

AN ABSTRACT OF THE THESIS OF

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Title: Pressure Sensitive Adhesives based on Oleic Acid

Abstract approved:

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Existing pressure sensitive adhesives (PSAs) are mostly based on petrochemicals. In this study, a novel PSA based on a renewable material, methyl oleate, was prepared and characterized. Methyl oleate was first epoxidized to form epoxidized methyl oleate that was subsequently hydrolyzed and acidified to form epoxidized oleic acid (EOA) which is an AB-type monomer containing both a carboxylic acid group (A) and an epoxy group (B). Various methods for the preparation of EOA with high purity were extensively studied. EOA was homopolymerized in the presence of a catalyst to generate a polyester that could serve as a PSA. Various catalysts were investigated for their effectiveness on the homopolymerization, and chromium (III) tris(acetylacetonate) was found to be the most effective catalyst. Effects of the EOA purity on the PSA properties of the resulting polyesters were investigated in detail; the EOA purity of at least 97% was found to be required for the preparation of the PSA with superior properties. The crosslinking of the polyesters with very small amount of crosslinking agents was able to further improve the overall properties, especially the aging resistance of the resulting PSAs. Among various

crosslinking agents investigated, polymeric methylene diphenyl diisocyanate was the most effective in improvement of the PSA properties. The PSAs were evaluated for their peel strength, tack force, shear resistance, and aging resistance. The PSAs were characterized for their viscoelastic properties, thermal properties, thermal stability, and chemical structures.

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Pressure Sensitive Adhesives based on Oleic Acid

by
Yili Wu

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Dr. Kaichang Li was involved with all experimental design and revision of the thesis.

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Pressure Sensitive Adhesives based on Oleic Acid

Chapter 1 - Literature review

1.1 General introduction of pressure sensitive adhesives (PSAs)

PSAs are self-adhesive materials that can bond to adherends instantaneously under a light pressure [1]. The ability to bond without the activation by water, solvents, heat or radiation distinguishes PSAs from other types of adhesives [2]. Due to their permanent tack, the adhesion by PSAs is a convenient way to apply the backing to different surfaces and fulfill different tasks [1]. Another important feature of the PSA products is their easy and clean removal and their reusability. PSAs must have adequate adhesive strength so that the PSA products cannot be easily peeled off from the adherend [3]. PSAs also must have adequate cohesive strength so that the PSA products can be removed from the surface of the adherend without leaving any adhesive residue [3]. The Post-it® note is a good example of a PSA product.

Pressure sensitive tapes were first used in 1840s [4]. Pressure sensitive labels and pressure sensitive protective films came to the market in 1930s and 1940s, respectively [4]. Today, PSA products such as packaging tapes, labels, sticky notes, duct tapes, and medical tapes are almost indispensable in many aspects of our daily lives. The applications of PSAs could be divided into two categories based on performance requirements: removable such as Post-it® notes or masking tapes and permanent such as safety labels or product-description labels [1]. The PSA products can be divided based on the product types into tapes, labels, and miscellaneous products.

Tapes are considered the most important PSA products [3]. Tapes can be subdivided according to the backing materials into fabric tapes, paper tapes, film tapes, nonwoven fabric tapes, foil tapes, foam tapes, and transfer tapes. Tapes can also be subdivided according to their functions into electrical tapes, office tapes, packaging tapes, medical tapes, and masking tapes. One-sided pressure sensitive tapes usually consist of four layers and an enlarged structure is shown in Figure 1.1. In a typical visual inspection of a PSA tape, the backing layer and the pressure sensitive adhesive layer can be readily recognized, but the release coat layer and the primer coat layer are sometimes hard to recognize. The backing layer typically provides the basic properties required for targeted applications. For example, the backing of packaging tapes provides the strength in keeping a box closed, the backing of electrical tapes provides electrical insulation, and the backing of decorative papers provides visual images. The PSA layer fulfills characteristic pressure sensitive adhesion, including the quick adhesion upon a simple contact, the good adhesion under a light pressure without the use of solvents or heat, the clean removal after the contact, and the repetitive stickiness to the adherend. The primer coat layer is used for improving the bonding strength between the backing layer and the PSA layer. Sometimes, the primer coat layer also contains a crosslinking agent that is able to crosslink the PSA after the PSA is coated [5]. The release coat layer is used for facilitating the unwinding of the tapes.

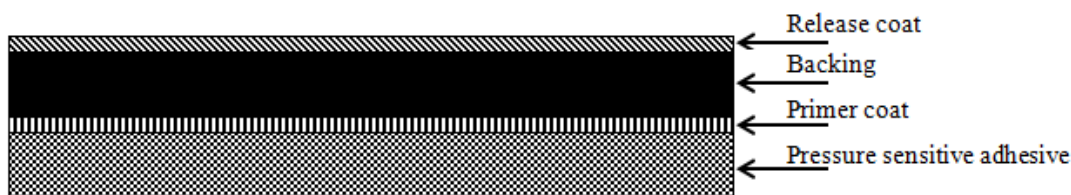


Figure 1.1 Four layers of a typical pressure sensitive tape

Labels are another important type of PSA products. PSA labels can be used as pricing labels, product-description labels, safety labels, inventory labels, stickers, automotive labels, and mailing labels. Besides tapes and labels, PSAs can also be used in products such as protective films, floor tiles, and automotive wood-grained films [6]. Because of the high flexibility in selecting the backing materials and tuning up the PSA properties, PSA products are growing rapidly and diversely for accommodating more and more different end uses in the modern world.

1.2 General composition of PSAs

Commercial PSAs are usually based on an elastomeric polymer and a tackifier [7]. Plasticizers, fillers, pigments, and stabilizers can also be included in the PSAs for helping achieve desired properties.

1.2.1 Base polymers

PSAs are based on a film-forming elastomer that has viscoelastic properties. The viscoelastic properties are required for the contradictory behaviors that a PSA has during bonding and debonding processes [8]. During the bonding of a PSA to an adherend, the

PSA must be able to deform and spread onto the surface of the adherend for achieving good adhesion. During a debonding process, the PSA is expected to behave as a solid and shows good resistance to deformation for holding the adherend and the backing material in place.

Viscoelastic polymers that are mainly used for the preparation of commercial PSAs include natural rubber, polyacrylates, styrenic block copolymers, and silicone [1]. PSAs based on each individual base polymer will be discussed in more detail later.

1.2.2 Tackifiers

Tackifiers, or tackifying resins, are used for improving the tack or the stickiness of PSAs. They are usually low-molecular weight brittle materials with a glass transition temperature (T_g) higher than the room temperature (typically 30-60 °C [9]). An effective and desirable tackifier must be compatible with the base polymer. The tackifier may migrate to the surface of the PSA and seriously affect the performance of the PSA if it is not fully compatible with the base polymer [9]. There are three major classes of tackifiers for PSAs: hydrocarbon resins, rosins/rosin derivatives, and terpene resins [10]. Hydrocarbon tackifying resins are carefully selected low molecular weight fractions from oil refinery, including C_5 aliphatic hydrocarbons, C_9 aromatic hydrocarbons, and $(C_5)_2$ cycloaliphatic hydrocarbons such as dicyclopentadiene [9]. Depending on the sources and the methods of obtaining them, rosins can be subdivided to gum rosins, wood rosins, and tall oil rosins [9, 10]. The gum rosins are oleoresins from living pine trees and are obtained by collecting the exudates from the wound of a tree. The wood rosins are

obtained from the extraction of the aged stump of harvested pine trees with organic solvents. The tall oil rosins are obtained by the distillation of the crude tall oil, a byproduct from a kraft pulping process in the pulp and paper industry. The major components of these rosins are rosin acids [10]. Besides rosins, rosin derivatives such as hydrogenated rosin acids and rosin esters from the esterification of rosin acids are also useful tackifiers. Terpene resins are low molecular weight polymers from turpentine such as the wood turpentine from wood stump and the sulfate turpentine from a kraft pulping process.

1.2.3 Plasticizers

Plasticizers are used for increasing the plasticity or fluidity of PSAs. They are low-molecular-weight and nonvolatile liquid at room temperature. Commonly used plasticizers for PSAs include mineral oils, low- T_g oligomers such as polybutenes and polyethers, and long-chain esters of aromatic and aliphatic acids such as phthalic acids, adipic acids, sebacic acids, and trimellitic acids [5]. Plasticizers weaken molecular interactions such as Van der Waals' forces between the polymer chains, resulting in increase in chain flexibility and decrease in melt viscosity and elastic modulus of adhesive polymers [11]. The improved chain flexibility can enhance tack properties of PSAs. However, the use of excessive plasticizers in PSAs may result in large reductions in the molecular interactions, which may significantly reduce the cohesion of the adhesive polymers [11].

1.2.4 Antioxidants

Antioxidants are added in PSAs for protecting the PSAs from oxidative degradation. Antioxidants are especially needed for PSAs that are based on natural rubber and other base polymers that contain carbon-carbon double bonds [12]. The oxidative degradation is an autocatalytic chain reaction, which can be initiated by free radicals generated from the exposure to heat, light, or shear stress. There are two basic types of antioxidants: primary antioxidants and secondary antioxidants [13]. The primary antioxidants capture the existing free radicals and thus terminating the oxidative chain reaction [13]. Commonly used primary antioxidants in PSAs are phenolic compounds such as 2,5-di-*tert*-amyl hydroquinone and aromatic amines such as N-phenyl-2-naphthylamine and N,N'-di-2-naphthyl-*p*-phenylenediamine [14, 15]. Hydroperoxides are intermediate species in the oxidative degradation reaction that can split and form free radicals. The secondary antioxidants decompose the hydroperoxides (ROOH) to alcohols, thus preventing the formation of free radicals [13]. Commonly used secondary antioxidants include phosphites such as tri(nonylated phenyl)phosphite and thiol compounds such as dilauryl 3,3'-thiodipropionate [12, 16]. The secondary antioxidants are often used with the primary antioxidants for providing the PSAs with synergistic stabilization [16].

1.2.5 Fillers

Fillers are used in PSAs for reducing material costs and adjusting colors and other properties such as thermal expansion, electrical and thermal conductivity, heat resistance, creep resistance, flame retardance, and removability [17]. Commonly used fillers for

PSAs include natural pigments such as kaolin and limestone, carbonates such as calcium carbonate, silicates such as calcium silicate and sodium aluminum silicate, silica, carbon black, metallic powder such as nickel particles, metallic hydroxides such as aluminum hydroxide and magnesium hydroxide, and metallic oxides such as zinc oxide, titanium dioxide, antimony oxide, and calcium oxide [7]. Microspheres made from glass such as borosilicate glass or from polymers such as the copolymer of vinylidene chloride and acrylonitrile can also be used as fillers in PSAs [18, 19].

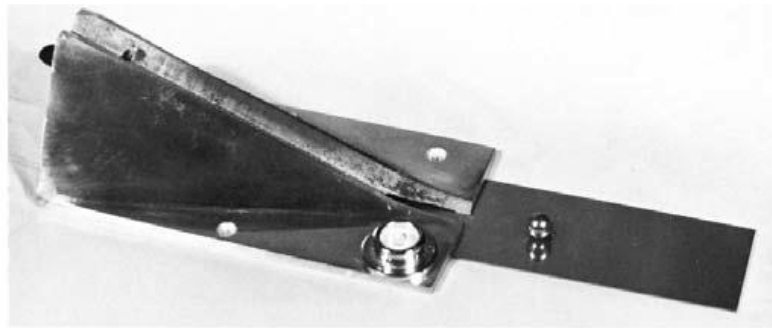
1.3 Testing methods

All PSAs are typically evaluated for the following three properties: tack, peel adhesion, and shear resistance. Tack, also called instant “grab” or quick stick, measures the PSA’s abilities to wet the surface of an adherend and to adhere to an adherend under a light pressure at a short contact time [20]. Peel adhesion, also called peel strength, is a measurement of PSA’s resistance to be removed by peeling [21]. The peel strength results from the combined effects of three works: the work required to deform the backing layer, the work to deform the PSA layer, and the work to debond the PSA from an adherend [21]. Shear resistance indicates the PSA’s ability to hold in position when a shear force is applied. It is a measurement of the internal strength or cohesive strength of the adhesive itself [22]. The adhesive polymer should possess enough cohesive strength for resisting a shear movement by its own weight of a PSA product or by an extra load. A sufficient cohesive strength also ensures the clean removal of a PSA product from the surface of an adherend. A proper balance among tack, peel adhesion, and shear resistance is necessary for most PSA products [2].

1.3.1 Tests for measuring tack

1.3.1.1 Rolling-ball tack test

The rolling-ball tack test is simple, fast, low-cost, and easy to perform. It is probably the oldest and most widely used tack test. ASTM D3121–06 provides a standard test method for measuring the tack of a PSA by the rolling-ball method [23]. Figure 1.2 shows a test apparatus for the rolling-ball tack test. The apparatus is placed on a hard and horizontal surface such as a metal plate. The steel ball placed at the top of the incline (21.5° with horizontal) rolls down to the adhesive surface of a PSA specimen. The distance that the ball travels before it stops determines the rolling-ball tack of the PSA. The forces against the rolling ball are generated by the adhesion between the steel ball and the adhesive mass, and by the energy required to push the adhesive out of the ball's rolling path. This test is used primarily for quality control and is not recommended for the specification of a product. The rolling-ball tack results do not correlate well with the tack requirements for most PSA applications [23].

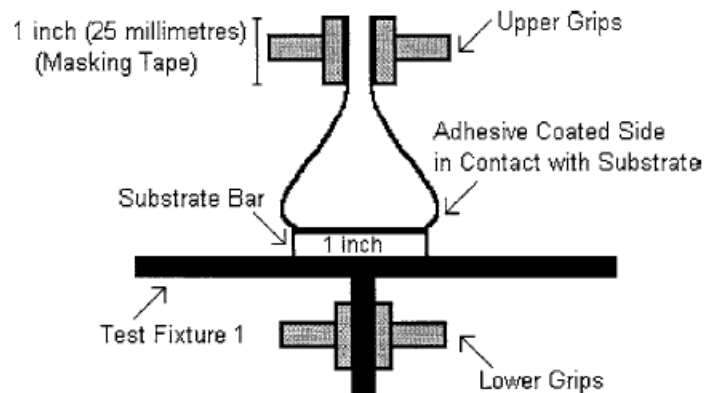


Adopted from ASTM D3121 – 06 [23]

Figure 1.2 Test apparatus for rolling-ball tack test

1.3.1.2 Loop tack test

The loop tack of a PSA product can be measured according to ASTM D6195–03 (2011) [24]. In a loop tack test (Figure 1.3), a loop of tape in a tear-drop shape with the PSA layer facing outside is allowed to be brought into contact to the surface of a stainless steel panel, with a contact area of 25 mm by 25 mm and with a contact pressure generated only by the PSA product itself. The loop of tape is then removed immediately from the surface of the panel by the tester. The maximum force required to break the adhesive bond is recorded and used as a measurement of the tack for the PSA. The loop tack test can be performed using a loop tack tester or a regular tensile tester. The loop tack test is designed for providing a quantitative measurement of the tack properties of a PSA and can be used for quality control and research purpose [24].

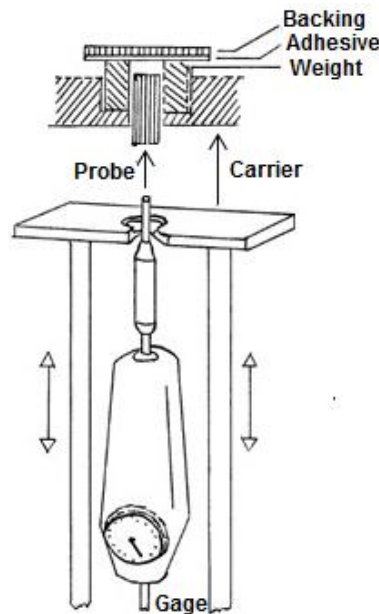


Adopted from ASTM D6195 – 03 (2011)

Figure 1.3 Schematic diagram of a loop tack test

1.3.1.3 Probe tack test

ASTM D2979 - 01(2009) describes a standard test method for measuring the probe tack of a PSA using an inverted probe machine [25]. In the probe tack test (Figure 1.4), a stainless steel rod (5 mm in diameter) is used as a probe; the tip of the probe is allowed to be brought into contact with the PSA layer under a fixed pressure and at a controlled rate. After a known short time such as one second, the probe is removed from the PSA at the controlled rate. The maximum force required to break the adhesive bond is recorded and used as a measurement of the probe tack for the PSA. Like the loop tack test, this test method is designed for providing a quantitative measurement of the tack properties of the PSA and can be used for quality control and research purpose [25].



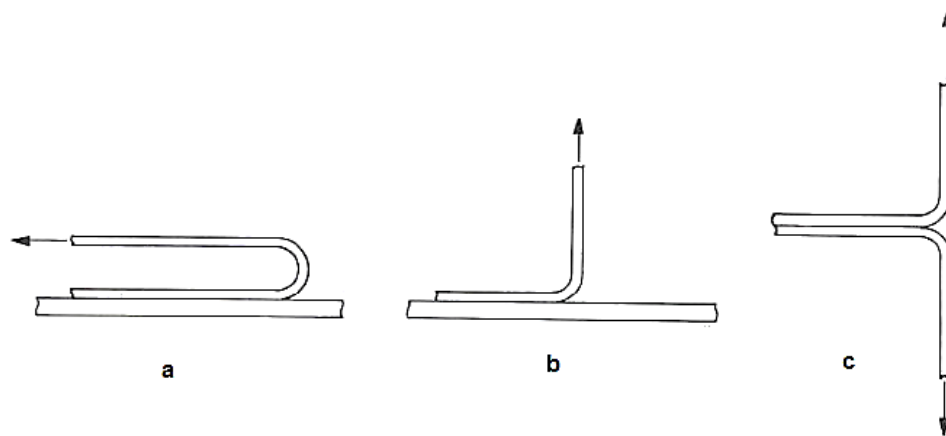
Adopted from ASTM D2979 - 01(2009) [25]

Figure 1.4 Schematic diagram of a probe tack test

1.3.2 Tests for measuring peel adhesion

The peel adhesion of a PSA product can be measured according to ASTM D3330/D3330M–04 (2010) [26]. In the peel adhesion test, a tape specimen of a certain width is applied to a test panel under the pressure generated by rolling a standard roller mechanically or by hand twice in each lengthwise direction at a controlled speed. After one minute, the tape specimen is peeled off at a fixed angle from the test panel at a specified speed. The average force during the peeling is recorded. The peel adhesion is reflected by the force per unit width of the specimen tape [N/cm]. The commonly used peeling angle is 180° (a in Figure 1.5) and 90° (b in Figure 1.5). The 180° peel adhesion test is easier to run than the 90° peel adhesion test, because maintaining a constant angle of 180° during peeling is easier than maintaining a constant angle of 90° . However, at a large angle of 180° , the backing layer deforms more than it does at a smaller angle [21]. The backing layer of some tapes such as glass-filament- reinforced tapes may fracture when bent at 180° [21].

For the determination of the force required to separate an adhesive-to-adhesive bond or the force required to separate a tape specimen from a flexible adherend, a T-peel test can be used (c in Figure 1.5). ASTM D1876–08 describes a standard test method for conducting the T-peel test [27]. The peel adhesion of pressure sensitive label stocks is measured in a similar way to that of pressure sensitive tapes. ASTM D6252/D6252M–98 (Reapproved 2011) describes a standard test method for measuring the peel adhesion of a label at a 90° peeling angle [28].



