Prevulcanization of Natural Rubber Latex

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Natural rubber latex is the sap of the *Hevea brasiliensis* which is commonly known as the rubber tree or Pará rubber. It is a colloidal dispersion of *cis*-1,4-polyisoprene particles in water and is an important polymeric raw material for manufacturing both latex-based products and dry rubber products, such as gloves, balloons, mattresses, and tires. Traditional vulcanization of rubber mainly refers to the vulcanization of dry rubber, which occurs after molding and shaping, where heat and chemical additives induce crosslinking in the solid state. Prevulcanization, by contrast, involves the controlled formation of crosslinks while the rubber remains in its latex stage, without disturbing its colloidal stability. This an important modified latex-based raw material offers significant advantages in process efficiency, energy consumption, and control over final material properties, especially for latex-based products such as gloves.

Pervulcalization:

Prevulcanized natural rubber latex is defined as modified latex grade in which the dispersed rubber particles undergo partial chemical crosslinking while retaining their fluidity and colloidal stability. This early-stage crosslinking is typically achieved by the addition of sulphur, accelerators, activator and other compounding agents. Importantly, the latex maintains its original dispersion characteristics, enabling storage, transport, and processing similar to unvulcanized latex. Commercial centrifuged natural rubber latex can be vulcanized using sulphur curing system, peroxide system, or high-energy radiation such as gamma-ray or electron beam irradiation. Among the methods sulphur prevulcanized latex is still the dominant industry accepted method to date.

Sulphur prevulcanization

In this process, natural rubber latex is first stabilized with a surfactant such as Sodium dodecyl sulfate (SDS) and KOH to maintain the colloidal stability of the latex during the reaction. Then the latex is compounded with sulphur, accelerators, activators such as zinc oxide, and other necessary ingredients, allowing controlled crosslinking to occur within the dispersed rubber particles. Commonly for the prevulcanization ultra-fast accelerators such as Zinc 2-Mercaptobenzothiazole (ZMBT), zinc-dibutyldithiocarbamate (ZDBC), Zinc Diethyldithiocarbamate (ZDEC) are used. During the prevulcanization process, sulphur crosslinks are formed within the rubber particles as shown in figure 1.

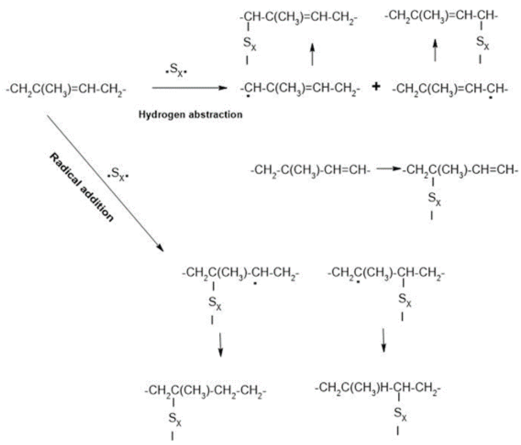

Figure 1: Two proposed mechanisms for sulphur pre vulcanization.

A study by Tangboriboonrat et al. (2002) demonstrated that a homogeneous network of sulphur-crosslinked isoprene chains develops within each rubber particle, independent of particle size. In this system, the vulcanizing agent (sulphur) dissolves in the rubber phase more rapidly than in peroxide-initiated systems. By adjusting the ratio of sulphur to accelerators, it is possible to form mono-, di-, or polysulfidic linkages, enabling the production of prevulcanized latex with varying moduli and mechanical properties. This flexibility allows the formulation of latex suitable for a wide range of applications, from soft, flexible films to high-modulus dipping products.

The degree of crosslinking achieved during prevulcanization has a profound effect on film formation and mechanical properties. Highly crosslinked particle surfaces restrict chain mobility, impairing particle coalescence and producing weak films. Conversely, homogeneous crosslinking within the latex particles promotes uniform fusion during film formation, resulting in films with superior tensile strength, elasticity, and tear resistance. Hence, controlling the extent of prevulcanization is critical for ensuring reproducible product performance. The degree of crosslinking is usually measured using equilibrium-swelling test (in toluene), Modulus test or estimated via Chloroform coagulation test.

Peroxide Vulcanization

Peroxide vulcanization is an alternative crosslinking mechanism, where thermal decomposition of organic peroxides generates free radicals that induce carbon–carbon crosslinks as shown in figure 2. Peroxide-vulcanized latex exhibits high thermal stability and low compression set, rendering it suitable for specialized applications. Nevertheless, peroxide systems are less prevalent industrially due to higher material costs, handling considerations, and generally lower tensile strength compared to sulphur-based systems.

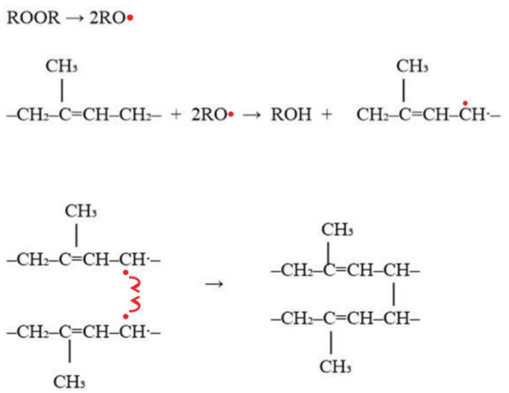

Figure 2: Reaction mechanism of peroxide curing.

Radiation Vulcanization

Radiation vulcanization employs high-energy ionizing radiation, such as γ-rays or electron beams, to induce crosslinking in latex. Free radicals generated within the rubber macromolecules lead to crosslinks without requiring elevated temperatures or chemical accelerators. γ-radiation, commonly sourced from Cobalt-60, is preferred for its high penetration power, whereas Caesium-137, despite a longer half-life, is rarely used due to lower γ-energy.

Electron beam irradiation has emerged as a controllable alternative, allowing precise adjustment of crosslink density. Low to moderate doses enhance mechanical properties, including modulus, tensile strength, elongation at break, and tear resistance. Excessive doses can cause chain scission and degradation, highlighting the importance of dose optimization. Transmission electron microscopy studies have confirmed that radiation vulcanization produces relatively homogeneous crosslinking within latex particles, favoring film formation and mechanical performance.

Radiation vulcanization offers several advantages: reduced chemical usage, room-temperature processing, and formation of carbon–carbon crosslinks with superior thermal stability. These characteristics are particularly advantageous for latex-based products subject to strict regulatory constraints, such as nitrosamine limits, accelerator- and protein-induced allergies, zinc discharge control, and environmental considerations during disposal. Despite these benefits, high capital and operational costs, coupled with safety and regulatory requirements, have limited widespread industrial adoption.

Industrial Applications and Advantages

Prevulcanized latex is ideally suited for dipping applications, such as gloves, condoms, and elastic coatings. Sulphur-based prevulcanization remains the preferred industrial route due to its cost-effectiveness, reproducibility, and scalability. Radiation and peroxide methods provide alternatives for high-performance or regulatory-sensitive applications, offering cleaner, chemically stable, and mechanically robust latex.

Overall, the prevulcanization of natural rubber latex represents a critical strategy in modern rubber technology. By precisely controlling crosslinking at the particle level and optimizing maturation conditions, manufacturers can produce latex products with tailored mechanical properties, enhanced stability, and compliance with environmental and health regulations.

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