INFLUENCE OF SILANE SOLUTION pH ON THE RUBBER-METAL BONDING

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INFLUENCE OF SILANE SOLUTION pH ON THE RUBBER-METAL BONDING

Submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

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I hereby, declared this report entitled "Influence of Silane Solution pH on The Rubber-Metal Bonding" is the result of my own research except as cited in reference.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for the degree of Bachelor of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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(Dr. Chang Siang Yee)

ABSTRAK

Ejen gandingan silana adalah satu pendekatan baru ikatan getah-logam disebabkan oleh kelemahan sistem pelekat, dan kecekapannya bergantung kepada keadaan ikatan. Penyelidik mendapati bahawa silana campuran akan meningkatkan rekatan ikatan getah-logam, tetapi kecekapan ikatan getah-logam bergantung pada sifat kimia larutan silana dan keadaan silana. Tujuan kajian ini adalah untuk mengkaji sifat kimia terhadap larutan individu dan campuran silana dan untuk mengkaji kesan pH larutan silana terhadap kekuatan ikatan pemasangan getah-logam. Nilai pH larutan silana campuran dilaraskan kepada pH 4-5 dan 7-8 pada komposisi tetap 1:3 iaitu nisbah silana amino:sulfur untuk menyelidik pengaruh larutan silana pH pada ikatan getah-logam. Analisis FTIR dilakukan untuk menggambarkan sifat kimia terhadap larutan silana dan mendapati larutan silana bis-amine, bis-sulfur dan campuran menunjukkan puncak Si-O-Si terletak pada julat 1000-1100 cm^{-1}. Setelah berjaya mengikat getah dan aluminium melalui pembentukan mampatan, ujian ASTM D 429 B dilakukan untuk memeriksa ikatan rekatan antara getah asli dan aluminium manakala mikroskop optik digunakan untuk mengenalpasti ragam kegagalan pada ikatan. Walaubagaimanapun, proses ini tidak dapat dilakukan dan penganalisaan melalui ulasan berkritis berdasarkan kajian lepas dilaksanakan akibat kekangan pandemic. Kajian ini menjangkakan kekuatan rekatan optimum akan tercapai pada pH rendah dengan kegagalan jelekitan disebabkan hidrolisis pantas tetapi kondensasi perlahan yang menghasilkan rangkaian yang padat dan bermolekular tiga dimensi manakala pada keadaan neutral dan pH tinggi, ikatan akan gagal pada mod kegagalan perekat. Hal ini dikemukakan kerana pengegelan pramatang yang terhasil akan mengurangkan ikatan kalis air. Oleh itu, pengaplikasian pH larutan silana dicadangkan antara pH 4-5 untuk mencapai rekatan optimum pada ikatan getah-logam.

ABSTRACT

Silane coupling agents is a new approach of rubber-metal bonding due to the disadvantages of existing adhesive system, and its efficiency depends on the bonding conditions. Researchers found that mixed silanes promote adhesion of rubber-metal bonding, but the efficiency rubber-metal bonding depends on the chemical properties of silane solutions and pH condition of silanes. The aim of this study are to study the chemical properties of individual and mixed silane solutions and the effect of silane solutions pH on bond strength of rubber-metal assembly. The pH value of the mixed silane solutions was adjusted to pH 4-5 and 7-8 at fixed composition of 1:3 to amino:sulfur in order to study the effect of pH value of mixed silane solution on bond strength of the rubber-metal assembly. FTIR analysis was conducted to characterize the chemical properties the silane solutions and was found that all bis-amine, bis-sulfur and mixed silanes showed Si-O-Si peak located in the range of 1000-1100 cm^{-1} in the spectra, indicating that siloxane bond was present in the solutions. Once the rubber was successfully bonded with aluminium under compression moulding, peel test was performed under ASTM D429 B to examine the adhesion bond between natural rubber and aluminium while the optical microscope was used to identify the failure mode of the bonding. However, this process could not be conducted and analysis through critical review based on previous research was done due to the pandemic constraint. It is expected that an optimum adhesion strength would be achieved at low pH with cohesive failure mode due to fast hydrolysis but slow condensation reactions that producing a dense and three-dimensional molecular network while under neutral and high pH condition, the assembly would fail with adhesive failure mode. This is rendered to the premature gelation formed in the silane solution which reduces the number of water-resistant bonds. Therefore, application pH of silane solution is recommended between pH 4-5 in order to obtain optimum adhesion for rubber-metal bonding.

DEDICATION

My beloved father, Mohd Ali Piah Bin Pandak Ibrahim

My beloved mother, Habsah Binti Mohd Hassan

My lovely sisters, Hanizah and Hazirah

My respected supervisor, Dr Chang Siang Yee

Thank you for the motivation, encouragement and endless support was given to me in completing this research.

