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Components used in the vulcanization of rubber

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Abstract

Elastomers, which are rubber-based materials, are among the important raw materials used in the industry today, as they have a wide area of use in many sectors such as textile, food, livestock, armature, construction, etc., especially in the automotive industry. The business world, which is developing day by day with the advancement of technology, is rapidly consuming the raw materials we have, and unfortunately, our resources are gradually decreasing due to the fact that most of these raw materials are not recycled. For these reasons, it is of great importance to know the material used very well and to analyze its static, dynamic, thermal, physical, chemical, etc. properties according to their usage areas. In this study, the materials used during the preparation and vulcanization of rubber-based materials, which have a wide area of use in many sectors such as automotive, textile, food, livestock, armature, construction, and their intended use will be emphasized.

1. Introduction

The rubber compound is a recipe consisting of rubber polymers and other additional materials for the rubber to exhibit the desired properties in the industry. The successful functioning of rubber products depends on choosing the right polymers and mixing the rubber chemicals and fillers in the appropriate ratio. The mixture of materials selected for this purpose and providing proportional integrity with each other is called rubber recipe or rubber formula [1].

In the rubber mixture, a recipe is prepared so that the sum of the elastomer or elastomers is 100. All materials except elastomer are put on the prescription as “phr”, which is defined as "parts per hundred of rubber" [2]. A rubber compound usually contains 40-50% by weight of the rubber polymer. The typical content of a mixture is given in Table 1 [1].

Table 1. Typical rubber composition

Amount of material (phr)	Quantity (phr)
Rubber	100
Fillers	20-100
Plasticizers	5-30
Vulcanization Agent	5-10
Accelerators	0-30
Activators	1-5
Antioxidants	1-3

The first usable rubber formulation was prepared by Charles Goodyear with NR rubber with cooking a sulfur [3]. In order to develop a rubber mixture, a material that can determine the necessary properties for the dough, knowledge of chemical mixture preparation, and experience in this regard are required [3].

A typical rubber mixture; rubber polymer, cooking materials that provide cross-linking, fillers used to reinforce and/or cheapen the mixture, plasticizers that give the dough softness in the processing process and then give it the desired flexibility and low temperature flexibility, protect the material from deterioration both during processing and during the use of the piece [4]. Stabilizers are added to the mixture according to the need and amount. The main purpose of rubber additives; to improve the properties of the material to be worked [4].

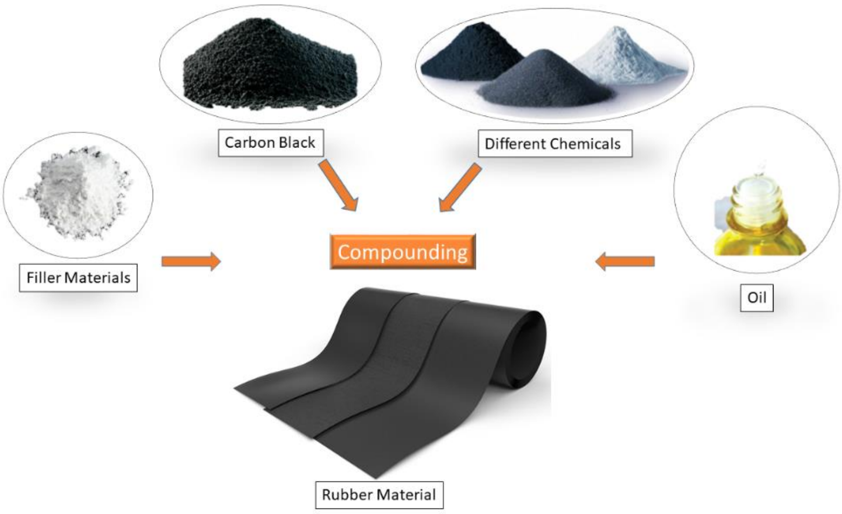

Figure 1. The scheme of rubber compounding

Added additives interact with the elastomer physically or chemically. Industrial applications will be limited as the mechanical and thermal properties of rubbers cannot be adequately provided without suitable fillers and additives [5].

