

# Sustainable Raw Materials in Hot Melt Adhesives: A Review

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**How to cite this paper:** Vineeth, S.K. and Gadhave, R.V. (2020) Sustainable Raw Materials in Hot Melt Adhesives: A Review. *Open Journal of Polymer Chemistry*, 10, 49-65.

<https://doi.org/10.4236/ojpcchem.2020.103003>

**Received:** June 28, 2020

**Accepted:** August 22, 2020

**Published:** August 25, 2020

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## Abstract

Hot-melt (HM) adhesives offer advantages over their contemporary water-based and solvent-based adhesives like low volatile organic compounds (VOCs), 100% solid, fast drying, setting etc. In recent years, to reduce their dependence on dwindling petroleum resources and due to the enormous use of HM adhesives in packaging areas that demand 100% recyclability, efforts have been devoted to making these formulations completely bio-based, sustainable and biodegradable. In this attempt, research and developments have been focused on using starch, modified starch, soy protein, polylactides, polyamides, lignin and vegetable oils as a partial/fully replacement to the petrochemical-based polymers. The huge amount of research going on in the field of bio-based polymers has still not reached its complete potential in the field of HM adhesives. In this review paper, HM adhesives based on sustainable raw materials namely starch, modified starch, polyamides, poly (lactic acid), soy protein and lignin are discussed.

## Keywords

Sustainable Polymers, Hot Melt Adhesives, Starch, Lactic Acid, Soy Protein, Polyamides, Lignin

## 1. Introduction

Increases in the demand for adhesive for various applications have resulted in the investigation of various types of adhesives. Polymer-based adhesives can be generally classified into water-based adhesives, solvent-based adhesives, reactive adhesives and hot melt (HM) adhesives depending on a curing or solidification/drying process. As hot melt adhesive uses no solvent, it provides a solution to environmental concern. Hot melt adhesives were introduced to the market in the 1950s, and then have become increasingly important in the adhesive seg-

ment. HM adhesive covers 15% - 21% of the global volume of production and consumption of adhesives. More importantly, the total average annual growth rate of the consumption of HM adhesives is 1.5 - 2 times higher than that for other types of adhesives [1] [2] [3]. The HM adhesives are designed to be applied in consumer goods, packaging, construction, transportation, electronics, health-care, and for other applications like bookbinding, furniture etc. [4] [5]. **Figure 1** shows the global demand of hot melt adhesive.

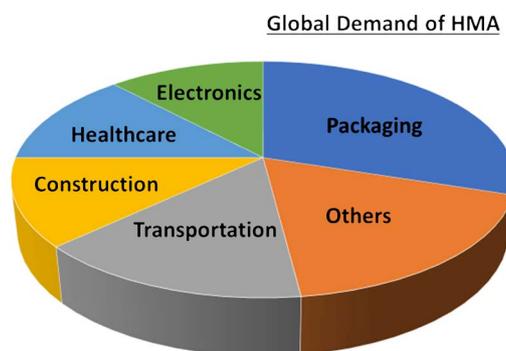
***HM adhesive. How to apply and how does it work?***

HM's are basically thermoplastics that are used after melting the polymer beyond its melting point. These are generally available as granules, powder, slats, blocks, foils, ribbons etc. HM adhesive is thermally activated or by solvent-based method, and becomes a liquid. 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 HM adhesives 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. Another applicator is a hotmelt dispenser that delivers the adhesive through its nozzle from a tank containing molten adhesive by the means of a dosing pump.

Cooling of the drop largely depends on the size of the droplet, the nature, temperature of the substrate and environmental conditions. In case the substrate is not insulated, it may take longer for the HM to cool down. The second substrate is placed on the adhesive, in order to join the two substrates with the help of the HM applied between them. The second substrate is pressed, and the adhesive can be seen oozing out in case the contact surface with the substrate is large. The large surface area of the substrate allows for quicker cooling of the HM. This HM sets after cooling, making it impossible to separate the two substrates. HM adhesives are 100% solid materials which do not contain or require any volatile solvents or any other carrier/medium. On cooling, the adhesive regains its solid form and gains its cohesive strength [6].

