Additives for the processing of natural rubber and their application in small rubber plantations[1]

Aditivos para el procesamiento del caucho natural y su aplicación en pequeñas plantaciones de caucho[1]

Recieved: 20- 09 - 2014 Accepted: 18-11-2014

Gabriel Jaime Peláez Arroyave[1]
Sandra Milena Velásquez Restrepo[2]
Diego Hernán Giraldo Vásquez[3]

[1] Final study report from the executed study, financed by the Gobernación de Antioquia. (Colombia), started in November 2013.

[2] Colombian, Materials Engineer, candidate to M.Sc., SENA researching instructor for the Leather Design and Manufacture Center in Itagüí, Antioquia. BIOMATIC group – Biomechanics, Materials, TIC, Design and Quality for the leather, plastic and rubber sector and their production chains.

[3] Colombian, M.Sc. in Engineering, M.Sc specialist in Management, leader of SENA Leather Design and Manufacture Center in Itagüí, Antioquia. BIOMATIC group – Biomechanics, Materials, TIC, Design and Quality for the leather, plastic and rubber sector and their production chains.

[4] Colombian, M.Sc in Engineering, professor of the Materials Engineering program of Universidad de Antioquia. Mechanical Engineer, Polymeric Materials Group.

Abstract

This study presents a literature review about how additives used in the production of natural rubber (NR) modify the properties of the liquid latex or dry rubber in the form of sheets or coagulate, products that can be obtained from small rubber plantations, which are abundant in Colombia. The advantages and disadvantages of using additives are considered, highlighting the reduction of the environmental impact and providing criteria to replace substances traditionally used that imply health risks. Few researches were found whose the main objective was to study the effect of the additives used during the production of liquid latex or solid rubber. Therefore, an attempt to identifying sections regarding the effects of the use of additives on liquid latex and solid rubber properties in natural rubber processing studies was conducted. A clear tendency to totally or partially remove the use of ammonia as latex stabilizer, and using natural substances such as some natural vinegars to replace formic and acetic acid in the fresh latex coagulating process, was identified. These are viable alternatives to be implemented in the processes that take place in small rubber plantations in Colombia.

Keywords: Processing; rubber cultivation; latex stabilization; latex coagulation.

Introduction

Since the discovery of vulcanization, in the mid-XIX century, rubber has increased its participation in the market to a level where it has become a highly utilized material in industries such as automotive, aerial (Hirata, Kondo and Ozawa, 2014), clothing and footwear (Smith and Burger, 1992), sealing of fluids (Chandrasekaran, 2010), hoses (Tully, 2011) and sports goods (De and White. 2001), to quote the most relevant examples. Some sources claim that the usage of rubber is an indirect measurement of global economic growth and the industrialization level of a country (Brunisma, 2003), in particular of the automotive sector growth, since between 65 and 70 % of the worldwide rubber production in tire fabrication (Original Equipment, Support, Industry and Service [OESS], 2008).

Although the development of synthetic rubbers in the mid-XX century markedly displaced natural rubber consumption, in the last two decades the natural rubber still represented the 40 % of the worldwide rubber market. (International Rubber Study Group [IRSG], 2014). A decisive factor for this tendency is the impossibility to develop synthetic rubbers that can meet the mechanical properties and hysteresis that natural rubber provides (Beilen and Poirier, 2007), due to its capacity to crystallize as effect of deformation (Le-Gac et al., 2014; Kohjiya et al., 2007; Murakami *et al*., 2002) and the amino acids present at the endings of their polymeric chains (Tuampoemsab, 2008); it is important to emphasize that after 60 years of research and development, there is no synthetic rubber with the same excellent cost/benefit of natural rubber (Beilen and Poirier, 2007; Vaysse, Sainte-Beuve, and Bonflis, 2003; Silva *et al*., 2012).

The tendencies described above have increased the worldwide demand for natural rubber in the last decades (OESS, 2008; FPT Securities Joint Stock Company, 2013), considering it as a commodity even comparable to palm oil or cacao. (Food and Agriculture Organization [FAO], 1990). Projections of the International Rubber Study Group – IRSG mark that for the year 2015, the world natural rubber demand will grow 4.4 % in comparison to 2014 (IRSG,2014), keeping the increasing behavior of the last years; it is estimated that by 2023, the demand of natural rubber will increase 60 % in respect to the actual consumption (IRSG, 2014; Alves *et al*.,2013).

