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# Epoxy-Based Chain Extenders in Polylactic Acid (PLA): A Comprehensive Review of Structure, Performance, and Challenges

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## Abstract

Amid the escalating plastic pollution issue, the development of biodegradable and recyclable polymeric materials has become a focus within the scientific community. Chain extenders, which are an important class of compounds, facilitate the elongation of polymer chains through reactive functional groups, thereby enhancing the performance of the materials. Epoxy-based chain extenders, due to their cost-effectiveness, low toxicity, high reaction efficiency, and effective reactivity with hydroxyl and carboxyl groups, have emerged as a promising class of chain extenders. This manuscript comprehensively elaborates on the varieties, structural characteristics, and performance of chain extenders, the challenges they face, and the methods for their modification. Special emphasis is placed on the application of epoxy-based chain extenders in biodegradable polymers, such as polylactic acid (PLA), and their subsequent influence on the structural and performance properties of these materials.

## Keywords

Chain Extender, Epoxy Type, GMA, Biodegradable, PLA, Recycle

## 1. Introduction

Polymer materials, especially plastics, play an important role in multiple fields such as packaging, home appliances and building materials due to their advantages of light weight, ease of processing and cost-effectiveness. [1] Nevertheless, the extensive use of these materials has led to serious environmental issues. Disposable plastic products, such as straws, tableware, cups and bags, which can hardly be recycled owing to their lightweight nature, have become a focus of social concern. According to statistics, in 2020, China's output of primary plastics exceeded 100 million tons, while the global recycling rate of plastic products is only 9%. A large amount of wasted plastics eventually pile up in landfills or enter the natural environment, causing soil damage, water pollution and ecological impacts, and even threatening human health. [2]

The impact of plastic pollution on the environment and living organisms has drawn global attention. [3]-[10] Microplastic particles may potentially enter the human body via the food chain. Meanwhile, the slow degradation of plastic waste results in the accumulation of persistent organic pollutants in the environment. Additionally, carbon dioxide emissions during the production of plastics and the depletion of fossil resources are also serious issues that the industry is confronted with. [11]-[15] Under the Framework Convention on Climate Change, the United Nations has proposed the "Race to Zero" strategy. However, the situation regarding achieving this goal remains challenging. [16]-[22]

To address these challenges, academia and industry are exploring two main solution approaches. The first is the concept of circular economy, which aims to improve resource utilization efficiency through reduction, reuse, and recycling. For example, the European Union, the United States, South Korea, China, and Japan have issued various regulations on handling plastic waste to improve recycling efficiency. [23]-[29] For the traditional recycling method, such as re-extrusion, impurities such as moisture and cleaning solution introduced during the cleaning process may cause the degradation of polymers and a drop in viscosity after high-temperature shearing and melting. The mechanical properties of polymers are directly correlated with molecular weight. A decline in molecular weight leads to the deterioration of mechanical properties. Eventually, the recycled plastic products fail to meet the usage standards and thus cannot be reused. [30]-[33] To address this issue, researchers have attempted to inhibit the degradation and enhance the performance of recycled plastics by applying chain extenders. [34]-[39] Through this particular approach, recycled plastics can be effectively redirected and reused in the production of plastic products, thereby reducing the need for new plastic production. Specifically, the production of 1 kg of traditional plastics, such as polyethylene, requires approximately 73 to 81 MJ of energy and results in 2.5 to 3 kg of $CO_2$ equivalent emissions. [40] Replacing new plastics with recycled ones avoids excessive energy consumption and $CO_2$ emissions, thus realizing the benefits of environmental protection and cost reduction. Particularly, it was estimated that recycling could reduce the environmental impacts caused by fossil fuel depletion by 40% to 60%. [41]

Another approach is to develop degradable polymers to achieve an environmentally friendly substitution for plastics. [42]-[47] As a biodegradable material, polylactic acid (PLA) has attracted attention due to its good optical, mechanical, thermal and barrier properties. [48]-[55] In industry, PLA has been produced in large quantities. According to statistics, in 2015, the production of PLA reached

0.2 million tons, and by 2019, it had increased to 0.3 million tons. This figure has continued to grow in recent years. [56] PLA is manufactured from lactic acid, which is obtained through the fermentation of starch found in sugarcane and corn. It takes approximately 28 MJ of energy to produce 1 kg of PLA, and 1.8 kg of $CO_2$ is emitted. [57] Without considering the biodegradability of PLA, the energy required for its production and the greenhouse gas emissions are much lower than those of traditional plastics. Additionally, its demand for non-renewable energy is also considerably less. The end-of-life (EoL) options for PLA include landfilling, composting, and recycling. The landfilling of PLA products exerts a comparatively minor influence on the environment. Merely 1% of it will be decomposed after a span of 100 years, and the $CH_4$ generation is less than 0.1%, accompanied by negligible $CO_2$ emissions. [58] The composting process of PLA products is generally regarded as one of the worst EoL options due to the lack of energy recovery and low compost quality. [59] Recycling, on the other hand, is the most promising EoL option for PLA, which can significantly reduce $CO_2$ emissions and environmental problems. [60] Nevertheless, regardless of whether it is virgin or recycled PLA, only the high molecular weight PLA possesses commercial value within industries like fiber, textile, plastics, and packaging. [61]-[63] Therefore, enhancing the molecular weight of PLA to improve its comprehensive properties is a hot topic in current research and using chain extenders is one of the most promising ways to solve this problem.

