

INVESTIGATION OF THE FACTORS AFFECTING THE STRENGTH OF A METAL-RUBBER INTERFACE JOINED BY VULCANIZATION: A REVIEW

PREGLED OPRAVLJENIH RAZISKAV, KI OBRAVNAVAJO FAKTORJE KI VPLIVAJO NA KOHEZIJO MEJNE PLOSKVE Z VULKANIZACIJO SPOJENE GUME IN KOVINE

Ramazan Cagri Kutlubay^{1*}, Tezcan Sekercioglu²

¹Faculty of Technology, Pamukkale University, Department of Biomedical Engineering, 20160 Denizli, Turkey

²Faculty of Engineering, Pamukkale University, Department of Mechanical Engineering, 20160 Denizli, Turkey

Prejem rokopisa – received: 2024-05-09; sprejem za objavo – accepted for publication: 2024-09-12

doi:10.17222/mit.2024.1183

Metal-rubber parts are used in many sectors because of their ability to combine the advantages of both rubber and metals. Thanks to the advances acquired as a result of the studies carried out by researchers and industries, the usage area of metal-rubber parts expands day by day. The focus of researchers in this field continues to be on achieving effective joints, improving their durability, and ensuring their preservation, as these composites find wide-ranging use. In particular, the positive effects of newly developed surface treatments and adhesive materials on bond strengths have been observed in recent years. Within the scope of this study, the metal-rubber bonding mechanism, vulcanization, bonding during/after vulcanization, some standards related to rubber, bond failures, and their causes are investigated. This review focuses on studies addressing the factors influencing the interfacial strength of metal-rubber bonds joined by vulcanization. Additionally, it provides information on studies and their findings up to date regarding the effects of vulcanization parameters, corrosive environments, components in the bonding process, and different substrates on the bond strength.

Keywords: rubber-to-metal bonding, vulcanization, surface treatment, rubber-metal interface

Izdelki iz medsebojno spojene gume in kovine se uporabljajo na mnogih področjih zaradi sposobnosti kombiniranja lastnosti obeh materialov. Zahvaljujoč naprednim znanstvenim in industrijskim raziskavam na tem področju se izdelki na osnovi medsebojno spojene gume in kovine danes vse več uporabljajo. Raziskovalci so v svojih raziskavah osredotočeni predvsem na problem, kako doseči čim bolj učinkovit spoj guma-kovina, izboljšanje njegove dobe trajanja in ohranitve, saj se te vrste kompoziti uporabljajo na različnih področjih. Razvoj novih metod površinske obdelave in novih lepil ima pozitiven učinek na trdnost spojev te vrste. V tem članku avtorja opisujeta študijo v kateri obravnavata literaturni pregled raziskav s področja mehanizmov spajanja, vulkanizacijo, spajanje med in po vulkanizaciji. Obravnavata tudi nekaj standardov, ki se nanašajo na gumo ter odpovedi oziroma poškodbe spojev in vzrokov zanje. V tem literaturnem pregledu sta se avtorja osredotočila predvsem na faktorje, ki vplivajo na kohezijo (trdnost) spoja guma-kovina izdelanega s postopkom vulkanizacije. Dodatno avtorja predstavljata študije in najnovejše informacije, ki se nanašajo na parametre vulkanizacije, korozijska okolja, komponente v procesu spajanja in različne dodatke, ki vplivajo na trdnost spoja.

Ključne besede: spajanje gume in kovine, vulkanizacija, površinska obdelava, mejna ploskev guma-kovina

1 INTRODUCTION

The latex required for rubber production is derived from the *Hevea* genus tree, and although South American natives were familiar with this material before Columbus, it was first reported by Columbus in 1495. Priestly, who discovered that pencil marks could be erased with latex, named this product rubber. The recognition of rubber broadened with Macintosh's (1823) production of waterproof garments using rubber, utilized in the American Civil War, and further attention came with Hancock and Goodyear's (1839) discovery of the vulcanization method. In the 1880s, John Dunlop achieved great success by using it as the basic material for pneumatic tires.^{1,2}

Rubber finds applications across diverse sectors, including agriculture, aerospace, medical, and automotive. Rubber can be obtained in various degrees of hardness to offer different characteristics, and it can be reinforced by incorporating steel wire, fabric, and textile cords to enhance its strength.³ The use of modern synthetic fibers as reinforcement materials provides advantages such as flexibility, cost-effectiveness, corrosion resistance, and structural properties similar to steel.⁴ A wide variety of rubber types can be found in the market, including but not limited to, natural rubber (NR), styrene-butadiene copolymer (SBR), solution polymerized styrene-butadiene rubber (SSBR), polyisobutylene (IIR), polydimethylsiloxane (PDMS), and hydrogenated nitrile rubber (NBR).^{3,5}

Rubbers, while varying according to their type, generally propose advantages such as light weight,⁶ flexibility, elasticity,⁷ very low glass-transition temperatures,

*Corresponding author's e-mail:
rckutlubay@pau.edu.tr (Ramazan Cagri Kutlubay)

ability to return to their initial dimensions upon release of an applied stress,⁸ resistance to abrasion, impact resistance, efficient heat dispersion,⁹ providing corrosion resistance,¹⁰ and high damping capacity.¹¹ The disadvantages of rubber types can be listed as, in natural rubbers; weak air permeability, weak solvent, and oil resistance,¹² allergenicity due to its proteins,¹³ poor crack-initiation resistance,¹⁴ in EPDM rubbers; resistance to oils, susceptibility to burning,¹⁵ low adhesion of raw blends, low thermal stability,¹⁶ weak solvent resistance,¹⁷ potential colonization of microorganisms in prostheses made of silicone rubber,¹⁸ in SBR rubbers; slow curing kinetics, low mechanical strength,¹⁹ high flammability,²⁰ weak oxidation and ozone resistance,²¹ in NBR rubbers; low tensile strength,¹⁹ weak ozone resistance, weak electrical insulation property.²² Attempts are made to overcome the disadvantages observed in rubbers using additives to recipes, vulcanization methods, modification, or blending with different polymers.^{12,14,15,19}

The vulcanization process, which occupies a significant place in the rubber industry, improves the mechanical properties of rubber materials by facilitating cross-linking. Therefore, the parameters of the vulcanization process have an important impact on mechanical properties, and this process has evolved over time.^{23–25} Additionally, the efficiency of the vulcanization process can be increased by additives.^{25,26}

Different rubbers and metals can be bonded to each other using various primers and adhesives through cold bonding (with vulcanized rubber) and hot bonding (with non-vulcanized rubber) techniques. Bonding through the vulcanization method is a form of hot bonding.²⁷ The surface treatment of metals is a crucial step to achieving a quality bonding connection. Prior to the bonding process, oxide layers and contaminants (such as oil and grease) on the metal surface should be removed through physical, chemical, electrochemical, etc., methods or various combinations of these methods. This enhances the surface properties and enables the attainment of high mechanical strength joints.^{27–29} Sandblasting, sandpaper roughening, plasma treatment, sol-gel process, laser treatment, acid etching, and anodization methods are surface treatment techniques applied to different metals.^{28–30}

Within this study, comprehensive literature reviews were conducted, delving into the factors that influence the bonds established via vulcanization between rubbers and metals treated with diverse surface-treatment methodologies. Moreover, included were investigations examining the effects of modifying various vulcanization parameters on the bonding between metal and rubber.

2 RUBBER-METAL ADHESION MECHANISM AND THE IMPORTANCE OF SURFACE TREATMENTS FOR ADHESION

An adhesive enables the joining of multiple materials, and adhesion and cohesion events occur during the

bonding process. Cohesion denotes the internal bonding within the adhesive substance, while adhesion describes the bonding interaction between the adhesive and the adherend material.³¹ Numerous theories exist on the mechanisms of adhesion, synergistically contributing to the adhesive bonding process. These theories are categorized based on their operative scale: atomic scale, characterized by chemical bonding; molecular scale, encompassing diffusion, wettability, weak boundary layer, and acid-base interactions; microscopic scale, involving mechanical interlocking; and macroscopic scale, which encompasses electrostatic interactions.³²

When bonding rubber and metal, two approaches are commonly employed: using only adhesive, which must react with both the metal and the rubber, or employing both adhesive and primer simultaneously.^{33,34} A primer is frequently used for purposes of protecting the applied surface, promoting adhesion, facilitating wetting of the applied surface, and resisting corrosion, while adhesive provides adhesion of rubber and metal materials by physical and/or chemical bonds.^{33,35,36} Additionally, primers are utilized to augment the bond strength.³⁶ Nevertheless, in certain instances, the application of primer may result in weaker bond formation. One study reports that in composites made by bonding nylon 6,6 and rubber, the absence of a primer improves the bond strength.³⁵

In products made with rubber and metal, it is often preferred to bond rubber and pre-treated metal by vulcanization.³⁷ The formulations of primers and adhesives utilized for creating rubber-metal composite materials typically consist of proprietary mixtures of various substances.³⁴ However, there is a lack of comprehensive understanding regarding the effect of the variables in the composite-production process and the components in the adhesive on the bond to be formed.³⁸ The selection of adhesive is typically determined through an experimental investigation, and it should possess the capability to withstand temperatures similar to those encountered during the vulcanization process.^{38,39}

Emphasizing the importance of the filler content in rubber, one study highlights the significance of a high filler content, identifying carbon black as the best filler.⁴⁰ Adhesives contain polymeric materials, often halogenated, which facilitate the wetting on metal surfaces. These materials contribute to adhesive bond maintenance while remaining compatible with the primer and rubber. Throughout the rubber-metal bonding process, interactions occur among the rubber, primer, and adhesive materials, both internally and with the materials they encounter. Primers typically incorporate organic resins, forming robust chemical bonds through chemisorption with metals and facilitating surface adhesion.³⁴ Adsorption and interdiffusion mechanisms operate between the adhesive and the primer.³⁹ The curative in the adhesive establishes chemical bonds with both the primer and the rubber. Also, additional cross-links form between the

rubber and the adhesive, facilitated by sulfur in the rubber.³⁴

There is also an alternative joining technique, which saw growing use in the 1970s and early 1980s for bonding metal and vulcanized rubber, known as post-vulcanization.^{34,39} In this approach, the adhesive application occurs directly onto the metal surface according to one source,³⁴ while another study suggests that adhesive application may be onto either the primed metal or the rubber.³⁹ Despite its benefits, such as reduced mold costs and the ability to perform the process at lower temperatures, this method presents drawbacks, including additional production steps and a limited rubber-adhesive interface.³⁴

In an investigation concerning metals treated via shot blasting, two bonding methodologies were employed: one conducted during vulcanization and the other post-vulcanization. The research revealed that bonding during vulcanization yielded superior adhesion on rough metal surfaces. This superiority stems from the more effective filling of voids on metal surfaces by rubber during the vulcanization process.⁴¹

In the formation of composite materials through bonding, the strength of the rubber plays a pivotal role. Moreover, the rubber utilized must meet specific criteria, including high tensile strength, good heat resistance, be free from grit, have compatibility with the intended adhesive, filler content, and compatibility with softening or processing oils.^{40,42} Among general-purpose rubbers, nitrile rubber (NBR) is identified as the most readily bondable, whereas isobutylene-isoprene rubber (IIR) is the most difficult.³⁴ Effective rubber adhesion, characterized by a high bondability index, diminishes the necessity for employing a two-coat bonding system.⁴⁰ Additionally, curing rubber without sulfur or with peroxide complicates the bonding process.³⁴

Surface cleaning is required for the substrate materials to be bonded. Corrosion-preventive oils, silicone sub-

stances, oils used in the manufacturing process, mold-release agents, atmospheric contaminants, oxide and scale layers formed on metal surfaces, etc., both organic and inorganic layers, should be removed from the surface.^{34,43} In the process of bonding the rubber, the surface energy of the counter material should be increased, and the weak oxide layer on the metal surface should be removed. This facilitates the creation of an active surface, allowing the liquid adhesive to spread more effectively. Furthermore, because the primer interacts with the oxides present on the metal surface, the removal of the weak oxide layer prevents damage to the bonds being formed.^{34,36} The methods used for the surface treatment of metals are fundamentally grouped into mechanical and chemical methods. For mechanical methods, degreasing and blasting, and for chemical methods, phosphate coating, galvanizing, and anodizing can be given as examples.³⁴ The critical aspect lies in selecting the appropriate method tailored to the specific metal being utilized.

