

Recent Synthetic Approaches and Emerging Bio-Inspired Strategies for the Development of Sustainable Pressure-Sensitive Adhesives Derived from Renewable Building Blocks

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ABSTRACT: In this review, we provide a bird's eye view of recent developments in the field of pressure-sensitive adhesives (PSAs) derived from renewable monomeric building blocks. This emerging research field has been driven by increasing sustainability requirements in the adhesive industry and bridges the gap existing between highly optimized petroleum-based synthetic PSA systems, which display superior performance but lack biobased content, and historical PSAs derived from naturally occurring biopolymers (e.g., starch and natural rubber), which provide more environmentally friendly bonding solutions but have inherent technical limitations that prevent their more widespread implementation in today's technically demanding applications. We critically reviewed a representative (and exhaustive) survey of recent synthetic approaches to the development of biobased PSAs from the academic (articles) and industrial (patents) literature categorized in two families: chain-growth and step-growth polymerization routes. Finally, we draw a parallel between renewable synthetic PSAs and nature's self-adhesive glues, highlighting how the synergy between green chemistry and biomimetic concepts could inspire the emergence of a new generation of smart, synthetic, biobased PSAs with differentiated properties that approach the ones that are found in the natural world and with a wide spectrum of potential applications in the industrial and medical sectors. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40669.

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INTRODUCTION

Pressure-sensitive adhesives (PSAs) are soft polymeric materials that show permanent stickiness at room temperature and adhere to surfaces via noncovalent forces when light pressure is applied.^{1,2} PSAs stick in their solid state and, therefore, differ drastically from other types of adhesives, such as glues, which are liquid upon application but solidify after a chemical reaction, or hot-melt (HM) adhesives, which are tacky in the molten state and harden when they are cooled to room temperature.³ PSA are extremely complex and multiform materials that should simultaneously possess ambivalent properties, such as a high molecular mobility, long relaxation times, a substantial cohesive strength, and conformational restructuring upon aging.⁴ To date, important families of polymers for PSA applications belong to acrylic copolymers, natural rubbers, styrene-isoprene-styrene block copolymers (SBCs), styrene-butadiene-SBCs, styrene-butadiene rubbers, and polysiloxanes.⁵ In addition to these well-established chemical families, polyesters

have recently emerged as a viable and sustainable alternative for pressure-sensitive adhesion.^{6,7}

Modern PSAs are subjected to a number of highly demanding requirements: they must join materials efficiently in a fast and safe way according to the required technical specifications (permanent or removable applications), and they must also have a satisfying aging profile and be economically viable. On top of this, ecological aspects are playing an increasingly important role in today's environmentally conscious society. This is why many adhesive manufacturers are putting a lot of effort into reducing the environmental impact of their production processes (through less energy use, less solvent use, and less waste) and to implement ecodesign concepts that will allow bonded parts to be reused or recycled (e.g., through the development of adhesives that could be debonded on demand).⁸

The use of renewable raw materials derived from biological sources also provides an interesting option for increasing the sustainability of self-adhesive products because, with the

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Walter Eevers joined Nitto Europe after receiving his Ph.D. in electrical conductive polymers from Antwerp University (1993). He was responsible for research and development and business development until he became the general manager of technomarketing and started working internationally within the Nitto Group. He got involved in global technology sourcing and marketing by setting up multiple collaborations with universities and research institutes. During this period, he obtained his master's degree in business administration from Hasselt University (2001). In 2012, he founded the Nitto Denko Europe Technical Centre in Lausanne, which is dedicated to research activities in medical devices. In September 2013, Eevers joined VITO, a research organization in Belgium dedicated to sustainability as director for contract research and commercial affairs.



exception of natural rubber, important families of polymers for PSA applications are still based on petroleum. From a strategic sourcing perspective, renewable resources contribute to a decrease in the oil dependence of the adhesive industry. Although shale gas constitutes a new and cheap source of fossil resources, its extraction process tends to favor small carbon fractions (e.g., C₂ and C₃) and create a shortage of larger fractions (C₅ and more), which are very important for adhesives. A diversified sourcing strategy could thus support the sustainable development of adhesive manufacturers in many ways.

The interest of the chemical community toward green chemistry and biobased products is seeing a resurgence today^{9,10} but is by no means new for the adhesive industry. Naturally occurring biopolymers, such as natural rubber, starch, casein, gelatin, and animal glues, have been used as bonding technologies for millennia and have a long history in PSAs.¹¹ The early use of natural biopolymers for bonding purposes was largely inspired by the observation of nature's adhesive systems, such as the sticky glues produced by plants or small animals for self-defense or predatory purposes. However, although man-made adhesives formulated from natural biopolymers are still very useful today for specific applications, they do not possess the structural refinement of nature's glues and have significant technical limitations. Natural adhesives are usually employed in their virgin state (as extracted from biomass or with only

limited modifications) and suffer from several drawbacks associated with their intrinsic chemical nature, such as poor UV resistance, insufficient water resistance, and compositional variability. Because of these inherent technical limitations and despite their renewable character, it is extremely unlikely that natural adhesive biopolymers could displace or even partly substitute current petrochemical-based PSAs, which reach the astonishingly high degrees of sophistication required to meet stringent customer specifications.

Only biobased products able to compete with their highly optimized petrochemical counterparts could become commercially viable and contribute to the successful development of the bioeconomy.¹² To increase the renewable content of PSAs while maintaining their good performances, an alternative scenario has recently emerged; in this scenario natural biopolymers are not used as such in adhesive formulations, but renewable feedstocks are used to supplement standard fossil-based petroleum resources. Recent advances in biorefining have allowed the production of a wide range of renewable building blocks that can be used as monomers by adhesive manufacturers and formulators.^{12–15} Conceptually, synthetic biobased PSAs take full advantage of the specific molecular structures that can be derived from biomass and the modern tools of polymer chemistry necessary for tailoring the structure–properties relationship of PSAs (Figure 1).

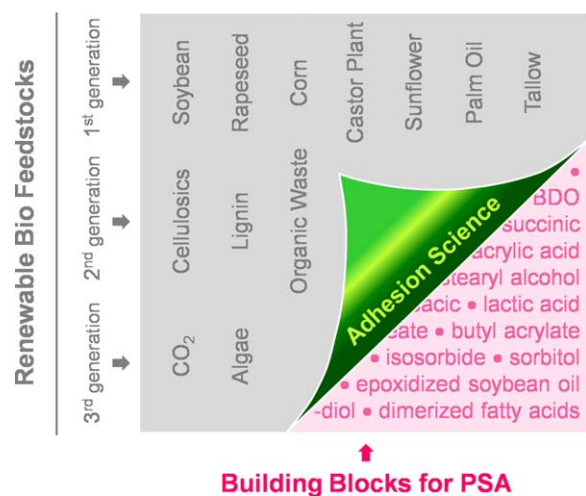


Figure 1. Functional and green PSAs can be obtained by the polymerization of renewable building blocks derived from a variety of renewable resources. Synthetic biobased PSAs take full advantage of the specific molecular structures that can be derived from biomass and the modern tools of polymer chemistry and physics necessary to tailor their structure–properties relationships. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Finding sustainable and efficient ways to transform biomass-derived building blocks into functional PSAs is an attractive idea, but of course, it is not an easy task. The aim of this review is to provide a bird's eye view of the significant developments that have happened in this emerging field over the last few years. At first, the origins and requirements of biobased building blocks are summarized; then, we briefly describe the materials science of stickiness. Recent approaches toward synthetic biobased PSAs are reviewed and divided in two families: radical polymerization routes and step-growth polymerization routes. Finally, we draw a parallel between renewable synthetic PSAs and nature's self-adhesive glues, highlighting how the synergy between biobased chemistry and biomimeticism is inspiring the emergence of a new generation of synthetic PSAs with differentiated properties approaching the ones that are found in the natural world.

MATERIAL REQUIREMENTS OF BIOBASED ADHESIVES

Origins of Renewable Building Blocks

Carbon-based renewable building blocks suitable for designing PSAs are typically derived from agricultural feedstocks, such as polysaccharides (sugars), fats and oils (fatty acids), proteins (peptides and amino acid), and forest resources (tannins, natural rubber), and are usually classified into three categories (or generations). The first generation of renewable building blocks is related to agricultural biomass that is generally (with few exceptions) edible. The second generation is defined as compounds produced from a wide array of different feedstocks, which range from lignocellulosics to municipal solid wastes. Finally, the third generation is related to algal biomass but could to a certain extent be linked to the utilization of CO₂ as a feedstock.

