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Design, preparation and properties of bio-based elastomer composites aiming at engineering applications

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Bio-based polymer products derived from renewable agricultural and biomass feedstock have become increasingly important as these sustainable and eco-efficient products bring a significant reduction in greenhouse gas emissions and saving of fossil energy in comparison with conventional pertrochemical-based materials. A series of bio-based elastomers from large-scale produced and petroleum independent monomers such as succinic acid, sebacic acid, itaconic acid, 1,3-propanediol, 1,4-butanediol, soybean oil, glycerol, citric acid, etc have been developed by authors. Same as conventional elastomers, bio-based elastomers possess low glass transition temperature, high elasticity and low strength, and this implies that they must be reinforced by nano-fillers. However, they also possess particular and novel properties due to their characteristic macromolecular structures and aggregation structure. For example, the existence of abundant ester groups, terminal carboxyl groups, and terminal hydroxyl groups in bio-based polyester elastomers endow polar fillers like silica disperse homogeneous in the elastomer matrix without surface modification. Even though, for incorporation of easily agglomerated fillers like graphene and layered silicates, elaborately dispersion and interfacial tailoring technique is necessary. Combined with specific structures and relevant effective composite technology, bio-based elastomer composites exhibit versatile potential applications in tire tread, PLA toughener, thermoplastic vulcanizates, and dielectric elastomer, etc.

1. Introduction

At the time of great challenge to energy, resource and environment, with large energy and resource consumption, chemical industry is facing serious problems. It's with great significance to encourage world economic development by using recyclable resource and reducing dependence on non-renewable fossil fuels [1]. Biomass resource ranks first in the renewable energy and ranks fourth in the world's total energy consumption, preceded only by coal, oil and natural gas. Countries all over the world are making great efforts to support and encourage technological innovation of biomass energy and resource. Conversion from fossil energy to biomass energy will be the greatest challenge and opportunity in the coming fifty years. Polymer materials play irreplaceable role in people's diary life and the volume consumption has already exceeded steel. Even though, except natural rubber and few other materials, most polymer materials are highly depended on fossil resource (mainly oil and coal). Developing bio-based polymers meets the requirements and trend of sustainable development and circular economy concept. Many efforts have been paid and various materials have been fabricated from bio-based chemicals, for example, polylactic acid (PLA) [2], starch based polymers [3], polyhydroxyalkanoates (PHAs) [4], 1,3-propanediol based polymers [5,6] and polybutylene succinate (PBS) [7], etc. PLA is the most successful bio-based polymer with great potential market by far. Dow Chemical has built a 140,000 tons/year PLA plant and is planning to raise the capacity to 450,000 tons/year. Toyota has made car automobile parts from sugar cane and potato based plastics [8] and Fujitsu has made computer shells by corn starch-based plastics [9]. DuPont has developed an engineering thermoplastic polymer by PTT which produced from a corn-based PDO.

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Showa Japan and United States Eastman have experienced industrial production of PBS, and the production capacities are 5000 tons/year and 15,000 tons/year, respectively. There is an emergence of fossil resources replacing by biomass resources to get novel polymer materials in plastic field, even though bio-based plastics like PLA still has shortcomings like low heat-resistant temperature and poor toughness. It's worth noting that the current bio-based plastic is always aimed at fast biodegradable performance, which to some extent limits its application and development. We believe efforts also should be taken to develop environmental stable and bio-based polymers to meet high-performance demands.

Elastomer is widely used in industry, agriculture, national defense, and our daily life as its unique high elasticity. Natural rubber (NR) is a valuable elastomer material with excellent comprehensive properties from *hevea brasiliensis*. However, *hevea brasiliensis* need to be cultivated in the high-temperature and great rainfall environment. Therefore, they can only be large-scale cultivated in certain tropical areas. After years of development, NR production has been up to the top limit. On this situation, researching and developing various high-performance synthetic elastomers to replace NR or used in the complicated conditions (NR cannot meet the requirements) have been the focus in elastomer science and engineering field. There is no doubt that raw chemicals used in synthetic elastomer production are basically derived from fossil resources, including butadiene, styrene, isoprene, chloroprene, ethylene, and propylene. Compared with bio-based plastics and fibers, research and development of bio-based elastomers aiming at engineering applications are quite few. Clearly, in order to meet the growing demand for sustainable development, the preparation of such elastomers derived from biomass as the next-generation engineering elastomers is extremely significant. The objective of present article was to introduce design, preparation, and applications of these bio-based elastomers and related composites.

