The importance of the order of addition of ingredients in the natural rubber (NR) mixing process: A qualitative analysis through molecular modeling

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ABSTRACT
The order of addition of ingredients in an elastomeric formulation of natural rubber was investigated using molecular modeling and the hypothetical adsorption process. Two sequences were evaluated, the zinc oxide system (ZnO) and the stearic acid system (C18), through the AMBER force field methodology. The theoretical data allow us to suppose that, although there is no statistically relevant difference between the adsorption energies, the C18 system does not seem to bring advantages in its adoption while the ZnO system only seems to be effective when the sequence suggested by the ASTM standard is obeyed. A seemingly ideal addition order in the ZnO system is suggested, but the nature of the adsorption process is changed, as is the arrangement of the additives.

Keywords: Molecular modeling, adsorption, mixture, elastomer.

1 INTRODUÇÃO

The formulation of a rubber can be understood as the art and science of the correct choice of various ingredients in a composition, as well as the quantities to be mixed. Thus, adequate elastomeric compositions are achieved from the point of view of processing and meeting or exceeding the performance expectations of the generated product. In addition, such compositions must be cost-effective. Consequently, the three P's of elastomeric composition are price, processing, and properties. It is still necessary to consider the issue of health, safety and environmental aspects related to the ingredients present in the composition and the derived compounds, which are found both in rubber and in the final artifacts (DICK, 2001; Campbell, 2016).

When the mixing process is completely performed in an open mixer, the uniformity of the process is conditioned to a program, which indicates the times and sequence of addition of the various ingredients of the elastomeric formulation, as well as the number and type of "cuts" to1 be made. In addition, it is necessary that the mixer has an efficient cooling system, so that the temperature of the cylinders does not rise progressively and without control. Although there are process variables (temperature and distance of the cylinders; order and times of addition of the ingredients; and, number, type and times of the cuts to be made), what often happens in practice is that the mixing processes are

carried out in a more or less empirical way, that is, with additions of ingredients made at any time and without defined order (CTB, 2022).

Thus, the objective of this manuscript is to investigate, through molecular modeling, the possible modifications that may arise when the different chemical species, present in the elastomeric formulation, interact in different orders of addition in the natural rubber matrix (NR). Therefore, the adsorption energies were analyzed through molecular mechanics using the family of force fields designated as AMBER.2

2 EXPERIMENTAL

In order to obtain the conformational analysis of the molecules and the minimum energy state, the HyperChem 8.0 programÔÒ was used. The guidelines chosen for the determination of adsorption energy were: molecular mechanics with AMBER force fields; Polak-Ribiere optimization algorithm; convergence conditions of the RMS gradient equal to 10-2 kcal/Å.mol; and, modeling under vacuum conditions. In order to determine some specific parameters of the chemical species such as polarizabilitya (), dipole momentm (), hardnessh (), electrophilicity (w) and the electrostatic potential map (MPE), the semi-empirical method PM3 was chosen.

Figure 1: Spatial model of overlapping spheres for the crystal that simulates the elastomeric matrix of natural rubber
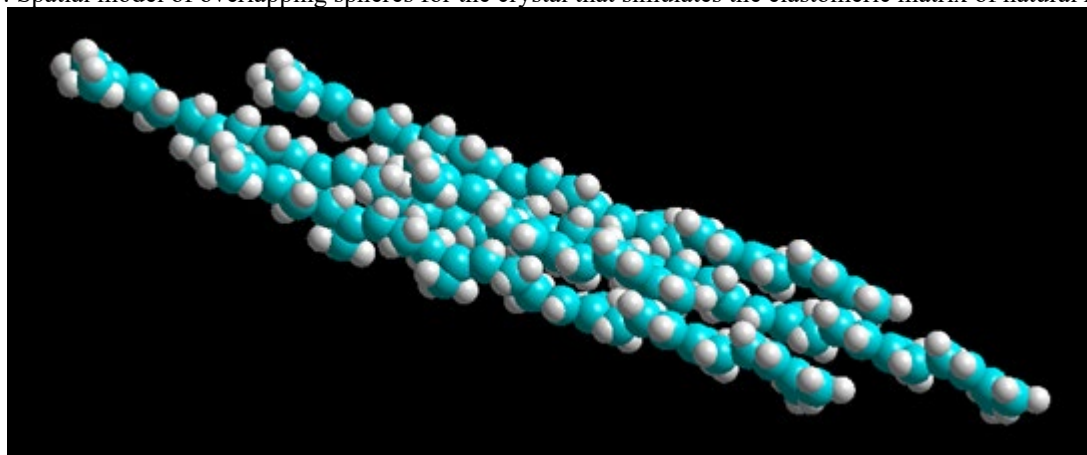

The molecule of squalene (C30H50) or 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahhexene was selected as the model compound for natural rubber. In order to simulate the elastomeric matrix, a hexagonal crystal was generated (lengths of edges a, b and c equivalent to 10 Å, 10 Å and 20 Å, respectively; and, the angles, and a of the edges equivalent tob 90, 90g and 120, ° ° °respectively) containing a number of unit cells of 1 x 1 x 1, as shown in Figure 1.

The Hypothetical formulation for the theoretical study of the effect of the order of addition of ingredients in the NR matrix was based on the following additives: activators – zinc oxide (ZnO) and stearic acid (CH3(CH2)16COOH or C18); vulcanizing agent – sulfur (S8); accelerator – N-[1,3-

benzothiazol-2-yl) sulfanyl]cyclohexanamine (CBS)3; and, the antioxidant – 2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione (TMQ)4. The zinc oxide structure constructed for the molecular simulation is shown in Figure 2.