Adopted from [21]

Figure 1.5 Schematic diagrams of different peel adhesion tests: a, 180°; b, 90°; c, T-peel

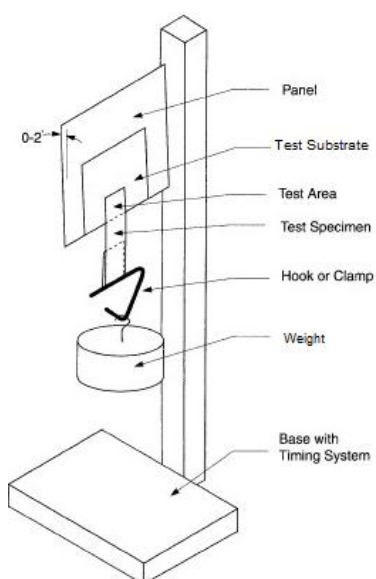
1.3.3 Tests for measuring shear resistance

1.3.3.1 Determination of time to failure

Shear resistance of a PSA product is measured in a static manner. ASTM D3654/D3654M describes a standard test method for measuring the shear resistance [29, 30]. In the shear resistance test (Figure 1.6), a pressure sensitive tape is applied to a test panel with the contact area of 12 mm by 12 mm or 24 mm by 24 mm. The panel is at an angle of 0 to 2° with the vertical direction. The tape is then pressed by a standard roller mechanically or by hand twice in each lengthwise direction. After one minute, a weight of a known mass (500 or 1000 g) is attached to the free end of the tape. A timing system is used to record the time when the pressure sensitive tape fails to adhere to the test panel. The time to failure (i.e., the time between the attachment of the constant mass and the complete separation of the tape from the test panel) is used as the indication of the shear resistance of the PSA. The shear resistance can be used for predicting the end-use

properties of a PSA product, such as die cutting quality, an ability to seal packages, and a vertical holding power [30].

Sometimes, the capacity of a PSA product to hold at an elevated temperature is of interest [29]. For the measurement of the capacity, a test specimen free of an extra weight is applied to the test panel used in the measurement of the shear resistance as described previously (Figure 1.6). The panel and the stand are subsequently moved to an oven that is maintaining at 50 °C. The test specimen is allowed to be conditioned at 50 °C for 10 min. After that, a weight (1000 g) is attached to the free end of the test specimen and the time to failure at 50 °C is recorded.

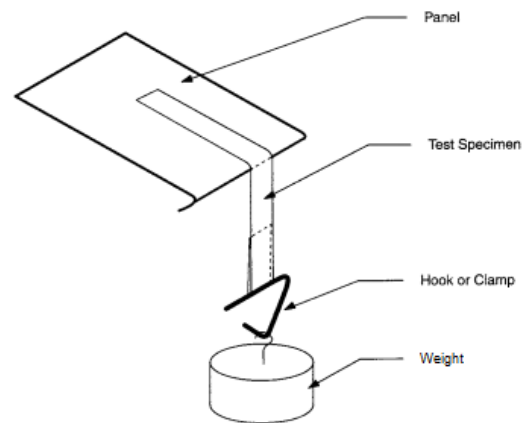


Modified from ASTM D3654/D3654M – 06 (Reapproved 2011) [29]

Figure 1.6 Schematic diagram of a shear resistance test for the determination of the time to failure

1.3.3.2 Determination of shear slippage

For some PSA products such as a filament-reinforced packaging tape used for closing corrugated fiberboard boxes, the shear slippage is more meaningful than the time to failure [29]. For the determination of the shear slippage (Figure 1.7), a tape specimen with the size of 12 mm by 100 mm is pressed by a standard roller mechanically or by hand twice in each lengthwise direction. The panel is mounted horizontally with one end bended downward at an angle of 120° with the horizontal. After one minute, a 4.5 kg mass is attached to the free end of the tape specimen. The shear slippage was measured at the end of 48 h.



Adopted from ASTM D3654/D3654M – 06 (Reapproved 2011) [29]

Figure 1.7 Schematic diagram of a shear resistance test to determine shear slippage

1.4 Early history of PSA products

The earliest PSA products such as adhesive tapes, plasters, and dressings were intended for medical applications [1, 3]. In 1845, William H. Shecut and Horace H. Day invented and patented “a new and improved mode of preparing adhesive plasters for medicinal

purposes” [31]. Before their invention, the then commonly used plasters were stiff, easy to crack, impervious, odorous, and difficult to remove [31]. For solving these problems, they formulated new adhesive plasters with India rubber, pine gum, cayenne pepper, balsam of Peru, litharge, and spirits of turpentine. They also made the new adhesive plasters “pervious to fluids by perforating them with numerous minute holes”. The porous adhesive plasters were coated on cotton cambric or muslin for surgical uses.

In 1874, Robert Wood Johnson and George Seaburg started a plant in New Jersey. This marked the beginning of the industrial production of PSA-coated surgical tapes in the United State [3]. In 1882, Paul C. Beiersdorf, a German pharmacist, developed and patented an improved adhesive plaster based on gutta-percha [6]. He established a company for the business in medical PSA products, which is now known as Beiersdorf, a famous German personal care company. In 1886 Robert Wood Johnson, James Wood Johnson and Edward Mead Johnson founded Johnson & Johnson Company in New Jersey, which is still a major manufacturer of medical tapes [3]. In 1921, Earle Dickson, an employee of Johnson & Johnson, added a piece of gauze to a surgical tape and covered the tape with crinoline. This helped to prevent the tapes from falling off the wound and led to the invention of Band-Aid® [32].

For quite a long time, the applications of PSAs were limited to the medical uses. In the 1920s, the first electrical tapes were produced [33]. Although the cohesive strength of the tapes was low and the adhesive failed cohesively during the unwinding of the tapes, those tapes can be viewed as the very first attempt of industrial application of PSAs [6].

In the late 1920s, the modern history of multifunctional PSA tapes began [3]. Richard G. Drew, an engineer of Minnesota Mining and Manufacturing Company (3M), noticed several problems of using surgical tapes as masking tapes in automobile body painting. For examples, the paint was removed by the adhesive, adhesive residues were left on the car, and marginal edges of the paint were blurry [34]. Drew then developed and patented a rubber-based pressure sensitive masking tape in which saturated paper was used as a backing material [34]. The use of this new masking tape resulted in a clean removal of adhesives and “a clear and clean cut line of demarcation between several colors” [34]. This is also the first use of paper as a backing material. The paper-based backing material had lots of advantages over the commonly used cloth-based backing materials. As Drew depicted, the paper tapes had flexibility, low material costs, high tensile strength, and no surface fibers breaking away and sticking to the PSA layer during the unwinding of a roll; the paper backing also allowed a sharp definition between colors [34]. The use of paper as a backing material widened the applications of PAS tapes [3]. In 1930, Drew used cellophane as the backing material and invented the first transparent film tape, creating the now well-known Scotch® tapes [35]. During the World War II in 1942, in order to meet the need of the US Army for waterproof tapes used for sealing ammunition boxes, Johnson & Johnson invented Duct tape® by coating the fabric backing material with polyethylene [36]. Also because of the high gripping ability, the Duct tape® rapidly found itself to be useful in many other applications such as emergency equipment repairs, and modifications and manufacture of clothing [3].

PSA labels were developed in the 1930s. In 1935, Ray Stanton Avery invented and patented the world's first "self-adhesive, die-cut labeling machine" [37]. He found the company, Kum Kleen Products, for promoting the label business. The company is now known as Avery Dennison Corporation [6].

Today, various PSA products abound in the market and there is a trend for development and production of PSAs from renewable materials such as plant oils and carbohydrates instead of petrochemicals from oil refinery.

1.5 Natural-rubber-based PSAs

1.5.1 Chemical structure and properties of natural rubber

During the 19th century, natural rubber became an important industrial material. Natural rubber is the first natural base polymer used in PSAs [12]. Natural rubber is obtained in the form of latex from the sap of some plants and trees. *Hevea Brasiliensis* trees are the most important sources of natural rubber because they produce a higher yield and a higher quality of rubber than other plants [38]. Today, Thailand, Indonesia, and Malaysia are the top three countries of natural rubber production.

The natural rubber latex may have various compositions. The water content of the latex can be in the range of 50-80 wt% [39]. Besides water, the latex contains a large amount of polyisoprene and a small amount of other organic/inorganic compounds such as proteins, fatty acids, and salts [40]. In the late 1920s, Kurt H. Meyer and Herman Mark discovered that the double bond in the natural rubber molecule had a *cis* configuration

[41]. The natural rubber is a linear poly(*cis*-1,4-isoprene) with the repeating isoprenic unit (C_5H_8). It has a specific gravity of about 0.93 at 20 °C [38].

The molecular weight of the natural rubber is very high. The number-average molecular weight ranged from 2.5×10^5 to 2.7×10^6 g/mol and the weight-average molecular weight ranged from 3.4×10^6 to 1×10^7 g/mol [42]. The molecular weight of the natural rubber is so high that chain entanglements make the dissolution of the natural rubber in organic solvents difficult. Therefore, in the production of the natural-rubber-based PSAs, the natural rubber is often masticated for reducing the molecular weight, thus facilitating its dissolution in an organic solvent [40]. Toluene and heptane are the most widely used solvents for the dissolution of the natural rubber for PSA applications [12]. The masticated rubber is also more plastic and easier to process than the rubber without mastication [12].

Natural rubber has a very low T_g of about -73 °C [43]. The backbone of the natural rubber molecules is very flexible. The carbon-carbon single bonds of the backbone can rotate with respect to each other relatively easily and the natural rubber molecule chains tend to coil up randomly [43]. The chains can be straightened out to a certain degree under tension. Due to the coil-like structure, the natural rubber is an elastic material. The backbone chains of the natural rubber molecules are unsaturated, i.e., containing carbon-carbon double bonds. The double bonds are subject to oxidative degradation, which will lead to chain scission and weaken the cohesive strength of the natural rubber [12]. The natural rubber is often crosslinked or vulcanized. The crosslinking prevents the polymer chains from moving independently, which can harden the natural rubber and

improve the elasticity, cohesive strength, and heat and chemical resistance [40]. Goodyear's sulfur process patented in 1844 is one of the many methods of crosslinking the natural rubber [44].

1.5.2 General composition of the natural-rubber-based PSAs

The natural rubber was first used for PSAs by Schecut and Day in 1845 [31]. They employed India rubber, pine gum, cayenne pepper, balsam of Peru, litharge, and spirits of turpentine to make adhesive plasters for surgical uses [31]. The wide-spread industrial applications of the natural-rubber-based PSAs did not start until the development of masking tapes for automobile painting in the late 1920s [45].

The commercial natural-rubber-based PSAs generally consist of the natural rubber, tackifying resins, and antioxidants [12]. Crosslinking agents, plasticizers, fillers and pigments can also be added. The natural rubber has to be masticated for the reduction of its molecular weight before it can be used for PSAs [46]. The mastication is a very energy-consuming milling process. The degree of milling depends on the desirable pressure sensitive properties required by end uses [46]. Without mastication, the natural rubber does not have the desired level of tack for PSA applications. The milling can also reduce the usage of an organic solvent in the dissolution of the natural rubber and reduce the viscosity of the resulting rubber solution [12]. When the light color of the final natural-rubber-based PSA products such as clear film tapes is an important consideration, the pale crepe grade of the natural rubber is often used. The dark grades of the natural

rubber such as the smoked sheet are less expensive and are often used when the color of the final products is not important [47].

Tackifiers are also used for improving the low tack property of the natural rubber [46]. Within certain limits, increase in the usage of a tackifier improves the tack and the peel adhesion, but decreases the cohesive strength [12]. Besides tackifiers, antioxidants are often added in the natural-rubber-based PSAs, because the natural rubber is susceptible to oxidative degradation. The oxidative degradation can result in a loss of cohesive strength, and can be promoted by heat and UV light [48]. There are generally three main classes of antioxidants for the natural-rubber-based PSAs: aromatic amines, phenolic compounds, and dithiocarbamates such as zinc dithiodibutyl carbamate [49]. Aromatic amines are effective antioxidants, but will stain the surfaces of substrates [12]. Phenolic compounds are the most widely used antioxidants. They are effective against UV degradation and don't stain the PSAs [12]. Dithiocarbamates are also non-staining and provide good protection against heat and also UV to some extent [12]. Antioxidants are often used as a blend to give full protection to the natural-rubber-based PSAs.

The crosslinking of the natural rubber can improve the cohesive strength, heat resistance, and solvent resistance of the resulting PSAs [50, 51]. Sulfur curing agents and phenol-formaldehyde resins such as formaldehyde-nonylphenol resins are commonly used [52]. Diamines or polyamines such as ethylene diamine or hexamethylene diamine [53], titanate esters such as tetraisopropyl titanate or tetrabutyl titanate [54], and isocyanates such as toluene diisocyanate [55] are also used as crosslinking agents for the natural-rubber-based PSAs. Other materials such as plasticizers and pigments may also be used

for lowering the overall cost of materials and for some special applications. For example, mineral oil or lanolin is used as a plasticizer for lowering the unwinding force of the natural-rubber-based PSA tapes [56]. Titanium dioxide is used as a white pigment [57].

1.5.3 Applications of the natural-rubber-based PSAs

The natural-rubber-based PSAs generally don't have good aging resistance because of their high amounts of carbon-carbon double bonds. Therefore, the natural-rubber-based PSAs have limited applications in which high aging resistance, high temperature stability, and non-yellowing are required [12]. Major applications of the natural-rubber-based PSAs include packaging tapes, masking tapes, double-face tapes, electrical tapes, protection masks, and pressure sensitive labels.

Packaging tapes are widely used at home and in industries. The natural-rubber-based PSAs have good tack with respect to paper, making them a good choice for the production of packaging tapes [58]. The natural-rubber-based PSAs are used in the masking tapes that are mainly used in automobile industry during spray-painting operations [51]. The natural-rubber-based PSAs are also used as surface protective films that can be used for protecting various surfaces against damage during production, storage, and transportation [59]. The protective films often require low tack and sufficient cohesive strength for an easy and clean removal. The low tack is typically achieved through a low usage of tackifying resins and a low coating rate [12].

1.6 Polyacrylate-based PSAs

1.6.1 Chemical structures and properties of polyacrylates for PSAs

The tacky properties of some polyacrylates were first reported in the 1930s [60]. Those polyacrylates were homopolymers of the *n*-butyl, 2-ethylbutyl, and isooctyl acrylates [61]. However, those polymers were generally too soft and too weak to be used as PSAs. In 1959, copolymers of isoamyl acrylate or *n*-butyl acrylate with acrylic acid or methacrylate acid were found to have desirable properties for PSA applications [62]. Those copolymers were found to be particularly useful for tapes such as packaging tapes [62].

Monomers that have been used for the preparation of PSAs include acrylic acid, methacrylic acid, *n*-butyl acrylate and 2-ethylhexyl acrylate, methyl methacrylate, ethylene glycol dimethacrylates, *N*-*tert*-butyl acrylamide, and acrylonitrile [60]. Other monomers such as styrene, vinyl acetate and *N*-vinyl pyrrolidone have also been used as comonomers in the preparation of polyacrylate-based PSAs [60]. Monomers are classified based on the T_g of their homopolymers [63]. Monomers are called soft monomers, medium monomers and hard monomers, respectively, if T_g values of their corresponding homopolymers are below -30 °C, between -30 and 30 °C, and above 30 °C, respectively.

Those homopolymers from soft monomers are generally tacky, but soft and weak, whereas those from hard (or medium) monomers are typically non-tacky, but strong [63]. Polyacrylates suitable for PSAs are generally copolymers of a high amount of a soft

monomer (50-90%) and a small amount of a hard (or medium) monomer (10-40%) [64]. The commonly used soft monomers are *n*-butyl acrylate and 2-ethylhexyl acrylate. The commonly used hard monomers include methyl methacrylate, vinyl acetate and styrene [60, 63].

Small amounts of acrylic acid and acrylonitrile are often used as comonomers with soft monomers for improvement of certain PSA properties [60]. For example, it was found that the copolymerization of *n*-butyl acrylate with acrylic acid significantly improved the peel adhesion of the resulting PSAs [65, 66]. The incorporation of a small amount of acrylonitrile in poly(*n*-butyl acrylate) through a copolymerization was found to significantly improve the cohesive strength of the resulting PSAs, which was explained by the formation of hydrogen bonding from the CN groups [60].

Polyacrylates do not contain carbon-carbon double bonds and are more resistant to oxidation than most of the other base polymers such as the natural rubber [67]. Polyacrylates are transparent, colorless, and do not discolor by sunlight, making them suitable for the production of clear tapes [68]. In addition, polyacrylate-based PSAs can be prepared as solutions in organic solvents and as aqueous emulsions, and can easily be coated onto backing materials. They may melt and flow very well at elevated temperature, thus being coated onto backing materials as hot-melt adhesives [60].

1.6.2 Polyacrylate-based PSAs from a solution polymerization method

A solution polymerization method was first used for preparation of polyacrylate-based PSAs in 1940s [69]. An emulsion polymerization method for making polyacrylate-based

PSAs was developed later in 1950s [62]. The solution polymerization is a homogenous free radical polymerization process. Polyacrylates from the solution polymerization are relatively pure, e.g., without undesired surfactants, and can be easily coated onto backing materials [60]. The organic solvent can be readily evaporated, which makes the high speed production of PSA products possible. However, the molecular weight of polyacrylates from a solution polymerization is usually not very high because the free radical addition of the monomers onto the chain ends of polyacrylates becomes more and more difficult when the solubility of the polyacrylates in the reaction medium decreases because of the increase in the molecular weight. Commonly used solvents for the solution polymerization include ethyl acetate, cyclohexane, toluene, and *n*-heptane [60]. The molecular weight of the resulting polyacrylates from the solution polymerization can also be affected by the monomer concentration and the initiator concentration [60]. Low molecular weight polymers are preferred when the monomer concentration is low or the initiator concentration is high [60, 70]. The most frequently used initiator in the solution polymerization is 2,2'-azobisisobutyronitrile [71, 72]. The resulting PSAs generally do not have good adhesive properties if the molecular weight is not sufficiently high. The adhesive properties of PSAs from low molecular weight polyacrylates are usually improved by the chemical crosslinking of polyacrylates [60].

Another disadvantage of polyacrylates from the solution polymerization is that the solution can be very viscous and become very difficult to handle. In addition, the use of an organic solvent for the production and coating of polyacrylates may result in

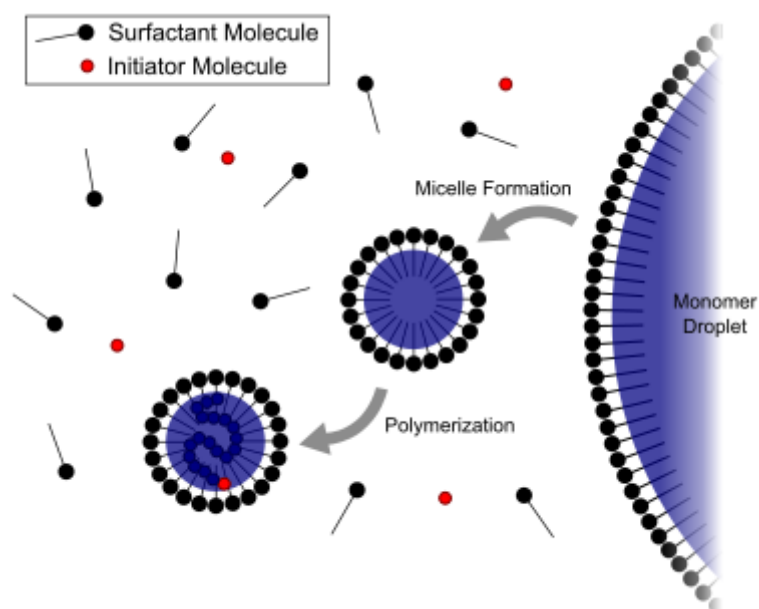
environmental pollution and health issues. The recovery of organic solvents also increases the production cost.

