



**INFLUENCE OF CHEMICAL MODIFICATION ON ENERGY
ABSORPTION OF STARCH MODIFIED NATURAL RUBBER BASED
COMPOSITES**

This report is submitted with requirement of the Universiti Teknikal Malaysia Melaka
(UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials)

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By

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ABSTRACT

Nowadays, there are abundant of vulcanized rubber waste, especially in automotive industries which lead to environmental pollution. In order to overcome the problem, the natural rubber composite was recently combined with natural filler to produce biodegradable rubber product. In this research, the influence of chemical modification on energy absorption of starch modified natural rubber composite was studied. The objectives of this research are to evaluate the effect of chemical modifications on energy absorption properties of starch modified natural rubber composites and to correlate the energy absorption of starch modified natural rubber based composites with its hardness and morphological characteristics. This research involves preparation of raw material, chemical modification of starch, fabrication of composites as well as testing and analysis of the final product. For chemical modification of starch, the starch was treated by using 5% of silane and 5% of glycerol to enhance their matrix-fiber interaction. For the composites fabrication, NR and CB were undergoing a mixing process in the internal mixer with mixing temperature 60 °C, rotor speed 120rpm, mixing time 11minutes and hot pressing machine at temperature 150 °C under compression 110kgf to produce a Polymer Matrix Composites (PMC) blend. The mechanical and physical testing involve in this research were impact, hardness and density, respectively. The morphology was observed by using Scanning Electron Microscopy (SEM). Furthermore, to identifying types of chemical bond, X-ray Diffraction and Raman Spectroscopy were used. It was observed composites without chemical surface modification produced high impact strength with 126.5 J/m properties than composites with chemical surface modification. However, to be compare among the treated starch, silane shows the highest impact strength 120.57 J/m regarding to its higher interfacial interaction of treated fiber matrix.

ABSTRAK

Pada masa kini, terdapat banyak sisa getah tervulkan, terutamanya dalam industri automotif yang membawa kepada pencemaran alam sekitar. Bagi mengatasi masalah ini, komposit getah asli telah digabungkan dengan pengisi semula jadi. Dalam kajian ini, pengaruh pengubahsuaian kimia untuk penyerapan tenaga komposit kanji diubahsuai getah asli telah dikaji. Objektif kajian ini adalah untuk menilai kesan pengubahsuaian kimia pada sifat penyerapan tenaga kanji diubahsuai komposit getah asli dan untuk mengaitkan penyerapan tenaga komposit getah asli berasaskan kanji diubahsuai dengan kekerasannya dan ciri-ciri morfologi. Kajian ini melibatkan penyediaan bahan mentah, pengubahsuaian kimia pada kanji, fabrikasi komposit serta ujian dan analisis produk akhir. Bagi pengubahsuaian kimia pada kanji, kanji dirawat dengan menggunakan 5% daripada silana dan 5% daripada gliserol untuk meningkatkan interaksi matriks-gentian mereka. Bagi fabrikasi komposit, getah asli dan karbon hitam telah menjalani proses pengadunan di dalam pengadun dalaman pada suhu pencampuran 60°C, kelajuan rotor 120rpm, masa campuran 11 minit dan mesin panas menekan pada suhu 150°C dibawah tekanan 110kgf untuk menghasilkan komposit matriks polimer (PMC) campuran. Ujian mekanikal dan fizikal yang terlibat dalam kajian ini adalah kesan, kekerasan dan kepadatan,. Analisis morfologi telah dijalankan dengan menggunakan Mikroskop Imbasan Elektron (SEM). Tambahan lagi, untuk mengenal pasti jenis ikatan kimia, difraksi sinar-x (XRD) dan spektroskopi raman telah digunakan. Didapati, komposit tanpa pengubahsuaian permukaan bahan kimia menghasilkan kesan kekuatan yang lebih baik dengan 126.5 J/m daripada komposit dengan pengubahsuaian permukaan kimia. Walau bagaimanapun, untuk dibandingkan antara kanji yang dirawat, silana menunjukkan kesan kekuatan paling tinggi 120.57 J/m mengenai interaksi antara muka yang lebih tinggi iaitu gentian-matriks.