Figure 2: Hypothetical structure of ZnO created for molecular simulation. Spheres in red represent the oxygen atoms, while the spheres in violet represent the zinc atoms
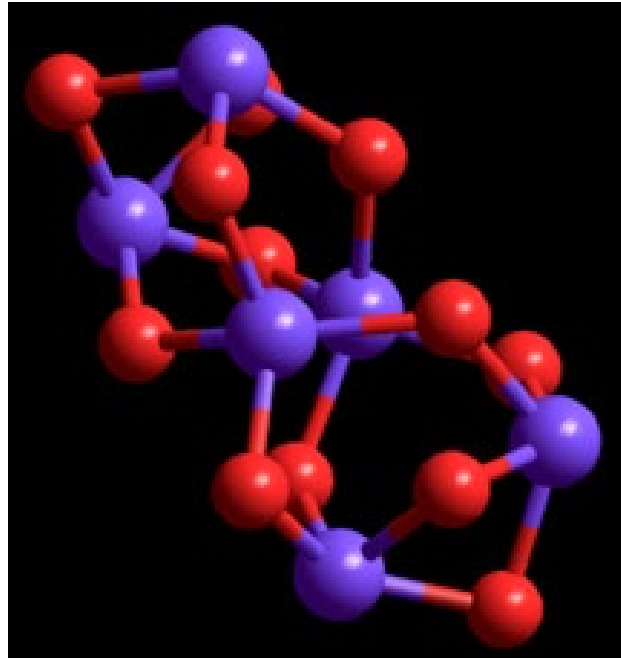
The experimental procedure followed the following steps:

    i.   Calculation of the potential energy of each molecule of each ingredient in the most stable conformational state;

    ii.   Calculation of the potential energy of the hypothetical crystal of NR;

    iii.   Calculation of the potential energy of the system: NR and additives; and

    iv.   Calculation of the adsorption energy using Equation 1:

$$E_{adsor\,ção} = U_i^{sistema} - \sum U_i \quad Eq.\,1$$

Where: U_i is the potential energy of the additive i or the crystal of NR; and, $U_i$system is the potential energy of system i created by the order of addition.

It is important to note that the The potential energy of the AMBER fields obeys a function of four sums, according to Equation 2. The first three summations refer to the potential energy of the covalent bond, while the last term refers to the non-covalent interactions (electrostatic and van der Walls).

The meanings of each term are (AMBER, 2022):

- Sum of bond: represents the energy between two covalently bonded atoms. The bond is considered a spring, and for this reason, it is described by the harmonic function of the ideal spring. The term Kr refers to the spring constant of the bond, there are also the terms of the bond distance and the equilibrium distance (field parameter);

- Sum of the angle: represents the angular energy between three covalently bonded atoms. Following the same principle of the item mentioned above, the energy will refer to the perturbation of the angle considered compared to the equilibrium angle of the trio of atoms;

- Dihedral summation: represents the energy of the torsion of a bond over its order and the bonds of the surroundings or isolated pairs of electrons; and

- Last term: represents the non-covalent forces acting on the system, such as electrostatic interactions and van der Walls interactions. The first two terms within this summation refer to van der Walls interactions, which in the case of this family of force fields, uses the Lennard-Jones potential. The latter term, in turn, describes the electrostatic interactions described by Coulomb's laws.

3 RESULTS AND DISCUSSION

3.1 ANALYSIS OF INDIVIDUAL SPECIES

Polarizability (a) of the molecules corresponds to the ease of deformation of the electron clouds. Very polarizable molecules are those in which the charge of the nucleus has little control over the surrounding electrons, perhaps because the atoms are bulky or because the valence electrons are shielded effectively by the electrons inside. Electron density can fluctuate a lot, and therefore very polarizable molecules can have instantaneous dipole moments and strong London interactions (ATKINS and JONES, 2012).

In turn, when atoms with different electronegativities are bonded, the resulting molecule has polar bonds and an electric dipole is formed, a partial positive charge close to an equal but negative partial charge. The greater the electronegativity difference, the more polar the bond, and the size of the electric dipole – a measure of the magnitude of partial charges – is called the electric dipole moment (m). Molecules with dipole moments interact electrostatically with each other and with other polar molecules. When the dipoles are large enough, the molecules orient themselves with the positive end of one molecule toward the negative end of the other (ATKINS and JONES, 2012; MIESSLER et al., 2014).

In Figure 3 The dipole moment and polarizability values of the chemical species of interest are arranged. The molecule of squalene, the model compound used for natural rubber, is the one with the

highest polarizability value (a = 54.7 Å3) and therefore the highest distortion capacity of the electronic cloud. This characteristic makes squalene able to develop more significant intermolecular interactions with other chemical species, even though it has an extremely low dipole moment value (m = 0.13 D). At the opposite extreme, ZnO is the least polarizable species, although the value of m is approximately 4.3 times greater than the value of m of squalene.

It should also be noted that the TMQ antioxidant molecule exhibits a value of m close to zero as a function of the symmetry in the spatial arrangement of the atoms in its structure. The CBS and C18 species are the molecules with the highest values of m - 1.98 D and 2.06 D, respectively - and, therefore, with greater capacity for electrostatic interaction with each other or, through induced dipoles, with the other species present in the formulation.

Figure 3: Dipole moment versus polarizability of the chemical species present in the formulation of natural rubber
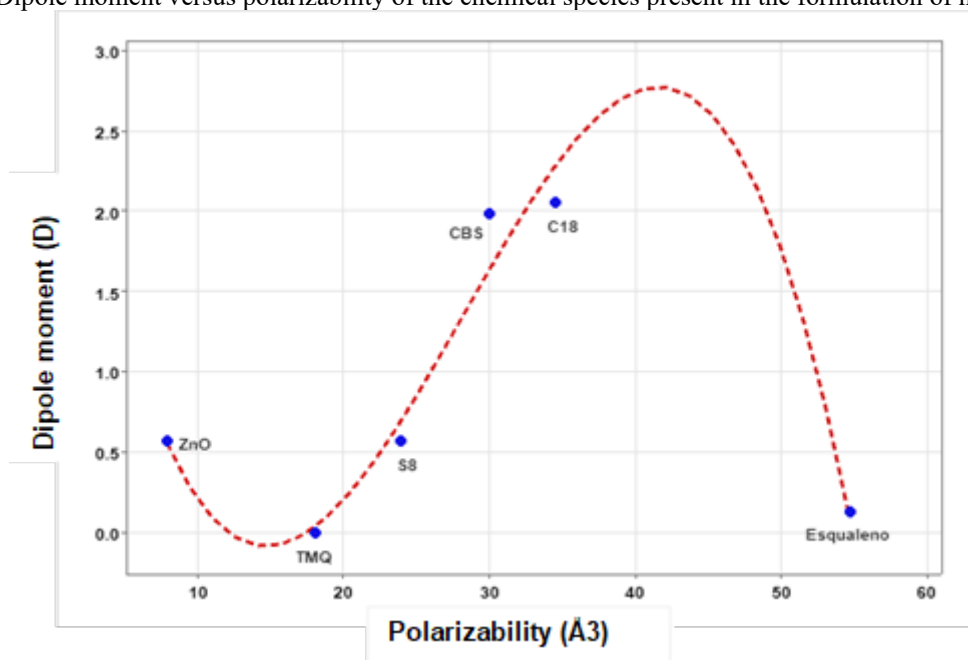
In Figure 4 the theoretical data of hardnessh () and electrophilicity () w of the chemical species are shown. In order for the data to be properly interpreted, it is necessary to consider the following important points:

