

## EFFECT OF CALCIUM CARBONATE ( $\text{CaCO}_3$ ) ON DEGRADATION OF PVC/NBR COMPOUND USED IN AUTOMOTIVE FUEL SYSTEM WITH B30

C. G. Herbert<sup>1</sup> ; C. C. Gonçalves<sup>1</sup>; L. R. P. de Andrade Lima<sup>2</sup>

[1cherbe13@ford.com](mailto:cherbe13@ford.com)

<sup>1</sup>Ford Motor Company

<sup>1</sup>Avenida Henry Ford, 2000 42810-970 Camaçari, BA - Brazil

<sup>2</sup>Department of Materials Science and Technology

<sup>2</sup>Federal University of Bahia

### ABSTRACT

*The compatibility of rubber used in automotive fuel system has been investigated with biodiesel in response to the increase of the biodiesel content of governmental policies in commercial diesel adopted by many countries. Elastomeric compounds based on nitrile rubbers (NBR) showed a lower resistance to degradation. The change of the base polymer formulation may increase the degradation resistance but with higher costs. The rubber formulations generally are composed of a list of ingredients and fillers that could interact as reinforcing or non-reinforcing. Carbon black is generally used as reinforcing filler and calcium carbonate as non-reinforcing due to widely usage of a larger particle size with reduced cost. Through the tensile test and SEM analysis, the effect of addition of a larger particle size calcium carbonate on the degradation of polyvinyl chloride (PVC) and nitrile butadiene (NBR) blend was evaluated after 1008h immersion at 80°C with B30. The results showed that  $\text{CaCO}_3$  should be avoided of PVC/NBR formulation to improve degradation resistance when in contact to biodiesel.*

Key-words: biodiesel, rubber formulation, degradation, calcium carbonate

## 1. INTRODUCTION

Due to the introduction of biodiesel usage in the past 10 years and trends to continue increasing until B20 in Brazil, changes of non-compatible materials with high concentration of biodiesel will be required by automakers. Using biodiesel as fuel source would generate many benefits such as: reducing the country's dependency on fossil fuels, the potential for increasing local industries, the strengthening of agricultural social programs in Brasil and overall benefits to the environment.[1] As the chemical composition of biodiesel is significantly different from petroleum diesel, biodiesel interacts with rubber compounds causing excessive swelling and loss of strength depending on the type of polymer based chain[2].

Biodiesel can be made from different types of oils by the trans esterification process. Sources of oil commonly used to produce biodiesel in Brazil are soybean, cotton seed, and animal fats. The participation of soybean oil to produce biodiesel in Brazil was of about 75% in the last year [3].

Biodiesel is commonly blended with petroleum diesel and blend concentration is indicated by the number following the letter B (B7 is a blend of 7% biodiesel and 93% petroleum diesel). Recently the Federal Senate in Brazil approved a 1% increase in the biodiesel portion of the blend to be implemented in July 2014 and 1% more in November 2014. Water content for distributors adopted was 150 mg/L and the oxidation stability was increased from 6 to 8 hours. The acidity number limited to 0,5 mg KOH/g have not changed [4].

Unsaturated points on NBR rubber may be the weakest point in the chain to react with biodiesel [2]. Higher percentages of acrylonitrile in nitrile rubber may be able to prevent such degradations [5]. Despite this fact, previous studies suggested rubber compounds seems to swell or degrade through reactions with polymer backbone and crosslink system or by reactions with filler system [2, 6].

Coronado et al. [7], evaluated the effect of different mixtures diesel-biodiesel with nitrile rubber fuel hoses at temperatures of 25 and 70°C. They concluded that higher

blend levels of biodiesel lead to higher material deterioration and the acid number of biodiesel increased with the exposure time.

The resistance to degradation of certain types of elastomers should be analyzed in depth because of the wide usage of rubber in the automotive industry. Many parts made from rubber materials could cause potential failures affecting safety among other attributes. NBR blended with PVC is used widely to mold automotive fuel hoses and fuel sender gaskets and these components come in constant contact with fuel. The manufacturers of such parts own the rubber formulation which is a mix of various components which could interact with biodiesel and there are multiple combinations, however, the formulation should meet the material specification or part performance.

