STUDY ON THE ADHESION PROPERTIES OF LINEAR AND CROSSLINKED ADHESIVES IN THE PRESENCE OF FILLER

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LIST OF ABBREVIATIONS AND SYMBOLS

ASTM	American Standard for Testing and Materials, USA
BPO	Benzoyl peroxide
CI	Coumarone–indene resin
° C	Degree Celsius
DSC	Differential scanning calorimetry
ENR	Epoxidized natural rubber
FTIR	Fourier transform infrared spectroscopy
T_g	Glass transition temperature
h	Hour
kg	Kilogram
MgO	Magnesium oxide
MPa	Megapascal
µm	Micron metre
min	Minute
Mc	Molecular weight between crosslinks
N	Newton
N m-2	Newton per metre square
NR	Natural rubber
Phr	Parts per hundred parts of rubber
PET	polyethylene terephthalate
PSAs	Pressure sensitive adhesives
SEM	Scanning electron microscopy
SMR	Standard Malaysian Rubber
TGA	Thermogravimetric analysis
V	The value of crosslinked density
ZnO	Zinc oxide

KAJIAN MENGENAI KESAN PENGISI TERHADAP SIFAT KEKUATAN LEKATAN PEREKAT LELURUS DAN DIPAUTSILANGKAN

ABSTRAK

Permintaan yang semakin meningkat untuk peranti elektronik mendorong permintaan yang pesat untuk perekat berketahanan haba. Kebanyakan perekat ini diperbuat daripada polimer sintetik yang diperoleh daripada petroleum yang merupakan biopolymer yang tidak mampan dan juga bertoksik. Oleh itu getah asli yang mampan dan merupakan biopolymer dikaji sebagai alternatif untuk meningkatkan penggunaan perekat berasaskan getah asli yang dipaut silang (ENR-25, ENR-50 dan SMR L) dengan menambahkan pengisi zink oksida (ZnO) dan magnesium oksida (MgO). Benzoil peroksida (BPO) digunakan sebagai pemula penghubung silang untuk menyediakan perekat bersilang. Manakala coumarone-indene (CI), toluena, dan polietilena tereftalat (PET) masing-masing digunakan sebagai bahan pelekat, pelarut dan substrat. Penyalut tangan SHEEN telah digunakan untuk melekatkan formulasi perekat pada substrat. Semua sifat rekatan perekat dicirikan oleh penguji lekatan Llyod. Objektif pertama kajian ini ialah untuk mencirikan saiz, kecenderungan terhadap air dan morfologi bagi pengisi ZnO dan MgO dan ia menunjukkan bahawa saiz pengisi, bentuk dan kecenderungan terhadap air pengisi mempengaruhi sifat rekatan perekat. Objektif kedua kajian ialah menganalisis sifat-sifat perekat apabila jenis pengisi dipelbagaikan. Penyebaran pengisi yang baik dalam setiap sistem perekat telah dibuktikan melalui TEM. Termogram DSC menunjukkan kebolehupayaan campuran sistem perekat terisi. Termogram TGA menunjukkan penambahan pengisi oleh MgO dan ZnO meningkatkan kestabilan . Objektif ketiga kajian ialah untuk menyiasat kesan pengisi,

ketebalan salutan, kadar ujian dan jenis getah ke atas sifat lekatan perekat. Keputusan menunjukkan sifat rekatan perekat ENR-25, ENR-50 dan SMR L meningkat dengan pertambahan pengisi sehingga mencapai nilai optimum masing-masing pada 10 phr, 30 phr dan 20 phr bagi MgO dan 30 phr, 40 phr dan 30 phr bagi ZnO. Kekuatan ricih ENR-25, ENR-50 dan SMR L meningkat secara langsung masing-masing kepada 147 x 10^3 N/m², 113 x 10^3 N/m² dan 91 x 10^3 N/m² bagi MgO dan 132 x 10^3 N/m², 107 x 10^3 N/m² dan 74 x 10^3 N/m² bagi ZnO apabila bertambahnya pengisi disebabkan bertambahnya kekuatan kohesif. Peningkatan ketebalan penglitupan dan kadar kelajuan ujian akan meningkatkan tindak balas elastik perekat dan menyebabkan kegagalan rekatan. Mikrograf SEM menunjukkan kegagalan perekat lebih dominan bagi perekat berasaskan ENR manakala kegagalan kohesif bagi perekat SMR L. Kesimpulannya, perekat berasaskan getah asli dipaut silang terisi dengan MgO dan ZnO sesuai sebagai alternatif kepada perekat berasaskan sintetik yang berada di pasaran.

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ABSTRACT

Increasing demand for electronic devices is driving rapid demand for thermal resistance PSAs. Most of these adhesives are made from synthetic polymers derived from petroleum which are unsustainable and toxic biopolymers. Therefore, sustainable natural rubber, which is a biopolymer, is being studied as alternative to increased use of cross-linked natural rubber-based adhesives (ENR-25, ENR-50 and SMR L) by adding zinc oxide (ZnO) and magnesium oxide (MgO) fillers. Benzoyl peroxide (BPO) was used as crosslinking initiator to prepare the crosslinked adhesive. Coumarone-indene (CI), toluene, and polyethylene terephthalate (PET) used as tackifier, solvent and substrate, respectively. A SHEEN hand coater used to coat the adhesive on the substrate. All adhesion properties of adhesives were determined by a Llyod Adhesion Tester. The first objective of study to characterize the size, water affinity and morphology of ZnO and MgO fillers and it shows that filler size, shape and water affinity affect the adhesion properties of the adhesive. The second objective is to analyze adhesive properties when type of filler varies. TEM shows both fillers are well distributed in all adhesive systems. DSC thermogram confirms the miscibility of all adhesive systems. TGA thermograms show the addition of MgO and ZnO increases thermal resistance of adhesive. The third objective is to investigate effects of filler, coating thickness, test rate and rubber type on adhesive adhesion properties. The adhesive properties of ENR-25, ENR-50 and SMR L adhesives increased with addition of fillers until reaching optimum values at 10 phr, 30 phr and 20 phr for MgO and 30 phr, 40 phr and 30 phr for ZnO, respectively. Shear strength of ENR-25, ENR-

