra violet barrier, water resistance, and adjustable permeability [4].

4. Composition

PLA composites have different properties when composited different materials. Josef et al. studied the result of grating lamination on properties of three dimensional (3D) printed PLA. They studied the ensuing toughness, strength and stiffness, especially toughness. Results reveal the stiffness and strength of the standard lamination with 90° alternating directions were almost isotropic, while the toughness was highly anisotropic. In addition, it shows that materials with this type of lamination might even amendment their behavior from breakableness to malleability per the loading direction. Finally, they planned a replacement stacking theme, which provided higher toughness and better strength compared with the quality methodology. For unidirectional laminations, if the fibers were parallel with the loading direction, all the toughness, strength and stiffness area unit the best. For laminations with a 90° offset within the layer direction (this is normal in Fused Deposition Modeling (FDM) printing), they found that the fabric was utterly identical in stiffness and strength, but completely different in toughness. especially, the fabric exhibited higher toughness once loaded diagonally onto the grating than once loaded parallel/perpendicular to the grating. Additionally, most behaviors of materials altered with the loading direction. Such phenomena were because of the harm beginning within the inter-fiber bonding, and that made the fibers re-orient toward the loading direction, resulting in a big increase in elongation at break. On this basis, researchers have studied a novel interlacing scheme, in which the alternate layers are symmetrically arranged relative to the loading direction. If this scheme is applied, the optimized material properties that provide high strength and high toughness can be obtained at the same time [5]. In another study, zirconium phosphate (ZrP), a nano filler were blended into PLA to move forward its warm steadiness. The nanocomposite PLA/ZrP/ethylene-methyl acrylate-glycidyl methacrylate polymer (E-MA-GMA) was obtained with superb toughness. The quality of the nanocomposites was expanded to 71.5 kJ/m2, and the composition proportion was 72/3/25. Transmission electron microscopy (TEM) characterized the typical core-shell structure that could lead to a large amount of shear yield deformation, which made the nanocomposites have excellent toughness. From the research of Zhu et al., super-toughness PLA/ZrP/E-MA-GMA nano composites were arranged by responsive soften blending strategy. After counting 15% E-MA-GMA, the nanocomposites possessed these properties: prolongation at break were 41.6 times of unadulterated PLA; The pliable quality remained at 39.1MPa. It was suggested that there was extended compatibility between PLA and ZrP. Electron microscopy observations indicated an ordinary core-shell structure, which gave the orchestrated nanocomposites awesome sturdiness [6].

In the research by Jiang et al., PLA was strengthened and made tougher through the process of dynamic vulcanization using SiO_2 and (epoxy natural rubber) ENR treated with silane coupling agent KH550. A bicontinuous phase structure was discovered in PLA/ENR/SiO2 thermoplastic vulcanizate (TPV) with balanced stiffness and toughness. The hydrophobic SiO2 was inside them, and they were carefully controlled to be evenly dispersed in the ENR phase. This was important for strengthening rubber, which helped toughen PLA while maintaining satisfactory rigidity. Through combining SiO_2 nanoparticles with KH550, TPV can achieve 23.7 kJ/m2 impact strength at 0 °C while maintaining 42.1 MPa tensile strength, which is 1.62 times and 1.03 times greater than those values prior to modification. Through a series of tests and analysis, the synergistic toughening mechanisms were discovered, that provided a straightforward and effective technique for making ready superior PLA materials [7].

In the study of Huang et al., dynamic vulcanization was induced using diisopropylene peroxide to produce PLA/polymethylmethacrylate grafted natural rubber (NR-PMMA)/NR blends with enhanced compatibility. The co-continuous morphology of simple blends and the obtained ternary TPV was

DOI: 10.54254/2755-2721/3/20230556

evident. Additionally, in the dynamic vulcanization processes, PLA and rubber became compatible in-situ. The hardness increases initially and then reduces as dicumyl peroxide (DCP) content increases. The highest impact strength of TPV, 760.7 J/m, was achieved with 2.5 parts of DCP. At the same time, the tensile strengths of TPV and simple blends were similar (about 44 MPa) [8].

To increase the tensile toughness of pure PLA, a set of PLA biological blends and branched polycaprolactone (PCL) grafted polysaccharide biological toughening agent (CghbP) were simply manufactured and characterized in Zafar et al'study. The ready PLA/CghbP biological mix is physically complete and only partially compatible at the dimensions of ca. 10-30 nm. Characterization confirmed that implementation of CghbP to PLA might cause additional disorder of PLA in ready PLA/CghbP blends. The study determined that the enhanced tensile toughness containing five skyscraper CghbP was associated with the additional ordered arduous PLA evoked by loading acceptable CghbP into PLA α Crystallization is closely associated with the synchronous formation of extremely branched soft phases. additionally, compared with different PLA/CghbP blends and PLA/traditional low-molecular-weight plasticiser blends, the 5% PLA/CghbP5 bioblend showed considerably higher migration stability when additive overflow take a look at, with a weight loss of concerning 0.1% CghbP [9].

In Chen et al' study, the effect of extrusion temperature on reactive PLA/epoxy-containing elastomer was studied. The mix framework of acrylic-butyl acrylate/glycidyl methacrylate (EBA-GMA) and metallic element particle crosslinking operator [magnesium particle crosslinking operator of ethylene/methacrylate polymer (EMAA-Mg)] was examined. The reliance of morphology advancement on responsive admixture temperature was investigated. The degree of response compatibilization between PLA/EBA-GMA and EBA-GMA crosslinks started by EMAA-Mg was determined, torsion rheometer, energetic mechanical examination and gel substance once chloroform extraction of the dioxane freed buildup. The stage morphology was examined by negatron magnifying lens perception and energetic natural philosophy take a look at. Compared with the ternary mixes containing metallic element neutral EMAA polymer (EMAA-Zn), the scored have an effect on quality of the mix containing EMAA-Mg was less subordinate on the expulsion temperature. With the increment of expulsion temperature, the taking once ternary mixes appeared distinctive "Salami-like" scattered stage structure [10].

5. Conclusion

The above are some methods collected to solve the toughening of PLA. There are three main approaches, blending, copolymerization and composition. Blending modification refers to the blending of PLA and other polymer materials to achieve the purpose of toughening PLA by compounding the properties of each component. It is the most direct toughening method of PLA at present. A large number of non-biodegradable and biodegradable flexible polymers have been used to toughen PLA. Copolymerization modification is a modification method based on micro-molecular structure. It refers to the effect of reducing the regularity of PLA chain, reducing its crystallinity or weakening the interaction between PLA molecular chains by introducing flexible chain segments into the side chain or main chain of PLA, to improve the toughness of PLA. Currently, the commonly employed copolymerization modification can be mainly divided into graft copolymerization and block copolymerization. Although copolymerization modification can fundamentally improve the brittleness of PLA through structural control, most of the modification methods have the disadvantages of complex preparation process and high cost. Composition is now one of the hottest topics in terms of PLA toughening. It is most flexible and promising approach for there can be a wide variety of both polymer and inorganic materials which can be composited with PLA. It is of great importance to develop PLA composites with improved toughness and reduced cost toward mass production.

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