According to Fang et al [8], calcium carbonate has been widely used as filler in plastics and rubber industry. The principal reason for this application is to reduce cost with less impact on tensile strength. It could be found in natural or could be chemically produced. In general this filler could be considered as a non-reinforcing. On the other hand, carbon blacks have been widely used as principal reinforcement element in rubber industry for more than one century [9]. With the incorporation of carbon black, the mechanical properties and fatigue resistance of rubbers can be greatly improved [10].

Although there are other rubber based polymer types with better degradation resistance against biodiesel such as fluorinated rubber (FKM) and hydrogenated nitrile butadiene rubber (HNBR), the interactions with fillers have not been investigated in depth. Therefore, the aim of this work is to investigate the degradation of carbon black and carbon black with calcium carbonate filled on PVC/NBR rubber matrix against B30.

In the review of state of the art [2, 5-10], there were not founded studies in which the assessment of the degradation of PVC/NBR rubber with different fillers has been made following the methodologies proposed in the current research.

## **2. MATERIALS AND METHODS**

### **2.1. MATERIAL SELECTION**

PVC/NBR with a proportion of 30/70 respectively and 45% of acrylonitrile in the NBR polymer were selected as the polymer base chain. Two samples with different type of fillers were tested. The type of filler of each sample carried was carbon black and carbon black with CaCO<sub>3</sub>.

### **2.2. TEST COUPONS PREPARATION**

The compounds were made in a standard internal mixer according to ASTM D3182 with the content according to Table 1 and the amount of ingredients used in each composition was proportional to 1.5 kg of NBR/PVC.

The mixing chamber produced a pre-mix without the accelerators in about 4 minutes. The NBR was first masticated for 1 minute and then the fillers, plasticizers, stearic acid and zinc oxide are added to the standard internal mix. The accelerator (TBBS) and cure agent (DTDM) was added only after the premix cooled for 2 hours at room temperature. Then the composition was passed through rollers at least six times and folded each time therefore there was complete dispersion of the ingredients added.

A small sample of each composition was analyzed on a moving die rheometer (MDR) series 2000 made by Alpha Technologies for 1hour at 170°C to determine the scorch time and cure time. Vulcanization was conducted in a hydraulic press in order to obtain square sheets (150 x 150 mm). The following mechanical test specimens were performed on the sheets: tensile strength, volume and hardness.

### **2.3. FUEL SAMPLES BIODIESEL**

B30 was obtained by a mix of B10 low sulfur (S10) with B100 both supplied by Ipiranga Produtos de Petróleo S/A. The biodiesel was obtained from soy bean oil. The standard ASTM D664 was applied for fuel acidity number measured after biodiesel B30

was blended. Acid number for biodiesel is lower than 0,5 mg KOH/g according to EN 14214 and ASTM D6751 standard fuels. This parameter is quite significant since it reveals fuel aggressiveness.

#### **2.4. TENSILE STRENGTH TESTING, SWELLING AND HARDNESS**

The tensile tests were conducted according to ASTM D412 on Alpha Technologies tensile tester T 2000. Dumbbell shaped specimens (Die C model) were used, with lengths of 115 mm. To determine the cross sectional area, the average thickness and width of each test specimen was the average value of three different measurements. The specimens were placed in the machine grips, which had a separation rate of  $500 \pm 50$  mm/min. The hardness test was performed on a durometer Shore A, Parabor, following ASTM D2240, and the tensile bars were plied to raise the thickness to 6 mm. The swell was measured according to ASTM D471.

#### **2.5. SEM ANALYSIS**

Test coupons were analyzed on a cryogenically fractured surfaces using a scanning electron microscope FEI model Inspect S50 in order to know about the changes occurred in their morphologies after 1008 hours in contact to B30 at 80°C.