HM adhesives are solid materials at low temperatures (typically < 80°C) and



**Figure 1.** Global demand of hot melt adhesive [5].

can melt to liquid or viscous-flow state at elevated temperatures, in which form they are applied on the surface of substrates [7] [8]. In this regard, HM adhesives differ from other types of adhesives which achieve the solid state through evaporation or removal of solvents or by polymerization. The major advantage of HM adhesives is the lack of a carrier fluid which eliminates the need for drying the adhesive film once it is applied to the substrate. This elimination of the drying step overcomes hazards associated with solvent usage and also allows for faster production line speeds and lower costs [9]. The application area of HM adhesives is vast, including for example carton and case sealing, paper industry, and bookbinding [10] [11]. As the regulative pressure for moving towards degradable or reusable packaging increases, there is a growing interest in HM adhesives that not only have adequate technical properties for the desired application, but also meet the requirements related to biodegradability [12] [13].

## 2. Advantages over Existing Adhesive Systems

The HM adhesive has illustrated a high growth rate as compared with the existing solvent-based adhesive due to its advantages of high productivity caused by process automation, eco-friendliness, a wide range of applicability, and re-adhesion possibility. The HM adhesive requires a small working space and has high-speed adhesion without a drying process as compared with a solvent-based adhesive or water dispersed adhesive. High-speed adhesion of the HM adhesive enables automation of the production line. Thus, the HM adhesive has considerable economic advantages such as improvement in productivity, reduction of labor costs, reduction in the amount of material usage caused by regulation of spread, and the like [14]. Compared with conventional solvent-based adhesives which generally involve evaporation and/or removal of solvents or polymerization to bond substrates together, HM adhesives show significant advantages. For example, the elimination of a carrier fluid or solvent in HM adhesives formulations not only overcomes the hazards associated with solvent usage and emissions of volatile organic compounds (VOCs), but also allows for faster production speeds and lower costs of transport/inventory maintenance [15].

## 3. Conventional HM Adhesives

The ability to modify the properties of the adhesive composition with the addition of various resins, oils, waxes and other additives makes HM adhesives commercially useful in a wide variety of applications [16]. Last but not the least, they are clean and easy to handle. Currently, almost all the base/major polymers for HM adhesives on the market are primarily derived from petroleum resources, such as ethylene vinyl acetate (EVA), block copolymers of styrene and butadiene (SBS) or isoprene (SIS), polyesters, polyamides, polyurethanes and polyolefin's [17] [18] [19]. Recently, there has been an increase in research on fatty acid-derived dimers and different diamines-based HM adhesives. Overall,

the basic resin highly affects adhesion strength and cohesion strength is the most important desirable properties of the HM adhesive [20].

#### 4. Dependency of HM Adhesives on Petroleum Resources

In recent years, there has been an increasing drive in the entire chemical industry to improve the sustainability of processes and products. This is due on one hand to the environmental awareness of customers and the ensuing regulations and on the other to the looming shortage of oil from which many chemicals are derived and the associated threat of petroleum price volatility. In the adhesive industry, this has manifested itself most notably in the switch from solvent- to water-based or high solid adhesives, and in the renewed interest in traditional natural adhesive materials such as polysaccharides and proteins [21] [22] [23].

Biopolymers are man-made polymers which are based on renewable raw materials such as agricultural feedstock. Such feedstock includes those that are well known and used in everyday practice like corn starch, soy and those that are extracted from biomass and further refined into polymers. It is extremely unlikely that biopolymers will completely displace petrochemical-based raw materials in all adhesive formulations. However, a more plausible scenario foresees renewable raw materials supplementing the petrochemical resources.

Even an adhesive formulation that is only partly based on renewable feedstock can be an environmentally useful approach especially if the value proposition is not degraded by high cost or inferior properties.

