

Lactic Acid-Sustainable Raw Material for Biodegradable Hot Melt Adhesive: Review

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Abstract

Currently, due to scarcity of hydrocarbon resources and the extensive use of water based, solvent based and hot melt adhesives in wood bonding in furniture industries and packaging industries that demand recyclability, compostability and bio-degradability, recently attention has been concentrated to making these formulations completely bio-based, sustainable and biodegradable. Biodegradable hot melt adhesives (HMAs) prepared from natural sources have a potential for use in furniture and packaging industries because of an increase in awareness of environmental issues, the replacement of conventional petroleum-derived hydrocarbon raw materials by renewable, biodegradable and sustainable materials has developed. In terms of environmental issues, such as climate crisis due to an increase of carbon dioxide emission, attempts have been made to produce HMAs using non-hydrocarbon resins, such as polylactic acid (PLA)-based resins, containing no petroleum as a raw material. Polylactic acid was prepared by self-condensation reactions of lactic acid or by lactide ring opening polymerisation, and used for packaging materials, sanitary pads, diapers etc., especially adhesives owing to its excellent processability and the excellent mechanical properties of its HMAs products. Therefore, recently the use of PLA materials as a substitute for non-biodegradable hydrocarbon-based polymers can be considered to be environmentally favourable. Here, we discussed the various uses of PLA as a sustainable and bio-degradable and sustainable hot melt adhesive.

Keywords

Lactic Acid, Hot Melt, Sustainable, Bio-Degradable, Adhesive

1. Introduction

Bio-based and Bio-degradable materials

Recently, to reduce their dependency on hydrocarbon materials, focus has

been concentrated to making these adhesive recipes completely bio-based, sustainable and biodegradable. To reach this, research and developments are targeting on the uses of starch, lignin, tannin, soy protein, polylactides and vegetable oils based fatty acid as a partial/fully replacement to the hydrocarbon-based polymers [1]. **Figure 1** is showing the classification of bio-degradable, renewable, non-biodegradable and petrochemical raw materials.

Definitions:

Bio-based materials: Fully or partially obtained from biomass e.g., plants;

Bio-degradable materials: The breakdown of organic matter into carbon dioxide, water and biomass by the action of microorganisms such as bacteria or fungus.

Currently, Hot melt adhesives (HMAs) are based on petroleum-based materials and those are not biodegradable. To reduce the dependency on the petroleum sources and achieve biodegradability, bio-based raw material can be used in HMAs. Here, we review the uses of PLA in the hot melt adhesive segment.

2. Hot melt Adhesive

Hot melt adhesives (HMAs) are one of the most growing sectors within the adhesive industry [2] [3]. HMAs can be useful for high-speed manufacturing and applications that require bonding versatility, large gap filling, and minimal shrinkage. HMAs do not require a carrier fluid such as an organic solvent or water, which eliminates the need for drying the liquid adhesive layer once it is applied to a substrate. Elimination of the drying step reduces solvent usage, increases production line speeds, and lowers transportation costs [4] [5].

HMA is a thermoplastic material which is solid at room temperature and is applied on the adherend in its molten state. The adhesive bond is formed after

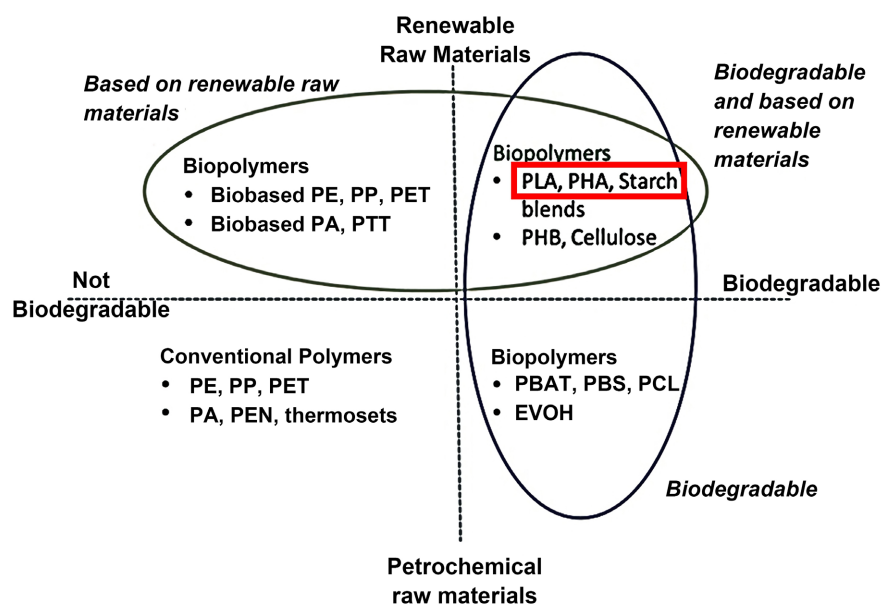


Figure 1. Bio-based and biodegradable materials.

