

## A review on the cords & plies reinforcement of elastomeric polymer matrix

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**Abstract.** Steel, polyester, nylon and rayon are the main materials of cords & plies that have been reinforced in the natural rubber to produce quality tyres but there is few research reported on cord and plies reinforcement in silicone rubber. Taking the innovation of tyres as inspiration, this review's first objective is to compile the comprehensive studies about the cords & plies reinforcement in elastomeric polymer matrix. The second objective is to gather information about silicone rubber that has a high potential as a matrix phase for cords and plies reinforcement. All the tests and findings are gathered and compiled in sections namely processing preparation, curing, physical and mechanical properties, and adhesion between cords-polymer.

### 1. Introduction

Cord is a structure composed of two or more strands and can formed as plied yarns [1]. Plies are locally represented as unidirectional assembly of cords [2]. Silicone rubbers have unique characteristics as it acts like both organic and inorganic compound properties. They have special properties, including biocompatibility, thermal stability, fine electrical properties, good chemical stability, oxidation resistance, and resistance to temperature [3,4]. Therefore, silicone rubber is chosen in a lot of industries to improve the quality and functionality of product such as electric and electronic equipment, households goods, footwear, and dental application [5-7].

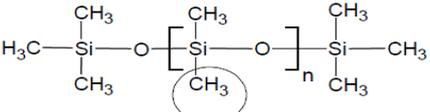
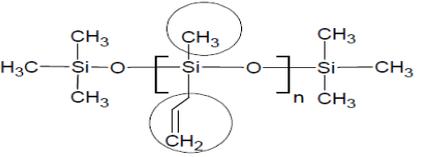
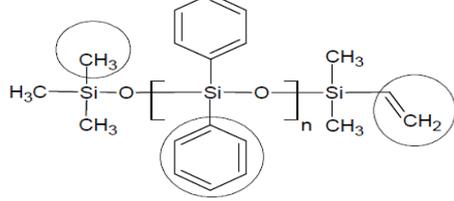
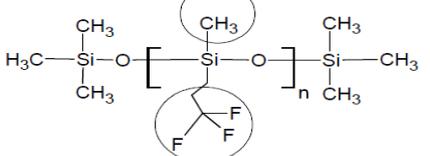
Silicone rubbers were classified into four as shown in table 1, polydimethyl siloxane elastomers (MQ) that have only methyl substituent groups on the polymer chain; second is polydimethyl/vinylmethyl siloxane elastomers (VMQ) which exist with both methyl and vinyl substituent groups on the polymer chain. The third is polymethyl/vinyl/phenol siloxane elastomers (PVMQ) which have methyl, phenyl and vinyl substituent groups on the polymer chain and fourth is poly-Y-trifluoropropylmethyl/vinylmethyl siloxane elastomers (FVMQ) with fluoro, vinyl and methyl substituent groups on the polymer chain. The Q is an abbreviation for silicone rubber that represents quaternary group because silicone atom has four valence electrons [8]. MQ elastomers are rarely used since the methyl groups are difficult to vulcanize. The VMQ elastomer that represents vinyl groups

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shortens the curing time of the elastomeric because it reduces the activation energy. The fluorine of FVMQ is distributed in increase the oil and heat resistance while phenyl groups of PVMQ incorporated into the chain to make sure the material remain elastomeric in lower temperature [9].

**Table 1.** Classification of silicone rubber [10-14]

Class of silicone rubber	Velocity ( $\text{ms}^{-1}$ )
MQ	
VMQ	
PVMQ	
FVMQ	

There are two types for silicone rubber which are room temperature vulcanizing (RTV) and high temperature vulcanizing (HTV) [15]. HTV was cured at high temperature that mainly used as a weather shed and RTV used as hydrophobic coating on ceramic surfaces and cured around room temperature [16].

Many research have been written about the upgrading the properties of silicone rubber. Yet, only a few reports were published on used of various cords and plies reinforcements in silicone rubber. Therefore, this paper aims at gathering all information and literature review to design and fabricate silicone rubber with various materials of cords and plies reinforcements. The others study such as the results on mechanical and physical properties, curing and adhesion behaviour of silicone composite also will be summarized.