However, such compositions are derived from depleting petroleum resources, and there are concerns over their degradation ability [24]-[33]. Lactic acid-based polymers, starch-based or cellulose-based polymers, protein-based polymers, and bio-based polyamides have been studied as bio-based alternatives for cohesive polymers. Currently, tackifiers are mainly tall oil resins, rosins, rosin esters, polyterpenes, and hydrocarbon resins [31]. Their function is to improve the wetting of the substrate by lowering the viscosity of the base polymer. Earlier reports have described HM adhesives composed of starch- or cellulose-based polymers together with transglycosylated products or hemicellulose derivatives as tackifiers and a plasticizer [34]. The crosslinked, resin like structure of lignin could, similarly to compounds such as terpene-phenol resins, offer suitable properties as a tackifier [35] [36].

In this review, HM adhesives based on sustainable, renewable and economical raw materials namely starch, modified starch, polyamides, poly (lactic acid), soy protein and lignin are discussed.

#### 5. HM Adhesive—Constituents and Role

There are three primary components used for formulating HM adhesives, represented in **Figure 2**, namely:

- 1) Base Polymer
- 2) Tackifier

### 3) Wax

In addition to these main components, other additives like antioxidants, UV stabilizers and plasticizers are added in small amounts to control and enhance their service properties.

*Base polymer:* The adhesive strength with tack properties are provided by the base polymer. It is generally a high molecular weight polymer with glass transition temperature greater than room temperature. Thermoplastic base polymers which fall into the categories of vinyl polymers, olefinic polymers, styrene block copolymers and thermoplastic polyurethanes. An important criterion for the usefulness of the HM adhesive is the melt viscosity of the base polymer and it directly depends on the molecular weight of the polymer. Hence it should be low, because too high melt viscosity results in adhesives which are hard to apply, less coverage and involve higher power costs [37].

*Tackifiers:* The tackifiers are used to improve the flow and leveling properties of base polymer. They are amorphous in nature with low molecular weight. Glass transition temperature should be lower than room temperature. As shown in Figure 3, tackifier works by reducing the modulus and increasing the Tg

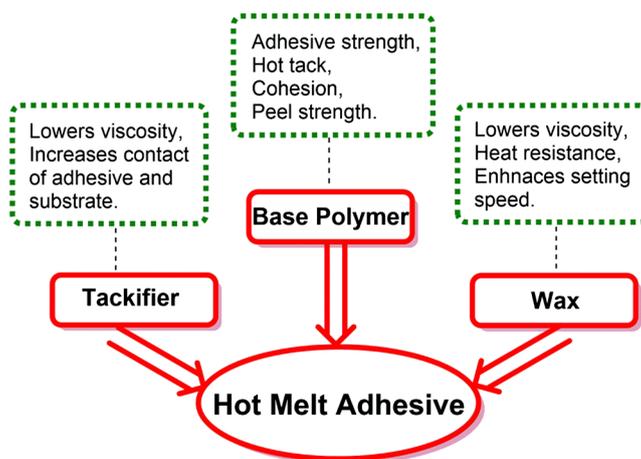


Figure 2. Main constituents of a hot melt adhesive.

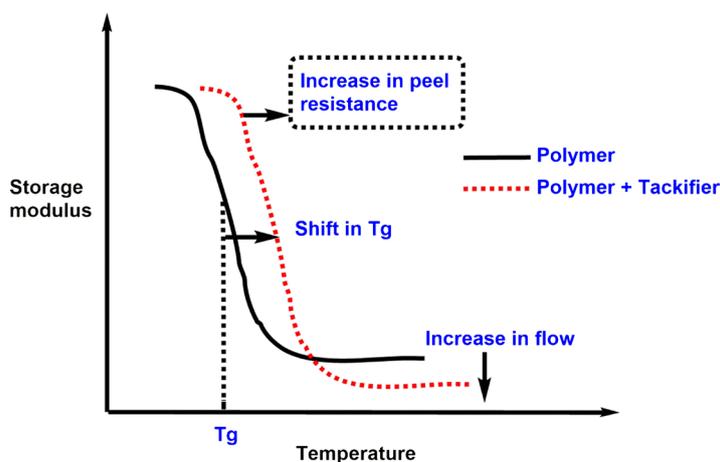


Figure 3. Effect of tackifier of adhesive formulation [38].

of the resulting adhesive formulations. Most conventional tackifiers are derivatives of tall oil resin or hydrocarbon resins [38]. Some natural product based tackifiers are mainly rosin acid derivatives. There are some tackifiers which are petroleum cracked products which also come under natural products [37].

