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Development of Biodiesel-Resistant Nitrile Rubber Compositions

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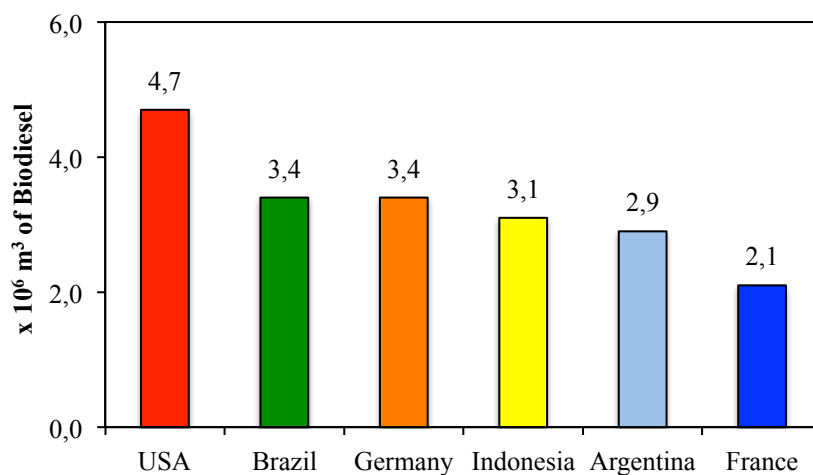
## INTRODUCTION

Substantial efforts have been made to control pollutant gas emissions to minimise global warming effects. Based on the fact that these emissions are mainly a result of fossil fuels use, researchers are constantly motivated to find replacements for these pollutant fuels.

Biodiesel is currently the most ready-to-use substitute for petroleum diesel (PULLEN; SAEED, 2014; AKHLAGHI et al., 2015b), owing to its similar performance in compression ignition engines (ALI et al., 2016; MOSER, 2016; RASHED et al., 2016) to that of diesel and its lower level of pollutant gas emissions (SHAHIR; JAWAHAR; SURESH, 2015). Moreover, biodiesel is considered to be non-toxic, renewable, and biodegradable (MOFIJUR et al., 2013b; TORREGROSA et al., 2013; ÖZENER et al., 2014; DAUD et al., 2015).

The world's biodiesel production is rising quickly. According to the Organisation for Economic Co-operation and Development (OECD, 2015), the production of biodiesel has risen from  $4 \times 10^6$  tons to  $36 \times 10^6$  tons of biodiesel from 2005 to 2015. In 2014, the world's production (Figure 1) was led by the USA followed by Brazil, Germany and Indonesia (STATISTA, 2015).

Figure 1 – Biodiesel production per country in 2014 (in millions of m<sup>3</sup>).



Source: STATISTA, 2015.

Biodiesel is no longer considered a “fuel of the future” but rather can be considered an actual fuel option. However, biodiesel is not commercially available in its pure form and is currently sold worldwide as a blend in small proportions with petroleum diesel. Blending biodiesel and petroleum diesel is mandatory in some countries: for example, Brazil

implemented a policy in 2005 stating that diesel in petrol stations must be sold as a 2% biodiesel/diesel blend, and in 2014 the required concentration in the blend was raised to 7% (ANP, 2015). In the European Union, biodiesel consumption rose from 2.5 million tons of oil equivalent in 2005 to 11.5 million tons of oil equivalent in 2012 (STATISTA, 2015).

Nevertheless, despite the similarities and advantages between biodiesel and petroleum diesel, they possess significant chemical differences, which has raised concerns about material compatibility, especially with respect to their use in the automotive industry. Because of these differences, studies on the compatibility of biodiesel and several types of materials have become of vital importance (BÖHNING et al., 2014a; 2014b; CORONADO et al., 2014; FAZAL; HASEEB; MASJUKI, 2014; RESTREPO-FLÓREZ et al., 2014; AKHLAGHI et al., 2015b). To date, the compatibility of biodiesel with materials that are widely used in diesel engines has not been fully explained or understood.

Automotive units are built with a wide variety of materials, including metals and polymers (AKHLAGHI et al., 2015a; SORATE; BHALE; DHAOLAKIYA, 2015). Among the polymers used, there is also a wide diversity of plastics and rubbers that can be employed. Nitrile rubber (NBR) is widely employed in automotive parts that require constant contact with fuels and oils in automotive parts, e.g., hoses and seals, owing to its high polarity (AKHLAGHI et al., 2015a; AKHLAGHI et al., 2015b).