Chain extension is an effective chemical modification approach. Compared with solid-state polycondensation, it is not only more effective in increasing molecular weight but also simple to operate, with milder reaction conditions that are easy to regulate. Epoxy-based chain extenders represent a class of promising chain extenders due to their broad availability, low cost, safety and non-toxicity. They are capable of improving the viscoelasticity, thermal stability, melt strength and processability of PLA-based materials. Moreover, they contribute to the blending modification, enhancing capacity and functionalizing of PLA, and even in its recycling. [64]-[69]

This manuscript comprehensively introduces the structure, performance, challenges faced and modification approaches of chain extenders, and discusses the development and application of degradable materials. Future research may focus on exploring the relationship between the structure and performance of chain extenders, optimizing the chain extension process and developing new degradable polymers to achieve an environmentally friendly substitution and recycling of plastic materials. This requires not only the efforts of researchers but also the joint participation of policymakers, industry, and consumers. Through interdisciplinary cooperation and innovation, the sustainable development of plastic materials and the solution to environmental problems can be promoted.

## 2. Categories of Chain Extenders

In terms of the chemical structure of chain extenders, there are usually multiple reactive functional groups on a single molecular chain. Through the reaction of these reactive functional groups with the active groups in polymer materials (usually end groups), the molecular chains of the target polymer are promoted to extend and expand. The common chain extenders applicable to PLA include epoxy-, isocyanate-, anhydride- and oxazoline-based chain extenders. The following sections will present a detailed introduction to each of them.

## 2.1. Epoxy-Based Chain Extenders

As one of the most common functional groups in chain extenders, the epoxy group has unique chemical properties and reactivity. It can react with hydroxyl, carboxyl and amino groups in polymers through ring opening to form new chemical bonds, thereby increasing their molecular weight, mechanical properties and processability. Owing to their cost-effectiveness, low toxicity and high reaction efficiency, epoxy-based chain extenders have a broad application prospect in polymer modification and are currently the most commercially mature systems. [64]-[69] In **Figure 1**, the chain extension reactions of the epoxy-based chain extenders with the carboxyl and amino groups are illustrated.

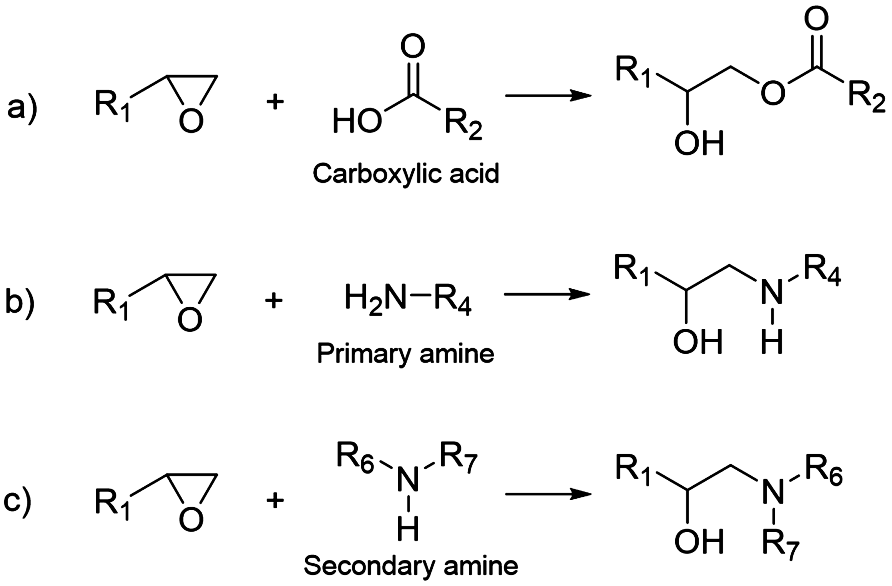

**Figure 1.** Chain extension reactions based on epoxy groups. [64]

The incorporation of chain extenders has a remarkable impact on the properties of polymers. Pilla *et al.* employed the epoxy-based chain extender (Joncryl® series) to enhance the extrusion and injection foamability of PLA. The addition of the epoxy-based chain extender significantly increased the molecular weight of PLA, but decreased its crystallinity. [70] CORRE *et al.* incorporated the epoxy-based chain extender into PLA during the reactive extrusion. Upon chain extension, the enhancement in the melt rheology of the modified materials in terms of melt strength and thermal stability during stretching and shearing has been observed. [71] Mihai *et al.* fabricated branched PLA with the epoxy-based chain extender.

