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Biomass-sourced polymers for pressure-sensitive adhesive applications

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Abstract. Pressure-sensitive adhesives are self-adhesive chemical products that have gradually supplanted traditional glues in recent years. Most of the commercially available pressure-sensitive adhesives are derived from petrochemical resources. The increasing attention to environmental protection, coupled with the introduction of stringent regulations and rising oil prices, has led to widespread attention being paid to the development of sustainable pressure-sensitive adhesives from biomass sources. This paper summarizes the biomass-sourced pressure-sensitive adhesives and their modification methods that have been reported in recent years as promising alternatives to petrochemical resources.

1. Introduction

Pressure-sensitive adhesive is a self-adhesive material that can adhere to the surface of objects with only slight pressure, and is widely used in automotive film, daily office, medical, packaging and other fields [1]. The formation of pressure-sensitive adhesion does not require a chemical reaction with the surface of the object in contact, which is achieved by the van der Waals forces between the pressure-sensitive adhesive and the substrate. Therefore, it is necessary that the pressure-sensitive adhesive material has a certain degree of fluidity to infiltrate the surface of the object to be adhered to, as well as the elasticity of the solid and the creep resistance required for the separation process [2]. Pressure-sensitive adhesives can be divided into six types: rubber, polyester, polyether, silicone, polyurethane and acrylate [3]. The use of pressure-sensitive adhesives has increased dramatically in recent years due to the rise of the courier industry. Most of the pressure-sensitive adhesives today come from petrochemical resources, and with the increasing demand and the contradiction between non-renewable raw material reserves, the development of new, recycled pressure-sensitive adhesives has become an inevitable trend for the future. The use of naturally occurring macromolecules, such as natural rubber, starch, egg whites and animal glue, glutinous rice, etc., for the production of adhesives began long ago, and these traditional adhesives are still in use and still exist in many ancient buildings today. Although these natural pressure-sensitive adhesives are renewable, they often contain a variety of impurities and are costly, limiting their large-scale industrial production. Natural pressure-sensitive adhesives have significant limitations, such as poor UV resistance and lack of water resistance, and are not suitable for today's complex applications, but it is still possible to extract raw materials from biomass and use polymerization and chemical modification to obtain new renewable pressure-sensitive adhesives that are comparable to today's commercial pressure-sensitive adhesives [4].

2. Polyester pressure-sensitive adhesives of bio-sourced

Polyester pressure-sensitive adhesives are becoming a hot topic of research due to their good biocompatibility and availability of raw materials from a wide range of biomass sources, as well as their rapid degradability in nature [5]. Kim and Shin et al. used diethylene glycol (DEG) as initiator and tin (II) ethylhexanoate $Sn(Oct)_2$ as catalyst to achieve sequential ring-opening polymerization of the bio-sourced monomers ε-decalactone (DL) and L-LA to prepare ABA-type tri-block polymers (PLLA-PDL-PLLA). The soft segment PDL has a molecular weight of up to 100 kg/mol, which effectively enhances the energy storage modulus and creep resistance of the polymer. The authors noted that tackifiers and other additives are necessary components of most polyester-based pressure-sensitive adhesives, and the addition of bio-derived rosin ester tackifiers and epoxidized soybean oil plasticizers blended with PLLA-PDL-PLLA yielded renewable pressure-sensitive adhesives [6]. The optimal formulation has a peel strength of 2.6 N/cm, a probe tack of 3.0 N, and hold tack test results greater than 2000 min, which is comparable to commercially available pressure-sensitive adhesives.