## 2. Motivation for studying

In 1960s, the cords materials for rubber were introduced such as polyester[17], steel [18], nylon[19-21]. The fabric cord-inserted rubber compounds was applied in manufacturing of tyres, conveyer belts, and hoses [21,22] and also practiced in materials such as clay [23]. The cross-ply or bias ply tyres design is the first design introduced the cords at angles between +60 until -60 degrees from the direction of travel. After that, the radial tire is approached by laying all of the cord plies at 90 degrees to the direction of travel. This is because the radial design can avoids the plies reinforced in tires to rub against each other as the tire flexes, and reducing the tire's rolling friction that will allowed the vehicles with radial tires design had fuel save economy. In order to have an adequate rigid at the contact with the ground, the entire tyre is surrounded by additional belts that can be made from steel, polyester, and Kevlar [20,24]. Thus, an important aspect that can be taken to produce a better

reinforcement polymer product is the specimen directions on recovery behaviours of cords- rubber composites. As reported by Choi & Kim [21] the cutting direction also significant to estimate the aging properties of calendared fabric cord. Then, a new composite for external reinforced polymer had been reported by Figeys et al. [25] material steel plates and carbon fibre reinforced polymers (CFRP) dealt with new material that can be used as external reinforcement which was steel cord reinforced polymer (SCRIP) that has a low price and flexible lamination. Other than steel cords, the other types of cords such as nonwoven hemp that replaced glass fibres also being approach by Richardson & Zhongyi [26] in order to provides technological, economical and environmental benefits.

**Table 2.** Examples types of material reinforcement

	Reinforcement Material	References
Polypropylene	Carbon, Kevlar	[27]
Epoxy resin	Kevlar	[28]
Natural rubber	Steel, Brass plate steel	[20,29-33]
Liquid Phenolic resin	Non-woven hemp	[26,34]
Elastomer matrix	Rayon, nylon	[35]
Polyethylene	Aramid	[36]
Urethane, Silicone rubber	Cotton, fibreglass	[37]

### 2.1. Cords and plies-rubber composite processing & preparation

Tian et al. [28] explained on the preparation of three-ply Kevlar fiber in epoxy composites. The epoxy resin and curing agent were dried in an oven at 60°C for several hours to get rid of moisture and then soaked in the epoxy resin for some hours until the fibers totally penetrated. After that, Kevlar and epoxy resin were coiled to the mandrel and let to cure at 70°C for 5 hours. Chandra et al. [31] studied on the adhesion of rubber to steel cord by a new testing technique and was further explored by Shi et al. [30]. The base used was natural rubber that being mixed for 8.5 min at 55 rpm and 60°C using an internal mixer. The material of cord used was brass-plated steel cord and was treated by ethanol. The specimens adhere behavior in a carcass was observed. Then, Richardson & Zhang [26] looked out the potency of organic material such as hemp as reinforcement material and liquid phenolic resin as base in their study. The sample without hemp and with two layers nonwoven hemp fabric was fabricated using a resin transfer molding. Sample were kept in the mould at 65°C for four hours as preliminary curing and transferred to an oven at a temperature of 80°C for three hours as post curing. Samples were cut by using diamond saw. Another report published by Carbone et al. [38] introduced the PET cord-rubber composites in order to asses its micromechanical behavior. The PET cords were coated with a Resorcynhol-Formal-dheyde-Latex (RFL) to have a good adhesion with the rubber matrix. The matrix was prepared by mixing all the ingredients using Haake Rheomix 600/610 batch mixer for 12 min at 30 RPM. The mixed compound was processed in a two-roll mill at 80°C and vulcanized by mechanical press at 160°C for 10 min under 1.37 Mpa as to obtain rectangular pads with thickness of c. 1 mm. The two composite types were prepared as discontinuous cord embedded and also as continuous cords completely crossing the specimen over the full length. There also an investigation on high strain rate tensile behaviors of steel cord-rubber composite conducted on the servo-hydraulic machine prepared by Elamnipon et al. [29]. The 45° and 90° cord angles were chosen as respecting the cord axis and 0° cord angle tested with single steel cord. Moghadam et al. [39] prepared HTV Silicone Rubbers by melt mixing in an internal mixer at a rotational speed of 60 r/min and 30 min of mixing times. Then, the blend sample was vulcanized in hot press (Carver hydraulic unit model 3912) at 180°C and pressure of 44482 N/cm<sup>2</sup> for 10 min and post-cured in an oven at 200°C for 2 hours under nitrogen.

