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Rheological and physical characteristics of bio-derived block co-polymers for adhesive applications

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Rheological and physical characteristics of bio-derived block co-polymers for adhesive applications

by

Zahra Sotoodeh Nia

A thesis submitted to graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Civil Engineering (Civil Engineering Materials)

Program of Study Committee:
R. Christopher Williams, Major Professor
Erich W. Cochran
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Iowa State University

Ames, Iowa

2016

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ABSTRACT

Over the past decade, due to the economic and environmental concerns about the excessive usage of oil and its unstable price, development of renewable resources such as vegetable oils as substitutes for petroleum-based products has received considerable attention. Recently, commercial synthesis of oil-based (e.g. soybean, corn, fish, etc.) polymers has prevailed in several applications including food packaging, biomedical devices, paints, coatings, adhesives, and many other applications. Commercial development of Poly-Styrene Poly-Acrylated Epoxidized Soybean Oil (PS-PAESO) as a bio-polymer is currently in progress through ongoing research at Iowa State University.

This thesis focuses on investigating the commercial viability of PS-PAESO block copolymers for adhesive applications, in particular, Pressure Sensitive Adhesives (PSAs). A library of candidate materials has been synthesized based on the recommended formulations by industry experts, and the most important physical, rheological, and adhesion properties of the adhesives have been evaluated and compared to petroleum-based counterparts. The results indicate promising potential of the material to perform as well as the commercially available petrochemical PSAs. However, more comprehensive studies on several factors influencing the behavior of bio-renewable PSAs is recommended before commercialization.

CHAPTER 1. INTRODUCTION

1.1 Background

“Green” polymers, or “biopolymers” are described as polymers derived partially or entirely from renewable natural non-petroleum resources. These materials could be either derived from biological sources such as plants, trees, or microorganisms, or, be produced by synthetic chemistry from such sources [2, 3]. In recent years, various aspects have been utilized through the comparison of biopolymers with today’s synthetic polymers to identify their potential advantages. As such, higher biodegradability, lower energy requirements for processing, smaller environmental footprint, and higher biocompatibility are shown as benefits attributed to biopolymers, leading to considering them as ideal candidates to replace tens of billions of pounds of petroleum-based polymers[2, 4, 5]. Soybean oil, as one of the most abundant renewable natural resources, has been incorporated into the formulation of a variety of promising polymeric materials including thermoplastic elastomers. The polymerized form of modified soybean oil has shown its potential to serve as replacement of the non-renewable polymeric components of materials such as asphalt paving mixtures [6] and surface coatings [7]. The application of this “biopolymer” can be further broadened in technologies such as pressure sensitive adhesives (PSAs) in which the polymeric components exhibit a variety of novel characteristics. Despite extensive research in the technology of PSAs, many challenges regarding the biocompatibility and biodegradability of such materials still remain beyond their lifetime.

The pressure sensitive adhesives should possess three important properties to meet functional requirements: (1) provide some degree of stickiness or tack upon application of light pressure, (2) exhibit proper peel strength with no residue on the substrate once peeled, in case they are classified as removable PSAs, and (3) minimize the creep during long term application

of stresses, if they are designed as permanent PSAs [8]. The proposed PSAs in this study are presumed to fulfill these requirements and perform comparably to their petroleum-based analogues.

1.2 Problem Statement and Objectives

The concerns regarding the finite availability of fossil oils and the instability in their price (Figure 1) prompted the research to focus on developing a substitute for Styrene-Isoprene-Styrene (SIS) triblock copolymer as the most common petroleum-derived polymeric component of pressure sensitive adhesives (PSAs). To achieve this goal, the experimental work was focused on formulating the new PSA system composed of soybean oil-based block copolymers (PS-PAESO) combined with commercial tackifiers and plasticizers, in accordance with the recommendations from industry experts. The characteristics of the synthesized PSAs were then evaluated by the most common laboratory techniques, and the viability of scaling up their production to commercial levels was determined.

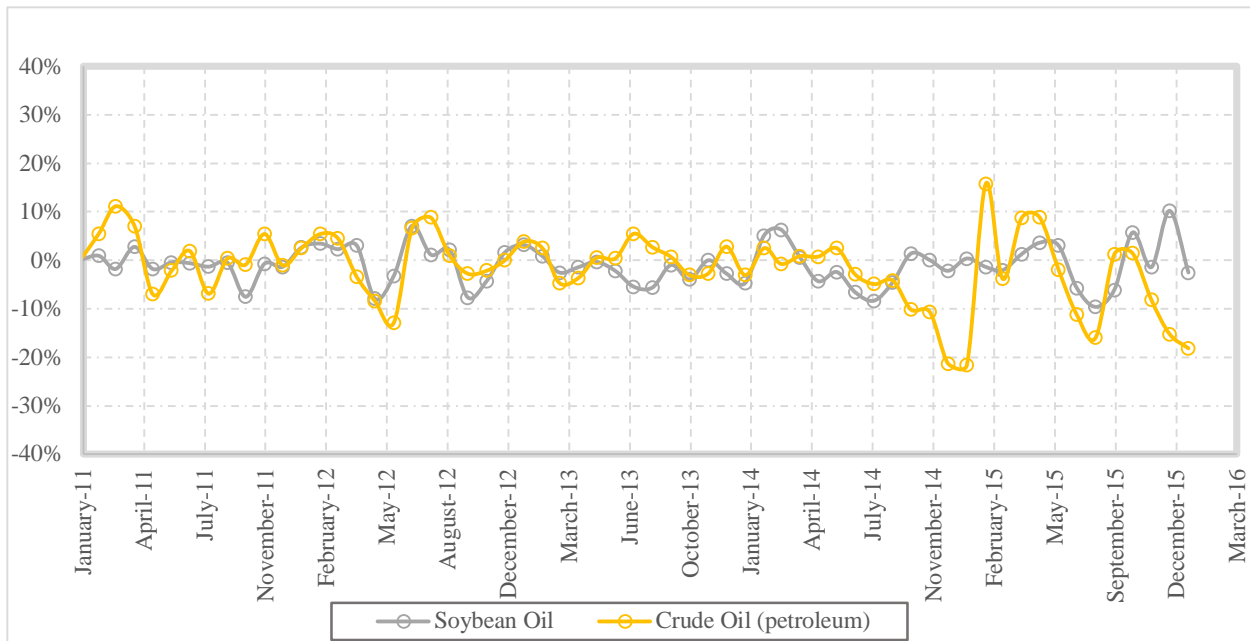


Figure 1 Monthly comparison between the rate of change in the price of Soybean Oil versus Crude Oil [9]

1.3 Methodology and Approach

A library of candidate materials was synthesized based on the recommendations by industry experts. The most important physical, rheological, and adhesion properties of the adhesives were evaluated and compared to petroleum-based counterparts, and a techno-economic analysis was conducted for future commercial purposes.

1.4 Significance of Work

The ongoing research attempts to investigate the viability of replacing non-renewable PSAs by bio-renewable substitutes as well as develop a foundation from which “green” materials with novel properties comparable to those of conventional materials can be produced for a wide range of applications.

1.5 Thesis Outline

The thesis is organized into five main chapters as follows: Chapter 1 presents a background on the current status of pressure sensitive adhesives, problem statement and objectives, methodology and approach, significance of work, and the report organization. In Chapter 2, a review of the literature has been provided regarding the history of pressure sensitive adhesives (PSAs), the composition of PSAs, different methods employed in the manufacture of them, and some remarkable physical, mechanical, and rheological properties of the PSAs identified by other researchers around the world. Chapter 3 presents the experimental program including materials, testing methods, and the equipment used for this study. In Chapter 4, an analysis of the results is provided followed by a discussion on findings. Conclusions and recommendations regarding the application of the proposed material can be found in Chapter 5 of this thesis. The references are provided following Chapter 5.

CHAPTER 2. LITERATURE REVIEW

2.1 Background of Pressure Sensitive Adhesives

An adhesive is defined as a nonmetallic material applied to surface of other materials to join them together through adhesion and cohesion [10, 11]. Adhesives have been used in several applications including cement, glue, and paste for many centuries. However, the significant evolution in science and technology of adhesives has occurred since the middle of the 1940s, when the development of synthetic polymers pioneered the scientific investigation for improving the adhesion strength of adhesives. Adhesives can offer many advantages including: joining dissimilar materials, joining thin sheet-materials, improving stress distribution in joints, increasing design flexibility and allowing wider selection of materials for implementing novel design concepts, improving the appearance of bonded areas, and improving the corrosion resistance of structures [11]. These advantages have provided opportunities for adhesives to meet the service life requirements of many industrial products including pressure sensitive adhesives.

Pressure sensitive adhesives (PSAs) have been widely used since the late 19th century when solvent-based PSAs were first developed, followed by the manufacturing of hot-melt PSAs in the 20th century. Various products such as adhesive tapes, labels, protective films [8], and postage stamps [12] represent the wide variety of applications provided by PSAs in the industry [10]. Pressure sensitive adhesives are most commonly identified in the form of tapes [13]. According to the Pressure Sensitive Tape Council (PSTC), “Pressure sensitive adhesive (PSA) tape can be defined as a continuous flexible strip of cloth, paper, metal or plastic coated on one or both sides with a permanently tacky adhesive at room temperature which will adhere to a variety of surfaces with light pressure (finger pressure) with no phase change (liquid to solid) and usually on a roll.” Another definition of PSA by Dahlquist has been referenced by many researchers in the literature:

a material that exhibits measurable adhesion to the substrate upon application of a light pressure or a brief contact at room temperature [14-16], without any required activation energy [8, 17]. Technologies associated with PSAs are discussed in section 2.2.

2.2 Materials used in Pressure Sensitive Adhesives

PSAs were first developed on the basis of natural rubber (NR) and natural resins. After a couple of years, adhesives were formulated by blending synthetic elastic rubbers and viscous materials such as tackifiers and plasticizers, resulting in the development of viscoelastic raw materials, in particular styrenic copolymers, in the technology of pressure sensitive adhesives and products [18]. The latest type of PSAs are composed of copolymer(s) as the base component, a tackifying resin as the tacky component, and other materials such as oil, fillers, and antioxidants as the complementary components used for improving the performance of PSAs with regard to the target application [19]. The most common components of a typical PSA are introduced in the following subsections:

Polymers

Polymers, as the base component of a pressure sensitive adhesive, can be classified into three categories: natural rubbers, acrylics, and Styrenic Block Copolymers (SBCs) [8]. Polymers can balance the adhesion properties of the adhesives in such a way that adequate strength for transferring loads between substrates can be achieved. Substrates or adherends are materials that bond to adhesives.

Common petroleum-based polymers used in PSA production

As discussed earlier, PSAs were first developed on the basis of rubbers, followed by acrylic PSAs, which are composed of: random copolymers of a long side-chain acrylic, a short-side chain

acrylic, and acrylic acid. PSAs in this category are inherently tacky meaning that it is not necessary to include tackifiers in their formulation [8, 20].

Over the past twenty years, PSAs based on block copolymers have been increasingly developed and used in the industry. Block copolymers have a typical structure of A-B-A, where A end-blocks with glass transition temperatures (T_g) higher than room temperature provide hardness for the mixture and the B mid-block with a T_g lower than room temperature plays the role of a soft, elastomeric component [21-23]. At room temperature, the A blocks provide cohesive strength by performing as physical cross-linking domains, while the B mid-block behaves as the soft, amorphous domain providing viscoelastic properties [23-25]. According to Yuhong and Charles, the most common block copolymers used in the production of PSAs are Styrenic Block Copolymers (SBCs) among which Styrene-Isoprene-Styrene (SIS) and Styrene-Butadiene-Styrene (SBS) are the most commercially available ones used [23]. Since 1964 when the Shell Chemical Company first made SBCs commercial, they have been extensively used as the base polymers for PSAs. SIS and SBS triblock copolymers have the two phase structure of A-B-A, which is discussed above. The rigid styrenic domains are dispersed in the soft matrix of polybutadiene or polyisoprene. Above the T_g of styrene, the cohesive strength of these polymers decrease and they melt and flow, while below this temperature the styrenic component increases the cohesive strength [26]. When these polymers are mixed together with the tackifiers and plasticizers at the adequate proportions, they can ensure the cohesion and adhesion of the PSAs [16].

Vegetable oil-based polymers

Due to economic and environmental concerns regarding the increasing use of fossil oils, the growing demand for them, and the dramatic fluctuations in the price of oil and its by-products, considerable effort is being devoted to development of renewable resources as complete or partial

substitutes for petroleum-based products [27]. Over the past decade, vegetable oils have been vigorous competitors for petroleum-based chemicals, especially polymers.

Generally, oils are composed of a mixture of triglycerides each of which contain a glycerol molecule and three fatty acids, as shown in *Figure 2*, where R_1 , R_2 , and R_3 , are fatty acid chains. A list of 16 of the most common oils can be found in Table 1. The most representative oils used in the composition of vegetable oil-based polymers are also shown in Figure 3. Fatty acids can have a chain length from 14 to 22 carbons and contain an average of 3.6 double bonds [1, 6] per molecule. The nature and the distribution of fatty acids, their different positions along the chain, their conjugated sequences, and the number of double bonds primarily prescribe the physical and chemical properties of vegetable oils [1]. The most important properties of some triglyceride oils and fatty acids are summarized in Table 2.

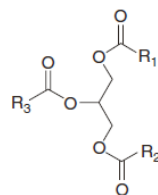


Figure 2 General structure of vegetable oils, R_1 , R_2 , and R_3 fatty acids [1]

Table 1 Names of the most common fatty acids with their specific chemical structures [1, 28]

Chain length: Number of DB	Systematic name	Trivial name	Double bond position
12:0	Dodecanoic	Lauric	–
14:0	Tetradecanoic	Myristic	–
16:0	Hexadecanoic	Palmitic	–
18:0	Octadecanoic	Stearic	–
18:1	9-Octadecanoic	Oleic	9
18:2	9,12-Octadecadienoic	Linoleic	9,12
18:3	6,9,12-Octadecatrienoic	γ -linolenic	6,9,12
18:3	9,12,15-Octadecatrienoic	α -linolenic	9,12,15
20:0	Eicosanoic	Arachidic	–
20:1	Eicosaenoic	–	9
20:4	Eicosatetraenoic	Arachidonic	5,8,11,14
20:5	Eicosapentaenoic	EPA	5,8,11,14,17
22:0	Docosanoic	–	–
22:1	Docosenoic	Erucic	13
22:5	Docosapentaenoic	DPA	7,10,13,16,19
22:6	Docosahexanoic	DHA	4,7,10,13,16,19

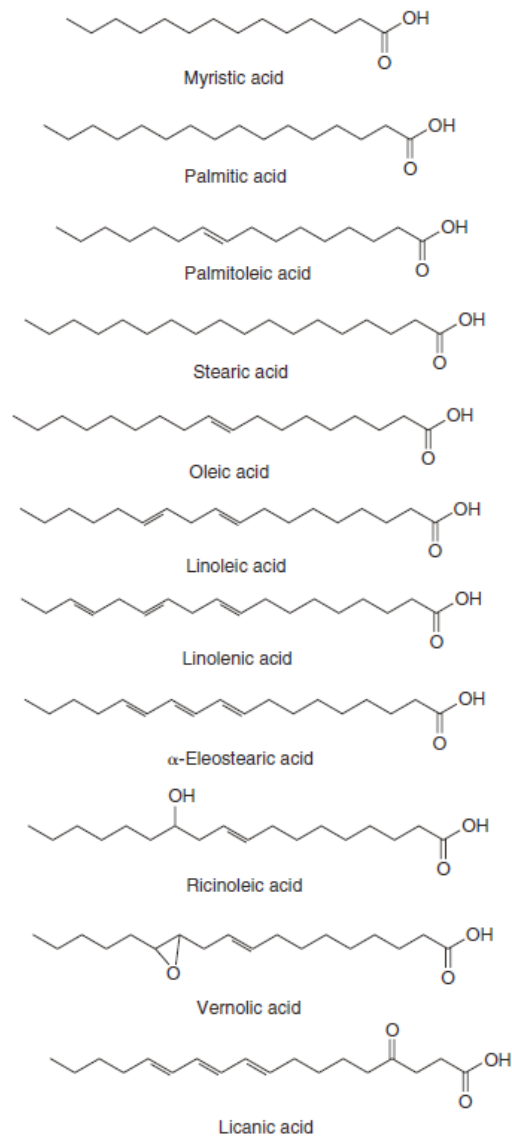


Figure 3 Chemical structure of common fatty acids in vegetable oil-based polymers [1]

Table 2 physical properties of some vegetable oils and fatty acids [1, 28, 29]

Name	Viscosity (mPa · s)	Specific gravity	Refractive index	Melting point (°C)
Castor oil	293.4 at 37.8°C	0.951 at 20°C	1.473–1.480 at 20°C	–20 to –10
Linseed oil	29.6 at 37.8°C	0.925 at 20°C	1.480–1.483 at 20°C	–20
Palm oil	30.92 at 37.8°C	0.890 at 20°C	1.453–1.456 at 20°C	33–40
Soybean oil	28.49 at 37.8°C	0.917 at 20°C	1.473–1.477 at 20°C	–23 to –20
Sunflower oil	33.31 at 37.8°C	0.916 at 20°C	1.473–1.477 at 20°C	–18 to –16
Myristic acid	2.78 at 110°C	0.844 at 80°C	1.4273 at 70°C	54.4
Palmitic acid	3.47 at 110°C	0.841 at 80°C	1.4209 at 70°C	62.9
Stearic acid	4.24 at 110°C	0.839 at 80°C	1.4337 at 70°C	69.6
Oleic acid	3.41 at 110°C	0.850 at 80°C	1.4449 at 60°C	16.3

Over the past decade, polymers based on triglyceride oils have been used for various applications in different forms such as oxypolymerized oils, polyesters, polyurethanes, polyamides, acrylic resins, epoxy resins, and polyesteramides [30]. In order to enable the vegetable oils to participate in polymerization, their active sites must be capable of reacting with other monomers. The active sites of the triglycerides cooperating in chemical reactions could be double bonds, allylic carbons, ester groups, and the carbons alpha to the ester group [31]. In the unmodified vegetable oils, the active sites are mostly isolated with low reactivities; therefore, they are not viable for polymerization reactions. In order to reach a higher level of reactivity, the active sites can be modified through different processes, such as epoxidation and acrylation, hydroformylation and hydrogenation, oxidation and reduction, etc., among which, epoxidation and acrylation is the most common method used in industry. The epoxidized functional triglycerides can be synthesized from unsaturated oils, such as soybean oil, through a standard epoxidation reaction. Epoxidized soybean oil (ESO) has been widely studied in the polymers and composites areas. To further increase the reactivity, the ESO can then be reacted with vinyl functionalities such as acrylic acid, thus forming acrylates, which can be polymerized via different polymerization techniques, including free radical, condensation, and cationic polymerization. Among the variety of triglyceride monomers, acrylated epoxidized soybean oil (AESO) has been reported as a promising candidate for use in engineering fields [6, 31]. Figure 4 shows the epoxidation and acrylation processes of soybean oil. To improve the processing ability of AESO and reach acceptable engineering requirements, it can be incorporated into a reactive diluent, such as styrene. Depending on the objectives, the amount of styrene can be adjusted to produce polymers with different engineering properties. Other than that, the molecular weight of monomer and the functionality of the acrylated triglyceride can control the properties of the produced polymer.