Nitrile rubber resistance has already been tested by several different authors under different conditions; a unanimous consensus has been made, stating that nitrile rubber presents low resistance to biodiesel (FRAME; BESSEE; MARBACH JR., 1997; FRAME; MCCORMICK, 2005; TERRY, 2005; TRAKARNPRUK; PORNTANGJITLIKIT, 2008; WALKER, 2009; ZHANG et al., 2009; HASEEB et al., 2010; CHAI et al., 2011; HASEEB et al., 2011b; ANDRIYANA et al., 2012; ALVES; MELLO; MEDEIROS, 2013; CHAI et al., 2013; LINHARES et al., 2013; CORONADO et al., 2014; AKHLAGHI et al., 2015b; CH'NG et al., 2015; DUBOVSKÝ; BOŽEK; OLŠOVSKÝ, 2015; ZHU et al., 2015). Nevertheless, most of the authors failed to provide complete information on the type of nitrile rubber that was tested, which impedes a thorough understanding of the interaction between the rubber and biodiesel. Fluorine-based elastomers are, however, highly resistant to different biodiesels and have consequently been proposed as a substitute for nitrile rubber in automotive parts. However, in Brazilian market, fluoro-elastomers are ten times more expensive than nitrile rubber (ALICE Web, 2015), and these higher prices of the material would have an impact on vehicles prices.

Biodiesel can degrade easier and faster than petroleum diesel through oxidation during storage (SORATE; BHALE, 2013) because of its low stability and therefore is considered more corrosive than petroleum diesel (SORATE; BHALE, 2013; CURSARU et al., 2014). Because this corrosiveness can be drastic in a CI engine system (FAZAL; JAKERIA; HASEEB, 2014), a complete understanding of the interaction between biodiesel and various types of materials is of great importance (BÖHNING et al., 2014b; RESTREPO-FLÓREZ et al., 2014).

It is widely agreed that corrosion rates for metals are higher for biodiesel than for petroleum diesel; in addition, higher temperatures intensify corrosion attacks on metal surfaces (CHEW et al., 2013; CURSARU et al., 2014; JIN et al., 2015). Copper has proved to be less resistant to biodiesel compared to other metals and alloys, e.g., aluminium and carbon steel (CURSARU et al., 2014; FAZAL; JAKERIA; HASEEB, 2014). Chew et al. (2013) showed that magnesium exhibits poor resistance to palm biodiesel. The higher resistance of some metals or alloys can be explained by the formation of a passivation layer on the metal surfaces (KOVÁCS et al., 2015). Stainless steel, carbon steel and aluminium have been suggested as the most suitable metals for use in applications that come in contact with biodiesel (SORATE; BHALE, 2015). Moreover, Sorate and Bhale (2013), and Mojifur et al. (2013b) also reviewed the compatibility of other metals with different types of biodiesel.

Less attention has been given to the interaction between biodiesel and polyethylene (PE), which is one of the most commonly used polymer for the fabrication of fuel tanks (THOMPSON et al., 2013; BÖHNING et al., 2014b; RESTREPO-FLÓREZ et al., 2014). The few available studies tested different types of PE, e.g., linear low density polyethylene (LLDPE), crosslinked polyethylene (XLPE), and high density polyethylene (HDPE). Petroleum diesel seemed to swell LLPE, XLPE (THOMPSON et al., 2013), and HDPE (BÖHNING et al., 2014a; 2014b) to a higher extent than biodiesel. Böhning et al. (2014a) mentioned that the swollen HDPE samples possessed higher molecular mobility and that this plasticisation effect changed the fracture mechanism and gave the material more ductile behaviour.

### **1.3 Compatibility of biodiesel with elastomers**

The effects of biodiesel on different elastomers have been discussed over the years under different conditions. Although interesting conclusions have been drawn, the interaction between the two has not been fully explained.



Fluoroelastomers are considered to be fully compatible with biodiesel from different sources under any condition (FRAME; BESSEE; MARBACH JR., 1997; FRAME; MCCORMICK, 2005; TERRY, 2005; TRAKARNPRUK; PORNTANGJITLIKIT, 2008; WALKER, 2009; HASEEB et al., 2010; ALVES; MELLO; MEDEIROS, 2013). Mass and volume changes, after immersion in pure or blended biodiesel, were negligible regardless of the times lengths and temperatures of the tests. Trakarnpruk and Porntangjitlikit (2008) found an almost 4% change in volume after immersion in palm biodiesel for 1008 h at 60°C. The results of this observation were close to those reported by Terry (2005), who reported a variation of 6.8% in volume after immersing a sample in a B20 blend of soybean biodiesel for 1000 h at 60°C. Tensile strength was reportedly as unchanged (TERRY, 2005; HASEEB et al., 2010; ALVES; MELLO; MEDEIROS, 2013), or only slightly decreased (FRAME; BESSEE; MARBACH JR., 1997; TRAKARNPRUK; PORNTANGJITLIKIT, 2008) after immersion in biodiesel.