- The molecular orbitals that are typically of most interest to chemical reactions is the highest-energy occupied molecular orbital (HOMO) and the lowest-occupied energy molecular orbital (LUMO), collectively known as boundary orbitals because they lie at the boundary between the occupied and unoccupied orbital. The energy of HOMO measures the electron-donor character of a compound and the energy of LUMO measures the electron-acceptor character (LOBATO et al., 2012; HOUSECROFT and SHARPE, 2013);

- The difference between the energies of the HOMO-LUMO orbitals is called the GAP, and is an important indicator of molecular stability. Molecules with low GAP value are reactive, while molecules with high GAP value indicate high stability of the molecule, so they have low reactivity in reactions (HOUSECROFT and SHARPE, 2013; MIESSLER et al., 2014); and

- The hardnessh, is defined numerically as h = GAP/2. In turn, softness is the inverse of hardness. The concepts of hardness and softness help rationalize much of inorganic chemistry, and much of the distinction between hard and soft depends on polarizability, the degree to which a molecule or ion is distorted by interaction with other molecules or ions. According to Pearson: "Hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases." Interactions between two soft or two hard species are stronger than those between a hard and a mole species (SHRIVER and ATKINS, 2003; MIESSLER et al., 2014); and

- An electrophile is an atom, ion, molecule or even a compound that has an affinity for electrons, meaning it is inclined to become negatively charged. Electrophiles are also classified according to their degree of reactivity or their tendency to accept electrons. One measure of this reactivity is the so-called electrophilicity index (w), which indicates its macroscopic electrical energy. A higher electrophilicity index indicates that a compound is more electrophilic. Electrophilic substances are Lewis's acids (compounds that accept electron pairs), and many of them are Brønsted acids (compounds that donate protons) (SILVA and PAES, 2018).

In Figure 4, it is possible to observe that stearic acid (C18) is the species with the highest hardness among those investigated, with an h approximate of 6.1 eV. At the same time, sulfur (S8) is the substance of lower hardness or greater softness with one h of about 3.1 eV. Since = h GAP/2, a theoretical conclusion is that C18 is a less reactive species than S8 and therefore of less effective interaction with the other ingredients of the composition. In addition, sulfur not only has the lowest hardness (high reactivity), but is also the molecule with the highest electrophilicityw (= 6.4 eV) next to zinc oxide (ZnO), that is, S8 and ZnO are the most acidic species among the ingredients present in the composition. In contrast, the lowest index w was squalene with about 1.7 eV, which means that, supposedly, the model compound of natural rubber is the species with the greatest basic character.

Figure 4: Electrophilicity versus hardness of the chemical species present in the formulation of natural rubber
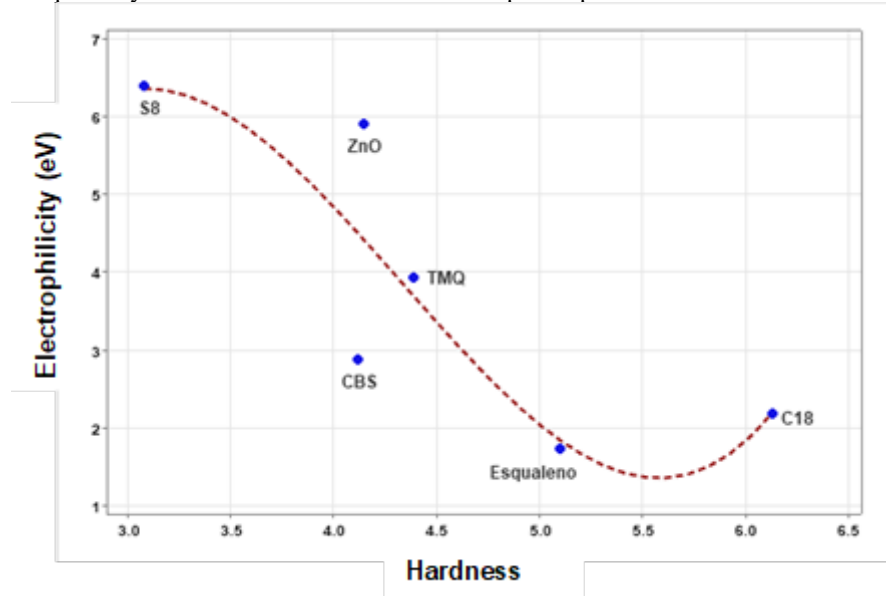

In Figure 5, the electrostatic potential (MPE) map of the species is displayed. The MPE serves to evaluate the regions of higher and lower electron densities reflecting the boundaries of the molecule. By calculating the MPE one can obtain a region in three dimensions that demonstrates how the electrons are energetically distributed around the molecule. The MPE on a surface can be a positive or negative quantity, in general: red means more negative electrostatic potential and is used for regions that attract more positively charged molecules; and, blue is used for areas with more positive electrostatic potential, that is, regions that attract more strongly negatively charged molecules. Other colors indicate intermediate levels of attraction. Therefore, this map is important to describe molecular sites of electrophilic attacks, nucleophilic reactions, and hydrogen bonds. The negative regions are correlated with electrophilic attack sites and the positive regions are nucleophilic reaction sites (CARVALHO et al., 2018).

The squalene molecule exhibits red regions distributed along its structure, essentially located along the C=C double bonds present. A bond is p weaker than a bond s and therefore it is the bond that breaks most easily when an alkene reacts. In addition, an p alkene bond consists of a cloud of electrons above and below the bonds. As a result of this electron cloud, an alkene is an electron-rich molecule – it is a nucleophile5. Comparatively, the stearic acid molecule (C18) exhibits the region of greatest accumulation of electron density concentrated only next to the oxygens of the group – COOH. The central body of the C18 molecule is essentially neutral and the density accumulation of positive charges is distributed across the hydrogens.

