

生物质基环保型聚氨酯的制备与应用研究进展

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摘要: **目的** 从利用生物质资源制备环保型聚氨酯树脂的角度揭示聚氨酯的结构调控机制及性能影响因素, 为植物油基聚氨酯及其印刷包装材料提供多种有效的制备途径, 为印刷包装材料提供丰富的原料。**方法** 通过对比不同种类的植物油制备不同聚氨酯原料, 综述包括蓖麻油、大豆油、葵花籽油、亚麻子油等油脂, 以及木质素、腰果酚等制备生物质基多元醇、异氰酸酯作为扩链剂的二元醇原料。**结果** 详细讨论了生物质转化为活性原料用于合成环保型聚氨酯, 并介绍了主要的机理和方法, 认为环氧开环法仍是植物油转化为多元醇的主要途径。**结论** 利用生物质资源及其废弃物制备环保型聚氨酯是未来绿色聚氨酯类产品的最有效途径, 在绿色化学和纳米科技的推动下, 植物油基的绿色、高性能的环保型聚氨酯能成为印刷油墨、包装胶黏剂及涂层的关键原料, 具有广阔的应用前景。

关键词: 水性聚氨酯; 生物质; 油墨

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Preparation and Application Research of Biomass-based Environmental-friendly Polyurethane

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ABSTRACT: The work aims to reveal the structural regulation mechanism and affecting factors of polyurethane from the perspective of preparing environmental-friendly polyurethane resin with biomass resources, so as to provide a variety of effective preparation methods for vegetable oil-based polyurethane and its printing and packaging materials and abundant raw materials for printing and packaging materials. Different raw materials of polyurethane were prepared by different kinds of vegetable oil. The oil such as castor oil, soybean oil, sunflower oil, linseed oil and lignin, cardanol, etc. were used to prepare biomass-based polyols, isocyanates, and diol raw materials as chain extenders. The conversion of biomass into active raw materials for the synthesis of environmental-friendly polyurethane was reviewed in depth and the major mechanism and approach were also introduced. It was considered that the epoxy ring-opening method was still the most common way to convert polyols from vegetable oil. The use of biomass resources and its waste to produce environmental-friendly polyurethane is the most effective way to prepare green polyurethane products in the future. Driven by green chemistry and nanotechnology, vegetable oil-based green and high-performance environmental-friendly polyurethane can become the key raw materials of printing ink, packaging adhesive, and coating, and has vast application potential.

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KEY WORDS: waterborne polyurethane (WPU); biomass; printing ink

水性聚氨酯 (Waterborne Polyurethane, WPU) 是由分散在水中的聚氨酯 (Polyurethane, PU) 分子链卷曲形成的纳米颗粒组成的重要材料, 水分散液一般呈现为乳白色液体, 偶尔表现出轻微的蓝色或红色光^[1]。WPU 产品形式主要有纤维涂料、替代基材黏合剂、油墨黏合剂、金属底漆、嵌缝材料、涂料添加剂、消泡剂、缔合增稠剂、颜料浆和纺织染料等, 广泛应用于运输、建筑、工业、机械、电子设备、家具、服装、纺织、印刷和包装、食品加工、生物医学等领域^[2-8]。聚氨酯由低聚物多元醇 (二醇)、多异氰酸酯 (二异氰酸酯)、扩链剂和其他添加剂通过逐步聚合或乳液聚合合成。PU 的主要原料都来自石油, 容易被石油资源危机、世界政治及环境污染等问题所影响。同时, 由于聚合物链的缓慢扩散特性, 在保持机械强度的同时制造出具有优异愈合能力的 PU 具有较大的挑战性, 尤其在合成具有高韧性、快速自愈能力和抗菌性能的功能性及高耐性的 PU 材料方面具有更大的需求^[9]。因此, 为了保障广泛应用的 PU 产品有充足的原料来源, 且提升其综合性能, 有必要对 WPU 原料进行开发研究。其中, 生物质作为来源广泛的可再生自然资源, 成本相对较低、容易获得且能大量生产, 可避免石化资源造成的限制^[10]。植物油很早就被用于印刷油墨的生产, 将植物油进行深度开发进而制备综合性能良好的 WPU; 不同的植物油已经被用于制备酯交换产物, 即二醇, 可以作为合成 PU 的原料或其改性原料的前驱体, 具备成本低的优势, 且结构中存在的长脂肪酸链, 可赋予涂层以优异的柔韧性和光泽, 能有效为印刷包装油墨, 涂料及胶黏剂等材料提供绿色、丰富的原料^[11-13]。

1 水性聚合物分散液的性能

为了理解和制备 WPU 分散体, 首先应了解水性聚合物的特性。众所周知, 水性聚合物的聚集状态通常是热力学不稳定的, 表明它是分散体而不是溶液。由于分散聚合物颗粒的内表面积较大, 相分离和凝固会受到明显阻碍, 因此通常需要添加稳定剂。颗粒团聚的驱动力来自于减少内表面所获得的能量。最后, 在水相中产生微相分离的聚合物链段以形成具备自支撑性或者非自支撑性的聚合物颗粒。通常, 具有高稳定性的聚合物分散体因其优异的综合性能而备受关注。这可以通过提供离子基团来实现, 例如通过二羟甲基丙酸 (Dihydroxymethylpropionic Acid, DMPA) 将离子基团并入聚氨酯链, 或在乳液中使用阴离子或阳离子表面活性剂以获得高稳定性的 WPU^[14-15], 因此, 制备 WPU 或者其他水性聚合物, 原料的结构及性能特点成为了关键因素。

2 植物油基聚氨酯

2.1 植物油基原料种类及其在聚氨酯中的应用

植物油基 PU 被誉为 PU 工业最重要的技术创新之一^[16]。根据是否采用异氰酸酯作为原料, PU 可分为异氰酸酯型 PU (Isocyanate Polyurethanes, IPU) 和非异氰酸酯型 PU (Non-Isocyanate Polyurethanes, NIPU)。在 IPU 中, 植物油基原料可以用于制备低聚物多元醇、扩链剂二元醇、异氰酸酯等; 在 NIPU 中, 植物油基 PU 可以通过含有环碳酸酯键的植物油基主体和脂肪族或脂环伯胺反应得到^[17], 因此, 植物油基原料在 PU 中有巨大的应用价值, 后文将详细介绍不同种类的植物油基原料的制备原理及性能。