This enhanced the shear viscosity and melt elasticity and, crucially, induced strain-hardening during uniaxial deformation in the molten state. [72] According to Elhassan *et al.*, the capping and connecting of the epoxy-based chain extender into PLA led to significant improvement in tensile strength and modulus. [73] Yousefzade *et al.* studied the impact of the epoxy-based chain extender on the crystallization rate of PLA. A high percentage of the epoxy-based chain extender promoted primary nucleation and increased the overall crystallization rate constant. [74] Cailloux *et al.* demonstrated that the reaction selectivity between epoxy groups and carboxyl groups was greater than that between epoxy and hydroxyl groups, owing to higher polarity. [75] In addition, Cai *et al.* investigated the chain-extending effect of a small-molecule epoxy-based chain extender on polyamide 6 (PA6). The addition of such an epoxy chain extender in the process of melt extrusion enabled the shear viscosity of PA6 to decrease by 52.2%, while simultaneously increasing the notched impact strength from 62.4 J/m to 105.9 J/m. [76] These findings provide definite directions for the application of epoxy chain extenders.

The chain-extending effect of the epoxy-based chain extenders is directly related to their functionality. Xanthos *et al.* compared the chain-extending effects of multifunctional anhydride- and epoxy-based chain extenders on polyethylene terephthalate (PET). Pyromellitic dianhydride, tetrafunctional and trifunctional epoxide exhibited strong reactivity. These modifiers could not only increase the molecular weight but also enhance the mechanical properties and processability of the material. [77] Dong *et al.* found that multi-epoxy functional chain extenders can effectively improve the compatibility and reduce the interfacial tension between PLA and PBAT. Chain extenders with a higher epoxy functionality have higher reaction efficiency. With a 1 wt% addition of the chain extender having 9 epoxy groups in its structure, the average PBAT phase size was reduced to 0.5 μm. While for the other chain extender with 2 epoxy groups in its structure, it was reduced to only 1 μm. [78]

The functionality of the chain extender also influences the structure of the polymer. Wu *et al.* that chain extenders with higher epoxy functionality tended to react with the carboxyl group of the oligomers, leading to the formation of branched structures in addition to linear growth. Polymers modified by bi-epoxy functional chain extenders exhibited a linear structure and desirable rheological properties, while polymers modified by multi-epoxy functional chain extenders had long-chain branched structures and better crystallinity, e.g., a higher crystallization rate. The higher the epoxy functionality of the chain extender is, the higher the level of branched structures of the polymer after chain extension will be. Moreover, the branched polymers show a higher shear thinning sensitivity, which is beneficial for large-scale processing and production. [79] [80] According to Eslami *et al.*, incorporating the epoxy-based, multifunctional chain extender into the biodegradable PLA/PBSA blends led to the formation of a long-chain branched topology and an increase in molecular weight and viscosity. The appearance of both linear and randomly branched structures improved the melt strength and strain hardening of the material, which consequently enhanced its processability and inhibited its thermal degradation. [81]-[84] The growth of melt strength facilitates post-processing, such as film blowing and extrusion, which is of significant significance for the expansion of PLA applications.

**Table 1** presents a compilation of commercially available epoxy-based chain extenders. [64]-[68] Examination of the data reveals that the majority of these epoxy-based chain extenders possess relatively low molecular weights. In an effort to overcome the limitations associated with the chain extension efficiency of traditional small molecule epoxy chain extenders, Li *et al.* have employed a secondary chain extension strategy. This approach involves the utilization of small molecule chain extenders with distinct structural features and the implementation of multiple chain extension reactions. Consequently, this methodology has resulted in a pronounced alteration in the structure of PLA, characterized by an increase in molecular weight and the formation of an extensive network of long-chain branching. These changes have been correlated with an enhancement in storage modulus and complex viscosity, which subsequently influence the crystalline structure. The alterations in crystalline morphology are evidenced by reduced spherulite sizes and increased crystallinity, culminating in a marked improvement in tensile strength and modulus. [69] However, the complexity of this approach may present challenges for its adoption in industrial-scale applications.

**Table 1.** Commercial epoxy chain extenders [64]-[68].

| Model | Specification | Epoxy equivalent | Mw | Appearance |
|---|---|---|---|---|
| Joncryl® | ADR 4468<br>ADR 4368<br>ADR 4370 | 285 - 320 | 6800 - 7300 | Powder/Flake |
| Ever Sun | X-U993 | −280 - 310 | 6500 - 7200 | Powder |
| Shanxi Chemical Industry | KL-E4370 | 270 - 300 | 6500 - 7000 | Powder |
| Bio-Master® | HPC-3510/P | 280 - 310 | −50000 | Powder/Particle |
| Eco-Batch® | Eco-1180 | 280 - 310 | 40,000 - 60,000 | Powder/Particle |
|  | Eco-1120 | 450 - 600 | 50,000 - 80,000 |  |
| Thyosil | CXP-5045 | −450 | −7000 | Powder |
|  | CXP-5030 | −285 | −7000 | Powder |

## 2.2. Isocyanate-Based Chain Extenders

Isocyanates (NCO) are a class of highly reactive compounds, which are able to interact with various functional groups, such as hydroxyl, carboxyl and amino groups. Isocyanates-based chain extenders also play an important role in polymer modification. For instance, the application of isocyanate-based chain extenders can effectively increase the viscosity, energy storage modulus and molecular weight of recycled PET and transform PET from a brittle material into a ductile one. [85] [86] They can also be utilized in biodegradable materials like PLA.