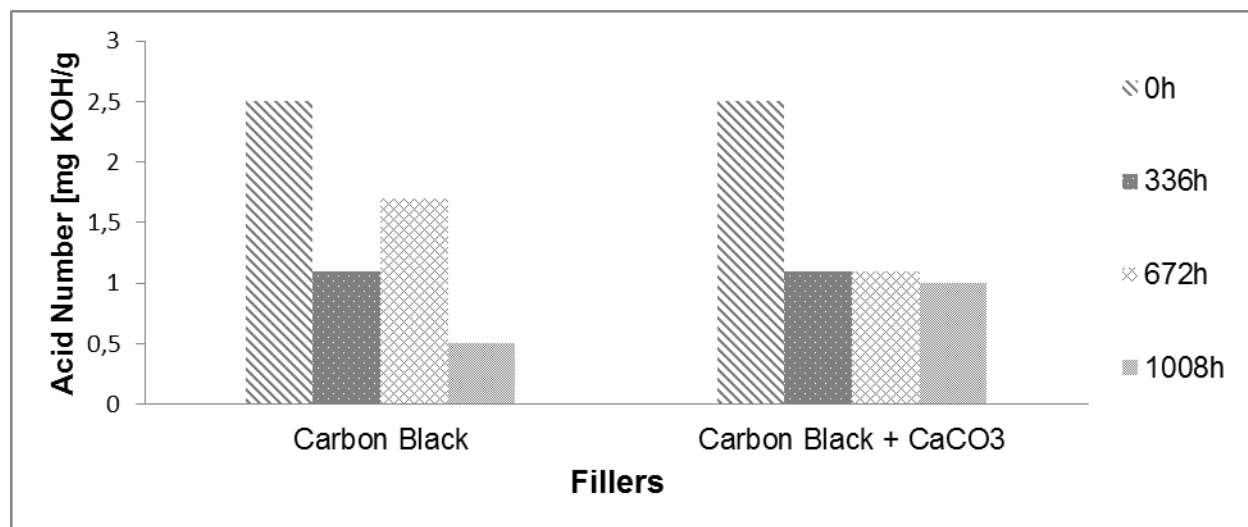
#### **2.6. EXPERIMENTAL CONDITIONS**

The specimens were placed in a fluorinated HDPE bottles and immersed in B30 at 80°C for 1008 hours. Every day the bottle is agitated and every two weeks the aged fuel is replaced and measured the acidity number. Mechanical proprieties were measured as follows: 0 and 1008 hours. Duplications of bottles with immersed samples were placed in a sand bath to improve the confidence level of values measured after the periods of removing samples. Values for hardness and swell were reported as an average of three measurements, tensile strength and elongations were reported as an average of five for original and ten for aged samples. Microscopy analysis was evaluated on the surface of a cryogenic fracture from original samples and 1008h after immersion in B30.

### 3. RESULTS AND DISCUSSION

#### 3.1. BIODIESEL ACIDITY CHANGE AFTER IMMERSIONS

In Figure 1 are presented the values of B30 acidity number before and after the immersions with the rubber compounds at 80°C. Before immersed this parameter is above the Brazilian regulation (0,5 mg KOH/g) and after in contact with rubber compositions the acidity number has reduced significantly for the compounds tested. The impact of carbon black to reduce acidity number was the most significant in the last change of fuel. The antioxidant present in the rubber compounds may have migrated to fuel portion and reacted to stabilize the products of biodiesel oxidation contributing to reduce acidity number.