Countries as Malaysia, Thailand, Viet Nam, Indonesia (Barlow, Jayasuriya, and Tan, 1994) and Guatemala (BusinessCol.com, 2008) found in the farming and processing of natural rubber, an important economic activity. Emulating these experiences, private and state entities have been decisively promoting the rubber culture in Colombia, taking account of the availability of land with the appropriate climate and soil conditions, as an attempt to mitigate poverty and exclusion, which is observed in some of the rubber producing regions, simultaneously, generating new opportunities for economic development (Clavijo, 2004; Espinal, *et al*., 2005). However, it is important to consider that nowadays, the national production of natural rubber is insufficient to meet the domestic market demand and unable to achieve the technical requirements demanded by the international market, therefore, the national natural rubber industry must upgrade and improve its productive processes, obtaining better technical specifications according to the industrial needs, and therefore, increasing their competitiveness (Blanco, 2009). The national production must implement rigorous quality standards to obtain latex and solid rubber with standardized properties satisfying the requirements of the national and international industries.

One of the main challenges for natural rubber culture in Colombia is that during the implementation of the plantations that currently exist, the vegetal material was not properly labeled, or was mixed with other clonal varieties, and consequently, there are plantations in which the species planted cannot be genetically identified with certainty. Because of this situation, some research studies have been conducted to solve this question (Blanco, 2009), gaining experience in the selection and handling of clones, which should be reflected in improvements of the material quality and the productivity of the plantations. Another relevant factor is the need to apply technology to the plantation management and processing, especially in small plantations because they have the largest need for retrofitting and upgrading; the lack of technology has turned into low productivity, and inadequate quality standards that have subtracted competitiveness to Colombian natural rubber (Espinal *et al*., 2005).

Considering that several additives can be used to control the properties of the natural rubber latex colloidal dispersion depending on the desired product: stabilized latex, sheets, coagulate, strip, crepe rubber or technically specified rubber (De and White, 2001; Espinal *et al*., 2005; Ministerio de Agricultura y Desarrollo,Rural MinAgricultura, 1992; Souza, 2013; Sridee, 2006), an interesting alternative to produce materials with low variability and high quality standards, consists in implementing the use of additives during harvesting, according to the studies reported in the specialized literature. This work presents a review of the published studies about this topic and describes the way that the additives modify the product's final properties when they are applied during latex harvesting process . It is also intended to propose alternatives that improve the processing of natural rubber that is effectuated in the small plantations that are plentiful in the national rubber industry, reducing variability of the product's properties, generating added value and fulfilling the technical requirements of the national and international industry.

Additives used in the processing of natural rubber

Several studies about the influence that the additives used during the mixing, vulcanization and forming have on the physical and mechanical properties of composites based on natural rubber have been published. Descriptions about the influence of the amount and types of vulcanization agents, activators (González, Álvarez, and Abreu, 2008), accelerants, (Travas- Sejdic *et al*., 1996; Kamoun, Nassour, and Michael, 2009), flame retardants (Na *et al*., 2013) and lubricants (Menon *et al*.,2002) on the mechanical properties of the natural rubber products can be found. Nevertheless, the influence of chemical additives and substances that are in contact with the rubber during the first processing stages and its effects on the properties of the final product are practically unknown and unexplored, even though the additives are known to affect these characteristics (Kongkaew *et al*., 2012; Intapun, 2009).

Among the main additives used in the rubber harvesting process, the latex stabilizers are needed to maintain the colloidal dispersion and preventing spontaneous coagulation, the preservatives help to avoid rubber putrefaction , the solvents are used to reduce the latex concentration facilitating its filtration and later lamination process, the acidifiers that regroup the molecules dispersed throughout the latex and separate them from the existing non-elastomeric products and the coagulants that take on concentrate the particles.