## 2.2. Curing

Definition of curing refers to the hardening the polymer material by crosslinking of polymer chains. The crosslinking of polymer does not need a fully cure process for certain cases. [40]. As presented in guidelines [8], there were two types of curing for solid silicone rubber product namely peroxide curing grades and addition curing with platinum catalyzed. For Liquid silicone rubber, it was always addition curing with platinum catalyzed. Curing had been approved to be a better technique for interfaces with silicone rubber compared only using silicone glue such as sealant [41]. Currently, Xue et al. [3] reported that the commercial silicone rubbers were prepared by three curing systems namely platinum-catalyzed hydrosilylation between vinyl groups and Si-H bond, tin- or Titanium-catalyzed condensation reaction of alkoxy silane and thermal-initiated free radical cross linking reaction. However, they had approached a new mechanism of curing namely UV-curing silicone rubber via thiol-ene reaction as to invent a cure mechanism that can unlimited the application of silicone rubber in medicine and biology. Ganesh & Unnikrishnan [42] developed on silicone rubber blend with Ethylene Vinyl Acetate (EVA) and revealed the curing reactions follow first order kinetics. There was also the other research that observed curing characteristics using the same blending of silicone rubber with another polymer [43][44]. Dai et al. [45] had proposed polymeric curing agent (PCA) reinforced silicone rubber composites with low viscosity and volume shrinkage. PDMS/PCA curing system exhibits lower volume shrinkage and longer curing period [45]. The cure characteristics were determined using a moving die rheometer (MDR, Mosanto, USA) at temperature 160°C.

## 2.3. Physical and mechanical properties

In 1999, the hydrophobicity changes in silicone rubbers based on polydimethylsiloxane (PDMS) already reported by Hillborg & Gedde [46] as their properties of water repellency, high surface resistivity, vandalism resistance, low density and good process ability are suitable for outdoor insulation. Momen & Farzaneh [16] have study three factors namely electrical discharge, adsorption of pollution layers, and UV radiation that cause the loss of hydrophobicity. Tian et al. [28] discovered the three-ply Kevlar/epoxy composites possess low density and have high specific strength and specific modulus. Their low density can be introduced in harsh environment such as a static ring of ship propeller.

The experiment result from Chen et al. [47] shows the mechanical properties of the novel RTV silicone rubbers were better in result compared to reference material such as divinyl-hexa[(trimethoxysilyl)ethyl]-POSS (DVPS). The influence of the temperature on the mechanical behavior of filled and unfilled silicone rubbers is studied by Rey et al. [5]. The other research made up to approach taguchi method as monitor the significant factor affecting the response and gives the optimum condition to most desirable performance [48]. Heiner et al. [9] discussed on mechanical analysis of two different silicone rubber namely peroxide-cured silicone elastomer and platinum-cured silicone elastomer. The hardness result of peroxide-cured showed 50% higher than platinum-cured. This is because of the side product produce by peroxide-cure in formed of radicals. The radicals tend to crosslinked with the elastomer and improved the hardness. Park [49] investigate the effect of fillers such as glass fiber, wollastonite and fluoro rubber towards silicone rubber composite. The tensile strength of silicone rubber with glass fiber filler increased by 26% compared to silicone without filler [50]. The silicone rubber with glass fiber hardness strength also shows slightly larger than the wollastonite filler. Recently, Brian Swanton from Dow Corning Corporation had introduced a new company product of RTV silicone rubber that was designed to assist in providing more reliability, added cost-efficiency, and reduced performance risks in subsea environments. The new RTV silicone rubber designed as insulation pipeline coating in saltwater production shows an excellent physical properties after curing. [51][52]. In aerospace, silicone rubbers also have contributed as addition-type silicone rubber (ASR) that prepared by vinyl-terminated polydimethylsiloxane (VPDMS) and polymethylhydrosiloxane (PMHS) [6].