2.2 植物油基多元醇

来自不同植物 (大豆、棕榈、油菜籽等) 的植物油由于其丰富的可再生资源, 固有的生物降解性和低廉的价格, 已成为 WPU 行业最有前途和吸引力的原料。植物油的化学成分是甘油三酯和 3 种不同组成的长链脂肪酸, 反应性取决于碳-碳双键 ($C=C$) 和酯活性位点^[18]。此外, 一些植物油可以直接用作具有反应活性的天然羟基多元醇。但有些油中没有羟基, 需要通过对双键和酯基等活性基团的改性将羟基引入分子结构中。主要方法是通过植物油 (甘油与 C_6 至 C_{22} 碳原子脂肪酸的甘油酯) 中的天然甘油三酯的水解^[19]。普通植物油的脂肪酸组成和不饱和度是区分植物油的主要指标, 见表 1^[12]。除蓖麻油外, 由于缺乏化学反应活性羟基, 其他植物油很难直接用于制备 WPU。植物油甘油三酯中的 $C=C$ 键和酯键允许引入此类基团与异氰酸酯反应。值得注意的是, 相当多的大于 2.5 个 $C=C$ 键的甘油三酯倾向于满足反应 (表 1)。PU 分散体中使用的主要植物油 (蓖麻油、大豆油、葵花油、亚麻籽油、麻疯树油和棕榈油) 见图 1。

蓖麻油是一种脂肪酸甘油酯, 化学结构见图 2, 可以直接与异氰酸酯反应, 形成天然植物油多元醇形式的 PU^[20]。由于蓖麻油链上羟基的均匀分布, 使得合成的 WPU 具有较大的交联度、较高的力学性能和热稳定性从而可以直接用于制备 PU 黏合剂、涂料、泡沫塑料, 也可改性使用。Dang 等^[21]采用蓖麻油制备的阴离子 WPU, 将蓖麻油作为软链段添加聚合物链中, 显著改变了薄膜的力学性能和柔韧性。此外, 通过向醇解和酯交换反应中添加低分子多元醇, 如乙二醇、甘油、季戊四醇等, 可生成具有不同羟基值和分子量的蓖麻油衍生物多元醇。相较于橄榄油、大豆油和葵花籽油等其他植物油, 蓖麻油具有显著优势。

蓖麻油约 90%的成分是蓖麻油酸，每 12 个碳上有一个羟基，第 9 和第 10 个碳之间有一个碳碳双键（如图 2）。本体聚合过程中通过单点方法制备的蓖麻油基聚氨酯弹性体^[22-24]，然而，所得的弹性体不溶于常

见的有机溶剂，从而有毒的催化剂和未反应的原料不能轻易从交联弹性体中去除。蓖麻油的羟基官能度平均为 2.7，导致聚合过程中形成聚合物结构的三维网络，从而赋予聚合物以更高的黏弹性^[25-26]。

表 1 常见植物油的不饱和度组成^[12]
Tab.1 Degree of unsaturation and composition of common vegetable oils^[12]

植物油	Double bonds*	脂肪酸组成/%					碘值/(mg.g ⁻¹)
		C16:0	C18:0	C18:1	C18:2	C18:3	
蓖麻	3.0	1.5	0.5	5.0	4.0	0.5	81 ~ 91
椰子	—	9.8	3.0	6.9	2.2	—	—
玉米	4.5	10.9	2.0	25.4	59.6	1.2	118 ~ 128
棉籽	3.9	21.6	2.6	18.6	54.4	0.7	98 ~ 118
亚麻籽	6.6	6.6	5.5	3.5	19.1	15.3	>177
橄榄	2.8	13.7	2.5	71.1	10.1	0.6	76 ~ 88
棕榈	1.7	42.8	4.2	40.5	10.1	0.6	50 ~ 55
棕榈仁	—	8.8	2.4	13.6	1.1	—	—
花生	3.4	11.4	2.4	48.3	31.9	—	84 ~ 100
菜籽油	3.9	4.1	1.8	60.9	21.0	8.8	100 ~ 115
芝麻	3.9	9	6	41	43	1	—
大豆	4.6	11.0	4.0	23.4	53.3	7.8	123 ~ 139
葵花籽	4.7	5.2	2.7	37.2	53.8	1.0	125 ~ 140
棉籽	3.9	21.6	2.6	18.6	54.4	0.7	98 ~ 118