Figure 5: Map of electrostatic potential of the different chemical species present in the composition of natural rubber
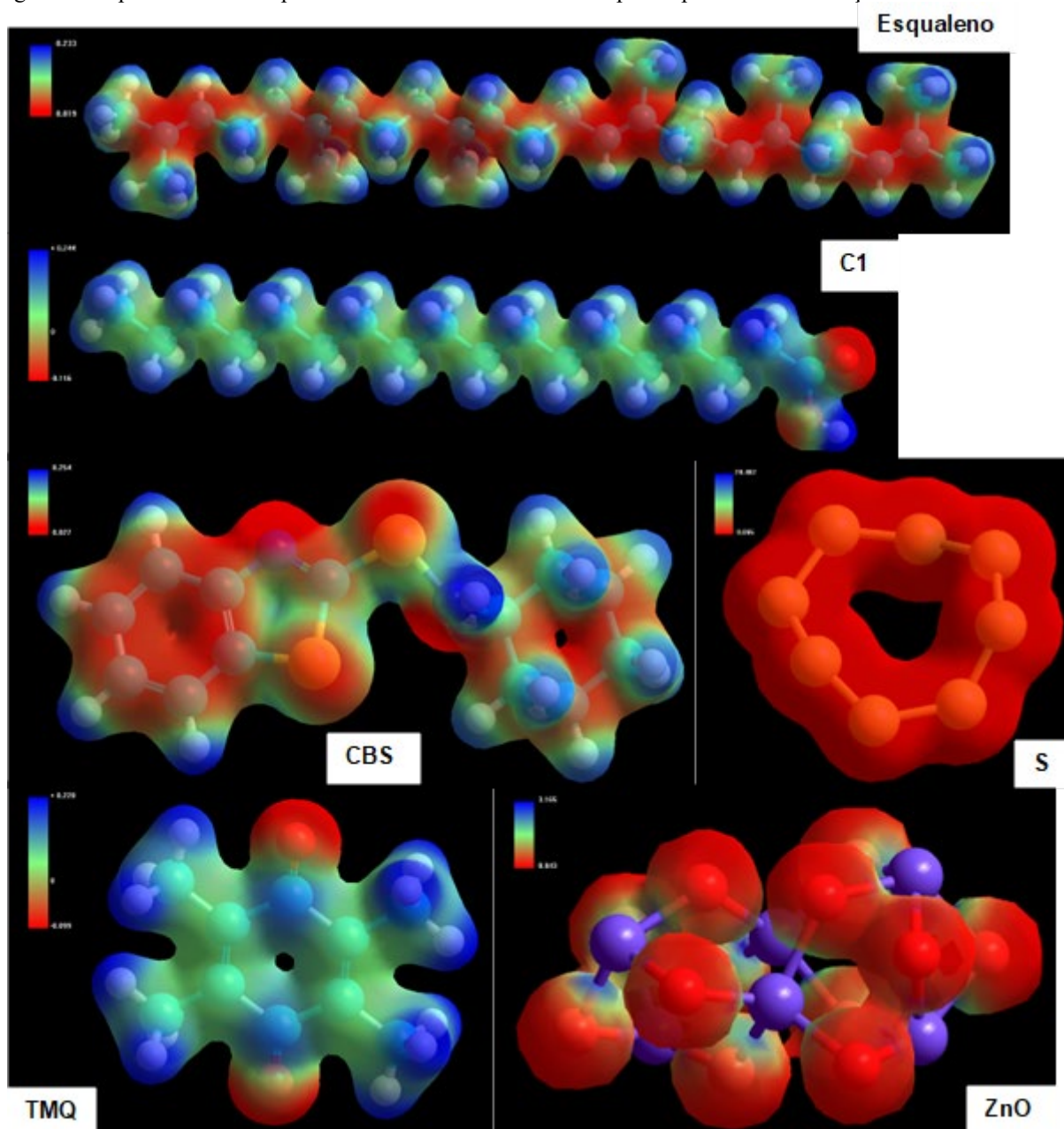
In the TMQ molecule there is a marked symmetry in the molecule, where the regular arrangement of the regions of higher or lower electron density can explain the dipole moment (m) approximately equal to zero. Only the oxygens, bound to the benzene ring, essentially concentrate the negative charge. As for the CBS organic accelerator molecule, the regions of negative charge accumulation are distributed throughout the structure - either by the C atoms of the benzene ring, or by the N and S atoms present or also by the C of the cyclohexyl radical. Finally, the structures of the S8 and ZnO reveal, through the MPE, the most expressive concentrations of negative charges, that is, of high electron density. The regions in red take the entirety of the molecule, in the case of S8; or, they are neatly allocated next to the atoms of O, in the case of ZnO.

3.2 ADSORPTION ENERGY ANALYSIS – ZNO SYSTEM

In order to evaluate the adsorption energy (Eads.) of the mixing process, initially the ZnO system was selected. This system implies the addition of the ingredients to the natural rubber matrix using the following order: squalene crystal, ZnO and the combinatorial analysis of the other additives. The adoption of the procedure generated 24 different ways of hypothetically conducting the elastomeric mixture. The energy associated with the adsorption of each individual mixture is found in the bar graph in Figure 6.

The adsorption energies of the combinations ZnO / C 18 / others, ZnO / S 8 / others, ZnO / CBS / others and ZnO / TMQ / others, were compared according to the analysis of variance of one factor in Kruskal-Wallis ranks, because the Shapiro-Wilk normality test was flawed with $p < 0.050$. With H = 0.080, in three degrees of freedom, and $p = 0.994$, it was possible to determine that the differences in median values between the treatment groups are not large enough to exclude the possibility that the difference is due to the variability of random sampling, that is, there is no statistically significant difference for a 95% confidence level.

Although there is no statistical difference, Figure 6 reveals how the choice of the order of addition of the different additives directly impacts the variation of the adsorption energy. Although the process tends to be predominantly endothermic in nature, there were five combinations, among the 24 possible, with negative Eads. values, that is, of an exothermic nature. In particular, the mixing sequence ZnO / C18 / S8 / TMQ / CBS stands out with about 58.5 kcal/mol (@245 kJ/mol) of heat released as a function of the adsorption of the additives next to the NR matrix.

Figure 6: Values of the adsorption energy for the ZnO system, according to the order of addition of the different additives to the NR matrix

RUSSEL (2000) describes two general types of adsorptions: relatively weak adsorption, physical adsorption or van de Waals; and, the strongest, chemical adsorption or chemisorption. The evidence that the chemisorvida molecule is more strongly bound to the surface comes from the fact that during chemisorption considerably more heat is released than during physical adsorption. Chimsorption is common in heterogeneous catalysis and apparently occurs, preferably, over certain surface sites, called active sites or active centers. The chemisorlife molecule is somehow modified at the active site so that it can react more easily with another molecule.