Biorefineries are developing an ever-increasing range of chemical and biotechnological processes to efficiently transform these vari-

ous feedstocks into synthetic building blocks that can be polymerized and formulated into various products.¹⁶ Two types of renewable monomers can be distinguished here: impendent ones that just substitute conventional monomers already used in the adhesive industry and ones that are newcomers to the adhesive world. In general, the first group of biobased monomers can be associated with lower financial risk and shorter times to market. However, rather than just mimicking the properties of fossil-based products, the second category of renewable building blocks is driven by a more ambitious idea of developing biobased products with specific structures and functionalities that are not available with petrochemicals and taking full advantage of the native structural properties of biomass and its derived components.

In the development of biobased adhesives, the procurement of renewable raw material has to be handled in a responsible and pragmatic manner, as the utilization of agricultural feedstocks for chemical purposes could raise legitimate concerns. Some industrial users of adhesives have already established their own guidelines regarding the integration of molecules derived from genetically modified organisms in their final product. In addition, the food versus nonfood question is still being debated. The idea that all food crops should be excluded from the biobased industry seems an oversimplistic argument that does not take into account the complexity of the biomass valorization chain, because very often food and nonfood applications are complementary and both contribute to optimized land use.¹⁷ In any case, the actual trend is going toward the second and third generations of biofeedstocks, which will not contribute to the food debate. From a carbon footprint point of view, renewable chemicals produced from plants generally have a strong advantage over petrochemicals because they release only the amount of CO₂ that they have taken from the atmosphere during their growth. However, a life cycle analysis is always a must for the evaluation of their real environmental footprint because the use of renewable raw materials is only one way to achieve sustainability, and global solutions should always be viewed in terms of the entire product lifecycle.¹⁸

Biobased Building Blocks in PSAs: Monomers, Additives, and Filmic Materials

In this review, we focus on the utilization of renewable building blocks as monomers and crosslinkers for PSAs. The elastomeric component of a PSA has a critical role as it directly influences key properties, such as tack and cohesive strength. However, the use of renewable building blocks for PSAs is not solely limited to monomers and can be extended to additives and/or base films [Figure 2(B,C)]. Almost all adhesive formulations contain additives to adjust their properties. Some biobased additives can be used as process aids during manufacturing (e.g., rheological modifiers based on chemically modified cellulose), whether other compounds will bring specific properties that are important for the service life of the adhesive.¹⁹ Examples of the second category include the natural tackifying resins derived from coniferous trees and widely known as rosins or adhesive plasticizers based on natural oils, such as ricinus and castor oils.

For practical use, biobased PSA glues are often be coated on a base film to form various tape constructions, such as single-

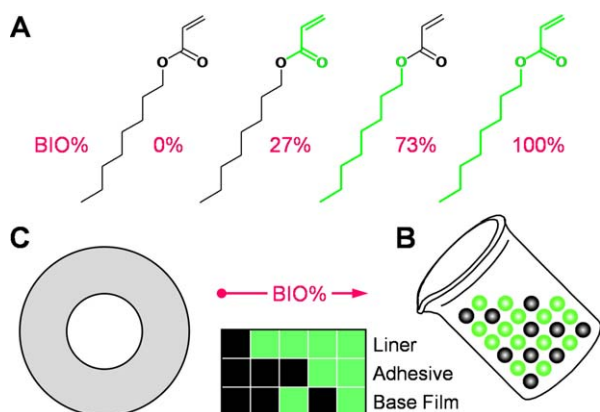


Figure 2. Step-wise introduction of biobased content (abbreviated as BIO%) into PSA at the (A) monomer, (B) formulation, and (C) tape levels: (A) Modulation of the biobased content of octyl acrylate by a combination of 1-octanol and AA derived from biobased (green) and/or petroleum (black) carbon. (B) PSA formulation containing both biobased and fossil compounds. (C) Tape constructions obtained by a combination of a glue layer, a carrier film, and a release liner derived from renewable and/or fossil resources. In this review, we mainly focus on biobased monomers and crosslinkers (strategy A). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coated or double-coated tapes, which can eventually be combined with an antiadhesive liner. In view of further increasing the biobased content of PSA products, a natural move is to coat renewable adhesives onto renewable carriers, such as cellulose-based films (e.g., paper, cellophane) or bioplastics [e.g., poly(lactic acid) (PLA), polyhydroxyalkanoates (PHAs), sugar-cane-based biobased polyethylene]. Interesting developments in biobased additives and renewable filmic materials suitable for PSA applications undoubtedly require separate investigation and were not considered to be within the scope of this review.

Materials Science of Self-Adhesive Materials

The physical origins explaining the stickiness of PSA materials can be encapsulated in a single word: viscoelasticity. PSAs must be designed with a subtle balance between flow and resistance to flow: the bond forms because the adhesive is soft enough to wet the adherent, but the bond also has a suitable strength because the adhesive is cohesive enough to resist the stress of the debonding stage.^{20,21} In practice, PSAs are soft polymeric materials with a low glass-transition temperature (T_g ; typical $T_g < -15^\circ\text{C}$) and can be characterized by three key properties: shear resistance, tack, and peel strength.⁵ The tack and peel strength describe the ability of the PSA to form a bond with a given substrate under a light pressure within a short application time or after a prolonged dwelling time, respectively, whereas the shear resistance is related to the flowing behavior (creep) of the PSA with longer application times. These three properties are related to the PSA response to various mechanical solicitations.

The formation, development, and strength of the adhesive bonds can be tuned through the thoughtful adjustment of the bulk viscoelastic properties of the glue and through the incorporation of functional monomers within the base-polymer

structure.²² The bonding, adhesion strength, and failure mode of a PSA can be correlated to its rheological profile [Figure 3(A)], and oscillatory frequency sweeps are well suited for such investigations. In an oscillatory frequency sweep, the lower frequencies of the PSA window (ca. 0.01 Hz) characterize the bond formation, whereas higher frequencies (100 Hz) refer to the debonding behavior. As an illustration, the graph displayed in Figure 3(B) represents the typical rheological profile of a polyester viscoelastic adhesive derived from fully renewable monomers, such as isosorbide (IS) and fatty acids (the chemical structure of this glue can be found in the corresponding reference).²³ This is also the viscoelasticity of the PSA layer, which is responsible for the phenomena of cavitation and fibril formation that are so important for the dissipation of mechanical

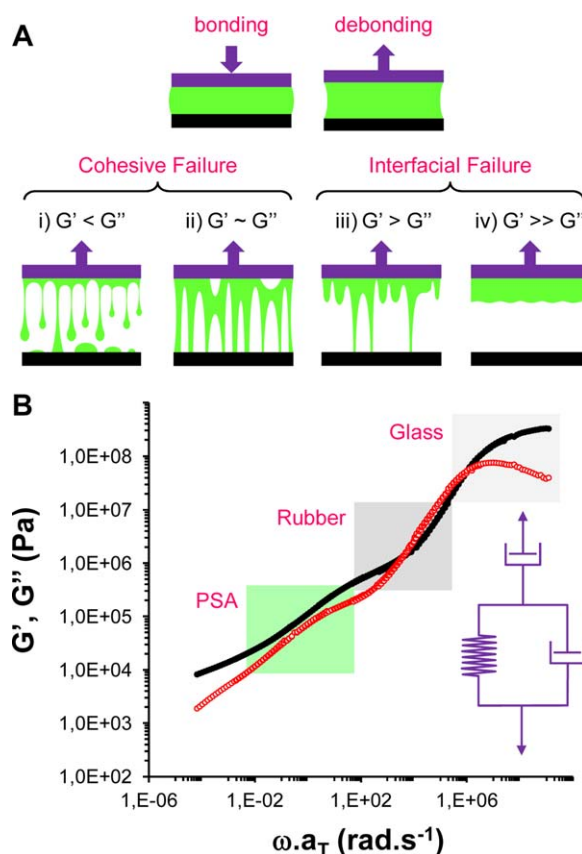


Figure 3. (A) Schematic representations of the phases of bonding under light pressure and debonding at small strain. The failure modes at large strains could be correlated with the bulk rheological response of the adhesive. Key: (i) viscous fibrils, (ii) cohesive fibrils, (iii) interfacial fibrils, and (iv) crack propagation. (B) Typical rheological profile (master curve at 25°C) of a renewable polyester-based adhesive highlighting the PSA window of the material. The real (G' , filled symbols) and imaginary (G'' , empty symbols) shear modulus components of the adhesive are plotted against the reduced frequency ($\omega \cdot a_T$) of the mechanical sollicitation. In terms of the constitutive models of linear viscoelasticity, the glue layer can be depicted as a Kelvin element combined in series with a dashpot (viscous) element, as shown in the inset. (Adapted from ref. 23, Copyright 2013 American Chemical Society). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stresses during the debonding step and modulation of the adhesion force.^{24,25}

CHAIN-GROWTH SYNTHETIC ROUTES

Recent strategies for synthesizing functional PSAs from renewable monomers fall within the chain-growth and step-growth polymerization mechanisms. In general, the direct polymerization of carbon-carbon double bonds of vegetable oils via a radical mechanism is difficult because the unsaturation of common fatty acids is nonconjugated, and consequently, they have a low reactivity. To overcome this problem, biobased synthons can be modified to form conjugated double bonds with increased reactivity toward radical polymerization. Chain-growth synthetic approaches to the development of biobased PSAs are mainly represented by the large chemical family of poly(meth)acrylates and, to a lower extent, by the ring-opening polymerization of renewable epoxides.