Through reacting with the end groups of PLA, ester-polyurethane linkages are formed, as illustrated in **Figure 2**. This process leads to an increase in molecular weight and an enhancement of mechanical properties. In addition, the branched or cross-linked structures generated in this process may lead to an increase in the glass transition temperature of the material. [87]-[90] Tuna *et al.* compared the chain-extending effects of 1,4-phenylene diisocynate (PDI) and the epoxy-based chain extender (Joncryl® series) on recycled PLA, and both were found to be effective. The viscosity of PLA experienced a more rapid increase when PDI was incorporated than when the epoxy-based chain extender was added. This was attributable to the higher reactivity of isocyanate. However, an overly high reaction rate led to the PDI being consumed too quickly during processing. In the absence of PDI for a long time, the thermomechanical effect caused chain scission and thus a reduction in molecular weight. In contrast, the epoxy-based chain extender enabled PLA to remain in a high-temperature processing state for a longer period. [91] Although isocyanate-based chain extenders show efficient reactivity, their use may lead to the discoloration of the product and may produce toxic or potentially carcinogenic degradation products, which restricts their application. [92] Research has indicated that isocyanate-based chain extenders, with hexamethylene diisocyanate (HDI) and diphenylmethane diisocyanate (MDI) in particular, possess stronger toxicity in contrast to other types of chain extenders like anhydride-based, phosphite-based, and oxazolidine-based ones. These substances are capable of impeding the growth of organisms, reducing their lifespan, and triggering locomotor impairments, neuronal damage, as well as reproductive deficiencies. [93] Consequently, it is essential to carry out more rigorous environmental safety evaluations regarding the application of such chain extenders.

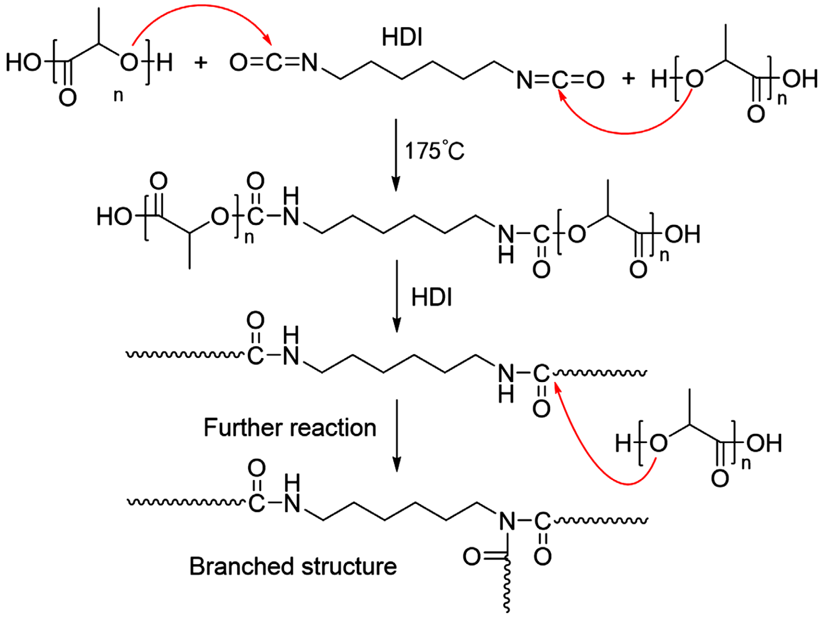

**Figure 2.** Chain extension reactions of PLA by using isocyanate-based chain extender. [88]

## 2.3. Anhydride-Based Chain Extenders

Anhydride-based chain extenders, such as homophthalic tetracarboxylic acid dianhydride (PMDA), are essential in the field of polymer modification due to their high reactivity and high functional group content. These chain extenders are capable of reacting with the hydroxyl groups of polymers, such as polylactic acid (PLA), through the ring-opening reaction of the anhydride group to promote chain extension and thus improve the melt strength. The concentration of anhydride-based chain extenders, processing temperature, and reaction time have a significant influence on the material properties. Studies have demonstrated that with the increasing PMDA concentration, the chain extension reaction rate of PET actually decreases. This phenomenon can be explained by the reaction mechanism of PMDA, as shown in **Figure 3**. At a high PMDA content, the ring-opening of the anhydride functional groups forms more carboxylic acid groups. The generated carboxylic acid groups may react with the end group of the PET, known as the slower second reaction step, which competes with the first step. Consequently, the overall chain extension reaction rate is reduced. [94]