注：*表示每个甘油三酯的 C = C 双键数目。

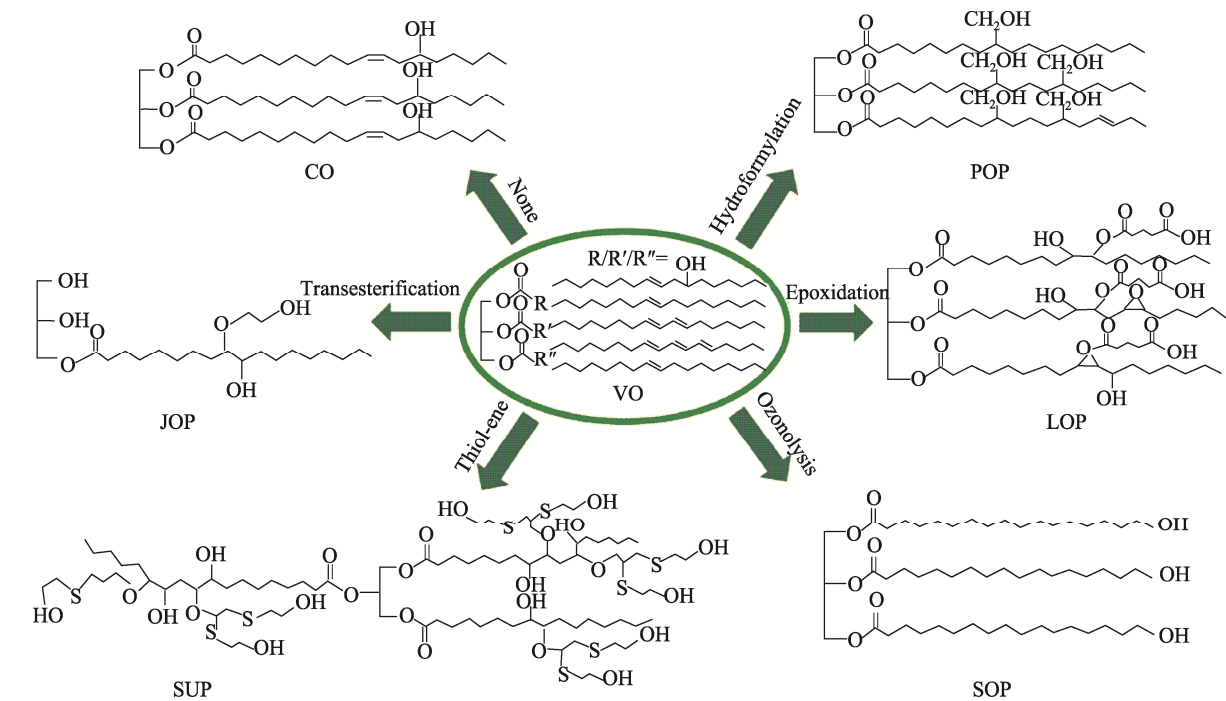


图 1 聚氨酯分散体中主要使用的植物油的分子结构^[2]
Fig.1 Molecule structure of mainly used vegetable oil in polyurethane dispersion^[2]

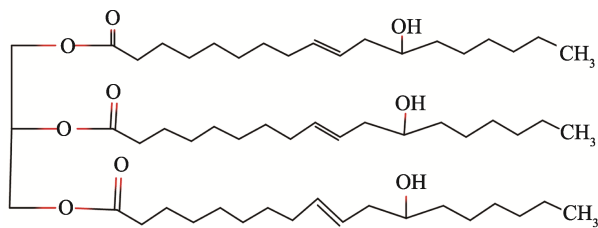


图 2 蓖麻油化学结构^[18]
Fig.2 Chemical structure of castor oil^[18]

大多数植物油,如大豆、向日葵、亚麻子、桐油、麻疯树油和棕榈油中都没有化学反应活性羟基,因此,需要对 $C=C$ 键反应位点进行化学修饰引入羟基。它们通常是通过双键的环氧化,然后环氧化物与乙醇开环而得到的,这可能会产生具备化学反应活性的二级羟基^[27]。当前主要有 5 种合成路线,分别是环氧化环氧乙烷开环反应、硫醇烯反应、氢甲酰化加氢、臭氧分解和酯交换跨酰胺反应^[10,18-19,28-39]。

大豆油是一种多不饱和或亚油酸,极易受到油脂氧化型油脂的影响,但大豆油不含天然羟基。同时,由于改性后大豆油基多元醇的多官能团,在合成 PU 时容易出现高交联和凝胶化。它优选于 PU 泡沫和弹性体,但不适用于 WPU 分散体。降低羟基官能度是调整多元醇可用于制备 WPU 的有效途径^[40],主要方法为通过环氧开环反应将大豆油转化为活性多元醇,通过环氧化和羟基化,大豆油的官能度为 1~6,羟值为 50~700 mg/g。Zhang 等^[41]以 1,8-二氮杂二环戊烯-7-烯为催化剂,研究了环氧化大豆油和蓖麻油脂肪酸之间的开环反应动力学。结果表明,环氧树脂与羧基的开环反应活化能为 72.2 kJ/mol,而以质子为催化剂的开环活化能为 75.1 kJ/mol,较高的能量可能归因于蓖麻油长碳链的空间位阻效应。Feng 等^[42]通过巯基烯与 2-巯基乙醇反应制备大豆油基多元醇(见图 3),并且由于初级羟基的存在,所得多元醇对二异氰酸酯具有较高的反应活性。此外,利用这种环氧化大豆油和戊二酸可以得到生物基乳化剂,可以取代传统石油基乳化剂^[43]。

葵花籽油可用作多元醇、异氰酸酯和扩链剂制备 PU。通过环氧化和环氧基的开环作用将羟基引入植物油的 $C=C$ 键结构中,进而形成化学反应活性多元醇^[44]。Omran 等^[45]通过硫醇-炔反应从葵花籽油中合成了高一级羟基官能度多元醇,如图 4 所示,新型葵

花籽油基多元醇由于具有高羟基官能度,可高度调节以生成具有广泛交联密度的 PU 热塑性塑料。这些生物基聚氨酯具有合理热稳定性,可用作透明膜。同样,高羟基多元醇在紫外线固化 PU、聚酯合成等领域有着广泛的应用^[46-47]。另外,Shendi 等^[48]提出了一种新的含羧基基团的多元醇以取代价格昂贵的二羟基酸,该多元醇由葵花籽油经环氧化、开环和皂化反应制备而成,并作为亲水性扩链剂制备 WPU。

亚麻籽油是从亚麻籽中提取的廉价可再生资源之一。最新研究表明,亚麻籽油基多元醇是通过甘油的酯交换反应合成的,然后用作扩链剂与二异氰酸酯合成 WPU。Cheng 等^[49]介绍了通过酯交换法从亚麻籽油合成 WPU,实验结果表明,显著提高 WPU 中的生物基含量,改善了其热性能和力学性能。同时,亚麻籽油基涂料对木材具有优异的附着力、耐用性和耐光性。此外,亚麻籽油被成功用作取代二羟甲基丙酸的亲水性扩链剂制备阴离子 WPU。同时,将亚麻籽油环氧化,然后用乙二醇和盐酸开环,可皂化为多羟基脂肪酸^[50]。

麻疯树油是从麻疯树种子中提取的,含有高浓度的佛波酯有毒成分,因此不能食用^[51]。麻疯树油的含油量约为 40%~60%,这对于提取具有良好的经济意义^[52]。Saalah 等^[53]通过环氧化和环氧乙烷开环工艺从麻疯树油中制备了麻疯树油基多元醇,并研究了麻疯树油基 WPU 中硬段、羟基数和离子乳化剂含量对胶体稳定性和流变性能的影响,制备出来的聚氨酯分散体平均粒径较小,胶体具备良好的稳定性,见图 5。

棕榈油由油棕制成,由甘油三酯和甘油三酸酯组成,化学结构见图 6。为了制备 PU,将羟基引入棕榈油骨架中制备具有反应活性多元醇较为关键,通过小分子多元醇的环氧化和酯交换是引入羟基制备棕榈油基多元醇的替代方法。Yeoh 等^[54-55]制备了棕榈油基聚酯多元醇,该多元醇由环氧化物棕榈油酸和戊二酸衍生而来,并与异佛尔酮二异氰酸酯反应生成脂肪族 PU,无需再加入任何商用石化多元醇。