Liquid latex stabilizers

One of the mostly used latex stabilizers in the conventional natural rubber harvesting process is ammonium (normally as ammonia), which has favorable characteristics such as being a bactericide and deactivator of the magnesium ions. However, it also presents important disadvantages such as the generation of ammonium vapors that are harmful for the staff that works in the rubber production chain, and even it can be corrosive for the facilities where it is produced; another disadvantage is because its volatility, the concentration of the latex can vary with short storage periods, affecting the properties of the final product (Kongkaew, Loykulnant, and Chaikumpollert, 2012; Singh *et al*., 2014). It is common to find also the stabilization system composed by low concentration ammonia, tetramethyltriurane disulphite (TMTD) and zinc oxide (ZnO)(De and White, 2001), while being more easily manageable than the traditionally used ammonia, it does not completely solve the difficulties related to the use of ammonia. Due to the disadvantages of ammonia, tests of other alternatives for a stabilizing substance to substitute it have been done for 60 years, such as formaldehyde, sodium sulphite or bisulphite, sodium cyanide and sodium hydroxide, although none of them is as efficient as ammonia (Wisniewski and Rohnelt, 1947). Other compounds such as alkaline phenols, sulphurated acid salts, esteric acid salts, mixes of cinnamic acid, butylic alcohol, sulphuric acid and formaldehyde, amongst others (Kongkaew *et al*., 2012; Booten,Hashim, and Singh, 2011) have been developed and tested.

In a study conducted in Thailand, (Chaikumpollert *et al*.,2000), the country with the highest production of natural rubber in the world, a quest for a substitute for the ammonia/TDMT/ZnO stabilizer, which is the stabilizer mostly used in the country, was done with the objective of reducing the amount of ammonia present in the rubber harvesting to attenuate the negative effects already mentioned. Chemical additives such as Zinc Sulphate ($ZnSO_4$), silver nitrate ($AgNO_3$), proteic silver or colloidal silver, lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethanolamine (C_2H_7NO), 1,4-methyl hydroxybenzoate and 1,4-propylhydroxybenzoate were tested. The efficacy of the stabilization was measured through the determination of the number of volatile fatty acids (VFA number) and the microorganism count in a solution of the stabilized latex. It was found that the use of $ZnSO_4$ together with a low ammonia concentration (0.4 % in comparison to the 0.7 % used normally), as substitute for the TDMT/ZnO mix, it has the advantage of not forming the carcinogenic substance nitrosamine, besides that, it can be added as an aqueous solution. This new stabilizer reduced the VFA number in relation to the common mix after one month of stabilization process, keeping practically unaltered other characteristics of the latex, such as particle size and viscosity; besides, this compound helped to increase the antimicrobial effect of the stabilizer. The authors concluded that strong alkalis and organic alkalis also possess latex stabilization qualities.

In addition to the additives with anticoagulant properties, other phenol and crisol derivatives behave as germicide and fungicides, but acting by themselves they are not able to avoid the latex coagulation. Its effect is obtained when they are used in parallel with the anticoagulant properties of the stabilizers. One of the most known compounds is sodium chloropentane, commercialized as Santobrite® (Wisnewski and Rohnelt, 1947). However, in this review, no studies were found evaluating the influence of these type of additives in the final properties of natural rubber latex.

Additives for the production of sheets

In some occasions, some kind of diluent is used with the latex to facilitate filtering and laminating processes, being water the most used (Ministry of Agriculture and Rural Development, 1992), taking in account that this dilution process has a great influence in the viscosity and the colloid's structure (Cecil and Mitchell, 2005). The water dilution process is also used for the extraction of low molecular weight proteins present in the latex's colloidal solution, which are a cause of diverse allergies when they are in contact with the skin of those people that process latex and even those that manipulate the final product (Sussman, Beezhold, and Kurup, 2002; Tomazic-Jezic and Lucas, 2002; Shah and Chowdhury, 2011).

Some authors affirm that the dilution process done with water is not completely effective when removing proteins (Maznah *et al*., 2008a), thus, in their work, they submerged prevulcanized natural rubber latex films in a KOH solution and measured the protein content , the tensile mechanical properties and the crosslink density as a function of the solution's hydrogen potential (pH), which is a measurement of the acidity or alkalinity of the solution, indicating the concentration of hydronium (H_3O^+) ions. The investigation showed that the KOH solution allows reducing the amount of extractable proteins due to the fact that they are degraded, which facilitates their removal. However, the process causes a significant reduction in the crosslink density, which reduces the tensile strength and the elastic module, while the elongation at break increases.

Since the process of washing with alkali solutions reduced the final mechanical properties of the natural rubber (Maznah *et al*, 2008b), the same authors tried a new work on natural rubber latex with an acidifying solution of HCL at 7 % w/w, and evaluated the influence of this procedure on the same properties mentioned in the previous study, again, as a function of pH. The results showed that differently from the alkali solution washing process, this acidifying procedure reduced the amount of extractable proteins (due to the action of the acid, which turns them insoluble), with slight decreases in the crosslink density and the properties of tensile strength and elongation at break, and practically non altering the elastic module.