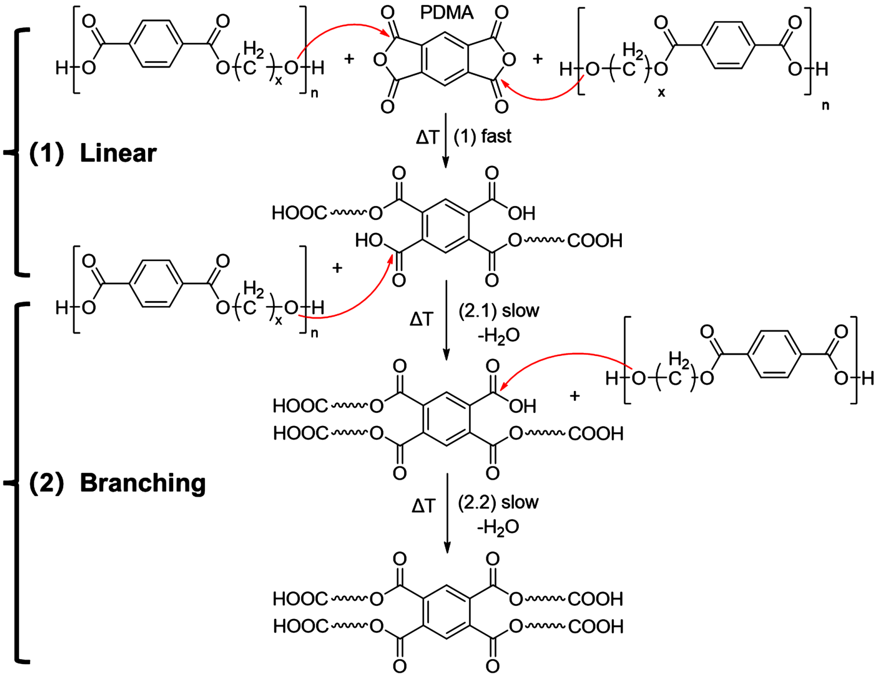

**Figure 3.** Chain extension reactions of a polyester by using an anhydride-based chain extender. [94]

Polymers modified by anhydride-based chain extenders exhibit excellent physical properties. For example, PET, after being chain-extended by PMDA shows significantly increased viscosity, storage modulus and molecular weight, while improving the toughness of the material. [95] In biodegradable materials such as PLA, the application of anhydride-based chain extenders has also been widely studied. By generating carboxyl groups through the ring-opening reaction of anhydride, the reaction between PLA and the epoxy group can be promoted. As a result, the molecular weight and heat resistance of PLA can be significantly enhanced. [96]-[102] However, the application of anhydride-based chain extenders in large-scale production is restricted because of the complexity of the two-step chain extension reaction. Hence, researchers are seeking more efficient and cost-effective approaches to realize the extensive application of anhydride-based chain extenders in industrial production. For instance, Yahyaee *et al*. simultaneously incorporated two chain extenders, namely Joncryl® series and PMDA, into PLA. The intention of adding PMDA was to increase the number of carboxyl groups by means of the anhydride ring-opening reaction. In comparison with hydroxyl groups, epoxy groups exhibit a greater preference for reacting with carboxyl groups. Hence, the reaction between PLA and the epoxy chain extender could be more easily facilitated. The PLA extended with both chain extenders demonstrated a synergistic enhancement in shear rheological characteristics and elongational rheological properties, owing to the longer segments between the branching points within their structure. [95]

## 2.4. Oxazoline-Based Chain Extenders

Oxazoline, a five-membered heterocyclic compound containing nitrogen and oxygen, exhibits remarkable application prospects in the area of polymer chain expansion owing to its high reactivity and rapid reaction rate. It realizes the chain extension by forming an ester-amide bond with the carboxyl group through ring-opening reaction. In this process, no small molecule by-products are generated, making it an ideal choice as a chain extender. Inata *et al*. proposed the reaction mechanism of oxazoline with carboxyl groups, namely coupling and blocking, as depicted in **Figure 4**. Moreover, oxazoline has a higher reaction efficiency with carboxyl groups than with hydroxyl groups. [103]-[106]

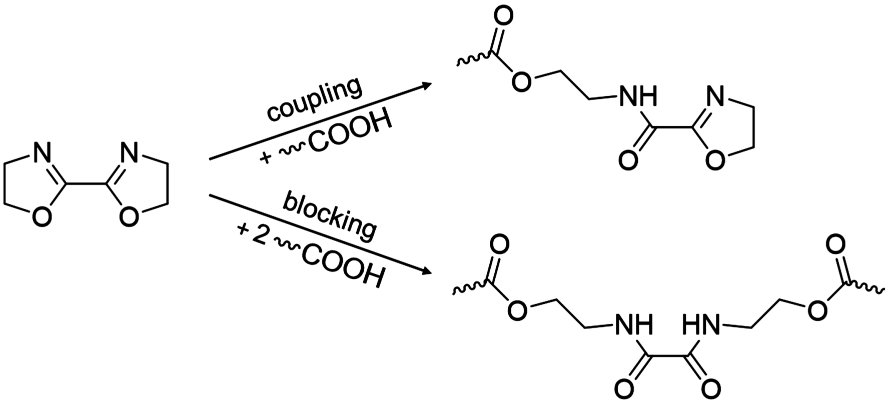

**Figure 4.** Chain extension reactions based on oxazoline. [106]

According to Kylmä *et al*., in case all the polymer ends are hydroxyl groups, applying 1,6-hexamethylene diisocyanate (HMDI) as the chain extender yields remarkable chain-extending effect and can effectively increase the molecular weight.