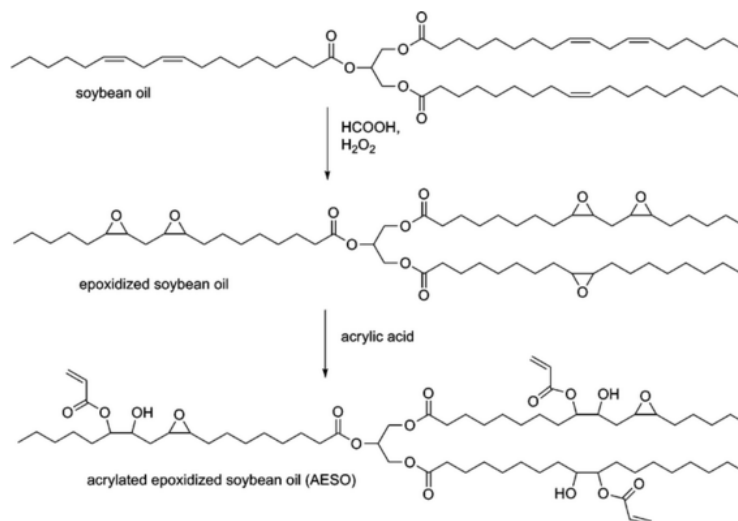


Figure 4 Synthesis of acrylated epoxidized soybean oil (AESO) from soybean oil [32]

With respect to environmental benefits of “green” polymers, Figure 5 illustrates the life cycle of vegetable oil-based polymers based on which, such polymers significantly contribute to the decrease in the large amount of solid wastes, as one of the major environmental issues that the world is facing.

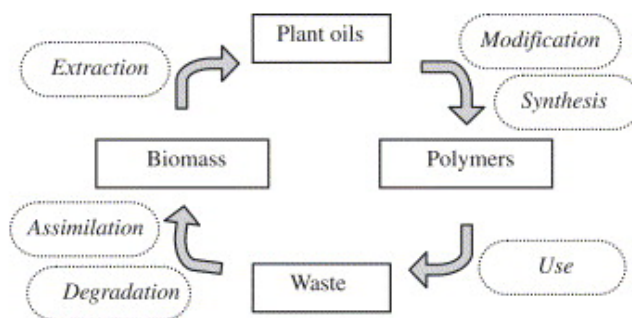


Figure 5 Life cycle of vegetable oil-based polymers [30]

Thus, soybean oil-based polymers have the potential to be synthesized as polymers and be employed in various applications as alternatives to petroleum-based polymers. These “green” materials are also distinguished from their conventional counterparts by some novel characteristics such as biocompatibility and biodegradability, adding significant value to the current studies on the use of renewable sources in the preparation of distinctive industrial materials.

Thermoplastic elastomers derived from soybean oil

Elastomers are a class of polymers characterized by their mechanical response rather than their chemical structure. Linear, reversible, and immediate response to an applied load, as well as weak intermolecular forces and high strains, are attributed to elastomers. These properties are highly related to each other, as the reversible and immediate response is obtained with molecules possessing flexible chains with weak intermolecular forces, and high strain is achieved with polymers due to uncoiling of their random molecular coils [33]. However, after molding or shaping, elastomers become cross-linked i.e. they cannot be reprocessed or recycled anymore. Thus, to overcome this shortage, thermoplastic elastomers (TPEs) have been introduced into a variety of applications requiring materials with all the same features as elastomers, but also involving the advantage of deforming after molding. A network of physical cross-links enables thermoplastic elastomers to behave as two-phase systems containing an elastic part with high molar mass, and a restraining part to resist viscous flow and creep. Therefore, an amorphous domain as a soft phase, and a crystalline domain as a hard phase, are the two major components of TPEs. The main advantage of such compounds is that they improve the properties of PSAs by creating a multiphase composite structure, yielding viscoelastic characteristics which provide both elasticity and viscous flow depending on the temperature and the formulations [6, 10, 33]. Six main classes of TPEs have been found commercially available: (1) styrenic block copolymers, (2) polyolefin blends, (3) elastomeric alloys, (4) thermoplastic polyurethanes, (5) thermoplastic copolyesters, and (6) thermoplastic polyamides [6]. Among these classes, styrenic block copolymers are the most commonly used TPEs for PSAs. Since 1964, when the first styrenic TPEs were introduced to the market, many variations have been made to their structure leading to a wide range of grades with different physical properties, among which SIS grades possessing low polystyrene content are the most commonly used ones. The chemistry of most common petroleum-

based TPEs was discussed earlier in section 2.2.1.1. However, few studies have studied the opportunities in developing TPEs from sustainable resources such as vegetable oils.

Vegetable oils, due to their biodegradability, relatively low price, low toxicity, ease of functionalization, etc., are attractive sources for the derivation of TPEs [7, 27, 34, 35]. As discussed in section 2.2.1.2, soybean oil can be used as a renewable substitute of the soft phase of non-renewable block copolymers, through appropriate modification processes such as epoxidation and acrylation. Iowa State University scholars have synthesized a diblock copolymer named PS-PAESO via controlled radical polymerization techniques (RAFT and ATRP), which is composed of styrene as the hard domain, and acrylated epoxidized soybean oil (AESO) as the soft domain [2, 6]. Until this study, the end use application of this diblock polymer had only been performed for modification of asphalt paving mixtures. This thesis, however, focuses on the incorporation of PS-PAESO into pressure sensitive adhesives formulation for complete replacement of Styrene-Isoprene-Styrene polymer, used as the most common polymeric component of PSAs. The new polymer will be further introduced in the next chapter.

Tackifiers

Tack is a unique property of pressure sensitive adhesives with which they bond to substrate upon application of a light contact pressure during a short time [10]. In order for an elastomer to exhibit tack, two important criteria must be met: (1) entanglement of the molecules in the polymeric chain with the molecules in the substrate in order to develop contact across the interface, and (2) development of high cohesive strength after formation of bond to prevent easy separation. As discussed in the previous section, due to their inherent very low T_g , elastomers do not exhibit viscous flow exclusively; therefore, to achieve tacky PSAs, elastomers must be replaced by thermoplastic elastomers, or blended with some viscous components such as tackifiers and

plasticizers. According to Benedek [10], tackifiers are described as low molecular weight resins, used to improve rheological behavior of base polymers in the PSA formulation. Rosin derivatives, phenolic, ketone, and hydrocarbon resins are examples of different natural or synthetic resins used as tackifiers, among which hydrocarbon resins are the preferred ones in PSA formulations. Most tackifying resins have a T_g above ambient temperature and are near 40 to 50°C, which enable the PSA composed of styrenic block copolymers to behave viscoelastically at room temperature [26]. The good performance of a tackifier is usually characterized by its compatibility with other components of the PSA [36]. According to Class and Chu [36], a compatible system is identified by a depression in the storage modulus in the plateau region so that an adequately low value is obtained for forming a bond upon application of a light stress. The compatibility can also be characterized by PSAs exhibiting only one glass transition temperature through differential scanning calorimetry (DSC) testing [37].

There have been several studies to evaluate the effect of tackifier properties on the performance of PSAs. For instance, Kim et al. have investigated the effect of tackifier on SIS-based hot-melt PSAs; they have observed that the increase in the tackifier content leads to a gradual increase in the peel adhesion followed by a decrease in this property. Therefore, they have found that the maximum value of peel adhesion occurs at 60 wt% of tackifier content for those blends made by using low softening point resins, and between 40 and 50 wt% of tackifier content for blends made by high softening point resins [38].

Da Silva et al. also studied the interaction between the components of PSAs and their effects on the mechanical and rheological properties of PSAs, varying the type of elastomers, type of tackifiers, and the plasticizer content [16]. They have concluded that the final characteristics of the PSA are dictated by the compatibility between the elastomer and the tackifier with relation to

the different combinations of these components which lead to acquiring the minimum values of tack for PSA applications.

The tackifier content depends on the end-use requirements such as level of removability, cost factors, etc. [10].

Plasticizers

It has been shown that blending a tackifier with rubber results in an increase in the glass transition temperature of the blend. The increase in T_g could be attributed to segmental frictions in the blend, which can be eliminated by using plasticizers to loosen the entangled network [39, 40]. Plasticizers are the additives incorporated into the formulation of pressure sensitive adhesives in order to improve their flexibility by providing more free volume. The composition will therefore require lower temperatures to reduce the free volume, thus lowering the glass transition temperature [33], and widening the rubbery region for improved performance at temperatures lower than room temperature. However, excessive amounts of plasticizer can reduce the adhesion and resistance to heat and deformation of the PSA [8, 16, 37].

2.3 Common Methods Used in Blending and Coating the Materials of PSA

Tapes are the common form of pressure sensitive adhesives (PSAs). PSAs can be blended and coated as tapes by either melting at high temperatures, or dissolving in an appropriate organic solvent, or dissolving in water. Aqueous adhesives have been found as generally lower in quality and performance than solvent-based and hot-melt PSAs due to the following deficiencies listed by Benedek [10] and cited by others [41-43]: lower water and humidity resistance, limited heat resistance, inferior balance of tack, peel, and shear properties, bad plasticizer migration resistance, and concerns about machinability and/or coatability. On the other hand, because of their unique structures discussed earlier, thermoplastic elastomers provide the option of both solvent processing

and melt processing [44]. Therefore, a comparative study has been performed to investigate the effect of the first two methods on PSA characteristics.

Solvent-based formulations

Throughout solvent blending and coating procedures, the first step is to dissolve the PSA components in an appropriate solvent so that they combine thoroughly. Next, the PSA is coated onto an appropriate substrate, and finally dried at a suitable temperature in a dust free environment. This method has been commonly utilized in PSAs based on acrylics [10, 45, 46]. Dissolution of the polymer in the solvent occurs when the attractive forces existing in the polymer-polymer and solvent-solvent networks are weakened. The solubility of the polymer can be determined by three-dimensional solubility parameter, δ^2 , proposed by Hansen [47]:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{Equation 1}$$

Where δ_d is the attractive molecular force from the temporary dipole formation, δ_p is the attractive force from dipole/dipole interactions, and δ_h is the attractive force from hydrogen bonding. Considering the solubility parameter of a solvent as a vector, then the polymer will dissolve in the solvent provided that the vector falls within the three-dimensional volume defined as the solubility parameter range of the polymer. The molecular weight, chemical nature, and the solids content in the formulation, are the most important factors affecting the solubility of the solids content in the solvent [10].

Solvent-based PSAs have been found to exhibit better shear strength and better durability upon exposure to high temperature, compared to melt coatings [48, 49]. However, as with any technology, there are some disadvantages in relation to environmental and toxicity concerns [13], high costs, and fire hazards due to the presence of solvents [10]. Therefore, hot-melt PSAs were developed to overcome these issues.

Hot-melt Pressure Sensitive Adhesives

PSAs produced by the hot-melt technology exhibit a solid state at room temperature and a liquid state at higher temperatures. Several advantages including good peel strength, good water resistance, and aggressive tack have been identified by researchers. This technology decreases the production time by eliminating drying steps as well as reducing material and energy costs. Coating at high temperature enables the PSA to achieve its cohesive strength at room temperature [13].

O'Connor and Macosko have reported a study on structure and properties of block-copolymer-based PSAs blended and coated through both hot-melt and solvent processes [15]. In summary, they have found the following results: upon peel testing, materials with the same composition and heat history exhibited higher tack and peel resistance values when prepared by hot-melt coating. Regarding the microstructure of materials, those prepared via solvent-casting procedures revealed narrower T_g and have a more uniform microstructure. This attribute could be due to the cooling temperature and cooling rate in a hot-melt coating process, where the chain ends are not able to entirely separate in an ordered lattice. Uniformity in composition, however, was found to be less in solvent coating products, due to the enrichment of low molecular weight tackifiers at the bottom of the coating during the evaporation period required by solvents.

In summary, when trying to find the appropriate adhesive technology for the desired applications, Table 3 presented by Benedek provides a great starting point.

Table 3 Selection of adhesive preparation technology based on the application field [10]

PSA label		Adhesive Technology	
Application field	Properties	Solvent-based	Hot-melt
Permanent	Label converting	G	E
	Adhesion	G	E
	Application temperature range	E	G
	Formulation flexibility	E	F
Removable	Label converting	F	F
	Adhesion	G	F
	Application temperature range	E	F
	Formulation flexibility	E	F
Cold temperature	Label converting	F	F
	Adhesion	F	F
	Application temperature range	G	F
	Formulation flexibility	G	F
Clear film	Label converting	E	F
	Adhesion	E	F
	Application temperature range	G	F
	Formulation flexibility	G	F

E=Excellent; F=Fair; G=Good.

2.5 A Review of Mechanical, Physical, and Rheological Properties of Pressure Sensitive Adhesives

The main difference between pressure sensitive adhesives and other types of adhesives is that PSAs bond to the surface without forming any chemical reaction. Therefore, they are basically used in nonstructural applications, as opposed to epoxies, which are used as structural adhesives.

This instance emphasizes the employment of PSAs in variety of applications due to their ease of use upon application of a light pressure at room temperature [8]. Significant debonding resistance is another important characteristic of PSAs [26]. To be designed for various applications, PSAs must meet three technical requirements (1) tack, (2) peel resistance, and (3) shear resistance [50]. They are differentiated from non-PSAs by their ability to develop immediate adhesion to the substrate, called tack. Dahlquist [14], discovered that the tack of PSAs is primarily dependent on the molecular motions, thereby is a modulus-controlled process. Dahlquist then found that when the storage modulus of the PSA exceeds 3×10^5 Pa, the tack will deteriorate. This phenomena, known as the “Dahlquist criterion”, has since been the foundation in adhesion and adhesives studies as applicable to rheological evaluation of PSAs [51].

The majority of PSA applications require films to be peeled from the substrate with no residue left behind [52]. This property is related to the two primary modes of failure of PSA films, that have been identified by several researchers: adhesive and cohesive failure [38, 53]. Cohesive failure usually occurs at low rates of peel, leaving a rough appearance of the adhesive on the substrate, while adhesive failure, occurring at higher rates of peel, reveals a rubbery response of the molecules, thus leaving a smooth surface on the substrate [39]. Based on the combination of adhesion, cohesion, and tack properties, PSAs can be classified as removable, semi-permanent, or permanent adhesives. The composition of the adhesive plays the most critical role in finding the balance between these properties [54].

According to Benedek, the viscoelastic performance of many commercial pressure sensitive adhesives can be evaluated by two important physical properties: elastic modulus E , and glass transition temperature T_g [10]. The viscoelastic behavior of PSAs allows them to perform in both solid (elastic) and liquid (viscous) states depending on the surrounding conditions. The

dynamic viscoelastic parameters G' (storage modulus) and G'' (loss modulus) demonstrate the behavior of materials as a function of frequency of applied stress or strain. The elastic behavior of PSAs is ascribed to the storage modulus, while the viscous behavior is attributed to the loss modulus [55]. It is obviously believed that the chemical structure of the PSAs affects their rheological properties. For instance, chain backbone structure with or without side groups which can restrict or facilitate rotation, modulates the flexibility of PSAs. The ratio between the elastic and the viscous component of the polymer can also affect the rheological behavior considerably [19].

Regarding physical properties, the glass transition temperature (T_g) represents the temperature above which the material has a liquid, rubber-like state, and below which it turns to a glassy, hard state. A low T_g enables the polymer to establish contact with the adherend through wetting the surface, where chain segments can diffuse into each other. As the T_g increases, the stiffer polymer will result in poor adhesive properties and decreased wettability [10].

2.6 Summary of studies

- PSA raw materials can be selected primarily based on their glass transition temperature, modulus, and the degree of miscibility in other components.
- The molecular weight of the polymer plays a key role in controlling the performance of PSA composition towards specific applications.
- PSAs are generally produced in the form of films by two methods: (1) from solution by coating and evaporation of a solvent, which is a more traditional method, used where specific requirements must be achieved only by dissolving the components in a solvent, and (2) from hot melts in the absence of any solvent. For PSAs based on block copolymers, the latter has been found to be the preferred method, since temperatures

higher than the glass transition temperature of the styrene phase yield a melting transition to the phase-separated structure of polymer [8]. Moreover, coating at high temperatures enables the PSA to achieve its cohesive strength at room temperature [13], which is a fundamental property related to debonding resistance of removable PSAs.