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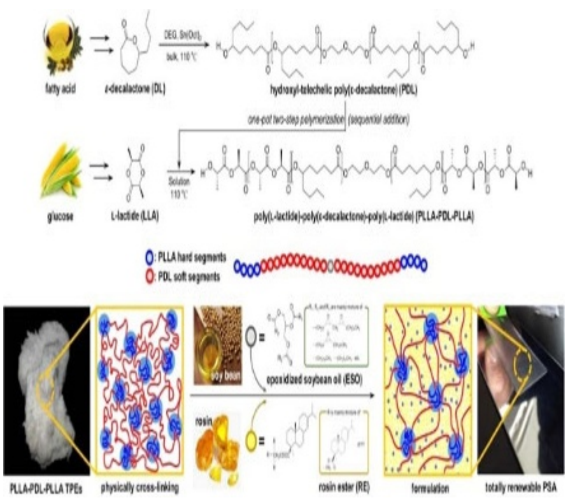

Figure 1. Synthesis of PLLA-PDL-PLLA from ε-decalactone (DL) and L-LA and preparation of renewable pressure-sensitive adhesives [6]. Reprinted with permission from ref. 6. Copyright (2015) American Chemical Society.

The cashew nut industry produces more than 2.2 million tons of cashew nuts per year, while cashew nut shells go unnoticed. these cashew nut shells can be produced by a simple extraction process to produce cashew nut shell liquid and are available in more than 450,000 tons per year. Hillmyer and Ellison et al. used cashew nut shell liquid as a raw material to prepare a new seven-membered ring polyester with long alkyl substituents, poly(pentadecyl caprolactone) (PPDCL) and polymerized it with L-LA blocks to obtain the tri-block polymer LPL (Figure 2) [7]. By blending with renewable rosin resin tackifiers, a series of pressure-sensitive adhesives with different adhesion properties can be obtained by changing the ratio of tackifiers. Among them, the 180° peel strength is 10.2 N/cm at 60 wt.% of rosin resin tackifier addition, which is higher than most commercial pressure-sensitive adhesives, and the ring adhesion is 10.0 N/cm and hangs vertically for 500 min without failure, with good creep resistance. The pressure-sensitive adhesive can be degraded in acidic aqueous solutions, which can effectively solve the problem of "adhesive residue" in pulping facilities.

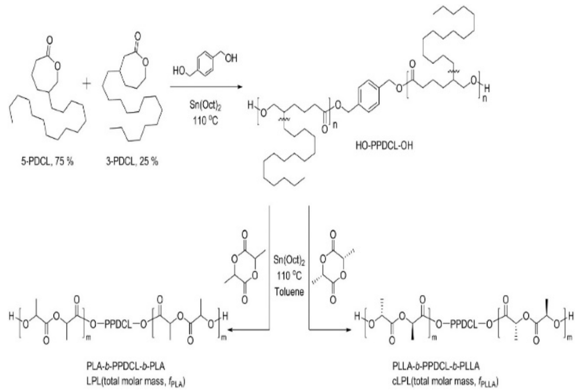

Figure 2. Synthesis of tri-block copolyesters from PDCL and LLA [7]. Reprinted with permission from ref. 7. Copyright (2020) American Chemical Society.

Williams et al. in 2020 reported a class of fully degradable bio-based pressure-sensitive adhesives. Hard segments were obtained by alternating copolymerization of biomass-derived monomers limonene oxide (LO), tricyclic anhydride (TCA), which had better properties than PLLA hard segments, where OL was derived from waste citrus peel [8]. Seven ABA-type polyesters were synthesized by a "one-pot" method through the selective polymerization of OL, TCA (1-4) and ε-decalactone using a single catalyst. These polyesters exhibited tunable peel strength (4-13 N/cm) and outperformed commercial adhesive or bio-based polyester formulations, and more importantly, did not require tackifiers or various additives. The authors further investigated the hydrolysis reaction of these polyesters and found that they degrade rapidly within 5 h of immersion in organic acid solutions at 60°C, with a mass loss of more than 98% of the polymer. Since these block polyesters can be used as pressure-sensitive adhesives without the addition of tackifiers and various additives, they are expected to be recyclable for reprocessing.