DEDICATION

Only
My beloved father, Azly bin Amron
My supportive mother, Zaida Binti Mail
My brothers Muhammad Shahmi Bin Azly and Muhammad Zahin Bin Azly
for giving me moral support, money, cooperation, encouragement and understandings.
Thank you so much

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CHAPTER 1

INTRODUCTION

1.1 Background

Natural rubber chemical properties naturally it is soft and sticky solid. Due to weak van der Waals forces, natural rubber has low tensile strength and low elasticity of its intermolecular attraction and occasional crosslinking (Chollakup *et al.*, 2015). Nowadays, rubber product are been found in everywhere and the application of rubber are well known by people. In 1839, Charles Goodyear and Thomas Hancock invest the first important chemical modification of natural rubber that improved tensile strength. Then, the request of rubber manufacturing has been growth rapidly since 1920 due to automotive industry is the biggest consumer of rubber product. Rubber also is used in kitchen appliance mattress, clothing and footwear (Hakimi, 2014).

There are various scopes of energy absorption in natural rubber but this study focus on impact in natural rubber. The focuses that will affect the impact energy absorption in natural rubber are vulcanization process, filler used in reinforcement, the interfacial interaction between rubber and filler and chemical modification. As for mechanically factor, are circumscribe with tensile strength, elongation at break, stiffness, mechanical and thermal properties (Nardin *et al.*, 2015). All are depend on filler be used after the reinforcement process of the natural rubber for improving the properties of natural rubber.

However, the innovation of natural rubber keeps going on with as a new approach to technology development. Rubber composite has gain attraction and interest among industry and academic nowadays due to their exhibit remark in improvise material properties. Reinforcing on rubber technologist has widely used as to improve the mechanical properties. In most research, the reinforcement material that widely used in vulcanized rubber is carbon black and silica. Carbon black mostly used as reinforcing filler as to improve abrasion resistance, tear strength, tensile strength and stiffness. While, silica has been used for mineral reinforcing filling to improve

abrasion resistance, tear strength and reduce rolling resistance (Ika Maria Ufah 2016). There is also reported, dispersion of natural rubber energy absorption by blend with resin; such as sodium lauryl sulfate, toluene, or ammonia as dispersion aids (Sabu Thomas 2011). The reinforcement of natural rubber gives an introduction of NR composites. Composite is a multiphase of material that opposed to one that forms naturally. The constituent phases must be dissimilar chemical and separated by distinct interface.

The recent development for energy absorption of natural rubber is by chemical modification with addition of filler such as natural starch and the quantity and activity of coupling agent. This chemical modification of natural rubber is essential to overcome some of the natural rubber properties drawback. Starch appears in plant as granules, the sizes and shapes depend on their origin resource. Even though the main component of all starch are polymer amylose and amylopectin, the natural starch granules characteristic and structure are consider in record. The degradation process of starch is very slow. The properties of starch have been extensively studied and directly related to biodegradation rate, availability, renewability, non-toxicity and affordability. Natural starch available in various plant such as sugar palm, kenaf tree and banana leaf.

1.2 Problem Statement

Natural rubber has superior mechanical properties but poor environmental resistance with respect to low heat ageing resistance and is prone to degradation to oxygen and ozone attack. It also cause so many rubber scraps. In Malaysia, the scarps of rubber mostly had been burned and buried as rubber has low degradability. This cause environmental effect which air and soil pollution. There are variety type of fillers are been used for various purpose in rubber industry as the reinforcement is important to reduce cost, improve processing and physical properties of vulcanize rubber The reinforcement natural rubber is to produce product which are good in cushioning, excellence shock absorption, elasticity and fatigue properties, with suitable filler is known as natural rubber based composites.

Many studies have been carried out to improve mechanical properties of natural rubber such as maize stalk as reinforcement in natural rubber composites (Chigondo *et al.*,2013), influence of

carbon black and silica filler on the rheological and properties of natural rubber compound (Ulfah *et al.*, 2015) and properties of natural rubber based composites containing fullerene (Al-Hartomy *et al.*, 2012). However, the research in natural rubber based composite still narrow especially on impact or dynamic stress properties and mechanism involve due to lots of information needed even though natural rubber composites material gained attention in various rubber articles and industry. The reinforcement of carbon black in natural rubber as the will properties of natural rubber will give different result with improved properties. Nevertheless, there are some innovations on rubber composition due to low compatibility between hydrophobic natural rubber matrix leads and hydrophilic fiber to weak interface gives result low mechanical properties and high swelling properties when adding natural filler as biodegradable agent in natural rubber. In order to enhance the interfacial bonding between fiber and matrix, the fiber surface needs to be chemically modified.

The research about natural rubber composited must be link with chemical modification of natural rubber composites. As natural rubber reinforce reinforced carbon black is known for environment effluence and inflict black colour (Mente *et al.*, 2016), the natural filler is introduce biodegradability of NR composites and reduce the air and soil pollution as NR composites is cannot to be decomposed. With introduction of natural filler in NR composites, the stress transfer of the composites decrease and decreasing in mechanical properties. This is due to different surface properties between filler and rubber matrix (Mente P1 *et al.*, 2016) that cause low compatibility of hydrophobic rubber matrix with natural filler (Chigondo *et al.*, 2013) which result poor mechanical properties. As to improve compatibility of matrix and filler, the treatment on fiber surface needs to be chemically modified (Chigondo *et al.*, 2013).