- The composition of the PSA should be properly balanced such that the T_g is below 10°C [50, 56], or 30 to 70°C lower than the application temperature [10], or falls in the range between -10 to -113°C [57]. This can be achieved through the addition of adequate concentration of plasticizers.
- For SIS-based adhesives, Lim et al. have found the appropriate tackifier content for providing sufficient flow ability in the region of 30-50% [13], which has been confirmed in other studies [10, 58]. Lim et al. have also reported that the higher the T_g of tackifier, the higher cohesion of PSA, and the higher peel strength. At higher contents of tackifier, however, they have observed that the peel strength drops as the PSA becomes brittle, showing a stick-slip behavior, and a considerable loss in shear strength.
- Taking into account the various factors affecting the miscibility of the tackifier in other components of the adhesive formulation, it has been concluded that the nature of polymeric base is the key factor in determining the choice of the tackifier [10]. Therefore, the most compatible tackifier in SIS-based PSAs may not serve similarly in PSAs based on other block copolymers.
- To ensure the necessary cohesion at room temperature, the amount of styrenic domains should be optimized so that cohesive failure of PSAs is prevented [16].
- The peel test is the most common method to evaluate the performance of adhesives by measuring the force required to peel a strip of the adhesive, which has been coated on a flexible backing, from a rigid or flexible substrate at a constant velocity [59, 60].

- In regards to rheological characteristics, the plateau region of the PSA which is attributed to the tack properties of PSAs, must be wide enough so that the applied frequency would not influence the shear resistance of the adhesive. Therefore, modulation of viscoelastic properties such as G' and G'' plays an important role in distinguishing PSAs from other types of adhesives.

CHAPTER 3. EXPERIMENTAL PLAN AND TEST METHODS

3.1 Materials and Formulations

The experimental pressure sensitive adhesives consisted of PS-PAESO block copolymer as the base polymer. The PS-PAESO block copolymer system is produced via RAFT polymerization technology [6]. Styrene was provided by Fisher Scientific and purified at Iowa State University chemical laboratories. Acrylated Epoxidized Soybean Oil (AESO) was purchased from Sigma-Aldrich Company and used as received. styrene-isoprene-styrene (SIS) was purchased from Kraton Company as well.

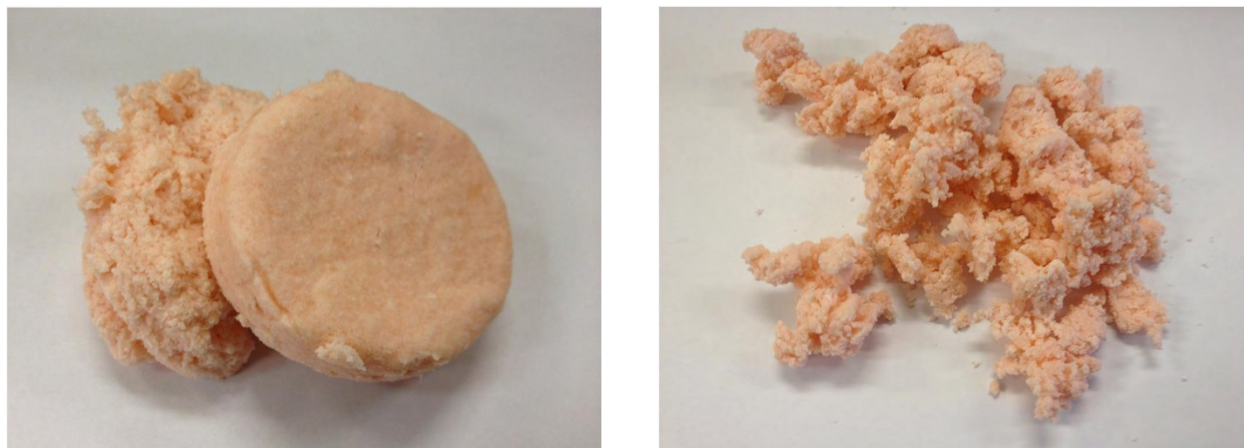


Figure 6 PS-PAESO di-block copolymer [6]

Eastman Chemical Company provided five hydrocarbon resins as tackifiers (see Figures 7 and 8) and three other chemicals as plasticizers (see Figure 9). All eight chemicals were used as received from the commercial source. An inhibitor called Methylhydroquinone (MHQ), purchased from Sigma-Aldrich, was also used in this study (see Figure 10). The PSAs were developed using 45% polymer, 49% tackifier, and 6% plasticizer, according to recommendations from industry experts.



Figure 7 Tackifiers, left to right: Piccotac 1095, Piccotac 8095, Staybelite 10-E, Foral AX-E

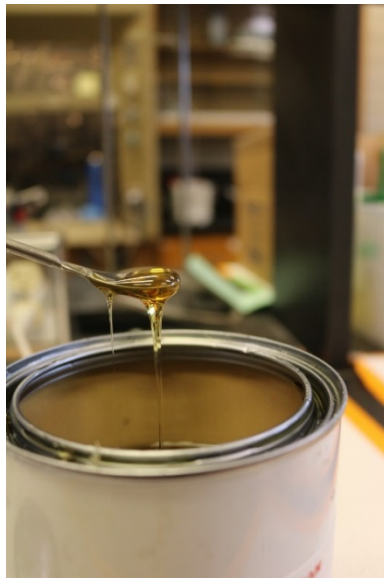


Figure 8 Staybelite 3-E as a tackifier

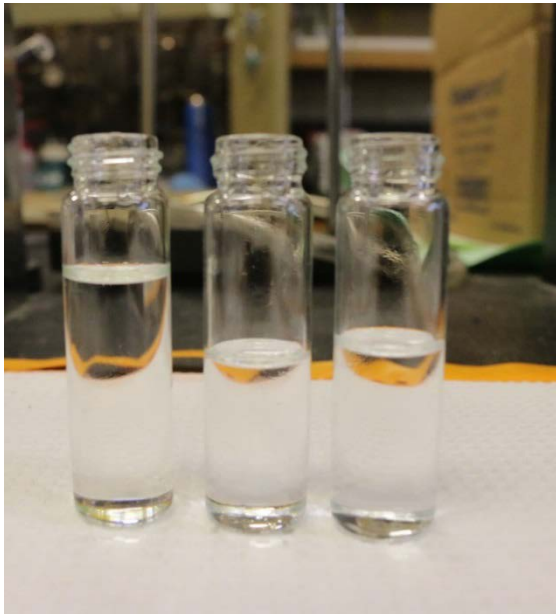


Figure 9 Plasticizers (left to right):
Benzoflex, Eastman 168, and Triacetin

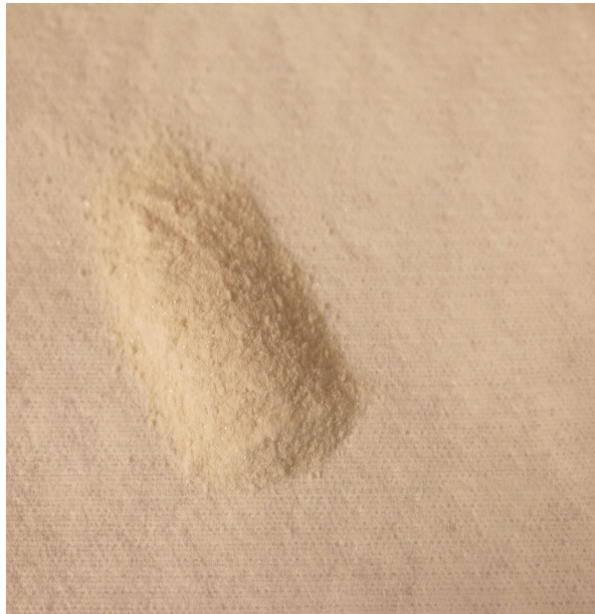


Figure 10 Methylhydroquinone (MHQ)

Some physical properties of the tackifiers found on the safety data sheets provided by Eastman Company are listed in Tables 4 and 5.

Table 4 Typical properties of Piccotac 1095 and Piccotac 8095 [61, 62]

Property Name	Molecular Weight (Da)		Density at 25°C (kg/L)	Softening point (°C)	Softening point method	Melt viscosity (°C)			Tg from data sheet(°C)	Tg from DSC test(°C)
	Mn	Mw				10 poise	100 poise	1000 poise		
Piccotac™ 1095	800	1700	0.94	94	Ring & ball	160	135	110	43	45
Piccotac™ 8095	850	2200	-	95	Ring & ball	190	155	130	41	45

Table 5 Typical properties of Staybelite 3-E, Staybelite 10-E, and Foral AX-E [63-65]

Property Name	Acid number mg KOH/g	Density at 25°C (kg/L)	Softening point (°C)	Softening point method	Melt viscosity (°cP)			Viscosity Brookfield LVDT mPa.s	Tg from DSC test(°C)
					120°C	140°C	160°C		
Staybelite™ 3-E	8	-	-	-	-	-	-	22000	-17.84
Staybelite™ 10-E	9	1.07	95	Ring & ball	1800	330	90	-	36.33
Foral™ AX-E	165	-	80	Hercules drop	-	-	-	-	30.21

Some key attributes and descriptions are also mentioned for the five tackifiers as follows:

- Piccotac™ 1095 Hydrocarbon Resin: Excellent adhesion to styrene-isoprene-styrene (SIS) block copolymers, excellent peel and tack properties, aliphatic low molecular resin, soluble in aliphatic, aromatic, and chlorinated hydrocarbon esters and ethers, as well as insoluble

in alcohols, glycols, and water. Applications include: hot-melt adhesives, pressure sensitive adhesives, tapes and labels, wax modification, packaging, etc. [62]

- Piccotac™ 8095 Hydrocarbon Resin: Compatible with SIS and SBS block copolymers, amorphous poly-alpha olefins, paraffin and microcrystalline waxes, soluble in aliphatic, aromatic, and chlorinated hydrocarbon esters and ethers, as well as insoluble in alcohols, glycols, and water. Applications include: hot-melt adhesives, pressure sensitive adhesives, tapes and labels, wax modification, packaging, footwear and leather, laminating, etc.[61].
- Staybelite™ Ester 3-E Ester of Hydrogenated Rosin: a pale, viscous, balsamic liquid with good resistance to oxidation and discoloration, compatible at all ratios, or in limited but practically useful proportions with resins, plasticizers, chlorinated rubber, waxes, nitrocellulose, and ethylcellulose. It is soluble in esters, ketones, higher alcohols, glycol ethers, aliphatic and aromatic hydrocarbons, and chlorinated solvents, but insoluble in water and methanol. Applications include hot-melt adhesives, pressure sensitive adhesives, tapes and labels, wax modification, packaging, caulks and sealants, assembly, etc. [63].
- Staybelite™ Ester 10-E Ester of Hydrogenated Rosin: a pale, thermoplastic resin with excellent resistance to oxidation and discoloration, which has found wide acceptance as a tackifying resin for many adhesive applications, especially pressure sensitive adhesives, hot melt and emulsion types, and is compatible with other resins, waxes, and plasticizers; with low molecular weight polyethylene, SIS and SBS block copolymers; with acrylic resins, etc. Applications include hot-melt adhesives, pressure sensitive adhesives, tapes and labels, wax modification, packaging, caulks and sealants, assembly, etc. [64].
- Foral™ AX-E Fully Hydrogenated Rosin: a thermoplastic, acidic resin produced by hydrogenating rosin to an exceptional high degree. It is soluble in alcohols, esters, ketones, hydrocarbons, chlorinated solvents, and mineral oils. It has a very light color, medium

softening point, and excellent resistance to oxidation. It is used as the tackifier and resin modifier in solvent adhesives and hot-melt applied coatings and adhesives [65].

Some descriptions and key attributes of the plasticizers are provided below in Table 6:

Table 6 Typical properties of plasticizers[66-68]

Name	Property	Boiling point (°C)	Dynamic viscosity at 25°C (mPa.s)	Molecular Weight	Freezing point (°C)	Flash point (°C)	Pour point (°C)	Specific gravity at 20°C/°C	Kinematic viscosity 25°C (mm ² /s)
Benzoflex™ 2088		356	71	332	< 16	202	-25	1.16	-
Eastman™ Triacetin		258	17.4	218	3.2	153	-	1.16	-
Eastman 168™		400	-	-	< -67.2	238	-	0.984	66.9

- Benzoflex™ 2088: a high solvating plasticizer known for its excellent performance in water-based adhesives and PVC and displays exceptional wet tack in adhesives. Its applications include Latex sealants, pressure sensitive adhesives, flooring/interior surfaces, etc. [67]
- Eastman™ Triacetin: used as a plasticizer for cellulosic resins and is useful for imparting plasticity and flow to laminating resins, particularly at low temperatures. Its applications include coatings, pressure sensitive adhesives, PVA water based adhesives, graphic arts, food contact, etc. [68].
- Eastman 168™ non-phthalate plasticizer: an excellent non-phthalate plasticizer for PVC, offering good low temperature flexibility and resistant to extraction by soapy water. Its

applications include: latex sealants, pressure sensitive adhesives, automotive, flooring/interior surfaces, wire/cable, etc. [66]

The formulations, as mentioned earlier, were designed as shown in Table 7. During the study, it was decided to perform solvent blending on smaller amounts of materials to synthesize the fifteen PSAs, in order to evaluate their general thermal and tack characteristics. Later on, based on testing the visual adhesion of these fifteen solvent-based PSAs and the miscibility of tackifiers in the blends, nine formulations were selected for hot-melt blending processes for the remaining portion of the study.

3.2 Experimental Layout

The experimental layout is shown in Table 8. Figure 11 also illustrates the sequential experimental test plan.

3.3 Synthesis of the PSAs

The PS-PAESO/tackifier/plasticizer blend ratios were estimated as 45/49/6 for both solvent-blending and hot-melt blending methods.

Upon solvent blending, a total of 3 grams of the PSA was mixed with approximately 7 g of toluene, as a typical organic solvent in a glass vial. MHQ was also added to the blend by 1.5 wt % of the polymer. As illustrated in Figure 12, the materials were then stirred by means of an IKA magnetic stirrer until entirely blended. To pull the solvent off after blending, PSAs were put into a schlenkline apparatus (see Figure 13). However, since this procedure required observation and adjustment of the vacuum pressure for more than a day, an alternative method was used as shown in Figure 14- the solution was poured into PYREX® petri dishes and the solvent was evaporated under circulating air over night.

Table 7 Experimental Formulation Plan

Sample Code	Formulation (Poly./Tack./Plast.)	Tackifier	Polymer Wt. (grams)	Polymer Code	Tackifier Wt. (grams)	Plasticizer	Plasticizer Wt. (grams)	Adhesive Wt. (grams)	Blending Method	Toluene Wt. (grams)
#1	45/49/6	Piccotac 1095	1.35	ADH_PSPAESO	1.47	Benzoflex	0.18	3	Solvent: Toluene	7
#2	45/49/6	Piccotac 1095	1.35	ADH_PSPAESO	1.47	Triacetin	0.18	3	Solvent: Toluene	7
#3	45/49/6	Piccotac 1095	1.35	ADH_PSPAESO	1.47	Eastman 168	0.18	3	Solvent: Toluene	7
#4	45/49/6	Piccotac 8095	1.35	ADH_PSPAESO	1.47	Benzoflex	0.18	3	Solvent: Toluene	7
#5	45/49/6	Piccotac 8095	1.35	ADH_PSPAESO	1.47	Triacetin	0.18	3	Solvent: Toluene	7
#6	45/49/6	Piccotac 8095	1.35	ADH_PSPAESO	1.47	Eastman 168	0.18	3	Solvent: Toluene	7
#7	45/49/6	Staybelite 3-E	1.35	ADH_PSPAESO	1.47	Benzoflex	0.18	3	Solvent: Toluene	7
#8	45/49/6	Staybelite 3-E	1.35	ADH_PSPAESO	1.47	Triacetin	0.18	3	Solvent: Toluene	7
#9	45/49/6	Staybelite 3-E	1.35	ADH_PSPAESO	1.47	Eastman 168	0.18	3	Solvent: Toluene	7
#10	45/49/6	Staybelite 10-E	1.35	ADH_PSPAESO	1.47	Benzoflex	0.18	3	Solvent: Toluene	7
#11	45/49/6	Staybelite 10-E	1.35	ADH_PSPAESO	1.47	Triacetin	0.18	3	Solvent: Toluene	7
#12	45/49/6	Staybelite 10-E	1.35	ADH_PSPAESO	1.47	Eastman 168	0.18	3	Solvent: Toluene	7
#13	45/49/6	Foral AX-E	1.35	ADH_PSPAESO	1.47	Benzoflex	0.18	3	Solvent: Toluene	7
#14	45/49/6	Foral AX-E	1.35	ADH_PSPAESO	1.47	Triacetin	0.18	3	Solvent: Toluene	7
#15	45/49/6	Foral AX-E	1.35	ADH_PSPAESO	1.47	Eastman 168	0.18	3	Solvent: Toluene	7

Table 8 Experimental Plan

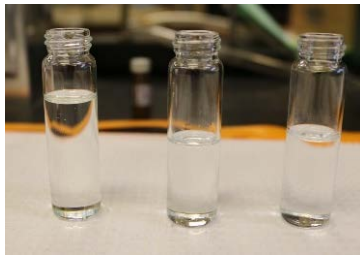
Sample Code	Tackifier	Plasticizer	Solvent Blending	DSC Test	Hot Melt Blending	DSC Test	Rheology Test	Peel Test			
								10 μm	50 μm	100 μm	125 μm
1	Piccotac 1095	Benzoflex	x	x	Not viable based on DSC test						
2	Piccotac 1095	Triacetin	x	x							
3	Piccotac 1095	Eastman 168	x	x							
4	Piccotac 8095	Benzoflex	x	x							
5	Piccotac 8095	Triacetin	x	x							
6	Piccotac 8095	Eastman 168	x	x							
7	Staybelite 3-E	Benzoflex	x	x	x	x	x	xxx	xxx	xxx	xxx
8	Staybelite 3-E	Triacetin	x	x	x	x	x	xxx	xxx	xxx	xxx
9	Staybelite 3-E	Eastman 168	x	x	x	x	x	xxx	xxx	xxx	xxx
10	Staybelite 10-E	Benzoflex	x	x	x	x	x	x	x	x	x
11	Staybelite 10-E	Triacetin	x	x	x	x	x	x	x	x	x
12	Staybelite 10-E	Eastman 168	x	x	x	x	x	x	x	x	x
13	Foral AX-E	Benzoflex	x	x	x	x	x	x	x	x	x
14	Foral AX-E	Triacetin	x	x	x	x	x	x	x	x	x
15	Foral AX-E	Eastman 168	x	x	x	x	x	x	x	x	x

x: number of samples test

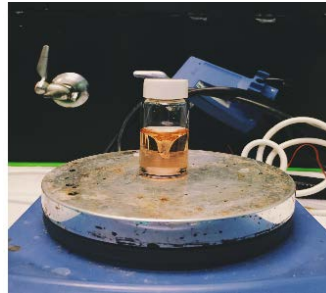
Raw materials



- Polymer (Cochran's group)
- Tackifier (Eastman Co.)
- Plasticizer (Eastman Co.)