As commented in the first section of the results discussion, the chemical species revealed, after molecular modeling, values of polarizability, dipole moment, hardness, electrophilicity and electrostatic potential map, remarkably different from each other. Consequently, it is to be expected the development of different mechanisms of interaction between the additives and between the additives and NR matrix. This would explain the distinct behavior in the values of Eads. seen in Figure 6. A proof for this hypothesis is the visual observation of how the additives are distributed next to the squalene crystal, after the completion of the molecular modeling. We found 7 characteristic arrangements, whose frequencies are shown in Figure 7.

Figure 7: Sector graph for the seven different categories of additive arrangements in the adsorption process with the NR matrix
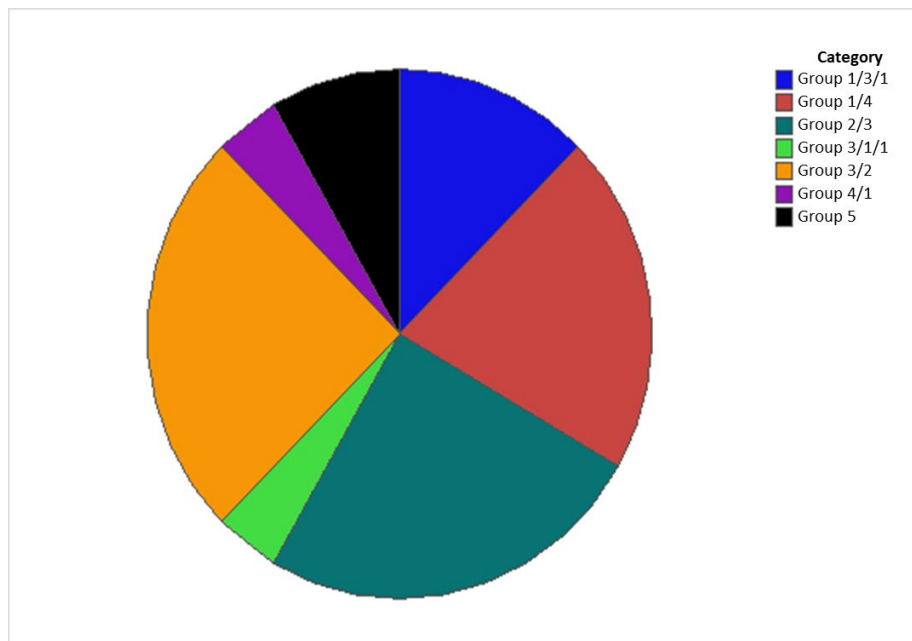

The arrangements called 2/3 and 3/2 account for 50% of the hypothetical situations found, while the 1/4 arrangement accounts for about 21%. Such more frequent situations are exemplified in Figure 8. The 2/3 arrangement was concentrated in the ZnO/C18/other mixes. In turn, the 3/2 arrangement was distributed in three subcases: ZnO/S 8/C18/others, ZnO/CBS/C18/others, and

ZnO/TMQ/C18/others. The designated arrangement of 1/4 was also shared in three subcases where, after the addition of ZnO, the next ingredient was S8, CBS or TMQ.

Figure 8 shows that ZnO tends to approach the surface of the squalene crystal probably due to intermolecular forces such as London scattering forces and induced dipole-dipole. This assumption is based on the electrostatic potential maps of the species and the high polarizability of the squalene molecule.

Figure 8: Arrangement of ingredients, according to the order of addition, most often found in the molecular modeling of the adsorption process during NR mixing
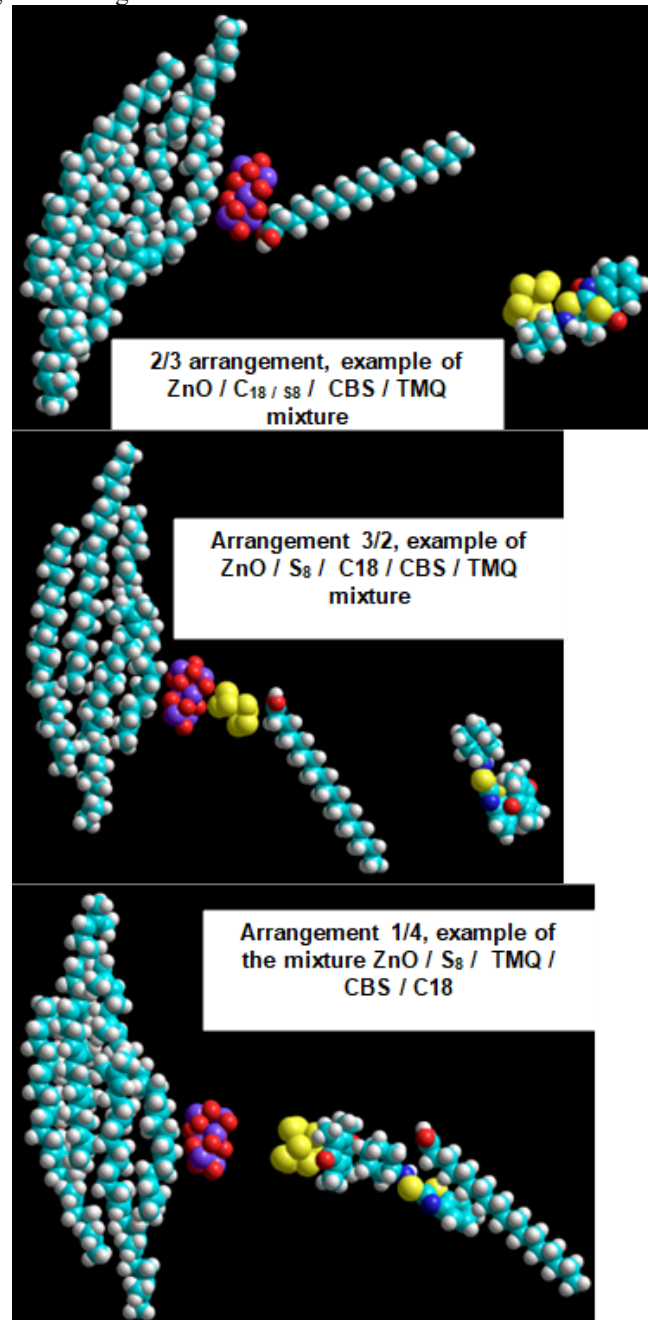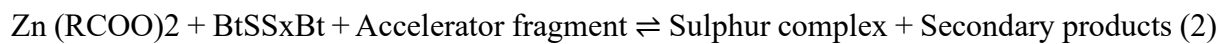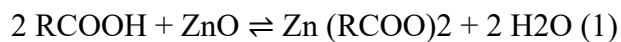

However, the sequence of addition of the other ingredients seems to impose a dispute between the preferred intermolecular interactions. In the 2/3 arrangement, for example, ZnO brings the stearic

acid molecule (C18) close to the squalene matrix, while the other ingredients cluster distant and organized into trios. In the 3/2 arrangement, the reverse occurs, i.e., ZnO/S 8/C18 (see Figure 8), ZnO/CBS/C18 or ZnO/TMQ/C18 cluster next to the squalene matrix, while the remaining additives are segregated into binary clusters. The extreme situation, shown in Figure 8, concerns the 1/4 arrangement in which only ZnO approaches the elastomeric matrix and all other ingredients remain in an isolated cluster.

