中国材料大会 2024

暨第二届世界材料大会

CMC 2024 & WMC 2024

July 8-11, 2024

Guangzhou, China

E14-生物基可持续材料

E14-Biobased and Sustainable Materials

Organized by

Chinese Materials Research Society

Website: https://cmc2024.scimeeting.cn

E14. 生物基可持续材料

分会主席：张立群、应汉杰、胡国华、Patrick Maestro、Philippe Dubois、Giuseppe Lacidogna、Elvira Fortunato、Hyacinthe Randria

E14-01

（题目）

陈学思

E14-02

（题目）

Patrick MAESTRO

E14-03

Global Vibrational Modes in Proteins: Terahertz Spectroscopy and Discrete Element Method Numerical Simulation

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Proteins are chemical compounds with highly complex mechanical structures, characterized by several degrees of freedom. Although their direct analysis is very difficult, it is possible to assess many of their properties indirectly by identifying their natural frequencies: since these frequencies derive from a given protein's structure, they also reflect the spatial distribution of its composing elements, i.e., its chemical structure, which, in turn, is linked to a tissue's physiological properties. Therefore, such analysis may lead to a better understanding of several pathologies and their treatment by observing how drugs interfere with a protein's frequency distribution. This topic has been approached through a number of experimental techniques, such as the Raman Spectrum and the Terahertz Time Domain Spectroscopy (THZ-TDS), but its corresponding analysis through theoretical and numerical means is still lacking. In this work, we explore the analysis of two specific proteins, Lysozyme and ATPase, through a numerical model based on the Discrete Element method, which represents a medium as concentrated-mass nodes linked by rigid bars, which approximate the chemical bonds between the structure's parts. The simulated results are compared to experimental data from both THZ-TDS and Raman Spectrum studies, aiming to provide a broader understanding of the vibration patterns in the structures under study.

E14-04

生物基高分子材料研究新进展

朱锦

Research Progress of Bio-based Polymer Materials

Bio-based polymers are a class of polymers which were derived from renewable resources. Great attention has been paid from both academic and industrial society since they are sustainable and renewable materials. This talk will review the recent progress on bio-based polymer materials developed at NIMTE. It will cover conversion of cellulose into glucose, furan based polyesters, controllable biodegradable polymers and herb-plastic composites.

E14-05

"Enzymated" polylactide: biosourced materials with programmed biodegradation

Philippe DUBOIS*
University of Mons UMONS

Among biosourced synthetic polymeric materials, polylactides (PLAs) undoubtedly represent the family of polyesters the most widely studied and produced at large industrial scale nowadays. Current applications fields cover packaging, textile, electronic industries as well as many others.

In this contribution, addition of a selectively engineered enzyme in commercially available PLAs is performed by an original continuous extrusion process via a masterbatch approach. Interestingly, all thermomechanical properties of the starting PLA materials are fully preserved but programmed biodegradation can be now forseen in both aquatic medium, industrial compost and for the first time (for a PLA materials) in low termperature domestic compost. Furthermore, the resulting "enzymated" PLA can be valorized at its end-life for biomethane production.

As a key-illustration, “enzymated” PLA films were produced by blow-molding and proved to show complete degradation under home-compost conditions within less than 24 weeks, fitting home-composting standards. Moreover, the mechanical and degradation properties of the “enzymated” film, compatible with packaging industrial applications, were found to be maintained over long term storage.

This innovative material paves the way to composters and biomethane production and provides for the first time, an industrially implementable process to address PLA (bio)degradation.

E14-06

From forest to Electronics: Green graphene

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This talk aims to discuss a new manufacturing technology supporting flexible and organic/inorganics electronics by exploring single laser processes for direct generation of conductive and semiconductive structures on biodegradable substrates. By means of different kind of laser sources, conductive carbon nanostructures can be generated on carbon-based precursor materials and substrates via a thermo-photo pyrolysis: the so-called Laser Induced Graphene (LIG).

One of the main advantages of the LIG process is that the precursor materials and the substrates themselves can be bioderived and biodegradable, thus allowing new opportunities for sustainable electronics, all along the device’s life: from reuse of waste biomass materials to the safe deployment in the environment, to final biodegradation.

That is, a greener alternative will be discussed to use carbon derived precursors rom biomass, which can be graphitized to become conductive tracks as well to simultaneous functionalized any time of material like metal oxide remaining underneath the surface.

In this presentation, we report the use of biomaterials as cellulose as a material in the toolbox of LIG precursors, aimed at the development of both disposable and wearable smart biosensing.

E14-07

一种新的聚合物材料家族：phamily（A New Polymer Material Family: PHAmily）

陈国强*
清华大学

Polyhydroxyalkanoates (PHA) have evolved into versatile biopolymers, transcending their origins as mere bioplastics. This extensive review delves into the multifaceted landscape of PHA applications, shedding light on the diverse industries that have harnessed their potential. PHA has proven to be an invaluable eco-conscious

option for packaging materials, finding use in films, foams, paper coatings, and even straw logos. In the textile industry, PHA offer a sustainable alternative, while its application as a carbon source for denitrification in wastewater treatment showcases its versatility in environmental remediation. In addition, PHA has made notable contributions to the medical and consumer sectors, with various roles ranging from 3D printing, tissue engineering implants, and cell growth matrices to drug delivery carriers, and cosmetic products. Through metabolic engineering efforts, PHA can be fine-tuned to align with the specific requirements of each industry, enabling the customization of material properties such as ductility, elasticity, thermal conductivity, and transparency. To unleash PHA's full potential, bridging the gap between research and commercial viability is paramount. Successful PHA production scale-up hinges on establishing direct supply chains to specific application domains, including packaging, food and beverage materials, medical devices, and agriculture. This review underscores that PHA's future rests on ongoing exploration across these industries and more, paving the way for PHA to supplant conventional plastics and foster a circular economy.