Similar comments can be extended to changes in other mechanical properties of fluoroelastomers. In addition, Walker (2009) showed that differences in fluorine content and curing systems affected the resistance to biodiesel. Nonetheless, the higher price of fluoroelastomers compared with other elastomers is a major concern and major obstacle for spreading their use in automotive parts (AKHLAGHI et al., 2015a).

Polychloroprene rubber (CR) showed poor resistance to biodiesel, especially in comparison with other rubbers (HASEEB et al., 2010; CHAI et al., 2011; HASEEB et al., 2011b; ANDRIYANA et al., 2012). Haseeb et. al (2010; 2011b) reported losses from 50% to over 80% after immersion in palm biodiesel. Although CR is no longer employed in parts that are in contact with fuels, it is used in hose covers, which may come in contact with fuels in case of leakage (AKHLAGHI et al., 2015a).

Ethylene propylene diene monomer rubber (EPDM) also showed little resistance to biodiesel, increasing almost 75% in volume, and losing approximately 80% of its initial tensile strength after immersion in palm biodiesel for 100 h at room temperature (HASEEB et al., 2011b).

The resistance of nitrile rubber has been exhaustively reported because of its importance in the automotive industry (FRAME; BESSEE; MARBACH JR., 1997; FRAME; MCCORMICK, 2005; TERRY, 2005; LINHARES; FURTADO, 2008; TRAKARNPRUK; PORNTANGJITLIKIT, 2008; WALKER, 2009; HASEEB et al., 2010; CHAI et al., 2011; HASEEB et al., 2011b; ANDRIYANA et al., 2012; ALVES; MELLO; MEDEIROS, 2013; LINHARES et al., 2013; CORONADO et al., 2014; AKHLAGHI et al., 2015b; CH'NG et al.,

Table 3 – Main accelerators used in sulphur vulcanisation of elastomers and their classifications.

Generic chemical designation	Property	Chemical name	Abbreviation
Thiazole	Fast	2-mercaptobenzothiazole	MBT
		2-2'-dithiobenzothiazole	MBTS
Sulphenamide	Fast – delayed action	N-t-butyl benzothiazole-2-sulphenamide	TBBS
		N-cyclohexyl benzothiazole-2-sulphenamide	CBS
Thiuram	Very fast	Tetramethyl thiuram monosulphide	TMTM
		Tetramethyl thiuram disulphide	TMTD
Dithiocarbamate	Ultra-accelerators	Zinc dimethyldithiocarbamate	ZDMC
		zinc diethyldithiocarbamate	ZDEC

Source: DATTA; INGHAM, 2001; COSTA et al., 2003; GHOSH et al., 2003; APREM; JOSEPH; THOMAS, 2005; CORAN, 2005; ALAM; MANDAL; DEBNATH, 2012.