In the works of CAMPBELL (2016) and MARTINS (2021), the fundamental chemical reactions for the formation of cross-links in conventional elastomers are:

$$2 \ RCOOH + ZnO \rightleftharpoons Zn \ (RCOO)2 + 2 \ H2O \ (1)$$

$$Zn \ (RCOO)2 + BtSSxBt + Accelerator \ fragment \rightleftharpoons Sulphur \ complex + Secondary \ products \ (2)$$

where: reaction (1) is a metathesis reaction or "double displacement reaction", where displacement of the RCOO- base by the O2 base- is accompanied by the extraction of H+ by Zn2+ acid. Reaction (1) corresponds to the reaction between the fatty acid (coactivator) and zinc oxide (activator), which would make available in the reaction medium, in a soluble form, the Zn2+ cation. The zinc carboxylate formed in (1) would then have the ability to react with BtSS xBt polysulfides (Bt is a benzothiazil fragment and 6 x is the number of sulfur atoms ranging from 1 to 8) and form the sulfur complex in the reaction (2).

If reactions (1) and (2) are taken as a parameter for the quality of the cross-link network to be formed in the elastomer, it seems inevitable that the formation of clusters of ingredients distant from the NR matrix (squalene crystal), as illustrated in Figure 8, will have an adverse impact on the curing process. Negative impact that could be manifested: (i) in the increase of the pre-cure time (Scorch Time) promoted by the difficulty of homogeneous dispersion of ingredients; and/or, (ii) in the decrease in cross-link density, measured by the reduction of maximum torque (Mh) in the rheometric measurements of the compositions. The investigation of HASAN et al. (2018) on the effect of the sequence of addition of ingredients in natural rubber compositions containing two varieties of carbon black (N330 and N660) as a reinforcement charge corroborates with the hypotheses listed.

According to ASTM D3182 which deals with materials, equipment and procedures for the mixing of elastomeric compositions, the suggested sequence of addition in NR consists of: elastomer, ZnO, C18, antioxidant, S8 and accelerator. Such an order of addition corresponds to the second most exothermic sequence designed by molecular modeling with EAds. equivalent to 49,5 kcal/mol (@ 206.7 kJ/mol) of heat released. In addition, the ingredients are arranged in the 2/3 arrangement, which is represented in Figure 8.

Analyzing the 7 characteristic arrangements found for the mixing process, exemplified in Figure 7, in only two situations (8.3% of the determined cases) all the ingredients were clustered near the squalene matrix, as shown in Figure 9. In the arrangement to the left of Figure 9, the ingredients appear compacted toward the NR matrix, "pushed" by the C18 molecule. In turn, in the arrangement to the right of Figure 9, the ingredients together with the C18 molecule appear to form a single block. If we take such an arrangement, generically called group 5, as hypothetically ideal for the mixing process, since the additives would be available almost simultaneously in the interaction with the elastomeric matrix, the immediate consequences would be:

The adsorption process will have the modified nature, as it will be conducted under endothermic conditions. About 69 kcal/mol for the order ZnO / CBS / TMQ / C 18 / S8 or approximately 76 kcal/mol for the sequence ZnO / CBS / S 8 / TMQ / C18;

The order of addition determined by ASTM D3182 will therefore be changed. The second additive to be mixed will be the organic accelerator while the fatty acid will occupy the penultimate or last position in the mixture sequencing; and

If the adsorption process becomes endothermic, then, thermodynamically, there will be a need to remove energy from the environment (heat gain by the system) so that the additive molecules gain sufficient energy and, thus, the diffusion occurs appreciably next to the squalene matrix. In summary, if during chemisorption considerably more heat is released than during physical adsorption, as cited in RUSSEL (2000); then, adopting the change in the order of addition of the additives to favor the group 5 arrangement supposedly represents compensating for the energy of a stronger interaction between ZnO and the elastomeric matrix at the expense of heat transfer to the system – an estimated quantity of 69 kcal/mol or 76 kcal/mol, that is, 289 kJ/mol or 318 kJ/mol, respectively.

Figure 9: Arrangement of the hypothetically ideal ingredients, according to molecular modeling, for the adsorption process during NR mixing
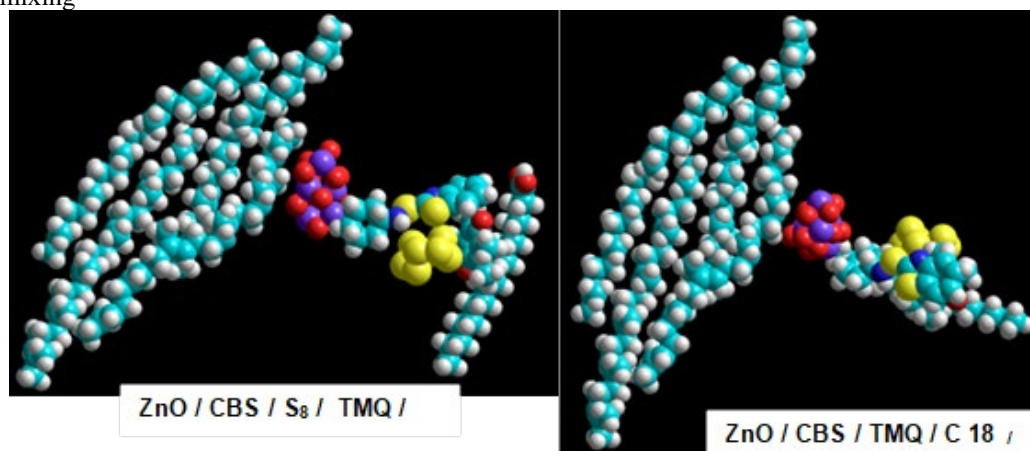
3.3 ANALYSIS OF ADSORPTION ENERGY – SYSTEM C18

For comparison purposes, the adsorption energy (Eads.) of the mixing process was also calculated for the C18 system. In this case, the addition of the ingredients to the natural rubber matrix followed the order: squalene crystal, C18 and the combinatorial analysis of the other ingredients. Again, the procedure resulted in 24 distinct ways of hypothetically conducting the elastomeric mixture. The energy associated with the adsorption of each mixture is found in the bar graph in Figure 10.