While preparing a rubber mixture, it is expected to gain the following properties;

- ✓ In the environment where it will work as a finished product; mechanical, chemical, thermal, electrical, etc. to have the desired characteristics.
- ✓ Compliance with the processes, molds and machines to which the mixture will be applied during preparation, and vulcanization.
- ✓ The cost of the prepared mixture is competitive.

The additives that make up the rubber mixture are given, respectively [5].

1.1 Filler Materials

Filler materials are included in the rubber mixture for the aim of reinforcing the rubber, increasing its usability and improving its character, coloring the rubber, and making it economical. They can be organic or inorganic in nature. Fillers can be divided into two groups like black and white fillers. Black fillers are carbon blacks. White fillers are fillers such as calcium carbonate, silica, clay, talc, zinc oxide [6].

Black fillers give the rubber a strength that is incomparable with white fillers. The white fillers used in addition to the black fillers, on the other hand, give the rubber homogeneous mixing and lubrication properties thanks to the weak polar bonds between it and the rubber. In other words, the black fillers used in rubber improve the properties of the rubber, while the white fillers are mostly used to cheapen the formulation and improve the processing properties of the rubber [2].

Carbon black is an amorphous carbon in a semi-graphite structure, which, when mixed with rubber, increases the tensile strength, modulus, abrasion resistance and tear strength of rubber. Carbon black is obtained as a result of the thermal cracking of liquid and gaseous hydrocarbons [7]. Properties that determine the quality of carbon black as a reinforcing agent; grain size or surface area, structure and surface activity. In general, each of the carbon black properties affects the workability and the cured product. If the grain size is small, an increase in hardness, abrasion resistance, breaking strength and electrical conductivity, and a decrease in elasticity are observed in the products after vulcanization [8]. As the grain size increases, the surface activity decreases and the strengthening effect decreases. That is, the breaking force, tear, and abrasion resistance are reduced [9].

White fillers, on the other hand, are used in rubber technology to improve the physical or mechanical properties of the rubber mixture and to reduce the cost. These properties can be achieved by blending mineral fillers with carbon black or using light-colored products, alone or in combination with other fillers [10].

1.2. Plasticizers

Plasticizers are macromolecules with short-chain lengths compatible with the main polymer structure. It does not make chemical bonds with the polymer but settles between the macromolecular. Those that do not adapt well can migrate to the surface over time [11].

Plasticizers reduce the hardness and swelling properties of rubber, improves its low temperature flexibility by decreasing it's the glass transition temperature (T_g), and increases its resistance to the flame by increasing its electrical conductivity from its physical properties. At the same time, reducing the viscosity of the mixture, before curing; provides convenience in mixing and extrusion processes by ensuring the fluidity of the mixture. Thus, energy savings are provided in the processes. In addition, they facilitate the mixing in the formation of rubber dough and ensure that the added substances are mixed homogeneously [12].

1.3. Antioxidants

Aging causes changes in physical and mechanical properties. The greater the unsaturation rate in the polymer, the greater the susceptibility to aging [13]. Because they are sensitive to double bonds, oxygen, ozone and other reactive substances. Oxygen causes the polymer bonds to break down. In addition, they continue to react with sulfur and cause hardening. Continuation of polymerization or intermolecular cross-linking in synthetic rubbers can lead to hardening and brittleness [14]. High temperature can lead to various deteriorations even in oxygen-free environments, such as; thermal breakdown of crosslinks, intermolecular and intramolecular crosslinking or displacement of crosslinks. Sunlight increases the effect of oxygen and forms a film of oxidized rubber. This layer consists of grooves that join each other in random directions [15].

1.4. Vulcanization Agents

The aim of using vulcanizing agents is to create a network chain structure by providing cross-linking between polymer chains. Sulfur is used for the unsaturated polymer group, while peroxide is used for the saturated polymer group [16]. The most known and frequently used crosslinking agent is sulfur [16]. There are two types of sulfur use, normal and insoluble. Normal sulfur has an octet ring structure. Since it increases the solubility with temperature, it can cause pre-vulcanization in mixture storages before curing. Since it has the possibility of free circulation within the structure, its homogeneous distribution in the mixture may deteriorate over time. Insoluble sulfur, on the other hand, is amorphous and does not dissolve during storage, so there is no pre-vulcanization problem and a homogeneous distribution can be achieved in the mixture [17].