Because of the drawbacks described previously, the solution polymerization method is being replaced by an emulsion polymerization method for production of polyacrylates for PSA applications [60]. However, the emulsion polymerization method has its own drawbacks. For example, polyacrylate-based PSAs from the emulsion polymerization typically have a lower water resistance and a lower drying speed than those from the solution polymerization. As a result, the solution polymerization method is still commercially used for production of polyacrylate-based PSAs.

1.6.3 Polyacrylate-based PSAs from an emulsion polymerization method

Polyacrylate-based PSAs can also be produced by an emulsion polymerization method. The emulsion polymerization is also a free radical polymerization process. The qualitative theory for the mechanism of the emulsion polymerization of a water-insoluble monomer has been described by Harkins in 1947, based on the studies of polystyrene [73]. In 1948, the quantitative theory for the mechanism of the emulsion polymerization was developed by Smith and Ewart [74]. In the emulsion polymerization process, water is used as the solvent. As shown in Figure 1.8, monomers are dispersed in water with the aid of a surfactant and form monomer droplets. The surfactant molecules associate with themselves to create lots of small-size micelles in water. A small amount of monomers diffuses from the monomer droplets through the aqueous solution into the micelles. After the addition of an initiator, the polymerization takes place, mainly in the micelles instead

of the monomer droplets, because the total surface area of micelles is much larger than that of the monomer droplets. As the polymerization proceeds and the monomers in the micelles are used up, more monomers will diffuse into the micelles and react with the growing molecules to form polymers. Eventually, the monomer droplets disappear with the formation of polymer particles. The polymer particles are protected from coalescence by the surfactants. The final product, a dispersion of polymer particles, is also known as a latex or an emulsion.



Adopted from [75]

Figure 1.8 Schematic diagram of emulsion polymerization

Anionic and nonionic surfactants are often used in the emulsion polymerization. Anionic surfactants are often used for improving the storage stability of the emulsion [76]. Electrolytes are used in the emulsion polymerization for increasing the size of the

polymer particles. Nonionic surfactants are typically used in the emulsion polymerization when a high tolerance for electrolytes is needed [60]. The usage of a surfactant is usually 2-5% based on the amount of monomers [60]. A high surfactant concentration may result in a high micelle concentration and thus a large number of polymer particles, which leads to small particle sizes and low molecular weights of the resulting polyacrylates. Surfactants remaining in the polyacrylates cause problems for PSA applications. Over time, the surfactants may migrate from the adhesive mass to the interface of the adhesive and the adherend, which will weaken the bonding strength of the PSAs [60]. In addition to the migration problem, the presence of a surfactant may also increase the water absorbency of the PSAs, resulting in poor water resistance of the PSA products. An excessive amount of a surfactant in the PSAs may also act as plasticizers, which may decrease the cohesive strength and the peel adhesion of the PSAs [60]. One method for preventing the migration of a surfactant is the use of a polymerizable surfactant, which can participate in the free radical polymerization. Sodium-2-sulfoethyl methacrylate, for example, was used as a polymerizable surfactant for producing a poly(isooctyl acrylate-*co*-isobutyl acrylate)-based PSA [77]. A small amount of sodium dodecylbenzene sulfonate having a long lipophilic chain was usually added for improving the initial emulsifying ability [77].

Various initiators can be used for initiating the emulsion polymerization. Initiators that can yield free radicals upon dissociation are called dissociative initiators. Persulfates including ammonium persulfate, sodium persulfate, and potassium persulfate are commonly used [76]. Initiators that can yield free radicals through a reduction-oxidation

reaction are called redox initiators. Commonly used redox initiators include hydrogen peroxide-ferrous ion initiators, hydroperoxide-ferrous ion initiators, and hydroperoxide-polyamine systems [76].

Thickeners are often added for increasing the viscosity of polyacrylate emulsions. The thickened emulsions wet substrates with a low surface energy such as silicone papers and polyolefin films more easily than the emulsion that is not thickened [60]. Poly(acrylic acid), for example, is a useful thickener for the poly(*n*-butyl acrylate-*co*-methacrylic acid) emulsion [78]. Wetting agents might also be added because polyacrylate emulsions with a high surface tension may contract after their application to the surface of an adherend [60]. Sodium alkyl aryl sulfonate, for example, has been used as a wetting agent for the poly(isooctyl acrylate-*co*-acrylonitrile) emulsion [79]. The use of a wetting agent or a surfactant can result in foaming, which is not desirable during a coating process. Defoamers such as fatty alcohols are used for resolving the foaming issue [80].

The emulsion polymerization method has many advantages over the solution polymerization method for the production of polyacrylate-based PSAs. The polymers obtained from the emulsion polymerization usually have higher molecular weights and can be produced at a faster polymerization rate than those from the solution polymerization. The amount of residual monomers in a polyacrylate emulsion is lower than that in a polyacrylate solution. A polyacrylate emulsion is easy to handle because the viscosity of the emulsion remains low during the polymerization. The viscosity of a polyacrylate emulsion does not significantly change until the total solids content reaches as high as 55% [60]. Therefore, a polyacrylate emulsion can have a much higher solid

content than a polyacrylate solution in an organic solvent. Another advantage of a polyacrylate emulsion is free of an organic solvent. Organic solvents are volatile, hazardous, flammable, and expensive. It is difficult to recycle organic solvents in 100%. Emissive organic solvent vapors can cause environmental pollution and creates unhealthy working environment. The recovery of organic solvents also increases operational costs.

However, the emulsion polymerization method also has its shortcomings. The surfactant remaining in the PSAs is usually difficult to remove, may migrate to the adhesive-adherend interface and weaken the bonding strength of the PSAs [77]. Water is more difficult to evaporate than most of organic solvents. It takes longer time and more energy to dry PSA products coated with a polyacrylate emulsion than those coated with a polyacrylate solution in an organic solvent [60]. Overall, the benefits of an emulsion polymerization method outweigh those shortcomings. More and more industrial processes that are currently using the solution polymerization method are being replaced with an emulsion polymerization method.

1.6.4 Hot-melt polyacrylate-based PSAs

Hot-melt PSAs (HMPSAs) are 100% solids. They melt and flow well at an elevated temperature, and can be coated to a backing material in a molten form [81].

The coating of a HMPSA onto a backing material is easy, convenient, and inexpensive. It only requires the input of heat for maintaining a low viscosity of the molten adhesive. An organic solvent or water is not required, thus eliminating the drying step required for the production of PSA products from a polyacrylate emulsion or a polyacrylate solution.

This increases production rates and saves the costs of drying equipment and drying operations [82]. The elimination of an organic solvent also makes the coating process environmentally friendly.

Desirable properties of a HMPSA include a sufficient shear resistance at room temperature for good holding power, a melting temperature of between 120 °C and 180 °C for hot-melt application, and a low viscosity of a molten adhesive for easy processing [83].

For polyacrylates, one commonly used approach for making HMPSAs is introduction of thermally reversible crosslinkings between polymer chains [83-85]. At room temperature, the crosslinkings are stable, and polyacrylates had a sufficient shear resistance to work properly as PSAs. At an elevated temperature, the crosslinkings are temporarily dissociated, and polyacrylates melt and flow well.

Satrijo et al. reported that poly(2-ethylhexyl acrylate-*co*-*n*-butyl acrylate-*co*-acrylic acid) containing pendent carboxylic acid groups was able to form thermally reversible crosslinkings on the addition of magnesium acetate tetrahydrate. [85]. Compared with the uncrosslinked polyacrylate copolymer, the crosslinked polyacrylate had a significantly higher shear resistance, and had a cleaner removal of the adhesive in the peel tests. The crosslinked polyacrylate also melted and flowed well at 150 °C, thus making it a suitable HMPSA [85].

Davis et al. disclosed that poly(2-ethylhexyl acrylate-*co*-acrylonitrile-*co*-4-vinylpyridine) with pendent tertiary amine groups was able to form thermally reversible crosslinkings

with zinc salicylate [83]. The polyacrylate had adequate shear resistance, and melted and flowed well at 180 °C, thus making it a suitable HMPSA [83].

Bartman et al. demonstrated that poly(*n*-butyl acrylate-*co*-*n*-butyl methacrylate-*co*-methacrylic acid) containing pendent carboxylic acid groups was able to form thermally reversible crosslinkings with zinc octanoate [84]. The introduction of zinc octanoate significantly increased the shear resistance of the polyacrylate. The polyacrylate also had a low viscosity at 175 °C, and was readily coated onto a backing material as a HMPSA [84].

1.6.5 Crosslinking of the polyacrylate-based PSAs

Polyacrylates from 2-ethylhexyl acrylate and *n*-butyl acrylate have superior PSA properties such as good tack and good aging resistance. However, PSAs based on those polyacrylates did not have sufficient shear resistance and often had cohesive failure when peeled off from an adherend [86]. Copolymerization of 2-ethylhexyl acrylate or *n*-butyl acrylate with a hard monomer such as acrylic acid or methacrylic acid was found to result in polyacrylate copolymers with increased shear resistance [79]. The crosslinking of polyacrylates was found to be an effective way for improving shear resistance and resistance to water or organic solvents [86].

Crosslinkable polyacrylates are derived from copolymerization of *n*-butyl acrylate or 2-ethylhexyl acrylate with a comonomer containing a reactive functional group on its side chain. The reactive functional group includes a carboxylic acid group, a hydroxyl group, an epoxy group, an amino group, an isocyanate group, and an allylic double bond [60].

The crosslinking reactions may take place during the polymerization of making polyacrylates. Guse et al. disclosed that copolymerization of glycidyl methacrylate, di-2-ethylhexyl fumarate, vinyl acetate, and monoisopropyl fumarate resulted in a crosslinked PSA [87]. The crosslinking reaction between the epoxy functional group from glycidyl methacrylate and the carboxylic acid group from monoisopropyl fumarate occurred during the copolymerization [87]. Ono et al. disclosed that polyethylene glycol dimethacrylate was used as a crosslinkable comonomer in the copolymerization of 2-ethylhexyl acrylate and methacrylic acid for the preparation of a crosslinked PSA [86].

The crosslinking reactions may also take place after a polyacrylate has been produced. Peterson disclosed that hexamethylene diamine was used for crosslinking poly(ethoxyethyl acrylate-*co*-acrylic acid) for PSAs [88]. Hexamethylene diamine reacted with carboxylic acid groups in the copolymer, resulting in crosslinked structures [88]. Polyisocyanates that were derived from reactions of toluene diisocyanate with 1,1,1-trimethylolpropane were also used for crosslinking poly(di-2-ethylhexyl fumarate-*co*-vinyl acetate-*co*-4-hydroxybutyl acrylate) [87].

1.6.6 Additives in the polyacrylate-based PSAs

A tackifier is theoretically not required for polyacrylates that are derived from 2-ethylhexyl acrylate or *n*-butyl acrylate because they are already tacky at room temperature [60]. However, a tackifier is often added for further improvement of the tack and the peel adhesion in actual practices [60]. Rosins and hydrocarbon resins are generally not suitable for the polyacrylate-based PSAs. Commonly used tackifiers for

polyacrylate-based PSAs include modified natural rosins such as dimerized or hydrogenated balsams and esterified abietic acids [80]. Plasticizers are also used in polyacrylate-based PSAs. They improve the flowability and wettability of the adhesive, resulting in improved tack and peel adhesion. Commonly used plasticizers for polyacrylate-based PSAs include phthalates such as dioctyl phthalate, dibutyl phthalate, and diisodecyl phthalate [89].

1.6.7 Polymer blends for polyacrylate-based PSAs

The plasticizers within the PSA layer, the backing layer, or the adherend may migrate to the adhesive-adherend or adhesive-backing interface, thus weakening the bonding strength at the interface, and resulting in losses of tack, peel adhesion and shear resistance [90]. This problem happens often when a plasticized PVC film is used as the backing material for polyacrylate-based PSAs or when PSA products are used to adhere to plasticized PVC plastics [60]. Poly(vinyl methyl ether) or poly(vinyl isobutyl ether) absorbs plasticizers and effectively prevents the migration of plasticizers [60]. It was demonstrated that the migration of the plasticizer was significantly alleviated when poly(vinyl isobutyl ether) was blended into poly(2-ethylhexyl acrylate-*co*-acrylonitrile)-based PSAs [80]. PSAs based on poly(2-ethylhexyl acrylate-*co*-acrylonitrile) and PSAs based on a blend of poly(2-ethylhexyl acrylate-*co*-acrylonitrile) with 20% of poly(vinyl isobutyl ether) were coated onto a PVC film backing material, respectively. The peel adhesion of the poly(2-ethylhexyl acrylate-*co*-acrylonitrile) decreased significantly after 14 days at 60 °C. However, the peel adhesion of the PSAs based on the blend was not significantly affected.

1.6.8 Applications of polyacrylate-based PSAs

Polyacrylate-based PSAs are the most widely used PSAs for labels. Their superior aging resistance makes them particularly useful for outdoor labels [1]. The polyacrylate-based PSAs are also widely used in various tapes, such as packaging tapes, splicing tapes, masking tapes, electrical tapes, and medical tapes [1, 60].

Compared to rubber-based PSAs, the polyacrylate-based PSAs are less irritant to skin, making them useful for applications in the medical field such as bandages and transdermal drug delivery patches. Poly(2-ethylhexyl acrylate-*co*-methacrylate-*co*-acrylic acid) was the first polyacrylate-based PSA suitable for those applications in the medical field [91]. Poly(acrylic acid-*co*-ethoxylethyl acrylate)-based PSAs were first used as splicing tapes for joining two rolls of papers together in paper making or printing operations, because they had superior adhesion to hydrophilic surfaces such as paper or even wet surfaces [92, 93]. Poly(2-ethylhexyl acrylate-*co*-methacrylate-*co*-N-vinyl-2-pyrrolidone)-based PSAs were found to be particularly suitable for electrical tapes, because they had superior gripping capacity and caused little electrolytic corrosion of a conductor [94].

1.7 Styrenic-block-copolymer-based PSAs

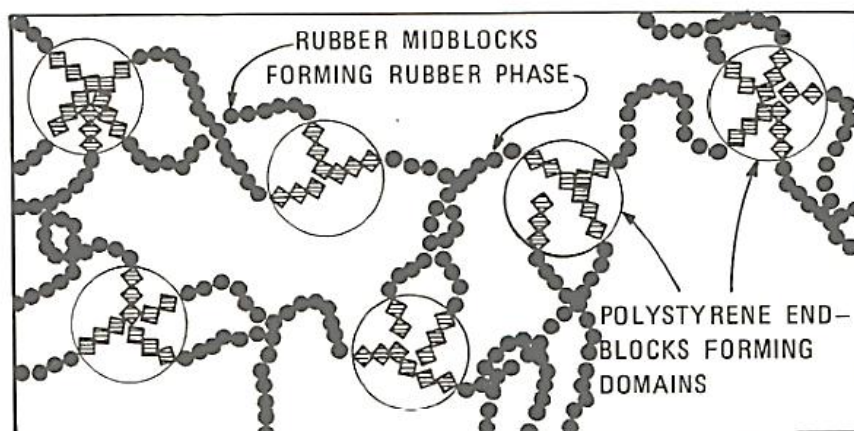
1.7.1 Chemical structure and properties of styrenic block copolymers for PSAs

Styrenic block copolymers (SBCs) are thermoplastic rubbers that have both thermoplastic and elastomeric properties [95]. SBCs that serve as PSAs are typically A-B-A triblock

copolymers containing two thermoplastic polystyrene endblocks (A) and one rubbery midblock polymer (B). A-B-A block copolymers were first used for making PSAs in 1966, including polystyrene-polybutadiene-polystyrene (S-B-S), polystyrene-polyisoprene-polystyrene (S-I-S) block copolymers [96]. Commonly used SBC-based PSAs include S-B-S, S-I-S, and polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S) block copolymers [97].

The rubbery midblock and the thermoplastic polystyrene endblocks are immiscible and incompatible [98]. The midblock polymers have T_g values well below the room temperature, and the polystyrene endblocks have a T_g well above the room temperature. The block copolymers have a two-phase structure: a midblock phase and endblock phases. The polystyrene endblock phases are discontinuous, and attract with each other to form domains that are dispersed in the continuous midblock phase (Figure 1.9) [98]. The difference between T_g values of the two phases has to be greater than 100 °C for ensuring a good phase separation [96].

The polystyrene domains act as crosslinkings between the ends of rubber chains [97]. Unlike the vulcanization of natural rubber, these crosslinkings are thermally reversible, making the A-B-A block copolymers very suitable for HMPSAs [96, 97]. The temperatures often used for the processing and coating of the S-B-S and the S-I-S block copolymers are in the range of 120-180 °C [98]. A high temperature promotes oxidative degradation of the unsaturated midblock. The midblocks of S-B-S and S-I-S block copolymers began to decompose at about 220 °C [98].



Adopted from [98]

Figure 1.9 Schematic diagram of a two-phase structure of A-B-A block copolymers

The practical and economical method for producing A-B-A block copolymers was first disclosed by the Shell Oil Company in 1964 [99]. A-B-A block copolymers are usually prepared by anionic polymerization in an organic solvent in the presence of an alkyl lithium catalyst such as butyl lithium (BuLi) [98, 99]. S-I-S block copolymers, for example, are prepared as shown in Figure 1.10. Styrene is first homopolymerized in the presence of BuLi to generate PS-Li (PS: polystyrene). After the homopolymerization of styrene finishes, isoprene is added and the polymerization continues to provide PS-PI-Li (PI: polyisoprene). After isoprene is all consumed, styrene is subsequently added and polymerized to form PS-PI-PS-Li. When the polymerization completes, a proton donor such as methanol is added for removing the lithium and finally afford the S-I-S triblock copolymers [99].

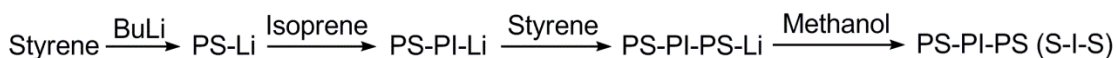


Figure 1.10 Synthetic scheme of the S-I-S block copolymers

A-B-A block copolymers are the latest PSAs joining the PSA markets [1]. They have many advantages for PSA applications. They are easily dissolved in organic solvents such as toluene without mastication [100]. The copolymer solutions have a lower viscosity than those of natural rubber, which allows the preparation of copolymer solutions with a high solids content [98]. A-B-A block copolymers melt and flow very well at 120-180 °C (the desirable processing temperature range without significant degradation of the copolymers), which make them suitable for HMPSAs. The high production volumes and low production costs make A-B-A block copolymers dominant base polymers for HMPSAs [101].