*Wax:* Polyolefin waxes are crystalline materials, low molecular weight which reduce the molten viscosity of the polymer while increasing setting speed [38]. Since waxes are hydro carbonaceous materials having lower surface tension than the base polymer of the HM, they lower the surface tension of overall liquid adhesive which helps in wetting the surface of substrate. Some waxes are micro-crystalline waxes which not only reduce the melt viscosity and surface tension but also reinforce the HM by formation of crystallites that resist deformation under load.

*Other raw materials:* Fillers and antioxidants are also used in the formulation of HM adhesives. Fillers like clay and talc are used to control melt viscosity of the HM, to provide opacity to the material and to reduce the cost of the final adhesive. Antioxidants are used when the chances of adhesives to spend time in the HM applicator before use are high. Most of the components which comprise an HM adhesive formulation are petroleum-based products.

### 5.1. Starch-Based HM Adhesive

Among these, starch has attracted much attention due to its abundant and guaranteed supply, low cost, renewability and biodegradability. However, natural starches are water/moisture unstable and mechanical properties of starches are poorer than those of synthetic polymers, something which hampers more widespread use of these materials in modern industry. Native starches are generally chemically and/or physically modified to overcome the limitations associated with starch and to improve its performance as an adhesive [39]. Starch is popularly being seen as a promising material for developing renewable, degradable plastics due to its easy biodegradability, durability, and low cost [40]. The commercially important sources include maize and rice starches, cassava and potato starches, and cereal starches like wheat [41]-[46]. However, access to these hydroxyl groups is significantly hindered due to the dense packing of polysaccharide chains within starch granules. Harsh pretreatments and chemical modification conditions are required to obtain desired starch derivatives [47] [48].

Starch has also been used in HMs but typically as a filler or extender as disclosed in a patent [49] by J. N. Coker. In another type of application, starch has been used in HMs as a pre-applied activator material which releases moisture into the subsequently applied HM adhesives: patent [50] by H. Schulte, *et al.* In adhesive application, starch ethers and esters have been found to be suitable as a part of HM adhesives. These adhesives have lower melting point which assists both compounding as well as application to thermally-sensitive substrates. Bio-based plasticizers such as triethyl citrate are often mixed with starch acetate

to impart flexibility and toughness. The resulting HM adhesive is claimed to be suitable for bonding Polylactic Acid (PLA) films, paper, paperboard, wood and certain plastics. These HM adhesives do not require water to melt and perform in HMs, and they provide good compatibility with diluents and other components. Also, they impart biodegradability to the system. Modified starch also provides a renewable raw material and increases the water dispersion of these adhesive formulations. To resolve the issue of immiscibility of starch with most commercial polymers, the route of chemical modification of starch has also been adopted [51]. Recently, HM adhesives based on intermediate or high degree of substitution (DS) starch esters have been disclosed in application Ser. No. 08/106,023 filed on Aug. 13, 1993. In European patent publication 511,916 of Nov. 4, 1992 hydrogenated starch hydrolysates were shown useful in forming HM adhesives. This invention involves a method for preparing an HM adhesive composition comprising a starch ester having a DS of 0.3 to 3.0 and a selected diluent wherein the starch ester is a wetcake having 40% or more by weight of moisture. More particularly, this invention is directed to a method of preparing an HM adhesive composition comprising a starch ester wetcake having a DS of from about 0.3 to 3.0 and 40% or more by weight of moisture and a non-volatile organic diluent, and heating to evaporate or boil off the water during the formulation step. In another embodiment, a starch-based HM adhesive is prepared by extruding a starch ester with a DS of from about 0.3 to 3.0 and a non-volatile organic diluent [52]. This invention is directed to the use of starch-based water sensitive HM adhesives for bonding the paper which wraps the filter element of a cigarette and to cigarette filter elements bonded therewith. The polar nature of such water sensitive HM adhesives generally precludes the use of triacetin plasticizers and the cigarette companies, seeking an environmentally friendlier cigarette, are eliminating triacetin in favor of less desirable plasticizers or other filter materials which do not require plasticizers [53]. The advantage of this type of material is that lower softening temperatures are achieved which assists both compounding and application to thermally sensitive substrates. For flexibility and toughness, the starch acetate is generally mixed with a bio-based plasticizer. The resulting HM adhesive is claimed to be suitable for bonding polylactic acid films, paper, paperboard, wood, and plastics. By varying the type and concentration of plasticizer, products with varying melt viscosity and softness are obtained.