Chemical Pathways to Biobased Acrylic Acid (AA) and Methyl Methacrylate (MMA)

Acrylic adhesives have been commercially available for more than 60 years and are the one of the most popular types of adhesive in use.⁵ The popularity of poly(meth)acrylates in PSAs stems from their optical clarity, UV- and light-oxidation stability, and relatively low cost combined with their highly tunable adhesion performances. For those reasons, new chemical pathways toward the development of (meth)acrylic monomers using biobased raw materials are the subject of intense research efforts, and biobased AA is a key building block.

Renewable AA can be obtained through the fermentation of sugar-based 3-hydroxypropionic acid or the metathesis transformation of fumaric acid.²⁶ Another chemical route for obtaining AA consists of first obtaining acrolein (propenal), which can be oxidized to AA. Acrolein can be obtained via the dehydration of glycerol (GLY),²⁷ which is a cheap bioderived molecule that is already available in large quantities. Venkitasubramanian²⁸ reported a process for making (meth)acrylic acid and its corresponding ester that started with propylene glycol or ethylene glycol. One of the methods proposed relies on the dehydration of propylene glycol, which leads to propanol. In the second step, propanol is desaturated to form acrolein. As an alternative, the same author also described a synthetic route with ethylene glycol to generate acetaldehyde (ethanal), which undergoes an aldol condensation with formaldehyde to yield 3-hydroxypropanal that can be rearranged into acrolein. Another approach toward biobased AA consists of the oxidation of methanol into formaldehyde. In a second step, the aldol condensation of formaldehyde with acetic acid generates AA. This chemical path uses methanol as starting compound; it can be obtained from both renewable and nonrenewable sources.²⁹ One can also obtain AA by first converting carbohydrates to lactic acid by fermentation and then dehydrating lactic acid or by the direct fermentation of biomass via strain improvement and metabolic engineering.³⁰

In addition to AA, biobased MMA is another key molecule, as it can be transesterified with various biobased alcohols to form methacrylic monomers. The current routes toward renewable

MMA involves either the use of biomass for feedstocks in the existing production process or the use of a novel route via the fermentation process of sugarcane.³¹

Concept of Hybrid Biobased Acrylic Monomers

Biobased AA can be integrated as such in adhesive compositions. It is well known that carboxylic acid functional monomers can improve wetting onto the adherent surface, tune the bulk rheological properties, and accelerate the rate of bond establishment via the formation of hydrogen bonding and/or noncovalent interactions.³² Alternatively, renewable AA can be esterified with biobased alcohols to form polymerizable monomers suitable for PSA applications. Although the reaction of biobased AA with a biobased alcohol will create a 100% biobased monomer, one can also imagine intermediate situations where a petroleum-based AA is reacted with a biobased alcohol or vice versa to create partially biobased acrylate monomers (or hybrid biomonomers) with intermediate biobased contents [Figure 2(a)]. The polymerization of hybrid monomers with additional (biomass-based and/or petroleum-based) monomers ultimately creates a hybrid biobased polymer in which the overall biobased material is determined by the respective weight fractions and individual biobased contents of each repeating unit. Similarly, partially (or fully) methacrylic monomers can be obtained by the transesterification of (biobased) MMA with renewable alcohols.

Acrylic Monomers Derived from Renewable Primary Alcohols

Acrylic PSAs are generally composed of sparsely crosslinked copolymers with a low T_g that have both an insoluble (gel) and soluble (sol) fractions. These compositions are formulated from a bulk of low- T_g alkyl acrylates combined with a lower fraction of functional (meth)acrylate monomers with higher T_g 's to improve the cohesion and add functionality.⁵ A wide range of renewable alcohols can be reacted with biobased AA to form acrylic esters suitable for adhesive applications. In short alcohols, *n*-butanol is undoubtedly a key biobased building block for PSA applications, as its acrylated derivative *n*-butyl acrylate (*n*-BA) is widely used in coating, adhesive, and ink markets.³³

Current petrol-based *n*-butanol is produced via the oxo petrochemical process, where propylene is reacted with syngas-forming butylaldehyde and subsequently hydrogenated to produce butanol. Alternatively, *n*-butanol occurs naturally as a minor product of the fermentation of sugars and can even be produced industrially by the fermentation of starch with *Clostridium acetobutylicum* bacteria according to the acetone-butanol-ethanol process initially developed by Chaim Weizmann.³⁴ More recently, a catalytic conversion technology involving the catalytic condensation of sugarcane-derived bioethanol to produce cost-competitive *n*-butanol through a Guerbet reaction was introduced. These developments toward the combination of *n*-butanol with the emergence of bio-AA could lead to the availability of fully biobased *n*-BAs for PSAs and coating applications in the future.

Fatty alcohols are interesting building blocks for adhesive applications because of their intrinsic flexibility and low T_g . Primary fatty alcohols with medium chain lengths usually have an even-

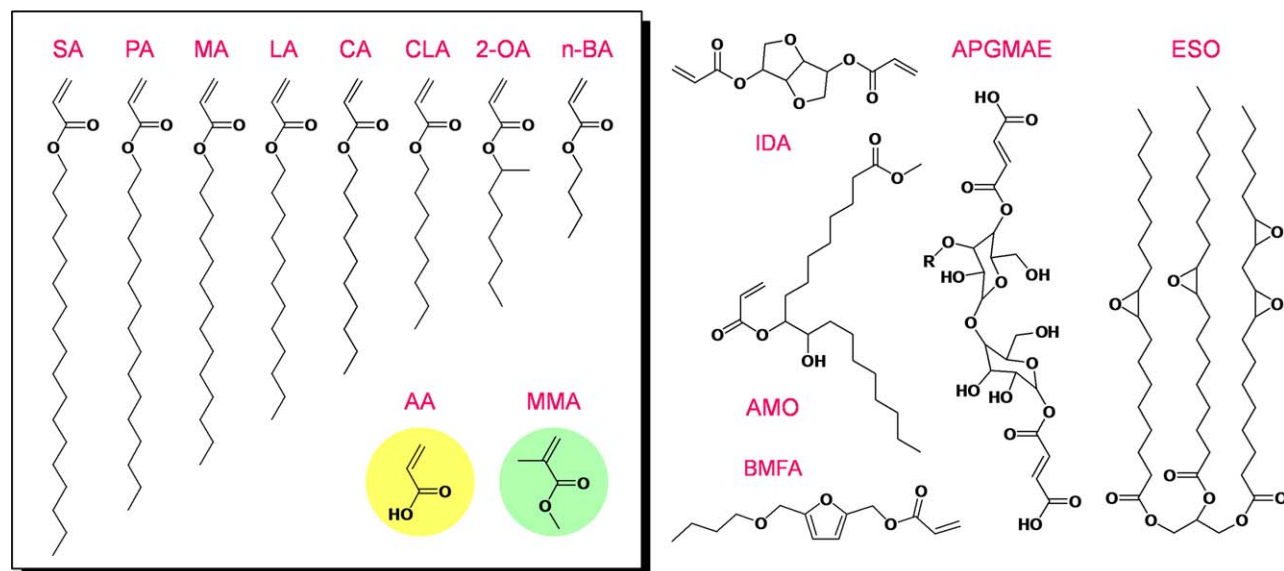


Figure 4. Structures of AA, MMA, SA, PA, MA, LA, CA, CLA, 2-OA, *n*-BA, AMO, ESO, IDA, and BMFA and hypothetical structure of a sugar-based APGMAE according to the general definition given in ref. 47. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