There are studies in combination of the non-biodegradable polymer with some biodegradable natural filler. The resulting of these combination makes the application is biodegradable and the mechanical properties are same as synthetic composites (Jeefferie *et al.*, 2011).

1.3 Objective

The purposes for this research are

1. To prepare natural filler modified natural rubber composites via melt compounding using internal mixer
2. To evaluate the effect of chemical modifications on energy absorption properties of starch modified natural rubber composites
3. To correlate the energy absorption of starch modified natural rubber based composites with its hardness and morphological characteristics

1.4 Scope

The main focus of this study is on energy absorption of natural rubber composites with modified starch by using silane and glycerol. The energy absorption was calculated by using izod impact strength (ASTM and drop ball testing). Then, for better interfacial interaction between matrix and filler, chemical modification has been introduced by using silane and glycerol. The machine used is internal mixer for blending material and additive together. Next, the mechanical and physical properties of treated starch in natural rubber composites were compared with untreated starch of natural rubber composites.

1.5 Project significance

The primary outcome of the study is research information which will facilitate the design of formulation of chemical modification as it is suitable with impact absorption applications. This analysis would be very useful in the design of energy absorbers. Such combinations are very effective in energy absorption applications, keeping the peak force below the limit in reducing the vulnerability of natural rubber.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Matrix Composites

There are 3 different types of polymer materials which are form from thermoplastic, thermoset and elastomer with vastly different performance by the way the atoms or molecules are bonded together (the main combination bonds) and one of it is polymer matrix composites (PMC) (Wang *et al.*, 2011). According to (Florea *et al.*, 2012), by the 1980s the term polymer composite referred exclusively to the systems consisting of a polymer matrix in which inorganic fillers or reinforcing textile materials were incorporated. The first combination was made due to economic reasons and later on, after the two-phase compatibility, out of performance reasons. In the 90s the term polymer composite material was extended to all systems with at least two components, one of which was organic with short or continuous fiber. The reinforcement of PMC primarily improved high strength and stiffness as its design for mechanical load structure which supported by the reinforcement. The matrix used is to transfer load between matrix and fiber as its bound together. The use of polymer from renewable resources is an environmentally advantageous alternative to synthetic polymer to some application. Many polysaccharide biopolymers have been examined this context with long term aim of value-adding to ‘waste’ agricultural byproducts such as sugar beet pulp and rice husks.

By referring to Princetonweb (2016), PMC have two categories, which are reinforced plastic and advance composites. The distinction is based on the level of mechanical properties (usually

strength and stiffness); however, there is no unambiguous line separating the two. Reinforced plastics, which are relatively inexpensive, typically consist of polyester resins reinforced with low-stiffness glass fibers. Meanwhile, advanced composites have been in use for about 15 years. It has been used primarily in the aerospace industry due to it has superior strength and stiffness, and is relatively expensive.

Nowadays, with very diverse properties (from good machinability and easily implementation to specific weight, very low thermal conductivity and electrical) polymeric materials have become indispensable and irreplaceable. The high diversity of polymer composites makes it impossible to treat these materials in a uniform manner. However, according to (Florea & Carcea, 2012) the polymer composites main criteria can be classified by the numbers of components of composite materials presuppose at least two components in their structure. Usually, the synthesis composite materials are limited to the use of 2-3 components. In composite structure, besides polymers, micro molecular substances can be included. Next is the nature of components. It depends on the nature of components, because polymer composites can be systems of: polymer-polymer (synthetic polymer-synthetic polymer, natural polymer-synthetic polymer, and natural polymer-natural polymer); polymer-inorganic compounds; polymer-organic compounds; polymer-metal. Macromolecular interactions system also is one of the main criteria in polymer composites classification. In terms of interactions between components, polymer composites can be: natural composites (interpolymeric complex) characterized by the fact that physical links (ionic, hydrogen, van der Waals, etc.) between components occur; chemical composites characterized by the fact that covalent bonds are established between compounds; physicochemical composites or interpenetrated networks (IPN), partially interpenetrated (semi-IPN) or totally interpenetrated (full-IPN). In full-IPN polymer composites, the chains of one component (cross-linked or not by covalent bonds) are "fixed" in the reticular structure of the second component. It also stated the composite in its functional form; solid, quasi-solid (gel), liquid (composite solutions). To achieve the mixture, the methods and processes at the molecular level, the mixing of two macromolecular compounds can be achieved through the following methods: melt mixing; solutions mixing; solution mixing and drying; solution mixing followed by freeze-drying, co-precipitation.

