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A novel promoter for enhancing adhesion between natural rubber and brass-plated steel cords

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ABSTRACT

In this study, a conventional manobond promoter as well as a newly synthesized kaolin modified resin (KMR) were applied in various concentrations into rubber mixes to investigate their performance in improving the adhesion between NR and brass-coated steel cords. Two types of steel cords were used to prepare T-shape samples for pullout test. The samples were aged under aerobic aging conditions or exposed to ionizing radiation and the adhesion force was examined. The analysis of variance (ANOVA) was used to obtain a general understanding of the impact of changing various parameters and their inter-relationships on the static adhesion between NR and brass-coated steel cords. The results revealed that the use of the prepared promoter has significantly resulted in the clear stability of the cure rate index of the NR mixes. Also, the presence of KMR in the rubber mix enhances the mechanical properties of the rubber to a great extent. The results showed also that the NR mixes with KMR promoter have higher adhesion levels than those of the manobond promoter.

1. Introduction

Natural rubber (NR) is among the most important elastomers used in the manufacturing of rubber products such as tires and conveyor belts. Many reviews were devoted to understanding the chemical, physical as well as compounding properties of NR [1–4]. NR is a material that is capable of rapid deformation and recovery, and it is insoluble in a range of solvents, though it will swell when immersed in organic solvents at elevated temperatures. Some of its many attributes include abrasion resistance, good hysteretic properties, high tear strength and high tensile strength. It can show poor tire performance in areas such as traction of wet skid when compared to synthetic elastomers such as styrene butadiene rubber (SBR). In some rubber items, natural rubber used alone does not have sufficient strength to withstand the forces encountered by the article during its use in applications. For example, in tires, belting and hoses, it is necessary to increase the strength of the rubber by incorporating either textile or steel reinforcement. For many applications, it is desirable or even imperative that the rubber be attached to a metal substrate in a reliable manner. There is a fundamental difference between bonding of natural rubber to metal involving cross-linking mechanisms and the physical sticking of rubber to metal using a non-vulcanizing adhesive. The former involves a chemical reaction (generally during cure) while the latter generally relates to a physical surface tension phenomenon. The increased use of rubber in automotive, aerospace, and industrial applications has driven the requirement for strong and robust bonds between rubber and metal. Much literature has been published on the history and technology of bonding rubber to metal [5–12]. The earliest historical methods of attaching rubber to metal involved attaching the rubber by mechanical means or by the use of ebonite. Mechanical attachment, which is still used today in some cases, creates an insecure union. Bonding with ebonite has several disadvantages. One significant drawback is that the ebonite is thermoplastic and becomes quite weak with moderate temperature exposure. Depending on the amount of sulfur, ebonite based on NR shows a thermoplastic transition temperature, i.e., softening, between 70 and 80 °C. At sulfur levels between 4 and 25 phr, NR goes through a transition where it becomes rather leathery and is of little use. Because there will be a gradient of sulfur between the ebonite adhesive and the soft rubber compound, at some point, the sulfur content of the compound must pass through this transition zone. This transition zone weakens the softer rubber in the interfacial region and it reduces the flexibility in that region. As a further drawback, bonding with ebonite limits the chemistry of rubber formulations that can be successfully bonded using this technique. In 1862, Sanderson submitted a British patent application for the use of electrodeposited brass as an intermediary for bonding rubber to

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iron or steel [13]. It was not until between 1920 and 1930 that the process of bonding to a galvanic layer of brass (brass plating) was commercialized. The bond is obtained by virtue of the chemical reaction that occurs between the brass and the sulfur curative in the rubber and it has the advantage over the ebonite process of not being heat sensitive. This process requires a large investment in processing machinery and it is difficult to keep all the variables in the galvanic bath constant. It is somewhat unpredictable and shows a high sensitivity to processing conditions. As with bonding to ebonite, it limits the chemistry of the formulations that can be successfully bonded to only those compounds with a high sulfur cure (2–4 phr). As a further complication, not all types of brass will bond to rubber and it appears that the best ratio of copper to zinc is somewhat compound dependent. However, the brass plating process has proven quite successful for certain applications such as steel cords for automotive tires. The last four decades have seen the introduction of many new rubber-to-metal adhesives designed to cover the ever increasing range of synthetic rubbers currently available for use in dynamic applications. These include one coat adhesives, adhesives for post vulcanization bonding, especially rubber adhesives for silicones, fluoro-silicones, fluoro-rubbers, acrylics, and hydrogenated nitrile rubbers, along with the recent introductions of water-based adhesives. Today, many companies make adhesives for chemically bonding rubber to metal. Rubber to metal primers contain organic resins which react with most metal (steel, aluminum, stainless steel, copper, brass) surfaces during the vulcanization process to form a chemical bond to the metal. They also contain polymers which allow for better film formation and act as an anchor for the subsequent application of the adhesive. Rubber-to-metal adhesives contain polymeric materials that are compatible with the ingredients in the primer, as well as the rubber compound to be bonded. Many are based on halogenated polymers or resins are known to wet metals efficiently and can be used in both the