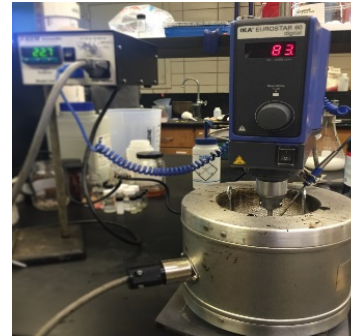
Solvent blending



- Compatibility study
Differential Scanning Calorimetry (DSC)
- Rheology (ARES G2 Rheometer)



Hot-melt blending

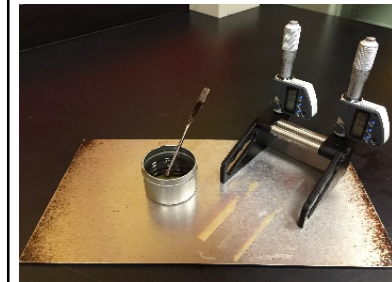


Evaluation

- DSC
- Rheology
- Viscoelastic windows



Film application



Peel Testing

- IMASS peel tester

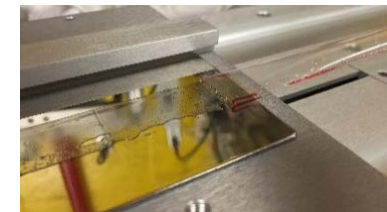


Figure 11 Experimental steps

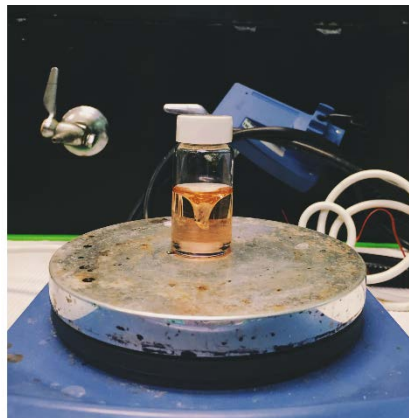


Figure 12 Solvent blending on a magnetic stirrer

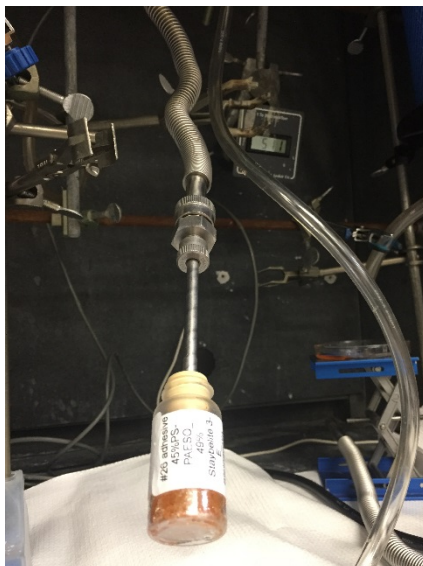


Figure 13 Drying of the PSA with schlenkline setup

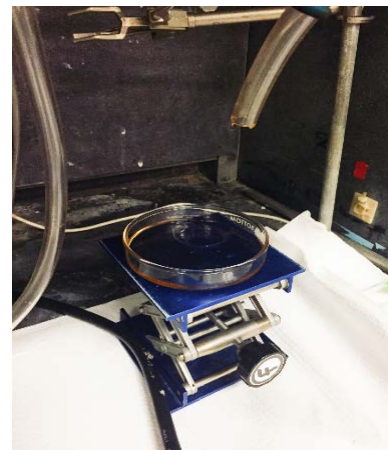


Figure 14 Solvent Casting by air circulation

Hot-melt blending was performed under an Argon atmosphere to minimize the effect of oxidation on PSAs. PSAs were blended with a EUROSTAR 60 IKA® stirring head, holding an R 1302 dissolver stirrer. Blending was conducted at 150°C at a rate of 200 rpm for one hour (see Figure 15).

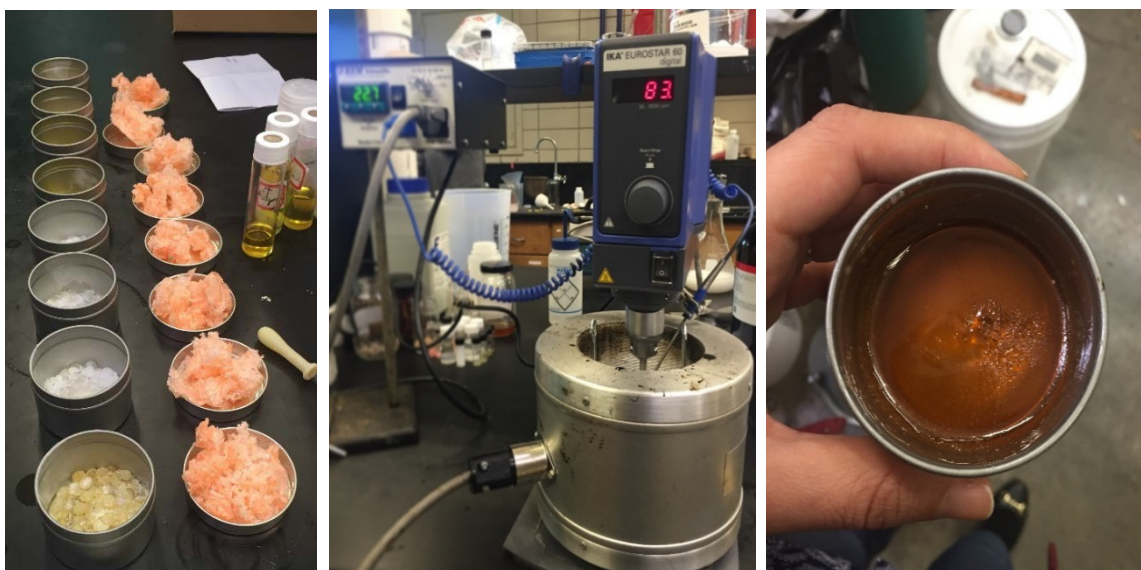


Figure 15 Hot-melt blending procedures

3.4 Preparation of the PSA Films

As discussed in the previous section, it was decided to prepare films just for hot-melt PSAs, since the solvent blended adhesives did not show sufficient tack and took several days to dry. The samples to be tested consisted of a 50 μm Mylar® polyester film backing coated with the PSA. The PSA blends were applied onto backing by melt coating procedure as following: the melted PSA was deposited on the Mylar films which were placed as substrates on a heated (90°C) metal plate, and spread over the film using a GARDCO® adjustable micrometer film applicator. The blade of the applicator was also heated to 90°C in the oven. The first 1.5 cm of the length of the tapes was not coated with the adhesive for the sake of transferring. The 2.5cm \times 14 cm stripes of PSA were then placed on steel plates for peel testing, discussed later in this chapter. (See Figure 16)

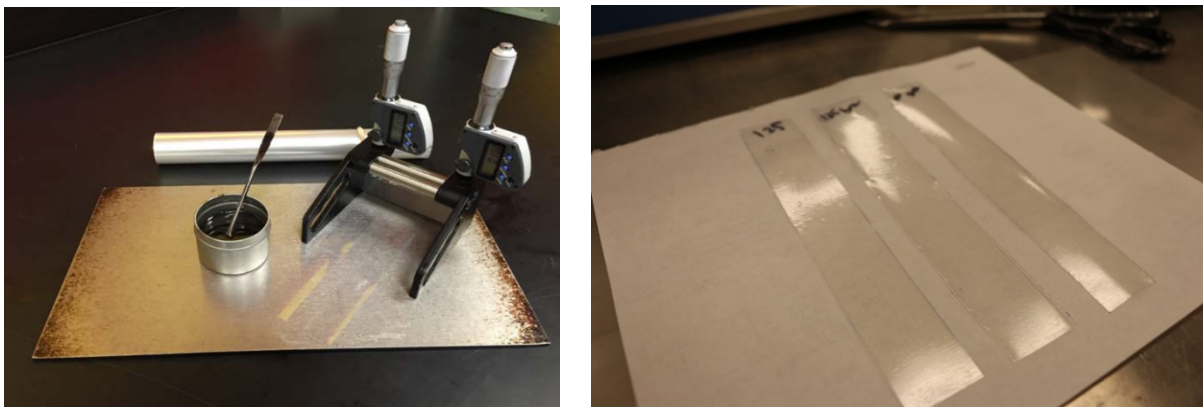


Figure 16 Film preparation

3.5 Testing Methodology and Equipment

3.5.1 Thermal properties and Differential Scanning Calorimetry (DSC)

The glass transition temperature of each formulation was characterized by a TA Instruments Q 2000 Differential Scanning Calorimetry (DSC), as shown in Figure 17, equipped with a liquid nitrogen cooling system (LNCS). A DSC measures the temperatures and heat flows

associated with transitions in materials as a function of time and temperature. Three or four consecutive heating and cooling cycles ranging from -60 to 130 with a rate of 10°C/min were applied on each sample weighing 5 ± 1 grams of material in standard aluminum pans. Each of the five tackifiers were first tested by a DSC in order to study their thermal behavior. To prepare DSC samples of solvent blend PSAs, they were further dried at 40°C in a vacuum oven to completely evaporate toluene and anneal overnight [69]. Hot-melt blended PSAs were tested as prepared without any further action.



Figure 17 Differential Scanning Calorimetry (DSC) apparatus

3.5.2 Viscoelastic properties and rheometer

The viscoelastic properties of the PSAs (storage modulus, loss tangents, and complex viscosities) were characterized using a TA Instruments ARES G2 rheometer, illustrated in Figure 18.

Approximately 2 grams of the PSA was deposited on a silicone mold and transferred to 8 mm parallel plates. The samples were then trimmed in the form of disk with a thickness of 1 mm. Using a frequency range of 1 to 100 rad/s at a temperature increment of 10°C between -50°C and

50°C, master curves at a reference temperature of 25°C were developed by means of TRIOS data analysis software, provided by TA instruments.



Figure 18 ARES G2 rheometer

3.5.3 Adhesion properties and peel tester

PSA films were adhered to a stainless steel panel such that the uncoated end of the sample was free to install in the peel tester clamps. The samples of tape were then rolled twice with a 2 kg roller to develop good bond to the steel plate [14, 45]. According to earlier publications [13, 38], an average thickness of 0.075 mm results in a sufficient peel resistance. Therefore, films were prepared in 0.01 mm, 0.05 mm, 0.075 mm, 0.1 mm and 0.125 mm thickness of PSA in order to investigate the effect of thickness on peel strength.

Pressure sensitive tapes were tested with the 180° peel test according to the Pressure Sensitive Tape Council (PSCT) Test Method 1. According to ASTM D907, the peel strength is defined as “the average load per unit width of bondline required to separate progressively a flexible member from a rigid member or another flexible member” [70]. The peel strength was measured

using an IMASS SP-2100 slip/peel tester (see Figures 19 and 20). In this test, the force was measured as a variable with time. A 1-inch wide piece of tape was peeled from a stainless steel panel as a substrate at an angle of 180° and at a rate of 12 in./min, as indicated by ASTM D903 [14]. Since during the actual peel test process a small finite amount of time is required for the peel forces to reach a dynamic equilibrium, the First 4 seconds were called delay time and were discarded to ensure that the initial readings obtained from peeling the free end of the tapes were not included in the results. The average peel force from at least three [20] tests over the remaining peel length was recorded for each formulation. These experiments took place at a room temperature of $24 \pm 1^\circ\text{C}$ and $35 \pm 1\%$ relative humidity.

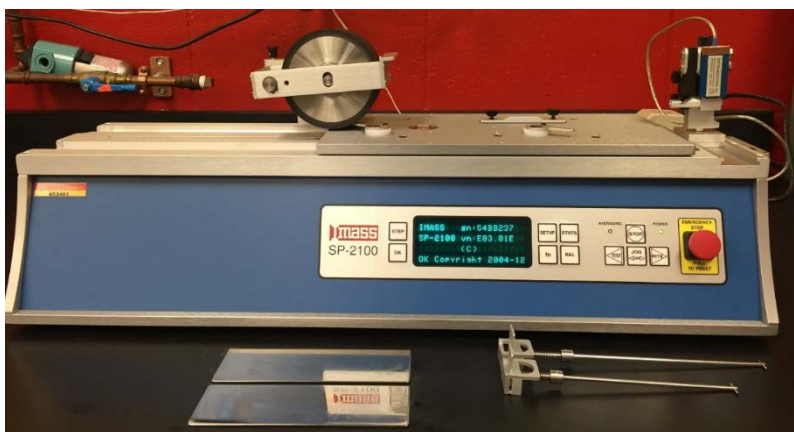


Figure 19 Peel tester apparatus

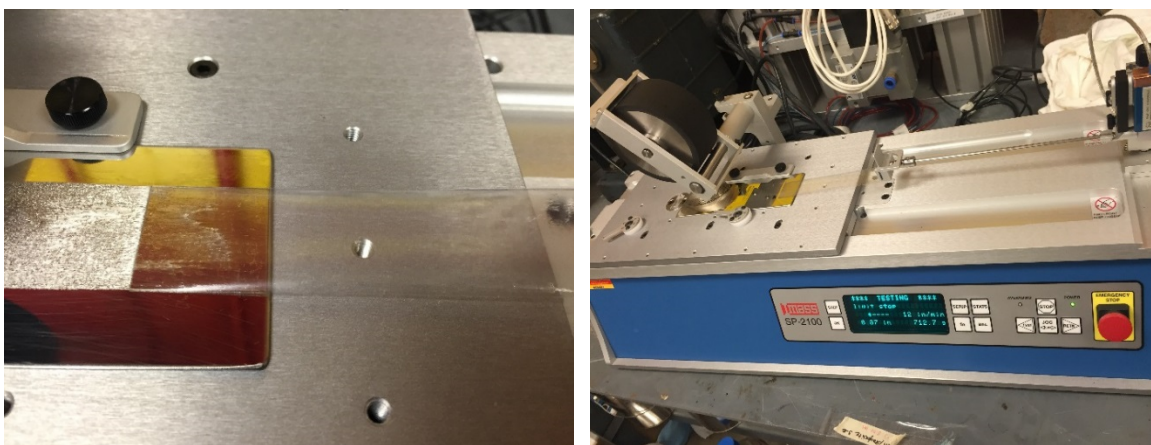


Figure 20 Peel testing procedure

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Thermal Properties and Compatibility Study

The compatibility of the polystyrene blocks and of the PAESO blocks depends upon their molecular weight and the volume fraction of each in the blend composition, however, the evaluation of the polymeric component of the PSAs was not included within the boundary of this study, since it was received as a patent pending material.

The glass transition temperatures of the PS-PAESO, as well as each of the tackifiers, were identified by means of a DSC instrument as shown in Table 9, Figure 21, and Figure 22. It should be noted that each material underwent three or four cooling/heating cycles; however, due to the transitions in the first one or two cycles, only the last two cycles were taken into account for analysis.