numbered carbon chain length and a single alcohol group attached to the terminal carbon. The saturated straight-chain *n*-C₆, *n*-C₈, *n*-C₁₀, *n*-C₁₂, *n*-C₁₄, and *n*-C₁₆ renewable fatty alcohols can be derived by the hydrogenation of naturally occurring fatty acids (or the methyl esters of fatty acids) from vegetable triglycerides, such as coconut and palm kernel oils, whereas odd-numbered carbon lengths can also be obtained by the modification of naturally occurring even-numbered raw materials by steam-cracking or ozonolysis.³⁵ As an illustration, the biobased monomers capryl acrylate (CLA), capric acrylate (CA), lauryl acrylate (LA), myristyl acrylate (MA), and palmityl acrylate (PA) represented in Figure 4 are conveniently obtained by the reaction of bio-AAs with their respective fatty alcohols, and their use as PSA monomers has been reported.³⁶ Fatty alcohols with longer chains can also be derived from renewable resources. Stearyl (*n*-C₁₈) alcohol is usually derived from animal fats (its name comes from the Greek word *stéar*, meaning “tallow”) or vegetable feedstock, such as cocoa and shea butters, and its (meth)acrylated derivative stearyl (meth)acrylate is already commonly used in adhesive formulations.

The polymerization behavior of fatty-acid-derived methacrylate monomers with chain lengths varying from C₁₀ to C₁₈ was investigated by Ayli and Meier.³⁷ This team reported that methacrylic monomers derived from capric, myristic, palmitic, and stearic fatty alcohols could be polymerized in bulk at 35°C via atom transfer radical polymerization (ATRP) and that optimized polymerization conditions allowed for the synthesis of high molecular weights, whereas the polymer properties were influenced by the side-chain length.³⁷ Importantly, the role of hydrophobic fatty acrylic esters in PSA is not limited to increasing the biobased content of the system but also to the addition of specific technical features. In that framework, Asua et al.³⁸ reported that stearyl acrylate (SA) influenced both the rheological properties and compatibility of the PSA layer with low-

energy substrates such as Teflon. These authors also noted that an optimum content of SA resulted in an optimal balance between adhesion and cohesion but that, above a certain point, an excess of SA could also have deleterious effects on the adhesive elasticity, performance, and failure mode. This key observation highlighted that the ratio of long, straight-chain acrylates in adhesive systems has to be thoughtfully adjusted to obtain optimal properties; this is in contrast with short- and medium-chain-length acrylates, which can form the bulk of the adhesive composition.

Acrylic Monomers Derived from Secondary Alcohols and Functionalized Fatty Acids

3M Co. disclosed an adhesive composition based on 2-octyl acrylate (2-OA), where 2-octanol can be specifically obtained from biomass through the treatment of ricinoleic acid (a derivative of nonedible castor oil) with sodium hydroxide followed by distillation from the coproduct sebacic acid (SEA; Figure 4).³⁹ These resulting 2OA-based adhesive demonstrated good peel and shear values in addition to high temperature stability. In a different approach, Wool and Bunker⁴⁰ reported PSA compositions containing acrylated methyl oleate (AMO; Figure 4), a fatty biobased monomer obtained by the acrylation of the epoxidized form of methyl oleate, the later compound being prepared by transesterification of plant oils such as high-oleic soybean oil. This monomer proved to be suitable for solvent-free waterborne latex processes and to have comparable adhesive properties as petroleum-based polymers.^{41,42} Another family of UV-polymerizable adhesive compositions containing acrylated mono-unsaturated fatty acid alkyl esters was also reported and included monomers such as acrylated methyl margaroleate (margaroleic acid is a C_{17:1} fatty acid), acrylated methyl palmitoleate (C_{16:1}), acrylated methyl myristoleate (C_{14:1}), acrylated methyl gadoleate (C_{20:1}), and acrylated methyl eruceate (C_{22:1}).⁴³ An extra advantage of fatty acids acrylic monomers is their nonvolatility, which

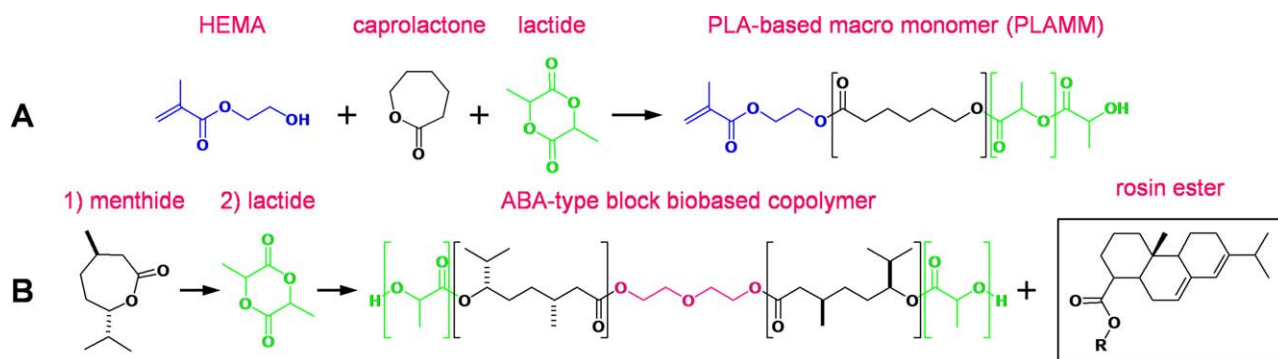


Figure 5. (A) Chain-growth and (B) step-growth approaches toward lactide-containing biobased PSAs. (A) Design of a PLA-MM via the ring-opening copolymerization of L-lactide and ε-caprolactone with HEMA. (B) Sequential synthesis of a biobased triblock copolymer from the cyclic monomers menthilde and lactide. The resulting copolymer displays an ABA-type structure, where A and B represents the polylactide and polymenthilde blocks, respectively. The formulation of the block copolymer with a rosin ester compatible with the menthilde-block formed a nanostructured PSA analogous with the well-known SBC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

turns out to be attractive in view of reducing the emission of volatile organic compounds from various polymer systems.⁴⁴

Multifunctional fatty acrylates, such as acrylated epoxidized soybean, are also commercially available. In general, the direct polymerization of these highly functional monomers leads to densely cured thermosets suitable for coatings⁴⁵ but not for PSA applications. However, tacky resins with suitable high molecular weights between crosslinks can be obtained by limitations on the number of reactive groups per triglyceride or by the copolymerization of these multifunctional monomers with low-molecular-weight acrylic monomers and/or prepolymers.⁴⁶

Acrylated Macromonomers Derived from Sugars and Carbohydrates

In addition to fatty acid-based acrylics, the development of unsaturated monomers derived from sugars is also appealing for adhesive applications because of the high functionality and low cost of carbohydrate building blocks. An inspiring example of sugar-based acrylate monomers was developed by the company Ecosynthetix.⁴⁷ In this technology platform, sugar-based macromonomers of alkyl polyglycoside maleic acid esters (APG-MAE; Figure 4) are copolymerized with conventional acrylic monomers in a water-based emulsion process to give synthetic copolymer structures that incorporate biobased sugar units. Interestingly, the polarity of the sugar repeating units can make the PSA water-dispersible and can make it suitable for paper-making and recycling processes (repulpable PSA).^{48,49}

Lactide (the dimeric form of the starch-derived compound lactic acid) is another interesting starch-based building block that can be used to increase the biobased content of various polymer systems but that cannot directly participate in free-radical (chain-growth) polymerization. A recent attempt to develop PSAs containing high levels of biomass was based on the design of poly(lactic acid) macromonomers (PLA-MMs) that could be polymerized with suitable acrylate monomers.⁵⁰ The acrylated PLA-MMs were first generated through the ring-opening copolymerization of L-lactide and ε-caprolactone with 2-hydroxyethyl methacrylate (HEMA) with respective molar ratios of 5:4:1 [Figure 5(A)]. The PLA-MMs were then copoly-

merized with *n*-BA or 2-ethylhexyl acrylate to produce PSA polymers with average biobased contents ranging from 40 to 60% and adhesive properties that met those of commercial water-based acrylic PSAs.⁵¹ Functional sugar-based unsaturated monomers derived from bioderived carbon have also been derived from various renewable building blocks, such as IS or furanic derivatives [isosorbide diacrylate (IDA) and 5-butoxymethylfurfuryl acrylate (BMFA) in Figure 4].⁵²

Ring-Opening Cationic Polymerization of Biobased Epoxy Precursors

Finally, biobased chain-growth mechanisms are also represented by the cationic polymerization of epoxies. In this case, the initiation step is created by a cation generated by a chemical reaction or an adequate source of irradiation, whereas propagation proceeds through an ozonium.⁵³ Chain polymerization of epoxy monomers bearing two or more epoxy groups in their structure ultimately leads to gels and networks with low T_g values and modulus properties that can meet the requirements of PSAs. Epoxidized vegetable oils, such as epoxidized soybean oil (ESO; Figure 4) and epoxidized linseed oil, are commonly used as plasticizers and stabilizers for poly(vinyl chloride), but they can also be used as PSA precursors in combination with epoxy acrylics or vinyl ethers cured via a photocatalyzed cationic process.⁴⁶ Sun et al. designed a solvent-free, fully biobased photocurable PSA by the UV-initiated cationic polymerization of ESO copolymerized with dihydroxyl soybean oil (DSO) and rosin ester.⁵⁴ The covalent incorporation of both ESO and DSO and rosin ester was shown to create a complex PSA structure of ether-crosslinked triglycerides functionalized with diols and rosin esters.