A method studied in Brazil for the processing of natural rubber sheets consisted in the use of acid smoke resulting from the local vegetal carbon production (Ferreira *et al*., 2005). Comparisons of the properties of sheets treated that way with sheets coagulated with acetic and formic acid solutions used traditionally were done. The results showed that hardness, tensile strength and elongation at break between all the sheets, did not present significant differences among them.

Vinegars of different plants such as coconut palm, bamboo, and eucalyptus have been tested as coagulating agents (Baimark and Niamsa, 2009; Prasertsit, Rattanawan, and Ratanapisit, 2011; Baimark *et al*., 2008; Mela *et al*., 2013). Comparing the coagulated sheets with those vinegars with sheets obtained by coagulation using traditional acetic and formic acids showed that those natural vinegars are efficient to be used as coagulating agents, since properties as dry rubber content, impurity content, Mooney viscosity and plasticity retention index are very similar for all coagulating agents, while the bactericidal properties and mechanical attributes like tensile strength and elongation at break of the coagulated sheets with natural vinegars were superior to those of the sheets coagulated with acetic and formic acids.

Antioxidants

Since natural rubber, like any other polymer, is susceptible to oxidative degradation which decreases some physical properties, other important additives for the processing of latex are the antioxidants (Abad *et al*., 2002). The oxidation of natural rubber is due to the formation of free radicals that can propagate the rupture reactions of the rubber molecule (Al-Malaika, 1991; Bernard and Lewis, 1988), therefore the antioxidants, whether natural or synthetic, prevent this oxidative reaction. The aminoacids non soluble in water, have shown to have antioxidant properties, such as cystine, asparagine and alanine, which have attenuated the aging of natural rubber latex (Abad *et al*., 2002; Sasiradhan *et al*., 2001). Looking to improve the low resistance of aged-epoxied natural rubber (ENR), Luo *et al*., (2012) showed that the use of neodymium stearate as thermal stabilizer, up to an optimal concentration, it can accelerate the vulcanization process and slightly increase the tensile strength and the elongation at break, however, slightly reducing the crosslink density. Yang *et al*.,(2013) showed that the addition of antioxidants as 2,2,4-polytrimethyl-1,2-dihydroquinoline, N-isopropyl-N'-phenyl-p-phenyl-enediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylendianine and 2-mercaptobenzimidazole generates different values of crosslink density, tensile strength and thermal aging resistance , therefore, the choice of the antioxidant must be based on the final properties desired.

Taking into account that in the international market, there are available over 40 types of different dry natural rubber specification profiles (De and White, 2001; Naranjo, 2013), among them: the technically specified rubbers (TSR) in blocks, the grades without technical specification types such as crepe rubber and sheets (Cecil and Mitchell, 2005), the choice of the additives must consider the type of rubber to be obtained since the classification system comprise the coagulation system and the dry rubber's properties (American Society for Testing and Materials, ASTM, 2011). For example, to obtain a TSR-L dry rubber type, the latex must be stabilized with ammonia or an ammonia/boric acid mix. Immediately after the coagulates formation, a 0.05 % w/w of sodium metabisulphate must be added to avoid the appearance of yellow color in the material, and finally, the latex should be coagulated without dilution using formic acid, up to a pH of 5. On the other hand, the SMR-CV type rubber is obtained by adding 0.15 % w/w of neutral hydroxylamine sulphate to the latex previously preserved with ammonia, before the acid coagulation process (Elastotec Industria e Comercio de Artefatos de Borracha Ltda, ELASTOTEC).

Environmental impact mitigation

A marked tendency observed in the most recent studies, has been the search for "green" additives, it meaning, substances that produce little or none environmental impact, that could be able to substitute some of the additives traditionally used, considering that mostly of them are toxic. In a study performed by Gong *et al*. (2013), biodegradable dialdehyde sodium alginate was exploited for the immobilization of the extractable proteins present in the latex, which cause allergies, looking to remove the dilution stage, previously described. The results showed that the use of this additive reduced the amount of extractable proteins below the maximum limits permitted by the standards that regulate this parameter such as ASTM D5712, without altering significantly the mechanical properties and even further, improving the degradability of coagulated latex sheets.