HMA is cooled. Therefore, HMAs provide several advantages e.g., rapid setting times and elimination of volatile organic compounds [6] [7] [8]. Main application area of the HMAs is in packaging [9]. HMAs are often used to bond two substrates together so as to maintain the two substrates in a fixed relation to each other. HMAs compositions have historically been based on petroleum-derived polymers, and these compositions are further tackifier, plasticized, and reinforced with a variety of resins, oils and waxes that can be derived from both petroleum and naturally occurring feedstocks such as wood, gum and tall oil rosin, and terpenes. Useful fillers and/or rheology modifiers are chalk, barite, quartz, gypsum, calcium oxide, magnesium oxide, silica [10] [11].

3. How Do Hot Melt Adhesives Work

HMAs offer advantages over their contemporary water-based and solvent-based adhesives like low volatile organic compounds (VOCs), 100% solid, fast drying, setting etc. The HMAs are designed to be applied in consumer goods, packaging, construction, transportation, electronics, healthcare, and for other applications like bookbinding, furniture etc. [12] [13]. These are generally available as granules, powder, slats, blocks, foils, ribbons etc. It is then applied by bringing it between two substrates. Once cooled, it will set and solidify. The solidification mechanism depends on open time and set time. Open time denotes the time during which sufficient tack is retained on the surface on the other hand, set time is referred as the time for developing acceptable bond strength at 20°C. As the HMAs need heating, special applicators are needed for its application. Special glue gun that can be loaded with the solid adhesive sticks or rods which are fed and heated in the gun nozzle producing liquid adhesive. HMAs are solid materials at low temperatures (typically < 80°C) and can melt to liquid or viscous-flow state at elevated temperatures, in which form they are applied on the surface of substrates [14]-[19]. Currently, almost all the base polymers for HMAs on the market are primarily derived from petroleum resources, such as ethylene vinyl acetate, block copolymers of styrene and butadiene or isoprene, polyesters, polyamides, polyurethanes and polyolefin's [20] [21] [22] [23].

4. Need of Renewable and Bio-Based Materials in Hot Melt Adhesive

“Renewable resource” is used herein to refer to a resource that is produced by a natural process at a rate comparable to its rate of consumption. “Bio-based” is used herein to refer to a component of the hot melt adhesive that is produced or is derived from at least 50% by weight of a renewable resource. Bio-based materials are not necessarily compostable [24].

Packaging materials contain small amount of adhesives but that can nevertheless have a significant effect on the repulpability of the package. Recycled paper from packaging material waste is used in combination with virgin fibers in the paper making process and traditional hot melt adhesives are likely to contami-

nate the paper made in this way. It is therefore desirable that the adhesives used in packages would degrade in the recycling process. Other issues related to adhesives and packaging materials are the increasing demands on compostability and the use of materials from renewable resources. In compost environments it is important that the major part of packaging material is degradable in a certain time, which also includes the adhesives used. Biodegradable hot melt adhesives prepared from renewable raw materials have a potential for use in packaging applications [25]. Renewability of the adhesive raw materials can be considered to be an asset compared to petroleum derived polymers due to increased environmental awareness [26] [27] [28] [29].

5. Polylactic Acid-Chemistry

Polylactic acid (PLA) has been a subject for numerous studies during the past decades and several attempts have been made in order to commercialise this polymer on industrial scale. Lactic acid is the simplest molecule showing optical activity. The l-stereo form is the most commonly occurring one in nature, while the d-form can be produced either by biological or chemical methods. Lactic acid-based polymers are interesting because the starting chemical, lactic acid, can be obtained from renewable sources by fermentation. PLA is also compostable which means that a CO₂-neutral life cycle can be established for the material [30]. PLA homopolymer has a glass transition temperature in the range 55°C - 60°C and a melting temperature of about 170 °C [31].