STEP-GROWTH SYNTHETIC APPROACHES

In addition to the chain-growth approaches, a new class of PSAs based on step-growth chemistries has recently emerged. These synthetic approaches are very innovative because, historically, the design of adhesives based on polycondensates has mainly been focused on HM applications and not on PSAs. For instance, polyester HM adhesives generally have a high degree of crystallinity and are only applied in specific niche applications. In this section, we show that recent advances in step-

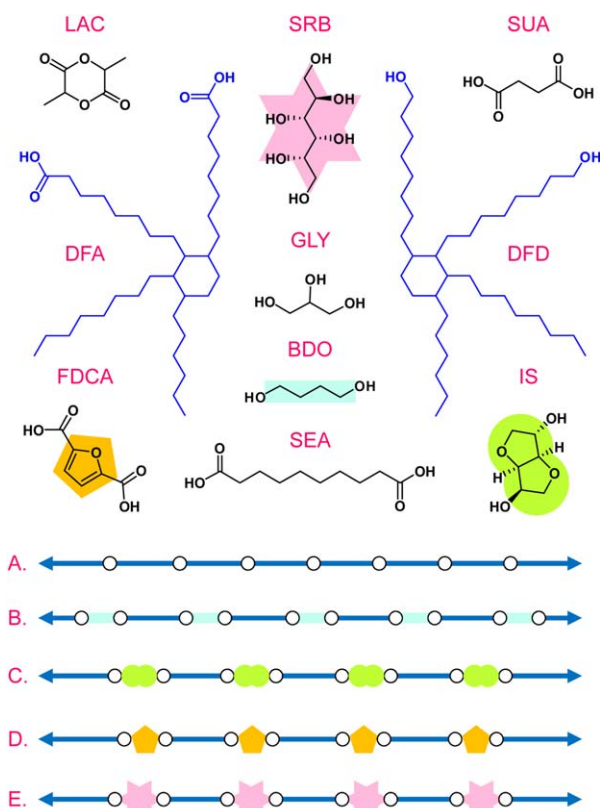


Figure 6. Molecular structures of a selection of renewable precursors for polyester-based PSAs. DFA, DFD, SEA, succinic acid (SUA), lactide (LAC), SRB, IS, FDCA, GLY, and 1,4-butane diol (BDO). The repeating units of amorphous low- T_g biobased polyesters: (A) poly(dimer diol dimerate), (B) poly(1,4-butane diol dimerate), (C) poly(isosorbide dimerate), (D) poly(dimer diol furan dicarboxylate), and (E) poly(sorbitol dimerate). The open circles and arrowheads (\rightarrow and \leftarrow) indicate ester bonds and the continuation of polymer chains, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

growth chemistry have enabled the design of a new generation of biobased polyesters suitable for PSA applications.

Emergence of (Renewable) Polyesters in the PSA Arena

Timothy Long was one of the first to recognize that amorphous low- T_g polyesters constitute promising candidates for PSA applications,⁶ and he was awarded the 2011 Dahlquist Prize from the Pressure-Sensitive Tape Council for this achievement. This interest in polyester chemistry was triggered by its intrinsic sustainable advantages: polyesters are readily synthesized in bulk without organic solvents, and they tend to degrade in an environmentally friendly manner because of the presence of hydrolytically degradable ester bonds. On top of this, a wide range of potential polyester building blocks (dicarboxylic acids and diols) are gradually becoming commercially available from biorefineries.^{9,55} To develop new polyester-based PSA, some fundamental questions have to be addressed; these include whether renewable dicarboxylic acids and diols are sufficiently reactive in polycondensation reactions to be smoothly incorporated into the polyester backbone and whether they have enough stability under the harsh conditions of melt condensation so that

decomposition or other secondary reactions can be excluded. If these elementary requirements are fulfilled, many novel monomers and polymer structures could be envisaged, which in some cases, are not even accessible via petrochemicals. This could enable access to innovative polyesters for the formulation of adhesives with improved properties.

As an illustration, a partially renewable polyester-based PSA was designed by the copolymerization of the starch-based monomer lactide with other cyclic monomers, including glycolide and caprolactone.⁵⁶ The resulting poly(D,L-lactide-co-glycolide-co-ε-caprolactone) was shown to be a tacky material that could, for instance, promote the adhesion of biomedical implants in a subject. The potential degradability and biocompatibility of these lactide-based terpolymers could be an advantage for various biomedical applications where the PSA is expected to degrade into components that can be metabolized by a microbial population *in vivo*.⁵⁶

Nanostructured Renewable Self-Adhesive Materials

Hillmyer et al.⁵⁷ recently described an inspiring concept of a nanostructured PSA developed from renewable triblock copolyesters prepared from the biomass-derived monomers menthite and lactide [Figure 5(B)]. The compounding of these microphase-separated copolymers with a biobased tackifying resin miscible with the flexible polymenthite-based middle block yields a structure of polylactide-based glassy physical crosslinks dispersed in the elastomeric matrix. The resulting nanostructured material is associated with PSA-like properties at room temperature, analogous with widely employed petrochemical-based SBC adhesives.²¹ In general, unformulated self-assembled block copolymers have very limited adhesion on their own, and the addition of a low-molecular-weight tackifier is essential for obtaining good tack and for lowering the network modulus via the dilution of the topological entanglements.

Dimer Fatty Acids as Versatile Building Blocks for Polyester-Based PSAs

An interesting class of renewable monomers for adhesive applications is dimerized fatty acids (DFAs; see structure on Figure 6), which are produced by the Diels–Alder oligomerization of C_{18} unsaturated oleic and linoleic acids derived from renewable resources, such as rapeseed oil or tall-oil fatty acids. The predominant products of the oligomerization reaction are C_{36} diacid compounds in which the C_{18} units are linked together by carbon–carbon bonds of various isomeric structures (acyclic, monocyclic, bicyclic, and aromatic). The vast number of C_{36} diacid compounds present in DFA is responsible for their liquidlike noncrystallizing nature and the properties they impart in their various applications. DFAs have a long history in polyamide HM adhesives, which are usually composed of a dimer acid copolymerized with two or more different diamines, where the DFA provides the amorphous nonpolar character.⁵⁸ Recently, DFAs have also been used to design supramolecular rubbers with striking self-healing capacities,^{59,60} whereas their nontoxic character make DFAs potential building blocks for medical devices.^{61,62} In addition, C_{36} dimer fatty diol (DFD; see

structure on Figure 6) and fatty dimer diamine can also be derived from DFAs.

The company Nitto Denko has recently developed a whole range of renewable polyester-based PSAs with differentiated properties with DFAs as key building blocks. Because of their specific molecular structure and hydrophobic nature, DFAs enhance the wetting properties of biobased PSAs, promote the adhesion to low-energy surfaces, provide humidity resistance, and bring about the suitable molecular flexibility required for PSA applications. Fully dimer-based polyesters obtained by the polycondensation of DFAs and DFD have been used as base polymers in various PSA formulations.^{63,64}

The viscosity, T_g , and formulation capacity are all essential parameters that determine the property profiles of PSAs, and the properties of sticky polyesters can be fine-tuned by the selection of the type and relative ratio of monomers. In that framework, Nitto researchers developed a unique type of renewable adhesive by copolymerizing fatty-acid-based monomers with more polar, sugar-based, monomers, such as IS,⁶⁵ furan-2,5-dicarboxylic acid (FDCA),⁶⁶ succinic acid (SUA), and lactide (LAC) (see the structures in Figure 6). The resulting renewable polyester adhesives combine the intrinsic properties of their precursors, such as flexibility, softness, and functionality, and form the basis of a new class of self-adhesive materials.