Sasidharan *et al*, (2001) vulcanized latex by exposing it to γ radiation, avoiding the use of some additives such as accelerants and zinc oxide that was used as stabilizer. The reduction in the amount of chemical agents is important for the fabrication of added value products such as surgery gloves, examination gloves, preservatives, catheters and so on. Meanwhile, the control of the mechanical properties of this type of products will depend indirectly of the action of other additives (coagulant agent mainly) and the influence of parameters of the process subsequent to latex treatment.

Aspects of the processing in colombia that should be evaluated

Some differences between certain stages of the natural rubber harvesting in Colombia and the one described in specialized literature were detected. The main difference found is that while in Colombia the stabilization of fresh field latex is only applied when seeking liquid latex (SENA, 2006; Andrade and Prada, 2005), in some studies that were consulted it was found that the stabilization stage is conducted even in the collection cups during the harvesting for production process of concentrated latex as well as dry rubber (How Products are Made; Intapun, 2009; De y White, 2001; Marimim *et al*., 2014). Additionally, in the Colombian plantations, there is no use of antioxidants, bactericides or solvents different than water, therefore it is relevant that the additives referenced in this document can be considered as options to improve the process.

Conclusions

Although few studies which evaluated the influence of the chemical additives used during the harvesting on mechanical and physical properties of natural rubber were found, there is relevant information that can be extracted from the studies related with the characterization and/or processing of natural rubber. There is far more information about the use of additives during the process of mixing and vulcanization of rubber compounds, that is to say, when using natural rubber in industrial formulations, nevertheless, it is pertinent to implement improvements from the harvesting process of natural rubber as a raw material.

It was identified that during the processing of natural rubber for the production of both stabilized latex as well as dry rubber, certain substances that can affect the health of those who work or participate in the rubber production chain have been traditionally used. In specialized literature, it can be found references of the use of better additives which are very promising to substitute these traditional substances, without altering the properties of natural rubber and even improving some of them. In addition, the fact that the natural rubber production is becoming an interesting alternative for economic and social development of some regions of Colombia that have available lands, apt soils and favorable climate, make the authors of this research, address and present some alternatives to implement additives that could improve the productive processes actually used in the national industry seeking to obtain natural rubber with international quality standards. but that this economic activity requires to improve the productive processes to,.

The main tendencies found in the literature have to do with the use of zinc sulphate to stabilize the latex, reducing substantially the use of ammonia and avoiding the formation of nitrosamine, which is a carcinogenic substance, with the additional advantage that it can be added as an aqueous solution. To obtain dry rubber, it was found research works that are well advanced, showing that an acidifying solution of HCl 7 % w/w helps to improve the effect of the dilution, as well as the use of natural vinegars of coconut palm, bamboo and eucalyptus or acid smoke generated throughout the production of vegetal carbon for coagulation, could be an option to replace the industrial acetic acid and formic acid. In addition, studies that report successfully use of non-water soluble aminoacids such cystine, asparagine and alanine to avoid natural rubber oxidation were found.

The results obtained show that there are viable alternatives to be implemented on small plantations, to facilitate processing, improving the resistance to oxidation of natural rubber and reducing the risks for the environment and the health of the staff working in the process. However, it was identified that it is also necessary to deepen in the effect of the use of these additives on the latex's properties and the dry rubber produced, because even though some of the studies report low influence of the additives on the final physical and mechanical properties of the product or improves in some of them, it is a research line that should be explored more deeply.

Greetings

The authors thank the Gobernación of Antioquia for the financing of the project "Improving productivity for development and increase of competitiveness in the natural rubber chain, through an applied research program and innovation in the department of Antioquia." which permitted and facilitated the elaboration of this work.

References

Ministerio de Agricultura y Desarrollo Rural. (05 de 1992). *Agronet.* Recuperado el 02 de 09 de 2014, de http://www.agronet.gov.co/www/docs_si2/El%20cultivo%20del%20caucho.pdf

OESS . STN C.N & su Industria. (2008). *Comportamiento del Caucho Natural en Colombia y el Mundo 2002-2008.*

Abad, L., Relleve, L., Aranjilla, C., Aliganga, A., San Diego, C., Dela Rosa, A. (2002). Natural antioxidants for radiation vulcanization of natural rubber latex. *Polymer Degradation and Stability*, págs. 275-279.

Al-Malaika, S. (1991). Mechanisms of antioxidant action and stabilization technology - the Aston experience. *Polymer Degradation and Stability*, págs. 1-36.