总而言之,以各种绿色天然植物资源为原料合成一系列植物油基多元醇,可以用作不同用途的聚氨酯产品中。植物油分子链上有酯基和不饱和碳碳双键等多种功能位点,易于转化为不同的功能单体,如二醇、多元醇和含羟基的聚合物,可用于合成聚氨酯,因此,它可以作为石油基聚合物的替代品,生产生物基聚氨酯的绿色前驱体。

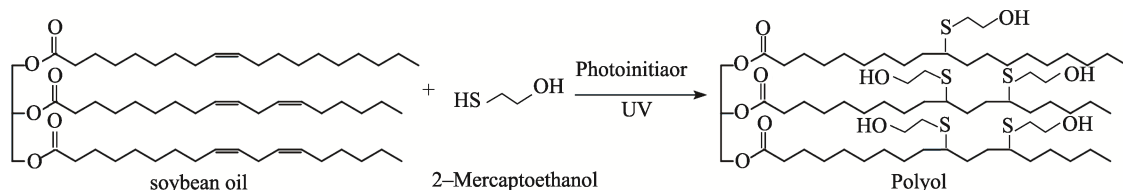


图 3 硫醇-烯光点击反应制备大豆油基多元醇^[42]
Fig.3 Preparation of soybean oil-based polyols by the Thiol-Ene Photo-Click Reaction^[42]

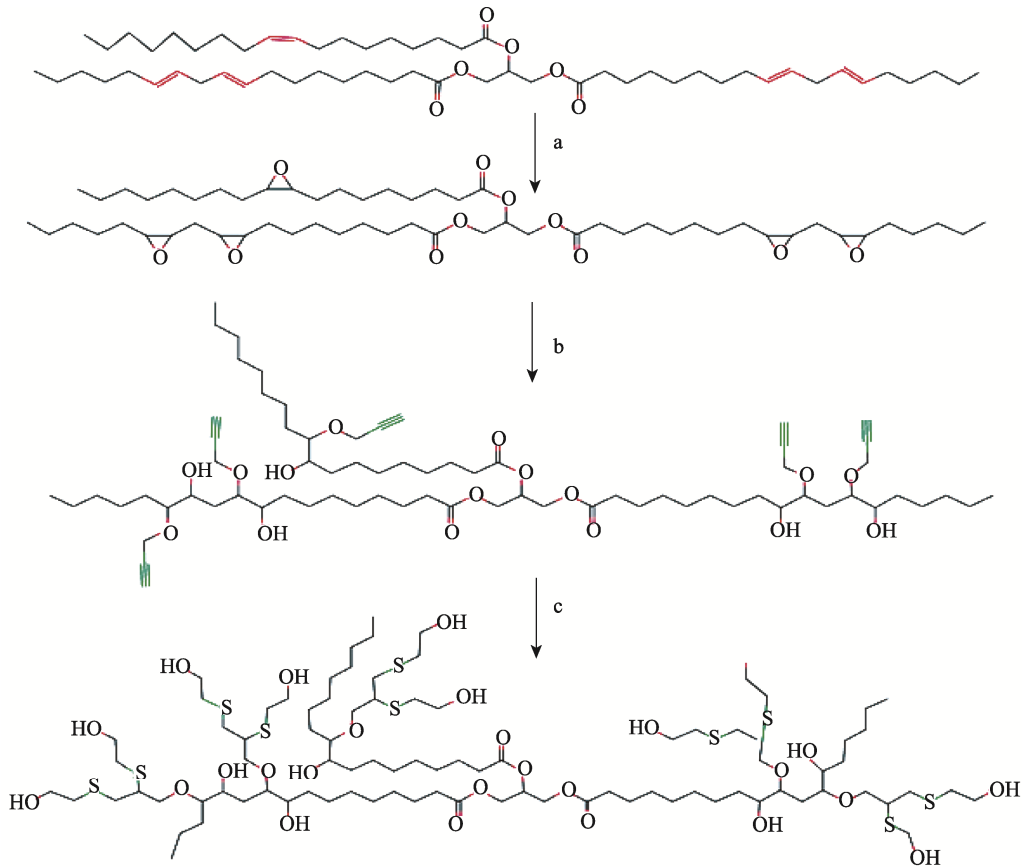


图 4 葵花籽油生物基超支化多元醇的合成途径^[45]
Fig.4 Synthesis method of bio-based hyperbranched polyol from sunflower oil^[45]

