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学位論文題目	Development of Tough Epoxidized Soybean Oil/Poly(lactic acid) Blends and Their Composites (強靱なエポキシ化大豆油/ポリ乳酸ブレンドおよびその複合材料の創製)	
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※本研究科以外に所属する場合はその所属を括弧書きすること

論文内容要旨 ※(20 ポイント)

As a biobased and biodegradable polyester, poly(lactic acid) (PLA) has been extensively utilized in many areas including packaging materials. The brittle nature of PLA is the key barrier for its broader application. Efforts on using epoxidized soybean oil (ESO) to enhance the ductility of PLA have been done; however, ESO is immiscible with PLA and would leach or migrate to the surface of PLA products when in use; thus, sufficient toughening efficiency is not achievable for the products. Therefore, fully biobased, thermally remoldable, and highly tough blends were successfully formulated from ESO and PLA via dynamic vulcanization. Two vulcanizing agents, i.e., cationic initiator and tannic acid (TA), were utilized to induce the crosslinking of ESO and its reaction with PLA matrix for performing dynamic vulcanization. The achieved TA-ESO/PLA blends with high toughness were further used as matrices for the development of nanocomposites and biocomposites.

In Chapter 1, the research background, significance, purpose and the construction of the thesis are particularly described.

In Chapter 2, the experimental materials used in this thesis are presented. The experimental methods and

characterizations are also described.

In Chapter 3, thermally processable and highly tough PESO/PLA blends were prepared by melt-blending of PLA with ESO using $\text{BF}_3\text{NH}_2\text{Et}$ as a cationic initiator for the self-polymerization ESO. The weight ratios of ESO to PLA ranging from 1:9 to 4:6 were designed to tailor the properties of the formed PESO/PLA blends. Results indicated the incorporated ESO could form a PESO phase dispersed on the PLA matrix and a superior interfacial compatibility with PLA matrix, which contributed to an improved toughening efficiency of PESO phase on the PLA blends. The PESO/PLA blends exhibited significantly increased elongation at break, tensile toughness, crystallinity, and complex viscosity when compared to pure PLA due to the formation of a two-phase separated structure in the blends; however, significant decreases in tensile strength, tensile modulus, storage modulus, and glass transition temperature of the blends were observed after the addition of ESO.

In Chapter 4, highly tough and biobased ESO/PLA blends were formulated through in-situ formation of TA-crosslinked ESO (TA-ESO) oligomer as a dispersed phase with PLA matrix by dynamic vulcanization technique. The crosslinking degree of ESO molecules and the interfacial compatibility between the ESO phase and PLA matrix were thus improved. The properties of the TA-ESO phase and its interfacial adhesion with PLA matrix were tailored by changing the molar ratio of TA to ESO, which significantly influenced the crystallization behavior, mechanical properties, thermal stabilities, and morphologies of the TA-ESO/PLA blends. After the incorporation of 10 wt% TA-ESO (based on the final blend) with a $-\text{OH}$ groups to epoxy rings molar ratio of 0.8 into PLA system, the elongation at break (242%) and tensile toughness (57.4 MJ/m^3) of the resulting PLA blend were 7 and 4 times higher than those of the blend with 10 wt% ESO, respectively. Compared to the 10 wt% ESO/PLA blend, the glass transition temperatures and thermal stabilities of the TA-ESO/PLA blends were slightly enhanced due to the increased crosslinking density of the TA-ESO phase; however, a slightly decreased crystallinity was observed for PLA after the addition of TA into ESO phase.

In Chapter 5, to repair the sacrificial strength of the TA-ESO/PLA blends and impart the composites with electrical conductivity, different concentrations of carbon nanotubes (CNTs), i.e., 0.5 to 10 wt%, were incorporated into the TA-ESO/PLA blends to prepare CNT/TA-ESO/PLA nanocomposites. The added CNTs selectively localized within the PLA matrix, leading to a reduced size of TA-ESO phase. The synergistic effects of CNTs and TA-ESO phase on the properties of the nanocomposites were fully investigated along with the

understanding of CNT reinforcing and TA-ESO toughening mechanism. The formation of TA-ESO phase significantly increased the fracture elongation and tensile toughness of the blends, while the incorporation of CNTs resulted in increased tensile strength, tensile modulus, and storage modulus of the nanocomposites; the combination of this two effects contributed to the obtained ternary composites with balanced mechanical properties and favorable electrical conductivity.