E14-08

Biobased thermoplastic elastomers with controllable properties

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Queen's University Belfast

Elastomers are used in various industrial sectors including automotive, construction, energy, electronics, and healthcare. However, most of the existing elastomers are either challenging to recycle or are derived from fossil fuels. A range of biobased thermoplastic elastomers (TPEs), including polyamide-based TPEs and thermoplastic polyurethanes, with different formulations, were prepared from renewable source. The TPEs were characterised by Fourier transform infared spectroscopy, nuclear magnetic resonance spectroscopy, gel permeation chromatography, differential scanning calorimetry, and different types of mechanical testing. The TPEs show a broad range of mechanical properties, with Shore A hardness varying from 16 up to 90. By changing the elastomer type, chain segment and/or monomer ratio, the properties of TPEs can be manipulated for target applications. Some of these TPEs demonstrate excellent self-healing properties. The potential applications of these biobased TPEs in anti-corrosion coating, elastic fibres, substrates for stretchable conductors and wearable devices, etc, have been explored. These biobased elastomers may be promising sustainable alternatives to some of the existing elastomers.

E14-09

Numerical-Experimental Study on Human Fascia Lata-Tissue

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There is an increasing number of soft-tissue reconstruction surgical interventions due to acquired defects, constituting a significant healthcare issue with important economic ramifications. Such procedures commonly include muscle grafts, both autogenous and allogenic, where the Fascia Lata is often used as the tissue source. From a biomedical engineering standpoint, modeling the mechanical properties of such tissues is a major challenge due to the inherent nonlinearities of their composing structures and the complex interactions between them, which severely restrict the application of conventional homogenization techniques used in the mechanics of continuous media. In this work, we pursue an alternative approach, based on interconnected discrete elements with distinct levels of strength, which vary according to a statistical distribution matching the modeled material’s overall characteristics. The results from simulating such a discrete-element model are compared to experimental data from testing human Fascia Lata tissues according to several methodologies.

E14-10

Modeling The Gas Phase Reaction Kinetics of Glycyrrhizic Acid: A Molecular Dynamics and Machine Learning Approach

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Solid propellants are vital energy sources for the performance of missiles and rocket engines, necessitating their development with a focus on energy density and combustion sensitivity. Nitrate Ester Plasticized Polyether (NEPE) propellant, a novel, high-energy solid propellant, consists of mixed nitrate ester plasticized polyether as the adhesive, solid oxidants like Ammonium perchlorate (AP), aluminum as metal fuel, and high-energy explosives such as octogen (HMX). This composition results in a high-pressure index and a narrow range of adjustable burning rates. However, there are challenges in adjusting combustion performance due to constraints between burning rate and pressure index adjustment technology. Additionally, existing solid propellant combustion mechanisms are ineffective for simulating the combustion process of NEPE propellants. This study develops a detailed chemical kinetic model for accurately predicting the burning rate of NEPE propellant. Specifically, a comprehensive gas-phase and liquid-phase reaction kinetics mechanism is developed by integrating detailed gas-phase combustion kinetics, solid-phase pyrolysis reaction mechanisms of NEPE propellant, solid-phase pyrolysis reaction rates, burning surface displacement models for NEPE formulations with polyethylene glycol (PEG), nitroglycerin (NG), 1,2,4-butanetriol trinitrate (BTTN), HMX, AP, and Al. The gas-phase reaction kinetic mechanism analyzes the sensitivity and reaction flux of the NEPE propellant combustion process, identifying key pyrolysis and combustion products, free radicals, and key elemental reactions across a wide range of equivalence ratio and pressure conditions. The modified prediction model accurately predicts the combustion rate of the vital oxidant HMX in NEPE and its formulation over a wide pressure range. Theoretical calculations are conducted on the propellant's gas-phase and solid-phase burning surface temperatures, and the model simulates with good agreement with relevant propellant burning rate testing experimental data from the literature. These research findings are significant for advancing the development of composite propellants, particularly high-energy propellants, and enhancing the performance level of rockets and missiles.

Key Words：Solid composite propellant; chemical kinetic mechanism; burning rate, model prediction; pyrolysis and combustion.

E14-11

Biobased mesoporous materials and their application exploration

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Biobased mesoporous materials are popular multifunctional materials, which have great application potentials in various fields. This is mainly because mesoporous nanomaterials not only have the properties of general porous nanomaterials, such as adjustable pore size, large pore volume, high specific surface area, etc, but also possess many advantages of unique morphologies or structures. It has a broad prospect in catalysis, hydrogen storage, separation and electrochemistry. So far, many methods have been developed to regulate the morphology and structure of mesoporous materials, including spraying, drip, Stober method, colloid assisted assembly, confined assembly and solid state reaction. However, the morphology and mesoscopic structure synthesized by the above methods still cannot meet the needs of the development of the times. At the same time, the research on the synthesis mechanism is not profound enough, and the application research is also very limited. Therefore, it is of great significance to further develop a simple and powerful method to construct bio-inspired porous nanomaterials, to conduct in-depth research on its synthesis mechanism, and to give full play to its application potential.

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E14-12

生物基材料创新发展机遇与挑战

翁云宣

Opportunities and Challenges for Innovative Development of Biobased Materials

利用可再生生物质资源加工生产的生物基材料，有望在部分应用领域逐步替代传统石油基材料，成为引领科技创新和经济发展的新型产业，并作为绿色低碳发展的主要途径及低碳经济增长的亮点。本报告将重点介绍生物基材料概念及范畴，国内外生物基材料产业发展现状，我国生物基材料发展面临挑战，并在此基础上提出生物基材料创新和产业高质量发展建议，以期推动生物基材料行业健康、可持续发展。本报告旨在为生物基材料研究者和企业提供参考和启示，促进生物基材料产业的蓬勃发展。

The utilization of bio-based materials, processed from renewable biomass resources, is anticipated to progressively substitute traditional petroleum-based materials in certain application fields. This will lead to a new industry that drives technological innovation and economic development, serving as the primary approach for green, low-carbon development and highlighting low-carbon economic growth. This report focuses on introducing the concept and categorization of bio-based materials, the present development of the bio-based materials industry domestically and internationally, the challenges encountered by the development of bio-based materials in China, and subsequently proposes suggestions for innovative and high-quality development of bio-based materials industries, aiming to promote the robust and sustainable growth of the bio-based materials industry. The objective of this report is to offer guidance and inspiration for researchers and enterprises in the bio-based materials sector, facilitating the strong advancement of the bio-based materials industry.