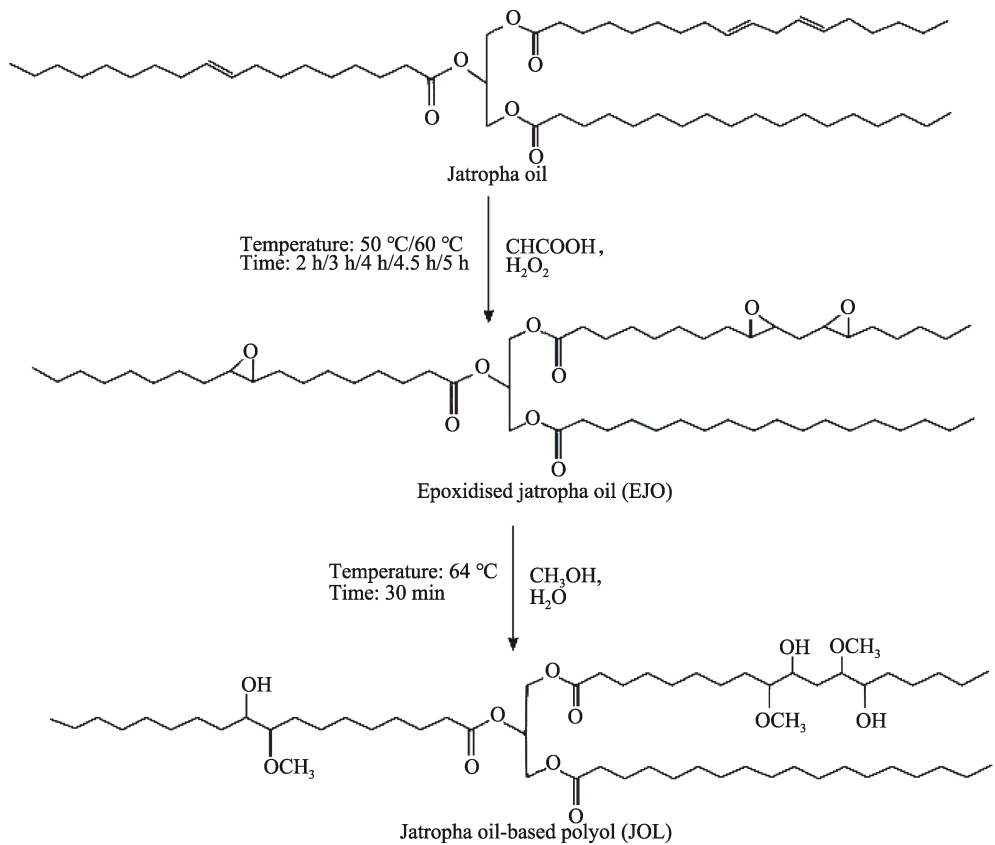


图 5 通过环氧化和环氧乙烷开环法合成麻疯树油基多元醇^[53]
Fig.5 Synthesis of jatropa oil-based polyol via the epoxidation and oxirane ring opening method^[53]

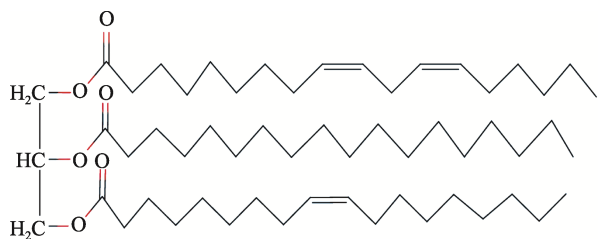


图 6 棕榈油化学结构
Fig.6 Chemical structure of palm oil

2.3 植物油基异氰酸酯

除了植物油基多元醇外,研究人员还致力于通过同时使用植物油来替代石油基异氰酸酯,从而实现异氰酸酯的绿色化。因为异氰酸酯具有高反应性和毒性,所以从植物油中合成适用于PU的二异氰酸酯仍然是一个巨大的挑战。据报道,汉高公司(Henkel Corporation Co)及通用磨坊公司(General Mills Co)提供了市场化的基于脂肪酸的二异氰酸酯,称为二聚二异氰酸盐^[56]。大豆油有望通过异氰酸酯官能化合成二异氰酸酯,当前主要有2种策略,其中一种是使用N-溴代丁二酰亚胺在烯丙基位置溴化甘油三酯,然后与AgNCO反应生成含异氰酸酯的甘油三酸酯^[57]。另一种是通过异氰酸酯碘和大豆油在室温下的反应,可进一步制备大豆油的异氰酸酯加合物,每甘油三酯含有3.1个异氰酸酯基团,见图7。这些异氰酸酯适合于制备WPU^[23]。此外,油酸也有可能通过将二羧酸氧化后,通过复分解合成不饱和的 α, ω -二羧酸,进而可被用于制备新型长链不饱和二异氰酸酯^[58]。

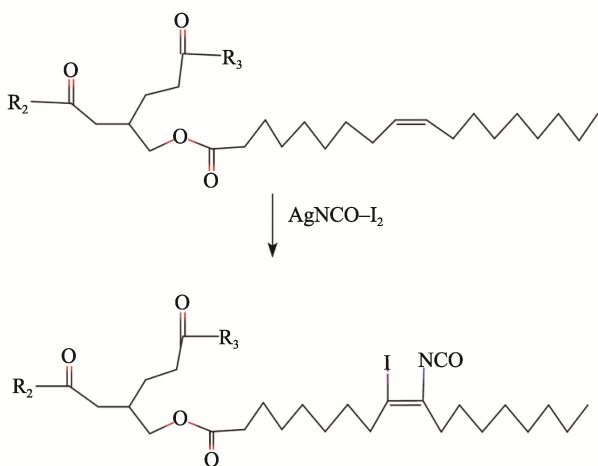


图 7 含碘植物油基聚异氰酸酯的合成
Fig.7 Synthesis of iodine-containing plant oil-based polyisocyanates

3 其他生物质基低聚物多元醇

3.1 木质素多元醇

木质素来源于木材,是自然界中可再生且丰富的

芳香族聚合物,它是由3种单体(松柏醇、对香豆醇和芥子醇)组成的交联网络结构化合物^[59-60]。木质素的三维网络具备足够的强度和硬度,可直接混合到聚合物基质中,以获得抗菌、抗氧化、抗紫外线、阻燃等性能^[61],在工业应用方面有巨大潜力。木质素的主要官能团有羟基、甲氧基、醚基、羰基和羧基^[62]。如图8所示,这些活性基团为木质素的改性,引入新的化学活性位点提供了可能,例如,羟基功能化开发的多功能木质素共聚物,可作为PU的原料^[63]。

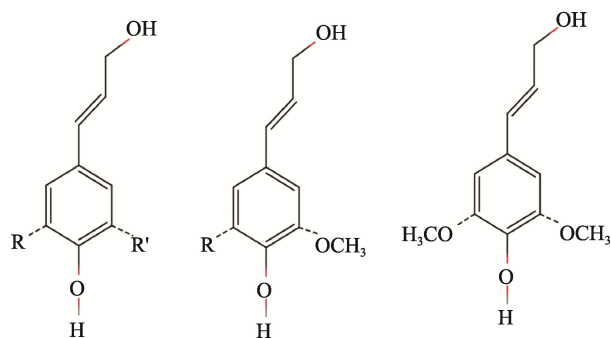


图 8 构成木质素的主要结构单元
Fig.8 Main structural units in lignin

由于羟基的存在,木质素可以直接与异氰酸酯作为多元醇前体反应,从而在较温和的条件下合成PU^[64]。通过溶剂分馏预处理方法可以有效提取均质木质素馏分,以获得清晰的特征结构和较高的纯度^[65-66]。Wang等^[67]探索了以未改性软木硫酸盐木质素馏分作为初级羟基制备木质素基PU的方法。结果表明,木质素分子量的增加可以提高木质素基聚氨酯的硬度或变形抗力。利用木质素作为单一多元醇开发的聚氨酯材料通常很脆且硬^[68],因此,可以对木质素进行化学改性以提高其反应性^[69],例如,木质素的氧化作为一种提高醇羟基含量和木质素功能性的方法被广泛研究^[70]。Ren等^[71]研究了环氧氯丙烷改性木质素用于WPU的合成,并分析了木质素对粒径分布、热稳定性、力学性能以及耐水性的影响。