50 and SMR L increased directly to 147 x 103 N/m², 113 x 103 N/m² and 91 x 103 N/m² for MgO and 132 x 103 N/m², 107 x 103 N/m² and 74 x 103 N/m² for ZnO respectively when filler was increased due to increase in cohesive strength. Increasing coating thickness and rate of testing becomes predominantly elastic resulting in adhesion failure. SEM micrographs show that adhesive failure is more dominant for ENR-based adhesives while cohesive failure is dominant for SMR L adhesives. As conclusion, cross-linked natural rubber-based adhesives filled with MgO and ZnO are suitable as an alternative to synthetic-based adhesives in the market.

CHAPTER 1

INTRODUCTION

An adhesive or commonly known as glue is a substance that holds items together to the surface of an object (adhesion) and the bond itself possesses a sufficient internal strength (cohesion). Adhesives can be cured (hardened) by either evaporation of a liquid or chemical processes that involve two or more components. Generally, adhesives can be derived naturally or generated from a variety of sources. Over time and during the development, several commercial adhesives are natural rubber-based, chemically modified natural rubber or synthetic rubber have achieved a stable position in an increasing number of fabrication processes (Pike, 2022).

Natural rubber (NR) was used in the adhesives industry for many years. Adhesives have become important in most industries that range from the food industry to manufacturing such as shoes, bags, tires, automotive, furniture, etc. NR latex was revealed to have been tacky when it dried, due to the properties that allowed rubber adhesives to hold porous materials for example paper, wood, and can hold different rubber together. NR has good resistance of peel, impact, and fatigue properties, but it has less shear resistance and heat resistance (Rohayzi et al., 2023). The excellent tack retention capabilities of this rubber, on the other hand, make it suitable for pressure-sensitive applications (PSAs), because the attraction of two different substances caused by intermolecular interactions will last for a long time after the adhesive has been applied. Hence, PSA needs to flow quickly and to withstand an additional deformational flow to stream over to wet the surface and ultimately create intermolecular forces to form a surface attachment with the adherents during the application process (Lee, 2013). Besides that, their remarkable features such as tensile

strength, hardness, and resilience when stretch. Epoxidized natural rubber (ENR) has been found to undergo strain induced crystallization like NR, but with oil resistance like a medium acrylonitrile NBR and gas permeability like butyl rubber resilience. ENR is also highly suitable for adhesive applications due to its polarity (Zainudin et al., 2021). The steady growth in the construction industry and increasing number of construction activities in developing countries are increasingly utilizing PSAs as an insulation barrier around doors and windows. PSAs prevent water and air from infiltrating the home, which enables enhancing energy efficiency as well as longevity and durability of buildings. Advancements in the design of customer electronics are projected to boost demand for PSA thermal resistant and drive revenue growth in the market during the forecast period (Songtipya et al., 2021).

However, if only NR is used, it is insufficient to offer good adhesion and tack strength in rubber-based adhesives, it is needed to be altered with other synthetic chemicals and resins i.e., tackifiers, fillers, and antioxidants to enhance adhesion or other properties like viscosity and shelf-life. Fillers are often used in rubber compounding either to obtain the desired properties for certain applications or to reduce the cost (Songtipya et al., 2021; Sanghvi et al., 2022). Fillers were used to increase strength properties of the PSA including talc, calcium carbonate, silica, carbon black, and montmorillonite are frequently utilized. ZnO and MgO, two common inorganic material types utilized in the creation of nanocomposite, are provided as reinforcement fillers for the metallic oxides (Sanghvi et., 2022). Highly thermally conductive inorganic fillers like carbon black, graphene, boron nitride, and alumina have been used as thermal resistant to be incorporated into polymeric materials. Another filler with appealing qualities is metal oxide like MgO and ZnO. This metal oxide has considerably superior bulk heat resistance than other inorganic

fillers. MgO and ZnO are also inert fillers. Recently inorganic oxide like ZnO and MgO is among the most used as filler in rubber adhesive to address the issue of high demands of thermal adhesive (Leitune et al., 2019; Arun et al., 2020; Kagenda et al., 2021; Sung et al., 2022).

Aside from fillers, curing agents are another ingredient added in the manufacture of natural rubber adhesives. This is another method of rubber modification is to change the chemical structure of the rubber molecules to recover certain properties or boost the rubber's resistance to various other chemicals (Kim et al., 2020; Yi et al., 2021; Li et al., 2022).

The chemical structure of natural rubber is a repeating unit with an unsaturated double bond that has limitless chemical modification potential. The unsaturated bonds can be used to produce sites for reacting with another chemical to form a new rubber structure. Thus, sulphur crosslinking agent commonly used as crosslink strategy, which involves introducing sulphur bridges between the natural rubber polymer chains to boost the strength qualities. The length and distribution of sulphur chain bridges can alter the qualities of the end rubber product in sulphur vulcanization, e.g., shorter sulphur chains give higher stiffness to the end rubber, while longer sulphur chains increase the aging properties of rubber compound (Cataldo, 2023)

Lately, BPO cured become more interesting method to crosslink the rubber adhesive. Peroxides cure by disintegrating into peroxy radicals, which remove a hydrogen from the elastomer and form a polymer radical, when heated. Most of these radicals generate cross-links almost instantly. Peroxides have the benefit of curing both saturated and unsaturated rubbers (since the reaction involves is hydrogen abstraction) and form carbon-carbon cross-links that are thermally stable, good elastic behavior at

higher temperatures, low moisture uptake, and lack of staining or discoloration of the final products are their key advantages as crosslinking initiator. The comparatively high hydrogen abstraction ability of commercially available peroxides makes them effective crosslinking initiator for a wide variety of organic polymers. The primary advantage is that NR that has been volcanized has less cytotoxicity and contains no residual compounds such as elemental sulphur, zinc oxide, or nitrosamines that have been used during sulfur crosslinking processes (Borova et al., 2020; Cataldo, 2023).