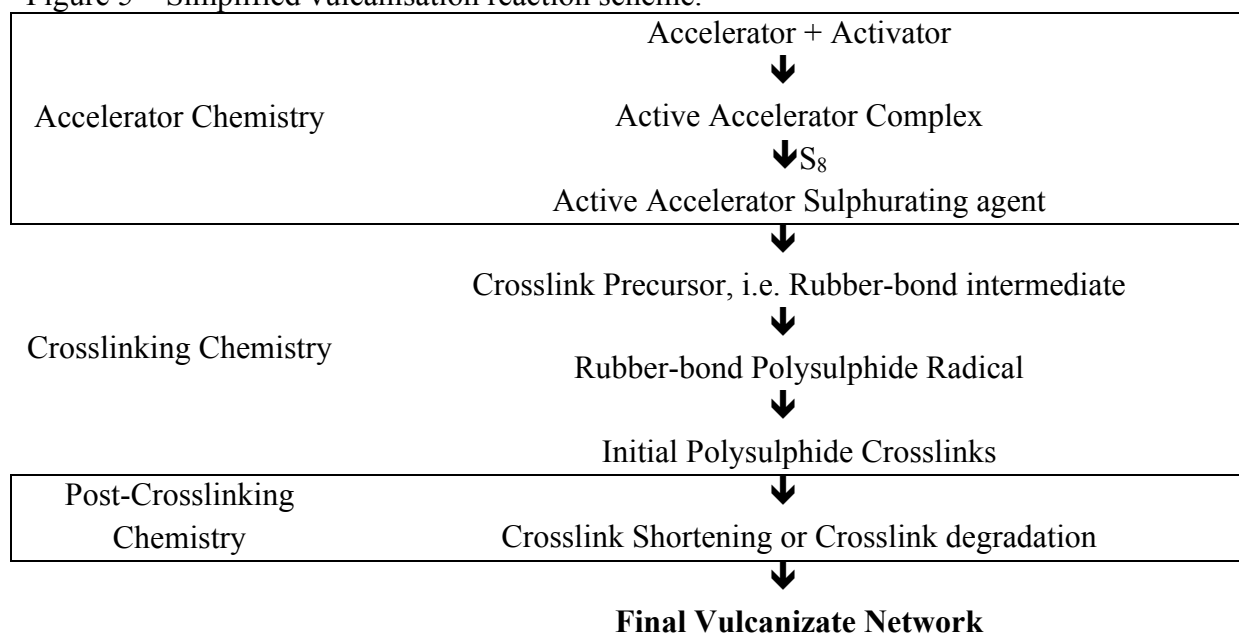
Sulphenamide accelerators, e.g., TBBS (N-t-butyl benzothiazole-2-sulphenamide) and CBS (N-cyclohexyl benzothiazole-2-sulphenamide), are known for having delayed action (DEBNATH; BASU, 1996; GHOSH et al., 2003; APREM; JOSEPH; THOMAS, 2005; NIYOGI, 2007; ANANDHAN et al., 2012; MOVAHED; ANSARIFAR; MIRZAIE, 2015). Usually, they are employed in binary systems, especially with thiuram accelerators (MOVAHED; ANSARIFAR; MIRZAIE, 2015). Thiurams, as TMTD (Tetramethyl thiuram disulphide), can improve reversion resistance, especially in binary systems (DATTA et al., 2007). In addition, TMTD contains 13.31% available sulphur (HOFMANN, 1989). However, the use of CBS was found to decrease crosslink densities, even in binary vulcanisations systems (DEBNATH; BASU, 1996). Moreover, TMTD can bloom on the surface of rubber products, when used at high concentration (FRANTA, 1989).

Until now, there has not been a solid agreement on the correct mechanism for the sulphur-accelerated vulcanisation process (NIEUWENHUIZEN et al., 1999; APREM;

JOSEPH; THOMAS, 2005; MARZOCCA; MANSILLA, 2007; DONDI et al., 2015). Additionally, the synergetic activity of binary vulcanisation has yet to be fully elucidated. It is believed that the formation of new chemical moieties occurs during the reaction (SUSAMMA; MINI; KURIAKOSE, 2001; MARYKUTTY et al., 2003; ALAM; MANDAL; DEBNATH, 2012b).

Ghosh et al. (2003) divided the general vulcanisation mechanisms into three sub-categories: (i) *accelerator chemistry*; (ii) *crosslinking chemistry*; and (iii) *post-crosslinking chemistry*. This general view of vulcanisation is shown in Figure 5 and Figure 6. The first step involves the formation of an activator-accelerator complex, which then reacts with sulphur to generate monomeric polysulphide species, which are the actual active sulphurating agents. These agents finally react with rubber and form crosslink bonds (CORAN, 2003; GHOSH et al., 2003; APREM; JOSEPH; THOMAS, 2005; ANANDHAN et al., 2012).

Figure 5 – Simplified vulcanisation reaction scheme.



Source: COSTA et al., 2003; GHOSH et al., 2003; APREM; JOSEPH; THOMAS, 2005; ANANDHAN et al., 2012.

A detailed discussion on the different reaction mechanisms for the different vulcanisation systems can be found in studies from Debnath and Basu (1996), Nieuwenhuizen (1999; 2001), Gradwell and Groof (2001), Susamma, Mini and Kuriakose (2001), Coran (2003; 2005), Ghosh et al. (2003), Marykutty et al. (2003), Aprem, Joseph and Thomas

Figure 27 – SEM fracture surface photomicrographs after cryogenic fracture of nitrile rubber composition with a high TMTD content. Composition 7(3/0/0.5).