Alves, L. C., Rubinger, M. M., Tavares, E., Janczak, J., Pacheco, E. B., Visconte, L. L., (2013). Synthesis, Spectroscopic Characterization, Crystal Structure and Natural Rubber Vulcanization Activity of New Disulfides Derived form Sulfonyldithiocarbimates. *Journal of Molecular Structure*, págs. 244-251.

American Society for Testing and Materials. (2011). *Standard Specification for Natural Rubber (NR) Technical Grades.* West Conshohocken: ASTM .

Andrade, A., Prada, L. (2005). *Diseño Básico de una Planta Procesadora de Látex de Caucho Natural para Diferentes Capacidades de Producción.* Trabajo de Grado, Universidad Industrial de Santander, Escuela de Ingeniería Química, Bucaramanga.

Baimark, Y., Niamsa, N. (2009). Study on wood vinegars for use as coagulating and antifungal agents on the production of natural rubber sheets. *Biomass and Bioenergy*, págs. 994-998.

Baimark, Y., Threeprom, J., Dumrongchai, N., Srisuwan, Y., Kotsaeng, N. (2008). Utilization of Wood Vinegars as Sustainable Coagulating and Antifungal Agents in the Production of Natural Rubber Sheets. *Journal* *of Environmental Science and Technology*, págs. 157-163.

Barlow, C., Jayasuriya, S., Tan, S. (1994). *The world rubber industry.* Londres: Routledge.

Beilen, J. B., Poirier, Y. (2007). Establishment of New Crops for the Production of Natural Rubber. *Trends in Technology*, págs. 522-529.

Bernard, D., Lewis, P. (1988). Oxidative ageing. *Natural Rubber Science and Technology*, págs. 21-75.

Blanco, F. E. (2009). Paternidad del Caucho Natural en Colombia. *Universidad Nacional.* .

Booten, K., Hashim, B., Singh, M. (2011). *Patente nº EP2132231 B1.* Francia.

Bruinsma, J. (2003). *World Agriculture: Towards 2015/2030 - An FAO Perspective.* USA.

Burger, K., Smit, H. (1997). *Rubber Market: Review, analysis, policies and outlook.* Cambridge: Woodhead Publishing Ltda.

BusinessCol.com. (24 de 07 de 2008). *Caucho guatemalteco destaca en mercado internacional.* Recuperado de http://www.businesscol.com/noticias/fullnews.php?id=4584

Cecil, J., Mitchell, P. (2005). *Processing of Natural Rubber.* FAO.

Chaikumpollert, O., Loykulnant, S., Chaveewan, K., Suchiva, K. (2000). Developmetn of Preservative for Natural Rubber Latex. *Proceedings of IV International Conference of Materials Science and Techonology*, (p.15). Bangkok, Tailandia.

Chaiprapat, S., & Sdoobee, S. (2007). Effects of wastewater recycling from natural rubber smoked sheet production on economic crops in southern Thailand. *Resources, Conservation and Recycling*, p. 577-590.

Chandrasekaran, C. (2010). *Rubber Seals for Fluid and Hydraulic Systems.* Oxford: Elsevier.

Clavijo, J. (2004). *El caucho natural, alternativa viable para tierras marginales cafeteras y cultivo promisorio para la sustitución manual de cultivos ilícitos.* Trabajo de grado de especialización, Universidad Nacional de Colombia, Facultad de ciencias y administración, Manizales.

De, S. K., White, J. R. (2001). *Rubber Technologist's Handbook Volume 1.* UK: Rapra Technology Limited.

Elastotec Indústria e Comércio de Artefatos de Borracha Ltda. (s.f.). *Elastotec Artefatos de Borracha.* Recuperado de http://www.elastotec.com.br/publicacoes_tecnicas/ELASTOTEC_Borracha_Natural.pdf

Espinal, C., Martinez, H. J., Salazar, M., Barrios, C. A. (03 de 2005). *La cadena del Caucho en Colombia. Una mirada Global de su Estructura y Dinámica.* Recuperado de Agrocadenas: www.agrocadenas.gov.co/caucho/documentos/caracterizacion_caucho.pdf.

Ferreira, V., Rêgo, I., Pastore, F., Mandai, M., Mendes, L., Santos, K., (2005). The use of smoke acid as an alternative coagulating agent for natural rubber sheets' production. *Bioresource Technology*, p. 605-609.

Food and Agriculture Organization of the United Nations. (1990). *Commodity Review and Outlook 1989-1990.* Roma, Italia: FAO Economic and Social Development Series.