However, the effect of crosslink to mechanical properties of adhesive has limitations. After the maximum amount of crosslinked, the properties of shear, peel and tack strength will reduce. Highly crosslinked networks produce mostly a negative effect on PSA flexibility and adhesion characteristics. To address this issue, at the limitation of this crosslinked, filler was used to enhance the adhesion characteristic. Besides that, inorganic fillers also were employed to enhance the thermal PSA properties (Kashihara et al., 2019). The goal of this study is to report the adhesion properties of crosslinked natural rubber-based adhesive in the presence of filler. Coumarone-indene resin was employed as tackifiers, and methylbenzene (toluene) used as the solvent. The amount of filler has been added into adhesive formulation, which is expected to increase the tackiness and certain strength of the adhesive.

1.1 Problem Statement

Nowadays, the pressure-sensitive adhesives (PSAs) sector has become important in the adhesive industry, due to the steady growth in a variety of industries, including manufacturing, packaging, electronics, automotive, and pharmaceuticals. Increasing demand for electronic devices that are continually decreasing in size and increasing in efficiency and functionality are driving rapid demand for thermal PSAs. Thus, the need for finding new PSAs products with high adhesion strength and thermal resistance is extremely contentious. Most of these PSA are often made from a variety of synthetic polymers, including acrylic polymers, polyisobutylene (PIB), styrene-isoprene block copolymer (S-I-S), chloroprene rubber (CR), and styrene-butadiene rubber (SBR). Synthetic polymer derived from modifiers of petroleum or petroleum by product is expensive production cost and unsustainable biopolymer. Other than that synthetic polymer is also toxic.

As the decrease on petrochemical resources and the disadvantages of the synthetic polymer, NR was introduced in PSA industry. However, NR adhesive lowers thermal resistance compared to synthetic adhesive. Thus, it is imperative to address the high demands of thermal resistance adhesive. Consequently, in this thesis MgO and ZnO were investigated as a filler to evaluate the thermal and other properties of BPO-crosslinked NR adhesive.

1.2 Scope of Study

This study aims to explore the potential for producing natural rubber-based pressure -sensitive adhesives (PSAs) filled with MgO and ZnO. The crosslinking reaction is initiated by BPO. ENR -25, ENR -50, and SMR L as based rubber and CI as a tackifier. The first part investigates to characterize size, water affinity and morphology of MgO and ZnO. The second part focuses on evaluating the properties of adhesive as filler type is varied. The third part focuses on the effects of fillers, coating thickness, rate of testing and type of rubber on adhesion properties. This research addresses the need for enhanced adhesion strength and thermal stability in natural rubber -based adhesives, contributing valuable insights to adhesive technology.

1.3 Objectives

1. To characterize size, water affinity and morphology of fillers: MgO and ZnO.
2. To analyse the properties of adhesive as filler type is varied.
3. To investigate the effects of fillers, coating thickness, rate of testing and type of rubber on adhesion properties of PSAs.

CHAPTER 2

LITERATURE REVIEW

2.1 Pressure Sensitive Adhesive

PSAs are non-metallic materials that use adhesion and cohesion to attach further materials, particularly to their surface area. Adhesion and cohesion have been defined as thermodynamically and chemical processes, it has been demonstrated that major bonding mechanisms are adhesion and PSA bonding. Although they had many flaws and errors, the combination of those various innovations contributed to their evolution. As the Egyptian Civilization began over 6000 years ago, adhesives had been identified as primitive tools, according to archeological data dating back to the beginning of time. An early kind of tape was created by applying a substance made of starch and water on sheets of cloth. It is used as tackifying resins in pressure-sensitive adhesive applications in the ship construction sector and in medicine as a mixture of fat and honey for surgical patches (Czech et al., 2011).

The first PSAs were created in 1845, and they became extensively utilized in the late 1800s. The earliest products were medical tapes and bandages. These tapes are made using NR as the base material alongside various ingredients such as wood turpentine, Peruvian balsam for medicinal uses, and tackifier (pine gum). Several decades later, Stanton Avery designed and introduced the self-adhesive label. This invention led to the growth of the PSA and label businesses. The transportation industry, which demanded tires soon after the first bicycle was invented in the early 1900s, allowed the rubber manufacturing sector to flourish. Higher standards have been placed on the industry to produce cutting-edge rubber-based products, although

the development of such technology does not directly include the adhesive tape business (Benedek, 2005).

Industrial tapes were invented in the 1920s, and by the middle of 1935, the self-adhesive labeling business had grown. While manufacturing was concentrated on surgical tape, cotton fabric remained the preferred material in the early 20th century, even though numerous rolled-shaped materials could be utilized as adhesive tape carriers. The Minnesota Mining and Manufacturing Company, better known by its corporate name 3M, supplied sanding paper to the automotive industry in the 1920s under the brand name "Wetordry." Working for 3M at the time, Richard Drew's sequence of patents on PSAs led to the creation of sanding paper samples and the industry for industrial adhesion tape. Cellophane films were, however, created in 1993 because of advancements in the pressure-sensitive film tape sector. His in-depth knowledge of masking tape was first applied to cellophane film in early 1930's, and the result was the first pressure-sensitive film tape in history, commonly referred to as "Scotch" tape (Urban and Egan, 2002).