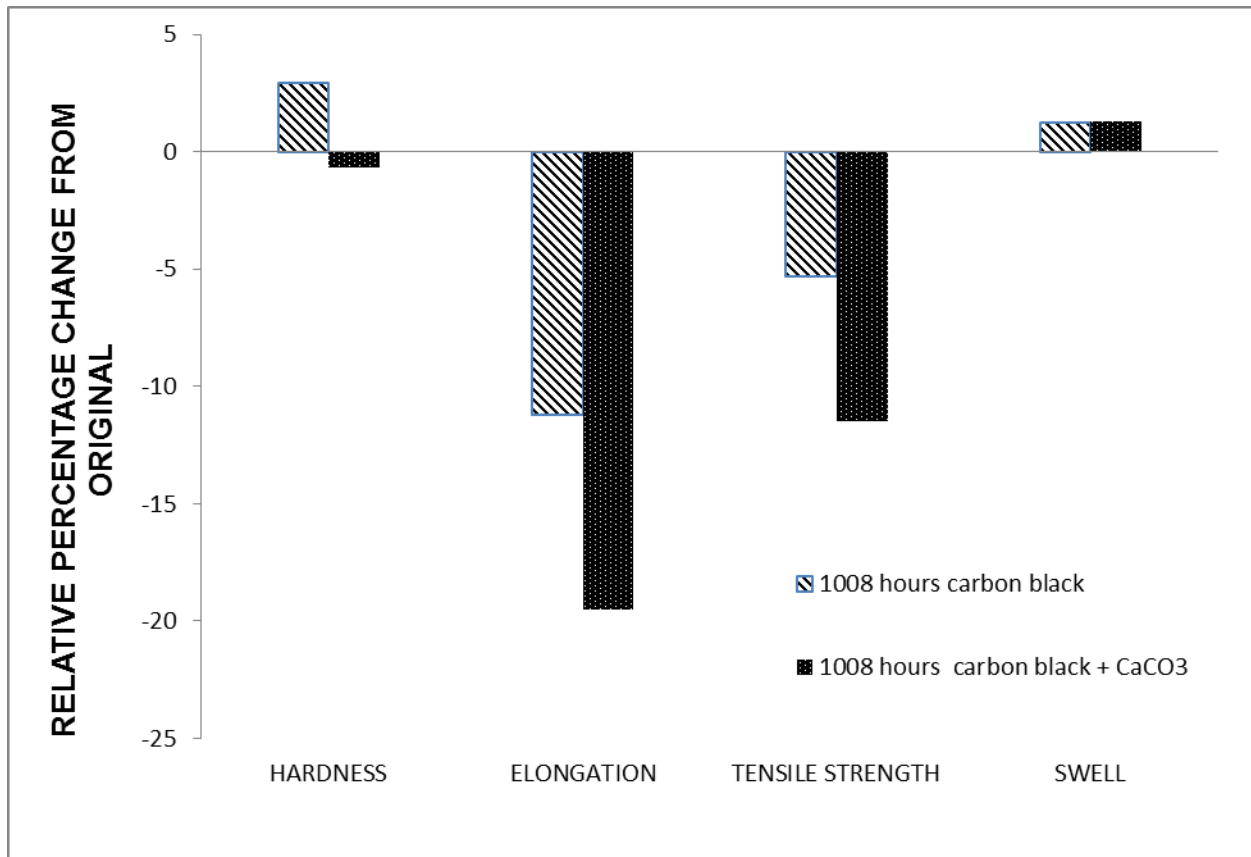


**Figure 1:** Acidity Change of B30 before and after contact with rubber samples

Acid number is a parameter directly related to the content of free fatty acids. It's considered as a measure of the corrosiveness and the degradation effect of biodiesel [7]. Antioxidants act to inhibit the oxidation process [11] and contribute to reduce the acidity number when added to biodiesel [12].

### 3.2. MECHANICAL PROPRIETIES CHANGE

Tensile properties are the most measured parameters after hardness. This is in part attributed to use of tensile strength as a general measure of quality [13]. Figure 2 shows the averaged results obtained by 2 replicated measurements of elongation at break, tensile strength at break and swelling after 1008 hours immersed in B30 at 80°C. The loss of elongation could represent the degradation of the polymer chain or an adsorption of fuel.