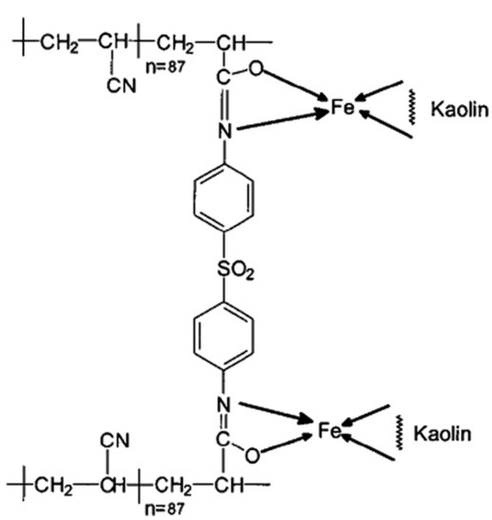

Fig. 1. Chemical structure of the modified kaolin/resin-iron chelate (KMR).

primer and adhesive formulation. They provide effective barriers to chemicals that can undermine the adhesive bond. The adhesive also contains very powerful curatives that react with both the polymers in the rubber and the polymers in the adhesive [14]. The selection of the best adhesive to use in a particular bonding situation depends on several factors [15]. They include: The rubber being bonded, the molding process employed, level of environmental resistance required, adaptability to existing adhesive application equipment and cost.

In the past years our research group investigated different factors contributing to adhesion between rubber and textile cords/fabrics [16–21]. In the present work, a newly prepared adhesion promoter is used together with a well-known promoter which is cobalt boron acylate [22–24]in order to judge the performance of the newly prepared promoter on the adhesion between NR mixes and brass plated steel cords. Aerobic aging and exposure to ionizing radiation are also investigated for both promoters using two different types of brass-plated steal cords. We also utilized the method of Analysis of Variance, known as ANOVA, to reach a statistical and mathematical understanding regarding the different factors affecting rubber adhesion.

2. Experimental

2.1. Natural rubber compounds

Natural rubber (NR) used in this study, SMR-20, was supplied by Tecnopolimeri srl, Russia. A tri component system consisting of resorcinol, formaldehyde resin and Silica was used as bonding system. The resorcinol component used is known as Cohedur-RS, supplied by Morgan Chem., Egypt; the resin was octylphenyl formaldehyde of grade (HR-0417), produced by Shinktady, England; and hexamethylene tetramine (HMT) acts as a methylene group donor, supplied by Bayer AG, Germany.

Cobalt boron acylate, named Manobond C-16, supplied by Rhodea, England is the well-known adhesion promoter, used in this study. Kaolin Modified Resin (KMR) is the adhesion promoter prepared via the reaction of acrylonitrile and a crosslinking agent to form a resin. The resin-iron complex was formed through the drop wise addition of $FeCl_3$ dissolved in acetone to the resin. The resin-iron complex was obtained by allowing it to cool. It was decanted, filtered, washed with acetone, then dried and milled into a fine powder. After that, kaolin was mixed with resin-iron chelate in a ratio of 2:1, respectively. The structure of the kaolin modified resin is shown in Fig. 1 [25].

2.2. Steel cords

Two types of steel cord, designated as cord 1 and cord 2, were used in this research. They were of the brass-plated type. These cords were supplied by Transport and Engineering Co., Egypt. The two cords differ mainly in the mechanical properties, cord constructer (rearrangement of filaments) and diameter. Cord 2 is

Table 1
Specifications of brass-coated steel cords.

Property	Cord 1	Cord 2
Nominal diameter (mm)	1.08	1.38
Cord construction	$(1\times3)\times0.2+(1\times6)\times0.35$	$(1\times3)\times0.2+(1\times9)\times0.2+(1\times6)\times0.2+(1\times9)\times0.2+(1\times1)\times(0.15)$
Breaking force (Kg)	135	350
Elongation at break (%)	4	5
Adhesion (Kg)	40	41
Tensile strength (kg/cm$^{2)}$	20,000	20,000
Linear density (g/m)	5.7	17