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LIST OF ABBREVIATIONS

A1170	-	Bis-(trimethoxysilylpropyl)amine
A1289	-	Bis-(triethoxysilylpropyl) tetrasulfide
Al 6061	-	Aluminum Alloy 6061
Al 6063	-	Aluminum Alloy 6063
ASTM	-	American Society for Testing and Materials
CRS	-	Cold Rolled Steel
EGS	-	Electrogalvanized Steel
EPDM	-	Ethylene Propylene Diene Monomer
FTIR	-	Fourier Transform Infrared Spectroscopy
HSS	-	High strength steel
HVLP	-	High-Volume Low-Pressure
IR	-	Polyisoprene rubber
MRB	-	Malaysian Rubber Board
NaOH	-	Sodium Hydroxide
NR	-	Natural Rubber
NBR	-	Nitrile Butadiene Rubber
OM	-	Optical Microscope
PHAs	-	Poly-Hydroxy-Alkanoates
SMR	-	Standard Malaysian Rubber
SBR	-	Styrene-butadiene Rubber
SR	-	Synthetic Rubber
UHSS	-	Ultra-High Strength Steel
UV	-	Ultraviolet

LIST OF SYMBOLS

θ	-	Angle
°	-	Degree
°C	-	Degree Celcius
λ	-	Wavelength X-Ray
µm	-	Micrometer
a	-	Lattice Parameter
cm/min	-	Centimeter per Minute
Cr	-	Chromium
Cu	-	Copper
d	-	Interplane Spacing
g/cm^3	-	Gram per Centimeter Cube
g/l	-	Gram per Liter
hPa	-	Hecto Pascal
mm	-	Millimeter
mm/s	-	Millimete per Second
mm/min	-	Millimeter per Minute
Mg	-	Magnesium
MPa	-	Mega Pascal
N	-	Newton
Si	-	Silicon

CHAPTER 1

INTRODUCTION

1.1 Background

Over the years, the rubber industry has seen steady and solid growth worldwide where a wide varieties of rubber products has been developed in the automotive industry. Vibration dampers, fuel flow controllers, automotive seals, suspension systems, pressure regulators and cruise controls are part of the full range of non-tire automotive products made from rubber (Barton, 2016). For wide range of applications, rubber-metal bonding is important as it dampens vibration, absorbs shock, fully seals, dissipates friction, and isolates noise. Due to the growing usage of rubber-metal applications, the need for a strong and long-lasting bond between rubber and metal has become more important and crucial. The efficient and long-lasting relationship of anti-vibration components is critical for each part of the bonding process, because rubber and metal are different substrates (Crowther, 2001; Whitford, 2019). The method varies completely from bonding of rubber to rubber or bonding of rubber to metal. Rubber-to-metal components are used in interconnected interfaces where strength and resistance are needed to deal with dynamic stress (Whitford, 2019).

Rubber-metal bonding can be mechanically bonded or chemically bonded. Some of the rubber-metal can be mechanically bonded. It is possible to use some mechanical bonds to hold the rubber to the metal. Holes are designed through the metal entirely. The rubber fills the holes and cavities on each side during the moulding process, leading to a mechanical bond. Ribs or cuts in the metal may be used to give both a mechanical and chemical bond to make an adhesive bond more robust (*Rubber to Metal Bonding*, n.d.).

Chemical bonding between rubber and metal would be the application of adhesive system and silane agent. Current adhesive systems used in the method of Chemlok® 205 and 220 rubber-to-metal bonding. This primer or adhesive system has allowed a wide range of available rubber to be bonded, thus allowing major improvements in service efficiency. Modern adhesive techniques use both single and two-coat adhesive formulations, with a choice dependent on the bonded assembly's service requirements. During elastomer vulcanization, the Chemlok ® 250 adhesive is a one-coat adhesive used to bind a variety of elastomers to different substrates. On the other hand, a two-coat system has a main layer and a topcoat adhesive. The primer provides a powerful adherence to the metal substratum whereas the topcoat adhesive provides the reactivity necessary. For the dried primer, an adhesive topcoat is added. The topcoat provides a reaction to unsaturation in the elastic base, normally during the moulding process. The topcoat also has to react to adhesive and primary intercoat adhesion with the first coating (*Adhesion Science - Rubber-to-Metal Bonding*, 2020).

Besides the adhesive mechanism, the silane coupling agents serve as a bonding or bridging agent for the area interphase between an inorganic substrate and an organic substrate to strengthen the adhesion of the two different materials. While various silanes have been discovered to aid bonding between metal substrates and a polymer layer, the results are highly dependent on the method used. Thus, several researchers developed mixed silanes to promote the adhesion of rubber-metal bonding so that different rubber compounds can be bonded to various metal substrates. Previous research has shown that the increase of cohesive failure from 50% (without silane mixture) to 90% after ageing with the cobalt-free compound has been caused by a greater linkage with the rubber compound module at the interface by the use of a combination of bis-(trimethoxysilylpropyl)amine and bis-(triethoxysilylpropyl) tetrasulfide silanes (Jayaseelan & Van Ooij, 2001).