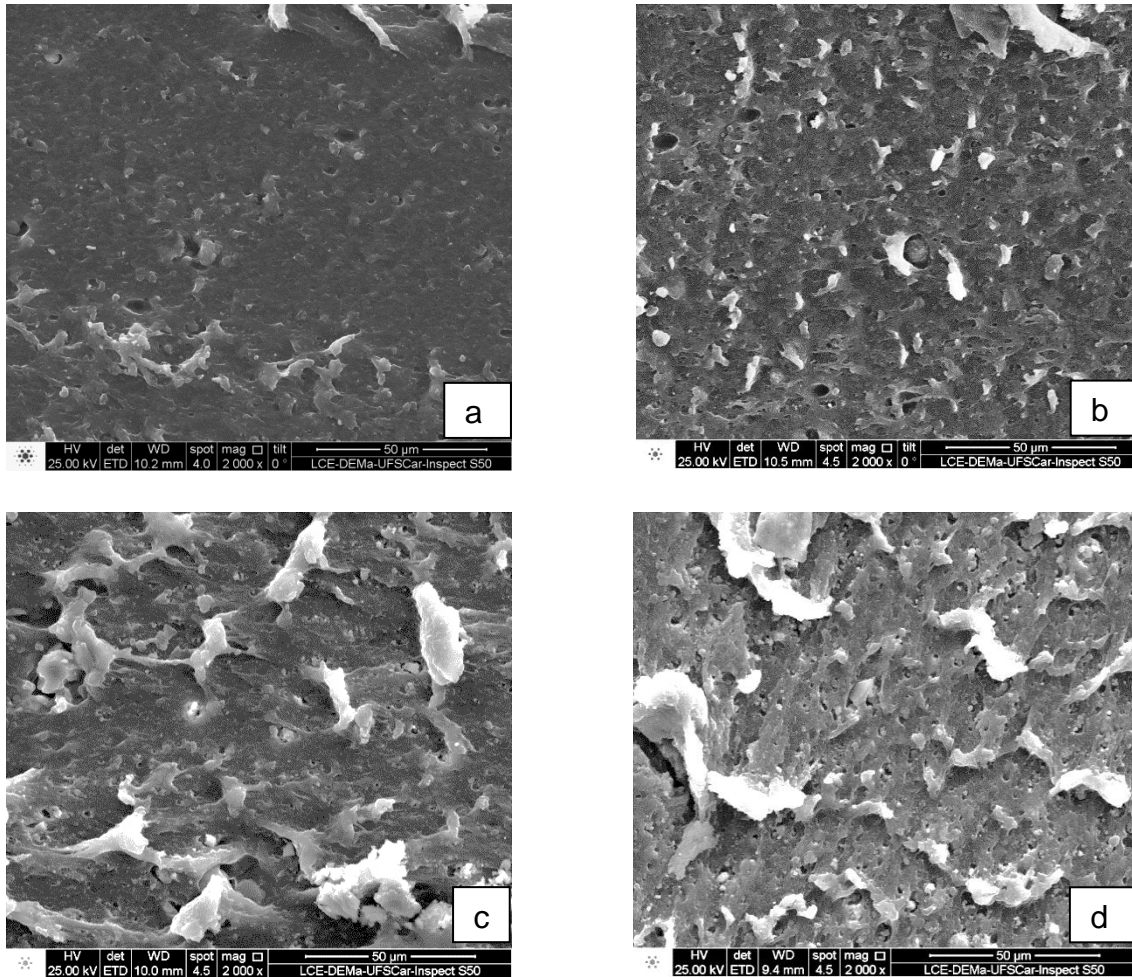
**Figure 2:** Loss of hardness, elongation at break, tensile strength, and swell after 1008 hours in B30 at 80°C.

As demonstrated in Figure 2, the compounds showed similar swell and the solvent action by fuel mixture contributing to changes in elongation at break since that the degradation process starts with the attack and penetration by solvent [7]. In addition carboxylic acids generated by biodiesel hydrolysis could react with sulfur crosslinks contributing to degrade the elastomer compound as reported by MITRA [12]. Elongation decreased greater in the sample containing carbon black with  $\text{CaCO}_3$  compound over the period tested compared with carbon black. A decrease of about 20% in the percentage change from original was observed for samples containing carbon black with  $\text{CaCO}_3$  while carbon black decreased of about 11%. Therefore it can be said that samples with only carbon black is more stable against B30 than carbon black  $\text{CaCO}_3$ .

### **3.3. SEM ANALYSIS**

Representative micrographs are presented in figure 3 for the surface of cryogenic fractured surfaces before and after aging for 1008h in B30 at 80°C. The surface morphology analysis through SEM of PVC/NBR with Carbon Black and  $\text{CaCO}_3$  showed more pits and cracks after aging in B30. This confirms the results obtained on higher loss of mechanical properties by adding a generic  $\text{CaCO}_3$  in the formulation of a carbon black filled PVC/NBR.





**Figure 3:** Scanning electron micrograph of cryogenic fracture surfaces: (a) PVC/NBR with carbon black unexposed to B30; (b) PVC/NBR with carbon black exposed 1008h with B30 at 80°C; (c) PVC/NBR with carbon black and CaCO<sub>3</sub> unexposed to B30; (d) PVC/NBR with carbon black and CaCO<sub>3</sub> exposed to B30

According to HASEEB (4), the reason to form pits can be attributed to the following steps:

- Macromolecular chain scission or crosslinking;
- Introduction of polar oxygen groups into elastomers.
- The microstructural changes can result in increasing of surface energy.
- Increasing the surface energy could lead to a localized decrease or increase in density.

This, in turn, may have modified the interactions of CaCO<sub>3</sub> particles generating a decoupling of elastomeric phase with a surface with more voids. As a result the loss in

mechanical properties almost double compared to the formulation only filled with carbon black.

#### **4. CONCLUSIONS**

Based on the results of mechanical tests which demonstrated the influence of PVC/NBR filled with carbon black and carbon black with  $\text{CaCO}_3$  of rubber fillers exposed to B30 over 1008h at 80°C it could be concluded that carbon black shows better resistance against B30 at 80°C than carbon black with  $\text{CaCO}_3$  that almost double the degradation and B30 acidity number seems to reduce after the contact with rubber specimens.