2. Bio-based chemicals, molecular design, and synthesis of bio-based elastomers

2.1. Biomass and bio-based chemicals

Biomass mainly refers to renewable or recyclable organic substances including crops, trees, other plants or residues, and animal waste, etc. Bio-based chemicals are chemicals produced from renewable bio-resources including grains, legumes, cotton stalks and other biomass as raw materials. Biological fermentation technology provides us a low cost and high efficiency method to produce bio-based chemicals in large scale. It is believed that bio-based chemicals and renewable energy are the only way to achieve sustainable development of mankind. With the depleting of petrochemical resources and increasing awareness of environmental protection, bio-based chemicals play more and more important role in the industry and people's daily life. With the rapid development of processing technology, large scale production of ethanol from lignin will be realized definitely and at that time, the ethanol can be used as fuel and chemicals directly. Developing renewable polymers and resembling existing petroleum dependent polymers by bio-based chemicals have been a universal consensus. Generally speaking, there are three major pathways toward synthesis of renewable monomers including fermentation (such as lactic acid, and 1,3-propanediol), chemical transformation of natural polymers (such as glucose, and furfural) and molecular biomass from nature (such as vegetable oils, terpenes, terpenoids, and resion acids) [10]. In 2004, the US Department of Energy (DOE) announced a group of top 12 bio-based building block chemicals including succinic acid (fumaric acid, malic acid), 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol (arabinitol) [11]. These chemicals can be produced via microbial fermentation or simple chemical process starting from sugars and can be further converted to other valuable or commodity products. After more than ten years developing, ten chemicals among these top 12 chemicals, excluding the aspartic acid and 3-hydroxybutyrolactone, have already been commercialized or are close to commercialization [12]. In addition to the top 12 chemicals, several other bio-based platform chemicals such as methanol, ethanol, isoprene, limonene, vegetable oils etc. are also highly emphasized and developed.

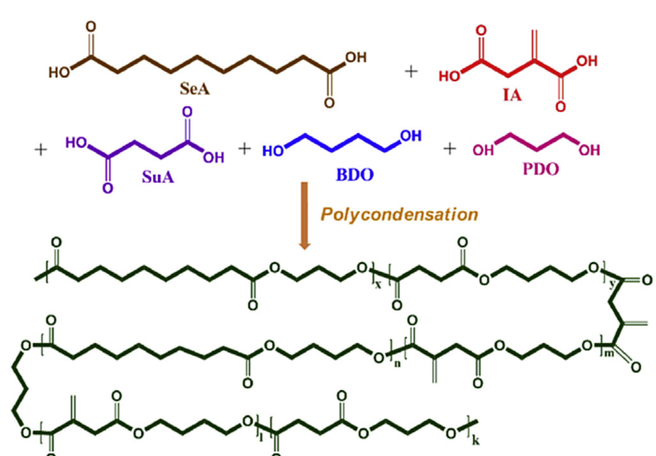
2.2. Design and preparation of bio-based elastomers

The motivation of our relative research is to prepare new elastomers aiming at engineering applications based on large scale produced bio-based chemicals. It is believed that following criteria are required [13]: (i) monomers should be obtained primarily from readily available and inexpensive renewable biomass feedstock; (ii) the chemically synthesized or biosynthesized elastomers should possess excellent environmental stability; (iii) they should be compatible with traditional rubber processing, such as mixing, molding and curing; (iv) the prepared elastomers should exhibit desirable mechanical properties.

2.2.1. Polyester elastomer prepared by condensation polymerization

Polyester elastomers were synthesized by the condensation polymerization of bio-based diacids and dialcohols [13]. Normally, polyester materials, for example PBS [7], are plastics as they possess high crystallization degree. In order to suppress the crystallization of polyester to form elastomer, five bio-based chemicals including itaconic acid, sebacic acid, succinic acid, 1,4-butanediol, and 1,3-propanediol were applied to increase the irregularity of the obtained polyester. The use of sebacic acid was to provide high flexibility and the use of itaconic acid was to provide double bonds for the further crosslinking. The pathway of the design and preparation of bio-based polyester elastomer was shown in Scheme 1.

The number average molecular weight of synthesized polyester elastomers was approximately 35,000 g/mol with PDI as 3.2, and the typical glass transition temperature (T_g) was −56 °C. Even though molecular weight of polyester elastomer was lower than conventional elastomers, the shortage can be compensated by further crosslinking. Ideal low T_g was attributed to the long carbon chain of sebacic acid and the disruption of polymer regularity. This linear polyester elastomer with double bonds can be processed



Scheme 1. Reaction formula of bio-based polyester elastomer.