E14-13

生物降解生物基材料的产业化与市场化

李建军

E14-14

生物基可降解聚酯橡胶产业化研究进展

王朝

South China University of Technology

Rubber has an irreplaceable role both in daily life and military field, because of its special flexibility. The annual consumption of rubber in our country reached more than 10 million tons, the output value of more than one trillion yuan. However, the natural rubber production capacity is insufficient in our country, more than 80% relied on imports. Synthetic rubber is synthesized from fossil resources, and each ton of synthetic rubber leads to about 10 tons of CO2 emissions over its life cycle. Therefore, developing a new generation of bio-based rubber is an important way to achieve sustainable development of rubber and low-carbon environmental protection. This report will be based on the design ideas, synthesis and performance, and industrialization progress of the original bio-based and degradable polyester rubber materials in our country. By using the bulk bio-based monomers obtained by biological fermentation, the regularity of molecular chain is broken by using multiple copolymerization through molecular structure design, so as to obtain completely amorphous elastomer materials. Furthermore, double bonds are introduced into the molecular structure to ensure the thermal vulcanization performance of the elastomer material, and finally the bio-based degradable polyester rubber composite with high performance is obtained. The structure-property relationship is regulated by monomer type and proportion, and

the catalyst and thousand-ton continuous production process are broken through. The obtained bio-based and degradable polyester rubber products can be used in degradable tires, degradable shoes, bio-based vulcanized rubber, oil resistant sealing ring, toughening agent, plasticizer and other application fields.

E14-15

多中心催化体系与序列可控降解高分子

庞烜*

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世界合成高分子材料年消耗超过 5 亿吨，是事关国民经济健康发展和国家安全的大宗基础材料，目前面临着难以持续发展和环境负荷过高的重大挑战。我国的材料领域未来的发展方向是：积极应对塑料污染，要牢固树立新发展理念，有序禁止、限制部分塑料制品的生产、销售和使用，积极推广可循环易回收可降解替代产品，增加绿色产品供给，规范塑料废弃物回收利用，建立健全各环节管理制度，有力有序有效治理塑料污染。环境友好高分子材料是材料科学领域的研究热点，具有很高的学术价值和广泛的应用前景。我们利用多中心催化体系，在分子水平上构建了与生物体机能有机融合的新型生物可降解高分子材料，提出了聚乳酸类生物可降解高分子材料的制备和回收的新方法。

E14-16

Synthesis of Sustainable Polymers from Bio-based Monomers

张兴宏

Zhejiang University

We have developed various synthetic routes for preparing sustainable polymers from bio-based monomers such as cyclic anhydrides, aldehydes, diols, diamine, and diacrylates. The polymerization mechanisms include chain-growth and step-growth mechanisms. Some of these polymeric materials obtained exhibit excellent mechanical and thermal properties. Some obtained polymers are easy to degrade and can even be directly depolymerized back into monomers. Some obtained polymers also have interesting fluorescence properties. Some obtained polymers can also be applied to polymer solid electrolyte materials for lithium batteries.

E14-17

聚烯烃高值化与循环利用

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中国科学技术大学

人类至今生产超过 90 亿吨塑料，其中约 2/3 成为废弃物，导致“白色污染”，产生涉及生态、环境、资源等影响社会可持续发展的一系列问题。聚烯烃是产量最大的一类塑料：2022 年聚烯烃产能约 2.3 亿吨，占合成树脂总产能的 70%。我们课题组在这一领域主要关注以下几个方面：

（1）传统聚烯烃材料的高值化，从而实现其长寿命服役以及拓宽其使用领域。通过对聚烯烃微结构在分子层面的调控可以有效的调控其一系列的宏观性质。更为重要的是，通过极性共聚单体的引入，我们可以制备出一系列极性官能化、可交联、自修复、光响应性的新型功能性聚烯烃材料。并且可以通过调节共聚单体含量等手段，制备热塑性塑料、弹性体和热固性材料等多种类型的聚烯烃材料。

（2）废弃塑料回收领域的一个非常大的挑战是混合材料的分离。我们需要针对不同聚烯烃材料以及聚烯烃与其他高分子材料的相容性问题，发展新型的策略实现混合材料的直接利用。为此我们需要发展新型、高效的手段来制备多嵌段聚合物。

（3） 发展高性能的催化体系，制备与传统聚烯烃材料性能相当的同时具有可降解、可循环性能的新型高分子材料。发展开环易位和配位聚合催化方法，精准制备遥爪型双末端官能化烯烃预聚物，在聚合物主链中引入“降解因子”，合成新型可降解“类聚烯烃”材料。

E14-18

天然橡胶的构效关系研究

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橡胶是国家安全和国民经济发展不可或缺的重要材料之一。以聚异戊二烯为橡胶烃的天然橡胶(NR)，具有合成橡胶无可比拟的优异综合性能。为了深刻理解和揭示其中奥秘，我们制备了 NR 的模型物，对比分析了模型物的微观结构、应变诱导结晶和分子运动，并提出了更全面和合理的天然网络模型。首先，制备和表征了三种含有不同非胶成分的模型物 NR，DPNR 以及 TEDPNR，通过对比研究它们对橡胶烃分子量及其分布、流体力学体积和粘度的影响以及介电松弛转变行为的变化，初步诠释了 NR 形成宽分子量分布和非键网络的原因；通过先进的随机光学重构显微技术第一次成功地将蛋白质和磷脂区分开来，观察到蛋白质和磷脂在胶乳和 NR 本体中的聚集状态及其自组装行为规律；采用同步辐射和固体核磁等深入分析非胶成分对分子运动和应变诱导结晶的影响规律，从多个角度揭示了天然网络的非均匀性，进一步离析出分子链的瞬态缠结和永久缠结，进而提出了由橡胶烃端基络合对分子链缠结的锚定而形成天然网络的机制；发现天然网络具有牺牲键的作用，证明正是其能量耗散功能，显著提高了天然橡胶的力学性能和耐疲劳性能。

E14-19

生物基呋喃二甲酸聚酯合成与性能研究

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聚呋喃二甲酸乙二醇酯（PEF）是一种具有比 PET 更高的 Tg、强度和模量的新型生物基芳香聚酯，有望替代 PET。但 PEF 的韧性差，成为限制其广泛应用的主要缺点。然而现有的增韧体系如添加增韧剂、柔性链共聚等均难以在保持 PEF 高 Tg、强度和模量的前提下获得优异的增韧效果。为了解决这一问题，本研究通过分子结构设计将含非平面环结构的二元醇引入到 PEF 分子链中，利用非平面环的空间构象转变提高了 PEF 的韧性。在此基础上，利用呋喃二甲酸结构横轴非对称和刚性合成了高耐热聚酯，利用其高结晶性能合成了生物基工程塑料和聚酯弹性体，利用其人体安全性和降解性合成了可降解聚酯，系统的总结了呋喃二甲酸结构特异性与聚合物的性能关系。

E14-20

Exploring Biomass and Paper-Based Materials as a Solution for Plastics Reduction

Xiaohui Wang*

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The international agreement to reduce plastic pollution and combat climate change has prominently featured the development of sustainable biomass and paper-based materials as substitutes for conventional plastics. Nevertheless, the inherent properties of biomass materials, including their natural hydrogen bonding network, high crystallinity, rigidity, and hydrophilicity, pose significant challenges to their processability and barrier performance compared to traditional plastics. Addressing these challenges requires enhancing the properties of these materials to facilitate their industrial application as plastic substitutes.