1.7.2 Additives in the SBC-based PSAs

SBCs, like natural rubber, are not inherently tacky. As a result, tackifiers must be added in the SBC-based PSAs [102]. Since A-B-A block copolymers have two incompatible phases, the selected tackifiers may be compatible with either the midblock phase or the endblock phase. Commonly used tackifiers that are compatible with the midblock phase include rosin esters, aliphatic resins, polyterpenes, and terpene phenolic resins [102]. Commonly used tackifiers that are compatible with the endblock phase include coumarone-indene resins and α -methyl styrene resins [103].

Plasticizers are used in the SBC-based PSAs for softening the adhesive polymers, lowering the T_g , increasing the tack, and reducing the melt or solution viscosity [98]. Mineral oils are often used as plasticizers for the SBC-based PSAs [96]. Plasticizers for the SBC-based PSAs should be incompatible with the endblock phases. Otherwise, they will soften the endblock domains and weaken the physical crosslinkings, resulting in a large decrease in the cohesive strength of the PSAs [96].

Stabilizers are often added for the protection of the SBC-based PSAs against oxygen, ozone, and UV degradation. The S-B-S or the S-I-S block copolymers contain an unsaturated midblock and thus especially require stabilizers [96, 104]. Stabilizers should be compatible with the midblock so that they can be in the proximity of the midblock for the protection [98]. Commonly used stabilizers for SBC-based PSAs include antioxidants such as zinc dibutyldithiocarbamate or tri(nonylated phenyl) phosphite, antiozonants such as nickel dibutyldithiocarbamate or N,N'-dibutylthiourea, and UV inhibitors such as *n*-octylphenyl salicylate or resorcinol monobenzoate [98, 104]. For full protection, a blend of different stabilizers is often used [96].

1.7.3 Applications of the SBC-based PSAs

The SBC-based PSAs have a large share of the tape market [1]. The SBC-based PSAs are used in good quality duct tapes [105]. These duct tapes typically have high coating rates and are coated with the SBC-based PSAs in the form of hot melt because solvent removal at high coating rates is difficult and expensive [98]. The SBC-based PSAs are also used as medical PSAs on transdermal drug delivery patches [106]. The SBC-based

PSAs are used in masking tapes in car-painting industry [107]. The polystyrene endblocks have a T_g of about 95 °C. A paint-baking oven having a temperature of up to 170 °C may melt the SBC-based PSAs, resulting in a significant decrease in the cohesive strength of the PSAs. For assuring sufficient cohesive strength in high-temperature environments, the unsaturated S-B-S or S-I-S block copolymers are usually vulcanized, typically with the aid of sulfur [98]. The SBC-based PSAs are also used in low-temperature environments. They are used in tapes or labels for frozen food packaging [98]. For displaying tack in low-temperature environments, a PSA should have a low T_g , because as the end-use temperature decreases and approaches to the T_g of a PSA, the PSA will become rigid, hard to deform, and thus non-tacky. Therefore, the selected tackifiers should have low T_g values for use in low-temperature environments [98]. For example, a S-I-S block copolymer having a T_g of -58 °C was tackified by a synthetic C₅ hydrocarbon resin having a T_g of -28 °C (commercially known as Wingtack® 10) to result in a PSA having a T_g of -45 °C; this PSA was capable of displaying good tack at -18 °C. Whereas, if the S-I-S block copolymer was tackified by a synthetic C₅ hydrocarbon resin having a T_g of 51 °C (commercially known as Wingtack® 95), the resulting PSA had a T_g of -12 °C and displayed no tack at -18 °C [98].

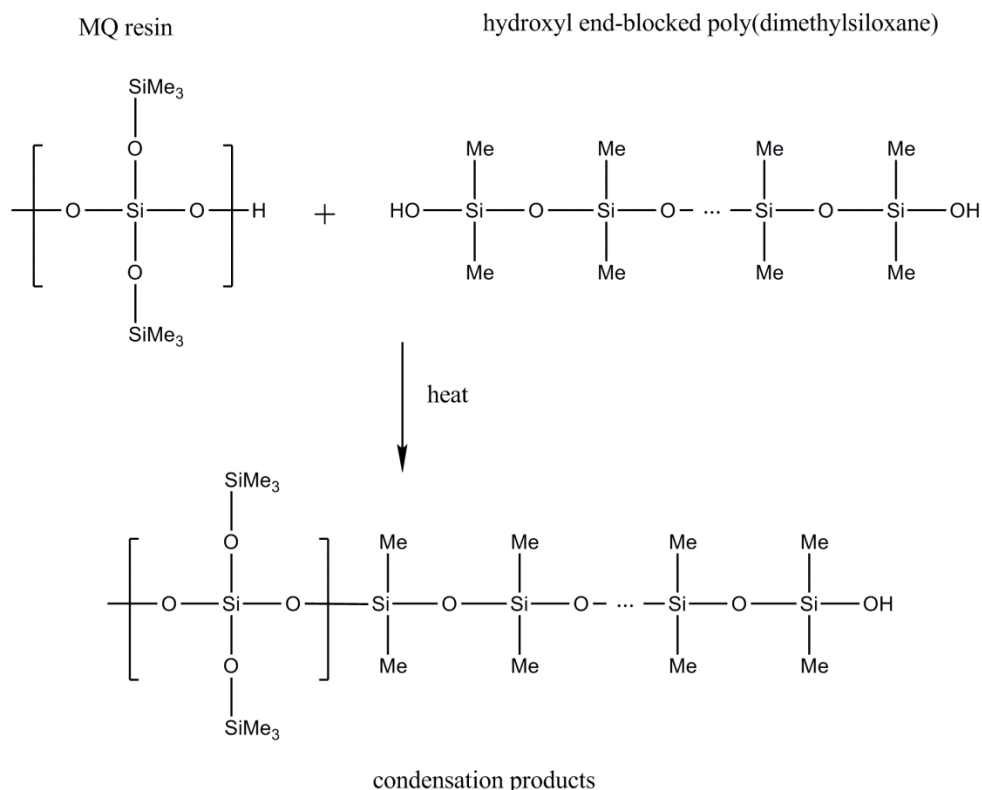
1.8 Silicone-based PSAs

1.8.1 Chemical structure of silicone-based PSAs

Silicone-based PSAs were invented for the need of bonding silicone rubbers to metals in the automotive industry [108, 109]. Before silicone-based PSAs were invented,

adhesives used for bonding the silicone rubbers to metals were not pressure sensitive and required heat for activation of the bonding. In addition, the bonding strength was usually not satisfactory and an appreciable amount of adhesive residues remained on metals when the silicone rubbers were peeled off [108]. The need of electrical PSA tapes that could be used in high-temperature environments for cable insulation was also a driving force [110]. The first silicone-based PSA was developed in 1956 by the Dow Corning Corporation [111].

Silicone-based PSAs are prepared from a siloxane polymer and a silicone-based tackifying resin. Siloxane polymers suitable for PSA applications include poly(dimethylsiloxane) and poly(dimethylsiloxane-*co*-diphenylsiloxane) [96, 97, 108]. Both poly(dimethylsiloxane) and poly(dimethylsiloxane-*co*-diphenylsiloxane) are linear polymers with the molecular weight between 500,000 to 1,500,000 g/mol and with terminal silanol functional groups [112]. The most commonly used tackifying resin in the silicone-based PSAs is MQ resin that comprises a core of Q units (“Q” for SiO_4) surrounded by M units (“M” for Me_3SiO), with a level of silanol functionality on the surface [113]. Typically, for producing the silicone-based PSAs, a siloxane polymer and a MQ resin are condensed usually in a hydrocarbon solvent such as benzene and xylene at an elevated temperature. The condensation reactions of poly(dimethylsiloxane) and a MQ resin are shown in Figure 1.11. Sometimes, condensation reactions between a siloxane polymer and a MQ resin are not required. PSAs based on a non-condensed mixture have good tack and moderate peel strength, but are usually low in shear resistance [97].

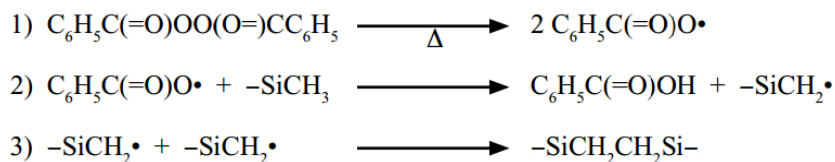


Reproduced from [114]

Figure 1.11 Preparation of silicone-based PSAs

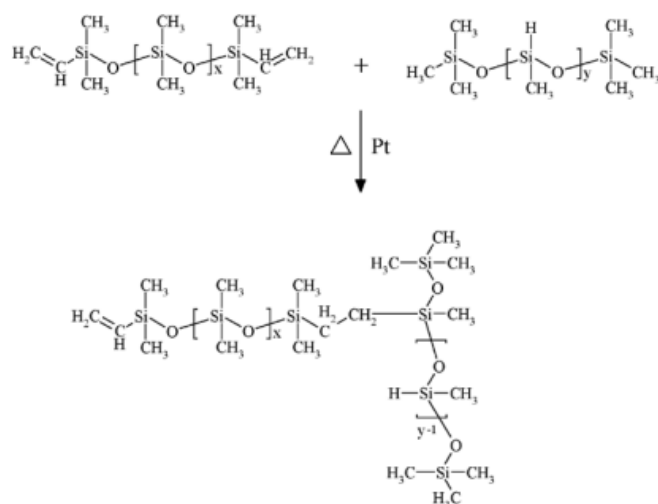
For some special applications in which a very high shear resistance is required, the silicone-based PSAs need to be further crosslinked [115]. Two types of catalysts are commercially available for crosslinking the silicone-based PSAs: peroxide catalysts and platinum-containing catalysts [113]. Peroxides including benzoyl peroxide and 2,4-dichlorobenzoyl peroxide were first used for the silicone-based PSAs in 1958 and are still the most widely used peroxides to date [97, 116]. Benzoyl peroxide is particularly effective [117]. As shown in Figure 1.12, at elevated temperatures between 130 °C and 200 °C, benzoyl peroxide decomposes to form free radicals. The free radicals extract

protons from methyl groups, generating $-\text{SiCH}_2\bullet$ free radicals which then combine to result in crosslinkings through ethylene linkages. The shortcoming of this method is the generation of the by-product, benzoic acid, in the PSAs, which may affect the stability of the adhesives [113]. Platinum-containing catalyst including metallic platinum and chloroplatinic acid were first used for crosslinking siloxane polymers containing silicon-bonded vinyl groups and silicon-bonded hydrogen atoms in 1963 [118]. The crosslinking chemistry is shown in Figure 1.13. At elevated temperatures between 100 °C to 150 °C, the platinum catalyzes the hydrosilylation reaction between silicon-bonded hydrogen atoms and silicon-bonded vinyl groups, resulting in a crosslinked structure with ethylene linkages [119]. Crosslinking by platinum doesn't generate undesirable by-products and requires a lower curing temperature than the crosslinking by peroxides.



Modified from [113]

Figure 1.12 Crosslinking of silicone-based PSAs by benzoyl peroxide



Adopted from [113]

Figure 1.13 Crosslinking of silicone-based PSAs by a platinum catalyst

1.8.2 Unique properties and applications of the silicone-based PSAs

Silicone-based PSAs are typically more expensive than PSAs from natural rubber, polyacrylates, and styrenic block copolymers, but have some unique properties that other PSAs don't have [113]. The silicone-based PSAs are capable of withstanding extreme temperatures and are usable from -80 to 250 °C [111]. They have a very low surface energy and are able to easily conform to various irregular surfaces. They can adhere to surfaces that are difficult to wet such as surfaces of polytetrafluoroethylene (PTFE) and silicone rubbers [97]. The silicone-based PSAs have very good electrical insulating properties [113]. They also have a very good durability and a long service life, and are resistant to biological degradation, moisture, ozone, UV, and most chemicals such as oils, acids, and bases [97].

Silicone-based PSAs are widely used in masking tapes for the production of printed circuit boards. These PSAs are typically based on poly(dimethylsiloxane-*co*-diphenylsiloxane) and the MQ resin, and are crosslinked by benzoyl peroxide or chloroplatinic acid [115, 120]. Polyethylene films are typically used as backing materials for the masking tapes. The masking tapes mask the finished circuits and protect the circuits from being corroded by water or chemical solutions [97]. Polyimide films are used as backing materials when the silicone-based PSA tapes are used for protecting the circuit boards during a solder process where environment temperatures can reach up to 250 °C [120]. The silicone-based PSAs are especially useful for bonding objects with a low-energy surface such as silicone rubbers, silicone coated fabrics, and PTFE [109]. One such product is silicone splicing tapes that are used for joining two rolls of silicone-coated release liners [113]. The silicone-based PSAs are also used in electrical tapes, especially those used for cable insulation in aircraft because of their good electrical insulating properties and ability to withstand extreme temperatures [111].

The silicone-based PSAs are also used in the medical field. Polyacrylate-based PSAs are widely used for transdermal drug delivery; but maybe cause skin irritation for some individuals or when they are used on the same area for an extended period of time [121]. The silicone-based PSAs are particularly useful in skin patches for transdermal drug delivery because they have a good biocompatibility with human skin and are permeable and inert to most drugs [97]. However, amine-containing drugs such as propranolol were found to diminish the tack of the silicone-based PSAs [121]. It has been reported that

reducing the content of silicon-bonded hydroxyl groups in the poly(dimethylsiloxane)-MQ-based PSAs significantly reduced the tack loss by amine-containing drugs [121].

1.9 PSAs based on plant oils and their derivatives

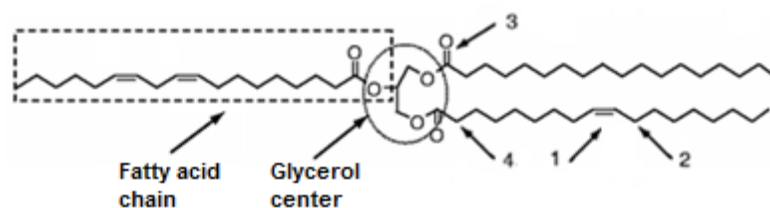
1.9.1 Triglycerides and their derivatives

The PSAs market is thriving and is projected to grow at a compound annual growth rate (CAGR) of 5.8% from 2013 and reach 3459.9 kilotons by 2018 [122]. However, most of the currently used elastomers for PSAs such as polyacrylates and SBCs are based on petrochemicals. Petroleum resources are limited, non-renewable, and non-sustainable. Petroleum-based synthetic polymers are also recalcitrant to biodegradation and their disposal may cause serious long-term environmental problems [123]. Therefore, it is desired to replace petroleum with renewable bio-based materials for the production of PSAs.

Plant oils are currently one of the most important renewable raw materials in the chemical industry. They are abundant and readily available. Soybean oil is one of the most important plant oils, which accounts for one quarter of the global plant oil production. Other important plant oils include palm oil, rapeseed oil, and sunflower oil [124]. Plant oils are mainly mixtures of triglycerides. Depending on the plant or the crop type and the growing conditions, the triglycerides can have a varying composition of long-chain saturated or unsaturated fatty acids [125,126]. Triglycerides offer a number of reactive sites for functionalization, such as the double bond, the allylic carbon, the ester

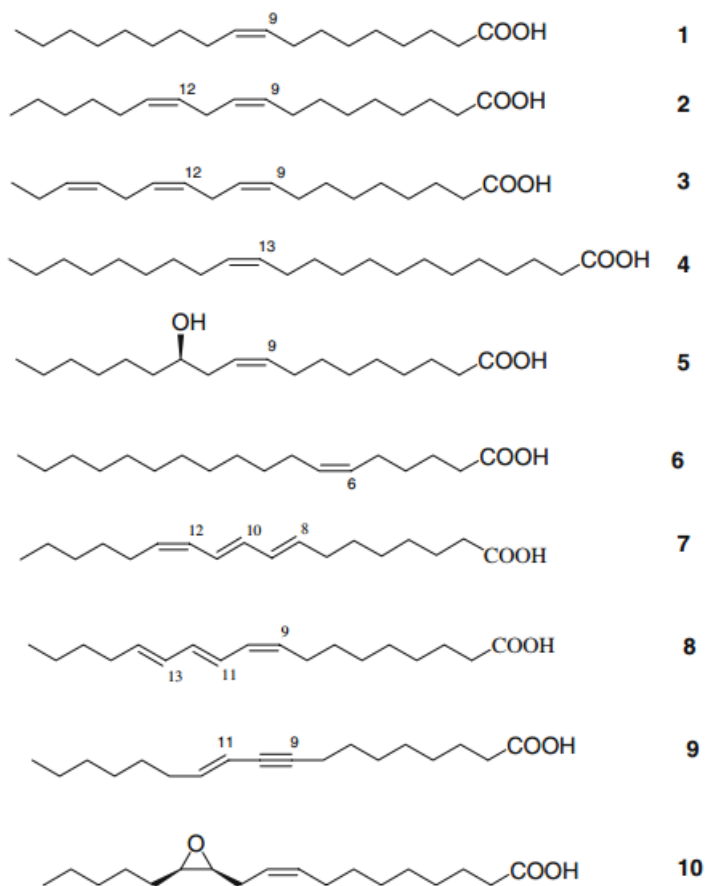
group, and the α -carbon to the ester group [127] (Figure 1.14). Fatty acids or fatty esters are derivatives of plant oils. Fatty acids that can be potentially used for preparations of PSAs include oleic acid from olive oil or high oleic sunflower oil, linoleic acid from soybean oil, linolenic acid from linseed oil, erucic acid from rape seed oil, and ricinoleic acid from castor oil (Figure 1.15) [123].

Plant oils and their derivatives have been widely used as raw materials for rubbers, plastics, coatings, paints, and various thermosetting composites [125, 128-130]. Extensive research efforts have also been made for development of PSAs from plant oils or their derivatives [70, 131-137]. The use of plant oils and their derivatives as starting materials for PSAs has many advantages such as low cost, low toxicity, and inherent biodegradability. Plant-oil-based products also have considerable environmental benefits because they don't lead to a net gain of CO₂ in the atmosphere [138].



Modified from [139]

Figure 1.14 Diagram of a triglyceride molecule. Fatty acids are connected to a glycerol center. Different functionalities are shown with the corresponding numbers: (1) double bonds, (2) allylic carbons, (3) ester groups, and (4) α -carbons



Adopted from [123]

Figure 1.15 Fatty acids as starting materials for the synthesis of novel fatty compounds: 1 Oleic acid, 2 linoleic acid, 3 linolenic acid, 4 erucic acid, 5 ricinoleic acid, 6 petroselinic acid, 7 calendic acid, 8 α -eleostearic acid, 9 santalbic acid, and 10 vernolic acid

1.9.2 Development of PSAs from fatty acids and fatty esters

Development of PSAs from fatty esters and fatty acids has been extensively studied and can be summarized into four approaches. In the first approach, fatty esters are first epoxidized to form epoxidized fatty esters. The ring-opening of the epoxy group with acrylic acid or methacrylic acid generates acrylated or methacrylated fatty esters, which

are subsequently polymerized via a free radical polymerization process to result in PSAs [70, 131, 132].