## 5.2. Soy-Based HM Adhesive

Soy protein is extracted from soybeans. Soy flour, soy concentrate and soy isolate are various products of soy protein containing 56%, 65%, 95% protein, respectively [54]. Soy protein is considered a potential replacement for petroleum-based polymer components due to its easy availability, low cost and excellent biodegradability [55]. Soy protein consists of 18 types of amino acids. Some of them are polar and some are non-polar. The non-polar ones work as cross-linking sites which results in improving physical, mechanical and thermal properties

and also increasing water resistance [56].

In this respect Choi *et al.* [57], studied HM adhesives based on Soy Protein Isolate (SPI) and polycaprolactone (PCL) blends and the effects of conventional and coconut oil plasticizers on their material properties such as thermal properties, softening point, morphology, tensile strength and shear strength. Coconut oil was found to be suitable in compatibilizing SPI and PCL and the blend demonstrated satisfactory properties as an HM adhesive [57]. Soy protein has low moisture resistance, high melt viscosity and brittleness. So it can be blended with PLA but also has some drawbacks like high cost and poor temperature resistance. Blending of these two helps in increasing processability and moisture resistance of soy and reducing cost of PLA [58]-[63]. Soy proteins can be used in HM adhesive formulations due to their thermoplastic-like behavior, their renewable origin, low toxicity and inherent biodegradability, and their ability to be processed by thermoplastic methods [64]. In the current study, we report the development and characterization of HM adhesives based on soy protein isolate with well-known adhesive ability, a synthetic biodegradable thermoplastic polymer, PCL, castor oil (CO) as a plasticizer/compatibilizing agent, and pine rosin (PR) as a tackifier. HM adhesives based on PCL, SPI and CO were developed and characterized. Based on the overall results, PCL-SPI based HM adhesives have potential as adhesives for lignocellulosic substrates and their properties can be tailored by changing the proportions, the tackifier, the thermoplastic or the biogenic polymer, in order to enlarge the potential substrates, with the additional benefit of having a high bio-based content and being potentially biodegradable [65].

### 5.3. Lactic Acid-Based HM Adhesives

For HM adhesives, PLA should either be of narrow molecular weight distribution or mono-dispersed high molecular weight resin. Poly (L-lactide) or PLLA homopolymer has glass transition temperature in the range of 55°C - 60°C and a melting temperature of about 170°C. In one such study, copolymers with PLLA: 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 HM adhesive is used in industrial glue lamination process. The measured properties were evaluated against commercial ethylene-vinyl acetate HM adhesives. The unique characteristics of PLLA/PCL HM adhesive 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 HM adhesive for food packaging applications [66]-[73]. HM adhesive compositions made from raw materials derived from renewable, natural resources can be composted or degrade naturally after coming in contact with the soil. For example, HM adhesive compositions prepared from homopolymers or copolymers of poly (lactide) (the bimolecular cyclic ester of lactic acid), also referred to herein as PLA,

can be useful in many bonding applications. The method of this disclosure differs from conventional techniques in which HM adhesive compositions are made from monomeric lactide with comonomers to build up molecule chains, or rely on high molecular weight base polymers, which can require significant amounts of tackifier and other modifying additives from non-renewable sources to achieve a desired level of HM adhesive performance. The method of this disclosure can produce base polymers with tailored molecular weight distribution, which in some embodiments require no tackifier, and in some embodiments can require fewer modifying additives to achieve good performance as an HM adhesive [74].