Whereas, when the polymers are entirely terminated with carboxyl groups, the addition of oxazoline-based chain extenders can not only reduce the acid value of the polymers but also perform chain extension. If both hydroxyl and carboxyl groups are present at the end of the polymers, a better chain-extending effect can be obtained by using HMDI and oxazoline-based chain extenders in combination, as shown in **Figure 5**. [105]-[108]

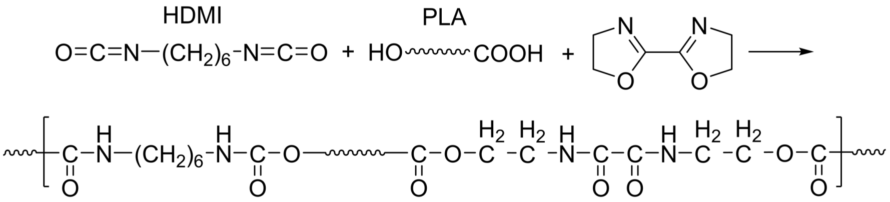

**Figure 5.** Chain extension reactions of poly(lactic acid) by using the oxazoline-based chain extender. [107]

Although oxazoline-based chain extenders demonstrate outstanding performance in improving polymer properties, they also suffer from the problems of high price and limited variety of derivatives, which restrict their widespread application. Therefore, the development of novel oxazoline derivatives, reduction of costs, and exploration of the applications of oxazoline in other polymer systems will become hot spots for the future research.

## 2.5. Other Chain-Extenders

Other chain extenders that can be applied to PLA include polycarbodiimide (PCDI) and tris (nonylphenyl) phosphate (TNPP). Polycarbodiimide (PCDI) is frequently employed as an anti-hydrolysis inhibitor since it reacts with moisture or water to prevent hydrolysis. PCDI is also capable of extending the PLA chains, as it is able to react with both hydroxyl and carboxyl groups, and exhibits a particularly higher reactivity towards carboxyl groups. [109] In several investigations, TNPP was incorporated into PLA as a chain extender. [110]-[113] According to Cicero *et al.*, the molecular weight of PLA underwent a 30% reduction after extrusion. However, following the addition of TNPP, the molecular weight of PLA was maintained in a stable condition. [110] The chemical structures of PCDI and TNPP are shown in **Figure 6**.

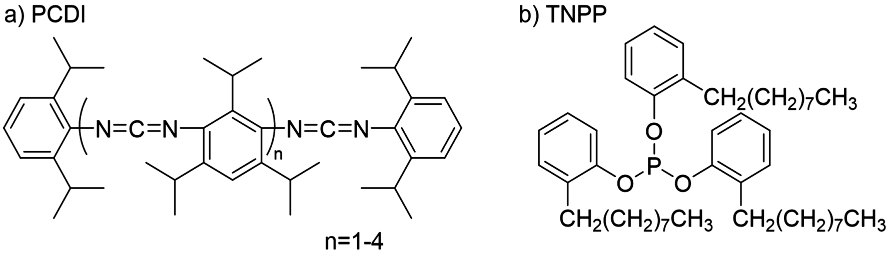

**Figure 6.** Chemical structure of a) polycarbodiimide (PCDI) and b) tris (nonylphenyl) phosphate (TNPP).

Different chain extenders have diverse impacts on the polymer crystallization rate and crystallinity because of the changes in molecular structure and compatibility following the chain extension. [112]-[117] The addition of TNPP results in a remarkable increase in crystallization rate and crystallinity of the polymer. However, excessive concentrations of TNPP have a negative impact on the crystallization behavior, and the residual by-products are susceptible to chemical degradation during storage. The application of PCDI leads to an increase in the cold crystallization temperature ($T_c$) but a decline in crystallinity of PLA. In the case of the epoxy-based chain extenders (Joncryl® series), as mentioned earlier, their incorporation leads to the formation of long-chain branching structures, which disrupts chain stacking. Consequently, the crystallinity is drastically reduced and the rate of crystallization may also decrease. Nevertheless, the chain-extending effect of epoxy-based chain extenders on PLA is remarkably superior to that of TNPP and PCDI. The enhancement in the molecular weight of PLA achieved by epoxy chain extenders is nearly several times greater than TNPP and PCDI. [111] [112]

## 3. Regulation of the Structure and Properties of Materials by Using Epoxy-Based Chain Extenders

Chain extenders are highly effective in improving the molecular weight of polymers. Due to chemical reactions, they may also exert an influence on the structure and other properties of the material. Among all the chain extenders mentioned above, epoxy-based chain extenders have the best overall performance, as they are cost effective, have low toxicity, possess high reaction efficiency and show effective reactivity with hydroxyl and carboxyl groups. Hence, they are currently the most commercially successful chain extenders on the market, which can effectively be applied to PLA. [64]-[68] The following sections will mainly introduce the impact of epoxy-based chain extenders on the properties of PLA or its alloys.