3 VULCANIZATION

Latex-derived natural rubber initially exhibits poor properties such as strength and elasticity, as well as being sticky and soft.⁴⁴ It partially returns to its former dimensions when the applied force is removed and has a thermoplastic structure.^{44,45} During the vulcanization process, uncrosslinked chains are crosslinked, leading to the formation of a three-dimensional network structure. This transformation represents a pivotal stage in acquiring elastomeric characteristics, as it alters the initial rubber structure and enhances its physical attributes. Furthermore, these modified properties exhibit applicability across a broader temperature range.^{44,46,47} Increasing the crosslink density results in the augmentation of certain properties such as elastic recovery, hardness, stiffness, and resilience, while others, including hysteresis, permanent set, heat build-up, solvent swelling, and creep, dem-

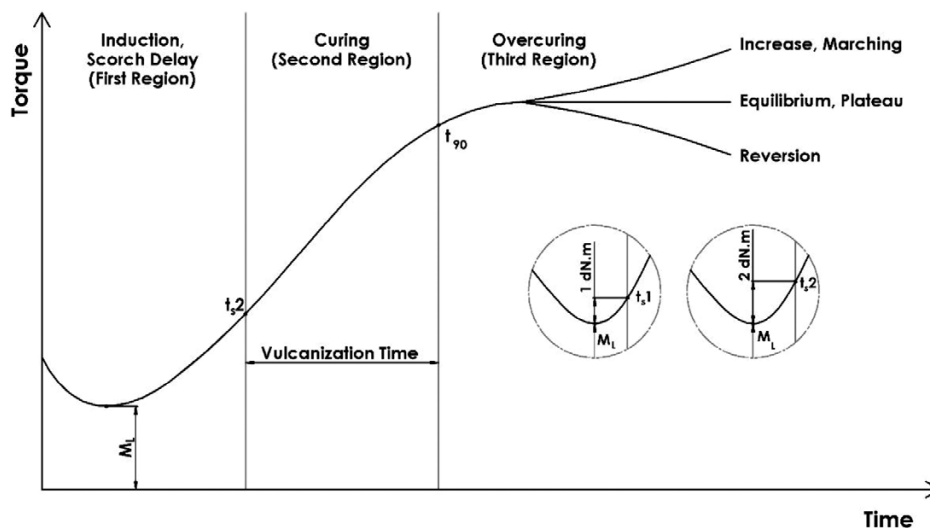


Figure 1: Typical vulcanization curve

onstrate a decline. Additionally, some properties exhibit an initial increment followed by a subsequent decrease, such as fatigue life, toughness, tensile strength, and tear strength.^{48,49} When cross-linking occurs within the range of 2–3 %, it results in the formation of a non-brittle and soft rubber, whereas cross-linking between 25–35 % yields a harder rubber.⁴⁵ This cross-linking process is typically facilitated using sulfur and stands as one of the most prevalent techniques in contemporary rubber manufacturing.^{44,50} Various additives are incorporated to achieve the desired rubber properties.⁴⁴ Additionally, the employment of accelerators in sulfur vulcanization confers a notable advantage by reducing the vulcanization time from hours to minutes.⁴⁷

The process steps are listed below according to the sequence of events and the different reactions occurring in the third region.^{11,51} A typical curve indicating these steps and highlighting some key points is presented in **Figure 1**.

Process steps:

1. Scorch delay, induction
2. Curing
3. Overcure
 - a) Increase, Marching
 - b) Equilibrium, Plateau
 - c) Reversion

The scorch times are referred to as t_{s1} and t_{s2} , respectively, corresponding to the time it takes to reach above 1 dN·m and 2 dN·m of minimum torque (**Figure 1**).⁵² The initial region of the curing process is known as the induction region, during which the rubber is transferred from the extruder to the mold for shaping. In this region, the rubber is in a fluid state, and the chemical reactions between the rubber and additives occur at a slow rate. The region’s duration should be at specific intervals to prevent premature vulcanization, which can cause surface roughness and shape distortion.^{11,44,53} The crucial point in the curing region where the network structures are formed is the optimum curing time, expressed as t_{90} , which determines the residence time of the vulcanized rubber in the curing line and thus ensures that the rubber has optimum properties. If the dough leaves the curing line before the optimum time, it does not achieve the desired shape and physical properties, whereas exceeding this time results in a hard and brittle rubber. Due to the reasons mentioned, it is desired that the rubber cures in a time equivalent to 90 % of the time required to obtain maximum torque.^{11,53} Although this time provides maximum tensile strength for certain rubber compositions, its applicability is not universal across all rubber types.⁵² In the third region, depending on the rubber, the materials used, and the process parameters, the torque value may increase due to the formation of additional cross-links,

Table 1: Standards related to rubber

Standard Number	Standard Name	Classification
ASTM D1566-21a	Standard Terminology Relating to Rubber	Terminology
ASTM D6085-97	Standard Practice for Sampling in Rubber Testing Terminology and Basic Concepts	
ISO 5893	Rubber And Plastics Test Equipment – Tensile, Flexural and Compression (Constant Rate of Traverse) – Specification	Test Equipment
ASTM E4-21	Standard Practices for Force Calibration and Verification of Testing Machines	Calibration
ISO 6502-1	Rubber – Measurement of Vulcanization Characteristics Using Curemeters – Part 1: Introduction	Vulcanization (Introduction)
ISO 6502-2	Rubber – Measurement of Vulcanization Characteristics Using Curemeters – Part 2: Oscillating Disc Curemeter	
ASTM D2084-19a	Standard Test Method for Rubber Property—Vulcanization Using Oscillating Disk Cure Meter	Vulcanization (Oscillating Disc Curemeter)
ISO 6502-3	Rubber – Measurement of Vulcanization Characteristics Using Curemeters – Part 3: Rotorless Curemeter	
ASTM D5289-19a	Standard Test Method for Rubber Property Vulcanization Using Rotorless Cure Meters	Vulcanization (Rotorless Curemeter)
ASTM D413-98	Standard Test Methods for Rubber Property Adhesion to Flexible Substrate	
ISO 36	Rubber, Vulcanized or Thermoplastic – Determination of Adhesion to Textile Fabrics	Determination of Bond Strength (Flexible Materials)
ASTM D429-14	Standard Test Methods for Rubber Property Adhesion to Rigid Substrates	
ISO 813	Rubber, Vulcanized or Thermoplastic – Determination of Adhesion to A Rigid Substrate – 90-Degree Peel Method	Determination of Bond Strength (Rigid Materials)
ISO 814	Rubber, Vulcanized or Thermoplastic – Determination of Adhesion to Metal – Two-Plate Method	
ISO 5600	Rubber – Determination of Adhesion to Rigid Materials Using Conical Shaped Parts	
ISO 1827	Rubber, Vulcanized or Thermoplastic – Determination of Shear Modulus and Adhesion to Rigid Plates – Quadruple – Shear Methods	
ISO 5603	Rubber, Vulcanized – Determination of Adhesion to Wire Cord	
ISO 6133	Rubber And Plastics – Analysis of Multi-Peak Traces Obtained in Determinations of Tear Strength and Adhesion Strength	Analysis

decrease due to the disintegration of the networks, or remain stable.¹¹

Torque-time curves, employed to assess vulcanization properties, are generated via testing conducted at a designated temperature utilizing rheometers. While oscillating-disc, reciprocating-paddle, and rotorless rheometers are frequently utilized, the application of reciprocating-paddle rheometers is currently less favored.⁵⁴ Although the determination of vulcanization properties falls beyond the purview of this study, interested readers can consult the vulcanization-related standards referenced in Section 4.

4 STANDARDS RELATED TO RUBBER

Numerous international standards have been developed by various institutions concerning rubber, including product properties, raw-material specifications, manufacturing procedures, product-testing protocols, and more. A comprehensive literature review unveiled a multitude of standards related to these subjects. **Table 1** illustrates the standards examined in this study that remain currently applicable.

When we examine the standards used in terminology first, we encounter the ASTM D1566-21a:2021⁵⁵ and ASTM D6085-97:2022⁵⁶ standards. ASTM D1566-21a:2021⁵⁵ includes terminology related to rubber, while ASTM D6085-97:2022⁵⁶ includes terminology related to testing and sampling.

To perform R&D studies, it is imperative to conduct tests of rubber specimens or bonding processes. The ISO 5893:2019⁵⁷ standard provides comprehensive guidance about the design specifications, force-measurement systems, accuracy, precision, and deviations associated with the constant rate of traverse tensile testing systems utilized for these evaluations. Moreover, ensuring the accuracy of data obtained from such tests is pivotal for research and development activities. Consequently, calibration of force measurement systems within the testing apparatus is deemed necessary. The ASTM E4-21:2021⁵⁸ standard includes information concerning calibration and verification procedures, outlining three distinct methods for verification. These methods can be utilized individually or in combination to verify the efficacy of test machines.