Acrylated epoxidized methyl oleate (AMO) was synthesized from the epoxidation of methyl oleate, followed by the ring-opening with acrylic acid [70]. Bunker and Wool reported that the copolymerization of AMO with acrylic acid generated a PSA through an emulsion polymerization method [70]. The peel strength of this AMO-based PSA was higher than that of a Post-it® note but lower than that of an office tape [70]. There are many different types of office tapes in the market; the exact type of the office tape used was not mentioned [70]. The failure mode, i.e., adhesive failure or cohesive failure, in the peel tests was not reported. Whether there were any adhesive residues remained on the testing panel was also not mentioned. The shear resistance of this PSA was low and not comparable to commercial PSAs [70]. Copolymerization of AMO with a crosslinkable comonomer, ethylene glycol dimethacrylate (EGDM), effectively improved the shear resistance of the resulting PSAs [70]. However, the change in the peel strength of the resulting PSAs was not reported. It was not clear if the introduction of EGDM had improved other adhesive properties in addition to the shear resistance. The rate of polymerizing AMO appeared to be slow, evidenced by that it took 18 h to achieve a monomer conversion of about 91% [131]. The amount of a surfactant needed in the emulsion polymerization was as high as 15 wt% based on the total weight of monomers [70]. The tack and the aging resistance of these AMO-based PSAs were not reported [70]. Without knowing these results, it is difficult to conclude whether these PSAs have all desirable properties for a commercially viable application.

Bunker and Wool later reported a new AMO-based PSA that was prepared by the copolymerization of AMO, methyl methacrylate (MMA) and 1,4-butanediol diacrylate (BDDA) through an miniemulsion polymerization method which effectively shortened the polymerization time to 1 h and lowered the usage of a surfactant to 2 wt% based on the total weight of monomers [131]. The new AMO-based PSA was evaluated for the tack, the peel strength, and the shear resistance. This PSA didn't appear to have a good balance among the tack, the peel strength, and the shear resistance [131]. The peel strength of this PSA was very low, although the tack and the shear resistance were satisfactory and comparable to those of a commercial PSA [131]. Lowering the usage of the crosslinkable monomer, BDDA, slightly improved the peel strength but significantly decreased the shear resistance. The improved peel strength was, however, still too low to be comparable to a commercial PSA [131]. No further work on improving the peel strength was reported. The new AMO-based PSA had better tack and better shear resistance than the previously reported PSA prepared from an emulsion polymerization method. However, it was not clear if the improvement was due to the new polymerization method or a new crosslinkable comonomer. The aging resistance of this new PSA and the failure modes in its tack and peel tests were not reported [131]. Without knowing these results, it is difficult to conclude whether this PSA has balanced properties for a commercially viable application.

Klapperich and Wool investigated the cytocompatibility of PSAs that were derived from copolymerization of AMO with MMA and EGDM with Alamar Blue and Live/Dead assay [133]. The PSAs were found to be compatible with human fibroblast cells, thus

having a potential of being used in the medical field [133]. The tack of the PSAs was measured, but was not compared with that of a commercial PSA. The PSAs had a clean removal during the tack tests. The peel strength, the shear resistance, and the aging resistance of the PSAs were not reported. Without knowing these properties, it is difficult to conclude whether the PSAs have all desirable properties for a commercial application.

Wool and Bunker disclosed two more AMO-based PSAs in a US patent [132]. One of them was prepared by the emulsion polymerization of AMO and acrylated linoleic methyl ester (ALM). The peel strength of this PSA was measured but was not compared with that of a commercial PSA. Another AMO-based PSA was prepared by the miniemulsion polymerization of AMO, MMA, and ALM. The peel strength and the shear resistance of this PSA were reported but were not compared with those of a commercial PSA.

In the second approach, epoxidized fatty esters or epoxidized fatty acids are polymerized for preparation of PSAs via a cationic ring-opening polymerization [137]. Koch mentioned in a patent application that epoxidized oleic acid or epoxidized erucic acid was homopolymerized or copolymerized with epoxy or vinyl ether monomers to form PSAs [137]. However, epoxy or vinyl ether monomers were not specified, experimental procedures for the preparation of the PSAs were not provided, and adhesive properties of the PSAs were not reported. It is hard to determine the approach mentioned in this patent application can actually generate polymers with all desirable properties for a commercial application.

In the third approach, conjugated fatty acids are used for preparing PSAs by the free radical polymerization method [137]. Carbon-carbon double bonds in natural fatty acid chains are typically not conjugated, except that tung oil contains a very high amount of conjugated α -eleostearic acid [140]. The unconjugated double bonds in fatty acids are generally not sufficiently reactive for formation of high-molecular-weight homopolymers or copolymers that have sufficient strength for PSA applications [70]. Koch mentioned in a patent application that tung oil was first hydrolyzed to provide fatty acids with conjugated double bonds and then PSAs were prepared through a free radical polymerization of the resulting fatty acids with acrylic monomers [137]. However, the composition of the resulting fatty acids was not determined and the acrylic monomers were not specified. Experimental procedures for the preparation of the PSAs were not provided, and adhesive properties of the PSAs were not reported [137]. It is difficult to determine whether the polymers mentioned in the patent application have all desirable properties of a commercially viable PSA.

In the fourth approach, glycidyl methacrylate (GMA) was reacted with lauric acid to form methacrylated lauric acid that was homopolymerized or copolymerized with acrylic monomers to generate PSAs [137]. However, the acrylic monomers were not specified, experimental procedures for the preparation of the PSAs were not provided, and adhesive properties of the PSAs were not reported [137]. It is hard to determine if this approach can really generate polymers that have all desirable properties of a commercially viable PSA.

1.9.3 Development of PSAs from plant oils

Development of PSAs directly from plant oils has been studied and can be summarized into three approaches.

In this first approach, plant oils are first epoxidized and then modified with acrylic acid to form acrylated epoxidized plant oils that can be copolymerized with acrylic monomers to result in PSAs [136, 137]. David et al. prepared a PSA based on the copolymer of acrylated epoxidized soybean oil (AESO) with *n*-butyl methacrylate [136]. In this study, soybean oil was first epoxidized and subsequently modified with acrylic acid, to generate the AESO. The AESO was copolymerized with *n*-butyl methacrylate by a free radical, bulk polymerization method to result in a copolymer with PSA properties [136]. The peel strength and the shear resistance of this PSA were measured but were not compared with those of a commercial PSA. This PSA had a clean removal in the peel tests which is desirable for any PSA applications. The tack and the aging resistance of this PSA were not reported [136]. Without these properties, it is hard to determine whether this PSA has all desirable properties for a commercial application. The antimicrobial activity of this PSA was also investigated for its potential applications in the biomedical field. It was found that this PSA had antimicrobial activity against gram positive bacteria *S. aureus* ATCC 25923, evidenced by that the normal growth of the gram positive bacteria on this PSA was inhibited [136]. However, this PSA didn't exhibit antimicrobial activity against gram negative bacteria *E. coli* ATCC 25922. It was mentioned that this PSA should be loaded with broad spectrum antibiotics like tobramycin or gentamycin for protection against gram negative bacteria for clinical applications [136].

Koch reported in a patent application that AESO was used for curing a polyacrylate that was derived from copolymerization of *n*-butyl acrylate, 2-ethylhexyl acrylate, and acrylic acid [137]. The peel strength and the shear resistance of the resulting PSA were measured, but were not compared with a commercial PSA [137]. This PSA didn't contain a high amount of bio-based materials, evidenced by that the usage of AESO was only about 10 wt% of the entire PSA [137]. The failure mode in the peel tests was not reported; the tack and the aging resistance of this PSA were not measured as well. Without these results, it is hard to determine if this work has any value.

Koch also mentioned in a patent application that acrylated epoxidized palm oil (AEPO) was first prepared from epoxidation of palm oil followed by modification with acrylic acid. A PSA was then prepared from copolymerization of AEPO with acrylic monomers. However, acrylic monomers were not specified, experimental procedures for the preparation of AEPO and the PSAs were not provided, and adhesive properties of the PSAs were not reported [137]. It is hard to determine whether the resulting polymer has any desirable properties of a commercially viable PSA.

In the second approach, the epoxidized plant oils undergo cationic ring-opening polymerization to form PSAs [137]. Vikoflex® 4050 is a commercially available epoxidized vegetable oils such as linseed oil [141]. Koch mentioned in a patent application that a PSA was prepared from copolymerization of Vikoflex® 4050 with epoxidized soybean oil (ESO) through a cationic polymerization [137]. Koch also mentioned in the patent application that 2-ethylhexylacrylate, *n*-butyl acrylate, acrylic acid, and GMA were first copolymerized in ethyl acetate to generate a polyacrylate and

then a PSA was prepared from copolymerization of Vikoflex® 4050, ESO, and the previously described polyacrylate through a cationic polymerization [137]. Adhesive properties of the resulting PSAs were not reported. It is hard to determine if the resulting PSAs have all desirable properties for a commercial application.

Koch mentioned in a patent application that a PSA was prepared from copolymerization of AEPO and other monomers including epoxy acrylics or vinyl ethers through a cationic polymerization [137]. However, epoxy acrylics or vinyl ethers were not specified, experimental procedures for the preparation of the PSA were not provided, and adhesive properties of the PSA were not reported [137].

In the third approach, ESO was cured by phosphoric acid for preparation of a PSA [134, 135]. Dihydroxyl soybean oil (DSO) was first prepared through hydrolysis of ESO in the presence of perchloric acid. A mixture of ESO and DSO was then cured with phosphoric acid at 110 °C for 60 s by a hot-air dryer to result in an EOA-based PSA [134]. This EOA-based PSA had a clean removal in the peel tests and had a peel strength comparable to that of a Post-it® note [134]. However, the tack, the shear resistance, and the aging resistance of the PSA were not reported [134]. Without these properties, it is hard to determine whether the PSA has desirable properties for a commercial application.

Phosphate esters of DSO (PDSO) was later prepared through reactions of ESO with phosphoric acid [135]. A mixture of ESO and the PDSO was then cured in the presence of phosphoric acid at 110 °C for 60 s to form a PSA [135]. The resulting PSA was found to have a higher peel strength than the previously reported EOA-based PSA from the

direct curing of a mixture of ESO and DSO with phosphoric acid [135]. However, the tack, the shear resistance, and the aging resistance of the resulting PSA were not reported as well. It is hard to determine if the PSA has desirable properties for a commercial application.

1.10 Development of PSAs from other renewable resources

In addition to plant oils, fatty acids, and fatty esters, the bio-based PSAs were also prepared from other renewable resources such as carbohydrates [142, 143]. A PSA based on polylactide-polymenthide-polylactide (PLA-PM-PLA) triblock copolymers and a rosin ester tackifier was reported [142]. The midblock polymer, polymenthide, was prepared from the ring-opening polymerization of (–)-menthide, a seven-membered lactone that was derived from naturally occurring (–)-menthol in mints, with diethylene glycol [144]. The endblock polymer, polylactide, was prepared from lactide that was derived from carbohydrates [143]. For the preparation of the PLA-PM-PLA triblock copolymers, the polymenthide was used as a macroinitiator in the ring-opening polymerization of lactide [142]. The triblock copolymers were tackified by a rosin ester tackifier (0~60% of total weight) to form PSAs [142]. The tack, the peel strength, and the shear resistance of the resulting PSAs were measured. It was found that the PSA tackified by 40 wt% rosin ester had a clean removal in the tack tests and the peel tests and had the highest tack and peel strength, which were comparable to those of a commercial PSA [142]. However, the aging resistance of these PSAs was not reported. It is not clear if the adhesive properties of this PSA can still remain satisfactory over time.

A PSA that was based on a polyacrylate but had a high content of bio-based chemicals has been prepared [143]. Lactide and ϵ -caprolactone can be derived from carbohydrates and can be considered bio-based chemicals [143]. The ring-opening copolymerization of lactide and ϵ -caprolactone with 2-hydroxyethyl methacrylate resulted in a macromonomer, acrylated poly(lactic acid-*co*- ϵ -caprolactone) [143]. The macromonomer was copolymerized with *n*-butyl acrylate, vinyl acetate, and methacrylic acid via a miniemulsion polymerization method to form a PSA that contained about 45 wt% of bio-based chemicals. The tack, the peel strength, and the shear resistance of the resulting PSA were comparable to those of a commercial PSA. The failure modes in the tack tests and the peel tests as well as the aging resistance were not reported. It is hard to determine whether this PSA has desirable properties for a commercial application.

1.11 Study objectives

Plant oils, fatty acids, and fatty esters are attractive raw materials for replacing petrochemicals in the preparation of PSAs. However, most of the reported bio-based PSAs still used a significant amount of petrochemicals, and were not fully evaluated for properties required for PSA applications [70, 131-137, 142-145].

In this study, we reported a novel and simple approach for the development of PSAs from epoxidized oleic acid (EOA). Preparation of EOA was extensively studied, starting from oleic acid or methyl oleate that is abundant and readily available from high oleic plant oils such as olive oil (oleic acid content, ~71%), canola oil (61%), sunflower oil (42%), palm oil (39%), and high oleic sunflower oil (>90%) [147]. The polymerization of EOA

for PSAs was extensively studied. The PSAs were characterized and were fully evaluated for the tack, the peel strength, the shear resistance, and the aging resistance.

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Chapter 2 - Pressure Sensitive Adhesives based on Oleic Acid

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2.1 Abstract

Existing pressure sensitive adhesives (PSAs) are mostly based on petrochemicals. In this study, a novel PSA based on a renewable material, methyl oleate, was prepared and characterized. Methyl oleate was first epoxidized to form epoxidized methyl oleate that was subsequently hydrolyzed and acidified to form epoxidized oleic acid (EOA) which is an AB-type monomer containing both a carboxylic acid group (A) and an epoxy group (B). Various methods for the preparation of EOA with high purity were extensively studied. EOA was homopolymerized in the presence of a catalyst to generate a polyester that could serve as a PSA. Various catalysts were investigated for their effectiveness on the homopolymerization, and chromium (III) tris(acetylacetonate) was found to be the most effective catalyst. Effects of the EOA purity on the PSA properties of the resulting polyesters were investigated in detail; the EOA purity of at least 97% was found to be required for the preparation of the PSA with superior properties. The crosslinking of the polyesters with very small amount of crosslinking agents was able to further improve the overall properties, especially the aging resistance of the resulting PSAs. Among various crosslinking agents investigated, polymeric methylene diphenyl diisocyanate was the most effective in improvement of the PSA properties. The PSAs were evaluated for their

peel strength, tack force, shear resistance, and aging resistance. The PSAs were characterized for their viscoelastic properties, thermal properties, thermal stability, and chemical structures.

2.2 Keywords

pressure sensitive adhesive; vegetable oil; epoxidation, oleic acid; methyl oleate; alkene

2.3 Introduction

A pressure sensitive adhesive (PSA) is an adhesive that is tacky at use temperature and forms a bond with a variety of substrates when light pressure is applied for achieving the wet-out of the adhesive onto the substrate surface. The ability to bond without activation by water, solvents, heat or radiation distinguishes the PSA from other types of adhesives. The PSA provides aggressive and permanent tack and adequate adhesion to an adherend, and has sufficient cohesive strength to be cleanly removed from the adherend [1]. PSA products such as labels and tapes are widely used in homes and workplaces. PSAs typically contain an elastomeric material and small amounts of tackifiers, processing oils, and waxes [1]. At present, the most commonly used elastomeric materials are petrochemical-based polymers such as polyacrylates and styrenic block copolymers. Tackifiers such as C-5 and C-9 resins and waxes used in PSAs are also typically derived from petroleum. Petroleum is non-renewable and thus not sustainable. Therefore, it is desirable to develop PSAs from renewable natural materials such as fatty acids.

Fatty acids or fatty esters can be derived from vegetable oils and kraft pulping of wood and other plant-based biomass, and are abundant, renewable, and readily available. Some

fatty acids have saturated hydrocarbon chains and some contain unsaturated hydrocarbon chains, i.e., carbon-carbon double bonds [2, 3]. Oleic acid is one of the most abundant unsaturated fatty acids in nature.

Development of PSAs directly from plant oils such as palm oil and soybean oil has been studied [4-7]. Development of PSAs from fatty esters or fatty acids has also been extensively studied, which can be summarized into four general approaches. In the first approach, fatty esters are first epoxidized to form epoxidized fatty esters. Ring-opening reactions of the epoxy groups in epoxidized fatty esters with acrylic acid or methacrylic acid generate acrylated or methacrylated fatty esters that are polymerized via a free radical polymerization process to result in PSAs. In this approach, fatty ester chains are used to replace butyl and 2-ethylhexyl groups in butyl acrylate and 2-ethylhexyl acrylate (these are two commonly used petrochemical-based monomers for PSAs). Petrochemical-based acrylic acid or methacrylic acid is still required [4, 8-11]. In the second approach, epoxidized fatty esters are polymerized to form PSAs via cationic ring-opening polymerization of the epoxy group. Some other petrochemical-based epoxy compounds or vinyl ethers have to be used as co-monomers in the cationic polymerizations [4]. Carbon-carbon double bonds in natural fatty acid chains are typically not conjugated, and polymerizations of unconjugated carbon-carbon double bonds typically cannot generate polymers with sufficiently high molecular weights for PSA applications. Therefore, in the third approach, unsaturated fatty acids are first converted into conjugated fatty acids followed by free radical polymerization with other acrylic monomers to form PSAs [4]. The fourth approach involves the reaction between

the carboxylic acid group of a fatty acid and glycidyl methacrylate to form methacrylate monomers, which can be copolymerized with other acrylic monomers to form PSAs [4]. In all these four approaches, significant amounts of petrochemicals are still required for achieving decent PSA properties. The second, the third and the fourth approaches were revealed in patent applications [4]. Petrochemical-based comonomers were not specified, experimental procedures for the preparation of the PSAs were not provided, and adhesive properties of the PSAs were not reported [4]. It is hard to determine whether these three approaches can really lead to PSAs with desirable properties for a commercially viable application. In addition, no reports can be found about the aging resistance of those bio-based PSAs reported so far, including PSAs from triglyceride [4-7], fatty acids or fatty esters [4, 8-11], and/or carbohydrate derivatives [12-16].

In this study, we report a novel and simple approach for preparation of PSAs from methyl oleate that can be derived from plant oils with a high oleic acid content, such as olive oil (oleic acid content, 71%), canola oil (61%), sunflower oil (42 to 90%), and palm oil (39%) [17]. The PSAs were characterized and evaluated for their adhesive properties in detail.

2.4 Experimental

2.4.1 Materials

Methyl oleate (MO) (99%), chromium (III) tris(acetylacetonate) (CTAA) (97%), dibutyltin dilaurate (DBTDL) (95%), hydrogen peroxide (35 wt% and 50 wt% aqueous solution), oleic acid (OA) (99%), peracetic acid (32 wt% in dilute acetic acid), N,N,N',N'-tetramethyl-ethylenediamine (99%), tetraphenylphosphonium bromide (97%),

dimethylbenzylamine (99%), trimethylolpropane triglycidyl ether (TMPTGE) (technical grade), bisphenol A diglycidyl ether (BADGE), and tris(2,3-epoxypropyl) isocyanurate (TEPI) were purchased from Sigma-Aldrich (St. Louis, MO). Formic acid (97%) was purchased from Alfa Aesar (Ward Hill, MA). Polymeric methylene diphenyl diisocyanate (pMDI) was obtained from Huntsman Polyurethanes (Woodlands, TX). N-methylmorpholine (99%) was manufactured Acros Organics and purchased from VWR International, Inc. (West Chester, PA). Epoxidized soybean oil (ESO) (iodine value of 2.0) was manufactured by Spectrum Chemical Mfg. Corp. (Gardena CA) and purchased from VWR International, Inc. (West Chester, PA). The BOPP (bi-axially oriented polypropylene)-based backing film, PET (polyethylene-terephthalate)-based release film, and a release liner were obtained from Avery Dennison Corp. (Pasadena, CA). All common chemicals and solvents were purchased from commercial sources and used as received.

