A Review of Blooming in Natural Rubber Products: Mechanisms, Challenges, and Solutions

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Introduction

According to the IUPAC, the definition of blooming is "the process in which one component of a polymer mixture, usually not a polymer, undergoes phase separation and migration to the external surface of the mixture" (Nouman et al., 2017). Chemical additives such as, vulcanizing agents, accelerators, activators, antioxidants, fillers, plasticizers and pigments are incorporated into rubber to obtain desired properties, durability, stability, strength, and performance. However, migration of those components to the surface of a rubber article has a considerable effect on the quality of the product. The bloomed chemicals are visible as a white powder deposit or a greasy liquid or a layer of wax on the product surface (Nouman et al., 2017; Pajarito & Arabit, 2016; Sharj et al., 2020).

Additives like sulphur, accelerators, activators, and fillers bloom as powders while plasticizers and lubricants bloom as oils. Blooming occurs when the concentration of additives exceeds their solubility limit. It can happen before, during or after vulcanization or when storing the rubber product. This process can be influenced by the processing, storing and service temperature of the article. For example, those additives are soluble at the processing temperature and when the product reaches room temperature or less storage temperatures, the additives can get oversaturated and migrate through the rubber matrix and will form a crystalline layer on the surface (Andries et al., 1975).

Effects of Blooming on Products

Sulfur Bloom

Based on literature, the commonly used curatives such as sulfur, sulphanaimide accelerators and sulfur doners diffuse quite readily across a rubber-to-rubber interface (Ignatz-Hoover et al., 2003). Migration of sulfur and other additives to the surface can reduce the adhesion properties and tackiness of rubber compounds (Saeed., et al, 2011); and when vulcanized, because of crosslink gradient, those products will not satisfy the expected durability (Jurkowski & Jurkowska, 1998). Also, coating adhesion and lamination peel strength can be decreased due to the inability of sealing the surface (Datta, et al., 2007). Moreover, discoloration and poor appearance of the products can result in blooming (Yasin et al., 2015). It is a drawback when marketing those products. Although blooming is often viewed as a disadvantage, it can also act as a protective layer on vulcanized rubber providing more resistant to aging in service conditions (Kuzminskiĭ et al., 1962).

Wax Bloom

Wax (petrolium wax) blooms and acts as a physical barrier against ozone attack and this is an advantage to protect rubber products from ozone attack (Dimauro et al, 1979). Blooming antiozonants at the surface is undesirable because it will lead to loss of considerable amount of antiozonant (Ignatz-Hoover et al., 2003).

Blooming Mechanism

Blooming is a diffusion-driven process (Yasin et al., 2015). It occurs when a partly soluble low molecular weight additive is added into a rubber compound at concentrations exceeding its solubility limit, leading to its migration to the surface (Ignatz-Hoover et al., 2003). When the surface of the rubber product crystallizes, a concentration gradient forms between the inner rubber matrix and the subsurface layer. This gradient drives the continued migration of the additive towards the surface until its concentration throughout the material drops below the solubility limit, thereby halting the blooming process (Ignatz-Hoover et al., 2003).

Factors Influence the Blooming

The rate of blooming increases with temperature due to the enhanced rate of diffusion. In the case of sulfur blooming, insoluble sulfur begins to migrate once it reverts to its soluble form, a transition that starts at approximately 110 °C (Ignatz-Hoover et al., 2003). At temperatures above 130 °C, all the sulfur converts into its soluble form, eliminating any difference in migration behavior between soluble and insoluble sulfur. Therefore, using insoluble sulfur in sulfur-based compounding systems processed at temperatures below 110 °C can help prevent sulfur migration (Ignatz-Hoover et al., 2003).

Conversely, as temperature decreases, the solubility of certain additives, such as waxes, also decreases. This reduction in solubility leads to an increased tendency for blooming (Datta et al., 2007). Additionally, in non-sulfur vulcanizing systems, a higher crosslink density has been shown to influence and increase the blooming rate (Yasin et al., 2015).

Recent Studies on Blooming

In 2019, Yasin et al. identified paraffin wax as the dominant blooming ingredient when natural rubber compounds were tested under varying loadings of dicumyl peroxide (DCP). The blooming substances were analyzed using Energy-Dispersive X-ray (EDX) spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy. Their findings indicated that higher peroxide loadings did not significantly reduce the amount of blooming. On this study, separate FTIR spectrums were analyzed for DCP and other additives. But a controlled vulcanized sample was not tested. They have varied DCP concentrations only for three samples. By including more formulations with varying the concentrations of DCP, more comprehensive study can be executed. Also, the crosslink density was mentioned in the paper, but it has not been measured. The blooming amounts of samples were tested over two weeks to study the actual behavior of blooming yet only tested in ambient storage conditions. The study does not address the blooming behavior in elevated temperature conditions. Also, the study shows the variation of bloom mass over time but has not done a statistical treatment on the mass.