It is also widely used in peroxide and phenol-formaldehyde resins. Peroxide forms direct bonds to carbon chains forming carbon-carbon bonds. These bonds take more energy to break, which often results in higher service temperatures and lower permanent deformation in finished products. Some polymers can only be cross-linked with peroxides. Peroxide is faster but more expensive than the sulfur crosslinking agent. It is a special process in cross-linking with high radiation energy [18].

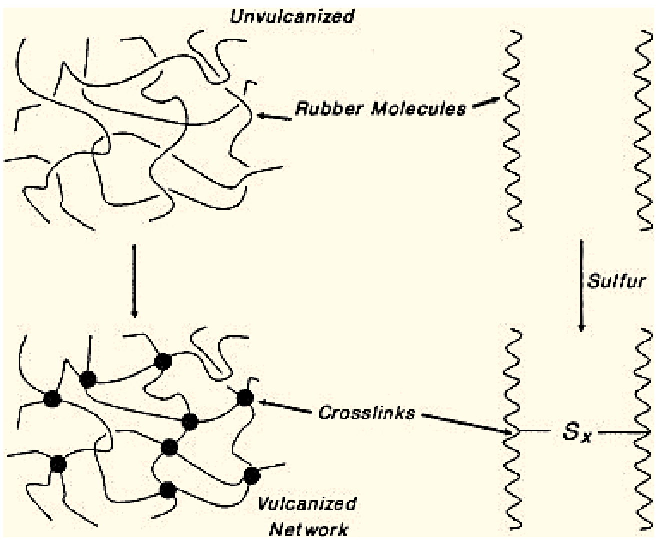

Figure 2. The formation of vulcanized rubber [19]

1.5. Accelerators and Activators

When using sulfur without accelerator in vulcanization, the crosslinking reaction rate will be slow. When sulfur and accelerator are used together, cooking occurs in a short time and economically. The resistance of the product to aging increases [20]. With the vulcanization method using the accelerator, the heat resistance, fatigue resistance, dynamic properties and aging properties of the rubber product are improved. Organic accelerators are used more as accelerators than inorganic accelerators. With the use of an accelerator, the crosslinking reaction is accelerated. Vulcanization is more economical [21,22].

Accelerators that accelerate vulcanization need organic substances. Activators are used to show the most efficient effect of accelerators. Metal oxide, fatty acids are examples of activators. Stearic acid can be used as an accelerator and softener activator in rubber. The activities of activators differ according to their types. One of the most important activators is zinc oxide. Stearic acid increases the solubility of zinc oxide in rubber [23,24].

2. Conclusion

Rubber, the use of which dates back many years, comes into our mix as a material that is needed more and more with the developing technology and especially the increasing automotive industry. In the world and in our country, rubber is used in many materials that make our daily life easier, both as a main and by-product. Increasing production potential, which is shaped according to consumer demand, is also becoming the focus of attention of investors in the chemical industry.

As mentioned in the study, there is an ongoing need for rubber for centuries and efforts to meet this need. It is important to know the preparation process and the used compositions of rubber, which is actively used in many fields today. It is extremely important to choose the components and their ratios according to the type of rubber used or to prepare a recipe for the area to be used. In this context, the preparation of rubber dough and knowing its vulcanization parameters increase its importance in terms of the production of products for the rubber industry.

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Conflicts of interest

The authors declare no conflicts of interest.