#### 2.4. Adhesion between cords or plies -polymer

Adhesive was used to bond two different structures together to form a composite and the forces or mechanism created by chemical bond results on good properties between adhesive and substrate was called as adhesion [53]. The destructive testing to identify the adhesion can be determined by shear, torsion, and peel test. The adhesion to rubber compound also can be determine by pulled out the cords from the rubber using tensile testing machine with the speed of 100mm/min [22]. Picard et al. [54] have compiled information regarding the chemical adhesion of silicone elastomers on primed metal surfaces. The review paper compiles the three mechanism on promoting a strong adhesion namely wetting, priming of the metal substrate and elastomer, and mechanical behavior of the final composite part[54]. Wang et al. [55] had determined the peel strength of different substrate surface to determine the adhesion with liquid silicone rubber. The different substrates used in their research were aluminum, glass, epoxy resin, polypropylene that being treated before coated with liquid silicone rubber and Pt catalyst. Jamshidi et al. [56] reported about the temperature can affect the adhesion between cords and rubber matrix. So, they had measured a wide range of temperatures between 25-170°C of cord-RFL-rubber system and compared with the other adhesion of different cords (N6, N66, and PET) to determine the best vulcanization temperature. Adhesion properties were measured by using three types of aging experiments was performed in Nah et al. [57]. Firstly, thermal aging that prepared in an air oven at 100°C, the second was humidity aging that setup in a humidity chamber (Weiss Technik, model 305B) at temperature 75 °C and 85% relative humidity. Thirdly, salt solution aging, the adhesion specimen were completely immersed in 20wt% NaCl solution at room temperature. After that, the specimens were tested by using a tensile Instron tester at a crosshead speed of 100 mm/min at room temperature in order to determine the maximum force exerted. The result analyzed by ranked a bare steel cord as 0%, and a fully covered cord as 100% [57] [58]. The effectiveness of silane as a primer towards silicone rubber is characterized accordingly to the type of inorganic substrate consideration in Fig.1 and their significance on mechanical and interfacial adhesion was discussed by George et al. [59].

<b>Inorganic Substrates</b>	
Silica	} Excellent adhesion
Quartz	
Glass	
Aluminium (AlO(OH))	
Alumino-silicates (e.g. clays)	
Silicon	
Copper	} Good Adhesion
Tin (SnO)	
Talc	
Inorganic Oxides (e.g. TiO <sub>2</sub> )	
Steel, Iron	
Asbestos	
Nickel	
Zinc	} Slight Adhesion
Lead	
Marble, Chalk (CaCO <sub>3</sub> )	
Gypsum	
Barytes	} Poor Adhesion
Graphite	
Carbon Black	

**Figure 1.** Effectiveness of silane adhesion according to the type of inorganic substrate [54].

### 3. Summary

The processing preparation for cords and plies reinforcement depends on type of rubber base whether in solid or liquid form. The substrate treatment preparation also can be varied in order to have a suitable primer formulation. In order to determine the suitable process preparation, the results will be shown in characterization of mechanical and physical properties. Not all cords and plies materials give a good adhesion to its rubber base as they also can results in poor adhesion because of some functional group that can inhibit the curing. Primer such as silane or cords and plies treatment can improve the crosslinking between silicone rubber and reinforcement material. The high crosslinking will in turn contribute to better adhesion.

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### Acknowledgement

The authors gratefully acknowledge the financial support received from Education Ministry of Malaysia through Research Acculturation Grant Scheme (RAGS) (RAGS/1/2014/TK04/UITM//8), Research Management Centre (RMC), Faculty of Chemical Engineering and Universiti Teknologi MARA, Selangor, Malaysia.