Natural rubber, pale crepe, wild rubber-based materials, or smoked sheet rubber-based materials, as well as mixers with other additives like tackifiers (coumarone gum resin, burgundy pitch, pine oil, wood resin, and gum olibanum), softeners (liquid paraffin, or mineral oil, lanolin, and beeswax), fillers (zinc oxide) with whiting for prime coats, and solvents (benzole or low-boiling-point aliphatic petroleum hydrocarbons) became the primary raw materials for PSA formulations in the mid-1930s. The synthetic elastomers e.g., polyisobutylene, or Oppanol B, polyvinyl isobutyl ether or Oppanol C, and styrene butadiene, or Buna S were also commonly used as elastomer. Early 1941, polypropyl acrylic ester has been being

employed as the main raw material used in the PSAs formulation and this is the beginning of acrylic PSAs produced (Czech et al., 2011).

Hot-melt adhesives were first introduced in the postwar years of the 1940s. Balloons were launched into the stratosphere as part of the initial study. It was determined that adhesives can be used at very low temperatures would be required. A series of research led to the development of Dow Corning's silicone PSA as one of the examples, which performed in the range of –62°C to +260°C and was the forerunner of later high temperature and low temperature silicone pressure-sensitive adhesive technologies. The process is then transformed over the years, and in the 1950s, the quandary of tack and adhesion is studied widely. Manufacturers of industrial adhesive tape actively collaborated with one another for the good of the sector. In the early 1970s, petroleum derivatives started to make up a sizable portion of the raw materials used in the adhesive tape business where it then continued to flourish in the 1980s, delivering new goods and improvements to raw materials, particularly in the form of a hot-melt adhesive alternative, but nothing in the way of advancements in PSA technology (Czech et al., 2011).

The term for the PSA has a specific technical interpretation, and it has been extensively discussed and analyzed in chemical literature and publications. PSAs are well-known polymeric materials with viscoelastic attributes, held extremity and persistent tack, and adequate cohesive strength sufficient cohesive strength to stick off a surface without letting the viewable residue (Mustafa and Fatimah, 2013). PSAs are intended to adhere immediately when applied with light pressure no more than finger pressure and, in most cases, to be quickly removed from the area where they were attached to with the least amount of pulling power. Furthermore, the PSA undergoes neither chemical nor physical changes when bonding, which is principally achieved

by van der Waals forces. Therefore, PSAs are characterized by their intrinsic capacity to form an instantaneous bond to a surface without the need for activation—such as a solvent or heating treatment—and by possessing sufficient internal strength to keep the adhesive material from disintegrating before the surface-adhesive bond breaks (Kiu, 2007).

It demonstrates that PSA bonding and debonding are energy-driven processes, which debonding system requires cavity on the interface and filaments growth inside a PSAs. During the bonding PSAs process, the viscosity properties become important to stream and can disperse energy. Hence, the glue or adhesive also needs to be elastic (it must withstand inclination to flow) and this storing bond breakage power to offer better peel and tack productivity. Appropriate viscoelastic properties will allow better response for both a bonding and debonding process. PSA polymers must fulfil partially contradictory requirements; have high shear strength and peel adhesion to display better adhere to substance but must without leaving a residue to substrate once the substrate has been deboned (Kiu, 2007).

Applying the PSAs, the adhesive does not change its physical form due to film formation inherent in PSAs. PSAs utilized in self-adhesive strips are adhesives that can build up a junction without changing its viscoelastic fluid condition during or after application because of its viscoelastic fluid state. Its liquid state also allows for controlled debonding, which lends it to a temporary bonding aspect. The matching quantity of adhesives (glue layer sizes) is limited because of the liquid nature of the adhered adhesive; typical applications include paper-thin layer adhesive tape, coats, and composites. Solid-state duct tape components have a significant impact on the properties of glue or adhesive within the composites. As a result, there is a difference between an adhesive's measurable property when it is unspoiled and an adhesive that

is encased in laminate. Shear endurance, peel durability, and tacking strength are the three main characteristics of natural PSAs. First, measurement adhesives must be able to attach rapidly; second, it must be able to resist removal by peeling; and third, it must be able to maintain its place when the force of shear is applied (Kiu, 2007).

PSAs are coated on the film as the carrier, and as soon as the solvent has evaporated, the tape is ready to be placed at the site of assembly. They're most seen in packaging and masking tapes. Nowadays, PSA technology is applied in many consumers and commercial products, including insulation tape, wrapping tape, sealant tape, self-adhesive tags, postage-paid stamps, removable adhesive notes, transdermal pads, and surgical dressings (He et al., 2023).

PSAs mainly the coating on a support material to form the PSAs tape. Frequently employed as carrier materials to uphold the delicate adhesive coating include materials such as cloth, cellophane, polypropylene, paper, and polyester. PSA tape is made by coating PSAs onto a backing material. The carrier materials as mentioned above are amongst of the major carrier materials used to hold a thin adhesive layer. Improved research on PSAs makes adhesives capable of withstanding electrical and thermal stress, insulating, resisting microbiological and ecological threats, and reducing certain adhesive effects such as skin irritation or corrosion (Mustafa and Fatimah, 2013)

PSAs will be used in a range of air conditioning, such as dry and wet, atmospheric, and subsurface, and in various temperatures. Because PSAs are utilized in so many different applications, it is essential to comprehend how they behave mechanically in a range of temperatures and conditions. PSAs are applied in the same way as contact adhesives and offer immediate tackiness. Unlike contact adhesive, the

PSA's adhesiveness is permanent, thus there have never been sets of ideal periods to link the substrates. Many PSAs are based on solvent solutions, either from thermoplastic or elastomer. Butyl, nitrile, and styrene butadiene thermoplastic elastomers, as well as acrylate or silicone resins, constitute the foundation of most widely used PSA formulations. The advantages and limitations of elastomer-based PSAs are summarized in Table 2.1.