Information is required during the vulcanization process of vulcanizable rubbers, acquired through torque-

time curves derived from conducted tests. These curves are generated using curemeters. The ISO 6502-1:2018⁵⁴ standard elucidates the insights attainable via curemeters regarding the vulcanization process. It offers clarification concerning the typical configuration of a vulcanization curve, its acquisition methodology, termination patterns of the curves, interpretations of the data extractable from the curves, mathematical computations associated with this data, and fundamental operational principles governing curemeters. Moreover, the standard addresses curemeters, which are extensively utilized, with oscillating disk and rotorless curemeters retaining their popularity. These curemeters constitute the second and third sections of the ISO 6502 standard. ISO 6502-2:2018⁵⁹ and ASTM D2084-19a:2019⁵² standards offer insights into oscillating-disk curing meters. Additionally, the ASTM D2084-19a:2019⁵² standard defines four distinct configurations for obtaining the curves. ISO 6502-3:2023⁶⁰ and ASTM D5289-19a:2019⁶¹ stand as standards for rotorless curing meters, which conduct torque measurement within cavities either entirely enclosed or non-enclosed. As per ASTM D5289-19a:2019⁶¹ and ISO 6502-1:2018⁵⁴ standards, rotorless curing systems achieve superior temperature distribution compared to oscillating disk curing systems by eliminating the unheated rotor from the setup.

Various standards exist for measuring the bond strength between rubber and the material to be bonded, facilitating an evaluation of the adhesion properties across different rubber formulations, adhesive types, production parameters (e.g., temperature, duration), and surface treatments (e.g., acid etching, phosphating, sandblasting). One such standard is ASTM D413-98:2017,⁶² which assesses bond strength between flexible materials (e.g., fabric, wire, sheet metal) and rubber, providing methods applicable to planar or smooth circular surfaces.

ASTM D429-14:2023⁶³ provides guidelines for evaluating the bond strength between rigid materials, predominantly metals, and the rubber bonded to them. This standard defines eight distinct measurement methodologies, including approaches like between two parallel metals measurement, 90° stripping, conical specimen assessment, and post-vulcanization bond adhesion testing. Within this standard, **Figure 2** shows surface images of failed specimens following testing conducted in accordance with Method C of ASTM D429-14:2023.



Figure 2: Surface images of the specimens tested by Method C of ASTM D429-14 standard

The ISO 813:2019⁶⁴ standard is utilized to determine the bond strength between a rigid plate and rubber using the 90° peeling method. The standard specifically notes that this method is not suitable for rubbers with a hardness greater than 85 IRHD. A measurement according to ISO 814:2017⁶⁵ involves using two parallel metal plates with rubber bonded between them. The force is applied perpendicular to the bond surface to measure the bond strength. The test is terminated when the specimen fails. To prepare samples according to the ISO 5600:2024⁶⁶ standard measurement procedures, two rigid materials with conical shapes, whose dimensions are provided in the standard, are used. After the materials are positioned facing each other with their ends on the same axis and at the distance specified in the standard, they are bonded with rubber using a suitable adhesive system.

ISO 1827:2022⁶⁷ is one of the standards also used to measure the bond strength. The four rigid or metal parallel plates are used for the samples. Tests are conducted by adhering rubber to metal plates. This standard is also used to determine the shear modulus. In assessing adhesion between wire cord and rubber, ISO 5603:2024⁶⁸ outlines methods applicable to where the exterior surface of the rubber is unreinforced or is reinforced. Specimens are prepared via vulcanization, followed by testing involving the pulling of the cord embedded within the rubber.

An accurate evaluation of the experimental data and the corresponding graphical representations is crucial. Force-time graphs, derived from tear and bond strength measurements may exhibit multiple peaks, introducing complexity to the analysis. ISO 6133:2015⁶⁹ offers guidance on five distinct methods for strength calculation, accounting for the number and shape of these peaks, aiming to enhance consistency and comparability. An example force-strain graph with multiple peaks obtained from an experiment to measure adhesion strength is shown in **Figure 3**.

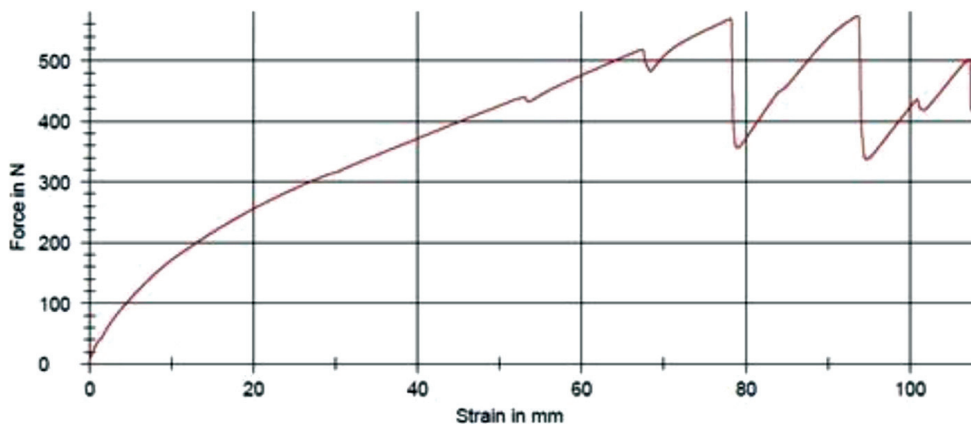


Figure 3: Force-strain graph with multiple peaks

5 FAILURE TERMINOLOGY

Many rubber composites are formed by bonding metal and rubber. The bonding process involves the use of primer and adhesive. The primer is often used in the bonding process to ensure corrosion resistance, while the adhesive bonds the rubber and the metal materials.^{35,70} The vulcanization method is commonly preferred for this bonding process.³⁷

These products have a wide range of applications and operate in various environments and under different stress conditions. Therefore, many factors can cause damage to metal and rubber structures, including overloading, corrosion, and vibration.^{71–73} Testing the reliability of the products is essential due to their impact on product performance and the potential hazards to employee safety.^{72,73} In most methods, the failure of prepared specimens is used to calculate the tensile force generated during the test.⁷⁴ Although peel testing is commonly used, other tests, such as shear (pure, simple), compression, etc., are also conducted.^{37,75} Static tests can be used to estimate the service life of products. However, these predictions often do not align with the service life of the products as they operate most of the time under dynamic loads.⁷⁶

It is necessary to analyze the failures and their causes using analysis methods that have different advantages over each other. The Scanning Electron Microscope (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), Electrochemical Impedance Spectroscopy (EIS), Secondary-Ion Mass Spectrometry (SIMS (Dynamic SIMS and Static SIMS)), Ion Scattering Spectroscopy (ISS), Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Nuclear Magnetic Resonance (NMR), and X-ray Photoelectron Spectroscopy (XPS) are among these analysis methods.^{71,77–79} These methods allow a detailed assessment of failure and can be used alone or in combination.⁷¹

The rubber composite may fail either individually or in combination, either within the rubber or at the interfaces. The ASTM D429-14:2023⁶³ standard defines these

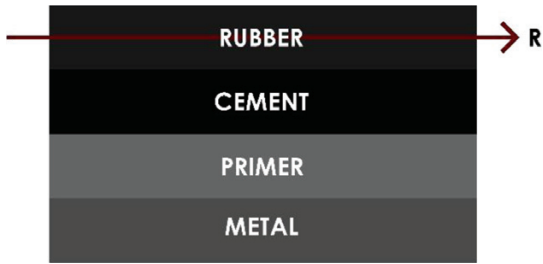


Figure 4: Rubber failure



Figure 5: Rubber-Cover Cement interface failure

failures. Figures 4 to 8 shows the failure patterns based on the failure location.

- 1-Failure of the rubber is indicated by R (Figure 4).
- 2-Failure of the rubber-cover cement interface is indicated by RC (Figure 5).
- 3-Failure of the cover cement-primer interface is indicated by CP (Figure 6).
- 4-Failure of the primer-metal interface is indicated by M or CM (Figure 7).

Although the relevant standard does not specify a separate item for it, it is stated that in the case of multiple failures, a definition can be made based on the percentages of failure. By the example from the standard, Figure 8 shows an example where 50 % of the failure is to the rubber and 50 % to the rubber-cover cement inter-

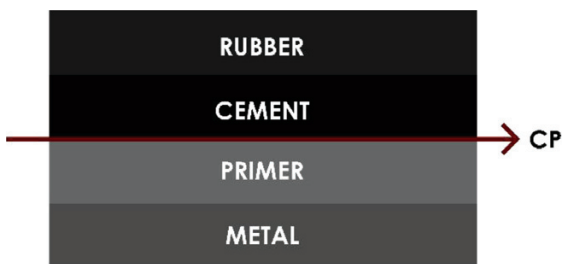


Figure 6: Cover Cement-Primer interface failure

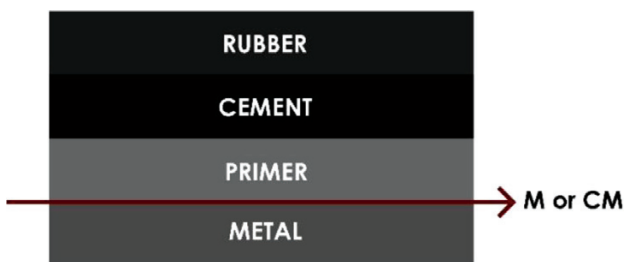


Figure 7: Primer-Metal interface failure

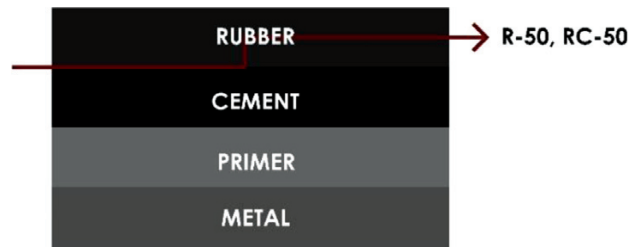


Figure 8: Multiple failures

face. In this case, all the failure is written according to the rules in the relevant terminology. The failure in the given figure is indicated as R-50, RC-50.

6 REVIEW OF SOME EXPERIMENTAL STUDIES

Ting⁸⁰ bonded neoprene rubber and steel (AISI 4130) using seven different adhesives and examined the samples using two different testing methods. Moreover, the samples were subjected to different aging conditions. Following the conducted tests, a notable finding was the adequacy of most employed adhesives concerning the dry bond strength. Furthermore, it was observed that thermal aging exhibited negligible impact, while the bond strength exhibited a decline when subjected to stress in a saltwater environment. In addition, it was determined that degradation levels escalated in correlation with elevated oxygen concentrations within the water medium.

Björk and Stenberg⁸¹ employed three distinct techniques, i.e., grit-blasting, centrifugal blasting, and detergent washing, to treat the surface of soft carbon steel. Subsequently, experimental samples were fabricated by bonding the treated steel with natural rubber using Chemosil 211+231. Evaluation of the resulting bonds was carried out via peel tests conducted under varying procedures and temperatures in an aqueous environment. The conducted analyses have conclusively identified grit-blasting as the most efficacious surface treatment method.

Östman and Persson⁸² indicated that the conventional peel test lacked adequacy and thus explored the characteristics of rubber-metal bonds through a novel approach termed peel-creep. Their investigation involved the utilization of natural rubber and steel materials to fabricate specimens subjected to accelerated aging. The surface treatment of the metals was executed via two distinct methods, i.e., air-blast tumbling, and grit-blasting. The study outlined an augmentation in effective surface adhesion facilitated by the grit-blasting process, attributable to the heightened particle velocity. Moreover, a longitudinal comparison indicated a sustained enhancement in adhesive properties relative to the alternative method. Furthermore, the presence of residual dust was noted to detrimentally impact the bond longevity, with the

grit-blasting method being identified as a superior cleaner owing to its elevated air velocity.