Figure 10: Values of the adsorption energy for the C18 system, according to the order of addition of the different additives to the NR matrix
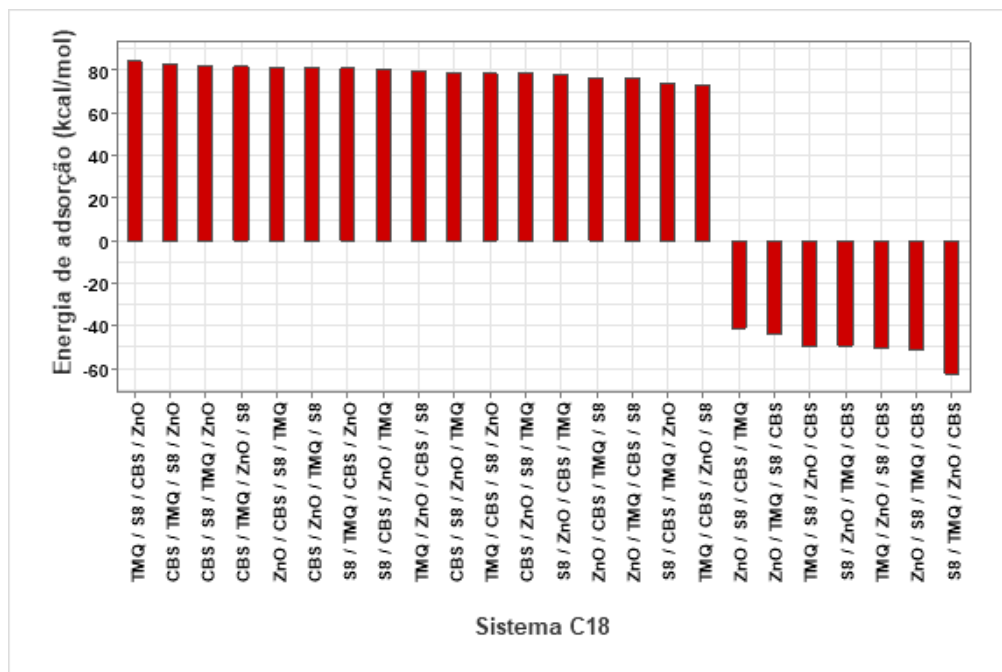
Automatically generated descriptionAs in the previous situation, when ZnO was the first additive of the mixture, in the so-called C18 system significant differences were also found in the adsorption energy depending on the selected addition order. According to Figure 10, there are both endothermic and exothermic processes, although the latter constitute only about 29% of the cases. The sequence S8 / TMQ / ZnO / CBS showed the highest exothermy of adsorption with about 62.5 kcal/mol released (@ 261.7 kJ/mol). However, when the adsorption energies of the combinations C18 / ZnO / others, C 18 / S8 / others, C18 / CBS / others and C18 / TMQ / others, are compared according to the analysis of variance of a factor in Kruskal-Wallis ranks, because the Shapiro-Wilk normality test was flawed with $p < 0.050$, an H of 6.753, in three degrees of freedom, and a p of 0.080 were determined. This means that the differences in median values between the treatment groups are not large enough to exclude the possibility that the difference is due to the variability of random sampling, i.e., there is no statistically significant difference for a 95% confidence level.

In addition, when all 24 possible combinations present in the ZnO and C18 systems are compared for adsorption energies, the non-parametric test called the Mann-Whitney U test7 demonstrates that the differences in median values between the addition groups are not large enough to exclude the possibility that the difference is due to the variability of random sampling, that is, there is no statistically significant difference for a 95% confidence level. The test parameters determined were W = 203.00 and p = 0.081.

If from a statistical point of view the C18 addition system and the ZnO addition system are not distinguished, as well as the sequences C 18 / ZnO / others, C 18 / S8 / others, C18 / CBS / others and C18 / TMQ / others, the observation of the way the additives are distributed in front of the squalene matrix is peculiar. While in the ZnO system 7 characteristic arrangements were found, in the C 18 system, regardless of the mechanism of addition, all 24 combinations were of the group 1/4 type. In this arrangement, only the stearic acid molecule (C18) tends to be very close to the surface of the squalene crystal and, in some cases, even appears to be "encompassed" by it. In turn, the other ingredients form a more or less compact agglomerate distant from the adsorption surface designed for the elastomer. In Figure 11, examples of this situation are illustrated.

According to the electrostatic potential map in Figure 5, squalene has an electronic distribution spread throughout the molecule as a function of the C=C double bonds present. At the same time, the stearic acid molecule essentially concentrates the electron density next to the O atoms of the -COOH grouping, while the hydrogen atoms scattered along the structure become places of concentration of the positive charge (blue regions). Thus, together with the considerable polarizability of the squalene molecule, the adsorption of C18 seems to be facilitated by dispersive and dipole-type interactions, which would justify the trend by the 1/4 arrangement illustrated in Figure 11.

As for the other ingredients (CBS, TMQ, S8 and ZnO), regardless of the order of addition, it is quite likely that a balance of intermolecular forces of the dipole-dipole and/or induced dipole-dipole type, in addition to the dispersive forces, is more relevant than any interactions with squalene or C18. This being true, the segregation of the ingredients and the formation of an isolated aggregate is justified.

Although there are no experiments to corroborate the observed effect, hypothetically it is expected that in the compositions of the C18 system there is a greater difficulty of homogeneous dispersion of the ingredients than the ZnO system. This fact will probably impact the pre-cure time and the optimal healing time of the elastomer, decreasing the cross-link density achieved. Thus, the sequencing of mixtures of the C18 system would not bring advantages in being adopted.