In our study, we have pioneered the thermal processing of biomass feedstocks, such as cellulose, chitosan, and starch, by reengineering the intermolecular interactions within biomass molecular chains. This was achieved by substituting the original hydrogen bonds with dynamic covalent bonds, thereby transforming the biomass into a pliable material with adjustable mechanical properties, enhanced processability, and remarkable resistance to moisture and solvents. This innovative approach also ensures good recyclability and biodegradability, aligning with the principles of sustainable development. Furthermore, we have developed solution-processable biomass materials, demonstrating their potential for scale-up production and industrial application. A significant breakthrough was achieved with the invention of novel biomass-based barrier coating materials, which endowed paper-based materials with plastic-like barrier properties, thereby enabling their industrial application. The processes, challenges, and breakthroughs in our research will showcase the promising future of biomass and

paper-based materials in reducing plastic use.

E14-21

生物基/生物可降解热塑弹性体超临界流体发泡技术和应用

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软质聚合物发泡材料如 EVA 泡沫、PU 海绵、橡胶泡棉等广泛应用于鞋材、运动防护、家具、缓冲包装等领域，其的全球市场容量在 2020 年已超过 3000 亿元人民币。不过传统软质发泡材料存在加工过程不环保、性能较差、发泡制品难以熔融回收等行业共性问题。面向双碳经济，聚合物软质发泡材料向着加工过程更环保、高性能化、可回收/可降解的方向发展，具有生物基/生物可降解特征的热塑弹性体以及具有环保低碳特征的超临界流体绿色发泡技术在软质发泡材料应用领域获得广泛关注。本报告聚焦商用生物基/生物可降解弹性体树脂，系统介绍弹性体超临界流体间歇发泡的基本特征、发泡方法和工艺，选择典型生物基和生物可降解弹性体材料，阐述其的超临界流体发泡行为和发泡材料的性能，最后，本报告介绍生物基/生物可降解弹性体发泡材料的应用领域和发展方向。

E14-22

Sustainable Development of Wood Cellulose Nanofibrils

陈文帅

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Amid the backdrop of the international carbon neutrality strategy, the high-value utilization of low-grade forest waste has become a focal point in forestry and materials science area. Through eons of evolution, trees have honed a remarkable adaptability to environmental fluctuations. At the cellular level, they are organized as composite structures where cellulose fibrils are embedded within a hemicellulose and lignin matrix. These nanofibrils, also termed as nanocellulose, represent the most abundant natural polymer nanofiber, and are lauded for their sustainability and distinctive nanostructural benefits. At this report, I will first delve into the multi-layered nanocomposite architecture of trees. Subsequently, I will outline the individualization techniques and nanostructural traits of plant cellulose fibrils, and the use of nanocellulose as building block to create sustainable responsive materials. Finally, I will discuss the exploration of cellulose fibril-based recombinant materials for various applications such as wastewater filtration, atmospheric water harvesting, dehumidification, moisture-induced power generation, and stimulus responsive structural color films.

E14-23

Design, Preparation and Industrialization of Bio-based Itaconate Elastomer

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Bio-based itaconate elastomer is a novel bio-based synthetic rubber prepared from bio-based monomer itaconic acid through esterification and copolymerization. This research designed the macromolecular chain structure based on bio-based itaconic acid for the first time, and has established the relationship between itaconate monomer and diene monomer, the third functional monomer and macromolecular chain structure and the properties of bio-based elastomers. New technology of free radical emulsion copolymerization with high conversion rate and low gel content were invented and complete technology for the industrial preparation of bio-based itaconate elastomers were developed. World's first 5,000 ton/year bio-based itaconate elastomers production line has been successfully established in China. Tires has been trial-produced and put on vehicles, and its wet skid resistance and fuel saving performance have both reached the Class A in the EU labeling law. Bio-based itaconate elastomers has been verified to be potenial to replace traditional petroleum-based rubber materials in treads, shoe materials, and oil-resistant products.

E14-24

木质生物质基生物塑料

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生物质材料来源丰富，是大自然赠予人类的宝贵资源。其中以木材为代表的木质生物质是自然界最为丰富的一类非粮基生物质材料之一，广泛分布于全球各地。木材作为一种古老的材料，在人类发展过程中扮演者重要的角色：人们用木材制作工具与家具、建造房子、甚至制造纸张，应用于生活的方方面面。可持续循环利用以木材为代表的非粮基生物质资源，特别是农林废弃生物质资源，是我国乃至全人类社会实现可持续发展及“碳中和”的重要途径之一。本报告将探讨木质生物质基生物塑料的化学合成策略及可持续利用路径，着重探讨古老的木质生物质如何应对人类社会可持续发展及“碳中和”实现过程中面临的材料-能源-环境挑战。

关键词：木质生物质；木质纤维素；生物塑料；生物基

E14-25

先进木质纤维可持续能源材料

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木质纤维生物质为自然界中最丰富、可再生的有机碳源，立足“双碳”减排目标，拓展开发木质纤维资源是解决未来碳基能源催化材料与化学品大宗制备与可持续发展的重要途径。本次会议报告人将分享在先进生物质炭材料构筑与性能调控方面的研究进展。一是“自上而下”从木材生物质的天然结构出发，以生物酶、路易斯酸预处理、冷冻导向结合高原子经济性的单分散金属掺杂等方法，制备了一系列木质等级孔炭并研究其对锌空气电池两极催化反应、生物质电氧化、电合成氘代药物的催化性能。二是“自下而上”以制浆废弃物木质素磺酸、纳米纤维素等组分为碳骨架，通过纳米焊接、异质结制造、无机盐介导热解途径等提升木质炭在催化过程中的电荷/传质能力，制备了高比表面积生物质基柔性碳基催化材料，并系统研究了其在氧还原及水分解反应过程的作用机制，探索了生物质糖分子选择性光、电、热催化转化为有机酸中反应过程；报告还将进一步揭示了木质炭的结构、电子结构和配位环境等理化特性与电化学活性的影响规律。