Aktepe⁸³ investigated the bonding between NBR rubber and steel material, employing the vulcanization method. Three distinct recipes were employed in the preparation of NBR rubber, while Chemosil 211 and Chemosil 220 were selected for rubber-to-steel bonding purposes. The experimental setup involved the creation of eight sample groups, distinguished by the utilization or non-utilization of the shot-blasting process (incorporating hard casting residues) or adhesive, as well as the adoption of different rubber formulations. Notably, in instances where adhesive application was omitted, the absence of adhesion was observed. Moreover, analysis of the peel test outcomes revealed a notable enhancement in bond strength for samples subjected to shot blasting.

Boulos and Petschel⁸⁴ conducted an analysis of samples employing various methodologies. These samples were derived from the bonding of natural rubber to metals coated with four distinct types of phosphate coatings, i.e., heavy zinc phosphates, calcium-modified zinc phosphates, polycrystalline zinc phosphates, and non-heavy metal (amorphous) phosphates, utilizing either solvent-based or water-based adhesives. Their investigation revealed that polycrystalline and amorphous transformation coatings contributed to enhanced adhesion, whereas coatings characterized by large crystal formations exhibited inferior performance, attributed to crystal damage upon impact exposure. Additionally, in the study where appropriate coating weights were specified, it was concluded that a polycrystalline phosphate coating should be prioritized for both adhesion improvement and corrosion protection.

Cook et al.⁸⁵ utilized the vulcanization method to bond steel materials (B.S. 6323, pt. 6 CEW 2BK) treated with two distinct phosphating techniques and an acid-etching method to natural rubber (SMR L). Adhesives Chemlok 205 and Chemlok 220 were employed in the process. The study revealed that respectively Phosphate-2 > Acid Etching > Phosphate-1 regarding peel energy. Notably, it was asserted that surface roughness does not play a crucial role in achieving optimal rubber-steel adhesion. Additionally, the research highlighted that the formation of crystals in the Phosphate-2 method, particularly at low coating weights, resulted in rubber damage by redistributing stresses away from the surface.

Ansarifar et al.⁸⁶ conducted investigations by bonding natural rubber (SMRL) to different materials such as steel (BS 6323 CEW 2 BK), nylon 6,6 (Dupont's Zytel 70G30 HSL), and aluminum (LM6) using Megum 3276 and Megum 101. The steel and certain aluminum materials were grit blasted with 30/40 brown alumina grit, while nylon 6,6 and the remaining aluminum materials were not grit blasted. The empirical investigations revealed the feasibility of employing water-based substances for cleansing purposes. Furthermore, varying degrees of surface roughness demonstrated minimal to no

impact on the peel energy. Additionally, substituting steel with nylon 6,6 and aluminum was deemed viable. Notably, the constant load-peel test emerged as superior in yielding precise outcomes compared to the constant rate peel test, attributed to its capacity for precise assessment of the crack-propagation rates.

Jeon and Seo⁸⁷ investigated the effect of curing temperature on the adhesion between brass-plated steel cord and rubber (natural+butadiene rubber). T bonding specimens were prepared with curing times of $t_{90}+5$ min after calculating t_{90} times every 15 °C between 130 °C and 190 °C. Furthermore, the samples underwent thermal and humidity aging processes for (5, 10, and 15) d. The research revealed a consistent decrease in pull-out force with escalating curing temperatures across both unaged and thermally aged specimens. Additionally, a noteworthy observation was made regarding the elevated rubber coverage in thermally aged samples, particularly outside of 190 °C. Furthermore, the analyses of specimens subjected to humidity aging revealed a pattern where the pull-out force exhibited an initial increase up to 160 °C followed by a subsequent decline, and a low coverage occurred in samples cured at 190 °C.

Jeon and Seo⁸⁸ examined the impact of curing time on the adhesion between natural rubber and brass-plated steel cord. At a temperature of 160 °C, T adhesive specimens were prepared with curing times of 0.25, 0.50, 1, 2, and 4-times the t_{90} duration. Furthermore, the samples underwent thermal and humidity aging processes for (5, 10, and 15) d. An increase in the pull-out force was noted as the curing time extended up to the t_{90} duration in both unaged and thermally aged specimens, followed by a subsequent decrease. Additionally, it was noted that the rubber coverage exhibited high levels in both the optimally and over-cured unaged samples, as well as in the under-cured thermally aged samples. Throughout humidity aging, the pull-out force increased to 0.5 times the t_{90} duration, followed by a subsequent decline, and the diminishing of rubber coverage with increasing duration.

Ansarifar et al.³⁵ conducted a study investigating the influence of primer application on the bond strength between rubber (SMRL) and nylon 6,6 (Dupont's Zytel 70G30 HSL). Two bonding systems, MEGUM 3276+MEGUM 101 or MEGUM W23501+MEGUM 23126, were employed in the bonding procedures. The specimens were divided into four groups based on whether they were primed or unprimed. Alkaline solution degreasing was employed, followed by the vulcanization method for bonding. Results from the constant-load peel test in solvent-based systems indicated a notable increase in the bond strength in the unprimed group. Conversely, in waterborne systems, a marginal enhancement in bond strength was observed in the unprimed group under either constant load or constant-rate peel tests. Comparative analysis of the unprimed groups revealed nearly identical strengths between the two systems, also sug-

gesting that primer application did not confer any discernible benefits.

Jeon and Seo⁸⁹ investigated the impact of curing levels on the adhesion between natural rubber and brass-plated steel cord. Five types of T adhesive specimens were prepared, including under-cured (130 °C for 20 min and 150 °C for 5 min), optimally cured (150 °C for 20 min), and over-cured (150 °C for 80 min and 170 °C for 20 min). The samples underwent humidity aging for 15 d. As a result of the tests, the highest pull-out force was obtained in the optimum curing condition in unaged and aged samples. In the unaged specimens, a low level of rubber coverage was observed in the case of under curing, whereas this ratio increased under over curing conditions. With aging, an increase in rubber coverage was observed in the case of under curing, along with an increase in pull-out force. Additionally, it was found that pull-out force decreased under over-curing conditions while the rubber coverage remained constant.

Durmuş et al.⁴¹ investigated the bond strength between the 7132-grade sheet material and EPDM rubber. The surface of the sheet materials underwent treatment via shot blasting using S-330 steel balls under varying durations. Bonding procedures were conducted through two methods: during vulcanization and post-vulcanization. Chemosil adhesives (211 and 411) were employed during vulcanization, whereas Rite-Lok EC-5 and Loctite 480 adhesives were utilized post-vulcanization. Tensile testing revealed that the highest bond strength was attained in samples subjected to 6 minutes of shot blasting during vulcanization and 3 minutes of shot blasting post-vulcanization.

Delattre et al.⁹⁰ investigated samples comprising plasma-polymerized thiophene (PPT_h) coated SAE 1010 steel bonded with synthetic rubber. Additionally, brass materials (63 % Cu and 37 % Zn) were incorporated for comparative analysis. Pre-treatment involved the use of argon, hydrogen, and oxygen gases while cleaning procedures encompassed either alkaline cleaner or acid etching. Following the peeling tests conducted across eight distinct sample groups, it was noted that samples subjected to acid etching and pre-treated with H₂/Ar plasma had the highest adhesion force, closely approaching that of polished brass samples. Optimal adhesion results were achieved at a film thickness of 5 nm, with an observed decrease in adhesion force with increasing film thickness.

Yeoh⁹¹ investigated utilizing finite-element analysis to examine the A, C, and F methods outlined in ASTM D 429. The study defined the radius of the metal material as "a" and the shortest distance between the rubber-bonded metals as "h". The analysis yielded a recommended *h/a* ratio of 2 for the test samples because of facilitated easier comparison as the height increased. Additionally, a novel method was proposed, wherein one of the metals composing the test sample would feature a spherical tip, while the other would possess a conical tip.

Del Vecchio and Ernest Ferro⁹² examined samples prepared using eight different metal surface treatment methods (primed or unprimed (solvent wipe, grit blast, phosphatize) methods and MetalJacket, Phosphatize + MetalJacket methods), three different adhesives (Chemlok 252X, Chemlok 6108, and Chemlok 8560S), and two different rubber components. The samples were prepared following ASTM D429 Method F, and forty-eight different working groups were created. The experimental findings revealed that surfaces treated with grit blasting displayed enhanced strength, contingent upon the adhesive type, whereas solvent wiping rendered them susceptible to corrosive attacks. Moreover, it was established that all MetalJacket combinations attained high levels of environmental resistance.

Zhang et al.⁹³ bonded NBR rubber to anodized LD7 aluminum alloys using Chemlok 250 adhesive. Basically, five distinct working processes were created for the treatments using two different anodization methods (180 g/L sulfuric acid and 100 g/L phosphoric acid). Furthermore, a comparison was conducted between the anodization process and the processes of burnishing and sandblasting. In addition, two different drying methods (vacuum and air drying) were also employed. Based on the findings of the peel-test analysis, it was noted that a phosphoric acid treatment yielded greater strength in comparison to a sulfuric acid treatment. Additionally, it was observed that augmenting film thickness and employing vacuum drying enhanced the strength of the anodized samples. Notably, anodized samples outperformed burnished and sandblasted samples in terms of strength.

Wang et al.⁹⁴ undertook investigations involving the bonding of liquid silicone rubber (LSR) to various substrates (aluminum, polyethylene, polypropylene, glass, and epoxy resin) after surface modification. In the experiments involving aluminum, the aluminum surface underwent pretreatment via corona discharge, followed by immersion in vinyltrimethoxysilane (VMS) solution and platinum (Pt) catalyst solution. Subsequently, the LSR coating was applied, and the curing process was executed. Results from the T peel test indicated optimal parameters for the connection between aluminum and LSR, with a VMS concentration of 5 g/L, immersion time of 5 min, and Pt catalyst concentration of 100 ppm, immersion time of 3 min. Furthermore, it was noted that the peel strength experienced a significant increase because of experiments conducted with other materials.

Latifi et al.⁹⁵ researched plasma surface oxidation treatment for better adhesion of silicone rubber coating to the surface after electropolishing and acid etching processes applied to 316L stainless steel. Investigations on seven different groups of samples revealed that the roughness of the plasma surface oxidation-treated samples was higher than the electropolished + acid-etched samples. On the other hand, it was observed that the roughness remained low compared to the electropolished surfaces. In terms of surface activity, empirical observa-

tions revealed a notable reduction in the water contact angle consequent to the plasma surface oxidation process. Based on the findings of the tensile tests, the oxidized samples had the highest bond strength, whereas the untreated samples had the lowest.