Table 2.1 Advantages and limitations of PSAs based on elastomer (Mustafa and Fatimah, 2013)

Chemical family	Rubbers	Acylates	Silicones
Advantages	(1) Good flexibility	(1) Good UV resistance	(1) Excellent chemical and solvent resistance
	(2) High initial adhesion (better than acrylic)	(2) Good hydrolysis resistance (better than rubber)	(2) Wide temperature used range (-73 to 260 °C)
	(3) Ease of tackification (with additives)	(3) Excellent adhesion buildup	(3) Good oxidation resistance
	(4) Lower cost	(4) Good solvent resistance	(4) Good adherence to low and high energy surfaces
	(5) Good shear strength	(5) Good temperature use range (-45 to 121°C)	
	(6) Good adherence to low and high energy surfaces	(6) Easier to apply than rubber	
	(7) Suitable for temporary or permanent holding	(7) Good shear strength and service life	
Disadvantages	(1) Low tack and adhesion (without additives)	(1) Poor creep resistance (compared to rubber)	(1) Higher cost compared than rubbers and acrylates
	(2) Poor aging, subject to yellowing	(2) Fair initial adhesion	(2) Lack of aggressive behavior
	(3) Limited upper service temperature used and moderate service life	(3) Moderate cost (compare to rubber and silicone)	

PSAs have been specifically engineered to exhibit exceptional flexibility, tack, and peeling strength. Solvents, water-based dispersions, or hot melts can be used for application. In hot melt PSAs, thermoplastic elastomers are frequently utilized. Double-sided tapes, or pressure-sensitive tapes, are offered with adhesive on either or both sides. Double-sided foam tapes are typically used for substrates with shaped, uneven surfaces and significant gaps in the connection area. Recently, extraordinarily strong binding adhesive tapes have been developed for semi-structural applications (González et al., 2017).

Using a foam carrier not only fills up gaps but also serves to disperse stress inside the joint region, enhancing the joint's final strength. These strips of tapes exhibited bond strengths to as much as ten times compared to the standard PSA by having sufficient stressed of cohesive for prolonged time in handling the unassuming loads. However, following quick application of mild pressure (often manually), PSAs produce a relatively low strength adhesive, and they are applicable to any clean, and dry surface of substrate. As a result, they can maintain only the light loads due to creep, they are not regarded as structural adhesives. However, the evolution of PSAs constructs a more powerful bond with time. They should not try out the PSA immediately after applying PSAs and the joint is conducted. The maximum strength takes several days to draw up, and these tapes need close enough to pair substrates. Consuming foam carrier e.g., polyethylene or vinyl in pressure-sensitive tapes can produce great gap tolerances. Such adhesives can be found in a variety of places, including for automobile protection, wall dispensers mounting tape, and so on (Mustafa and Fatimah, 2013).

2.2 Rubber-Based Pressure Sensitive Adhesives

Big molecules with substantial molecular masses form rubber. Increases in molecular mass have a direct impact on density, boiling temperature, and point of melting. It reveals that the increase in boiling point is the final attribute on rising to the point where the substance decomposes before evaporating. Sturdy and load-supporting rubbers need rubbers with a greater molecular weight. Rubber viscosity and molecular weight have a rough linear relationship. A vital process of breaking apart the structural regularity of the recurrent -CH2- segments to reduce the crystallization is very important in reducing the molecular weight in a rubber polymer (Mustafa and Fatimah, 2013).

Rubber can be inhibited normally in any of the following methods: either by adding side groups, such as methyl or chlorine, to keep nearby chain segments from aligning perfectly, or by adding unsaturation or carbon-carbon double bonds to the polymer chain. The recurrent segments are joined at the extreme carbon atoms with a distinct double bond presenting in each segment, due to diene monomers holding a pair of carbon-carbon double bonds and polymerizing inside the double bond. These double bonds between carbon atoms will stop rotating them, preventing the molecular segments from aligning correctly and interfering with crystallization. One example of a non-crystallizing polymer with unsaturation is styrene-butadiene rubber. To create robust and durable rubbers like polyisoprene rubber, both side groups and double bonds of carbon and carbon can be combined into the polymer structure. Rubber turns hard and delicate when the temperature is lowered (Vayyaprontavida Kaliyathan et al., 2020).

The entire rubbers mainly were stiffened to a firm, shapeless glass at the glass transition temperature (T_g). Alternatively, it indicates that the service limit of rubber is low at cooler temperatures. The structure, level of cross-linking (vulcanization), and the isomer structure of the rubber all affect its T_g values. Nevertheless, repeating unit structure and molecular mass primarily control rubber's physical characteristics. The rubber properties, which emanate from the adhesive's elastomers, dictate the adhesive's primary characteristics. The methodology may be tailored for a specific purpose by adding other components (Vayyaprontavida Kaliyathan et al., 2020).

Elastomeric adhesives, often known as rubber-based adhesives, are immensely utilized in commercial and domestic usage. There are a variety of elastomeric adhesive systems that are now proving to be important in industry, such as pressure-sensitive tapes and tagging, construction adhesives, contact adhesives, and hot-melt packaging and binding adhesives. Vulcanization is needed for the rubber-based adhesives to achieve acceptable ultimate strength, and chemical interactions at the interface are primarily responsible for adhesion. However, certain rubber-based adhesives, such as contact adhesives, do not necessitate the vulcanization process, however it does need sufficient process of compounding to compose the adhesives joints, equipped usually with permeable substrate (Chang et al., 2021).