E14-26

二氧化碳基塑料的结构和性能调控

王献红

Structure and performance control of CO2 based plastics

高分子量 PPC 是一类无定型高分子材料，同时其玻璃化转变温度处于室温附近，因此 PPC 的使用温度低，且尺寸温度稳定性很差，需要在保持生物降解性能的前提下对其进行低温增韧、高温增强为核心的双重改性，进而采用吹塑、流延等方法实现其超薄莫的快速成型加工，进而挖掘出选择性气体阻隔性能和无机粒子的分散促进性等特殊性能，推动其在多个工业应用场景的规模应用。/This talk will focus on toughening and plasticizing of high molecular weight PPC for practical application.

E14-27

Sustainable Cellulose-based Materials for Scattering Engineering

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To manipulate the light–matter interaction effectively, we often rely on high refractive index inorganic nanoparticles. However, as these nanoparticles can accumulate in the human body and environment, there is a strong need to replace them with more biocompatible counterparts. Inspired by the optimised performances of the random networks found in Cyphochilus beetles, we developed highly scattering materials using only sustaibale and biodegradable cellulose materials . We developed cellulose-based microparticles (CMPs) with optimized

dimensions for efficient light scattering that can replace traditional inorganic particles. By tailoring their size, these particles can be implemented to engineer light transport and produce highly reflective white materials to fully transparent films with high optical haze. The assemblies of CMPs were able to achieve materials with a scattering mean free path as small as □1 μm (refle
(92%) and haze (98%). We also achieved using only cellulose derivatives for efficient radiative cooling that is simple to fabricate, cost-efficient and avoids the use of polluting materials. The produced cellulose films reached up to about 5.2°C below ambient temperature. We believe that these sustainable cellulose-based optical materials combined with the simplicity of the production can find applications in the next-generation sustainable, biocompatible, and renewable coatings for light distribution devices and light management materials.

E14-28

基于呋喃二甲酸的新型生物基高性能聚酯弹性体设计制备

刘斐

Design and Synthesis of Novel Bio-based Polyester Elastomers with High Performance Based on 2,5-furandicarboxylic Acid

热塑性聚酯弹性体是一类应用广泛的高分子材料，兼具优异的加工性及弹性，在汽车、电子电气、建筑、工艺及日常生活等领域具有广泛的用途。其中，加工性来源于结晶性能好、熔点高、刚性大的聚酯硬段，而弹性则来源于无定型、玻璃化转变温度较低的聚醚软段。2,5-呋喃二甲酸（FDCA）是含有呋喃环芳香结构的刚性生物基单体。由于其具有与对苯二甲酸类似的刚性和对称的二羧酸结构，可以用来替代来源于石化资源的对苯二甲酸，用于合成聚酯、聚酰胺和弹性体等高性能生物基高分子材料，在工程塑料领域具有巨大的应用潜力和价值。本研究基于 FDCA 设计高熔点、高结晶能力聚酯 PNF 和 PCF 作为硬段，结合聚醚软段分子量及质量分数调控，获得具有高弹性和高耐热的新型生物基聚酯弹性体材料，200%形变弹性回复率最高超过 90%，耐热温度最高超过 200^{o}C。

Thermoplastic polyester elastomers are a type of widely used materials that possess excellent processability and elasticity. The processability comes from the polyester hard segments with good crystallization ability and high melting point, while elasticity comes from the amorphous polyether soft segments with low glass transition temperature. 2,5-Furanedicarboxylic acid (FDCA) is a bio-based monomer containing aromatic furan ring. Due to its rigid and symmetrical dicarboxylic acid structure similar to terephthalic acid (TPA), it can be used to replace TPA for the synthesize high-performance bio-based polyester, polyamide, and elastomer. In this study, FDCA was used to design polyesters with high melting point and crystallinity as hard segments, combined with molecular weight and mass fraction control of polyether soft segments, resulting in a new type of bio-based polyester elastomer with high elasticity and heat resistance. The maximum deformation elastic recovery rate under 200% strain exceeds 90%, and the maximum heat resistance temperature exceeds 200^{o}C.

E14-29

高强高韧木质素基生物聚酯弹性体

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开发源于可再生资源的生物基材料是解决环境污染和缓解化石资源短缺的关键战略途径。目前，生物质化工的主流技术之一是将生物质转化为平台化学品，再合成材料。虽然这种方法易于实现对材料结构的精确控制，但产业链流程较长，成本较高。另一种途径是直接将生物质转化为材料，这种方法更具有经济性及能源效率优势，但在材料结构调控方面更具挑战性。我们团队近来通过整合木质素的天然结构功能和成本优势，结合生物基平台化学品的结构调控灵活性，合成了一种高性能生物基聚酯弹性体。具体地，以生物基 2,5-呋喃二甲酸（FDCA）为原料，合成低分子量柔性聚酯预聚物（PPeF），再引入扩链剂将 PPeF 接枝到木质素上，成功合成了一种多功能木质素改性聚酯弹性体（LFPEe）。该材料表现出优异的力学性能，拉伸强度和断裂应变可达到 58.9 MPa 和 610%，弹性恢复率达到 88.9%以上，杨氏模量达到 332 MPa，远

高于商用聚酯弹性体，优于大多数先前报道的 FDCA 基聚酯、木质素基聚酯和木质素基聚氨酯弹性体材料。其优异力学性能归因于：木质素在聚酯体系中不相容形成的纳米微相分离结构，以及木质素与聚酯链段之间形成的界面动态氢键和动态共价键组成的动态双网络结构。得益于木质素自身优异的光热功能，以及动态键的自愈特性，LFPEe 可实现光热自愈合，并具有优异的光热驱动形状记忆功能。此外，引入木质素还赋予 LFPEe 优异的紫外线屏蔽性能、良好的热稳定性以及抗老化能力，在简单的加热条件下还能实现溶剂循环回收。