Renner⁹⁶ investigated the relationship between the parameters obtained by treating the surface of cold-formed or cold-rolled steel using EKF-24 corundum with a jet blasting device and using a GN-50 steel shot with a wheel blasting device and bond strength. Chemosil (211 and 411) were used as adhesives. According to the results obtained from both methods in the study, no correlation between rubber-metal bond strength and R_a values was shown, while a correlation between strength and S_v was noted.

Souid et al.⁹⁷ conducted research on specimens prepared by bonding steel and natural rubber by vulcanization method using a primer (Chemosil 211) and adhesive (Chemosil 425) at four different temperatures (120 °C, 140 °C, 150 °C, and 170 °C). The peel tests conducted revealed a noticeable trend wherein heightened vulcanization temperatures correlated with diminished peel resistance, especially evident beyond the threshold of 150 °C, alongside a decrease in peel energy.

Vandenabeele et al.⁹⁸ investigated a plasma treatment to improve the adhesion between filament and rubber by depositing an organo-chlorinated thin film on zinc-plated steel monofilament. Force measurement was performed by removing the embedded monofilament from the rubber patented by Goodyear. Upon comparing the pre-treatments administered to filaments, encompassing untreated, acetone + ethanol cleaning, Ar plasma cleaning, and Ar/O₂ plasma cleaning, it was discerned that Ar/O₂ plasma cleaning exhibited superior efficacy. Additionally, within the context of adhesion strength assessments performed on plasma layers of diverse thicknesses deposited at varying power levels (10 W, 30 W, and 50 W), optimal adhesion was consistently attained at a thickness of 75 nm across all power settings.

Pradhan et al.⁹⁹ examined the influence of electro-cleaning current density on the surface roughness of steel wire and the adhesion strength of the wire to rubber through the utilization of both the COMSOL Multi-Physics program and practical experiments. The findings from the examination suggest a decrease in the R_z value with escalating current density, while R_a demonstrates a comparable trend. In the pull-out experiments, an augmentation in force was noted alongside increasing current density up to 600 A/m², followed by a subsequent decline in force with further increases in density.

Günsoy¹⁰⁰ conducted studies on the adhesion of polyacrylic rubber and EN10130 DC01 steel using six distinct surface treatment groups. The bonding process utilized Chemosil 360 adhesive, and adhesion was attained via the vulcanization method. The results of the peel test suggest that the sandblasting (F54 SiC) + zinc phosphating and shot peening (S60 SS) + zinc phosphating

methods yield the highest strength. It was noted that the strength increased by over two times solely with the phosphating method. Despite the shot-peening and sandblasting procedures yielding comparable levels of surface roughness, the peel test revealed discoloration in the sandblasted specimens, which was attributed to corrosion. Furthermore, deep cracks were formed as a result of the sandblasting technique.

Mihçi¹⁰¹ conducted research on the bonding of EPDM rubber to 5754 aluminum alloy. In experiments involving Chemosil-coated aluminum specimens subjected to varying aging durations and temperatures, it was noted that the highest adhesion levels were attained within the temperature range of up to 150 °C. Based on the results obtained from six experimental groups that differed in terms of coating status, geometric shape, and surface treatments, it was discerned that cold plasma treatment elicited enhancements in surface adhesion properties among coated materials. Assessing the peel test outcomes across ten experimental groups, formed through the combination of diverse coating materials, it was determined that the Chemosil brand coating material showcased the most elevated peel strength. Moreover, it was uncovered that identical coating materials displayed differing peel strengths upon the coating application methodologies employed.

Ahsan et al.¹⁰² investigated the correlation between surface roughness and damping characteristics by conducting analyses utilizing the Obers Beam Method (OBM) subsequent to employing various surface treatments on A6061 aluminum alloys. Specifically, the damping properties at the interface of the rubber bonding were examined. A solvent-based adhesive was utilized for bonding the rubber, involving primer application followed by topcoat adhesive application. Following experiments conducted after roughness measurements of five distinct treated surfaces (namely untreated, sandblasting, blasting+graphene, phosphate anodizing, and graphene), it was established that damping behavior depends on surface roughness, with superior damping characteristics observed in samples subjected to sandblasting and blasting+graphene, which exhibited the highest roughness.

Gong et al.¹⁰³ examined the factors affecting interfacial strength in the bonding of 6063 aluminum alloys with nitrile butadiene rubber (NBR-80A) employing anodization and silane coupling agent (γ -aminopropyltriethoxy). Due to the elevation in the electrolyte temperature employed during the anodization process, the rate of formation of the oxide film was observed to escalate. However, an initial rise followed by a decline in bonding strength was noted. Similarly, it was observed that bonding strength exhibited an initial ascent then, a descent with increasing solution concentration of the coupling agent. Moreover, it has been established that with rising mold temperature, there is an initial increment followed by a decrement in bonding strength, coupled with a reduction in rubber tensile strength.

Grard et al.¹⁰⁴ investigated different experimental groups consisting of three different formulations of primers used in bonding AA6061 aluminum alloy and silicone rubber (HCR). The aluminum surface underwent five treatments, including sandblasting (corundum F36) or polishing (various degrees), resulting in different levels of surface roughness. Furthermore, it was determined that increasing roughness negatively affects adhesion on primed surfaces.

Sarlin et al.¹⁰⁵ prepared samples by bonding stainless steel materials (EN 1.4432 and EN 1.4410) with rubber (BIIR) using two different primers (PR500-1 and S500-2) and adhesive (TC5000) through vulcanization. The prepared samples were examined using different corrosive environments (at 95 °C, i.e., air, 95 % humid environment, and deionized water) and H₂SO₄ solution (at 25 °C, 80 °C, and 95 °C). Based on the peel tests conducted on super duplex stainless-steel samples, a slight enhancement in bonding in a hot-air environment was observed. Additionally, it was reported that the peel strength exhibited a declining trend over time in alternative environments, while superior resistance against sulfuric acid was attained at ambient temperature. Concerning the resistance to aging, it was noted that the stainless-steel variant did not induce noteworthy alterations, whereas degradation in rubber linings was attributed to polymeric constituents. Moreover, it was determined that primer failure occurred initially in pure water, whereas adhesive failure predominated in acidic solutions.

In another study, Sarlin et al.¹⁰⁶ fabricated specimens by bonding stainless steel materials (EN 1.4432 and EN 1.4410) with rubber (BIIR) employing two distinct primers (PR500-1 and S500-2) and adhesive (TC5000) via the vulcanization process. Four different grits (steel grit, feldspar, corundum F20, and F24) were used to treat the steel. An increasing trend was observed in austenitic stainless steel regarding the relationship between sandblasting media hardness and S_a , while this phenomenon was not observed in super duplex stainless steel. According to the relationship between sandblasting media hardness and S_{dr} , almost identical results were obtained in both steels, with an increase in hardness and roughness. There was no interaction between surface roughness and grit size. Based on the peel tests conducted prior to aging, it was seen that the surface roughness did not affect the peel strength. Following immersion in 95 °C water for durations of 4 weeks and 12 weeks, the specimens treated with steel grit exhibited the lowest peel strength. Additionally, it was observed that while the peel strength of austenitic stainless steels showed a positive correlation with increasing roughness, this phenomenon was not evident in super duplex steels.

Abdullah and Essa¹⁰⁷ conducted investigations on the adhesion of EPDM rubber and low-density polyethylene (LDPE) materials to brass material. The brass surfaces underwent treatment via either chemical or thermal oxi-

dation, where the thermal oxidation process was conducted at three distinct temperatures (100 °C, 200 °C, and 300 °C). Following the peel tests, the highest adhesive strength was achieved in both materials through the chemical oxidation process. Additionally, it was noted that the bonding strength of EPDM to brass surpassed that of LDPE to brass.

Andreikova et al.¹⁰⁸ treated titanium-alloy (Lider detergent degreasing, VPF-T paste processing, DChK cast-iron shot treatment) and stainless-steel (Nefras degreasing) surfaces in different ways. Then, preliminary chemically modified rubbers (SBR (water resistant), SBR+EPDM (heat resistant), NBR+PCP (oil resistant)) were bonded to these surfaces using Chemosil 211 and 51-K-10V adhesives, followed by examination under aging conditions. Titanium alloys bonded with water-resistant rubber and treated with either DChK shot or VPF-T paste are reported to exhibit adequate bond strength. The bond strength of stainless steel bonded with heat- or oil-resistant rubbers remained virtually unchanged.

Kuteneva et al.¹⁰⁹ bonded rubber (V-14-INTA) with three distinct metals (Fe-2Mn-1Si, Fe-1Al-Ti, Al-Mg3) via hot-hardening glue and conducted various tests to investigate the bond. With the materials available, five-layered and nine different composites were formed. As a result of the peel tests, it was observed that the steel/rubber joint (due to the oxides on the steel surface activating the surface) exhibited higher bond strength than the aluminum/rubber joint (due to the presence of passivating oxide layers on the aluminum surface). The impact test results indicated an augmentation in impact strength alongside a reduction in weight at lower temperatures within the steel/aluminum/steel configuration. Furthermore, it was noted that enhancing impact strength in the aluminum/steel/aluminum structure could be attained with minimal weight increment. The fatigue test indicated that due to the inconsistent metal/rubber interface in the steel/aluminum/steel structure, excessive stress was generated in the outer steel layer, resulting in premature damage.

7 CONCLUSIONS AND RECOMMENDATIONS

Within the scope of this study, information related to rubber-metal adhesion (adhesion mechanism, factors affecting adhesion), vulcanization (operation mode and key parameters), bonding processes during/after vulcanization, rubber-related standards (terminology, test equipment, calibration, vulcanization, determination of bond strength of flexible and rigid materials, evaluation of test results), and bond failures (causes, analysis, and terminology) is provided. Initially, the factors influencing the interfacial strength of metal-rubber joints bonded through vulcanization were investigated. In addition, an archive of about 40 years has been reviewed about other factors affecting bond strength.

From the conducted investigations, the utilization of adhesives is essential for establishing adhesive bonds, with many of these adhesives offering adequate dry bond strength. Nevertheless, detrimental effects induced by saltwater and heightened oxygen concentrations within water present challenges to the integrity of the bond. The use of primer is also recommended, although it is not always valid. Furthermore, it has been determined that the primer primarily fails in pure water, while the adhesive primarily fails in a H_2SO_4 solution. Moreover, bonding during vulcanization exhibits superior efficacy compared to post-vulcanization bonding, owing to rubber better fills of surface cavities on the metal substrate. Optimizing the duration and temperature during the vulcanization process augments bond strength in adhesive bonding procedures.

There are varying perspectives on surface roughness. Observations during the vulcanization process indicate a positive correlation between increased surface area and bond strength, while a reduction in S_m value detrimentally affects adhesion post-vulcanization. Furthermore, an alternative perspective proposes that the bond strength correlates with S_v , rather than R_a . In the process of bonding aluminum and silicone rubber, a rougher surface results in weaker adhesion on primed surfaces. On the other hand, it is worth noting that an increase in roughness contributes to damping. Some studies suggest that surface roughness has minimal or no effect on bond strength. Dynamic tests carried out in this domain may enrich existing literature.