In Chapter 6, fully biobased biocomposites with tailorable performance were successfully produced from renewable materials including bamboo fibers (BFs), TA-ESO and PLA via reactive blending technique. The properties of the composites were regulated by changing the TA-ESO concentration on the BFs surface, where the TA-ESO phase was designed to function as two roles in BF/PLA biocomposites, i.e., coupling agent and toughening agent. At a low content of TA-ESO, the TA-ESO was localized at the fiber-matrix interface via the formation of a flexible interfacial layer between BFs and PLA. This resulted in significant increases in tensile strength, tensile modulus, elongation at break, tensile toughness, impact strength, and storage modulus of the composites. When a high content of TA-ESO was used, the TA-ESO oligomer acted as a toughening phase inside PLA. The formation of phase-separated structure in TA-ESO/PLA matrix contributed to significantly increased elongation at break, tensile toughness, and impact strength of the composites. The TA-ESO rubbery phase induced cavity growth and matrix plastic deformation are proposed as the main toughening mechanism of TA-ESO on PLA matrix and composites.

In Chapter 7, general conclusions of the study were made.

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論文審査結果要旨

本論文は、優れた力学特性を有する生分解性複合材料の開発を目的として、バイオマス由来で高い靱性を示すエポキシ化大豆油/ポリ乳酸ブレンド (ESO/PLA) およびそれらのカーボンナノチューブ (CNT) や竹繊維 (BF) との複合材料を作製し、その材料特性を検討したものである。本論文は全7章で構成されている。

第1章は緒論として、PLAに関する既存の研究から本研究の背景を述べ、本研究の目的を示している。第2章では材料および試験方法として、使用した材料と PLA ブレンドの作製方法およびそれらの力学特性の評価方法、内部構造などの分析方法について説明している。第3章では、ESO の自己重合に対するカチオン開始剤として $\text{BF}_3\text{NH}_2\text{Et}$ を用いて熱成形可能な ESO/PLA ブレンドを作製し、その性能を評価している。結果として、ESO を 40wt% 添加した ESO/PLA ブレンド材は破断ひずみが 141%、引張靱性が 24.4MJ/m^3 を達成している。第4章では、環境に優しい加硫剤であるタンニン酸 (TA) を用いて、PLA と ESO のブレンドと架橋を同時に行う動的架橋により再生可能な PLA ブレンドを作製している。結果として、安定的な TA-ESO 相をブレンド材中で形成し、それにより PLA との界面接着性を高めたことで、ブレンド材の靱性が大きく向上している。例えば、エポキシ環に対するヒドロキシ基 (-OH) のモル比が 0.8 で、TA-ESO 含有量 10wt% のブレンド材において、破断ひずみが 242%、引張靱性が 57.4MJ/m^3 まで達している。第5章では、TA-ESO/PLA ブレンドの強度回復および導電性を付与するために、CNT を添加したナノ複合材料を作製している。結果として、TA/ESO と CNT の添加量がそれぞれ 10wt% の場合、引張強度が 63.2MPa 、導電率 $1.5 \times 10^{-2} \text{S/m}$ を達成している。第6章では、BF、TA-ESO、PLA などの再生可能な材料を用いて、リアクティブブレンドにより複合材料を作製している。結果として、TA-ESO が BF と PLA のカップリング剤としての機能を認められ、100% バイオマス由来の生分解性複合材料の開発に成功している。第7章は結論であり、研究結果をまとめている。

本論文の成果は、コスト競争力のある生分解性 PLA 複合材料を提供するだけでなく、PLA 複合材料の改質や強化およびそれらのメカニズムに関する学術的貢献も大きい。また、研究業績として、査読付国際学術論文3編、国際会議2件、国内会議2件を公表している。

よって、本論文は博士 (工学) の学位論文として合格と認める。