作为一种高生物基含量、高性能的多功能材料，新型木质素基聚酯弹性体有望作为石油基弹性体的替代品。该工作打破了 FDCA 基聚酯力学性能对高分子量的依赖，实现了由低分子量 FDCA 聚酯低聚物制备高性能生物基聚酯弹性体。此外，该工作也为木质素在高性能生物基聚酯弹性体开发中的创新设计和增值利用提供了新思路。

E14-30

生物基聚碳酸酯绿色合成新过程

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高性能聚碳酸酯是国家重大战略需求，本研究以“生物基聚碳酸酯设计制备及聚合过程创新”为方向，开展了功能单体创制、高效催化体系构筑及聚合过程调控的研究，形成了基于新型功能单体的离子液体催化制备生物基聚碳酸酯制备新技术：（1）阐明了单体结构、链段组成等对聚碳酸酯性能的调控机制，提出了基于多芳杂环和脂肪杂环的单体设计新策略；（2）揭示了离子/分子间协同作用对单体活化及产物选择性的影响机制，解决了生物基异山梨醇单体惰性羟基活化难、单体适用性差的问题；（3）解决了工程上高粘体系传热传质不均、副产小分子脱挥难的问题，实现了千吨级装置稳定运行，产品性能通过了下游用户企业验证，优于国外同类产品，在光学元件领域实现应用。

E14-31

Eucommia Ulmoides Gum Electromagnetic Interference Shielding Composites Based on Segregated Network

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沈阳化工大学

The research and development of electromagnetic shielding materials have become crucial in both social life and national defense. EMI shielding rubber composites are widely utilized and highly favored engineering applications due to their exceptional elasticity, ductility, and sealing capabilities. The recently rubber composites with exceptional EMI SE have been developed by incorporating novel nano-fillers such as carbon materials, MXene, ferrite, or composite fillers. Additionally, these composites feature intricate heterogeneous structures including porous architectures, segregated network and multilayers embedded within the material. Despite recent advancements in structural design and filler hybridization for enhancing their EMI shielding performance, challenges persist in terms of suboptimal mechanical properties, intricate processing techniques, and limited industrial scalability. To address these limitations, bio-based Eucommia ulmoides gum (EUG) composites with segregated network structures were prepared using a simple mechanical blending method and the characteristics of highly cross-linked rubbers with restricted molecular chains. Highly cross-linked EUG (HCE) effectively segregated the conductive fillers into the EUG matrix phase, while the crystallization of EUG promoted the dispersion of conductive fillers within the amorphous region of the EUG matrix through volume exclusion effect. Therefore, the segregated structure and crystallization significantly facilitated the formation of a highly efficient 3D conductive network by conductive fillers, enabling the EUG/HCE/CNT composite to achieve an exceptional shielding effectiveness value of 83.0 dB with a high absorption loss in the frequency range of X-band (8.2~12.4 dB).

E14-32

生物质基纤维材料的绿色制备与功能化应用

Green Preparation and Functional Applications of Biomass-based Fiber Materials

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西安工程大学

生物质是自然界赋予人类最宝贵的生产资料，对其进行绿色、可控的功能化开发是科学研究和生产实践持续努力探索的方向。 本报告围绕纤维素、海藻酸钠等生物质材料的绿色溶解、功能改性、纤维应用等方面开展了系列工作，通过创新性制备工艺和改性技术的开发，实现了复合纤维材料在柔性传感、焦耳加热、医用抗菌等方面的应用。此外，成果研究开发的原位改性技术大大增强了生物质高分子与功能材料之间的界面及分散。在保证所制备生物质纤维/薄膜的物理机械性能以及环境友好特性不受影响的前提下，赋予了复合材料多样的功能，极大提高了生物基材料的附加价值。

Biomass is one of the most valuable natural resources bestowed upon humanity by nature. The green and controllable functional development of biomass is a continuous focus of scientific research and production practice. This presentation centers on the green dissolution, functional modification, and fiber application of biomass materials such as cellulose and sodium alginate. Through innovative manufacturing processes and modification techniques, the research has achieved applications of composite fiber materials in flexible sensing, Joule heating, medical antibacterial uses. Furthermore, the developed in-situ modification technology significantly enhances the interface and dispersion between biomass polymers and functional materials. While ensuring the physical and mechanical properties of the prepared biomass fibers/films and their environmental friendliness remain uncompromised, diverse functionalities have been imparted to composite materials, greatly increasing the added value of bio-based materials.

E14-33

Design and Characterization of High Gas Barrier and Fully Biobased Poly(1,5-pentylene succinate-co-itaconate-cofuranoate) Elastomers

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Biomass feedstock is an accessible alternative to finite fossil chemical resources for fabricating durable and high-performance polymers. In this study, fully biobased poly(1,5-pentylene succinate-co-itaconate-co-furanoate) (PPeSIFs) copolyesters were synthesized by using transesterification and melt polycondensation methods from dimethyl furandicarboxylate, dimethyl succinate, dimethyl itaconate and 1,5-pentandiol. Dimethyl itaconate was incorporated to provide the cross-linkable reaction sites. Four kinds of monomers were employed to regulate the glass transition temperature and suppress crystallization. Silica/PPeSIF nanocomposites exhibited good mechanical properties, such as an ultimate tensile strength of 17.2 MPa and an elongation at break of 253 %. This elastomer displayed outstanding gas barrier properties comparable to butyl rubber, with O2 permeability 13 times lower than that of natural rubber. Positron annihilation lifetime spectroscopy tests demonstrated that furan moieties significantly reduced the free volume of PPeSIFs. This work provides a promising route for preparing biobased elastomer with intrinsic high gas barrier properties.