The integration of IS into PSAs is especially innovative because, until now, this promising renewable monomer has mostly been integrated into rigid polymer systems [Figure 6(C)].^{67–69} Vendamme and Eevers²³ showed that in soft materials, such as PSA, IS can play multiple roles, such as adjusting the T_g , modulating the viscoelastic spectrum, and tuning the cohesion and interfacial properties of the glue. In addition to adding polarity to the adhesive, cyclic sugar-based monomers such as IS are also very effective in adjusting the bulk rheological response of polyester PSAs. Fundamentally, Nitto's recent work on polyester-based renewable adhesives exemplifies that some well-established design principles for petrochemical-based adhesives could be advantageously transposed to the emerging world of green chemistry in view of speeding up the emergence of highly functional biobased adhesive solutions.

The incorporation of carbohydrates into nonpolysaccharide structures such as polyesters is a versatile strategy for attaining highly functional PSAs and complex systems that act as smart materials. According to a general synthetic protocol initially reported by Gross and coworkers,^{70,71} a new type of linear polyester adhesives bearing secondary hydroxyl groups in the main chain have been synthesized via the selective lipase-catalyzed condensation between diacids and sugar polyols such as sorbitol [SRB; Figure 6(E)].⁷² The concept of hybrid sugar-based and lipid-based adhesives is, therefore, a general and powerful concept for designing functional PSAs that embrace both chain-growth^{47–51} and step-growth^{23,65,66,72} synthetic strategies.

Percolative Step-Growth Reactions Involving Linear Polyesters

Linear amorphous polyesters synthesized by classical melt condensation have the appearance of transparent viscous honey

with typical molecular weights ranging from 20,000 to 90,000 g/mol and, in general, do not possess the subtle balance of properties required for PSA applications. As a result, these polyesters need to be crosslinked and/or formulated to reach useful levels of cohesion. In a first approach, a OH-terminated polyester was cured with classical multifunctional petrochemical compounds such as isocyanates.^{63,64} As a greener alternative, multifunctional biobased compounds could also be used for crosslinking purposes. For instance, Vendamme and coworkers^{7,73} reported that fully renewable polyester adhesives with tunable viscoelasticities could be obtained by the simple reaction of fatty-acid-based polyester polyols and maleinized triglycerides. Remarkably, the DBU-catalyzed alcoholysis curing reaction had the dual effect of branching/curing the base polymers while introducing carboxylic acid groups with adhesion-promoting characteristics. These functional crosslinked adhesives combined good peel properties with superior cohesion and tensile strength because of their percolated architectures. In a subsequent article, the same authors demonstrated that epoxy bio oils, such as ESO (Figure 4) and epoxidized linseed oil, are very efficient for curing acid-terminated polyesters.^{23,74}

Randomly Crosslinked Polyester Networks

The synthesis of a linear base polymer is not a prerequisite for designing polyester PSAs, and crosslinked biobased PSAs can also be synthesized by the direct condensation of multifunctional precursors. Li and Li⁷⁵ reported the elaboration of biobased PSAs by reacting one epoxidized vegetable oil (e.g., ESO) with at least one dibasic acid (e.g., SEA) or anhydride in molar ratios ranging from 3:1 to 1:3. After curing was performed at 160°C, a tacky coating was obtained with good adhesion to various substrates. In a different approach, Sun and coworkers^{54,76,77} prepared novel PSAs by polymerizing ESO in the presence of phosphate acid to form a copolymer matrix consisting of phosphoric ester and ether crosslinkages, whereas DSO could be added to ESO at a designed ratio to improve the tackiness. The resulting PSA display good thermal stability, transparency, and peel strength comparable to current PSAs.

Finally, it is important to mention that some recent developments in randomly crosslinked polyester networks for biomedical applications are also very relevant to the framework of biobased PSAs. This research field was initially pioneered by Robert Langer from Massachusetts Institute of Technology, who in 2002 reported the design of poly(glycerol sebacate) (PGS), a polyester that is physically analogous to vulcanized rubber.⁷⁸ When GLY and SEA are heated for several days, the alcohols and acids react to form prepolymers that can be melted for further fabrication processes. From a chemical standpoint, GLY is the basic building block for lipids, and SEA (Figure 6) is industrially obtained from castor oil. SEA is also a natural metabolic intermediate in the ω oxidation of medium- to long-chain fatty acids and has been shown to be safe *in vivo*. The initial motivation of Massachusetts Institute of Technology's team was to design a mechanically robust, biocompatible, and biodegradable polyester biorubber that could be useful in a wide range of biomedical applications, including tissue engineering and therapeutic delivery.⁷⁹ However, the

Langer group also reported that the mechanical properties of PGS could be tailored through the tuning of the polymerization degree and the molar ratio of the monomers. In particular, PGS networks with low degrees of crosslinking were found to be exceedingly sticky on a variety of substrates, including human skin, and even hard-to-stick substrates, such as polytetrafluoroethylene (PTFE).⁸⁰ On the basis of these observations, these authors suggested the use of PGS as a surgical glue. The integration of reactive acrylic groups into PGS prepolymers that could be subsequently UV-cured provide a faster curing strategy with enhanced applicability.⁸¹ Following the synthesis of PGS, researchers have designed a wide range of soft polyester networks from a variety of renewable (or even endogenous) compounds, including citric acid, xylitol, and SRB,^{82–84} which all have the potential to be tailored for PSA applications.

EMERGING BIOLOGICALLY INSPIRED STRATEGIES

In the two preceding sections, we demonstrated how adhesive chemists are gradually using naturally derived building blocks to design innovative synthetic PSA materials with differentiated features. A complementary scientific trend is to not limit the role of nature as a supplier of renewable feedstocks but to use it as a source of inspiration for new bonding strategies that sometimes outperform the most sophisticated currently available synthetic adhesives. The field of bio-inspired and biobased adhesives share some common traits because the specific properties of biological adhesives often arise from the unique structural features and functions of their biomacromolecular constituents.^{85,86} Although this research field is still in its infancy, some interesting design principles of nature's toolbox are already emerging.

Sticky Biological Substances Are Biobased, Biodegradable, and Viscoelastic

Insects and small animals often produce sticky viscous or viscoelastic layers of glue on their feet to be able to adhere to various surfaces with complex geometries for locomotion, self-defense, or catching prey.⁸⁷ The exact nature of most of these glues are still largely unknown, and their chemical analysis is only an emerging field in the biological sciences. Nevertheless, some glues found in the smooth and hairy adhesive pads of insects have already revealed the presence of hydrophobic, long-chained fatty hydrocarbons (C_{22} to C_{29}) in addition to more polar fatty acids and carbohydrates derivatives.^{88,89} Similarly, the glues produced by carnivorous plants are usually categorized as sugar-based (polysaccharide mucilages) or lipid-based (lipophilic) resins.⁹⁰

Although the chemical composition of such biological adhesives is extremely complex compared to synthetic polymers, it is notable that their stickiness principles often originate from their bulk material responses (halfway between the liquid and solid states) rather from their precise monomer sequences. For instance, Dhinojwala et al.⁹¹ elegantly demonstrated that the stickiness of the glue drops produced by the modern orb-weaving spider [Figure 7(A)] could be explained by the simple theory of viscoelastic solids and that this biomechanical stretchi-

ness was critical in the enhancement of the adhesion caused by specific adhesive ligands.