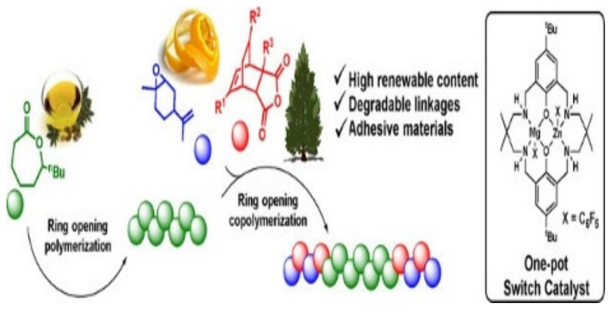

Figure 3. Fully renewable ABA type polyester synthesis [8]. Reprinted with permission from ref. 8. Copyright (2020) American Chemical Society.

3. Degradable pressure-sensitive adhesives derived from lignin

Lignin is the most abundant biopolymer in nature after cellulose, and it is attractive to use lignin as a raw material for pressure-sensitive adhesives to replace existing petroleum-based pressure-sensitive adhesives. Wang and Epps et al. reported a method to develop pressure-sensitive adhesives with high performance by obtaining chemicals directly from biomass [9]. The poplar was depolymerized in methanol solution using commercial Ru/C catalysts, and two aromatic compounds, 4-propylsyringol and 4-propylguaiacol, were obtained in a few purification steps (vacuum filtration and extraction), using the two aromatic compounds as hard segments, which allowed the synthesis of tri-block polymers with biologically derived poly(n-butyl acrylate) as intermediate segments. The polymers exhibit excellent adhesive properties with a 180° peel force of 4 N/cm and an adhesion force of 2.5 N/cm, comparable to many commercial pressure-sensitive adhesives and without the addition of any tackifiers or other additives.

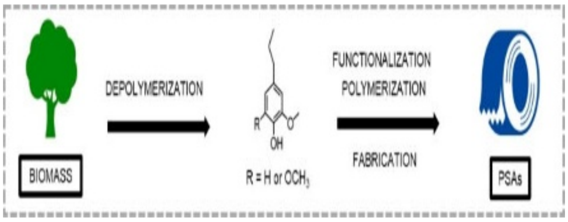

Figure 4. Monomers obtained from real biomass, not model compounds or lignin mimics [9]. Reprinted with permission from ref. 9. Copyright (2018) American Chemical Society.

The use of lignin, a non-toxic renewable material, as an additive to modify the performance of pressure-sensitive adhesives is an option to achieve sustainability, and the addition of new materials to the formulation usually results in significant changes in performance compared to conventional products, Nasiri et al. used acetyl bromide and acetic acid, methacryloyl chloride and maleic anhydride for modification to reduce the viscosity of latex [10]. Moreover, both the acrylic lignin and the maleated lignin obtained through the modification were effective in simultaneously improving the adhesion and shear strength in acrylic adhesive formulations while maintaining a constant peel strength.

4. Conclusion

Research on biomass-sourced pressure-sensitive adhesives has been one of the hot topics in recent years, with the main objective of developing a green material that can replace existing petroleum-based pressure-sensitive adhesives. With the global emphasis on environmental protection and sustainable development, the research and development of bio-sourced pressure-sensitive adhesives has become a trend. In this field, researchers have successfully developed a series of bio-sourced pressure-sensitive adhesives with excellent properties through the extraction and modification of various bio-based raw materials. This paper discusses the recent advances in biomass-derived pressure-sensitive adhesives and summarizes the methods reported in the literature in recent years for the preparation of pressure-sensitive adhesives using bio-based feedstocks. The performance of these pressure-sensitive adhesives is comparable to or even exceeds that of current commercial pressure-sensitive adhesives, making it possible to replace existing petroleum-based pressure-sensitive adhesives. Such substitution can reduce the dependence on petroleum resources and is also in line with environmental protection concepts.

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