Contaminants present on surfaces pose a hindrance to adhesion, necessitating their removal. In addition to solvent-based cleaning materials, water-based cleaning materials are also used in this process, and water-based cleaning materials also appear to be effective. There are also cases where solvent cleaning alone is insufficient in corrosive environments. The pre-treatment of metal surfaces is imperative to prime and activate them prior to bonding. It is emphasized that surface treatments tailored to the material and environmental conditions, along with active oxide layers, positively impact bond strength. Among physical surface treatment methods, grit-blasting offers advantages over centrifugal blasting and air-blast tumbling. The selection of grit compatible with metal substrates and operating environments is paramount. Grits possessing corrosion resistance exhibit advantages in humid and elevated temperature conditions compared to steel shot. Additionally, the application of zinc phosphate coating following the blasting process enhances durability. However, it is noted that deep surface cracks induced by grit-blasting can detrimentally affect fatigue life.

Phosphating, a chemical surface treatment method, stands out as a preferred choice due to its dual benefits of enhancing both metal-rubber bond strength and corrosion resistance of metal substrates. Given the damping properties inherent in rubber, metal-rubber components

are favored in applications involving dynamic and impact loads. The formation of large crystals in the phosphating process and inappropriately high coating weights were found to be detrimental to the joint under impact loading. Comparative evaluations of various oxidation methods on brass surfaces reveal superior bond strength with the chemical oxidation method over the thermal oxidation method. The application of Metal-Jacket has also been found to increase resistance to corrosive environments. Additionally, it has been observed that the results of different chemical surface treatments vary depending on the process parameters, usage environment, and system components. Among these, the optimal selection of gas and film thickness in the PPTH method has been identified as a positive contributor to bond performance. Furthermore, research has been carried out to establish the most effective process parameters for various chemical methods, including anodization, immersion in different solutions, etching with various acids, surface modification with plasma, and others, based on the materials used. The literature also includes comparative assessments of physical and chemical methodologies. Studies have shown that the anodization of aluminum materials yields superior outcomes compared to burnishing and sandblasting processes.

The selection and application of suitable surface treatments for both rubber and metal materials are crucial. Applying identical surface treatment techniques across diverse materials may yield disparate results. Within the existing literature, limited comparative analyses between physical and chemical surface treatments have been documented. Expanding the scope of such studies would offer valuable insights for researchers and users. Additionally, there is a pronounced need for further investigation to identify surface treatment methodologies and optimal parameters tailored to the specific components of adhesive systems.

Literature on resistance to corrosive environments includes studies predominantly focusing on stainless steel due to its renowned corrosion resistance. Despite this reputation, stainless steel is susceptible to corrosion. It is important to select the appropriate stainless steel for the working environment and to apply the correct surface treatment to this steel. Extensive aging tests have indicated that the bond strength remains relatively stable when the metal substrate, surface treatment technique, adhesive system, and rubber material are correctly selected.

Mechanical analysis of metal-rubber bonds predominantly occurs within laboratory settings through static and peel tests. Researchers often subject test specimens to various assessments, including thermal aging, acidic solution immersion, salt-spray exposure, and hot tearing, aimed at replicating real-life conditions. There are also studies on updating existing test methods or proposing novel ones. Notably, dynamic testing for metal-rubber

joints appears to be infrequent. To enhance efficiency and realism, parts should undergo dynamic tests tailored to their intended usage and environment. Ideally, the part itself should be used during testing; otherwise, it is important to apply standard test methods that are compatible with the shape of the part. Moreover, computational analyses should complement experimental efforts. Utilizing test models developed in a computerized environment, alongside collected data, can furnish valuable insights into diverse operating conditions of the parts and aid in cost reduction.

Upon analysis of the study results, it is evident that few issues have been agreed upon, and many remain subject to differing opinions. This disparity arises due to the utilization of diverse materials and parameters in bonding metal and rubber components. Conceptually, the metal-rubber system can be likened to a table supported by four legs: metal, rubber, adhesive-primer, and surface treatment. The surface of the table represents the environment in which the metal-rubber part will operate, and it is in contact with each foot. The incompatibility of any of these four legs with the working environment disrupts the equilibrium of the table, ultimately leading to its collapse or system damage. Furthermore, incompatibility of any leg within the system itself can also result in damage.

Acknowledgments

This study was conducted within the framework of the Scientific Research Projects Unit of Pamukkale University (project no. 2021FEBE076). The authors also extend their gratitude to HD Rubber & Metal Co. for their invaluable assistance in preparing the test specimens and conducting the experiments as part of this project.

8 REFERENCES

- P. E. Hurley, History of natural rubber, *J. Macromol. Sci., Chem.*, 15 (1981) 7, 1279–1287, doi:10.1080/00222338108056785
- W. Verheye, Growth and Production of Rubber, in Land use, land cover and soil science, (Ed: W. Verheye), UNESCO-EOLSS Publishers, Oxford, UK 2010
- T. R. Vijiyaram, A technical review on rubber, *Int. J. Des. Manuf. Technol.*, 3 (2009) 1, 25–37, doi:10.18000/ijodam.70043
- E. V. Klimentyev, A. O. Zvonov, E. U. Glazkova, Rubber-cord cushions application in modern engineering, 2014 Dynamics of Systems, Mechanism and Machines (Dynamics), Omsk-Russia, IEEE, 2014
- T. S. Natarajan, S. Finger, J. Lacayo-Pineda, E. S. Bhagavatheswaran, S. S. Banerjee, G. Heinrich, A. Das, Robust Triboelectric Generators by All-In-One Commercial Rubbers, *ACS Appl. Electron. Mater.*, 2 (2020) 12, 4054–4064, doi:10.1021/acsaelm.0c00846
- S. Muroga, Y. Takahashi, Y. Hikima, S. Ata, S. G. Kazarian, M. Ohsima, T. Okazaki, K. Hata, Novel approaches to in-situ atr-ftir spectroscopy and spectroscopic imaging for real-time simultaneous monitoring curing reaction and diffusion of the curing agent at rubber nanocomposites surface, *Polymers*, 13 (2021) 17, 2879, doi:10.3390/polym13172879
- F. Z. S. A. Hassani, W. Ouarhin, M. E. Achaby, Y. Tamraoui, M. O. Bensalah, D. Rodrigue, R. Bouhfid, A. E. K. Qaiss, Recycled tires shreds based polyurethane binder: Production and characterization, *Mech. Mater.*, 144 (2020), 103351, doi:10.1016/j.mechmat.2020.103351
- G. Zanchin, G. Leona, Polyefilen thermoplastic elastomers from polymerization catalysis: Advantages, pitfalls and future challenges, *Prog. Polym. Sci.*, 113 (2021), 101342, doi:10.1016/j.progpolymsci.2020.101342
- J. B. Van Beilen, Y. Poirier, Guayule and Russian dandelion as alternative sources of natural rubber, *Crit. Rev. Biotechnol.*, 27 (2007) 4, 217–231, doi:10.1080/07388550701775927
- M. W. Sabaa, A. F. Younan, R. M. Mohsen, M. L. Tawfic, Maleic anhydride grafted rubbers for metallic surfaces lamination, *J. Appl. Polym. Sci.*, 108 (2008) 2, 850–857, doi:10.1002/app.27699
- S. R. Khimi, K. L. Pickering, A new method to predict optimum cure time of rubber compound using dynamic mechanical analysis, *J. Appl. Polym. Sci.*, 131 (2014) 6, 40008, doi:10.1002/app.40008
- Y. Heping, L. Sidong, P. Zheng, Preparation and study of epoxidized natural rubber, *J. Therm. Anal. Calorim.*, 58 (1999) 2, 293–299, doi:10.1023/a:1010199013587
- H. Mooibroek, K. Cornish, Alternative sources of natural rubber, *Appl. Microbiol. Biotechnol.*, 53 (2000), 355–365, doi:10.1007/s002530051627
- A. B. Nair, R. Joseph, Chemistry, manufacture and applications of natural rubber, (Eds: S. Kohjiya, Y. Ikeda), Woodhead Publishing, UK 2014, Ch. 9
- E.E. Cömez, S. Öztürk, Etilen vinil asetat (EVA) ve etilen propilen dien (EPDM) karışımlarına eklenen huntit/hidromanyezit'in etkilerinin incelenmesi, *JournalMM.*, 3 (2022) 1, 33–49, doi:10.55546/jmm.1013165
- P. Rybinski, B. Syrek, A. Marzec, B. Szadkowski, M. Kusmirek, M. Sliwka-Kaszynska, U. Z. Mirkhodjaev, Effects of basalt and carbon fillers on fire hazard, thermal, and mechanical properties of EPDM rubber composites, *Materials*, 14 (2021) 18, 5245, doi:10.3390/ma14185245
- S. Samar ija-Jovanović, V. Jovanović, G. Marković, S. Konstantinović, M. Marinović-Cincović, Nanocomposites based on silica-reinforced ethylene-propylene-diene-monomer/acrylonitrile-butadiene rubber blends, *Compos. Part B Eng.*, 42 (2011) 5, 1244–1250, doi:10.1016/j.compositesb.2011.02.008
- L. Rodrigues, I. M. Banat, J. Teixeira, R. Oliveira, Strategies for the prevention of microbial biofilm formation on silicone rubber voice prostheses, *J. Biomed. Mater. Res., Part B*, 81 (2007) 2, 358–370, doi:10.1002/jbm.b.30673
- A. Fazli, D. Rodrigue, Waste Rubber Recycling: A Review on the evolution and properties of thermoplastic elastomers, *Materials*, 13 (2020) 3, 782, doi:10.3390/ma13030782
- R. Anyszka, D. M. Bieliński, Z. Pędzich, P. Rybiński, M. Imiela, M. Siciński, M. Zarzecka-Napierala, T. Gozdek, P. Rutkowski, Thermal stability and flammability of styrene-butadiene rubber-based (SBR) ceramifiable composites, *Materials*, 9 (2016) 7, 604, doi:10.3390/ma9070604
- K. Akshay, M. Arjun, S. S. Govind, V. Hrithwik, S. Akhil, N. Rahul, Mechanical behavior of silicon carbide filled SBR/NBR blends, *Mater. Today: Proc.*, 42 (2021), 1432–1436, doi:10.1016/j.matpr.2021.01.234
- X. Zhang, Y. Zhang, Z. Peng, X. Shang, Y. Zhang, Dynamically vulcanized nitrile rubber/polyoxymethylene thermoplastic elastomers, *J. Appl. Polym. Sci.*, 77 (2000) 12, 2641–2645, doi:10.1002/1097-4628(20000919)77:12<2641::AID-APP110>3.0.CO;2-0
- E. E. Cömez, S. Öztürk, Farklı vulkanizasyon parametrelerinin karbon ve kaolen-silika esaslı karışımların çapraz bağ yoğunluğuna ve mekanik özelliklerine etkileri, *ALKU Journal of Science*, 4 (2022) 2, 53–62, doi:10.46740/alku.1127332
- J. Wu, W. Xing, G. Huang, H. Li, M. Tang, S. Wu, Y. Liu, Vulcanization kinetics of graphene/natural rubber nanocomposites, *Polymer*, 54 (2013) 13, 3314–3323, doi:10.1016/j.polymer.2013.04.044