### 3.1. Impact of Epoxy-Based Chain Extenders on the Compatibility of PLA Alloys

Biodegradable polymers such as PLA have relatively few individual applications in industry due to the limitations of their own physical properties. However, the blending modification of different biodegradable materials has emerged as an important research trend. Reactive compatibilization is an extremely cost-effective and environmentally friendly processing technique as it is free of solvents, does not demand special facilities, and can be readily scaled up for industrial production. Epoxy-based chain extenders are highly reactive with the majority of biodegradable materials and can be utilized to enhance the compatibility of blended systems by means of in-situ compatibilization.

Regarding the blending modification of PLA, PLA/polybutylene terephthalate (PBAT) alloys have attracted much attention due to their capacity to improve the toughness of PLA. Nevertheless, due to the huge difference in solubility parameters between PLA ($10.1\ (\mathrm{cal/cm^3})^{1/2}$) and PBAT ($23.0\ (\mathrm{cal/cm^3})^{1/2}$), which leads to a typical incompatible system between them, the properties of the materials obtained by simple melt blending are not satisfactory. The application of epoxy-based chain extenders on the PLA/PBAT blends reduces the interfacial tension, enhances the interfacial adhesion, minimizes the size of the dispersed phase, and forms a more homogeneous morphology. As the compatibility between PLA/PBAT blends improves, the material's properties are enhanced in all aspects, which is conducive to further processing, molding, and application. [79]-[81] [118]-[120] Similar results have been reported by other researchers, where the incorporation of epoxy-based chain extenders improves the compatibility and mechanical properties of PLA/polyethylene glycol (PEG) blends. [121] [122]

Phase morphology has a significant impact on the properties of PLA/PBAT blends. The formation of blend morphology relies on extrinsic factors like viscosity ratio, shearing force, and temperature during melt processing. [123] [124] Arroda *et al.* investigated the relationship between viscosity ratio and morphology of PLA/PBAT blends in the form of blown films. They noted that PLA-g-PBAT copolymers, which were formed during the chain extension, could improve the compatibility of PLA and PBAT. In PBAT-dominated systems, the dispersed phase of PLA was fibrillar and elongated along the tensile direction in the absence of a chain extender, whereas the addition of a chain extender refined the morphology of PLA, which could be explained by the reduction of interfacial tension. In case the viscosity ratio > 1, the PLA dispersed phase appeared as ellipsoids oriented towards the film drawing direction. The rigid PLA particles became stress concentrators, which reduced the elongation at the break of the system. In the PLA-dominated systems, without the presence of chain extenders, the PBAT dispersed phase exhibited a coarse ribbon-like or sheet-like structure. The low adhesion to the PLA matrix resulted in the reduction of its ductility. As the chain extender was applied, however, finer and more homogeneous morphology and elongated fibrous structure were formed due to lower interfacial tension and viscosity ratio < 1, which led to a significant increase in ductility. [125]

The epoxy chain extender used in most studies was the Joncryl® series. In contrast, Wu *et al.* employed EMA-GMA as a chain-expanding compatibilizer in the PLA/PBAT blends system. At a high addition level, the interfacial adhesion was remarkably enhanced, forming a morphology similar to a core-shell structure, which substantially enhanced the impact strength. [126] Similar conclusions were reached by Hou *et al.*, in different concentrations and structures of epoxy-based chain extenders significantly affected the morphology and properties of the PLA/polycaprolactone (PCL) blends. Through the chemical reaction between the epoxy groups of EMA-GMA and the terminal carboxyl and hydroxyl groups of PLA and PCL, the compatibilizer acted as a bridge between the phases to improve the interfacial adhesion. By this means, adding 10 wt% of PCL to PLA increased the elongation at break up to 172% and the ductility continued to grow with further addition of PCL. [127] [128] Compared with the Joncryl® series, EMA-GMA has higher molecular weight. Despite the lower GMA content, its higher molecular weight and cohesive strength are conducive to the enhancement of the interfacial adhesion, thus further improving the morphology and properties of the blended system.

### 3.2. Impact of Epoxy-Based Chain Extenders on the Crystallization Behavior

During the chain extension of PLA, epoxy-based chain extenders not only lead to the linear growth of PLA, but also accompanied by the generation of branched structures. [78] On one hand, branched structures reduce the regularity of molecular chains. On the other hand, as chain length and chain linkage increase, under the same crystallization conditions, the melt viscosity rises. This restricts the movement of chain segments, making it difficult for them to form a highly ordered lattice through regular arrangement. However, the enrichment of chain segments around the branched structures is beneficial for the nucleation. An increase in the volume fraction of branched structures leads to a significant increase in the nucleation density of the polymer. Therefore, the chain-extended and branched PLA is more likely to form primary nuclei than linear PLA, thus causing a complex impact on the crystallization behavior. [129] Corre *et al.* noted that the increase in the epoxy-based chain extender content led to the decrease in the cold crystallization temperature ($T_{cc}$) and melting temperature ($T_m$). The crystallization rate of the chain-extended PLA was increased, but the crystallinity decreased. [130] Nofar *et al.* investigated the crystallization behavior of long-chain-branched PLA and found that the branched PLA possessed a more rapid crystallization rate compared to linear PLA. This is because the branched chains can serve as nucleation sites. Similarly, adding nucleating agents, such as talc, to linear PLA had the function of promoting the crystallinity and crystallization rate. However, they had less influence on the crystallinity and crystallization rate of the branched PLA, suggesting that in this case the branched structures dominated the crystallization process. In addition, the microstructure of branched PLA exhibited a smaller spherulite size. [131]