#### 5.4. Bio-Based Polyamides as HM Adhesives

Polyamide adhesives based on bio-based dimerized fatty acids have been available for some time. For example, they have been used for assembling shoes since the late 1980s. However bio-based polyamide HM systems have been developed that provide strength and durability similar to the best HM's. The drawback is high viscosity in molten state and poor shear-thinning behavior even for low molecular weight polymer. This implies that processing temperature for a polyamide HM adhesive is higher than that of conventional HM adhesives. Thus they find application in shoe, electronics, automotive, and wood industries [75]. Bio-based polyamide HM adhesives are primarily derived from dimer fatty acids from seed oils and ethylenediamine. However, use of mixed dicarboxylic acids and diamines is advocated to adjust the crystallinity, thermal, mechanical and adhesion properties of the resin [76]. Leoni *et al.* [77] studied the properties of polyamide HM adhesives synthesized from high purity fatty acid and propylene diamines. The polyamide prepared from this special type of diamine monomer has excellent adhesion to the metal substrate, wide range of softening point, low temperature flexibility, and can be easily activated [78]. For synthesizing polyamide with excellent low temperature properties the ratio of special diamine monomer and dicarboxylic acid is important. Chen *et al.* [79] synthesized polyamide based on dimer acid, ethylenediamine, sebacic acid and piperazine. The effect of the amounts of piperazine and sebacic acid on the properties, such as softening point, tensile strength, elongation at break, hardness, glass-transition temperature, low-temperature flexibility and impact strength, of the polyamides and the lap shear strength and T-peel strength, of the resultant HM adhesives were studied. In a recent study Kadam and Mhaske synthesized polyamides from low purity fatty acid composition. Polyamide hotmelt adhesives were synthesized by reacting mixtures of dicarboxylic acids and diamines. Polymeric fatty acid, sebacic acid, ethylenediamines and piperazine were utilized [80].

#### 5.5. Lignin-Based HM Adhesive

Lignin is a nonlinear phenolic biopolymer with a rather low molar mass. Lignin is also the most important byproduct of lignocellulosic biorefineries and is a

valuable renewable resource for bio-based materials. Generally, its low reactivity and low level of reactive sites restricts the utilization of lignin at high phenol substitution levels for these applications. In HM and pressure-sensitive gluing, the performance is based merely on physical interactions and the chemical reactivity is not as critical as it is in phenol formaldehyde resins. Research has been reported in which lignin has been used as an additive in HM adhesives [16], but the lignin quantities have been relatively low [81] [82].

### 5.6. Polylactic Acid and Starch Blend-Based HM Adhesive

Combinations of biodegradable and non-biodegradable materials are in general not recommended, since the packaging in that case cannot be considered biodegradable as a whole. Until now, no scientific papers have concentrated on blending of starch with a lactic acid-based HM composition in particular, although blends of poly (lactic acid) with different types of starch have been studied in several scientific publications. 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 [83]-[102].

## 6. Conclusions

Increasing global energy issues and dependency on petroleum resource focus has been shifted towards developing sustainable adhesives which are cost effective and renewable. Various biomaterials had been exploited as sustainable adhesives including starch, cellulose, lignin and chitosan. Biomaterials are one of the most studied materials by the scientific world due to their renewability, non-toxicity and biodegradability.

HM adhesives are formulated using base polymer, tackifier and wax as primary components. Starch has also been used in HMs but typically as a filler or extender. Modified starch also provides a renewable raw material used in HM adhesive formulations. HM adhesives based on SPI and PCL blends also developed with improvement in performance properties of HM adhesives such as thermal properties, softening point, morphology, tensile strength and shear strength. 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. However bio-based polyamide HM systems had been developed that provide strength and durability similar to the best HM's. Lignin had been used as an additive in HM adhesives. Blending of starch with a lactic acid-based HM adhesive proved to be a promising alternative for tailoring the degradation properties of the material.

An HM adhesive that is economical, even though partly based on renewable feedstock will be a significant achievement towards eco-friendliness and sustainability goal. Hence, HM adhesives based on natural raw materials like starch, polylactic acid, lignin, chitosan, bio-based polyamides, etc. will continue to have a huge potential and sustainable applications in adhesive industries.

### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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