1.2 Problem Statement

Over the years, many researchers improved the conventional adhesive system which has undesired qualities. These adhesive systems usually provide strong adhesion, however from the point of view of health and safety, they also imposed several undesirable characteristics. Typically, not only solvents are hazardous, they also can be difficult to add to certain substrates, are less efficient bonding agents for certain substrates, and generally cost more than their solvent-based counterparts (Wei, 2008). Therefore, silanes were chosen for the other alternatives due to the wide-ranging advantages over the existing conventional adhesive systems. While silane treatment takes less time to bond, this discovery efficiently and economically provides high adhesion and bonding force with minimal waste of silane solution compared with traditional adhesive systems.

The use of silanes for adhesion of different sulfur-cured rubber compounds to different metals was reported by Jayaseelan et al. (2012). The study demonstrated that the adherence of different rubber compounds to the different metal substrates was promoted by a mixture of two silanes, a bis-(trimethoxysilylpropyl)amine and a bis-(triethoxysilylpropyl)tetrasulfide, in ratio 1: 3 by volume. Generally, one of the silanes should be a former of dry film (only aminosilanes have this ability) and the other silane should be able to react with rubber. Meanwhile, the application of either silane alone did not lead to a cohesive rubber failure. Studies on the usage of mixed silanes are however limited.

This mechanism explains why the mixture of two silanes produces a high bond strength compared to single silane. Thus, it is important to determine the chemical properties of silane solution that will affect the bonding strength between two different substrates. On the other hand, it is important to understand the influence of application conditions such as the pH because the hydrolysis occurs only in a particular pH range and even a slight variation in those values causes condensation of silane (Sukumar, 2005). In this work, the chemical properties and pH value of mixed silanes solution on the rubber-metal bonding were studied further.

1.3 Objectives

The objectives of this research are:

1. To characterize the chemical properties of individual and mixed silane solution.
2. To analyse the effect of silane solution pH on bond strength of the rubber-metal assembly using reported experimental studies.

1.4 Scope

The silanes used in the experimental work were the mixture of bis(triethoxysilylpropyl)tetrasulfide and bis(trimethoxysilylpropyl)amine to bond with natural rubber and aluminum substrate. Aluminum substrate was roughened through sandblasting process and cleaned thoroughly prior to bonding. In order to achieve the first objective of this project which was to characterize the chemical properties of mixed silane solution, Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to identify chemical properties and bond structure of each individual silane solution and also the mixtures of both bis-(trimethoxysilylpropyl)amine and bis-(triethoxysilylpropyl) tetrasulfide silanes. Meanwhile, in order to achieve second objective which was to study the effect of pH value of mixed silane solution on bond strength of the rubber-metal assembly, the pH value of the mixed silane solution was tested and adjusted using acetic acid or sodium hydroxide to obtain different pH range, i.e. 4-5 and 7-8 at fixed composition of 1:3 to amino:sulfur and the silane mixtures were applied on the metal substrates. Then, the rubber-aluminum assembly was bonded under hot compression moulding and a peel test based on ASTM D 429 Method B was conducted in order to study the adhesion bond between natural rubber and aluminum. Last but not least, Optical Microscope (OM) was used for micro structural characterization and analysis of the silane film on the aluminium substrate. Due to the pandemic constraint, the experimental work for the second objective could not be carried out physically and the analysis was conducted through critical review using reported experimental studies.

CHAPTER 2

LITERATURE REVIEW

Rubber-metal bonding is critical for a wide range of applications in automotive industry because it dampens vibration, absorbs shock, completely seals, dissipates friction, and isolates noise. The need for a strong and long-lasting bond between rubber and metal has become more relevant and crucial due to the increasing use of rubber-metal applications in automotive industry.

There are few uses for rubber-metal bonding in the automotive industry, such as shock absorbers, engine mounts, suspension ball joints and so on. For instance, rubber-metal bonding of the shock absorber, which helps to regulate the impact or shock and rebound movement of the suspension and springs of the vehicle. The main function of the shock absorber is to ensure that the tyres of the vehicle remain in contact with the road surface at all times, ensuring timely braking response and the safest control of the vehicle and smoothing out vibrations and bumps (2U, 2015). In the meantime, rubber-metal bonding serves as vibration damping for the engine mount. As the engine is attached to the body, the static engine load is absorbed by the engine mounts. They restrict the movement of the engine, ensuring that the vibration is dampened and that the structure-borne noise is transmitted to the body. On the other hand, the rubber-metal bonding act as a suspension system for the suspension of the ball joints which attach the control arms of the wheel suspension to the wheel carrier and, consequently, to the wheel. Its role is to direct the wheel carrier and the wheel, in addition to allowing the spring deflection of the wheel, and to allow the steering movement on the front axle. The suspension ball joint usually transfers only longitudinal and lateral forces with less vertical forces and also carries the vehicle's weight (axial spring and damping forces) (*Supporting Joint and Suspension Ball Joint*, n.d.)