PSA Building Blocks Inspired by Amino Acids

Attachment devices developed by marine organisms rely on highly viscous adhesive secretions made of adhesive proteins. For instance, the strong adhesion ability of maritime creatures, such as the blue mussel *Mytilus edulis* [Figure 7(B)], has been ascribed to the presence of a rather unusual catechol-containing amino acid called *L*-3,4-dihydroxyphenylalanine (*L*-DOPA) found in the structure of secreted mussels adhesive foot proteins (Figure 8).⁹² Molecules that contain extensively repeating DOPA motifs tend to stick to a wide range of surfaces through the formation of various kinds of covalent and noncovalent bonds, even in underwater environments.^{93,94} Mussel adhesives have triggered tremendous interest in the chemical community, and a wide range of new catechol-containing polymer structures have been designed in view of the increasing need for adhesives that can be applied underwater or to already wet surfaces, such as boat hulls or medical devices.⁹⁵

Bio-inspired reactive DOPA monomers, such as dopamine methacrylamide (DMA; Figure 8)⁹⁶ or *N*-methacryloyl-3,4-dihydroxy-*L*-phenylalanine,⁹⁷ have been integrated into acrylic polymers structures via copolymerization with standard monomers, such as methoxyethyl acrylate (MEA) or AA. Washburn et al.⁹⁸ reported that in wet environments, DMA-containing soft acrylic networks displayed better adhesion than DMA-free gels and that subtle variations in the viscoelastic properties of the adhesives were also important for controlling the adhesion strength. The renewable compound eugenol (a catechol-related molecule that is the active ingredient in clove oil, Figure 8) was also integrated into siloxane elastomers and have been shown to improve wet adhesion.⁹⁹ In addition to these radical polymerization approaches, catechol-containing step-growth polymers have also been designed. For instance, Yang et al.¹⁰⁰ developed an injectable and biodegradable bioadhesives for surgical use by the polycondensation of dopamine with short poly(ethylene glycol) (PEG) segments and citric acid (a standard renewable building block obtained by fermentation of sugars). Very recently, Manolakis et al.¹⁰¹ directly integrated *L*-DOPA into a new class of fatty-acid-based polyesteramides with high renewable content and demonstrated the first example of a DOPA-containing bio-based adhesive tape.

The sandcastle worm is another marine creature that has attracted the attention of adhesives researchers. In this case, a mixture of highly charged proteins forms an insoluble and sticky complex coacervate that further solidifies via DOPA crosslinking. Synthetic mimics with polycations and polyanions have already been realized.¹⁰²

Self-Assembling Adhesive Systems Inspired by Nucleobases

In general, the DOPA-inspired approaches mostly aim at tuning the interfacial bonding of the adhesives and increasing the affinity with the substrate. However, in PSAs, the adhesion strength is also largely determined by the viscoelastic deformation of the glue layer. In this respect, Long et al.¹⁰³ demonstrated a very innovative concept of bio-inspired PSAs containing the complementary nucleobases adenine and thymine with the idea of

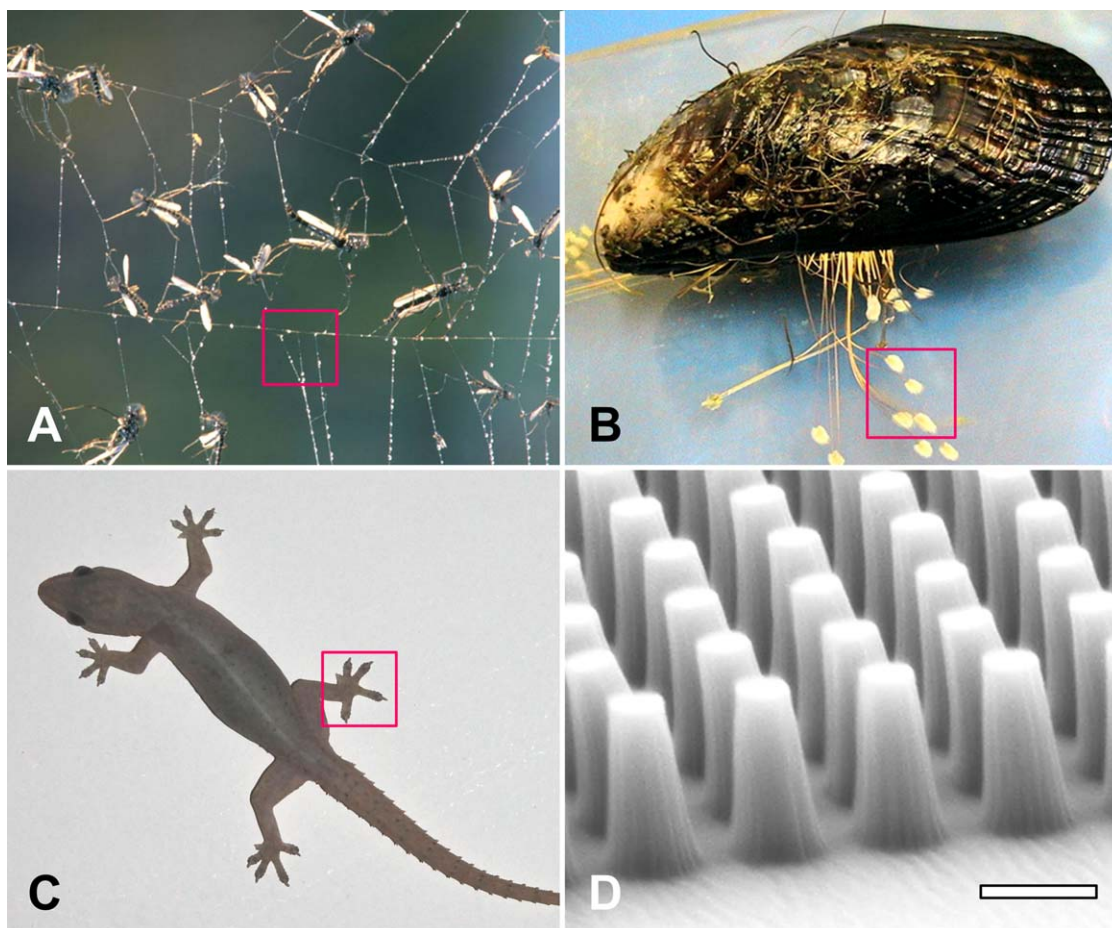


Figure 7. (A) The silk produced by modern orb-weaving spiders is coated by microscopic droplets of viscoelastic PSA-like glue that is very efficient for catching prey. (Reprinted with permission from ref. 86. Copyright 2010 Macmillan Publishers, Ltd.). (B) The blue mussel *Mytilus edulis* secretes DOPA-rich elastic adhesive threads with underwater sticking properties. (Reprinted with permission from ref. 94. Copyright 2009 American Chemical Society.). (C) The striking ability of geckos to climb on vertical walls stems from the gripping microsetae/nanosetae structures of their feet. (D) Gecko-inspired bioadhesives made of microstructured acrylated PGS. The scale bar represents 1 μm (Reprinted with permission from ref. 124. Copyright 2008 National Academy of Sciences.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

imparting some of the structural features of biomacromolecules (e.g., cooperative H bonding and noncovalent interactions) into emerging adhesive technologies. These authors showed that a blend of thymine- and adenine-containing statistical copolymers (see the structures of the monomers 4-[[3-(thymine-*l*-yl) propa-

noyl] oxy} butyl acrylate (TPOBA) and 4-[[3-(adenine-9-yl) propanoyl] oxy} butyl acrylate (APOBA) in Figure 8) associated into a thermodynamically stable complex because of adenine–thymine base pairing and that the nucleobase-functionalized polyacrylates exhibited a tunable viscoelasticity, enhanced

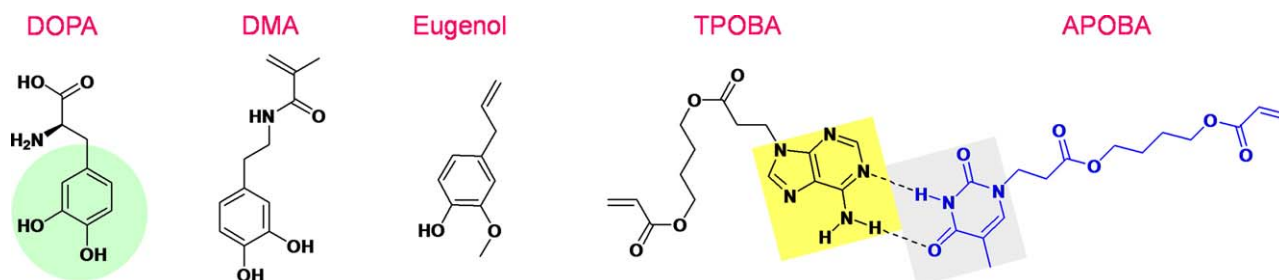


Figure 8. Molecular structures of L-DOPA, DMA, eugenol, TPOBA, and APOBA showing the adenine–thymine base pairing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adhesion, and cohesive strength.¹⁰³ Similarly, Creton et al.¹⁰⁴ demonstrated how the rheological profile of a bisurea-functionalized polyisobutylenes supramolecular PSA (and especially its long relaxation times) is affected by self-assembling mechanisms.