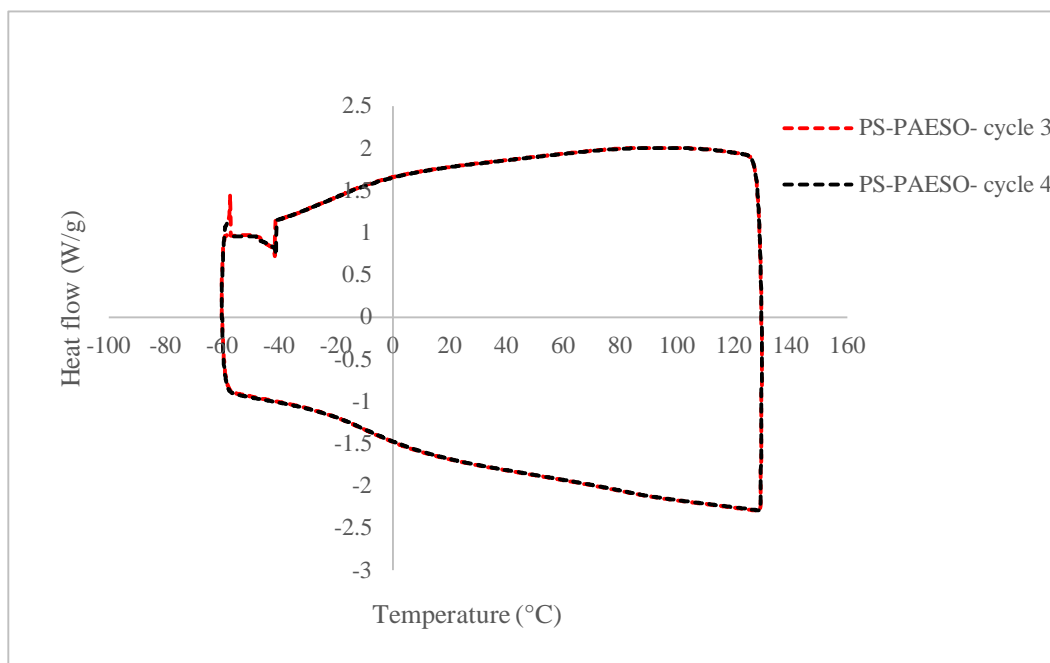


Figure 21 DSC plot of the PS-PAESO showing a T_g of -16 for the PAESO, no T_g for the PS

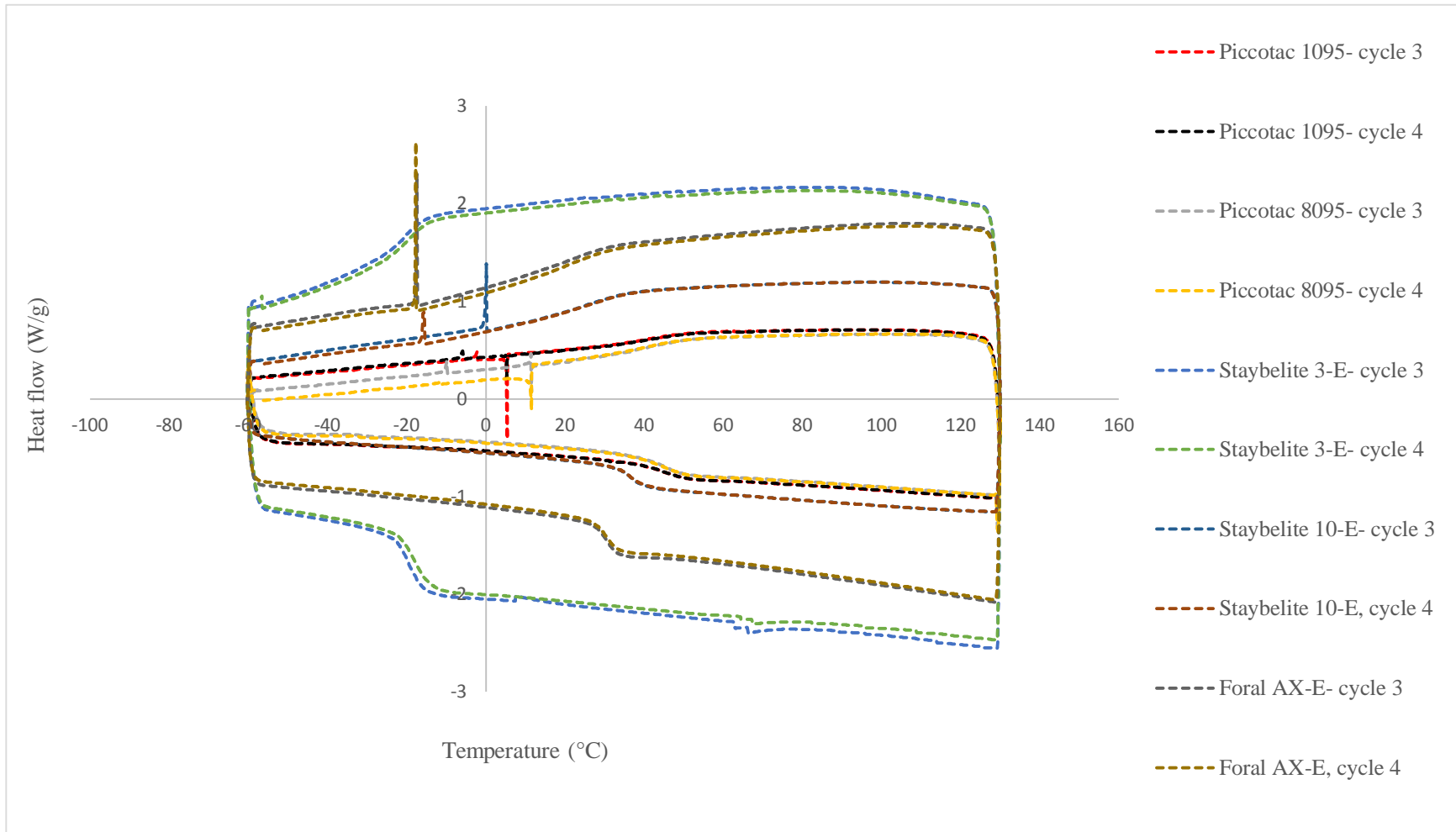


Figure 22 DSC plots of all the five tackifiers- last two cycles

Table 9 T_g results of tackifiers

Tackifiers	T_g (°C)
Piccotac 1095	45
Piccotac 8095	45
Staybelite 3-E	-20
Staybelite 10-E	35
Foral AX-E	30

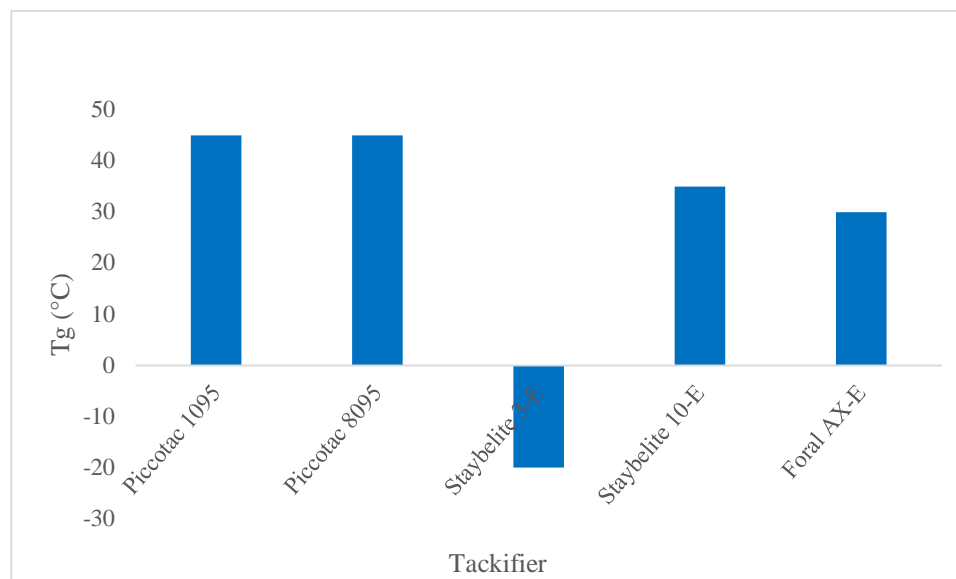


Figure 23 Comparison of the glass transition temperatures of the tackifiers

Among all tackifiers, the Piccotac formulations exhibited the highest T_g well above the room temperature, while Staybelite 3-E exhibited the lowest, well below ambient temperature.

The compatibility of the PS-PAESO with the five types of tackifiers and the three types of plasticizers was first evaluated by analyzing the DSC results of solvent-blended adhesives, as illustrated in Figures 24 to 28. Those compositions exhibiting full miscibility of tackifier in the blend, were selected for hot-melt blending processes and further testing. Although the values of the T_g for all the PSA formulations are consistent with the values suggested in the literature [10, 50, 56, 57], the Piccotac formulations were shown to be not fully miscible in PS-PAESO, while

other three tackifiers were fully compatible. According to Feldstein, the target glass transition temperature of a PSA blend should fall in the range between -10 and -113°C [57].

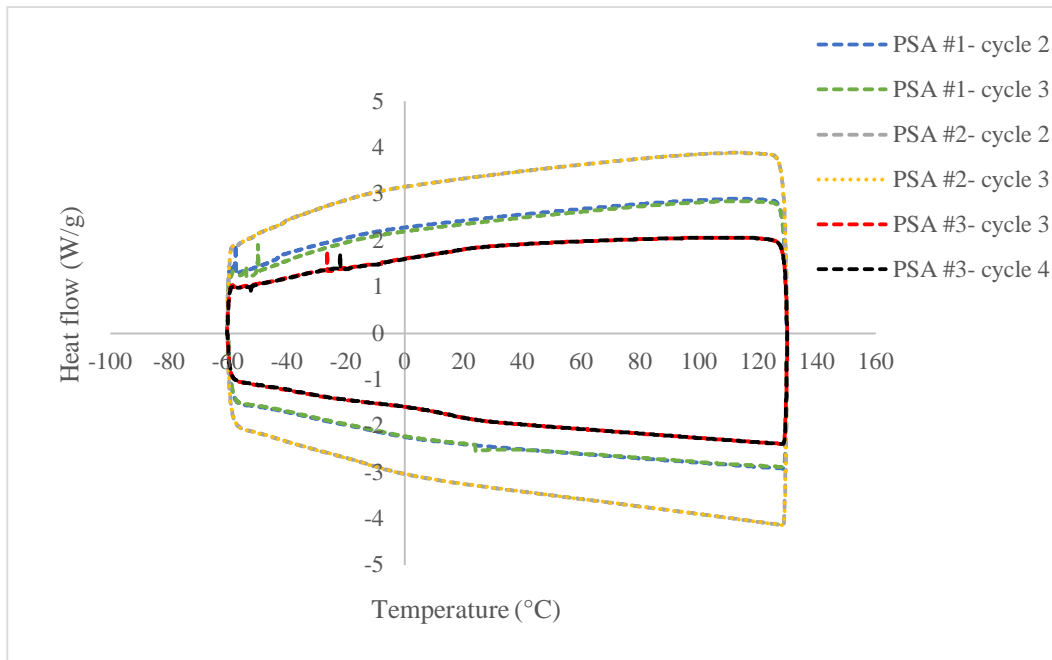


Figure 24 DSC plots of PSAs composed of Piccotac 1095 as tackifier blended with each of the plasticizers

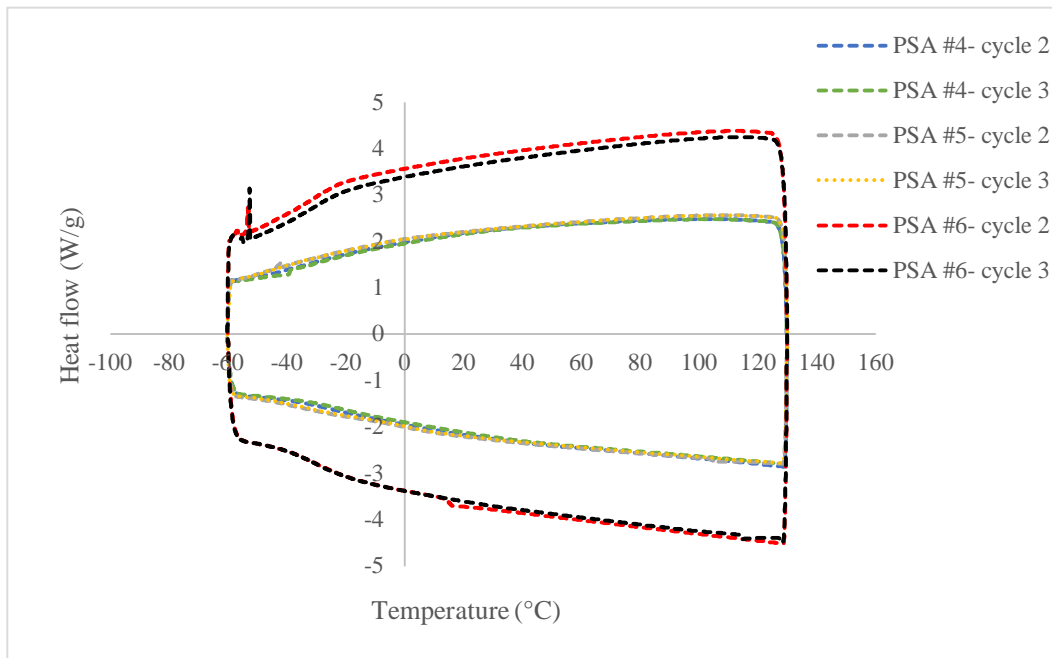


Figure 25 DSC plots of PSAs composed of Piccotac 8095 as tackifier blended with each of the plasticizers

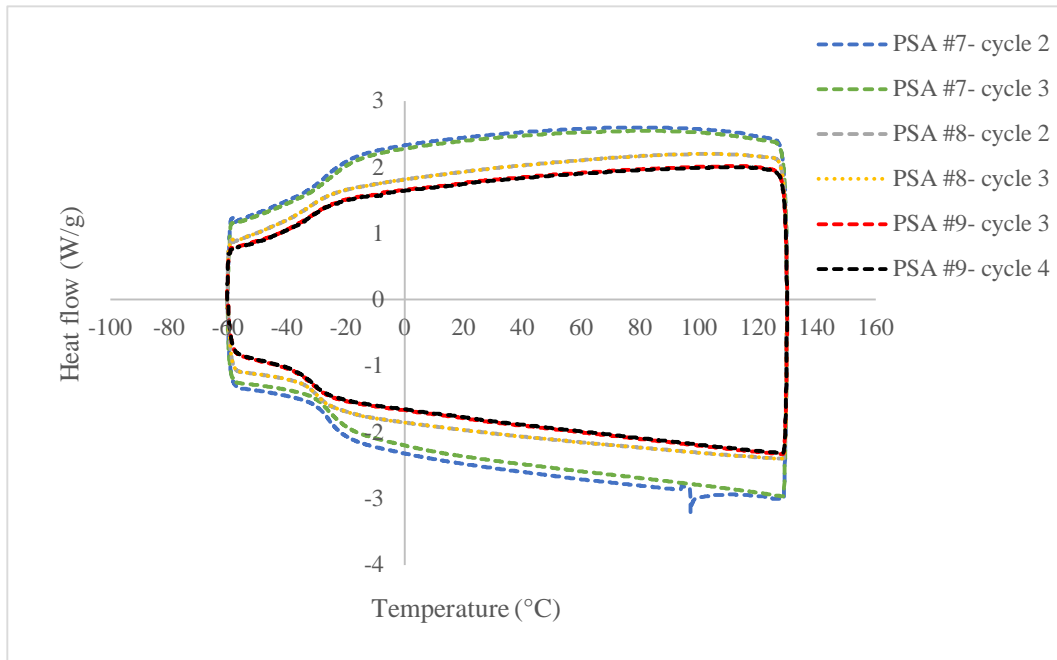


Figure 26 DSC plots of PSAs composed of Staybelite 3-E as tackifier blended with each of the plasticizers

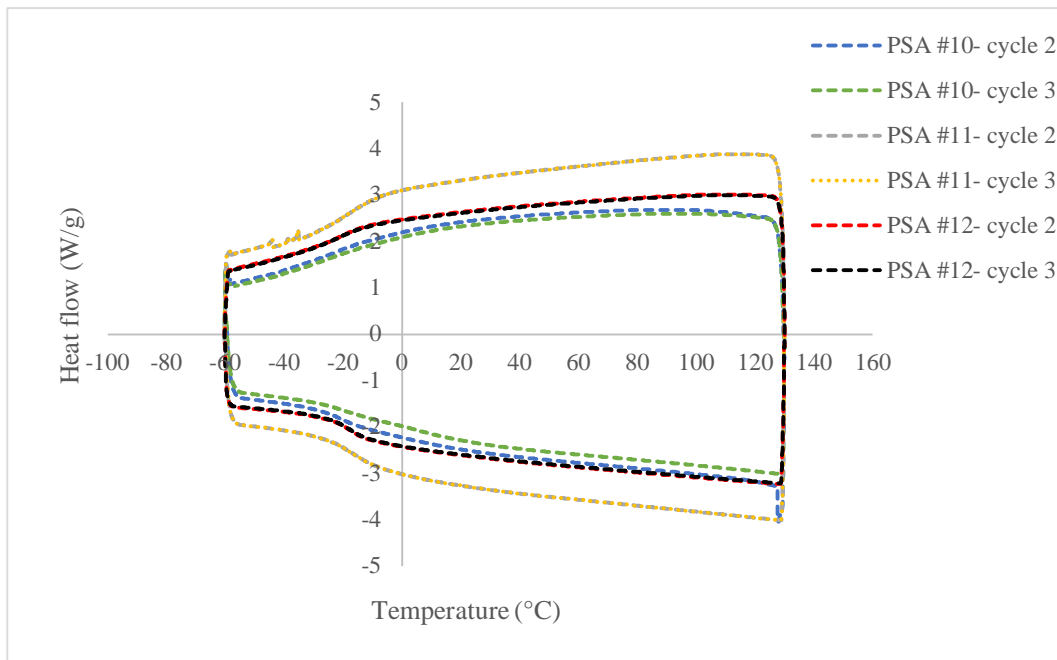


Figure 27 DSC plots of PSAs composed of Staybelite 10-E as tackifier blended with each of the plasticizers

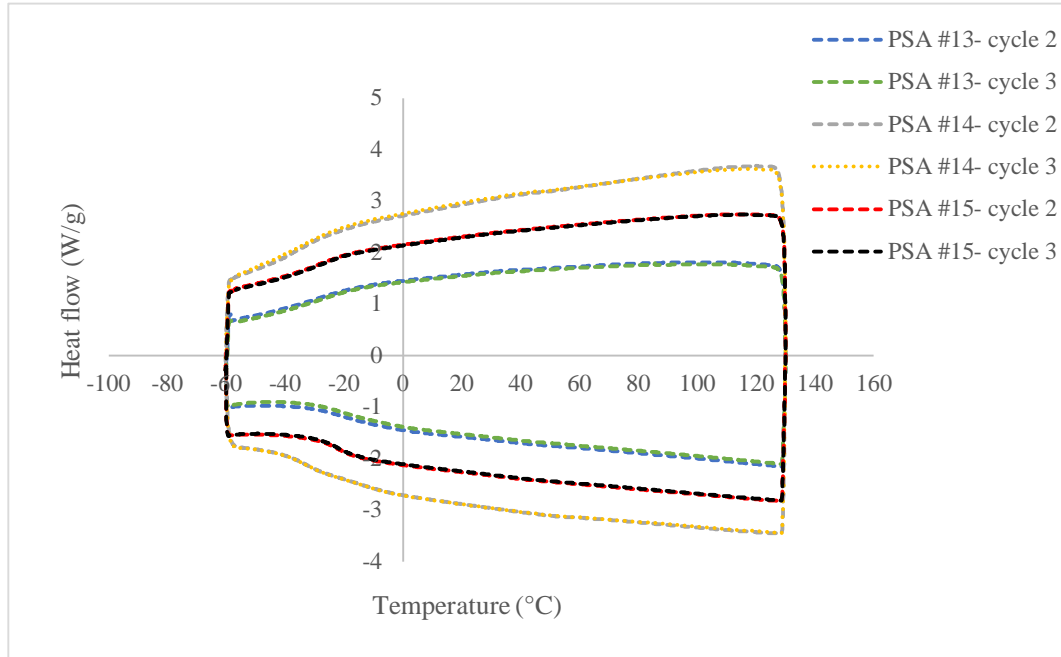


Figure 28 DSC plots of PSAs composed of Foral AX-E as tackifier blended with each of the plasticizers

As stated by Lim et al [13], at tackifier contents in the region of 30-50%, the higher the T_g of the tackifier, the higher peel strength of the adhesives based on SIS block copolymers. This hypothesis could be addressed in evaluating the T_g results of the PSAs based on PS-PAESO. Accordingly, the Piccotac formulations must result in better peeling resistance, however, since they did not exhibit compatibility with the polymer component, they were rejected for peel testing and rheology testing as they no longer appeared to be useful for this study. This hypothesis will be examined for the adhesives synthesized by the rest of the tackifiers later in this chapter. Table 10 and Figure 29 are provided to summarize the results of thermal properties of the solvent-blended adhesives.