3.2 腰果壳液基多元醇

腰果壳液是从腰果中提取出来的,含有许多具有高度疏水性脂肪链的活性酚衍生物,如腰果酚、腰果醇、2-甲基腰果酚和苦味柠檬酸^[70]。据报道,腰果壳液体通常用于环保型聚氨酯的开发,从腰果壳液中提取的一系列多元醇作为PU制备的组分^[72]。含有特征性长不饱和脂肪族链的腰果酚也用作多元醇或者合成环保型PU,Wang等^[73]通过硫醇基点击反应引入环氧化腰果酚多元醇,得到相对较高的羟值腰果酚(图9),在PU中具备潜在应用价值。

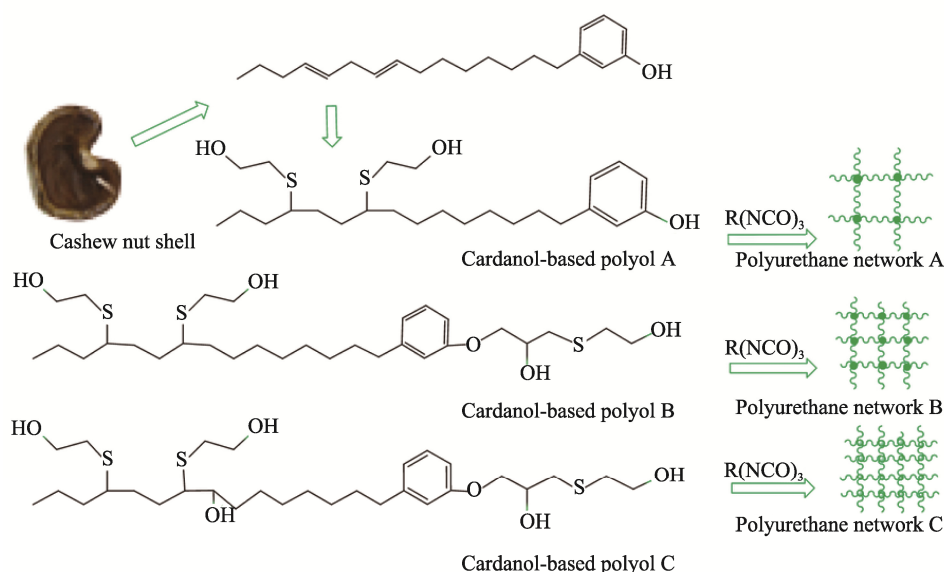


图 9 腰果壳衍生的多元醇作为聚氨酯的可持续原料应用
Fig.9 Application of cashew nutshell-derived polyols as sustainable raw material of polyurethane

3.3 植物秸秆多元醇

从纤维素中生产生物多醇一直是 PU 工业的常用方案。其中, 农作物秸秆中含有丰富的纤维素, 如大豆秸秆、油菜秸秆、小麦秸秆和玉米秸秆^[74]。这些植物秸秆可以通过液化过程, 由分解、酯化、缩聚等一系列反应, 转化为液体生物多醇^[75]。研究发现, 将各种植物秸秆材料在不同溶剂中液化, 生成多元醇, 作为溶剂的液化产物是富含羟基的聚酯或聚醚多元醇, 可与异氰酸酯反应生成 PU, 具备良好的综合性能^[76]。Hu 等^[77]提出了利用粗甘油从大豆秸秆中提取高质量生物多醇用于合成 PU。与传统的石油基 PU 相比, 含有 440 ~ 540 mg/g 羟基的多元醇可制备性能良好的 PU。Serrano 等^[78]研究了在甘油溶剂中通过液化反应制备麦草多元醇, 并将其用于合成可生物降解的 PU。

3.4 萜烯基多元醇

萜烯是从多种植物中提取的一类天然碳氢化合物, 广泛分布于自然界, 包括蒎烯、柠檬烯、匹罗卡酮、月桂烯、异罗卡烯、罗卡烯和法尼烯^[79]。结构的多样性 (即线性、环状或多环) 和双键的存在使萜烯具有多功能和高反应性。近年来, 在合成不同萜烯聚合物, 特别是聚氨酯方面有了长足的进展^[80]。

柠檬烯是从柑橘类水果中分离出来的廉价、可再生的原料, 由 2 个不同的双键组成的单萜烯^[81], 由于这种特殊的结构, 柠檬烯可以很容易地被改性为其他有价值的材料。通过环氧化或硫醇烯点击反应可以在其分子链上引入羟基, 以获得多元醇, 进而制备 PU (图 10a)^[82-84]。Gupta 等^[82-85]报道了以柠檬烯为基础合成具有芳香结构的新型多元醇, 并进一步用于制

备 PU。柠檬烯的双环氧化产物二氧化柠檬烯, 是制备生物基聚碳酸酯或非异氰酸酯 PU 的关键前体, 见图 10b。

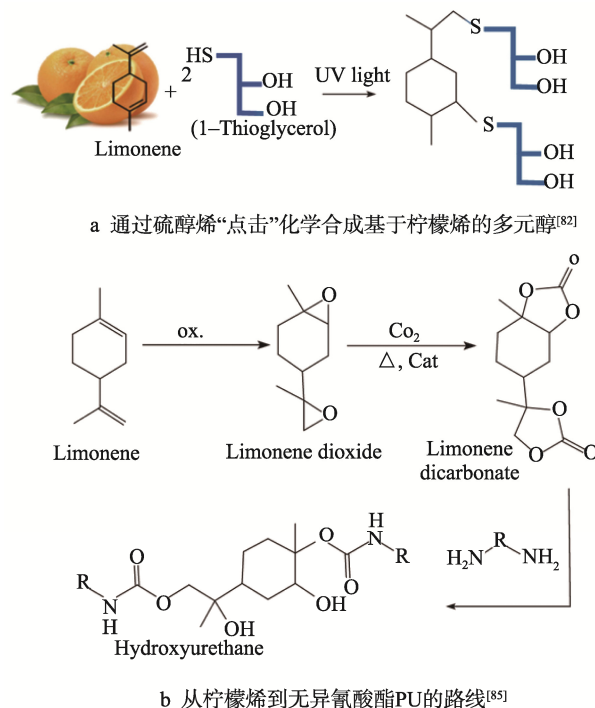


图 10 柠檬烯制备 PU 的不同途径
Fig.10 Different methods for preparation of PU with limonene^[85]