The lactic acid monomer of the amorphous polymerization product may be derived from one or more of L-lactic acid, D-lactic acid, L-lactide, D-lactide and meso-lactide [32]. Lactide is a chiral molecule and exists in two distinct optically active forms, L-lactide and D-lactide, which can be polymerized to form a crystalline polymer. Structure of PLA is shown in **Figure 2** as below.

Polymerization of a racemic mixture of L- and D-lactide monomeric units forms poly-D, L-lactide (PDLA), which is amorphous and has a glass transition temperature of 55°C - 60°C. The degree of crystallinity in the poly(lactide) polymer also can be tuned by altering the ratio of D to L enantiomers within the polymer. Selection of the PLA stereochemistry can have a major effect on polymer properties, processability and biodegradability. In some embodiments, poly(L-lactide) or PLA is used in the HMA precursor composition because it breaks down into L(+)-lactic acid units, a naturally occurring stereoisomer, and would

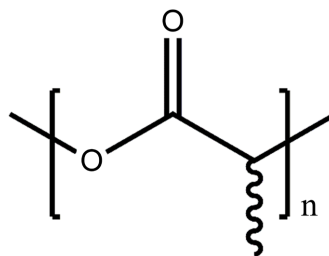


Figure 2. Structure of PLA.

be expected to degrade more quickly in the environment. Suitable polylactide polymers can include, for example, homopolymers or copolymers made up of (L-lactide), (D-lactide), and (meso-lactide) monomeric units. As noted above, while poly (D, L-lactide) and poly(meso-lactide) are essentially amorphous, poly(L-lactide, PLLA) or poly(D-lactide, PDLA) are crystalline in nature and have a crystalline melting point of about 186°C., depending on molecular weight and stereo purity. In some embodiments, the PLA polymer in the HMA precursor composition includes a predominant amount of (L-lactide) and (D-lactide) monomeric units, and in some embodiments the PLA polymer is a crystalline homopolymer or copolymer including (L-lactide) and (D-lactide) monomeric units. In other embodiments, the PLA polymer is a crystalline homopolymer including (L-lactide) monomeric units. The major component of the HMA composition, which is present in an amount of about 60 wt% to about 99 wt% of the composition, includes a homo- or copolymer of poly (lactic acid), referred to herein generally as PLA. [33]

6. Polylactic Acid in Hot Melt Adhesives

Polylactic acid (PLA) can be used for packaging materials, especially adhesives owing to its good processability and the excellent mechanical properties of its molded products. Therefore, the use of these materials as a substitute for non-biodegradable synthetic polymers can be considered to be environmentally beneficial. In one such study, copolymers with PLA: polycaprolactam (PCL) molar ratios 81:19 were tested for open time, adhesion, setting time, hot tack development, viscosity and weight loss of adhesives. To limit the unwanted thermal degradation, acetic anhydride is used as a stabilizer. This copolymer-based HMAs is used in industrial glue lamination process. The measured properties were evaluated against commercial ethylene-vinyl acetate HMAs [5].

The unique characteristics of PLLA/PCL HMAs are its excellent hot tack and a combination of long open time with moderate setting time. The same copolymer in the same molar ratio can also be used as biodegradable HMA for food packaging applications [34]-[42]. HMA includes: a lactic acid and caprolactone copolymer resin, a crystalline lactic acid oligomer wax, and said amorphous lactic acid oligomer tackifier, characterized in that the amorphous lactic acid oligomer tackifier includes an amorphous polymerisation product of 1) lactic acid monomer and 2) a multifunctional polymerization initiator containing three or more hydroxy and/or amino groups [43] The poor stability of lactic acid based polymers have been demonstrated in several publications and different approaches have been reported to be efficient in the improving the stability on of PLA. This PLA/PCL copolymer was stabilized by end-capping of the hydroxyl groups with acetic anhydride or by treating the polymer with peroxide. It was noticed, that these chemically stabilized polymers performed better during processing and also retained their mechanical properties better than the un-stabilized copolymer. Especially the acetic anhydride treated polymer seemed to be an interesting al-