FPT Securities Joint Stock Company. (2013). *Natural rubber industry report 2013.* Vietnam.

Gong, Y., Liu, G., Peng, W., Su, X., Chen, J. (2013). Immobilization of the proteins in the natural rubber with dialdehyde sodium alginate. *Carbohydrate Polymers*, pp. 1360-1365.

González, R. A., Álvarez, E., Abreu, K. (2008). Influencia de los Adtivos sobre las Propiedades Mecánicas de los Elastómeros. *Tecnología Química*, pp. 26-34.

Hirata, Y., Kondo, H., Ozawa, Y. (2014). Natural Rubber (NR) for the Tyre Industry. En S. Kohjiya, & Y. Ikeda, *Chemistry, Manufacture and Applications of Natural Rubber* (pp. 325-342). Cambridge: Woodhead Publishing Limited.

How Products are Made. (s.f.). Recuperado de http://www.madehow.com/Volume-3/Latex.html

Intapun, J. (2009). *Study of the Effects of biological Maturation fo Coagula of Hevea Brasiliensis Latex on Dry Rubber Properties.* Tesis doctoral, Montpellier SupAgro, Doctoral School "Process Sciences - Food Sciences".

International Rubber Study Group. (08 de 07 de 2014). *International Rubber Study Group*. Recuperado de http://www.rubberstudy.com/news-article.aspx?id=5071&b=default.aspx

Kamoun, M., Nassour, A., Michael, N. (2009). The Effect of Novel Binary Accelerator System on Properties of Vulcanized Natural Rubber. *Advanced in Materials Science and Engineering*, pp. 1-7.

Kohjiya, S., Tosaka, M., Furutani, M., Ikeda, Y., Toki, S., Hsiao, B. (2007). Role of stearic acid strain induced crystallization of crosslinked natural rubber synthetic cis-1,4 - polyisoprene. *Polymer, 48*(13), págs. 3801-3808.

Kongkaew, C., Dokkhan, C., Pattanawanidchai, S., Chaikumpollert, O., Loykulnant, S. (2012). Factors affecting creaming efficiency of bio-based polymers, vulcanization and mechanical properties of creamed skim rubber. *Biomass and Bionenergy*, pp. 233-241.

Kongkaew, C., Loykulnant, S., Chaikumpollert, O. (2012). *Patente nº 254424.* India.

Le-Gac, P.-Y., Arhant, M., Davies, P., Muhr, A. (2014). Fatigue behaviour of natural rubber in marine environment: comparison between air and sea water. *Materials and Design*, p. Accepted Manuscript.

Luo, Y., Yang, C., Wang, Y., He, C., Zhong, J., Liao, S., (2012). Effect of neodymium stearate on cure and mechanical properties of epoxidized. *Journal of Rare Earths, 30*(7).

Marimim, Darmawan, M., Machfud, Putra, M., Wiguna, B. (2014). Value chain analysis for green productivity improvement in the natural rubber supply chain: a case study. *Journal of Cleaner Production*, pp. 1-11.

Maznah, K., Baharin, A., Hanafi, I., Azhar, M., Hakim, M. (2008). Effect of soaking in potassium hydroxide solution on the curing, tensile properties and extractable protein content of natural rubber latex films. *Polymer Testing*, pp. 1013-1016.

Maznah, K., Baharin, A., Hanafi, I., Azhar, M., Hakim, M. (2008). Effect on acid treatment on extractable protein content, crosslink density and tensile properties of natural rubber latex films. *Polymer Testing*, pp. 823-826.

Mela, E., Arkeman, Y., Noor, E., Azam, N. (2013). Potential Products of Coconut Shell Wood Vinegar. *Research Journal of Pharmaceutical, Biological and Chemical*, pp. 1480-1493.

Menon, A., Aigbodion, A., Pillai, C., Mathew, N., Bhagawan, S. (2002). Processability characteristics and physico-mechanical properties of natural rubber modified with cashewnut shell liquid and cashewnut shell liquid–formaldehyde resin. *European Polymer Journal*, pp. 163-168.

Murakami, S., Senoo, K., Toki, S., & Kohjiya, S. (2002). Structural development of natural rubber during uniaxial stretching by in situ wide angle X-ray diffraction using a synchrotron radiation. *Polymer, 43*(7), págs. 2117-2120.