Hung *et al.* investigated the influence of the reactive block copolymers as chain extenders on the crystallization behavior of PLA. They noted that the GMA chain segments were able to enhance the molecular weight and melt strength of PLA, while the MMA and styrene chain segments improved the miscibility with PLA and act as nucleating agents to promote crystallization. In particular, the application of chain extenders containing MMA chain segments led to an increase in the crystallinity of PLA from 12.29% to 47.54%. In contrast, chain extenders without MMA chain segments did not exhibit good reactivity and nucleation ability. The MMA chain segments are the key structure of the chain extender, and the optimal ratio of styrene to MMA is 1.0 - 1.2. [132] The molecular structure design and selection of chain extenders are also important factors that further influence the structure and properties of PLA.

### 3.3. Impact of Epoxy-Based Chain Extenders on the Mechanical Properties

As previously mentioned, the application of epoxy-based chain extenders enhances the molecular weight, polydispersity, and forms branched structures of polymers. This leads to an accelerated crystallization rate, an increased number of spherulites and a decreased size. After being subjected to external forces, the more closely arranged crystal grains can better withstand stress and disperse around the surroundings, thereby preventing local stress concentrations. In parallel, the reduced crystallinity provides more space for intermolecular chain slip within the amorphous zone, which enables more energy to be absorbed. Under the combined action of these two factors, the flexural strength and impact strength are ultimately significantly improved. Furthermore, after chain extension and branching, the molecular spacing enlarges and the interaction force between molecular chains diminishes, leading to a decline in tensile strength. Nevertheless, as the degree of chain extension increases, the tensile strength can still exhibit a gradually increasing tendency. The dendritic long-chain-branched structure makes a remarkable contribution to the enhancement of strain hardening under tensile flow, thus greatly enhancing the melt strength and influencing the molding and processing.

### 3.4. Impact of Epoxy-Based Chain Extenders on the Degradation of PLA

The hydrolysis of PLA generally consists of three stages: First, water molecules gradually penetrate into the interior of PLA, leading to slight hydrolysis from the surface to the interior; secondly, rapid hydrolysis occurs inside PLA, leading to material embrittlement; finally, low-molecular-weight PLA is further hydrolyzed into soluble lactic acid oligomers. The kinetics of hydrolysis of PLA were investigated by Piedmont *et al.* in the temperature range of 140˚C to 180˚C. They tested PLA samples at concentrations ranging from 5 to 50 wt% and noted that the reaction kinetics were independent of PLA concentration. The experimental data revealed two different reaction mechanisms: one related to the biphasic reaction and the other to the autocatalytic effect of the carboxylic acid groups during depolymerization. The latter is observed in PLA hydrolysis and leads to a decrease in solution pH. The introduction of the chain extender reduces the concentration of PLA end groups, thereby decreasing its hydrophilicity. In addition, the chain extension produces a capping effect on PLA, which enhances its resistance to water erosion. [133]-[135] Palsikowski *et al.* studied the degradation of chain-extended PLA/PBAT. The presence of the chain extender has significantly reduced the degradation rate of pristine PBAT, which originally had a high degradation rate in soil. The functional groups of the chain extender could interact with the groups generated during the degradation of polymers, competing with molecular weight reduction and causing a delay in biodegradation. [119] By using chain extenders, the degradation stability and degradation cycle of PLA can be further regulated, providing great potential for its next application.

## 4. Future Prospects

In contemporary society, the development of environmentally friendly materials has emerged as a prominent concern. Of particular significance are the recycling and reuse of materials, along with the exploration of degradable materials. Chain extenders prove to be of great value in this context. Through the incorporation of chain extenders into recycled plastics or biodegradable plastics, such as PLA, the material's performance can be substantially enhanced, thereby broadening its range of applications. The substitution of traditional plastics with PLA and the replacement of virgin plastics with recycled ones not only lead to cost savings in production but also exert a favorable influence on environmental protection. This article reviews the different types of chain extenders for PLA and focuses on the influence of epoxy-based chain extenders on the properties of PLA. Epoxy-based chain extenders currently exhibit the most optimal overall performance, as they possess high cost-effectiveness, low toxicity, high reaction efficiency, and can react effectively with hydroxyl and carboxyl groups. Nevertheless, the majority of the chain extenders that are currently employed by researchers predominantly consist of small molecules or low molecular weight copolymers. Although they demonstrate excellent chain-extending effects, their low molecular weights may lead to potential processing limitations, such as extrusion. Understanding the most recent advancements in the application of chain extenders within biodegradable materials is of great significance for improving material performance, promoting the recycling of materials and driving the development of relevant industries. Future research will continue to focus on the invention of novel chain extenders and their potential applications in diverse materials. For instance, by augmenting the molecular weight of the chain extender and employing a high epoxy functionality, the chain-extending effect on PLA as well as the impact on the crystallization behavior can be investigated, with the aim of further improving the performance of the chain extender.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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