ternative. The rapid degradation of these PLA/PCL, HMAs is probably related to low initial molecular weight and the presence of a high amount of monomer residues. The low T_g -values of the PLA/PCL polymers also increase the chain mobility resulting faster degradation [44]. Utilizing biodegradable and renewable raw materials is a demanding challenge for the packaging industry. Many packages are of single-type use, which means rapid growth of municipal wastes [45] [46] [47]. Based on the previous studies, lactic acid-based polymers were chosen as candidate of a new generation hot melt adhesive. These samples degraded rapidly in the hydrolytic and compost environments. Additionally, these lactic acid-based polymers showed interesting adhesive properties [48]. In the case of biodegradable hot melt adhesives, the materials need to be stable enough during storage, in the process and in the application, but after the package has fulfilled its purpose, it should preferably degrade rapidly [49]. It can in any case be concluded that blending starch with a lactic acid-based HM adhesive proved to be a promising alternative for tailoring the degradation properties of the material. Because of the current high price of lactic acid-based polymers compared to conventional HM formulations, using starch blends would also be economically beneficial [17] [39] [50]-[69]. Patent [70] discloses a hot melt adhesive comprising polylactic acid and a polyvinyl alcohol-based resin. In addition, patent [71] discloses a hot melt adhesive composition comprising a thermoplastic resin and a tackifier as main components, wherein either one or both of these components comprise a lactic acid copolymer resin derived from PLA or lactic acid and other hydroxycarboxylic acids. This composition exhibits good self-life, high content of bio-degradable components, recyclable components and (or) components obtained from renewable natural materials [72]. The compositions with good adhesion and durability comprise lactic acid polymers to give a hot-melt composition showing softening point 101 °C, viscosity 6400 m Pa-s at 150 °C, and good biodegradability and adhesion in bookbinding [73]. Coconut oil appeared to be suitable for plasticization of Soy protein isolate (SPI): PCL HMA in improving compatibility between PCL and SPI and interfacial adhesion between PCL and SPI phases [74].

7. Testing of Hot Melt Adhesives

7.1. Viscosity Test Method

Viscosity is determined in accordance with ASTM D3236 entitled, "Standard Test Method for Apparent viscosity of Hot Melt Adhesives and Coating Materials," (Oct. 31, 1988), using a Brookfield Thermosel viscometer Model RVDV 2, and a number 27 spindle. The results are reported in centipoise (cP) and the test is performed at the specified temperature [75].

7.2. Peel Test Sample Preparation Method

Each hot melt adhesive composition was applied to substrates with a slot hot melt applicator set to an application temperature of from 110 °C to 150 °C, the

lamination equipment was set with minimal rewind and unwind tensions so as not to stretch the film.

7.3. Dynamic Peel Test Method

Dynamic Peel was determined per ASTM D1876-01 entitled, “Test Method for Determining Peel Resistance of Adhesive (T-Peel Test Method),” with the exception that the test was run at 30.5 centimeters per minute (12 inches per minute) over a period of 10 seconds and seven replicates were run. The samples were run on an IMASS Spec-type test instrument in a 7.62 cm (3 inch) width. The samples were peeled along the machine coating direction in a down web direction. The average peel value over 10 seconds of peeling was recorded and the results were reported in grams. The initial Dynamic Peel value is the value measured 24 hours after the sample is prepared. Seven replicates were tested and the average value was reported in units of grams of force (gf).

Glass Transition Temperature (T_g) Test Method.

7.4. Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of the samples was determined on the sample composition using Dynamic Mechanical Analysis (DMA) with a DHR-II instrument at 10 rad/second using the following conditions: the sample was heated to 140°C, held at 140°C for 1 minute, cooled to -20°C, at 10°C/minute, held at -20°C for 10 minutes and then heated from -20°C to 140°C at a rate of 3°C/minute. The temperature at the maximum value of Tan Delta on the heating curve was recorded as the T_g in °C.

7.5. Compatibility Test

If the hot melt adhesive composition formed a clear, homogeneous mixture when melted with no phasing upon mixing, it was rated as compatible (C). If the hot melt adhesive composition formed an opaque mixture when melted or formed two different phasing upon mixing, it was rated as not compatible (NC).

7.6. Transfer Test

Film of adhesive was held at room temperature for 24 hours, then a finger was pushed into the film and then removed. If there was transfer of adhesive to the finger, the film was rated: yes, if no transfer, the film was rated: no.

7.7. Loop Tac

The Loop Tack was performed according ASTM D 6195-97 Standard Test Methods for Loop Tack.