3.5 松香基多元醇

松香主要由 90% 的松香酸组成, 是松树树干分泌的一种脆性、透明的固体天然树脂, 具有优异的绝缘性、黏附性和乳化性, 能使聚合物具有较高的力学性

能,广泛应用于材料、化学、医药和化妆品等领域^[85]。由于松香分子结构中的共轭键和羧基等反应基团,通过加成、异构化、聚合、酯化等方式能得到不同的衍生物,因此,松香及其衍生物可被用作 PU 合成领域化学原料的替代品^[86]。Liu 等^[87]研究了松香基环碳酸酯与胺成功制备松香基非异氰酸酯 PU 涂料。通过对松香上的共轭双键和羧基进行改性,可得到松香基二醇扩链剂,将其引入 PU 硬段结构中,得到生物基 PU。Xu 等^[88-89]报道,从松香酸中提取的富马罗哌酸的聚酯多元醇可成功地用于合成一系列新型松香基 WPU,更有助于提升 WPU 的力学性能、热稳定性和耐水性。

3.6 纤维素

纤维素由线性和长链葡萄糖组成,是目前最丰富的天然聚合物。由于存在大量羟基,从而与其他聚合物的氢键功能引入化学活性位点提供了可能^[90-91]。纤维素种类可参照其微观形态分为纤维素纤维(微米级和纳米级)、纤维素纳米晶体(Cellulose Nanocrystals, CNC)和细菌纤维素(Bacterial Cellulose, BC)^[92-93]。由于具有优异的生物降解性、力学性能以及可再生性都被用于 WPU 的改性^[94-96]。在 PU 合成过程中,纤维素在分子水平溶解上存在难题,较难获得用于聚合均匀的纤维素溶液,因此,不同的纤维素产品主要用作改性 PU 的填料是提高 PU 性能的有效途径^[97-99]。

Głowinska 等^[100]研究了纤维素粉末参与生物基

聚氨酯复合材料的合成,其中取代基 R 可以作为油酸或棕榈酸的残基出现,见图 11。纤维素纳米纤维(Cellulose Nanofibers, CNF)可以分别通过化学接枝和物理共混工艺引入 WPU。研究表明,氢键与 PU 链形成化学键用于化学接枝,对提高 PU 的物理共混性能起着关键作用。由于纤维素的不溶性,化学结构无明显变化,PU 和通过 CNF 改性的 PU 热稳定性相似。值得注意的是,CNF 显著提高了聚氨酯的抗拉强度(约 41.8 MPa,高出纯聚氨酯约 26.3 MPa)^[101]。

由于纳米级氢键与 PU 链的相互作用,CNC 表现出具有高结晶度的棒状纳米形态,基于它良好的热性能和力学性能,它可能是最具吸引力的纳米级生物物质。在笔者之前的工作已经通过使用废纸中的 CNC 来增强 WPU 来证明了这一点^[102-103]。CNC 还可进一步改性以赋予 WPU 的新特性,包括导电性^[104]、耐水性^[105]和抗菌性能等^[106]。此外,CNC 还可与一氧化钒(Vanadium Oxide, VO)混合改性 WPU,以呈现高硬度和兼容性、弹性恢复和黏附性等多功能特性^[107]。

BC 是一种来自细菌菌株的独特纤维素产品。在医学、食品和组织工程领域发挥着重要作用。由于存在强的链间氢键,其呈现出具有显著力学性能的 3D 纳米纤维网络。独特的结构和性能为将 BC 用作水凝胶治疗伤口提供了可能^[108]。Urbina 等^[109]制备了具有形状记忆特性的凝胶状半透明 BC/WPU 复合膜,被认为是生物医学产品的最佳候选产品。形状记忆性能由温度调节,形状恢复率可达(92.8±6.3)%。

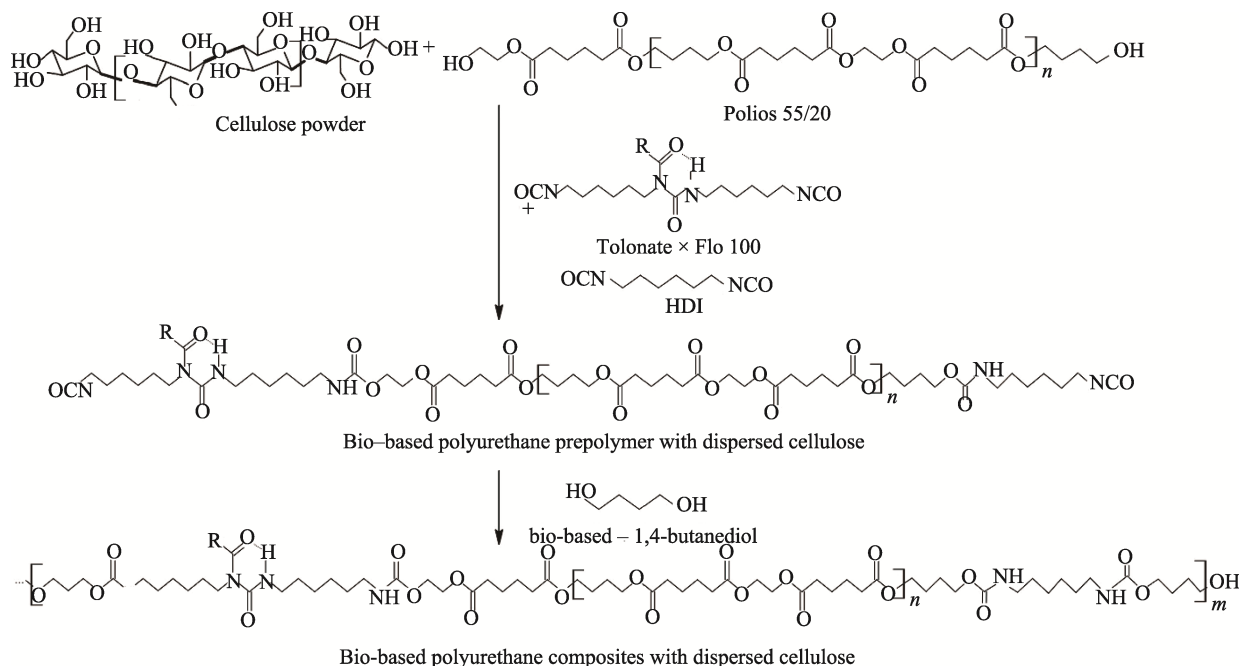


图 11 生物基聚氨酯复合材料的制备^[100]
Fig.11 Preparation of bio-based polyurethane composite^[100]