Table 10 DSC results of all the fifteen formulations- solvent blending

Solvent-based PSAs

Blend #	Blend	First Tg	Second Tg
1	Piccotac 1095, Benzoflex	-38	-
2	Piccotac 1095, Triacetin	-41	-10
3	Piccotac 1095, Eastman 168	-27	16
4	Piccotac 8095, Benzoflex	-36	-
5	Piccotac 8095, Triacetin	-49	-6
6	Piccotac 8095, Eastman 168	-38	-29
7	Staybelite 3-E, Benzoflex	-26	-
8	Staybelite 3-E, Triacetin	-33	-
9	Staybelite 3-E, Eastman 168	-36	-
10	Staybelite 10-E, Benzoflex	-29	-
11	Staybelite 10-E, Triacetin	-24	-
12	Staybelite 10-E, Eastman 168	-24	-
13	Foral AX-E, Benzoflex	-23	-
14	Foral AX-E, Triacetin	-39	-

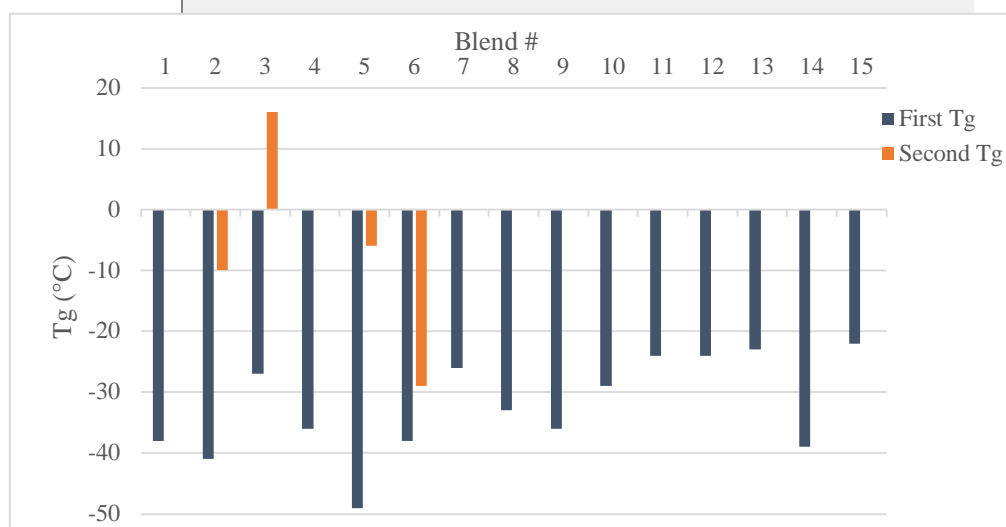


Figure 29 Glass transition temperature of all formulations- comparison of the values

Once the compatibility of the tackifiers with the block copolymer was identified, the miscible formulations (PSAs #7 to #15) were prepared for hot-melt blending. The DSC profiles indicated one and only one T_g for each formulation, confirming the hypothesis that the blending method- whether solvent or hot-melt- should not affect the miscibility of the materials. However, since it was found that the acceptable glass transition temperature for a feasible PSA falls below -10 °C, only those PSAs consisting of Staybelite 3-E were consistent with this criterion. Table 11 and Figure 29 summarize the results of DSC test on hot-melt blended formulations.

Table 11 Comparison of the DSC results of hot-melt blending and solvent blending

<i>Blend #</i>	<i>Blend</i>	<i>Tg- solvent blending</i>	<i>Tg- hot-melt blending</i>
7	Staybelite 3-E, Benzoflex	-26	-20
8	Staybelite 3-E, Triacetin	-33	-19
9	Staybelite 3-E, Eastman 168	-36	-25
10	Staybelite 10-E, Benzoflex	-29	1
11	Staybelite 10-E, Triacetin	-24	18
12	Staybelite 10-E, Eastman 168	-24	-4
13	Foral AX-E, Benzoflex	-23	-8
14	Foral AX-E, Triacetin	-39	6
15	Foral AX-E, Eastman 168	-22	-6

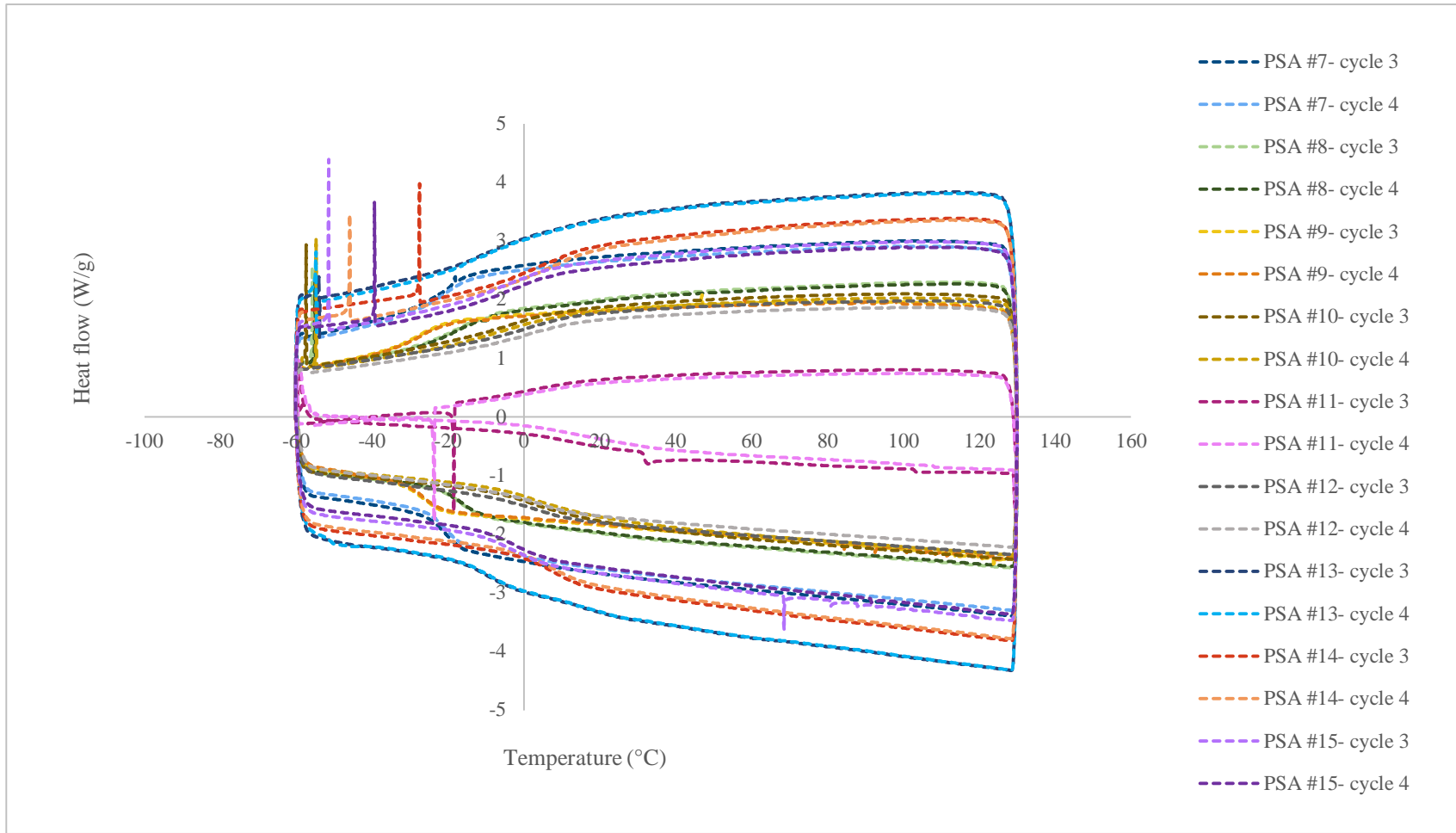


Figure 30 Comparison of the glass transition temperature of the hot-melt blended formulations

4.2 Adhesion Characteristics

Resistance to peeling is an important property of pressure sensitive adhesives. The energy dissipation required for the separation of the adhesive and the substrate, depends on peel rate, peel angle, the backing and the adhesive thickness, and the mode of failure[8, 39]; therefore, due to the difficulties arising from number of variables, only the effect of varying the adhesive thickness was studied in this research.

According to Satas [71], the peel strength increases with the increase in the thickness of the adhesive layer, up to a certain limit. The results are consistent to this general belief, however, in this study, increasing adhesive thickness up to 125 μm did not result in any maximum, indicating that the maximum thickness might be more than 125 μm . To determine the optimum thickness, the following studies were referred: O'Brien et al. selected a thickness of 17.5 ± 1 μm for their adhesives [26]. Shin et al. selected the target thickness of the adhesive as 20 μm [69]. O'Connor and Macosko coated the PET substrates with a 28 μm thickness film of PSA [15]. Poh and Kwo studied the effect of 30, 60, 90, and 120 μm coating thickness on the peel strength and observed that the 120 μm thickness resulted in greater peel strength [72]. Therefore, due to the economic considerations and recommendations found in the above literature, the optimum thickness was selected as 100 μm .

Figures 31 and 32 illustrate the three/four measurements of the force (in grams/25 mm width of film) required to peel the adhesive films off the steel panel for one formulation based on Staybelite 10-E and one formulation based on Foral AX-E.

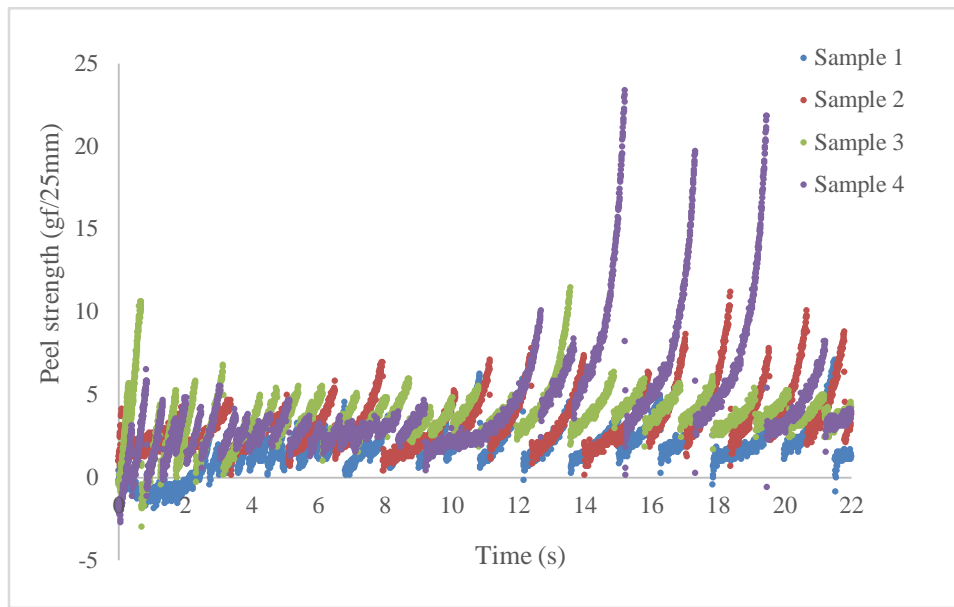


Figure 31 Peel Strength of Staybelite 10-E, Triacetin formulation with a thickness of 0.01 mm

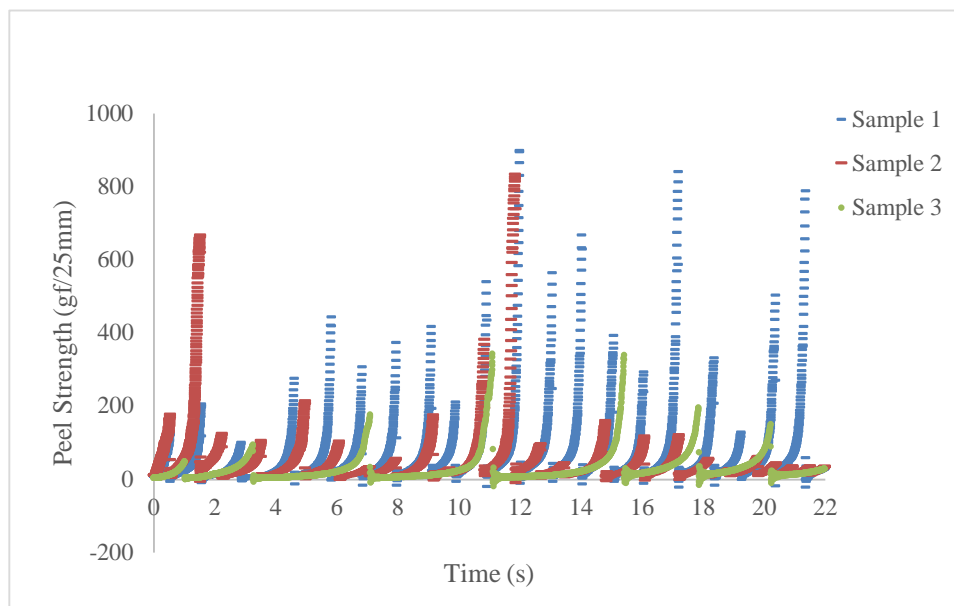


Figure 32 Peel Strength of Foral AX-E, Benzoflex formulation with a thickness of 0.01 mm

According to Figures 31 and 32, the Staybelite 10-E and the Foral AX-E tackifiers exhibited a discontinuous and very low peel strength upon application of a peel rate of 12 in/min, therefore the other two combinations of PS-PAESO with these tackifiers were not tested further. On the other hand, Figures 33 to 35 indicate that the Staybelite 3-E samples exhibited continuous and relatively higher tack to the surface, despite the low T_g of Staybelite 3-E. Therefore, the results

did not confirm the hypothesis proposed by Lim et al. [13] on the relationship between glass transition temperature of tackifier and the peel strength of the SIS- based PSAs.

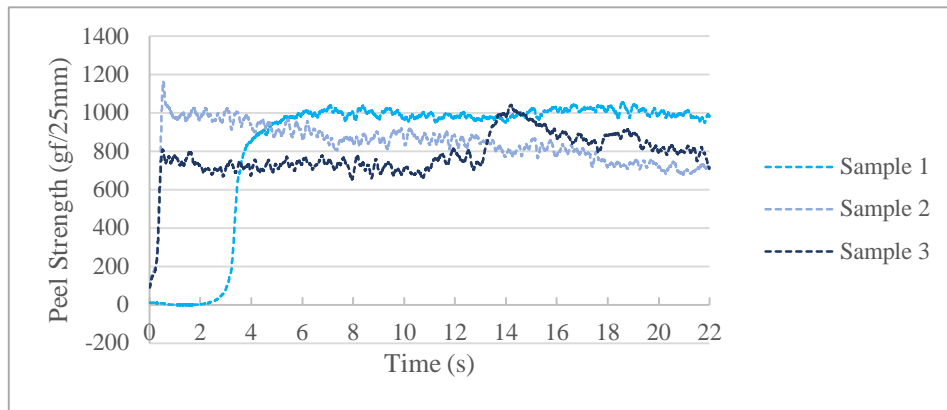


Figure 33 Peel Strength of Staybelite 3-E, Benzoflex formulation with a thickness of 0.01 mm

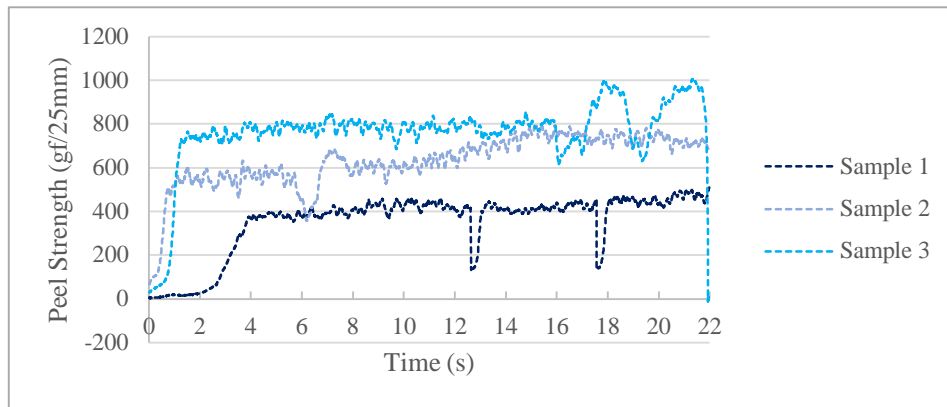


Figure 34 Peel Strength of Staybelite 3-E, Triacetin formulation with a thickness of 0.01 mm

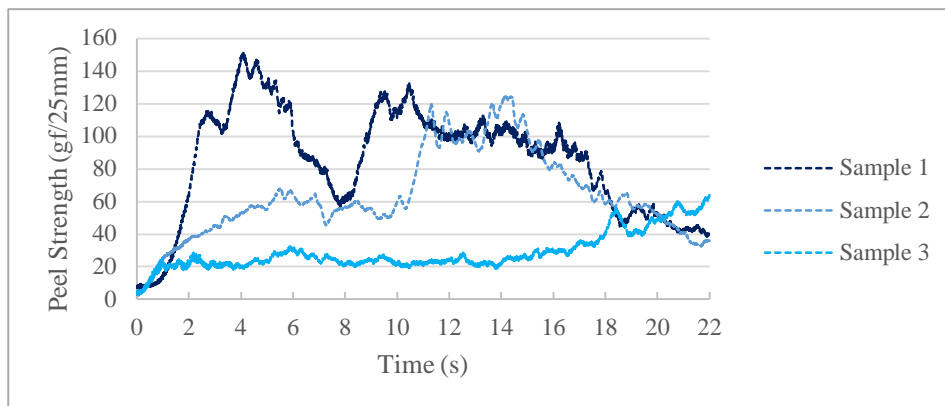


Figure 35 Peel Strength of Staybelite 3-E, Eastman 168 formulation with a thickness of 0.01 mm

In the case of adhesive failure, the existence of adhesive residue is a general judging standard. If the adhesive is to qualify as pressure sensitive, its cohesive strength must be such that the separation is apparently interfacial, meaning that there should be no adhesive residue visible to the naked eyes, on the testing panel [14]. As Figure 36 illustrates, after the test, the surface of the test panel for the PSAs composed of Staybelite 3-E was not entirely clean, therefore they are likely to exhibit both adhesive and cohesive failure. Likewise, for Staybelite 10-E samples and Foral AX-E samples, there was some residue left on the test panel, and the sharp lines observed on the test panel conformed to the discontinuities which appear in Figure 37.