7.8. Peel Force to Stainless Steel Sample Preparation Method

A laminate is prepared by coating a sample composition onto a treated Mylar film in a 2.54 cm (1.0 in) wide pattern at an add-on weight of 24 g/m² using a

slot applicator and then contacting the adhesive strip with a 0.09 mm (3.5 mil) siliconized release film to form a release treated Mylar/adhesive/siliconized release film laminate. Test samples having a length of 23.32 cm (9.18 inches (in)) in the machine direction and 2.54 cm (1.0 in) in the cross-machine direction are then cut from the laminate such that the adhesive pattern is centered in the cross-machine direction of the test sample. The release layer is then removed and the adhesive is applied to a stainless-steel panel having a length of 20.32 cm (8 in) and a width of 7.62 cm (3 in). In preparing the composite test sample, the adhesive is not pressed down onto the stainless steel.

7.9. Peel Force to Stainless Steel Test Method

Three samples are prepared per the Peel Force to Stainless Steel Sample Preparation Method. Each test sample is placed on a 2-kg mechanical roll-down device and the roller is allowed to pass over the film side of the sample two times, once in the forward direction and once in the backward direction, at a rate of 305 mm/min. A timer is then activated and the sample is placed into the jaws of INSTRON-type peel tester. After one minute, the sample is peeled at a 180-degree angle according to PSTC 101 entitled, "Peel Adhesion of Pressure Sensitive Tape," and the peel force is recorded. The average peel force of the three samples is reported in gf/25mm. [21]

7.10. Bio-Degradability and Compostability Test

The compositions used in the hot melt adhesive compositions formulated below when tested for biodegradability and compostability were tested under the ASTM D5338-92 Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions. In the context of the developing market in so-called "bio-based" products, the big players among the major supermarket chains are turning to their suppliers, demanding products that fulfil these expectations. These expectations are further increased as European directives require the progressive introduction of so-called "compostable" products that in particular satisfy the criteria set out in the European standard EN13432. In this connection, standard EN13432 specifies that the biodegradability of a product measured according to the released carbon-dioxide analysis method set out in EN ISO 14855 must be greater than 90% [76].

8. Application of PLA Hot Melt

More generally, typical markets for hot-melt adhesives as described herein may be packaging, non-woven, tapes and labels. The HMA may optionally be formed into sticks, pellets, blocks, pillows and the like. Hot-melt adhesives as described herein may also be useful in book binding, foam bonding, heat sealing applications, carpet sealing, bag end sealing, bonding filter media, insulation bonding, durable goods manufacturing, wood working, construction, automotive applications, appliance applications and assembly applications (e.g., filter media, insula-

tion, and bonding). Particularly preferred may be a method wherein the substrates are elements of a cardboard box. Suitable substrates also include plastics, in particular objects of, e.g., polyolefins or polylactic acid, textiles, foils used in packaging, e.g., the foils used in packaging flowers or plants, but also carpet backings. Suitable substrates further include metal foils and wood [24]. The hot melt adhesive according to the present invention is widely utilized for paper processing, bookbinding, disposable products and the like, and is particularly effectively utilized for disposable products because of excellent adhesion in a wet state. The “disposable products” are not particularly limited as long as they are the so-called sanitary materials. Specific examples thereof include disposable diapers, sanitary napkins, pet sheets, hospital gowns, operation white coats, urine liners, puerperant shorts, breast milk pads and armpit sweat pads. The present invention can provide a hot melt adhesive and an absorbent article coated with the hot melt adhesive. The absorbent article according to the present invention is particularly effective as a disposable diaper in which a nonwoven fabric is adhered to a polyolefin film [77].

9. Conclusion

Increasing global energy issues and dependency on petroleum resource focus has been shifted towards developing sustainable hot melt adhesives (HMAs) which are cost effective and bio-degradable. HMAs contain base polymer, tackifier and wax as primary components. In terms of environmental problems, such as global climate issues due to an increase of carbon dioxide emission, attempts had been made to produce HMAs using non-petroleum-based and bio-degradable resins, such as polylactic acid (PLA)-based resins. PLA copolymer-based HM adhesive was used in industrial glue lamination process. The unique characteristics of PLLA/PCL HM adhesive are its excellent hot tack and a combination of long open time with moderate setting time. Polyamide adhesives based on bio-based dimerized fatty acids had been available for HM applications. Blending of starch with a lactic acid-based HM adhesive proved to be a promising alternative for tailoring the degradation properties of the material. Hence, HMAs based on polylactic acid will continue to have a huge potential and sustainable and bio-degradable applications in packaging, sanitary and diaper adhesive industries. A lot of research has already been done on modification of PLA through copolymerization. However, the challenge remains to produce the PLA-based HMAs with high performance properties like synthetic resin HMAs.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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