2.4.2 Synthesis of epoxidized oleic acid (EOA) directly from OA.

2.4.2.1 Epoxidation of OA with hydrogen peroxide

OA was epoxidized in the presence of formic acid and hydrogen peroxide according to a slightly modified literature procedure [18]. Hydrogen peroxide (50 wt% aqueous solution, 2.93 g) was added dropwise to a mixture of OA (5.00 g) and formic acid (5.48 g) in a 100-ml three-neck flask equipped with a mechanical stirrer, a thermometer, and an addition funnel under vigorous stirring at 4 °C over 5 min. The reaction mixture was then stirred at room temperature for about 2 h, which resulted in the formation of a solid. The

solid was collected by vacuum filtration, washed with chilled water (5 °C, 4 × 150 ml), and dried under high vacuum. The resultant solid (4.79 g, 60% EOA, 34% unreacted OA, and 6% byproducts) was pale pink and slightly waxy and was characterized by nuclear magnetic resonance (NMR).

Increase in the reaction time of the exactly same experiment as described previously from 2 to 3.5 h at room temperature resulted in a white powder (4.15 g; 70% EOA, 6% unreacted oleic acid, 24% byproducts).

The EOA content was estimated by the ratio of the peak area of the two **CH**-protons of the epoxy ring at 2.91 ppm over the peak area of the α -**CH**₂ adjacent to the carbonyl group at 2.34 ppm (i.e., the epoxy/COOR ratio) in the ¹H NMR spectrum. The content of unreacted oleic acid was estimated by the ratio of the peak area of two **CH**-protons of the double bond at 5.35 ppm over the peak area of the α -**CH**₂ adjacent to the carbonyl group at 2.34 ppm in the ¹H NMR spectrum.

2.4.2.2 Epoxidation of OA with peracetic acid

Epoxidation of OA with peracetic acid was conducted in accordance with a literature procedure [19]. The usage of OA was proportionally scaled down from 500 g in the literature procedure to 2 g in this study. OA (2.01 g) was added to a well-stirred solution of peracetic acid (32 wt% in dilute acetic acid, 2.02 g) and de-ionized water (6.31 g) in a 50-mL round-bottom flask over 15 min at 18 °C with an icy-water bath. The reaction mixture was stirred for 3 h at 18 °C and then poured into a separation funnel which contained chilled water (5 °C, 50 mL). A layer of a solid was formed on top of the

aqueous phase and collected by draining the lower aqueous phase. The solid was further washed with chilled water (5 °C, 2 × 50 mL) and dried under high vacuum to afford a waxy white solid (1.61 g, 9% EOA, 90% unreacted oleic acid, and 1% byproducts) that was characterized by NMR.

2.4.3 Synthesis of EOA from methyl oleate (MO)

2.4.3.1 Preparation of epoxidized methyl oleate (EMO)

Epoxidation of MO was performed according to a modified literature procedure [20]. MO (12.00 g) and formic acid (6.00 g) were placed in a 100-ml round-bottom flask equipped with a magnetic stirrer and thermometer. After the resulting mixture was cooled to 0 °C in a salty-ice water bath, hydrogen peroxide (35 wt% aqueous solution, 8.32 g) was added dropwise over 15 min while stirring. The mixture was stirred at 5 °C for 2 h and then at 23 °C for about 11.3 h. The resulting mixture was then extracted with hexane three times (3 × 50 ml). The combined organic phases were washed successively with saturated sodium bicarbonate solution (2 × 100 ml) and brine (2 × 150 ml). The resulting neutral mixture was dried over anhydrous magnesium sulfate and then filtered. Evaporation of the hexane afforded clear, colorless oil (12.55 g, 91% of EMO). ¹H NMR (CDCl₃; δ, ppm): 3.67 (*s*, CH₃O-), 2.91 (*m*, CH- of the epoxy ring), 2.34 (*t*, -CH₂-COO-), 1.2-1.8 (methylene protons other than α-CH₂ to the carbonyl group), 0.88 (*t*, -CH₂CH₃). The EMO content was estimated by the ratio of the peak area of two CH- protons of the epoxy ring at 2.91 ppm over the peak area of the α-CH₂ adjacent to the carbonyl group at 2.34 ppm (i.e., the epoxy/COOR ratio) in the ¹H NMR spectrum.

2.4.3.2 Preparation of EOA with 91% purity

The crude EMO (12.45 g, 91% purity) was dissolved in acetone (300 mL), followed by addition of 0.4 N NaOH (300 mL). The resulting mixture was vigorously mixed with a mechanical stirrer at room temperature for 2 h to generate a homogeneous clear solution. After evaporation of the acetone, the remaining aqueous solution was extracted with ethyl acetate (110 ml), cooled to about 1 °C in a salty-ice water bath, and then acidified to pH 4 with 1.3 N H₂SO₄. The resulting acidified mixture was extracted with ethyl acetate three times (3 × 100 ml). The combined organic phases were washed with brine (2 × 150 ml). The resulting organic phase was dried over anhydrous magnesium sulfate and then filtered. Removal of the ethyl acetate afforded a white powder (11.60 g, 91% EOA) that was characterized by ¹H NMR.

2.4.3.3 Preparation of EOA with 93% purity

EOA with 93% purity was prepared through crystallization of EOA with 91% purity from hexane. The crude EOA (91% purity, 11.00 g) was dissolved in hexane (33 mL) in a 250-ml round-bottom flask equipped with a condenser at 60 °C. The solution was kept at 5 °C overnight and crystallization occurred. The crystal was collected by vacuum filtration, washed with chilled hexane (3 × 20 mL), and dried under high vacuum to provide EOA (93% purity, 9.88 g).

2.4.3.4 Preparation of EOA with 97% purity

EOA with 97% purity was prepared by crystallization of EOA with 93% purity from methanol. EOA (93% purity, 9.58 g) was dissolved in methanol (9.58 g) in a 250-ml round-bottom flask equipped with a condenser at 60 °C. The solution was kept at 5 °C

overnight and crystallization occurred. The crystal was collected by vacuum filtration, washed with chilled methanol (2×20 mL), and dried under high vacuum to provide a white and very fine powder (8.16 g, 72% overall yield based on MO, 97% purity). ^1H NMR (CDCl_3 ; δ , ppm): 10 (broad, $-\text{COOH}$), 2.91 (*m*, CH- of the epoxy ring), 2.34 (*t*, $-\text{CH}_2-\text{COOH}$), 1.2-1.8 (methylene protons other than $\alpha\text{-CH}_2$ to COOH), 0.88 (*t*, $-\text{CH}_2\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3 ; δ , ppm): 179.57 (HOOC-CH_2-), 57.31 and 57.27 (carbons of the epoxy ring), 20-35 (methylene carbons), 14.10 ($-\text{CH}_2\text{CH}_3$). FTIR (neat, cm^{-1}): 3050 and 2985 (C-H stretching of epoxy ring [21]), 2944 and 2871 (CH_3 stretching), 2911 and 2849 (CH_2 stretching), 1692 (COOH carbonyl stretching), 1469 (CH_2 bending), 1298, 1261, 1226 and 1194 (epoxy ring symmetrical stretching, or “ring breathing” [21, 22]), 918 (presumably due to carboxyl O-H [22]), 889 (C-C asymmetrical stretching of epoxy ring [21, 23]), 856, 840 and 825 (“12 micron band”, typical for epoxy ring [21, 22]), and 719 (CH_2 rocking motions, characteristic for at least four linearly connected CH_2 groups).

2.4.4 Polymerization of EOA with 70% purity

2.4.4.1 Polymerization of EOA with 70% purity with N-methylmorpholine

A mixture of EOA (70% purity, 10.06 g) and N-methylmorpholine (0.14 g) in a 50-mL round-bottom flask was purged with N_2 for 10 min and stirred at 180°C for 6 h, which generated a light yellow oil that had similar viscosity to soybean oil and was not sticky felt by hand.

2.4.4.2 Polymerization of EOA with 70% purity with N,N,N',N'-tetramethylethylenediamine

A mixture of EOA (70% purity, 8.00 g) and N,N,N',N'-tetramethylethylenediamine (0.10 g) in a 50-mL round-bottom flask was purged with N₂ for 10 min and stirred at 120 °C for 7.5 h, which generated a brown oil that was slightly more viscous than soybean oil and showed some stickiness felt by hand.

2.4.4.3 Polymerization of EOA (70% purity) with dimethylbenzylamine

A mixture of EOA (70% purity, 10.01 g) and dimethylbenzylamine (0.21 g) in a 50-mL round-bottom flask was purged with N₂ for 10 min and stirred at 160 °C for 9 h, which generated a brown oil that had similar viscosity to soybean oil and was not sticky felt by hand.

2.4.4.4 Polymerization of EOA with 70% purity with tetraphenylphosphonium bromide

A mixture of EOA (70% purity, 2.62 g) and tetraphenylphosphonium bromide (0.14 g) in a 50-mL round-bottom flask was purged with N₂ for 10 min and stirred at 140 °C for 12.5 h, which generated a dark brown oil that had similar viscosity to soybean oil and was not sticky felt by hand.

2.4.4.5 Polymerization of EOA with 70% purity with CTAA

A mixture of EOA (70% purity, 0.53 g) and CTAA (0.011 g) in a 50-mL round-bottom flask was purged with N₂ for 5 min and stirred at 160 °C for 4 h, which generated a viscous and sticky purple resin.

2.4.5 Polymerization of EOA with 91% purity

2.4.5.1 Preparation of PSA91A

A mixture of EOA (91% purity, 4.53 g) and CTAA (0.09 g) in a 50-mL round-bottom flask was purged with N₂ for 5 min and stirred at 160 °C for 9 min when the mixture was too viscous to be stirred with a magnetic stirring at 400 rpm. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 50 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA91A. PSA91A was evaluated for its peel strength.

2.4.5.2 Preparation of PSA91B

A mixture of EOA (91% purity, 1.00 g), CTAA (0.020 g) and succinic anhydride (0.20 g) in a 10-mL round-bottom flask was purged with N₂ for 5 min and stirred at 130 °C for 52 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 120 min only to give a wet and slightly tacky adhesive film. This adhesive film was designated as PSA91B and was not further evaluated as a PSA.

2.4.5.3 Preparation of PSA91C

A mixture of EOA (91% purity, 4.05 g), CTAA (0.082 g) and ESO (0.40 g) in a 25-mL round-bottom flask was purged with N₂ for 5 min and stirred at 130 °C for 42 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 50 min to give a dry, tacky adhesive film. This adhesive film was then transferred

onto a paper backing material and was designated as PSA91C. PSA91C was evaluated for its peel strength.

2.4.6 Polymerization of EOA with 93% purity

2.4.6.1 Preparation of PSA93A

A mixture of EOA (93% purity, 1.81 g), CTAA (0.037 g) and ESO (0.17 g) in a 10-mL round-bottom flask was purged with N₂ for 5 min and stirred at 130 °C for 37 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 75 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93A. PSA93A was evaluated for its peel strength.

2.4.6.2 Preparation of PSA93B

A mixture of EOA (93% purity, 1.25 g), CTAA (0.027 g) and TMPTGE (0.055 g) in a 10-mL round-bottom flask was purged with N₂ for 5 min and stirred at 130 °C for 47 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 70 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93B. PSA93B was evaluated for its peel strength.

2.4.6.3 Preparation of PSA93C

A mixture of EOA (93% purity, 2.0 g), CTAA (0.041 g) and TEPI (0.054 g) in a 10-mL round-bottom flask was purged with N₂ for 5 min and stirred at 130 °C for 40 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 75 min only to give a wet, slightly tacky adhesive film. This adhesive film was designated as PSA93C and was not further evaluated as a PSA.

2.4.6.4 Preparation of PSA93D

A mixture of EOA (93% purity, 1.23 g), CTAA (0.025 g) and BADGE (0.052 g) in a 10-mL round-bottom flask was purged with N₂ for 3 min and stirred at 130 °C for 87 min. The viscosity of the reaction mixture didn't significantly increase. The reaction mixture was still not viscous and had very weak cohesive strength after it was further stirred at 150 °C for 25 min and then at 160 °C for 120 min. This reaction mixture was not further cured for PSAs and was designated as PSA93D.

2.4.6.5 Preparation of PSA93E

A mixture of EOA (93% purity, 1.02 g), CTAA (0.021 g) in a 10-mL round-bottom flask was purged with N₂ for 3 min and stirred at 140 °C for 30 min. ESO (0.11 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140 °C for 10 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 35 min to give a dry, tacky adhesive film. This adhesive

film was then transferred onto a paper backing material and was designated as PSA93E. PSA93E was evaluated for its peel strength.

2.4.6.6 Preparation of PSA93F

A mixture of EOA (93% purity, 1.10 g) and CTAA (0.022 g) in a 10-mL round-bottom flask was purged with N₂ for 3 min and stirred at 140 °C for 70 min. TMPTGE (0.082 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140 °C for 7 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 20 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93F. PSA93F was evaluated for its peel strength.

2.4.6.7 Preparation of PSA93G

A mixture of EOA (93% purity, 1.21 g) and CTAA (0.024 g) in a 10-mL round-bottom flask was purged with N₂ for 3 min and stirred at 140 °C for 82 min. BADGE (0.11 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140 °C for 1 min. The reaction mixture was subsequently coated onto a release liner and covered by a PET release film by hand. The resulting laminate was cured in an air-circulating oven at 160 °C for 20 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a paper backing material and was designated as PSA93G. PSA93G was evaluated for its peel strength.

2.4.6.8 Preparation of PSA93H

A mixture of EOA (93% purity, 4.12 g) and CTAA (0.083 g) in a 10-mL round-bottom flask was purged with N₂ for 3 min and stirred at 140 °C for 70 min. TMPTGE (0.33 g) was then added to the reaction mixture and the resulting reaction mixture was further stirred at 140 °C for 13 min. The reaction mixture was subsequently coated onto a PET release film by hand. The resulting adhesive-coated film was cured in an air-circulating oven at 160 °C for 30 min to give a dry, tacky adhesive film. This adhesive film was then transferred onto a BOPP backing film and was designated as PSA93H (coating rate: 25 g/m²). PSA93H was evaluated for its peel strength, tack, shear resistance, and aging resistance.

2.4.7 Polymerization of EOA with 97% purity.

A mixture of EOA (97% purity, 5.50 g) and CTAA (0.11 g) in a 50-mL round-bottom flask was purged with N₂ for 3 min and stirred at 160 °C for 55 min to generate poly(epoxidized oleic acid) (PEOA). ¹H NMR (CDCl₃; δ , ppm): 4.83 (-CH-OCO-), 3.58 (-CH-OH), 2.35 (-CH₂-COO-), 1.2–1.8 (methylene protons other than α -CH₂ to carbonyl groups), 0.89 (-CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃; δ , ppm): 175 (-CH₂-C=O), 76.5 (-CH-OCO-), 72.7 (-CH-OH), 25–35 (methylene carbons), 14.9 (-CH₂CH₃). FTIR (neat, cm⁻¹): 3450 (OH stretching), 2952 and 2871 (CH₃ stretching), 2923 and 2853 (CH₂ stretching), 1730 (ester carbonyl stretching), 1713 (COOH carbonyl stretching), 1461 and 1376 (principally CH₂ bending), 1244 (ester C-O stretching), 1174 and 1100 (ester C-O-C stretching), 1065 and 1024 (C-OH stretching), and 723 (CH₂ rocking motions, characteristic for at least four linearly connected CH₂ groups).

2.4.8 Preparation of PSAs from PEOA.

2.4.8.1 Preparation of PSA97A

PEOA (6.73 g) was dissolved in anhydrous ethyl acetate (17.00 g) through refluxing for 30 min. The PEOA solution was cooled to room temperature, followed by the addition of a solution (0.164 g) of pMDI (0.51 g) and anhydrous ethyl acetate (1.97 g). The resulting solution was stirred at room temperature for 10 min and then coated on a sheet of BOPP film with a HLCL-1000 hot-melt coater (ChemInstruments, Inc., Fairfield, OH). The adhesive-coated BOPP film was put in a fume hood at room temperature for 10 min for evaporation of ethyl acetate and then cured in an air-circulating oven at 100 °C for about 20 min to give a dry, tacky adhesive film (coating rate: 25 g/m²). This adhesive was designated as PSA97A and evaluated for its peel strength, tack, shear resistance, and aging resistance.

2.4.8.2 Preparation of PSA97B

PEOA (5.50 g) was dissolved in anhydrous ethyl acetate (11.00 g) through refluxing for 30 min. The PEOA solution was cooled to room temperature, followed by the addition of a solution of pMDI (0.027 g, 0.5 wt% of PEOA) and anhydrous ethyl acetate (0.38 g), and a solution of DBTDL (0.027 g, 0.5 wt% of PEOA) and anhydrous ethyl acetate (0.38 g). The resulting solution was stirred at room temperature for 10 min and then coated on a sheet of BOPP film with the HLCL-1000 coater. The adhesive-coated BOPP film was put in a fume hood at room temperature for 10 min for evaporation of ethyl acetate and then cured in an air-circulating oven at 100 °C for about 45 min to give a dry, tacky

adhesive film (coating rate: 25 g/m²). This adhesive was designated as PSA97B and evaluated for its peel strength, tack, shear resistance, and aging resistance.

The solution of PEOA, pMDI, DBTDL, and ethyl acetate was coated onto a siliconized release liner with the HLCL-1000 coater. The adhesive-coated release liner underwent the same evaporation and curing processes as described previously. The cured PSA97B film was peeled off from the release liner for the characterization of its viscoelastic properties and its thermal stability.

2.4.9 Characterizations with NMR and Fourier-transfer infra-red (FTIR)

All NMR experiments were performed at room temperature with a Bruker 400 MHz spectrometer with CDCl₃ as solvent and internal reference. FTIR spectra were recorded on a Nexus 470 FTIR spectrometer equipped with a Golden Gate diamond ATR (attenuated total reflectance) accessory (Thermo Fisher Scientific Inc., Waltham, MA)

2.4.10 Determination of molecular weights of PEOA

The molecular weights of PEOA were determined with a gel permeation chromatography (GPC) by PolyAnalytik (London, Ontario, Canada). GPC experiments were performed on ViscoTek (Model 302) GPC System equipped with PolyAnalytik Columns PAS-105L, 104L, and 103L (in series) and triple detectors. The samples were fully dissolved in tetrahydrofuran (THF) at a concentration of 5 wt% and 200 µL of the solution was injected. The columns were operated at 35 °C and eluted with THF at a

flow rate of 1 mL/min. A universal calibration plot was constructed with NIST-traceable polystyrene standards. Reporting results were average values from three replicates.