Contact adhesives have been included into the joint research categories of rubber-based adhesives and the PSAs can also be considered within these categories, since the tackiness and applying pressure are among the vital properties before joining. The adhesive spreading process towards both surfaces that will be joined is the main process that bound the PSAs together. There are two important conditions required in optimizing the dispersion of the polymer chains: first, sufficient adhesive wettability on smooth or rough substrate surfaces, and secondly, suitable adhesive viscosity to

permeate voids and roughness of the substrate surfaces. The mentioned conditions are simply accomplished using adhesives in the form of liquid. Polymer rubber chains are required to diffuse over both film's surface to provide molecularly solidified adhesion to produce good adhesion. To reach enough auto adhesion, the dried adhesive films on the two joining surfaces must be brought into contact with one another. Application for the of pressure or heat in a designated period permits the needed degree of solidified intimacy exposure between both adhesives film interfaces. The intimate level at the contact will be composed of rubber-based adhesives' rheological and mechanical characteristics. Nevertheless, these attributes may be enhanced by other factors, such as choosing the right rubber grade, attribute, and quantity of tackifier and filler (Hu et al., 2023).

Rubber–based PSAs are made from natural or synthetic rubber, numerous resins, oils, and antioxidants. The qualities of PSA are determined by tackifier, which is blended with rubber to make high-quality PSAs. Other components such as antioxidants, particularly those that hinder the unsaturated backbone polymer from deteriorations, colors, plasticizers, and fillers are being added to minimize the cost principally for the natural rubber due to its expensive price tag. However, the long-time aging stability of the rubber can be low. Most PSAs are created by dissolving (35% solution) it in hexane, toluene, or some other petroleum component. Rubber PSAs' performance includes tack, peel adhesion, shear strength, UV resistance, solvent resistance, chemical resistance, plasticizer resistance, color, and cost. However, PSAs prepared from synthetic rubber have poor cohesive strength and greater manufacturing prices than natural PSAs rubber. It is important to examine the components which affect the performance of PSA tapes since adhesive systems are most incorporated in the tape production process (Mapari et al., 2021)

Natural rubber or synthetic rubber has numerous differences and distinctive characteristics respectively, but the exact performance of an adhesive cannot be predicted based just on the type of adhesive. However, each adhesive type has distinct features that exhibit its own adhesive particularities and hence, to be knowledgeable of these distinctive particularities might help you to avoid selecting the wrong tape for the wrong application. NR was recognized to be one of the earliest discoveries of adhesion technology implemented in conjunction with PSAs. The world's largest and most popular commercial application of natural rubber is in the tire industry. Owing to NR is not sticky or tacky by nature, tackifier resins need to be added to make a PSAs. The greatest advantage of NR is due to its lengthy polymer chains features that are intertwined with each other. This property makes this rubber highly flexible, even in low temperature and gives it inner sturdiness of NR. Owing to these properties, the NR adhesives for used in a variety of applications. Types of rubber in compounded resins and other additives affect NR adhesive performance. The advantages of natural rubber PSAs are as follows: they have more "grip" or tack, excellent peel adherence to both polar and non-polar surfaces, minimal time needed to attain the ultimate level of adhesion, and less residue left behind after detaching. Masking tapes is one example of such a product. However, there are some weaknesses to NR adhesives that must be considered when evaluating whether it is appropriate for a given application: poor cohesion strength at high temperatures (T>70°C), less aging resistance, poor environmental durability (which there is a need for stabilizer agent to protect from the UV light and ozone oxidation) and it also week chemical resistance and solvent resistance. Based on this weakness characteristic, NR adhesives are a great option for a wide variety of non-permanent applications, especially indoor ones (Khan et al., 2011).

There are several common synthetic rubber (SR) adhesives that have been used in PSAs, such as butyl rubber and styrene-butadiene-styrene. Is the unique molecular structure of SR polymer used for adhesive i.e., hard, and rigid block segments at both ends (styrene) and alternate block segments of soft and flexible elastic material (butadiene), so the chain chemistry is styrene – butadiene – styrene (SBS). Internal strength is determined by the styrene-end segment, whereas adhesiveness can be determined by the rubbery intermediate segment. SR alone does not sticky characteristics in the environment hence to produce PSAs product from SR polymer, tackifier resin is needed to add in the formulations of PSAs. The SR characteristic is across from the natural rubber compound properties in that SR has a short length of polymer chain and lower molecular weight. There are no adhesive qualities to SR on its alone. Tackifier resins are necessary to produce PSA. The SR polymer contrasts sharply with natural rubber polymers in that its length and molecular weight are both short. But the adhesive made from SR polymer can form a very strong initial bind to the substrate same as NR adhesive and it's also showing better peel resistance at both polar and non-polar surfaces. SR's advantages and disadvantages include limited temperature performance, better aging properties compared to natural rubber and less environmental resistance, it need to add the stabilizers to protect from the UV light, ozone affects and so on (Ilyin et al., 2022)

2.3 Natural Rubber

Industrialized natural rubber (NR) is approximately yielded from a latex of the Hevea Brasiliense's tree, where being planted in commercial plantations around the globe and it is biodegradable (Viet, 2008). Contemporary in polymer research areas, this term 'latex' refers to the milky fluid consisting of tiny droplets of organic matter

dispersed in an aqueous medium (a kind of natural colloidal suspension). As mentioned before, the NR latex, or also known as the plant latex, possessed a stable colloidal dispersion of cis-1,4-polyisoprene, in the form of high molecular weight in an aqueous medium. The NR latex is divided into two vital phases, consisting of a dispersion medium and a dispersion phase. The first important phase is the dispersion medium, in which is also well-known as the 'serum' of the latex. It is stated as aqueous fluid which is released from the latex because of the occurrence of colloidal destabilization and phase separation. The dispersion phase, or also known as the discontinuous phase, is the phase where there is a synthesis of the high molecular weight polymer spherical particles, in which the particle dimensions extend from 100 nm to 1000 nm in size. Table 2.2 shows the rough composition of fresh natural rubber latex (Min, 2012).