These conclusions points to a major influence of fillers compounds on mechanical properties degradation of PVC/NBR components applied in fuel system in contact to B30.

#### **5. ACKNOWLEDGEMENTS**

Support provided by Ford Poling funding and by the UFBA (Universidade Federal da Bahia)

#### **6. REFERENCES**

- [1] POUSA, G. P., SANTOS, A. L., & SUAREZ, P. A. (2007). History and policy of biodiesel in Brazil. *Energy Policy*, 35(11), 5393-5398..
- [2] HASEEB, A. S. M. A., MASJUKI, H. H., SIANG, C. T., & FAZAL, M. A. (2010). Compatibility of elastomers in palm biodiesel. *Renewable energy*, 35(10), 2356-2361.

[3] SOARES, Raquel Wayand; PINTO, Fernanda Vieira (Comp.). BOLETIM MENSAL DO BIODIESEL. 2015. Disponível em: . Acesso em: 01 jan. 2015.

[4] AGÊNCIA NACIONAL DO PETRÓLEO, GÁS NATURAL E BIOCOMBUSTÍVEIS. Lei nº 13.033, de 24 de setembro de 2014. Dispõe sobre a adição obrigatória de biodiesel ao óleo diesel comercializado com o consumidor final; altera as Leis nos 9.478, de 6 de agosto de 1997, e 8.723, de 28 de outubro de 1993; revoga dispositivos da Lei no 11.097, de 13 de janeiro de 2005; e dá outras providências.. Lei no 13.033, de 24 de Setembro de 2014. D.O.U., DF, 25 set. 2014. Seção 1, p. 3-3. Disponível em: . Acesso em: 17 mar. 2015

[5] LINHARES, F. N., CORRÊA, H. L., KHALIL, C. N., LEITE, M. C. A. M., & FURTADO, C. R. G. (2013). Study of the compatibility of nitrile rubber with Brazilian biodiesel. *Energy*, 49, 102-106.

[6] HASEEB, A. S. M. A., FAZAL, M. A., JAHIRUL, M. I., & MASJUKI, H. H. (2011). Compatibility of automotive materials in biodiesel: a review. *Fuel*, 90(3), 922-931.

[7] CORONADO, M., MONTERO, G., VALDEZ, B., STOYTCHEVA, M., ELIEZER, A., GARCÍA, C., ... & PÉREZ, A. (2014). Degradation of nitrile rubber fuel hose by biodiesel use. *Energy*, 68, 364-369.

[8] FANG, Q.; SONG, B.; TEE, T.-T.; SIN, L. T.; HUI, D.; BEE, S.-T. Investigation of dynamic characteristics of nano-size calcium carbonate added in natural rubber vulcanizate. *Composites Part B: Engineering*, Elsevier, v. 60, p. 561–567, 2014.

[9] TANG, Z., ZHANG, C., WEI, Q., WENG, P., & GUO, B. (2016). Remarkably improving performance of carbon black-filled rubber composites by incorporating MoS<sub>2</sub> nanoplatelets. *Composites Science and Technology*, 132, 93-100.

[10] ARABY, S., MENG, Q., ZHANG, L., ZAMAN, I., MAJEWSKI, P., & MA, J. (2015). Elastomeric composites based on carbon nanomaterials. *Nanotechnology*, 26(11), 112001.

[11] PULLEN, J., & SAEED, K. (2012). An overview of biodiesel oxidation stability. *Renewable and Sustainable Energy Reviews*, 16(8), 5924-5950..

[12] OBADIAH, A., KANNAN, R., RAMASUBBU, A., & KUMAR, S. V. (2012). Studies on the effect of antioxidants on the long-term storage and oxidation stability of Pongamia pinnata (L.) Pierre biodiesel. *Fuel processing technology*, 99, 56-63.

[13] MARK, J. E., ERMAN, B., & ROLAND, M. (EDS.). (2013). *The science and technology of rubber*. Academic press.

[14] MITRA, S., GHANBARI-SIAHKALI, A., KINGSHOTT, P., REHMEIER, H. K., ABILDGAARD, H., & ALMDAL, K. (2006). Chemical degradation of crosslinked ethylene-propylene-diene rubber in an acidic environment. Part I. Effect on accelerated sulphur crosslinks. *Polymer degradation and stability*, 91(1), 69-80..