- ²⁵ L. Chen, Z. Jia, Y. Tang, L. Wu, Y. Luo, D. Jia, Novel functional silica nanoparticles for rubber vulcanization and reinforcement, *Compos. Sci. Technol.*, 144 (2017), 11–17, doi:10.1016/j.compscitech.2016.11.005
- ²⁶ S. Mostoni, P. Milana, B. Di Credio, M. D'Arienzo, R. Scotti, Zinc-based curing activators: New trends for reducing zinc content in rubber vulcanization process, *Catalysts*, 9 (2019) 8, 664, doi:10.3390/catal9080664
- ²⁷ N. A. Nikiforova, M. A. Sheryshev, Estimation of the adhesion strength of rubber-metal bonds, *Polym. Sci., Ser. D*, 5 (2012), 53–59, doi:10.1134/S199542121201011X
- ²⁸ M. E. Mehr, H. Aghamohammadi, S. N. H. Abbandanak, G. R. Aghamirzadeh, R. Eslami-Farsani, S. M. H. Siadati, Effects of applying a combination of surface treatments on the mechanical behavior of basalt fiber metal laminates, *Int. J. Adhes. Adhes.*, 92 (2019), 133–141, doi:10.1016/j.ijadhadh.2019.04.015
- ²⁹ L. Guo, J. Liu, H. Xia, X. Li, X. Zhang, H. Yang, Effects of surface treatment and adhesive thickness on the shear strength of precision bonded joints, *Polym. Test.*, 94 (2021), 107063, doi:10.1016/j.polymertesting.2021.107063
- ³⁰ P. Molitor, T. Young, Investigations into the use of excimer laser irradiation as a titanium alloy surface treatment in a metal to composite adhesive bond, *Int. J. Adhes. Adhes.*, 24 (2004) 2, 127–134, doi:10.1016/j.ijadhadh.2003.06.001
- ³¹ T. Sekercioglu, *Makine elemanları hesap şekillendirme*, 5th ed., Birsen Yayınevi, Istanbul, Turkey 2021
- ³² S. Ebnesajjad, C. F. Ebnesajjad, *Surface treatment of materials for adhesive bonding*, 2nd ed., William Andrew, Oxford, UK 2014
- ³³ P. Sasidharan Achary, C. Gouri, R. Ramaswamy, Reactive bonding of natural rubber to metal by a nitrile-phenolic adhesive, *J. Appl. Polym. Sci.*, 81 (2001) 11, 2597–2608, doi:10.1002/app.1702
- ³⁴ B. Crowther, *The handbook of rubber bonding*, iSmithers Rapra Publishing, Shawbury, UK 2003
- ³⁵ M. A. Ansarifar, J. Zhang, A. Bell, R. J. Ellis, Role of primer in rubber to Nylon 6,6 bonding, *Int. J. Adhes. Adhes.*, 22 (2002) 3, 245–255, doi:10.1016/S0143-7496(01)00060-4
- ³⁶ I. Rezaeian, P. Zahedi, A. Rezaeian, Rubber adhesion to different substrates and its importance in industrial applications: A review, *J. Adhes. Sci. Technol.*, 26 (2012) 6, 721–744, doi:10.1163/016942411X579975
- ³⁷ M. A. Ansarifar, G. J. Lake, On the mechanics of rubber-to-metal bond failure, *J. Adhes.*, 53 (1995) 3–4, 183–199, doi:10.1080/00218469508009938
- ³⁸ J. Lasprilla-Botero, M. Álvarez-Láinez, D. A. Acosta, J. M. Martí'n-Martí'nez, Water-based adhesive formulations for rubber to metal bonding developed by statistical design of experiments, *Int. J. Adhes. Adhes.*, 73 (2017), 58–65, doi:10.1016/j.ijadhadh.2016.11.007
- ³⁹ A. K. Bhowmick, M. M. Hall, H. A. Benary, *Rubber products manufacturing technology*, Marcel Dekker, New York, USA 1994
- ⁴⁰ C. Chandrasekaran, *Anticorrosive rubber lining: A practical guide for plastic engineers*, William Andrew, Oxford, UK 2017
- ⁴¹ A. Durmuş, S. Ülkü, M. Güden, Ö. F. Otnar, *Kauçuk/metal yapışma mukavemetinin belirlenmesi*, Uludağ Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi, 10 (2005) 1, 33–39
- ⁴² J. M. Buist, W. J. S. Naunton, Rubber bonding, *Rubber Chem. Technol.*, 23 (1950) 4, 945–971, doi:10.5254/1.3547099
- ⁴³ L. F. M. Da Silva, A. Öchsner, R. D. Adams, *Handbook of adhesion technology*, Springer, Heidelberg, Germany 2011
- ⁴⁴ C. S. S. R. Kumar, A. M. Nijasure, Vulcanization of rubber, *Resonance*, 4 (1997), 55–59, doi:10.1007/BF02919629
- ⁴⁵ Ö. Kılınç, N. Toplan, Amorf Polimerler, *ALKU J. Sci.*, 5 (2023) 3, 131–148, doi:10.46740/alku.1299835
- ⁴⁶ A. K. Bhowmick, R. Mukhopadhyay, S. K. De, High temperature vulcanization of elastomers, *Rubber Chem. Technol.*, 52 (1979) 4, 725–734, doi:10.5254/1.3535236
- ⁴⁷ M. A. Akiba, A. S. Hashim, Vulcanization and crosslinking in elastomers, *Prog. Polym. Sci.*, 22 (1997) 3, 475–521, doi:10.1016/S0079-6700(96)00015-9
- ⁴⁸ N. J. Morrison, M. Porter, Temperature effects on the stability of intermediates and crosslinks in sulfur vulcanization, *Rubber Chem. Technol.*, 57 (1984) 1, 63–85, doi:10.5254/1.3536002
- ⁴⁹ A. Y. Coran, in *The science and technology of rubber*, (eds: B. Erman, J. E. Mark, C. M. Roland), Academic Press, USA 2013, Ch. 7
- ⁵⁰ J. Kru elák, M. Mikolajová, A. Kvasničáková, M. Džuganová, I. Chodák, J. Hronkovič, J. Pret' o, I. Hudec, Combined sulphur and peroxide vulcanization of filled and unfilled epdm-based rubber compound, *Materials*, 16 (2023) 16, 5596, doi:10.3390/ma16165596
- ⁵¹ R. Ding, A. I. Leonov, A kinetic model for sulfur accelerated vulcanization of a natural rubber compound, *J. Appl. Polym. Sci.*, 61 (1996) 3, 455–463, doi:10.1002/(SICI)1097-4628(19960718)61:3<455::AID-APP8>3.0.CO;2-H
- ⁵² ASTM D2084-19A:2019 – Standard test method for rubber property—Vulcanization using oscillating disk cure meter ASTM International, West Conshohocken, PA, doi:10.1520/D2084-19A
- ⁵³ S. Erkek, *Karbon siyahi/yağ ve karbon siyahi/dolgu maddesi oranının farklı vulkanizasyon sistemlerinde EPDM, NBR ve SBR elastomerlerinin fiziko-mekaniksel özellikleri üzerine etkisi*, Master's Thesis, Cukurova University, Adana, Turkey, 2007
- ⁵⁴ ISO 6502-1:2018 – Rubber – Measurement of vulcanization characteristics using curemeters- Part 1: Introduction ISO Committee, Geneve
- ⁵⁵ ASTM D1566-21a:2021 – Standard terminology relating to rubber, ASTM International, West Conshohocken, PA, doi:10.1520/D1566-21A
- ⁵⁶ ASTM D6085-97R22:2022 – Standard practice for sampling in rubber testing—Terminology and basic concepts ASTM International, West Conshohocken, PA, doi:10.1520/D6085-97R22
- ⁵⁷ ISO 5893:2019 – Rubber and plastics test equipment – Tensile, flexural and compression (Constant rate of traverse) – Specification ISO Committee, Geneve
- ⁵⁸ ASTM E4-21:2021 – Standard practices for force calibration and verification of testing machines ASTM International, West Conshohocken, PA, doi:10.1520/E0004-21
- ⁵⁹ ISO 6502-2:2018 – Rubber – Measurement of vulcanization characteristics using curemeters- Part 2: Oscillating disc curemeter ISO Committee, Geneve
- ⁶⁰ ISO 6502-3:2023 – Rubber – Measurement of vulcanization characteristics using curemeters – Part 3: Rotorless curemeter ISO Committee, Geneve
- ⁶¹ ASTM D5289-19A:2019 – Standard test method for rubber property – Vulcanization using rotorless cure meters ASTM International, West Conshohocken, PA, doi:10.1520/D5289-19A
- ⁶² ASTM D413-98R17:2017 – Standard test methods for rubber property – Adhesion to flexible substrate ASTM International, West Conshohocken, PA, doi:10.1520/D0413-98R17
- ⁶³ ASTM D429-14R23:2023 – Standard test methods for rubber property – Adhesion to rigid substrates ASTM International, West Conshohocken, PA, doi:10.1520/D0429-14R23
- ⁶⁴ ISO 813:2019 – Rubber, vulcanized or thermoplastic – Determination of adhesion to a rigid substrate – 90 degree peel method ISO Committee, Geneve
- ⁶⁵ ISO 814:2017 – Rubber, vulcanized or thermoplastic – Determination of adhesion to metal – Two-plate method ISO Committee, Geneve
- ⁶⁶ ISO 5600:2024 – Rubber – Determination of adhesion to rigid materials using conical shaped parts ISO Committee, Geneve
- ⁶⁷ ISO 1827:2022 – Rubber, Vulcanized or thermoplastic – Determination of shear modulus and adhesion to rigid plates – Quadruple – Shear methods ISO Committee, Geneve
- ⁶⁸ ISO 5603:2024 – Rubber, vulcanized – Determination of adhesion to wire cord ISO Committee, Geneve