Na, W., Long, M., Yuxian, W., Xiangzhou, W., Quinghong, F. (2013). Enhanced Flame Retardancy of Natural Rubber Composite with Addition of Microencapsulated Ammonium Polyphosphate and MCM-41 Fillers. *Fire Safety Journal*, pp. 281-288.

Naranjo, L. (2013). *Estudios sobre el Mercado del Caucho Natural para la Fabricación de Materia Prima y Productos en la Planta de Santa Clara en Tarazá Antioquia.* Trabajo de Grado, Universidad EAFIT, Medellín.

Prasertsit, K., Rattanawan, N., Ratanapisit, J. (2011). Effects of wood vinegar as an additive for natural rubber products. *Songklanakarin Journal of Science and Technology*, pp. 425-430.

Ranta, P., Ownby, D. (2004). A Review of Natural-Rubber Latex Allergy in Health Care

Workers. *Healthcare Epidemiology*, pp. 252-256.

Sasiradhan, K., Joseph, R., Rajammal, G., Viswanatha, P., Gopalakrishnan, K. (2001). Studies on the dipping characteristics of RVNRL and NR latex compounds. *Journal of Applied Polymer Science*, pp. 3141-3148.

Servicio Nacional de Aprendizaje. (2006). *Estudio de Caracterización Ocupacional del Sector del Caucho Natural en Colombia.* Observatorio, SENA, Mesa Sectorial del Caucho, Bogotá.

Shah, D., Chowdhury, M. (2011). Rubber Allergy. *Clincs in Dermatology*, pp. 278-286.

Silva, J., Scaloppi Jr, E., Moreno, R., Souza, G., Gonçalves, P., Scarpare, J. (2012). Producción y propiedades químicas del caucho en clones de Hevea según los estados fenológicos. *Pesquisa Agropecuária Brasileira, 47*(8): 1066-1076.

Singh, M., Esquena, J., Solans, C., Booten, K., Tadros, T. (2014). Influence of hydrophobically modified inulin (INUTEC NRA) on the stability of vulcanized natural rubber latex. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, pp. 90-100.

Smit, H., Burger, K. (1992). The Outlook for Natural Rubber Production and Consumption. En M. Sethuraj, & N. Mathew, *Natural Rubber: Biology, Cultivation and Technology* (págs. 26-50). Amsterdan: Elsevier.

Souza, A. (2013). *Estudo Experimental do Comportamento Viscoelástico Não Linear de Buchas de Borracha Sob Solicitações Estáticas e Dinâmicas.* Brasil: Universidad federal de Itajubá.

Sridee, J. (2006). *Rheological Properties of Natural Rubber Latex.* Tailandia: Suranaree University of Technology.

Sussman, G., Beezhold, D., Kurup, V. (2002). Allergens and natural rubber proteins. *Journal of Allergy and Clinical Immunology*, pp. 33-39.

Tomazic-Jezic, V., & Lucas, A. (2002). Protein and allergen assays for natural rubber latex products. *Journal of Allergy and Clinical Immunology*, pp. 40-46.

Travas-Sejdic, J., Jelencic, J., Bravar, M., & Fröbe, Z. (1996). Characterization of the Natural Rubber Vulcanizates Obtained by Different Acelerators. *European Polymer Journal*, pp. 1395-1401.

Tuampoemsab, S. (2008). *Control of the degradation of natural rubber: analysis and application of naturally occuring anti- and pro-oxidants in natural rubber.* Tesis de Doctorado, Mahidol University, Tailandia.

Tully, J. (2011). *The Devil's Milk: A Social history of Rubber.* New York: Monthly Review Press.

Vaysse, L., Sainte-Beuve, J., & Bonflis, F. (2003). Still current challenge for rubbertechnology: find new criteria for the prediction of manufacturing behavior of natural rubber. *IRRDB Annual Symposium "Challenge for natural rubber in globalisation".* Chiang Mai.

Whelan, A., Lee, K. (Edits.). (1979). *Developments in Rubber Technology* (Vol. 1). Barking, Essex, Inglaterra: Applied Science Publishers Ltda.

Wisniewski, A., Rohnelt, R. (1947). *A Prática da Concentração do Látex.* Brasil: Instituto Agronómico do Norte.

Yang, C., Luo, Y., Chen, B., Xu, K., Zhong, J., Peng, Z., (2013). Effect of types of antioxidants on crosslink density and tensile properties of epoxidized natural rubber. *Advanced Materials Research*, pp. 824-827.