Sticky Polymers Produced by Microorganisms

The viscoelastic biofilms produced by some microbes are another inspiring example of sticky natural substances.¹⁰⁵ Such biofilms typically flourish on moist surfaces and are made of a thin layer of densely packed microorganisms (microbes, bacteria) encapsulated within an aqueous matrix of proteins, nucleic acids, and polysaccharides. Although sticky biofilms are generally seen as a threat in various industrial fields (nautical shipping, cooling systems, medical devices, or food processing), this inherent stickiness could also inspire the development of new PSA compositions. In that respect, an interesting parallel can be drawn here with a special class of bacterial PHAs. PHAs are naturally occurring polymers produced by microorganism as an inert reserve of fatty acids.¹⁰⁶ Because of their inherent biodegradability and biocompatibility, PHAs are materials of interest for many industrial applications. The composition of a PHA depends on the bacteria used for its production and the substrate with which it is fed.¹⁰⁷

Among the different classes of PHAs, middle-chain-length polyhydroxyalkanoates (*mcl*-PHAs), in which the side group contains between 6 and 14 carbons, are of especial interest for adhesive and coating technology because they exhibit elastomeric and thermoplastic properties with a low crystallinity, low melting point, low T_g (typical values comprised between -50 and -60°C), and high tack.¹⁰⁸ Several studies have demonstrated the possibility of efficiently crosslinking *mcl*-PHA with γ rays,¹⁰⁹ UV-based processes,¹¹⁰ peroxide mediated reactions,¹¹¹ free-radical chemistry,¹¹² and electron-beam-assisted processes¹¹³ and have, thus, improved their cohesive properties in view of PSA applications.

To date, the use bacterial polymers for adhesive and coating applications has been sparsely explored. Metabolix, Inc., reported an adhesive-composition-based PHA.¹¹⁴ In this example, a solution containing PHA was evaporated; this led to an autoadhesive material with an adjustable surface tack value that depended on the casting condition. This adhesive could be used on several types of substrates, including paper, poly(ethylene terephthalate), and cellophane. In another example, Rutherford et al.¹¹⁵ synthesized PSAs made of a crosslinked PHA loaded with a tackifier additive. These PSAs exhibit a high cohesion and adjustable peel force that depended on the adhesive composition and processing conditions. van der Walle et al.¹¹⁶ reported an *mcl*-PHA-based coating having tunable adhesion levels on various substrates, such as glass and poly(ethylene terephthalate). This coating displayed a high gloss, a smooth surface, flexibility, and good cohesion. Interestingly the molecular design principles of *mcl*-PHAs are quite different than those of conventional PSAs and focus much more on genetic and biochemical engineering rather than chemical processes. Unfortunately, this innovative PSA technology has not been commercialized yet because of upscaling issues.

In addition to *mcl*-PHAs, Mancuso Nichols et al.¹¹⁷ investigated the role of microbial exopolysaccharides as adhesive materials

by screening a wide of microalgae cultures. Further expansion of these efforts could lead to new opportunities for natural and engineered biobased adhesives, but before that, close attention must be paid to research in the basic biological and biochemical sciences because biologically inspired research efforts should be always be based on a foundation of basic understanding.

Microstructured/Nanostructured Adhesives: Toward Hairy and Wrinkled Biomimetic PSAs

The reversible and dry bonding strategy of geckos [Figure 7(C)] has been studied extensively and has become model system for bio-inspired adhesive research.¹¹⁸ In sharp contrast with viscoelastic synthetic PSAs and semiliquid biological glues, the sticking (or gripping) ability of geckos stems from the hairy nanostructures that coat their feet and interact via reversible van der Waal's interactions with various substrates.¹¹⁹ The underlying principles of these adhesives is that a patterned surface can enhance adhesion compared with a smooth surface because of contact splitting.¹²⁰ A wide range of gecko-inspired synthetic adhesives have been developed from petroleum-based materials, such as polyimide, polydimethylsiloxane (PDMS), and even carbon nanotubes.^{121–123}

Langer et al.¹²⁴ further extended the concept of gecko-inspired adhesives to create a biobased, biodegradable, and biocompatible waterproof adhesive bandage that can be used to join sutures or for patching up surgical wounds. This gecko-inspired tissue adhesive is made from acrylated PGS, a biocompatible and biodegradable elastomer, combined with a thin tissue-reactive biocompatible surface coating (oxidized dextran). Tissue adhesion was optimized by the variation of dimensions of the nanoscale pillars [Figure 7(D)], including the ratio of the tip diameter to pitch and the ratio of the tip diameter to the base diameter. In addition, the coating of these molded pillars of biodegradable elastomers with a thin layer of a biobased glue (oxidized dextran) significantly increased the interfacial adhesion strength on porcine intestine tissue *in vitro* and in the rat abdominal *in vivo* environment.¹²⁴ This gecko-inspired medical adhesive may have potential applications for sealing wounds and for the replacement or augmentation of sutures or staples. Another breakthrough in that direction came from Messersmith et al.,¹²⁵ who developed a strong hybrid biologically inspired adhesive that could attach to both wet and dry surfaces. The strength of this adhesive came from the coating of an array of nanofabricated silicone pillars, similar in structure to the hair-like structures (or setae) of a gecko's foot, with a DMA-based polymer that mimicked the wet adhesive proteins found in mussel feet.¹²⁵ Wet adhesion of the nanostructured polymer pillar arrays increased nearly 15-fold when they were coated with the mussel-mimetic polymer, and the system maintained its adhesive performance for over a thousand contact cycles in both dry and wet environments. This hybrid adhesive, which combined the design elements of both gecko and mussel adhesives, should be useful for reversible attachment to a variety of surfaces in any environment.

A drawback of the current gecko-inspired PSAs made of fibrillar arrays is that their current fabrication processes are primarily

based on (soft) lithographic approaches, and consequently, there are issues related to the fabrication of these materials in an efficient and scalable manner. An emerging alternative method toward the design of structured and responsive PSAs is the use of self-organized surface wrinkling patterns, a spontaneous elastic instability that is readily apparent in natural systems,^{126,127} for instance, in aging human skin or drying fruits. Crosby et al.¹²⁸ created a reusable smart PSA that uses surface wrinkles as patterns to control the adhesion of a poly(*n*-butyl acrylate) elastomer (see the structure of *n*-BA in Figure 4). This material design offers several advantages over lithographic approaches including (1) an enhanced control of adhesion provided by well-defined surface wrinkle patterns, (2) the convenience and simplicity of the fabrication process without expensive lithography for patterning, and the amenability to the patterning of a wide variety of polymer systems. Subsequently, other examples of wrinkled PSAs have also been described.^{129,130}

The selected highlights mentioned in this section exemplify how combined advances in nanotechnology, microfabrication, and self-organization processes could contribute to the development of structured biobased materials with smart and tunable adhesive properties, a very important research direction when we consider that to some extent, most biological adhesives show complex structures on the micrometer and/or nanometer scales.

CONCLUSIONS AND OUTLOOK

Several routes for new materials have been explored since development activities toward a more sustainable adhesive industry took off around 10 years ago. The simultaneous development of new biobased raw materials from different sources have led to a multitude of new polymers and formulating agents that are now finding their way onto the market and providing an answer to the growing sustainability attention by the wider audience and consumers. This new class of biobased adhesives differentiates from traditional biobased glues and adhesives in the fact that through chemical synthesis, the properties of the materials have been improved; this allows them to compete with existing oil-based materials in technical high-level applications and to even outperform them in specific domains through the introduction of particular properties based on the specific characteristics of the biobased raw materials.

Simultaneously, great attention has been given by the industrial and academic societies to the sustainability aspects of these materials and their processes. Close monitoring of the real contribution to the 3 Ps (planet, people, and profit) of sustainability has been the focus point of many environmental research activities in the past decade.

The future of the biobased adhesive research is also guaranteed to grow further in diversity. Not only is the number of starting materials increasing, but also, the concept of hybrid materials is contributing to the facilitation of the introduction of biobased chemistry in real applications in a more acceptable fashion. Additionally, the most recent evolution in the scientific field of biobased adhesive research, where biomimetic principles are applied to biobased materials, is a trend that will bring nature even more close to traditional materials sciences. This scientific

evolution in this materials class will inevitably also lead to a wider application of these materials into potential medical devices, where the inherent biocompatible and eventual biodegradable properties will lead to more advanced life science materials and to improved health care.

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