E14-34

生物基高性能压电材料及其产业化进展

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压电材料是一种能够实现力学和电学信号相互转换的材料，目前被广泛用于生物医疗、环境发电、柔性电子等领域，是我国重点发展的功能与智能材料。现有的有机压电材料，如聚偏氟乙烯及其共聚物、聚酰胺等具有不可降解不可再生特性，而绿色环保的聚乳酸压电材料则因其压电性能不足存在性能瓶颈。本

报告针对上述研究需求，提出了通过柔性链段增强聚乳酸压电性能的新机制，合成了具有高性能高弹性的乳酸基压电弹性体，显著增强了聚乳酸压电性能的同时也保留其原有的可再生可降解特性。在此基础上，开发了乳酸基压电弹性体制备过程中的核心装备与工艺，并在能源传感、消费电子和智能医疗等领域探索了其产业化前景。

E14-35

木质素基碳点对天然橡胶的抗热氧老化性能的研究

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随着绿色化学获得全球共识，开发具有高抗氧化效率和环境友好的橡胶新型抗氧化剂受到广泛关注。木质素是一种重要的可再生生物质资源，对其进行研究和利用是当前的研究热点。作者通过采用双氧水和三乙烯四胺对木质素进行简单水热处理，制备了粗木质素基碳点(CLCDs)，其为准球形结构，表面拥有丰富的氮氧官能团，且具有显著的荧光性能和自由基清除能力。并以乙烯基吡啶-苯乙烯-丁二烯三元共聚物(VPR)为增容剂加入到天然橡胶(NR)中，VPR 的引入有效改善了 CLCDs 在天然橡胶基体中的分散性。结果表明 CLCDs 可赋予 NR 基体良好的抗氧化性能。值得注意的是，与纯化木质素基碳点(PLCDs)相比，粗木质素基碳点(CLCDs)对天然橡胶的抗氧化效果更佳。这一工作为从植物资源中制备低成本、高效的 CLCDs 提供了有价值的启发，为开发新型高效且环保的橡胶助剂提供了新思路。

墙报

E14-P01

Degradation behaviors of polylactic acid, polyglycolic acid, and their copolymer films in simulated marine environments

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Poly(lactic acid) (PLA) and poly(glycolic acid) (PGA) are extensively studied biodegradable polymers. However, the degradation behavior of their copolymer, poly(lactic-co-glycolic acid) (PLGA), in marine environments has not yet been confirmed. In this study, the changes in macroscopic and microscopic morphology, thermal properties, aggregation and chemical structure of PLA, PGA, PLGA-85, and PLGA-75 (with 85% and 75% LA content) in simulated marine environments were investigated. Results revealed that degradation occurred through hydrolysis of ester bonds, and the degradation rate of PGA was faster than that of PLA. The amorphous region degraded preferentially over the crystalline region, leading to cleavage-induced crystallization and decreased thermal stability of PLA, PLGA-85 and PLGA-75. The crystal structures of PLGAs are similar to PLA, and the higher GA content, the faster the degradation rate. This study provides a deeper understanding of the seawater degradation behavior of PLA, PGA, and their copolymers, and provides guidance for the preparation of materials with controllable degradation performance.

E14-P02

A natural protein-based high-performance, recyclable carbon fiber reinforced composite

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With the increasing emphasis on sustainable development, environmental protection and resource recycling have emerged as prominent global concerns. In the field of composite materials, the closed-loop recycling of carbon fiber reinforced composites (CFRP) holds substantial significance. In this study, we proposed a novel method for the preparation and recycling of bio-based, high-performance, recyclable CFRP. Using the silk protein

extracted from discarded silkworm cocoons or waste silk fabrics as the matrix material, CFRP with excellent mechanical properties could be prepared by simple processes including solution impregnation and solvent evaporation. The tensile strength and modulus of the as-prepared composites reached up to 1264.52 MPa and 38.59 GPa, respectively, which were superior to those of CFRP with other bio-based materials as matrix. Meanwhile, the closed-loop recycling of carbon fiber and silk protein matrix could be easily achieved by using the calcium chloride-ethanol-water solvent system. The recycled carbon fiber maintained its original chemical structure and mechanical property, and the recycled silk protein still exhibited great plasticity and biocompatibility. In addition, we trained a machine learning model to predict the mechanical performance of carbon fiber/silk protein composites by fiber contents, and found that there existed a strong correlation between the predicted values and the experimental values. Also, this model could be successfully extended to glass fiber/silk protein composites and aramid fiber/silk protein composites, which provided solid theoretical and experimental supports for the further study of silk-protein matrix composites. In conclusion, this study illustrated a new strategy for the closed-loop recycling and reuse of high-performance fiber-reinforced composites. This strategy could not only make full use of the waste bioresources, but also realize the green, gentle, and non-destructive recycling of carbon fibers, which will promote the sustainable development of the composites field.

E14-P03

Improving the barrier performance of PBAT by introducing epoxy soybean oil to form a cross-linked structure

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The biodegradable plastic polybutylene adipate-co-terephthalate (PBAT) shows great potential for widespread use as agricultural mulch film, but it suffers from poor water vapor barrier properties, hindering its large-scale application. This study presents a novel molecular design approach to prepare ESO-PBAT copolyesters which containing crosslinked structure using epoxidized soybean oil (ESO). Specifically, a certain molar ratio of ESO is reacted with adipic acid to form a multi-acid, which is then copolymerized with butanediol (BDO) and terephthalic acid (TA) to introduce a cross-linking structure into PBAT, resulting in ESO-PBAT. The ESO-PBAT copolyester has a melting temperature above 120°C and excellent thermal stability. The highest tensile strength and elongation at break are 22.3 MPa and 714%, respectively. Its water vapor barrier properties and hydrophobicity are significantly improved with increasing cross-linking structure content. The WVP of ESO-PBAT improved from 2.22×10-13 to 2.95×10-14g·cm/cm2·s·Pa. This work provides a direction for developing high-performance and biodegradable plastics, offering new insights into addressing the main drawbacks of PBAT.

E14-P04

Synthesis and Properties of Novel Bio-based Polycopolyether Ester Elastomers

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Due to the incessant depletion of fossil resources and deterioration of ecological environment, developing renewable and environment-friendly biomass elastomers has become the most urgent challenge faced by contemporary polymer materials.Herein, a series of bio-based poly(ester-ether) elastomers with different ether bond contents were designed and synthesized by multi-copolymerization firstly using poly(tetramethylene glycol)(PTMG) as the basic unit and other four bio-based aliphatic monomers.The impact of ether bond content on the microstructure and properties of the materials was investigated by 1H-NMR, FT-IR, DSC and GPC analyses.The chemical structure and composition of polyether ester elastomer were characterized by 1HNMR and FT-IR.And a series of bio-based poly(ester-ether) elastomers with number-average molecular

weights (42000~78000 g/mol) were obtained.The poly(ester-ether) elastomers exhibited tunable Tg from −48℃ to −65℃, which decreased gradually with the increase of ether bond content.The existence of ether bond structure endowed the elastomer with excellent flexibility and low-temperature elasticity.Additionally, the main chain structure of poly(ester-ether) elastomers contained the numerous ester groups, which gave it better oil resistance.The oil resistance results showed that the changes in mass and volume of the poly(ester-ether) elastomers remained below 4% after 72 h of immersion in 903# oil at 25℃, confirming that the ones superiority in oil resistance in contrast to several commercially avail-able oil-resistant rubber varieties.The synthesized novel bio-based poly(ester-ether) elastomer with low temperature oil resistance can be applied in aerospace, aviation and other fields that require harsh performance of elastomer materials.