2.4.11 Measurement of viscoelastic properties of PSAs

The viscoelastic properties of the samples were measured with an AR 2000ex Rheometer (TA Instruments, Inc., New Castle, DE) using 8 mm parallel plate geometry with an initial gap of about 0.1 mm (at room temperature) under nitrogen atmosphere; the strain amplitude was set at 1.5%. For frequency sweep, the samples were run at room temperature within the frequency range from 0.1 to 40 Hz; for temperature sweep, the samples were run at a fixed frequency of 1 Hz from -55 °C to 80 °C at 5 °C per step with 30 sec equilibration delay at each step. The Rheology Advantage Data Analysis version 5.6.0 software, supplied by TA Instruments, Inc., was used for plotting and analyzing the data.

2.4.12 Thermogravimetric analysis (TGA) of PSAs

TGA measurements were performed with a TA Q500 analyzer (TA Instruments, Inc., New Castle, DE). Temperature calibration of TGA was done according to the Curie point temperature of nickel. PSA samples of 18 mg in a standard aluminum pan without lid was heated at a heating rate of 15 °C/min from 50 °C to 600 °C in an air atmosphere. The balance was protected by a nitrogen flow. The flow rates of air and nitrogen were 60 mL/min and 20 mL/min, respectively. The Universal Analysis 2000 V4.7A software, supplied by TA Instruments, Inc., was used for plotting and analyzing the data.

2.4.13 Measurements of adhesive properties of the PSAs

2.4.13.1 Determination of peel strength of PSA tapes

The 90° peel adhesion test was performed on a stainless steel panel (type 302) according to Test Method F of ASTM D3330/D3330M-04 (Reapproved 2010). The PSA specimen tape (24 mm in width and 150 mm in length) was applied to the stainless steel panel by a roller (2040 g) once in each lengthwise direction by hand at the rolling rate of 10 mm/s. One end of the specimen touched the end of the test panel. The other free end of the specimen was attached to the grip of a tensile tester. The gap between the grip and the surface of the stainless steel panel was 25 mm. After 1 min of contact, the specimen was peeled off the stainless steel panel by the tensile tester at a speed of 5 mm/s. Data were collected after the first inch of specimen tape was peeled, and average peel strength (N/10 mm) was obtained by peeling the rest of the tape. Tests were performed at $23 \pm 1^\circ\text{C}$ and $40 \pm 5\%$ RH. The stainless steel panel was cleaned with acetone, dried with a heat gun, and conditioned for 10 min before a subsequent test. Three to five specimens were tested for each PSA sample and averaged values were reported as the peel strength. The failure mode (adhesive failure, cohesive failure, or adhesive transfer) was also recorded. The degree of cohesive failure (DCF) was used for quantifying cohesive failure and was defined as the ratio of the surface area covered by adhesive residues to the total contact area of the adhesive. The surface area covered by adhesive residues was estimated by visual inspection. The reported DCF was an average of all the test specimens.

2.4.13.2 Loop Tack test

The loop tack test was performed on a stainless steel panel (Type 302) in accordance with Test Method A of ASTM D6195-03 (Reapproved 2011). A loop of tape (24 mm in width and 150 mm in length) with adhesive facing outside was attached to the grip of the tensile tester and formed a tear drop shape. The gap between the grip and the surface of stainless steel was set to be 25 mm. The crosshead moved downwards at a speed of 5 mm/s. The adhesive loop was then brought into contact to the surface of stainless steel panel with a contact area of 24 by 24 mm and the contact pressure was generated only by the weight of the tape. Immediately after the contact, the crosshead moved upwards and the loop was separated from the surface of the stainless steel panel. The maximum force (peak reading) required to break the adhesive bond was recorded for each specimen. Tests were performed at 23 ± 1 °C and 40 ± 5 % RH. The stainless steel panel was cleaned with acetone, dried with a heat gun, and conditioned for 10 min before each test. Three specimens were tested for each sample and averaged values were reported as the tack force for the PSAs. The failure mode and DCF were also recorded.

2.4.13.3 Determination of shear resistance of PSA tapes

Shear resistance of PSA tapes was measured on a stainless steel panel (Type 302) in accordance with Procedure A of ASTM D3654/D3654M-06. A strip of PSA tape with 24 mm in width and 130 mm in length was applied to the stainless steel panel by rolling a roller (2040 g) on the tape twice in each lengthwise direction by hand at the rolling rate of 10 mm/s, with a contact area of 24 by 24 mm. The panel was at an angle of 2° vs. the vertical direction. After 1 min of contact, the free end of the specimen was attached to a

constant mass of 1 kg. The gap between the mass and test panel was 50 mm. A timing system was used to record the time when the tape separated from the panel. The time to failure (i.e., the time between the attachment of the constant mass and the complete separation of the tape from the test panel) was used as the indication of shear resistance (holding power). Three specimens were tested for each sample and averaged values were reported as the shear resistance for PSAs. Tests were performed at 23 ± 1 °C and 40 ± 5 % RH. The stainless steel panel was cleaned with acetone, dried with a heat gun, and conditioned for 10 min before each test.

2.4.14 Aging tests

The aging resistance of the PSAs was investigated by natural aging at room temperature and accelerated aging at 60 °C, respectively. For the natural aging test, the specimens were aged at 23 ± 1 °C and 40 ± 5 % RH. For the accelerated aging test, the specimens were aged at 60 °C in an Isotemp 625D Incubators (Thermo Fisher Scientific Inc., Waltham, MA). After being aged for one or two weeks, the sample tapes were tested for peel strength, tack force, and shear resistance according to the methods previously described. Specimens that have been aged at 60 °C were conditioned at 23 ± 1 °C and 40 ± 5 % RH for 10 h prior to the tests.

2.4.15 Statistical analysis

All data for adhesive properties of PSAs were statistically analyzed by permutation test using RStudio (RStudio, Inc., Boston, MA). The time to failure in minutes was

converted to its natural logarithm for analysis. All comparisons were based on 95% confidence interval.

2.5 Results and discussion

2.5.1 Preparation and characterization of EOA.

It would be ideal if EOA could be prepared from direct epoxidation of OA. The direct epoxidation of OA was first attempted with formic acid and hydrogen peroxide in accordance with a literature procedure [18]. When the reaction was conducted at room temperature for 2 h, the resulting crude product contained 60% EOA, 34% unreacted OA, and 6% ring-opening byproducts. Increase in the reaction time from 2 h to 3.5 h resulted in a crude product containing 70% EOA, 6% unreacted OA, and 24% byproducts. At the short reaction time of 2 h, a substantial amount of unreacted OA remained. Increase in the reaction time significantly decreased the amount of unreacted OA, but also significantly increased the amounts of byproducts. Extensive studies through variations of reaction time and temperature failed to generate EOA with its purity of higher than 70%. Epoxidation of OA with peracetic acid was also investigated in accordance with a literature procedure [19]. However, we were not able to re-produce the purity and the yield of EOA indicated in the literature [19]. The purity of EOA was never higher than 70% in our hands.

Attempts for increasing the purity of EOA through crystallization in various organic solvents were not successful. Pure EOA could be obtained from liquid column chromatography. However, it was too time-consuming and too expensive to use liquid

column chromatography for preparation of gram-scales of pure EOA. As discussed later in the polymerization of EOA, 70% purity was not high enough for generation of a polymer with adequate PSA properties. It was speculative that the carboxylic acid group in the oleic acid was responsible for the high amount of by-products during the prolonged epoxidation reaction. Therefore, our attention was turned to the extensively studied epoxidation of MO [8, 24, 25].

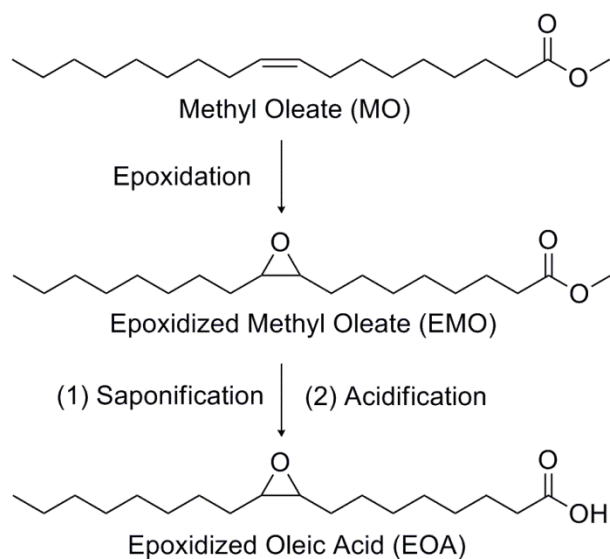


Figure 2.1 Preparation of EOA from MO

Preparation of EOA from MO is shown in Figure 2.1. Epoxidation of MO with hydrogen peroxide in the presence of formic acid as a catalyst readily generated EMO with 91% purity. The impurities included unreacted MO (2%) and byproducts (7%) that included those from ring-opening of the epoxy group by formic acid (4%) and water (2%). The crude epoxidized product was directly hydrolyzed with a NaOH solution at room temperature, followed by acidification to readily generate EOA. The ^1H NMR spectra of

the EOA revealed that the epoxy/-COOH ratio remained at 0.91, which implied that the ester group was selectively hydrolyzed to form a carboxylic acid group and the epoxy group virtually remained intact during the hydrolysis.

EOA with 93% purity was obtained through crystallization of EOA with 91% purity from hexane. EOA with 97% purity was further obtained through crystallization of EOA with 93% purity from methanol. Based on MO, the overall yield of EOA with 97% purity was about 72%. ^1H NMR spectra of EOA with 97% purity is shown in Figure 2.2. The impurities were mainly diols (1%) and (poly)ethers (0.6%), the byproducts from the ring-opening of the epoxy group with water or the hydroxyl group (the content of diols was estimated from the ratio of the peak area of two $-\text{CH}-$ protons of the diols at 3.4 ppm to the peak area of the $\alpha\text{-CH}_2$ adjacent to the carbonyl group at 2.34 ppm; and the content of (poly)ethers was estimated from the ratio of the peak area of protons of the ether linkages at 3.55 ppm (or those in the vicinity of the hydroxyl group β to the ether linkages at 3.23 and 3.33 ppm [6, 7]) to the peak area at 2.34 ppm). These side reactions could take place in the presence of acids such as hydrochloric acid and formic acid [6, 7].

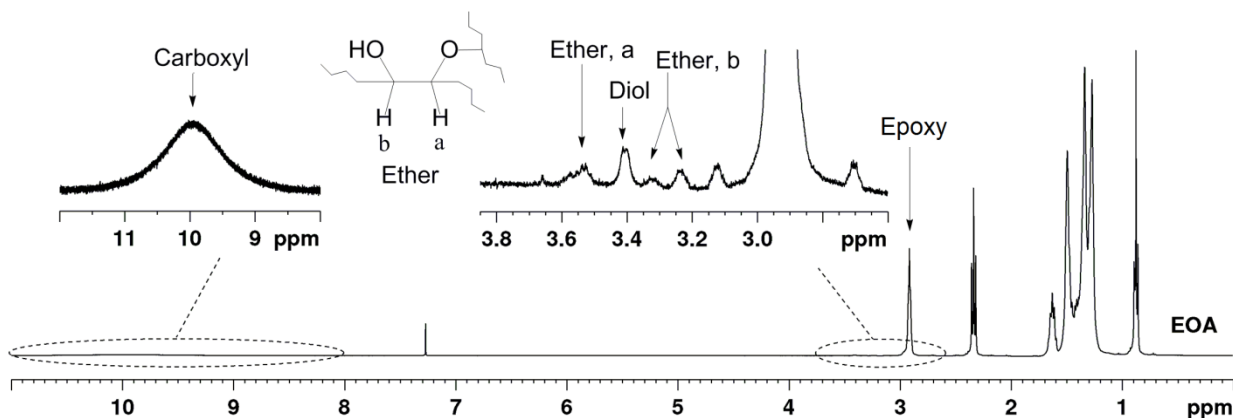


Figure 2.2 ^1H NMR spectrum of EOA with close-up views (64x original intensity) of the proton absorption signals of the epoxy, carboxyl, and impurities related to the ether and diol

2.5.2 Polymerization of EOA for PSAs

EOA is a bifunctional AB monomer containing a $-\text{COOH}$ (A) and an epoxy group (B). Theoretically, EOA may step-growth polymerize to form linear hydroxyl-functionalized polyesters via the ring-opening of the epoxy group with the carboxylic acid group (Figure 2.3). The ring-opening reaction can occur either at the 9-position or 10-position, thus generating PEOA with two regioselective linkages (a and b, Figure 2.3).

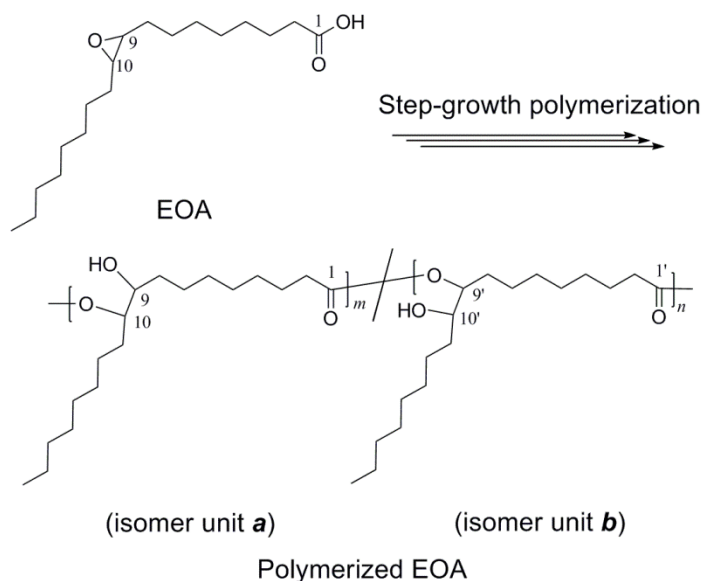


Figure 2.3 Step-growth polymerization of EOA

2.5.2.1 Polymerization of EOA with 70% purity

The thermal polymerization of EOA in the absence of any catalyst has been previously studied [26, 27]. However, the polymerization without any catalyst took a very long time

(several days), and applications of the resulting polymers was not investigated. Various catalysts such as tertiary amines, organometallic compounds [28], and some phosphonium salts [29] that have been demonstrated as effective catalysts for accelerating the reaction between a carboxylic acid group and an epoxy group were investigated for the polymerization of EOA (Table 2.1). EOA with 70% purity from the direct epoxidation of oleic acid was used for the polymerization study. N-methylmorpholine failed to serve as an effective catalyst for the polymerization of the EOA; only a non-viscous, non-sticky oil was formed after the polymerization at 180 °C for 6 h. The ineffective catalysis of N-methylmorpholine might be due to its evaporation from the reaction mixture during the polymerization reaction because the boiling point of N-methylmorpholine was 113-116 °C. Lowering the reaction temperature from 180 °C to 120 °C and use of a tertiary amine (N,N,N',N'-tetramethyl-ethylenediamine) with a similar boiling point of 120-122 °C were still not able to significantly polymerize the EOA (Table 2.1). In this reaction, the reaction temperature might be too low for the polymerization and was close to the boiling point of the amine, which might result in substantial loss of the amine from the reaction mixture. For eliminating the concerns over the low reaction temperature and evaporation of the catalyst, the reaction temperature of 160 °C, and dimethylbenzylamine with its boiling point (180 °C) being higher than the reaction temperature were investigated and also did not result in substantial polymerization of the EOA (Table 2.1). Tetraphenylphosphonium bromide, an effective catalyst for the step-growth polymerization of 10,11-epoxyundecanoic acid that has a terminal epoxy group [29], was also not an effective catalyst for the polymerization of EOA.

CTAA, an organometallic catalyst, appeared to facilitate the polymerization of the EOA. The polymerization product was a viscous and sticky resin, a good sign for PSA applications. However, 100% of cohesive failure, i.e., DCF of 100%, indicated that the cohesive strength of this product was still insufficient for PSA applications (Table 2.1). Subsequent investigations on the different usages of CTAA and different reaction conditions (temperature and time) failed to generate a polymeric material that had adequate tackiness and cohesive strength for a typical PSA application. The low purity of EOA was speculated to be the main reason for the inadequate PSA properties. Extensive efforts were then devoted to the preparation and polymerization of EOA with a higher purity than 70%. CTAA was used as a catalyst for the polymerization of EOA hereafter.

Table 2.1 Investigation of suitable catalysts for the polymerization of EOA with 70% purity

Catalysts	Product appearance	Product viscosity	Peel test [*]	
			Stickiness	DCF
N-methylmorpholine	Light yellow; oil	Not viscous	Not sticky	100%
N,N,N',N'-tetramethylethylenediamine	Brown; oil	Slightly viscous	Slightly sticky	100%
Dimethylbenzylamine	Brown; oil	Not viscous	Not sticky	100%
Tetraphenylphosphonium bromide	Dark brown; oil	Not viscous	Not sticky	100%
Chromium (III) tris(acetylacetonate)	Dark purple; resin	Viscous	Sticky	100%

^{*}Peel test: At the end of the polymerization reaction, the resulting product was coated onto a piece of printing paper by hand. The coated paper was stuck on and then peeled off different substrates such as

skin, paper, glass, plastic, and stainless steel under light pressure to see if the product was tacky and if there were residues left on the substrate surfaces;

2.5.2.2 Polymerization of EOA with 91% purity

The resultant adhesive film (PSA91A) from the polymerization of the EOA without a co-monomer was dry and tacky, and had a decent peel strength of 2.5 N/10mm (Table 2.2). However, DCF was only about 50%, which implied that the cohesive strength of PSA91A was still not desirable. The cohesive failure typically implied the internal strength, i.e., cohesive strength of the adhesive was lower than the adhesive strength, i.e., the bonding strength between the adhesive and the adherend. The insufficient cohesive strength typically implied that the molecular weight of the adhesive was not high enough for providing sufficient entanglement and adhesion among molecular chains of the adhesive.

For increasing the molecular weight, the EOA was co-polymerized with various co-monomers. Succinic anhydride was first investigated as a co-monomer, hoping that succinic anhydride could crosslink newly generated hydroxyl groups in the polymerized EOA (Figure 2.3), thus increasing the molecular weight of the adhesive. However, the resultant adhesive (PSA91B) was not dry and had the DCF of 100% (Table 2.2).

The ratio of the epoxy group to the carboxylic acid group was 0.91 for the EOA with 91% purity, which implied that about 9% of the impurities contained a carboxylic acid group, but didn't contain an epoxy group. The impurities could react with the epoxy group of the EOA and oligomeric EOA, thus terminating the chain growth and lowering

the molecular weight of the product. ESO had multiple epoxy groups on each ESO molecule, and could consume the carboxylic acid groups of the impurities and crosslink the carboxylic acid groups at the chain end of PEOA. ESO was theoretically able to increase the molecular weight. The adhesive (PSA91C) from the copolymerization of the EOA with ESO indeed had a higher peel strength and a lower DCF than PSA91A (Table 2.2). The DCF for commercially viable PSA-based products should be zero. Therefore, the DCF of PSA91C was still too high. The purity of the EOA was believed to have great impacts on the properties of the resultant PSAs. Our attention was turned to polymerization of EOA with a higher purity than 91%.