2.2 Natural Rubber based Composites

According to Mente P *et al.* 2016 , composite materials are a combination of two or more materials that have different properties, such as in the combinations render a product which has intermediary characteristics of the components. For example; rubber based composites normally produce composites which are good mechanical properties which are high elastic , high damping and strength due to in cooperated filler. Furthermore, natural rubber composites mostly need to be cure to gain the properties of rubber. Rubber composites are typical examples since curing is a recipe of rubber elasticity and strength. In addition, the properties of composite materials are influenced by the interfacial bond between filler and matrix. The properties for particle based composites depend on particle size, surface area, surface activity and aggregate structure; filler dispersion and concentration and filler-matrix interactions. In Al-Hartomy *et al.*, (2012) study, the usage of fullerene as a replacement filler of carbon black in rubber blends and rubber-based composites in order to achieve enhanced durability, lower heat-built up, and better fuel economy. Since 500 BC, composites have been in existence where pitch was used by the middle easterners as binders, papyrus, and reeds in building boats. There had reported to have used laminated wood veneers as decorations in Europeans, Asians, and Americans also as far back as first century AD. Shellac resin-based laminates have also been used by the Indians for over 300 years, while evidence of laminated wood is seen in Thebes dating as far back as 1500 BC (Olatunji & Richard, 2016).

2.2.1 Natural Rubber as matrix

One of type of polymer is elastomer. According to Kalle Hanhi *et al.*, (2007), elastomers are unique in polymers class and exhibit extraordinary reversible extension with low hysteresis and minimal permanent set. Elastomer is a high molar mass material when it deformed at room temperature reverts quickly to nearly original size and form when the load causing the deformation has been removed. Elastomer has high elastic recovery after deformation in compression or tension. Even after stretching an elastomer to several times its original length,

under ideal circumstances it will return to its original shape and length after removal of the tension. In addition, elastomers are characterized in great toughness under static or dynamic stresses, better abrasion resistance than that of steel, impermeability to air and water and in high resistance to swelling in solvents and attack by chemicals, like many other polymers. Elastomers show viscoelastic properties, which nowadays can be tailored for numerous special applications, e.g. tyres, vibration and shock isolation and damping. These properties are exhibited over a wide temperature range and are retained under various climatic conditions and in ozone-rich atmospheres.

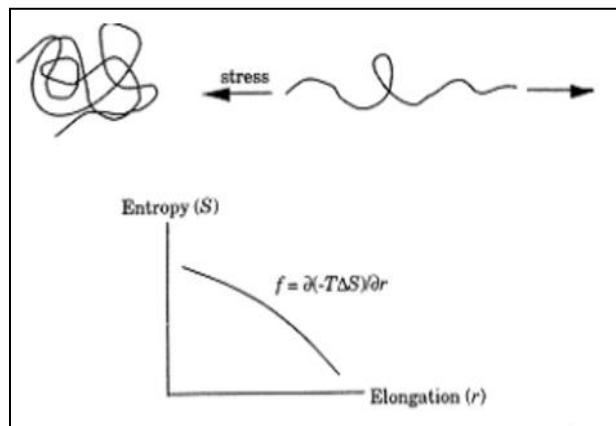


Figure 2.1: The structure of elastomers in strain and the dependence of elastic force on temperature T and entropy S Kalle Hanhi *et al.* (2007)

Thus, one of elastomer that mostly used in PMC is natural rubber. Natural rubber is obtained from latex, which is the emulsion of cis-1,4-polyisoprene and water. Latex is obtained from the tree by tapping the innerbark and collecting the latex in cups. A stabilizing agent, such as ammoniac, can prevent too early coagulation.

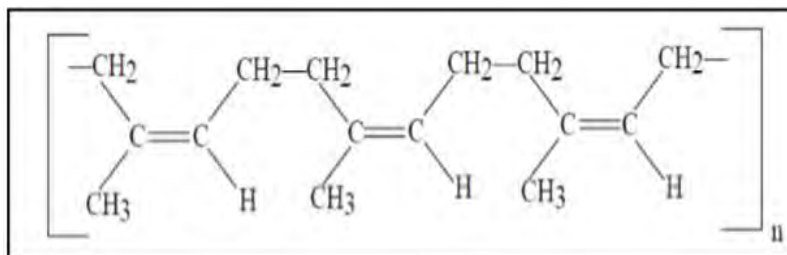


Figure 2.2: Structure of Polyisoprene (Kamarah, 2010).