Table 2.2 Composition of raw natural rubber latex (Min, 2012)

Constituent	**Amount (%)**
Rubber	30.0 – 40.0
Protein	1.0 – 2.0
Lipids	0.9 – 1.2
Carbohydrates	1.0 – 1.2
Inorganic matter	0.5 – 0.6
Water	55.0 – 60.0

Commonly, the negative charges on the rubber particles keep NR latex stable because they prevent the particles from clumping together. However, latex also can be destabilized upon the presence of the natural bacteria in the latex serum that will eventually cause the production of organic acid to neutralize the negative charges. Therefore, newly tapped NR latex is directly being conserved primarily with ammonia,

and secondary preservatives such as the tetramethyl thiuram disulphide, are also being used occasionally to neutralize the presence of the bacterial acids to maintain the latex consistency for future work processes. Presently during this phase, the NR latex is recognized as 'preserved NR latex'. The preserved NR latex is not the primary choice to be used commercially in the rubber industry due to its low content of rubber. Consequently, the NR latex should undergo the process to concentrate the latex to raise the latex's rubber content to the standard index of the NR latex at the rate ranging from 60.0% to 61.0%. The reason for the circumstances is to enhance the economic success rate of the NR latex commercially, as well as to adhere to the specific requirements and specifications of the latex industrialists. Evaporation, creaming, centrifugation, and electro decantation are the four basic processes used to focus the preserved NR latex. The most frequent method for concentrating preserved NR latex is centrifugation because of its rapidity and high dependability of the result. Although there are various configurations of latex centrifuge machinery, the fundamental concept applied is basically still the same. The machine used for the process is made up of a revolving bowl with a collection of con-shaped metallic divider discs. In the process of centrifuging the NR latex, it usually involves two preservative systems that normally depend on quantity of ammonia applied to preserve the NR latex colloidal stability. Hence, the preserved latex that possessed a high level of ammonia concentration is indicated as High Ammonia (HA) latex, and the latex with lower ammonia concentration is classified as Low Ammonia (LA) latex concurrently. ISO 2004:1997 standard is used to rigidly evaluate the quality parameters of the concentrated NR latex as shown in Table 2.3 (Min, 2012).

Table 2.3 Specification for centrifuged NR latex concentrate under ISO 2004 (Min, 2012).

Parameter	HA latex	LA latex	ISO test method number
Total solids content, min; %	61.5	61.5	124
Dry Rubber content, min; %	60.0	60.0	126
Nonrubber solids, max; %	2.0	2.0	-
Alkalinity, as ammonia, on latex weight; %	0.6(min)	0.29(max)	125
Mechanical stability time, min; s	650.0	650.0	35
Coagulum content, max; %	0.05	0.05	706
Volatile fatty acid number, max	0.20	0.20	506
Potassium hydroxide number, max	1.0	1.0	127
Copper content, max; mg/kg solids	8.0	8.0	1654
Manganese content, max; mg/kg	8.0	8.0	1655
Sludge content, max; %	0.1	0.1	2005

The NR is one of the most excellent categories of raw material sources. The NR is portrayed as a as a polymer chain-like molecule with replicating subunits. Term for the polymer originated from the Greek word “poly” which carry the sense of “many” and combined with the word “mer” which means “parts”. Polyisoprene is the chemical name for NR, while isoprene is the monomer name for it, which means "one part." (Miller, 2018).

2.3.1 Macrostructure of Natural Rubber

Even though natural rubber is made of repeated isoprene units, the natural rubber does not begin with isoprene monomer. The commencement of NR is the result of a sequence of metabolic reactions that begin inside the tree with isopentenyl pyrophosphate as shown in Figure 2.1.

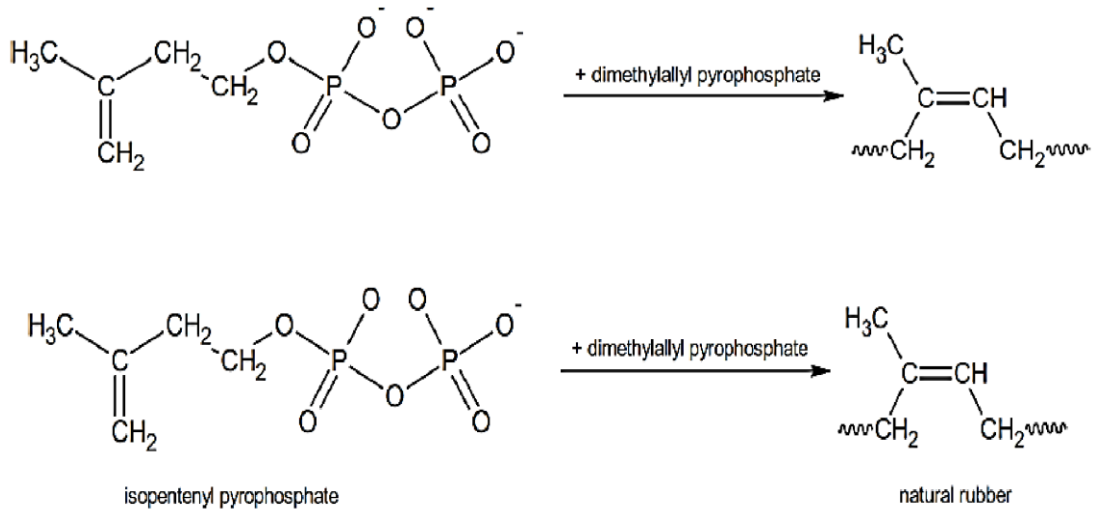

Figure 2.1 Biochemical production of natural rubber (Miller, 2018)