Figure 36 Peeling the PSA film containing Staybelite 3-E



Figure 37 Peeling the PSA film containing Staybelite 10-E



Based on the results, the PSA based on Staybelite 3-E and Benzoflex indicated best performance relative to other formulations. Therefore, it was decided to study the effect of increasing thickness on the peel strength of these combinations. According to Figures 38 to 40 and Table 11, increase of the adhesive thickness from 10 to 50, 100, and 125 μm resulted in more residue left on the test panel, thus exhibiting more cohesive failure. However, the average peel strength obtained from three samples at each thickness increased as the thickness was increased. The average peel strength for the Staybelite 3-E-based PSAs containing Triacetin and Eastman 168 are also summarized in Table 11.

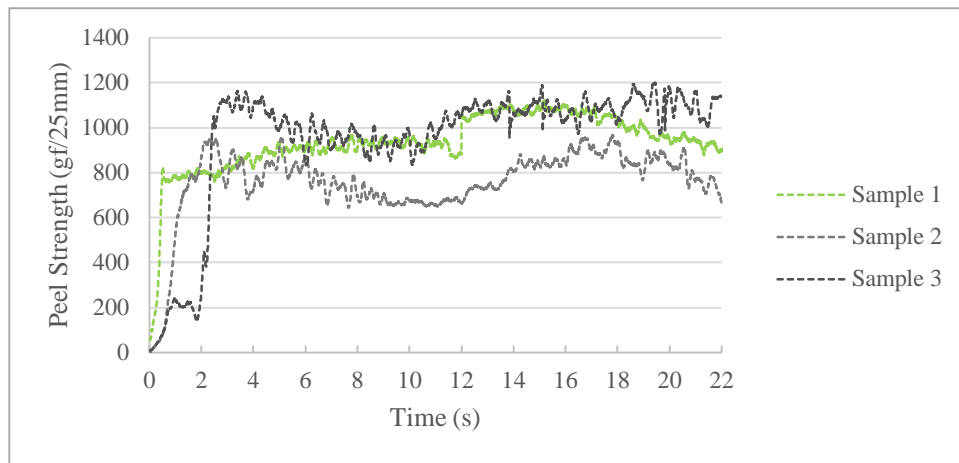


Figure 38 Peel Strength of Staybelite 3-E, Benzoflex formulation with a thickness of 0.05 mm

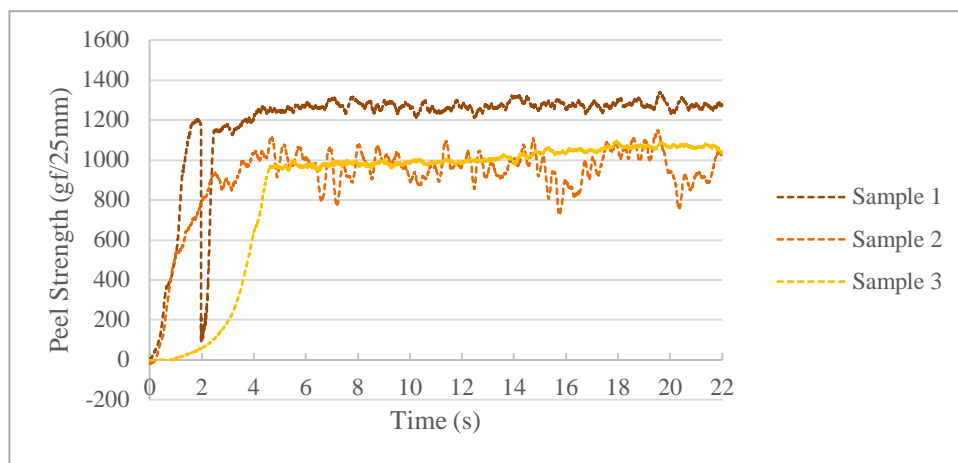


Figure 39 Peel Strength of Staybelite 3-E, Benzoflex formulation with a thickness of 0.1 mm

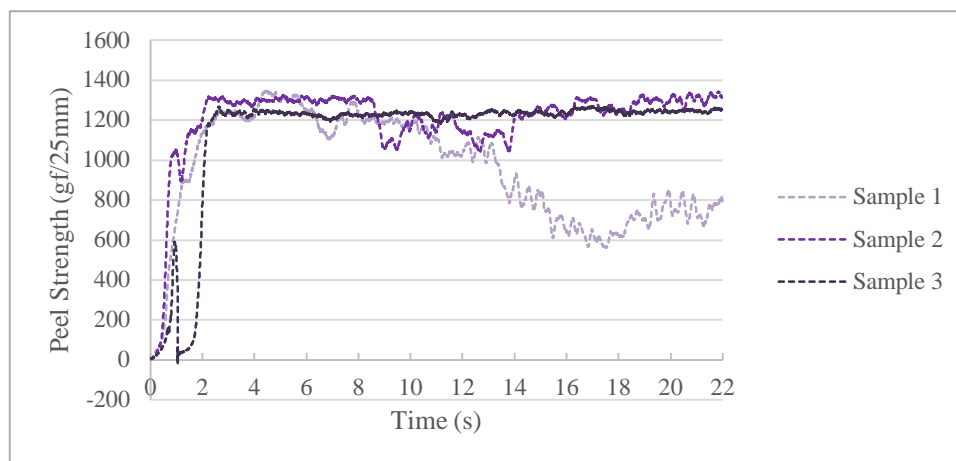


Figure 40 Peel Strength of Staybelite 3-E, Benzoflex formulation with a thickness of 0.125 mm

Table 12 Results of the peel testing

Code	Material, Thickness (mm)	Sample #	Averaging time	Peel force (gf/25 mm)	Average Peel Force (gf/25 mm)
A	Staybelite 3-E, Benzoflex, 0.01	1	18	991.41	872.60
		2	18	824.25	
		3	18	802.14	
B	Staybelite 3-E, Benzoflex, 0.05	1	18	941.78	921.58
		2	18	783.92	
		3	18	1039.04	
C	Staybelite 3-E, Benzoflex, 0.1	1	18	1271.56	1084.35
		2	18	971.09	
		3	18	1010.39	
D	Staybelite 3-E, Benzoflex, 0.125	1	18	961.48	1146.63
		2	18	1243.09	
		3	18	1235.31	
E	Staybelite 3-E, Triacetin, 0.01	1	18	411.13	625.37
		2	18	664.38	
		3	18	800.61	
F	Staybelite 3-E, Eastman, 0.01	1	18	89.23	63.54
		2	18	70.43	
		3	18	30.96	

In terms of the type of polymer used, a formulation based on SIS, Staybelite 3-E, and Benzoflex was compared to a formulation of PS-PAESO with same tackifier and plasticizer at 0.1

mm thickness. Results indicate that the peel strength of PS-PAESO-based PSA was higher on average than that based on SIS (Figure 41 and Table 12). In summary, Figure 42 provides a comparison of the results obtained in Table 11 and 12.

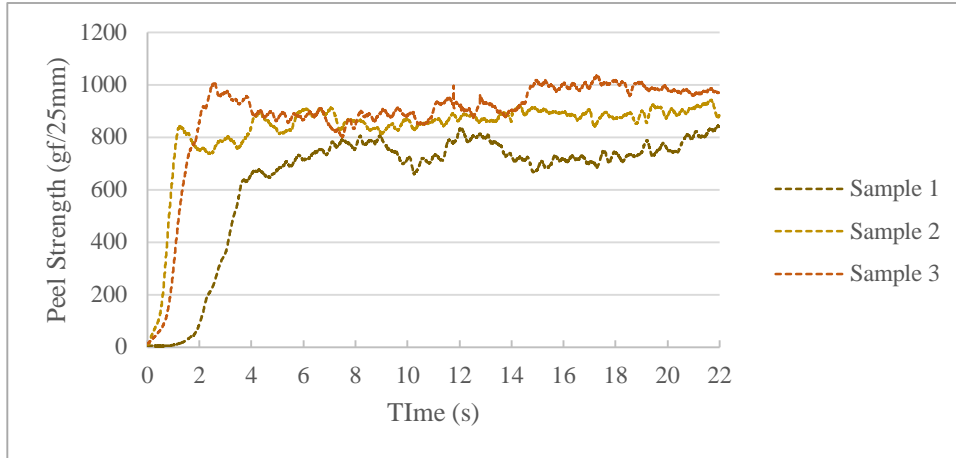


Figure 41 Peel Strength of SIS, Staybelite 3-E, Benzoflex formulation with a thickness of 0.1 mm

Table 13 Results of the peel testing of the SIS sample

Code	Material, Thickness (mm)	Sample #	Averaging time	Peel force (gf/25 mm)	Average Peel Force (gf/25 mm)
G	SIS, Staybelite 3-E, Benzoflex, 0.1 mm	1	18	741.58	850.11
		2	18	876.36	
		3	18	932.38	

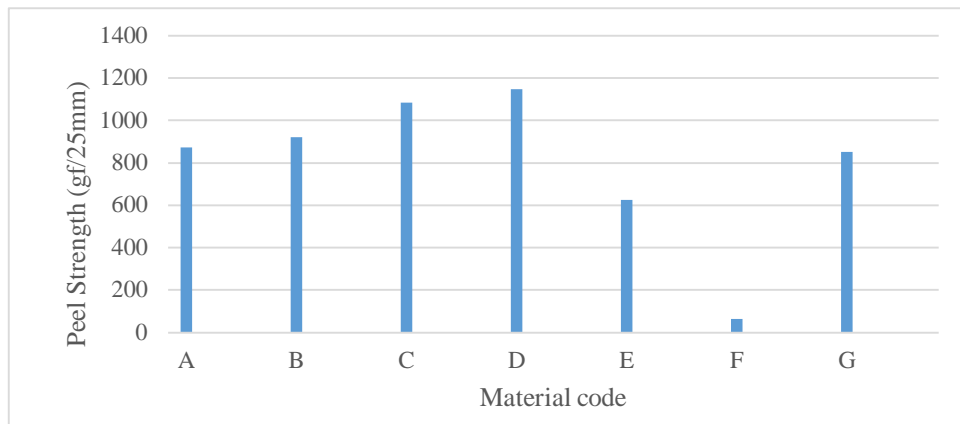


Figure 42 Comparison of the peel strength of the materials listed in Tables 12 and 13

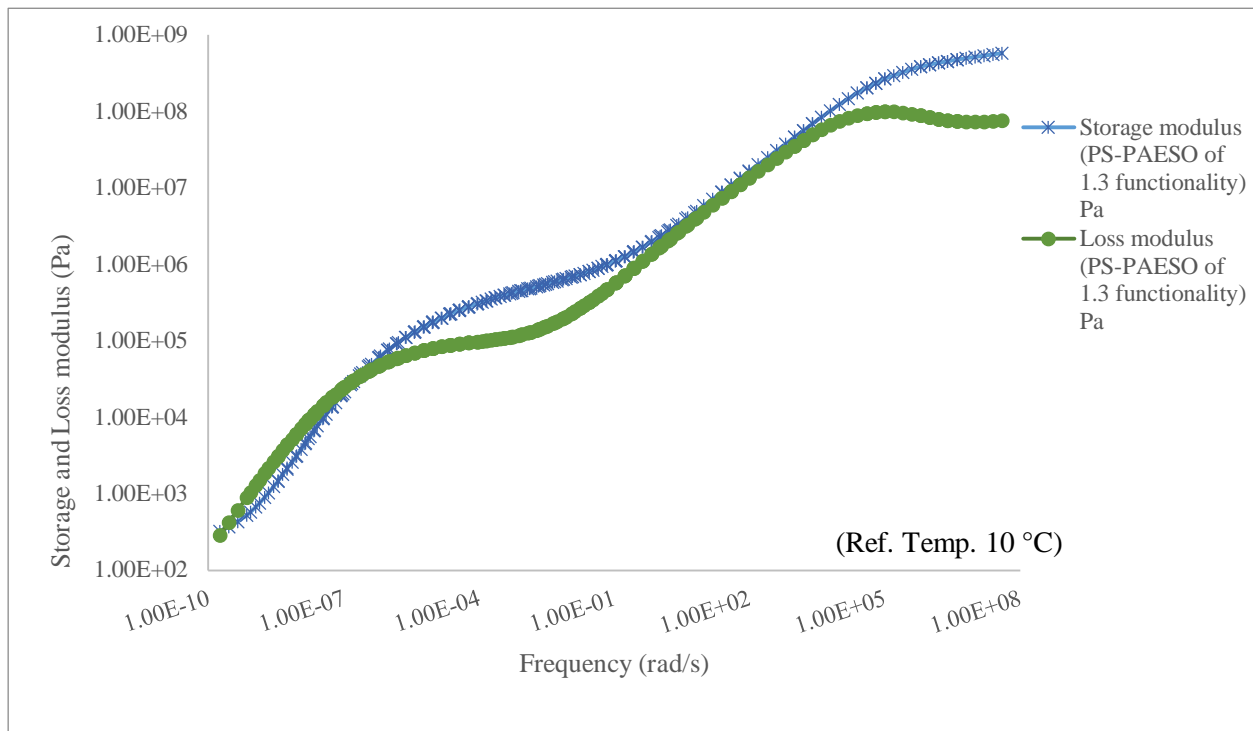
4.3 Rheological Characteristics

4.3.1 Master curves

To ensure quick and thorough coverage of the substrate, the adhesive must possess a proper viscoelastic flow, which can be characterized by two physical properties: storage modulus (G'), and loss modulus (G'').

The time-temperature superposition (TTS) master curves for the PS-PAESO polymer and the nine miscible formulations are shown in Figures 43-46. Each graph contains the storage and loss modulus of PS-PAESO-based formulations with the same tackifier, but varying with the three different plasticizers at the same dosage. Figure 47 also compares the master curves obtained from PS-PAESO, Staybelite 3-E, Benzoflex with the same PSA based on SIS as the polymer component.