- ⁶⁹ ISO 6133:2015 – Rubber and plastics – Analysis of multi-peak traces obtained in determinations of tear strength and adhesion strength ISO Committee, Geneva
- ⁷⁰ I. Ismail, M. K. Harun, Adhesion failure of rubber/metal composites undergoing corrosion, *Rubber Chem. Technol.*, 90 (2017) 3, 455–466, doi:10.5254/rct.16.83764
- ⁷¹ A. R. Madura, Investigation of rubber/metal bond failures by surface-analyses techniques, *Rubber Chem. Technol.*, 64 (1991) 2, 243–253, doi:10.5254/1.3538556
- ⁷² I. Ismail, M. K. Harun, Evaluation of rubber/mild steel bonds failure after exposure in marine environment, *Int. J. Chem. Eng. Appl.*, 4 (2013) 3, 119–123, doi:10.7763/IJCEA.2013.V4.276
- ⁷³ P. Kulkarni, S. Kshire, S. Patil, S. Vishwakarma, Design and manufacturing of rubber-metal bond testing machine for silent bush block, *Int. J. Eng. Res. Technol.*, 3 (2014) 9, 787–790, doi:10.17577/IJERTV3IS090725
- ⁷⁴ D. C. Leicht, O. H. Yeoh, A. N. Gent, J. Padovan, R. L. Mullen, Adhesion failure in bonded rubber cylinders Part 1: Internal penny-shaped cracks, *Rubber Chem. Technol.*, 76 (2003) 1, 160–173, doi:10.5254/1.3547731
- ⁷⁵ C. C. Lawrence, G. J. Lake, A. G. Thomas, New techniques for measurement of rubber-to-metal bond failure, *Rubber Chem. Technol.*, 78 (2005) 2, 271–285, doi:10.5254/1.3547883
- ⁷⁶ J. R. Beatty, E. C. Dalglis, A new tester for dynamic rubber-to-metal adhesion, *Rubber Chem. Technol.*, 47 (1974) 1, 188–201, doi:10.5254/1.3540424
- ⁷⁷ M. Nakache, E. Aragon, L. Belec, F. X. Perrin, G. Roux, P. Y. Gac, Degradation of rubber to metal bonds during its cathodic delamination, validation of an artificial ageing test, *Prog. Org. Coat.*, 72 (2011) 3, 279–286, doi:10.1016/j.porgcoat.2011.04.016
- ⁷⁸ I. Ismail, M. K. Harun, M. Z. A. Yahya, Effects of dissolved oxygen on the integrity of industrial chlorinated rubber-based primer used in rubber/metal composites, *Rubber Chem. Technol.*, 88 (2015) 3, 502–514, doi:10.5254/rct.15.84905
- ⁷⁹ Z. Wang, Research on fatigue failure mode and failure theory of rubber, *J. Phys.: Conf. Ser.*, 2076 (2021), 1–9, doi:10.1088/1742-6596/2076/1/012079
- ⁸⁰ R. Y. Ting, in *Adhesive joints: Formation, characteristics, and testing*, (Ed: K. L. Mittal), Plenum Press, New York and London 1984
- ⁸¹ F. Björk, B. Stenberg, Endurance of rubber-to-metal joints in hot water: comparison between two different stripping test methods, *Polym. Test.*, 6 (1986) 5, 369–377, doi:10.1016/0142-9418(86)90042-5
- ⁸² E. Östman, S. Persson, On the effect of metal surface texture on long-term resistance of vulcanized rubber-to-metal bonds under accelerated ageing, *Int. J. Adhes. Adhes.*, 10 (1990) 2, 102–107, doi:10.1016/0143-7496(90)90150-V
- ⁸³ Ş. Aktepe, *Kauçuk-Metal yapıştırılması*, Master's Thesis, Yıldız Technical University, İstanbul, Turkey, 1992
- ⁸⁴ M. S. Boulos, M. Petschel, Coating for rubber bonding and paint adhesion, *J. Mater. Eng. Perform.*, 6 (1997) 4, 421–425, doi:10.1007/s11665-997-0111-3
- ⁸⁵ J. W. Cook, S. Edge, D. E. Packham, Bonding of natural rubber to steel: surface roughness and interlayer structure, *J. Adhes.*, 72 (2000) 3–4, 293–315, doi:10.1080/00218460008029287
- ⁸⁶ M. A. Ansarifar, J. Zhang, J. Baker, A. Bell, R. J. Ellis, Bonding properties of rubber to steel, aluminium and nylon 6,6, *Int. J. Adhes. Adhes.*, 21 (2001) 5, 369–380, doi:10.1016/S0143-7496(01)00014-8
- ⁸⁷ G. S. Jeon, G. Seo, Influence of cure conditions on the adhesion of rubber compound to brass-plated steel cord. Part I. Cure temperature, *J. Adhes.*, 76 (2001) 3, 201–221, doi:10.1080/00218460108029626
- ⁸⁸ G. S. Jeon, G. Seo, Influence of cure conditions on the adhesion of rubber compound to brass-plated steel cord. Part II. Cure time, *J. Adhes.*, 76 (2001) 3, 223–244, doi:10.1080/00218460108029627
- ⁸⁹ S. G. Jeon, G. Seo, Effect of cure levels on adhesion between rubber and brass in the composites made up of rubber compound and brass-plated steel cord, *Korean J. Chem. Eng.*, 20 (2003), 496–502, doi:10.1007/BF02705555
- ⁹⁰ J. L. Delattre, R. d'Agostino, F. Fracassi, Plasma-polymerized thiophene films for enhanced rubber-steel bonding, *Appl. Surf. Sci.*, 252 (2006) 10, 3912–3919, doi:10.1016/j.apsusc.2005.05.069
- ⁹¹ O. H. Yeoh, Some geometric considerations for rubber-metal bond test specimens, *Rubber Chem. Technol.*, 79 (2006) 2, 320–337, doi:10.5254/1.3547940
- ⁹² R. J. Del Vecchio, Jr. Ernest Ferro, Strength vs. durability of rubber-metal bonds factor effects from processing and chemistry, *Rubber World*, 237 (2008) 4, 37–41
- ⁹³ X. F. Zhang, L. Fan, X. H. Zhao, L. Q. Zhang, L. Liu, Y. Zuo, Bonding properties between nitrile-butadiene rubber and aluminum alloy treated by anodizing methods, *J. Appl. Polym. Sci.*, 112 (2008) 1, 283–289, doi:10.1002/app.29378
- ⁹⁴ F. Wang, Y. Li, D. Wang, Adhesion enhancement for liquid silicone rubber and different surface by organosilane and Pt catalyst at room temperature, *Bull. Mater. Sci.*, 36 (2013), 1013–1017, doi:10.1007/s12034-013-0575-8
- ⁹⁵ A. Latifi, M. Imani, M. T. Khorasani, M. D. Joupari, Plasma surface oxidation of 316L stainless steel for improving adhesion strength of silicon rubber coating to metal substrate, *Appl. Surf. Sci.*, 320 (2014), 471–481, doi:10.1016/j.apsusc.2014.09.084
- ⁹⁶ T. Renner, Improvement in production of rubber-metal parts for the automotive industry, *Int. Polym. Sci. Technol.*, 41 (2014) 2, 779–784, doi:10.1177/0307174X1404100201
- ⁹⁷ A. Souid, A. Sarda, R. Deterre, E. Leroy, Influence of reversion on adhesion in the rubber-to-metal vulcanization-bonding process, *Polym. Test.*, 41 (2015), 157–162, doi:10.1016/j.polymertesting.2014.11.007
- ⁹⁸ C. Vandenaabeele, S. Bulou, R. Maurau, F. Siffer, T. Belmonte, P. Choquet, Organo-chlorinated thin films deposited by atmospheric pressure plasma-enhanced chemical vapor deposition for adhesion enhancement between rubber and zinc-plated steel monofilaments, *ACS Appl. Mater. Interfaces*, 7 (2015) 26, 14317–14327, doi:10.1021/acsami.5b02887
- ⁹⁹ D. Pradhan, R. Ghosh, A. Banerjee, M. Dutta, Effect of electro-cleaning roughness on steel wire-rubber adhesion strength, *Surf. Coat. Technol.*, 286 (2016), 293–302, doi:10.1016/j.surfcoat.2015.12.048
- ¹⁰⁰ C. Günsoy, *Mekanik ve kimyasal yüzey işlemlerinin poliakrilik kauçuk ve EN10130 DC01 çeliği yapışmasına etkilerinin incelenmesi*, Master's Thesis, Kocaeli University, Kocaeli, Turkey, 2018
- ¹⁰¹ F. Mihçi, *Improvement of Metal-EPDM rubber adhesion by plasma surface modification*, Master's Thesis, Sakarya University, Sakarya, Turkey, 2018
- ¹⁰² Q. Ahsan, A. F. A. Mawardi, S. Subramonian, M. R. Alkahari, A. Putra, (eds: M. N. O. Zahid, R. A. Aziz, A. R. Yusoff, N. M. Yahya, F. A. Aziz, M. Y. Abu), in *IMEC- APCOMS 2019: Proceedings of the 4th International Manufacturing Engineering Conference and the 5th Asia Pacific Conference on manufacturing systems*, Springer, Singapore 2020, Doi:10.1007/978-981-15-0950-6
- ¹⁰³ N. Gong, B. Wang, Y. Wang, X. Li, W. Lin, S. Fu, X. Chu, Effect of metal surface state on injection joining strength of aluminum-rubber composite part, *J. Manuf. Process*, 49 (2020), 365–372, doi:10.1016/j.jmapro.2019.12.006
- ¹⁰⁴ A. Grard, L. Belec, F. X. Perrin, Effect of surface morphology on the adhesion of silicon elastomers on AA6061 aluminum alloy, *Int. J. Adhes. Adhes.*, 102 (2020), 102656, doi:10.1016/j.ijadhadh.2020.102656
- ¹⁰⁵ E. Sarlin, A. Rosling, M. Honkanen, M. Lindgren, M. Juutilainen, M. Poikelispää, P. Laihonon, M. Vippola, J. Vuorinen, Effect of environment on bromobutyl rubber-steel adhesion, *Rubber Chem. Technol.*, 93 (2020) 2, 429–444, doi:10.5254/rct.19.80455
- ¹⁰⁶ E. Sarlin, M. Honkanen, M. Lindgren, P. Laihonon, M. Juutilainen, M. Vippola, J. Vuorinen, The effect of substrate pre-treatment on durability of rubber-stainless steel adhesion, *Surf. Interfaces*, 21 (2020), 100646, doi:10.1016/j.surfin.2020.100646

- ¹⁰⁷R. H. Abdullah, A. F. Essa, Measuring the peeling strength between polymers (low density polyethylene, ethylene propylene diene monomer (EPDM) rubber) and brass and evaluating the effect of thermal and chemical oxidation on the metal, *Mater. Today: Proc.*, 47 (2021), 5992–5998, doi:10.1016/j.matpr.2021.04.547
- ¹⁰⁸L. N. Andreikova, Y. O. Andriasyan, I. I. Abol'skaya, Simulation of the durability of adhesive joints during operation of rubber-metallic products, *Polym. Sci., Ser. D*, 15 (2022) 4, 586–589, doi:10.1134/S1995421222040335
- ¹⁰⁹S. V. Kuteneva, S. V. Gladkovsky, D. I. Vichuzhanin, P. D. Nedzvetsky, Microstructure and properties of layered metal/rubber composites subjected to cyclic and impact loading, *Compos. Struct.*, 285 (2022), 115078, doi:10.1016/j.compstruct.2021.115078