4 水性聚氨酯基印刷包装材料及发展

WPU 以其优异的综合性能而备受重视, 越来越多的应用于印刷包装领域, 尤其在印刷油墨、涂层、包装胶黏剂等产品中。在康师傅面碗表面印刷包装中, 大部分胶黏剂及上光油采用 WPU 系列产品。WPU 及其改性树脂也常用于镭射镀铝膜转移用背涂涂料中, 在高精度防伪印刷包装中被广泛应用。

WPU 因其广泛可调的软段与硬段交替结构, 具备良好的弹性及机械强度, 用于制备油墨时能赋予油墨良好的黏度、稳定性、细度等性能, 同时使墨膜具备优异的粘弹性、耐刮擦性、光泽度等, 在环保型油墨制造领域备受关注。俞胡斐等^[110]将 WPU 1 426/聚乙二醇 400 (质量比为 2:3) 混合树脂为油墨连结料, 制备水性变色油墨, 发现当溶剂、连结料、去离子水三者质量分数分别为 54.9%、17.4%、27.7% 时, 油墨样品印刷效果良好且变色效果最为显著。李海徽等^[111]使用聚丙二醇 (Polypropylene Glycol, PPG) 为低聚物多元醇, 以 DMPA 为亲水性扩链剂合成一系列醇溶性 PU。发现随着 PPG 分子量的逐渐增大, 油墨的黏度, 细度和稳态剪切黏度先增大后减小, 当 PPG 相对分子质量为 1 500 时, 所合成 PU 制备的油墨综合性能最佳, 在油墨黏度为 880 MPa·s, 细度为 5 μm , 析油率为 5%, 附着力为 93%, 初干性为 84 mm/s, 光泽度为 37 时, 印刷适性良好, 油墨在 15 s 的结构回复率为 94.47%, 触变性良好。

综上, 将 PU 作为油墨连结料制备水性环保型油墨, 具备较好的应用前景^[112]。将植物油用于制备新型环保型 WPU, 有望取代现有的溶剂型聚合物连结料体系。事实上, 植物油基油墨是出现最早的油墨之一, 在世界工业化进程中, 虽然因为印刷速度需求植物油基油墨逐渐被取代, 但是新世纪以来石油资源危机、环境保护等问题日益严重, 从而使得植物油基 PU 连结料及其油墨研究与植物油在涂料和印刷油墨中的应用中受到更广泛关注。Roy 等^[113]制备了植物油甲酯基“绿色”胶印油墨, 评估了油墨的流变特性, 并与使用石油基溶剂的标准印刷油墨进行了比较。得出酯类印刷油墨的性能与矿物油类产品相当, 酯基油墨相较于矿物油基, 其产品粘性、稳定性和光泽度更为优越。

在包装胶黏剂领域, WPU 因分子链含有大量的氨基甲酸酯基团、脲键、醚键等, 容易与不同基材表面产生多种相互作用, 因而对多种基材黏结力良好, 而且 WPU 中的亲水性羧基盐、羟基等活性基团在特定条件下容易形成交联, 为进一步提升 WPU 胶黏剂粘结性能提供可能。2020 年, 日本东洋油墨集团的成员 Toyochem 公司推出 Cyabine 系列聚氨酯压敏胶, 通过采用植物来源的原料制备环保型 PU 包装胶黏

剂, 且具备可生物降解性。Chen 等^[114]设计含有氨基磺酸基团 ($\text{NH}_2\text{SO}_3\text{H}$) 的桐油基 PU 预聚物制备 WPU 环保胶黏剂, 180 $^\circ\text{T}$ 型剥离强度实验结果表明该胶黏剂的胶黏强度可达 1.799 N, 表现出优良的黏合性和力学性能。

在涂层领域, PU 以其优异的力学性能和光泽度而成为上光油等保护印刷包装涂层的关键材料之一, 尤其是紫外光 (Ultraviolet, UV) 固化环保型聚氨酯涂层, 在木器、纸张、塑料、金属及玻璃等包装材料领域具备巨大的潜在应用价值。通常采用丙烯酸类的功能单体与 PU 预聚体进行接枝共聚, 制备分子链段上含有 $\text{C}=\text{C}$ 键的活性功能丙烯酸单体-聚氨酯共聚物, 与光引发剂在分散相中混合均匀后作为涂料使用。在 UV 光照下, 光引发剂产生的活性自由基引发 $\text{C}=\text{C}$ 双键发生自由基聚合, 进而促进 PU 产生交联, 形成综合性能优异的涂层^[115]。

5 结语

传统的 PU 工业及下游印刷包装材料严重依赖石油资源。随着人们对废物回收和环境污染问题的日益关注, 直接导致了工业生产中可持续 PU 的可再生和生物降解资源的使用。文中系统地介绍了利用生物质资源合成 WPU 分散体作为可持续材料的最新研究进展。近年来, 生物质基 PU 在印刷、包装、形状记忆聚合物等领域的材料功能化应用得到了进一步的探索。这些生物质中, 特别是植物油和纤维素在过去十年中受到了广泛关注, 为日益增长的环境和能源问题提供了有效解决方案。值得一提的是, 生物基 WPU 仍然存在许多问题需要未来的更多研究。

1) 植物油向多元醇 (或二元醇、异氰酸酯) 的转化效率相对有限。最常用的方法可能是环氧化物开环法, 这可能会降低产品的纯度。

2) 尽管设计了植物油基异氰酸酯, 但非异氰酸酯 WPU 仍然需要扩大原料来源。

3) 基于植物油基单体构建具有可控结构的 WPU 链段仍是研究焦点, 尤其是采用活性聚合方法来扩大这些生物基聚合物的应用。

总而言之, 基于生物基单体的环保型 WPU 应大规模设计和开发, 进一步扩大生物质基原料来源范围, 并实现规模化生产, 以满足日益增长的功能化和智能化聚合物技术的需求。

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