Figure 43 PS-PAESO neat Master Curve



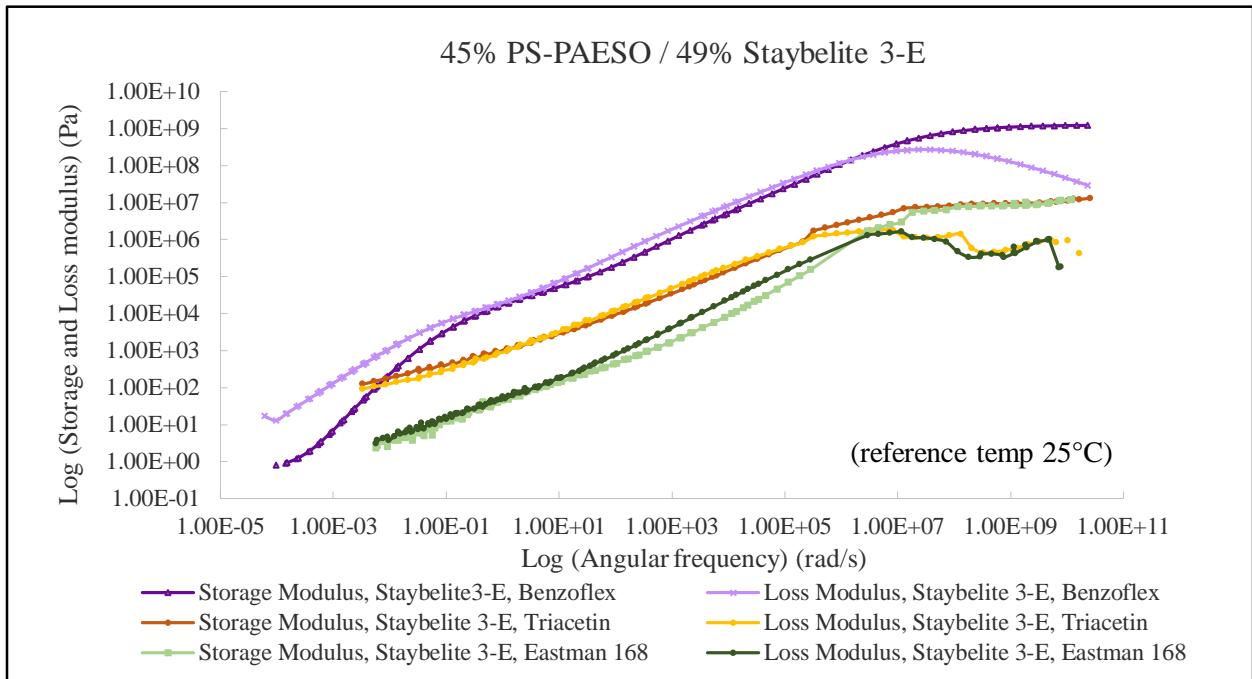


Figure 44 Master curves of the formulations based on Staybelite 3-E

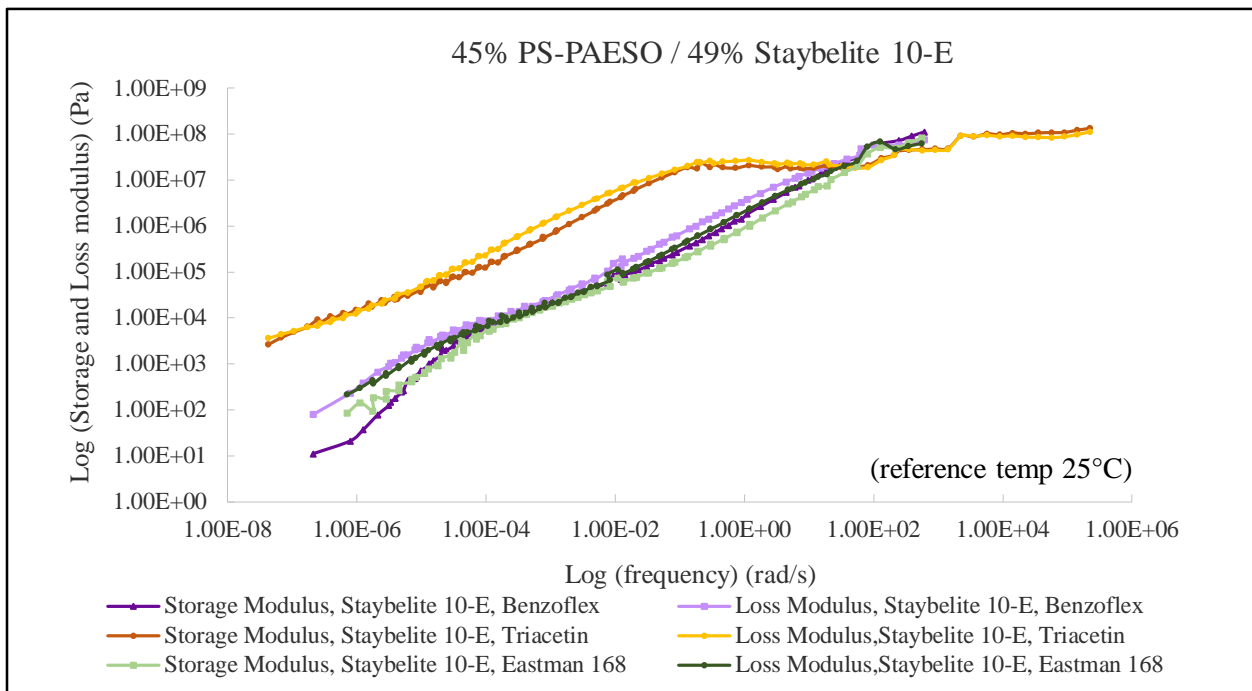


Figure 45 Master curves of the formulations based on Staybelite 10-E

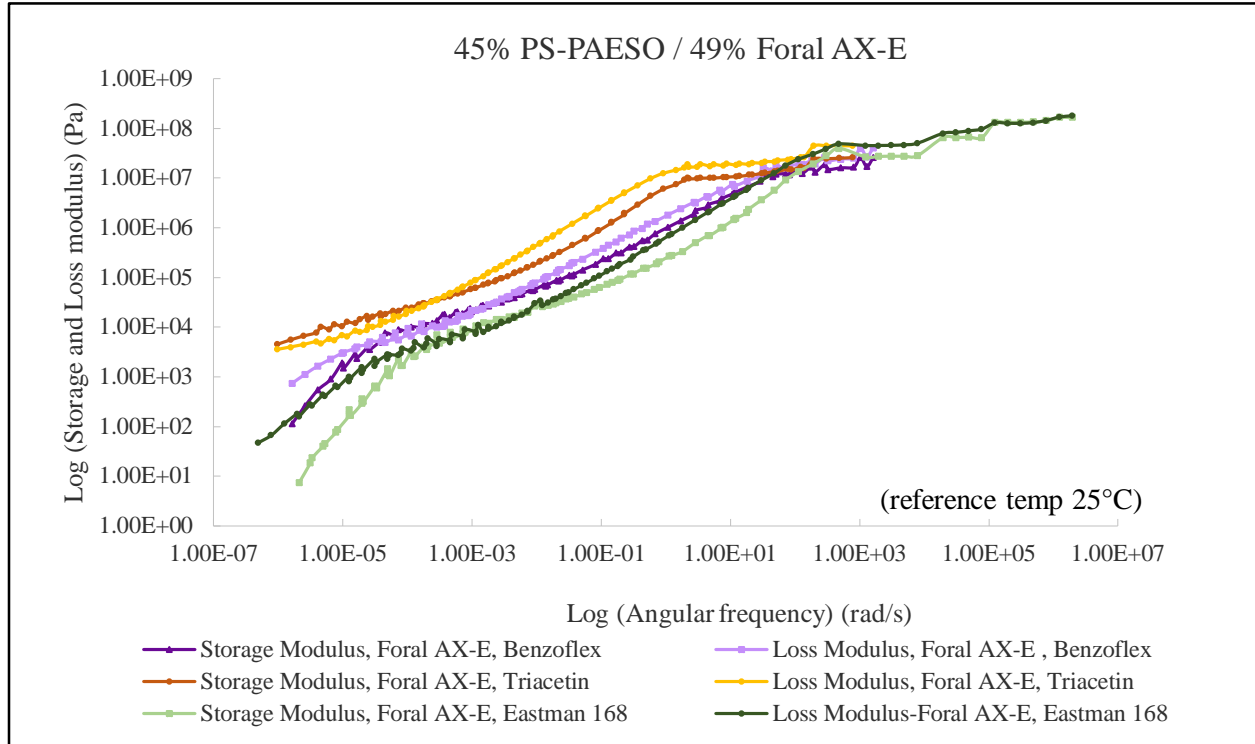


Figure 46 Master curves of the formulations based on Foral AX-E

According to Figures 44 through 46, the sample containing the Staybelite 3-E and Benzoflex possesses a higher G' plateau at high frequencies and low temperatures, indicating greater shear resistance at low temperatures. At low frequencies (around 1 rad/s), the crossover of the G' and G'' curves for this sample indicates a polymer melt behavior. The rubbery plateau region was observed at frequencies between 1 and 10 rad/s for this formulation. The plateau modulus of 5×10^4 Pa meets the Dahlquist contact criterion (the plateau modulus lower than 3.3×10^5 Pa), confirming the viability of this formulation to facilitate bonding and high energy dissipation at debonding frequencies [56]. Compared to the neat PS-PAESO master curve in Figure 43, although the plateau region has been shortened, the corresponding modulus has been decreased favorably to meet the Dahlquist criterion for the PSA.

The glass transition region, where the loss modulus is greater than the storage modulus, is relatively wide for all formulations. The stick-slip behavior of the adhesive films under peel testing, as well as the likelihood of the cohesive failure, may be attributed to this intermediate domain observed on the master curves at room temperature.

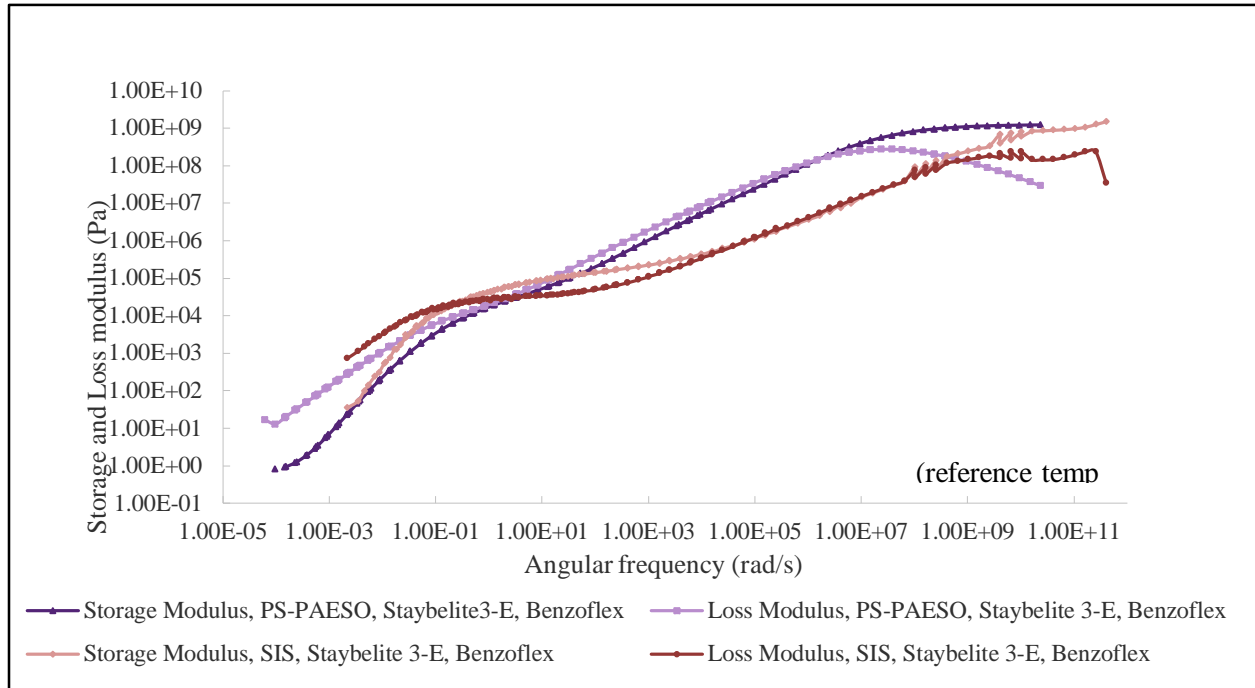


Figure 47 Comparison of PS-PAESO and SIS polymers

Figure 47 implies that the glass transition temperature for SIS-based PSA is lower than that for the PS-PAESO-based, and the SIS-based PSA exhibits a wider plateau region, indicating a broader temperature range in which the PSA retains the tack property.

4.3.2 Viscoelastic windows analysis and discussion

According to Dahlquist [14], performance of PSAs in terms of tack, shear resistance, and peel resistance is highly influenced by the bulk viscoelastic properties of these materials. To investigate this influence, viscoelastic windows were constructed by plotting the G' and G'' versus frequency on a log-log scale with the following four coordinates: (1) G' at 10^{-2} rad/s, G'' at 10^{-2} rad/s, (2) G' at 10^2 rad/s, G'' at 10^{-2} rad/s, (3) G' at 10^{-2} rad/s, G'' at 10^2 rad/s, and (4) G' at 10^2

rad/s, G'' at 10^2 rad/s (Figure 48). Based on the four-quadrant concept adopted by Chang [50], the Staybelite 3-E sample which roughly lies within all four quadrants, exhibits the most appropriate characteristics for general purpose PSAs as well as removable PSAs. Figure 49 is provided for the comparison of the nine formulations based on their behavior related to viscoelastic windows.

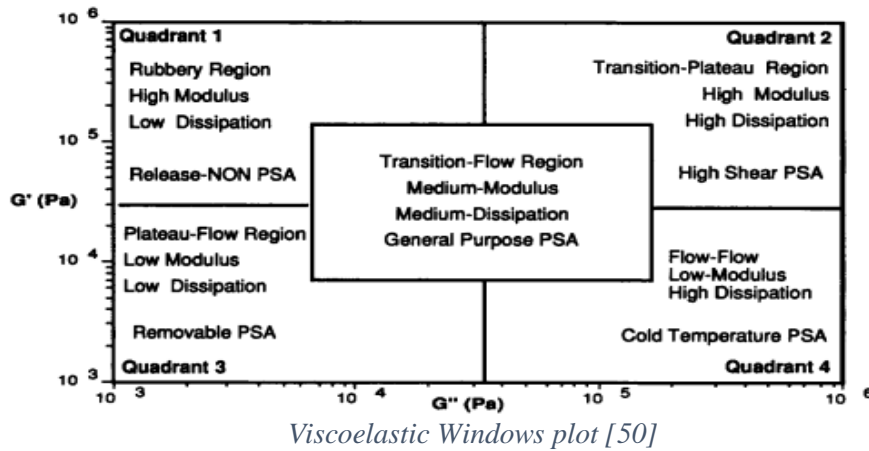


Figure 48

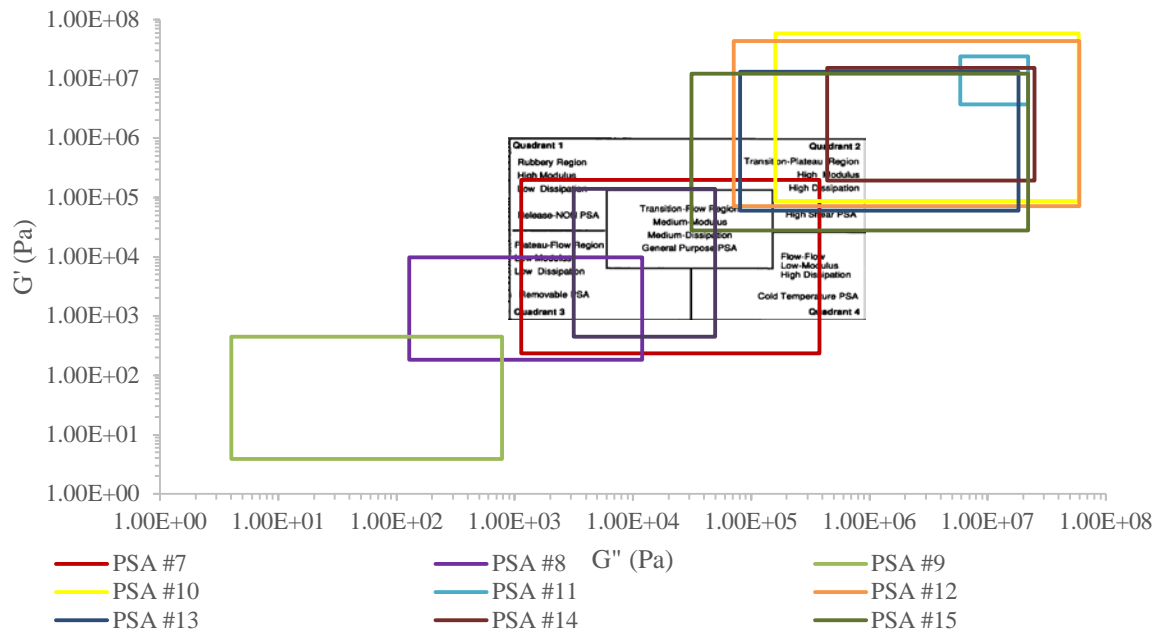


Figure 49 Viscoelastic Windows of PSAs

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

Based on the laboratory results, this thesis demonstrates the viability of the PS-PAESO polymer to be incorporated in the formulation of pressure sensitive adhesives successfully. The comparison of the rheological and physical characteristics of PS-PAESO-based PSAs with their petroleum-based counterparts indicates promising potential of the material to perform as well as or better than commercialized PSAs. The performance of the bio-polymer has also been reported successful in the formulation of modified asphalt. Therefore, the PS-PAESO polymer could be incorporated into several other formulations for more applications. The overall conclusions from this research can be drawn as follows:

- Incorporating a tackifying resin miscible with the PAESO phase into the PSA composition, renders an elastomeric PAESO+resin matrix enclosing a physical cross-linked structure provided by the glassy styrene domain. The existence of one T_g in nine formulations out of fifteen reveals that the PS-PAESO materials used in this study can be miscible with most of the commercial tackifiers.
- Among all tackifiers, the Staybelite 3-E was found the best tackifier well compatible with PS-PAESO, with respect to thermal properties, viscoelastic behavior, and peel resistance.
- Those hot-melt formulations with glass transition temperature above zero, may require higher concentrations of plasticizer, however, the adverse effects on the peel strength must be taken into consideration as well.
- Since the performance of commercial PSAs is strongly related to the glass transition temperature and plateau modulus, a viscoelastic window can help with characterizing the application of PSA for various purposes. The Staybelite 3-E and Benzoflex formulation

met the requirements based on viscoelastic windows for general-purpose and removable PSAs.

- In the case of peel resistance testing, it is important that the same testing conditions, including temperature, relative humidity, relaxation time of the PSA, and testing speed be performed on the samples, so that testing variability is minimized.
- The shift towards biopolymers will not occur until they can achieve a superior economic and performance opportunity for the industrial purposes.

The contributions from this work to future research can be summarized as:

- This study was limited to experiments in which the polymer was fixed at a specific molecular weight, and the tackifiers and plasticizers were the variables changed. Consequently, the reliability of the conclusions is restricted to the PSA systems based on PS-PAESO with a molecular weight of 20 kDa. Variables such as thickness of the backing film, peel angle, and annealing time must also be taken into consideration for more comprehensive results and a broad range of adhesive properties.
- It is also recommended to evaluate the performance of bio-polymers in PSAs with different molecular weight of tackifiers as well as different plasticizer concentrations to determine the optimum content of each of the components, to formulate additional alternatives that can perform not only as well, but also better than the petroleum-based counterparts with regard to mechanical, physical, rheological, and most importantly economic considerations.
- Future work in which the peel resistance of the PSAs is also estimated by means of master curves over a wide range of peeling rates, peeling angles, and temperatures could be useful for characterizing the performance of the PSAs with regard to their potential applications.

- The shear strength, which is a key characteristic of the PSAs and a measure of holding power, was not evaluated in this study. It is recommended to perform the standard test on bio-based PSAs to evaluate the resistance of the adhesives to flow upon loading. The probe tack test is also important to conduct on the PSAs to study the behavior of these materials when they are brought into contact with the underlying substrate.

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