Figure 11: Arrangement of the ingredients of the C18 system in group 1/4 format, according to molecular modeling, for the adsorption process during NR mixing
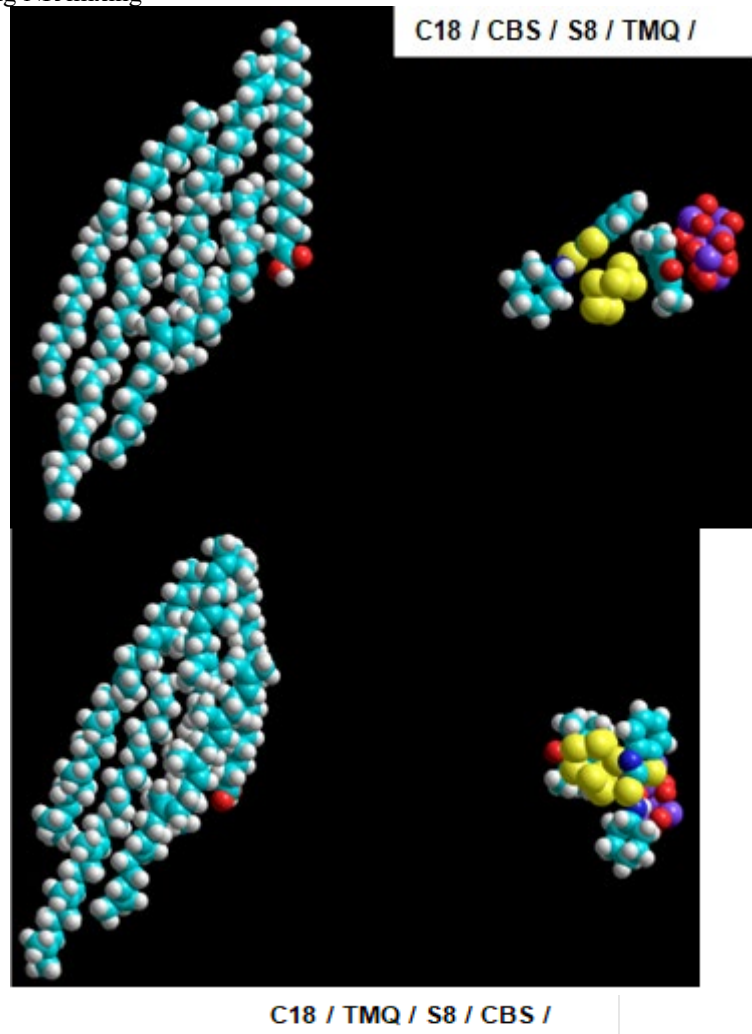
4 CONCLUSIONS

The effect of the sequence of addition of ingredients in an elastomeric mixture of natural rubber was theoretically evaluated through molecular modeling. The adsorption energy was estimated and the theoretical results allowed us to conclude that:

The mixing process conducted according to ASTM D3182, which adopts the sequence elastomer, ZnO, C18, antioxidant, S8 and accelerator, is of exothermic character. In addition to possibly providing the necessary energy conditions for adsorption to be characterized by chemisorption, there is a 2/3 arrangement present in the distribution of additives. If we take as a basis the reactions (1) and (2), suggested by CAMPBELL (2016) and MARTINS (2021), the reaction sequencing seems to be consistent with the analysis of the arrangement illustrated in Figure 8;

The proposal to adopt a mixture sequencing that allows the arrangement of the so-called group 5 (Figure 9) is not favored from the energetic point of view, because the adsorption process becomes endothermic and, possibly, of greater physical character to the detriment of the greater chemical character derived from the sequence standardized by ASTM D3182; and

The C18 system does not seem to bring any advantages in its adoption, since the ingredients, except stearic acid, are clustered and distant from the NR matrix.

REFERENCES

AMBER – MCPLWiki. Disponível em: http://www.iq.usp.br › mcplwiki › amber. Consulta em novembro de 2022.

ATKINS, P., JONES, L. Princípio de Química: Questionando a vida moderna e o meio ambiente. 5ed, Bookman Companhia Editora, 2012.

CAMPBELL, B. C. Análise térmica aplicada ao estudo das reações de vulcanização em elastômeros – efeito de óleos vegetais e da cera de abelha. Dissertação (Mestrado em Ciência e Tecnologia de Materiais) – Instituto Politécnico (IPRJ), Universidade do Estado do Rio de Janeiro (UERJ), Nova Friburgo, RJ, 2016.

CARVALHO, F. B., CAMARGO, A. J., OLIVEIRA, S. S. Estudo da estrutura eletrônica e da geometria da dihidroquinolinona sulfonamida utilizando Teoria do Funcional da Densidade. V Congresso de Ensino, Pesquisa e Extensão da UEG. Pirenópolis, Goiás, 17 a 19 de outubro, 2018.

CTB – Ciência e Tecnologia da Borracha. Disponível em: https://www.ctborracha.com/. Consulta em novembro de 2022.

DICK, J. S. Rubber compounding: Introduction, definitions, and available resources, In: Rubber Technology, compounding and testing for performance, cap.1, Dick, J. S. (ed.), Hanser Publishers, Munich, 2001.

HASAN, A., SULISTYO, H., HONGGOKUSUMO, S. The effect of ingredients mixing sequence in rubber compounding upon vulcanization kinetics of natural rubber: an autocatalytic model study. Indonesian Journal of Chemistry, v.18(4), p.709-717, 2018.

HOUSECROFT, C. E., SHARPE, A. G. Química Inorgânica. 4ed, LTC – Livros Técnicos e Científicos Editora Ltda., v.1, 2013.

LOBATO, C. C., SILVA, E. M., VIEIRA, J. B., MACEDO, W. J. C. et al. – Estudo computacional da reatividade dos produtos isoméricos em reações de halidrificação através da análise dos orbitais de fronteiras – HOMO e LUMO. 52o Congresso Brasileiro de Química, Recife, PE, 14 a 18 de outubro de 2012.

MARTINS, C. D. Modelagem molecular aplicada à vulcanização. Dissertação (Mestrado em Ciência e Tecnologia de Materiais) – Instituto Politécnico (IPRJ), Universidade do Estado do Rio de Janeiro (UERJ), Nova Friburgo, RJ, 2021.

MIESSLER, G. L., FISCHER, P. J., TARR, D. A. Química Inorgânica. 5ed, Pearson Education do Brasil, 2014.

RUSSEL, J. B. Química Geral. 2ed, Pearson Education do Brasil, v.2, 2000.

SHRIVER, D. F., ATKINS, P. W. Química Inorgânica. 3ed, Bookman Companhia Editora, 2003.

SILVA, F. M., PAES, L. W. C. Estudo teórico da eficiência de inibidores orgânicos de corrosão derivados do benzimidazol. Journal of Experimental Techniques and Instrumentation, v.1(1), p.11-26, 2018.