Pajarito and Arabit (2016) studied the relationship between the physical properties of natural rubber vulcanizates and blooming. They used two surfactants—cocamide DEA and glycerol monostearate (GMS)—in the rubber formulation. Blooming was measured before and after thermal aging at 50 °C, over 20 days using a weight-based method. Results showed that all formulations exhibited increased blooming after aging. As blooming increased, modulus also increased, while tensile strength, strain, and tensile set decreased. The study concluded that the deposited bloom on the surface contributes to resistance against deformation, thereby increasing stiffness. Here the samples were prepared using Taguchi L12 design, which leads to study multiple factors with a smaller number of trials. This study shows comprehensive statistical correlations between physical properties and blooming but lacks in molecular level explanations, surface morphology for the identification of bloomed materials and bloom composition. Here the amount of bloom has been measured using adhesive tapes. For more prices bloom measurement, a gravimetric or imaging-based quantification can be used.

In 2016, Santiago et al. investigated ambient blooming behavior in vulcanized rubber using ATR-FTIR and kinetic curve analysis. Using Taguchi L12 method, they examined how different ingredient loadings affect the rate and amount of blooming, as well as both tensile and compression properties. Anyway, Dynamic Mechanical Analysis and Fatigue tests could have been done beyond the above properties. The study showed that high loadings of stearic acid, paraffin wax, and oil increased the blooming rate, while high loadings of sulfur and coco DEA reduced it by enhancing crosslink density and filler dispersion. Increased sulfur also improved mechanical properties, whereas high amounts of oil and zinc stearate softened the rubber and reduced its strength. The study identified a non-Fickian bloom mechanism, with two distinct blooming rates observed. This study offers a good explanation on blooming behavior of rubber vulcanizates especially with non -ionic surfactants. Use of FTIR and kinetic modeling has provided evidence of non fickian diffusion. However, the limitation of replicates per sample can constrain the statistical power of the results. On this study, the samples were aged under ambient temperature for a long period of 64 days and the blooms were tested to show case the actual behavior. But using slightly elevated conditions can indicate real aging more accurately.

Yasin et al. (2015) examined the impact of compounding ingredients and peroxide loading on bloom formation in natural rubber. Among the six formulations, high wax content with 6 phr peroxide showed the highest blooming, while ZDEC with 1 phr peroxide showed the least. Statistical reliability could have been increased by increasing the replicates from each sample. In this study, the bloom has been only analyzed qualitatively by scrapping the surface of the sample. But FTIR could be used to analyze the bloom both quantitively and quantitively. The bloom texture and the distribution could be studied by adding Scanning Electron Microscopy (SEM) imaging. It’s a good initiative that they have considered the crosslinking density as well. The study highlighted how both additive type and crosslink density influence blooming behavior. Also lack of kinetic modeling has been limited the theoretical depth.

Saeed et al. (2013) investigated the effect of sulfenamide accelerator (TBBS) migration and re-agglomeration on the mechanical properties of natural rubber. By varying TBBS and ZnO loadings, it was allowed for a clear attribution of blooming effects only on those additives. Variation of other ingredients could broaden the study area. In this study they found that reduced TBBS blooming enhanced toughness and cyclic fatigue life. Bloom formation and internal structure were analyzed via SEM, while FTIR confirmed the blooming components. Apart from the blooming and fatigue, study has been focused on the variation of viscosity, hardness and the cure characteristics depending on the phr of TBBS and ZnO as well. Not using a mathematical model is a drawback of the study.

Blooming in natural rubber, caused by the migration of additives like curatives to the surface, negatively affects material properties such as hardness and fatigue life. Ansarifar et al. (2010) showed that TBBS blooming increases surface hardness and reduces cyclic fatigue life by over 100%, but lowering the TBBS to ZnO ratio can effectively eliminate this issue.

Huang et al. (2019) demonstrated that adding graphene oxide (GO) to natural rubber latex reduces blooming by forming a dense barrier and capturing excess additives through GO's oxygen-containing groups, thereby protecting the surface and reducing damage. These studies highlight effective methods to control blooming and improve rubber performance. The study has the novelty over the past studies done on blooming while showing innovative solution for the blooming issue. Comprehensive characterization has been conducted by using advanced analytical instruments such as SEM, quartz crystal microbalance (QCM), Energy Dispersive X- Ray (EDX) and Raman spectroscopy. The blooming was assessed under natural environmental conditions to add an ecological relevance. Anyway, this study could include other nano fillers to get more comparative results to highlight the GO performance. Also using a FTIR spectroscopy could provide more data on chemical changes on the surface. By addressing the compatibility with production methods, scalability and cost effectiveness of incorporating GO , could be beneficial to the industry.

Future Directions

When referring to the recently published available studies, it is obvious that there have not been many investigations done focusing on NRL products. Therefore, conducting such studies can be consequential for the industry. Especially focusing on GO incorporation on NRL can be beneficial to the industry. Also, the effect of blooming on the physical and chemical properties of NRL films, dependency of blooming on environmental factors, and sustainable solutions for blooming, can be further investigated.

Conclusion

In conclusion, according to the above studies, blooming shows both Fickian and non Fickian mechanisms with different compounding compositions. Paraffin wax has a high tendency to bloom. TBBS, oils also considerably contribute to the amount and rate of bloom. The addition of peroxide does not influence the decreasing of blooming. Thermal aging can speed up blooming and decrease tensile strength, strain and increase modulus. Blooming can be eliminated by reducing accelerator, activators ratio in rubber vulcanizates. The blooming issue in natural rubber latex films can be inhibited by incorporating even into very low amounts of graphene oxide.

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