The polymer mass of natural rubber is a single chain of polymers. The long chain polymer rubber makes it possible to entanglement, so that the bulk is held together. When a force is put on the polymer chain, the polymer structure tends to straighten with rotations occurring on the single bonds in the polymer chain. The individual polymer chain will also slide past each other, and the mass cannot go back to its original orientation when the force is withdrawn. The relatively very high molecular weight of the natural rubber is noticed when examining the macrostructure. The molecular weight of natural rubber in range to 3 x 10^4 to 1 x 10^7g/mol, it shows several times more at the high end than the most synthetic rubbers and this high molecular weight gives a less chain-ended and more entanglement than similar synthetic rubber of weight. The endpoints of the chain are a weak molecular-level point since these do not convey the strength of covalent bonds in the molecular chain; for larger molecular polymers such as natural rubber the tensile strength is greater. The macrostructure properties of natural rubber are the degree to which a polymer is branched. It is revealed how numerous bulky polymer side groups can be linked to the backbone of the polymer. The branch of the polymer affects the temperature of a glass transition (T_g) rubber, which is a stiffening that happens when the temperature is

lowered. However, if the temperature of glassy polymer increases, the transition from a glassy state e.g., hard and brittle to a rubbery state will occur. This transition usually takes place over a range of temperatures but is frequently noted in the middle temperatures of this range. This situation commonly is very distinct from the crystallization process and can develop from the bulky side groups of the polymer chain, which are usually lacking in natural rubber. The T_g of the natural rubber is -72°C and the specific gravity of the natural rubber is 0.93 which recorded at 20℃ (Miller, 2018)

2.3.2 Microstructure of Natural Rubber

Polyisoprene has several different isomers in its polymer chain. These are *cis*-1,4; trans- 1,4; 1,2; and 3,4. Each isomer has the same number of atoms of each element, but they are arranged differently. The numbers in the isomer name correspond to the carbon atoms that are bonded to neighboring units in each unit. In a 1,4 structure, carbon atoms 1 and 4 are linked together to create a chain. So, 1 and 4 carbon atoms are linked to the same side of the carbon-carbon double bond in a cis structure, while the 1 and 4 carbon atoms are attached to the opposite side of the double bond in a trans structure. Incidentally these isomers differ from single bonds in that there is no rotation around a carbon-carbon double bond. The pattern reveals that NR is almost entirely made up of the cis-1,4 structure, indicating that NR is a cis-1,4 polyisoprene chemically. It is called stereoregular when all the chain units in a polymer are the same isomer. The isomer of polyisoprene is presented in Figure 2.2.

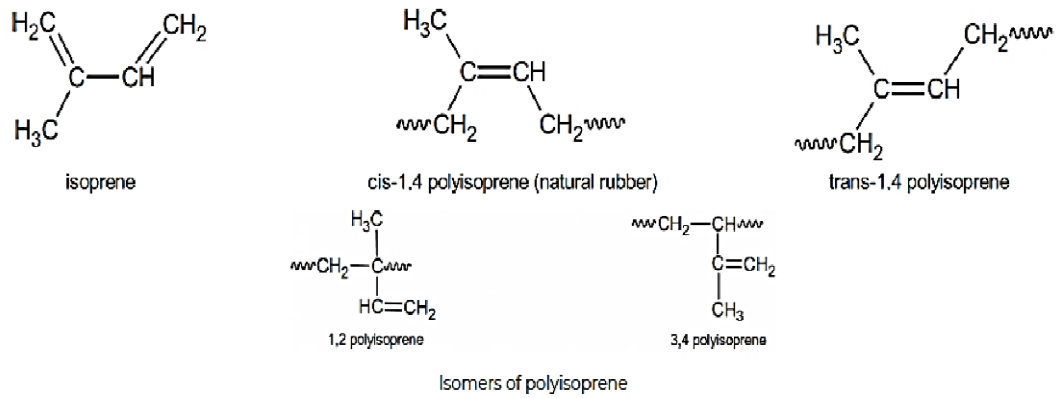

Figure 2.2 Isomer of polyisoprene (Kiu, 2007)

The stereoregularity of natural rubber's approximately 100 percent cis-1,4 polyisoprene structure provides numerous favorable features to the mechanical goods it is used to manufacture. This microstructure is responsible for the crystallinity of natural rubber. When the units of a polymer chain are arranged in a standard sufficient spatial configuration, interactions such as polar attraction, hydrogen bonding, and functional groups generate crystalline structures that stiffen the polymer. Owing to its stereoregularity, NR will form crystallites upon storage at temperatures below 20℃ and upon stretching. Unstretched rubber has no regular X-diffraction pattern and is therefore amorphous but in the stretched rubber there is an orderly crystalline-like X-ray diffraction pattern. Even though crystallization during storage can cause processing issues (it can be reversed with heat), the reversible crystallization during stretching, known as strain, induced crystallization is caused by intermolecular forces in the polymer and is responsible for many of natural rubber's unique properties (Miller, 2018).

Natural rubber comprises roughly 6% non-rubber elements in addition to the hydrocarbon portion: 2.2 percent proteins, 3.4 percent lipids (fatty acids), glycolipids and phospholipids, and 0.4 percent carbohydrates. Proteins are not contributing factors