References

1. Vayyaprontavida Kaliyathan, A., Varghese, K. M., Nair, A. S., & Thomas, S. (2020). Rubber–rubber blends: A critical review. *Progress in Rubber, Plastics and Recycling Technology*, *36*(3), 196-242.
2. Zhang, Y., Ge, S., Tang, B., Koga, T., Rafailovich, M. H., Sokolov, J. C., ... & Nguyen, D. (2001). Effect of carbon black and silica fillers in elastomer blends. *Macromolecules*, *34*(20), 7056-7065.
3. Greene, J. P. (2021). Elastomers and Rubbers, in: Automot. Plast. Compos., William Andrew Publishing, 127–147.
4. Rodgers, B. (2020). Tire Engineering, Academic Press.
5. Ibrahim, A., & Dahlan, M. (1998). Thermoplastic natural rubber blends. *Progress in Polymer Science*, *23*(4), 665-706.
6. Leblanc, J. L. (2002). Rubber–filler interactions and rheological properties in filled compounds. *Progress in polymer science*, *27*(4), 627-687.
7. Plagge, J., & Lang, A. (2021). Filler-polymer interaction investigated using graphitized carbon blacks: Another attempt to explain reinforcement. *Polymer*, *218*, 123513.
8. Khodabakhshi, S., Fulvio, P. F., & Andreoli, E. (2020). Carbon black reborn: Structure and chemistry for renewable energy harnessing. *Carbon*, *162*, 604-649.
9. Fan, Y., Fowler, G. D., & Zhao, M. (2020). The past, present and future of carbon black as a rubber reinforcing filler–A review. *Journal of Cleaner Production*, *247*, 119115.
10. Saad, A. L. G., & Younan, A. F. (1995). Rheological, mechanical and electrical properties of natural rubber-white filler mixtures reinforced with nylon 6 short fibers. *Polymer Degradation and Stability*, *50*(2), 133-140.
11. Koltzenburg, S., M. Maskos, O. & Nuyken, (2017). Polymer chemistry, Springer Berlin Heidelberg.

12. Callister, W. D., & Rethwisch, D. G. (2018). *Materials science and engineering: an introduction* (Vol. 9, pp. 96-98). New York: Wiley.
13. Xie, H., Li, H., Lai, X., Wu, W., & Zeng, X. (2015). Synthesis of A Star-Shaped Macromolecular Antioxidant Based on β-Cyclodextrin and its Antioxidative Properties in Natural Rubber. *Macromolecular Materials and Engineering*, *300*(9), 893-900.
14. Huangfu, S., Jin, G., Sun, Q., Li, L., Yu, P., Wang, R., & Zhang, L. (2021). The use of crude carbon dots as novel antioxidants for natural rubber. *Polymer Degradation and Stability*, *186*, 109506.
15. Wu, W., Zeng, X., Li, H., Lai, X., & Xie, H. (2015). Synthesis and antioxidative properties in natural rubber of novel macromolecular hindered phenol antioxidants containing thioether and urethane groups. *Polymer Degradation and Stability*, *111*, 232-238.
16. Akiba, M. A., & Hashim, A. S. (1997). Vulcanization and crosslinking in elastomers. *Progress in polymer science*, *22*(3), 475-521.
17. Saputra, R., Walvekar, R., Khalid, M., Mubarak, N. M., & Sillanpää, M. (2021). Current progress in waste tire rubber devulcanization. *Chemosphere*, *265*, 129033.
18. Wang M.-J., & Morris, M., (2021). Rubber Reinforcement Related to Tire Performance, Rubber Reinf. with Part. Fill., 394–507.
19. Ikeda, Y. (2014). Understanding network control by vulcanization for sulfur cross-linked natural rubber (NR). In *Chemistry, Manufacture and Applications of Natural Rubber* (pp. 119-134). Woodhead Publishing.
20. Coran, A. Y. (1965). Vulcanization. Part VII. Kinetics of sulfur vulcanization of natural rubber in presence of delayed-action accelerators. *Rubber Chemistry and Technology*, *38*(1), 1-14.
21. Nieuwenhuizen, P. J. (2001). Zinc accelerator complexes.: Versatile homogeneous catalysts in sulfur vulcanization. *Applied Catalysis A: General*, *207*(1-2), 55-68.
22. Zhong, B., Jia, Z., Luo, Y., & Jia, D. (2015). A method to improve the mechanical performance of styrene-butadiene rubber via vulcanization accelerator modified silica. *Composites Science and Technology*, *117*, 46-53.
23. Ducháček, V., Kuta, A., & Přibyl, P. (1993). Efficiency of metal activators of accelerated sulfur vulcanization. *Journal of applied polymer science*, *47*(4), 743-746.
24. Mostoni, S., Milana, P., Di Credico, B., D'Arienzo, M., & Scotti, R. (2019). Zinc-based curing activators: new trends for reducing zinc content in rubber vulcanization process. *Catalysts*, *9*(8), 664.