E14-P05

High strength bio-based eucommia gum wood adhesive design, preparation and properties

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At present, traditional petroleum-based adhesives such as epoxy resins, phenolic resins and urea-formaldehyde resins are non-renewable, and they release toxic and hazardous substances that are harmful to human health and the environment during production and use. Under the global trend of green and sustainable development, the design and development of environment-friendly, renewable, high-performance bio-based adhesives has become one of the hotspots of the moment!

In this paper, the synthesis of levodopa (LDOPA)-grafted liquid eucommia gum (LEUG) and its adhesive property on wood were investigated. First, the epoxidised eucommia gum (EEUG) was prepared by epoxidising the plasticized eucommia gum (EUG), and the oxidative degradation of the EEUG was converted into liquid eucommia gum (LEUG). then, the eucommia gum-grafted LDOPA (LEUG-g-LDOPA) was prepared by a ring-opening grafting reaction between the amino group of levodopa and the epoxy group of LEUG.

The effects of reaction temperature, LDOPA dosage and emulsion solid content on the grafting rate of the product were investigated by orthogonal experiments, and the optimum reaction conditions were determined. The grafted products were characterised in terms of structure, molecular weight, crystalline behaviour and viscosity by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance hydrogen spectroscopy (1H-NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and rotational viscosity instrument (RVI), respectively. The structure, molecular weight, crystalline behaviour and viscosity of the graft products were characterised by GPC, Differential Scanning Calorimetry (DSC) and Rotational Viscometer (RVI), respectively. The lap shear test was used to study the adhesive performance of LEUG-g-LDOPA on wood, and the average value of dry lap shear strength of LEUG-g-LDOPA was 5.74 MPa, and the average value of wet lap shear strength was 3.14 MPa, which was comparable to the strength of waterborne epoxy trees, and the wet lap shear strength was better than that of waterborne epoxy adhesives, exceeding the performance requirements of the national standard (GB T 17657- 2013). The contact angle test results show that LEUG-g-LDOPA has a wetting effect on wood; the SEM image results show that LEUG-g-LDOPA can be uniformly coated on the surface of wood or penetrate into the surface and internal structure of wood to form a glue nail and improve the adhesion performance.

E14-P06

Protic Ionic Liquids Catalyzed Polymerization of Isosorbide and Dimethyl Carbonate to Bio-based Polycarbonates

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Utilizing CO_2-based or bio-renewable chemicals as monomers in synthesizing polymers to replace

petroleum-derived plastics has recently received considerable attention. Herein, a strategy for the synthesis of poly(isosorbide carbonate) (PIC) via melt polycondensation of dimethyl carbonate (DMC) and isosorbide (ISB) catalyzed by organic base-derived protic ionic liquids (PILs) was presented. The influences of anion and cation alkalinity on the catalytic activity of PILs were systematically studied. Results show that ISB and DMC are activated by hydrogen bond interactions with the anion and cation of PILs, respectively, and that the hydrogen bond strength can be easily tuned by adjusting the pKa values of the anion and cation. Among them, [DBUH][Im] with moderate basicity showed the highest catalytic activity, and the weight-average molecular weight (Mw) of PIC reached 55700 g/mol. Combined with NMR analyses and DFT calculations, the mechanism that exhibits the synergetic catalytic effect of anion-cation for the polymerization of DMC and ISB is presented.

E14-P07

Switchable Circular Polarized Phosphorescence Enabled by Biobased composite film

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E14-P08

Combined Role of Stearic Acid and Maleic Anhydride in the Development of Thermoplastic Starch-Based Materials with Ultrahigh Ductility and Durability

Sixian Peng
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E14-P09

Optimizing Carbonized Cellulose Nanofiber Pore Structure Using Artificially Cultured Diatom Frustules for Advanced Shape-Stabilized Phase Change Materials

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仅发表论文

E14-PO01

Analysis of the patent technology of Poly(butylene adipate-co-terephthalate) (PBAT)

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Bioplastics is a general term for biodegradable plastics (degradable petroleum-based or bio-based plastics) and bio-based plastics (plastics synthesized from renewable resources). Poly(butylene adipate-co-terephthalate) (PBAT) can be completely degraded into small molecules or carbon dioxide and water under specific conditions, so it has broad application prospects. At present, PBAT is one of the biodegradable materials with the best market prospects in biodegradable plastics, and it is also the main material support for plastic restriction. Using the global patent database of PatSnap and the Derwent patent database (DII), the application trend, life cycle, global layout, and main innovative entities of PBAT patent technology were retrieved and analyzed globally, the patent technology branches were divided, the technical methods of PBAT preparation were summarized, and the evolution route of preparation technology was demonstrated. At the same time, the main innovative entities in this patent technology field and their patent technology branch directions, main preparation technical methods, and technology evolution routes were analyzed. The analysis results show that the global PBAT patent technology has entered a period of rapid development since 2016; the patent applications mainly come from China, the United States, Germany, South Korea, and Japan; the relevant technical branches of PBAT mainly include PBAT

preparation technology, PBAT modification technology, PBAT biodegradation technology, and the application technology of PBAT materials; the PBAT preparation methods include the co-esterification method, the separate esterification method, the tandem esterification method, etc.; among the main innovative entities, there are multinational enterprises including BASF SE in Germany, Carbios in France, Eastman Chemical Company in the United States, and LG Group in South Korea, and in China there are Kingfa Science and Technology Co., Ltd., Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Shanghai Changfa New Materials Co., Ltd., and Wanhua Chemical Group Co., Ltd. Through the analysis results, it provides information support for the technical layout of China's PBAT industry and provides a reference for formulating patent strategies.