Table 2.2 Co-polymerization of EOA with different co-monomers

PSA ID	Co-monomer	Curing time [*] (min)	90° peel test	
			Peel strength (N/10mm) ^{**}	DCF
PSA91A	/	50	2.5 ± 0.8	50%
PSA91B	Succinic anhydride	120	Adhesive film not dry	100%
PSA91C	ESO	50	3.6 ± 1.1	25%
PSA93A	ESO	75	2.5 ± 1.2	20%
PSA93B	TMPTGE	70	3.9 ± 1.7	25%
PSA93C	TEPI	75	Adhesive film not dry	100%
PSA93D	BADGE	/ ^{***}	/ ^{***}	100%

^{*} The curing was considered finished when the resultant adhesive film was dry and left no residues on fingers; ^{**} with paper backing; ^{***} the reaction mixture wasn't cured in oven because its viscosity didn't appear to increase even after reaction at 160 °C for 2 h in flask, indicating that BADGE interfered with the polymerization of EOA.

2.5.2.3 Polymerization of EOA with 93% purity

Increase in the purity of the EOA from 91% to 93% in the co-polymerization of the EOA and ESO resulted in a PSA (PSA93A) that had a slightly lower DCF than PSA91C (Table 2.2). However, PSA93A had a lower peel strength than PSA91C, which was still poorly understood. TMPTGE had three epoxy groups on each TMPTGE molecule and could play the same role as ESO. PSA93B from the copolymerization of the EOA with 93% purity with TMPTGE had comparable peel strength and DCF to PSA91C, but had a higher peel strength and a slightly higher DCF than PSA93A. TEPI also had three epoxy groups on each TEPI molecule. However, PSA93C from the copolymerization of the EOA and TEPI was a wet resin and had 100% DCF, which implied that TEPI interfered with the polymerization of the EOA and resulted in lower molecular weight of the adhesive. TEPI had a high melting temperature of 94-95 °C and was not very miscible with the EOA, which might account for the poor properties of PSA93C. BADGE with two epoxy groups on each BADGE molecule was also found to interfere with the polymerization. In summary, the strategy of copolymerization of the EOA with various co-monomers only had limited success in terms of enhancing the peel strength and lowering the DCF (Table 2.2). A different strategy that involved the pre-polymerization of the EOA with 93% purity followed by crosslinking of the resultant pre-polymer with various crosslinking agents was investigated (Table 2.3).

PSA93E had a higher peel strength and much lower DCF than PSA93A, indicating that the cohesive strength increased significantly (Table 2.3). The peel strength of PSA93F was comparable to that of PSA93G. Both PSA93F and PSA93G had a higher peel

strength than PSA93E, which implied that TMPTGE and BADGE were more effective crosslinkers than ESO (Table 2.3). These results were consistent with the fact that the epoxy groups in TMPTGE and BADGE were terminal and more reactive than the internal epoxy groups in ESO. As a matter of fact, the adhesive strength and the cohesive strength of PSA93F and PSA93G were so strong that the paper backing material broke instead of the test specimens being peeled off the stainless steel panel during the 90° peel tests. No DCF could be determined for PSA93F and PSA93G. BOPP film, a stronger backing material than the paper backing material, was employed for the preparation of PSA93H and subsequent PSA-tapes. PSA93H had zero DCF, i.e., no cohesive failure. PSA93H had a lower peel strength than PSA93F, which was probably due to the change of backing material. PSA93F and PSA93H can be based on 100% renewable materials because both EOA and TMPTGE can be derived from renewable material-based chemicals (TMPTGE can be derived from epichlorohydrin and trimethylolpropane. Epichlorohydrin can be derived from renewable glycerol [30] and trimethylolpropane can be derived from starch and sugars [31].)

Table 2.3 Crosslinking of pre-polymer of EOA with 93% purity with different crosslinkers

PSA ID	Crosslinker	Curing time [*] (min)	90° peel test	
			Peel strength (N/10mm) ^{**}	DCF
PSA93E	ESO	35	3.5 ± 0.4	<5%
PSA93F	TMPTGE	20	4.0 ± 0.5 ^{***}	/
PSA93G	BADGE	20	4.1 ± 0.3 ^{***}	/
PSA93H	TMPTGE	30	2.4 ± 0.8 [†]	0%

* The curing was considered finished when the resultant adhesive film was dry and left no residues on fingers; ** with paper backing material unless otherwise noted; *** the paper backing material split during peel test; † with BOPP film as the backing material.

Peel strength, tack force, and shear resistance of PSA93H with and without aging are shown in Table 2.4. The peel strength remained the same after 1WRT and decreased after 1W60C (Table 2.4). 1W60C also increased the DCF from 0% to 50% during the peel test. The tack force remained the same after 1WRT and 1W60C. 1W60C also increased the DCF from 0% to 25% during the tack test. The shear resistance of PSA93H remained unchanged after 1WRT and 1W60C (Table 2.4). PSA93H was disintegrated into an oily and flowable material after 2W60C. The aging studies on petrochemical-based PSAs revealed that one week of accelerated aging at 60 °C was equivalent to about 9 months of the aging at room temperature [32, 33]. If the aging results of petrochemical-based PSAs are applicable to PSA93H, PSA93H has the usable time of less than 9 months that are not long enough for a commercial PSA product.

Table 2.4 Adhesive properties of PSA93H before and after aging

	Peel strength (N/10 mm)	Tack force (N)	Shear resistance (min)
without aging*	2.4 ± 0.8 (DCF=0%)	5.8 ± 1.3 (DCF=0%)	9.0 ± 1.4
1WRT**	2.4 ± 1.1 (DCF=0%)	5.5 ± 0.3 (DCF=0%)	14.5 ± 7.5
1W60C**	1.6 ± 0.1 (DCF=50%)	5.6 ± 1.4 (DCF=25%)	15 ± 7.2
2W60C**	PSA disintegrated		

* That PSA samples were evaluated within 1 h after they were prepared was considered “without aging”; ** 1WRT and 1W60C represents the aging of a PSA sample for 1 week at room temperature or at 60°C; respectively; 2W60C represents the aging of a PSA sample for 2 week at 60°C.

2.5.2.4 Polymerization of EOA with 97% purity

Polymerization of EOA with 97% purity went smoothly. The viscosity of the reaction mixture increased quickly with time and after 55 min the reaction mixture was too viscous to be stirred by a magnetic stirring at its full torque. Further heating for about 10 min without agitation quickly led to gelation. The gel thus obtained was very tacky and strong, but could not be coated onto a face material because it did not melt at elevated temperature and could not be completely dissolved in common organic solvents such as chloroform, tetrahydrofuran, toluene, diethyl ether, ethyl acetate, acetone, N,N-dimethylformamide, and hexane. The polymerization reaction was stopped by removing the hot oil bath at 55 min, and the resulting PEOA was cooled to room temperature for further study.

PEOA was dissolved in ethyl acetate, and the resulting solution was coated onto a BOPP film. The PEOA-coated film obtained after evaporation of ethyl acetate at room temperature was clear, tacky, but wet. Further heating and curing at 130 °C for up to 100 min still didn't generate a dry adhesive film that had zero DCF. PEOA itself didn't appear to work well as a PSA. The further curing of the PEOA with a crosslinker was then investigated.

2.5.3 Crosslinking of PEOA for PSAs.

2.5.3.1 Crosslinking of PEOA for PSA97A

A small amount of pMDI (0.5 wt% of PEOA) was first investigated for crosslinking the numerous hydroxyl groups along the PEOA chain, resulting in PSA97A. PSA97A without aging had much higher peel strength, higher tack force, and longer shear resistance than PSA93H without aging (Tables 2.4 and 2.5), which indicated that the increase in the EOA purity from 93% to 97% and the use of pMDI as a crosslinker effectively improved the adhesive properties.

Typically, Post-it® notes and office tapes have peel strength of about 0.7 N/10 mm [8] and 3.5-8.8 N/10 mm [34], respectively. In our study, a commercial packaging tape (Duck® HP260™, ShurTech Brands, LLC) coated with polyacrylate-based adhesives with a coating thickness of 30 µm on a 50-µm-thick polypropylene film was used as a reference tape. The peel strength, tack force, and shear resistance were 3.5 ± 0.1 N/10 mm, 10.7 ± 1.2 N, and >1 month, respectively.

The peel strength of PSA97A decreased after 1WRT; but didn't decrease further after 2WRT. 1W60C decreased the peel strength as well. 2W60C didn't further change the peel strength; but cohesive failure was observed (DCF=10%). The tack force changed in the same way as the peel strength did, and cohesive failure occurred after 2W60C (DCF=5%). 1WRT and 2WRT did not result in significant changes in the shear resistance of PSA97A. 1W60C significantly increased the shear resistance of PSA97A. However, 2W60C reduced the shear resistance back to the level comparable to that

without aging. Effects of the aging on the shear resistance did not follow the same trend as those on the peel strength and the tack force. The sudden spike of the shear resistance of PSA97A after 1W60C was especially perplexing.

The decreases in the peel strength and the tack force implied that PSA97A might experience some kinds of disintegration during the first week of the aging at room temperature. The disintegration appeared to slow down after the first week of the aging, evidenced by the fact that the further aging at room temperature for two weeks and the aging at 60 °C for one week did not result in significant reductions in the peel strength and the tack force. After PSA97A was aged at 60 °C for two weeks, the disintegration was so severe that some adhesive residues remained on the stainless steel testing panels during the peel test and the tack test. Overall results from the effects of the aging on the peel strength and the tack force revealed that PSA97A was not very stable during the aging. The specific reasons for the instability were still poorly understood. It was speculated that the reaction between the isocyanate groups of pMDI and the hydroxyl groups of PEOA was not so effective that a small amount of the unreacted isocyanate groups might expose to air and were decomposed to form aromatic amino groups during the curing of PSA97A in an air-circulating oven. The aromatic amines could degrade the polyester chains of PEOA, thus resulting in the partial disintegration of the PSA97A during the prolonged aging (two weeks) at 60 °C.

Table 2.5 Adhesive properties of PSA97A and PSA97B before and after aging

	PSA97A			PSA97B		
	Peel strength (N/10 mm)*	Tack force (N)*	Shear Resistance (h)	Peel strength (N/10 mm)*	Tack force (N)*	Shear Resistance (h)
without aging**	3.6 ± 0.1	10.0 ± 0.9	3.4 ± 2.3	2.5 ± 0.1	5.7 ± 0.6	140.1 ± 83.1
1WRT***	2.6 ± 0.1	8.7 ± 0.7	12 ± 9.2	2.4 ± 0.1	6.0 ± 0.3	79.7 ± 75.3
2WRT***	2.3 ± 0.1	8.3 ± 1.9	2.5 ± 2.1	2.4 ± 0.2	5.8 ± 0.5	268.4 ± 64.3
1W60C***	2.1 ± 0.2	5.4 ± 0.4	> 1.8 month	1.9 ± 0.3	5.8 ± 1.2	> 6 months
2W60C***	2.4 ± 0.3 (DCF=10%)	6.8 ± 1.6 (DCF=5%)	3.7 ± 1.3	1.4 ± 0.2	4.4 ± 1.0	> 6 months

* DCF for the peel or the tack test was zero unless otherwise noted; ** That PSA specimens were evaluated within 1 h after they were prepared was considered “without aging”; *** 1WRT and 2WRT represents the aging of a PSA sample at room temperature for 1 week and 2 weeks; respectively; 1W60C and 2W60C represents the aging of a PSA sample at 60°C for 1 week and 2 weeks; respectively

2.5.3.2 Crosslinking of PEOA for PSA97B

DBTDL has been demonstrated to be a very effective catalyst for the reaction between isocyanate groups and hydroxyl groups [35,36]. PSA97B was prepared through the crosslinking of PEOA with pMDI in the presence of DBTDL. The peel strength of PSA97B without aging was comparable to that after 1WRT and 2WRT (Table 2.5). The peel strength after 1W60C was slightly lower than that after 2WRT, but slightly higher than that after 2W60C (Table 2.5). The tack force of PSA97B without aging, after 1WRT, 2WRT, and 1W60C were comparable to each other. However, the tack force of PSA97B after 2W60C was slightly lower than that after 1W60C. No adhesive residues could be found on the stainless steel testing panel for all test samples during the peel test and the tack test. The shear resistance of PSA97B without aging was the same as that

after the 1WRT and 2WRT. The 1W60C and 2W60C resulted in a much higher shear resistance than that after the 1WRT and 2WRT. The true values of the shear resistance for PSA97B samples after the 1W60C and 2W60C were not known because the shear resistance experiments were terminated at 6 months. Results shown in the Table 2.5 revealed that PSA97B was a very stable PSA.

2.5.4 Characterization of PEOA

When the FTIR spectrum of PEOA was compared with that of EOA (Figure 2.4, middle and bottom), PEOA had a new broad band of hydroxyl groups at 3450 cm^{-1} and a new peak of ester groups at 1730 cm^{-1} . The epoxy group peak at 840 cm^{-1} and the carbonyl peak of the $-\text{COOH}$ at 1692 cm^{-1} were very strong for EOA, but were very weak for PEOA. These results confirmed the ring-opening homopolymerization of the epoxy group with the $-\text{COOH}$ group. The FTIR spectrum of PEOA was almost identical to that of PSA97B, indicating the newly generated urethane functional groups from the reaction between PEOA and pMDI was too weak to be identified because of the very low usage of the pMDI.

The NMR analysis further confirmed the homopolymerization of EOA. When the ^1H NMR spectrum of PEOA was compared with that of EOA (Figure 2.5 and 2.2), PEOA had new peaks at 3.58 and 4.83 ppm that corresponded to protons on C^9 ($\text{C}^{10'}$) and C^{10} (C^9), respectively (Figure 2.3). The epoxy group peak at 2.91 ppm was very strong for EOA; but was very weak for PEOA.

The GPC results of PEOA showed that PEOA had a weight-average molecular weight (M_w) of 53800 g/mol and polydispersity index of 15.0, which implied that PEOA had a broad molecular weight distribution.

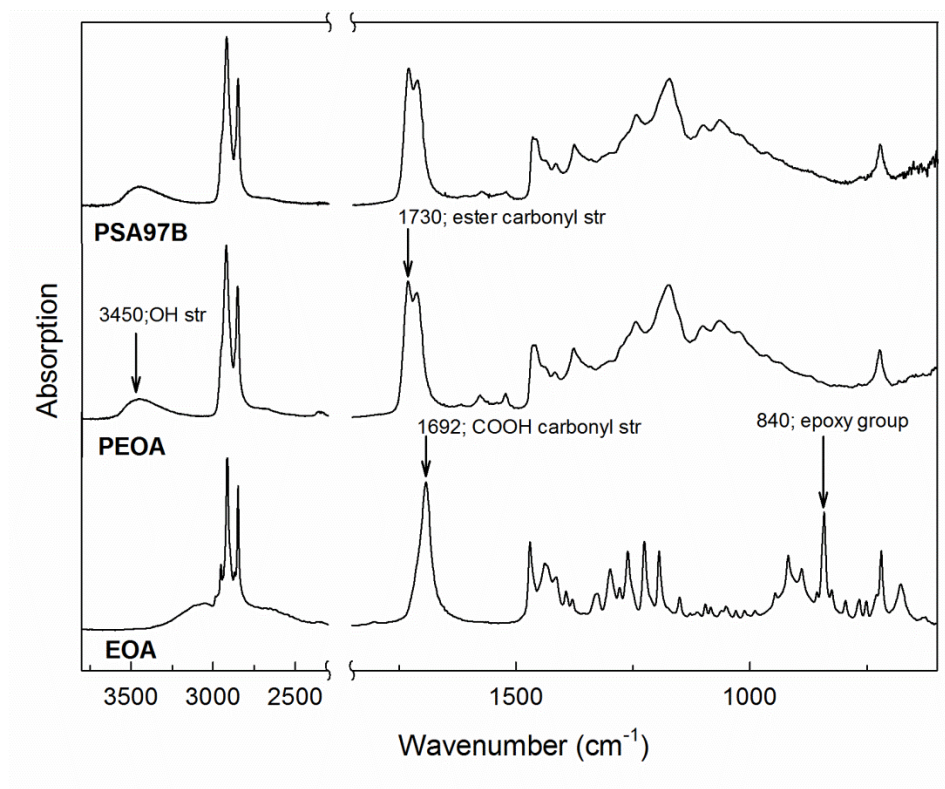


Figure 2.4 FTIR spectra of EOA (bottom), PEOA (middle), and PSA97B (top)

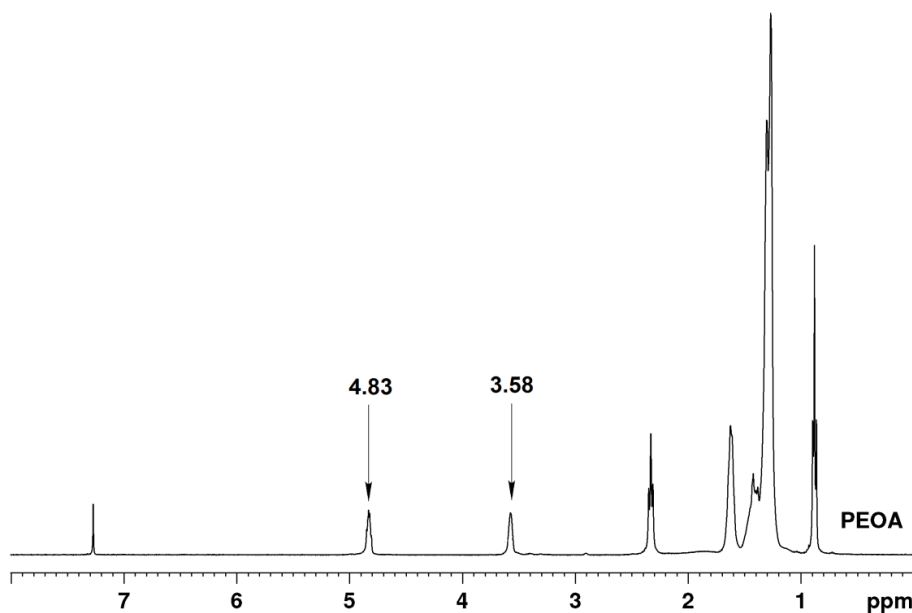


Figure 2.5 ¹H NMR spectrum of PEOA

2.5.5 Viscoelastic and thermal properties of the PSA97B.

Under a frequency sweep at 23 °C, PSA97B had the dynamic storage modulus (G') of 4.4×10^3 Pa at 0.1 Hz, 1.0×10^4 Pa at 1 Hz, and 4.6×10^4 Pa at 40 Hz, respectively. Under a temperature sweep at 1 Hz, the glass transition temperature (T_g) of PSA97B was determined to be -13 °C and the G' was 6.5×10^3 Pa at 23 °C. The TGA of PSA97B indicated that the thermal degradation (5% loss of the total mass) did not start until the temperature reached 275 °C, which implied that PSA97B had a high thermal stability.

2.6 Conclusion

EOA samples with different purities were prepared and characterized from oleic acid and methyl oleate, and were investigated for preparations of PSAs. CTAA was found to be the most effective catalyst for the homopolymerization of EOA. The purity of EOA

significantly affected the adhesive properties. The 97% purity was found to be required for achieving superior adhesive properties and aging resistance of the resulting PSAs. PEOA from homopolymerization of EOA with 97% purity had the M_w of 53800 g/mol and the polydispersity index of 15.0. The crosslinking of PEOA with a small amount of pMDI and DBTDL resulted in PSA97B with superior peel strength, tack force, long shear resistance, superior aging resistance, and high thermal stability.

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