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Effect of Curing Temperature on the Chemical and Mechanical Properties of Natural Rubber from Accelerator-Free Vulcanization Catalyzed by Dicumyl Peroxide

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Natural rubber films, commonly crosslinked using sulfur and accelerators such as zinc diethyldithiocarbamate (ZDEC), zinc-2-mercaptobenzothiazole (ZMBT), and tetramethylthiuram disulfide (TMTD), have been implicated in allergic reactions on human skin. To mitigate these effects, an alternative crosslinking system using peroxides has been proposed. While preliminary studies have shown that this peroxide system can produce satisfactory films, mechanical properties such as film strength have yet to be optimized. This study aims to enhance the mechanical properties of natural rubber films by eliminating accelerators from the formulation and employing peroxide crosslinking. Dicumyl peroxide, a long-chain organic peroxide, was selected for vulcanization to replace accelerators. Three different concentrations of dicumyl peroxide (1.5, 2.0, and 4.0 phr) were tested with continuous stirring for 48 hours. Curing of the latex films was performed at three different temperatures (100, 120 and 140 ºC) to identify the optimal drying temperature. The latex films underwent FTIR analysis to determine their chemical characteristics. FTIR analysis of the latex films containing dicumyl peroxide revealed characteristic peaks indicative of successful crosslinking, including C-H symmetric stretching vibrations and distinctive bands around 2964 cm^{-1} representing asymmetrical and symmetrical stretching modes of methyl groups. Tensile tests were conducted to assess the maximum tensile strength. There were notable trends in tensile strength, with the control set exhibiting an increase in strength up to 12.1 MPa at 140 °C, while sets containing dicumyl peroxide approached similar strengths to the control set at 100 °C. The results demonstrate the effectiveness of dicumyl peroxide in improving the properties of latex films and facilitating the production of allergen-free latex films with satisfactory mechanical characteristics. The tensile strength findings revealed significant variations across different curing temperatures and dicumyl peroxide concentrations, with sets containing dicumyl peroxide exhibiting comparable strength with the control set. By eliminating accelerators from the formulation and applying peroxide crosslinking, this study offers a promising avenue for mitigating allergic reactions on human skin caused by conventional sulfur-based vulcanization methods.

Keywords: Accelerator-free; peroxides; tensile strength; natural rubber

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Natural rubber latex is widely employed in the production of medical gloves due to its array of beneficial properties, including excellent infection control performance, durability, tear resistance, elasticity and tactile sensitivity [1]. It consists of long isoprene polymer chains that facilitate stretching and shape retention. Beyond medical gloves, natural rubber latex finds utility in the manufacturing of balloons, bladder catheters, dental dams, and rubber bands [2].

Natural rubber latex compounds are formulated by blending natural rubber latex with various chemical compounds to enhance its properties. Stabilizers like ammonia and potassium hydroxide are incorporated to enhance stability and maintain the colloidal system of the latex [3]. Vulcanizing agents, such as sulfur, are employed to improve rubber elasticity and mechanical properties by fostering crosslinks between rubber particles. Unvulcanized rubber inherently lacks strength and elasticity. Accelerators, like zinc diethyldithiocarbamate (ZDEC) and zinc mercaptobenzothiazole (ZMBT), are added to enhance vulcanization efficiency at lower temperatures (50-80 °C). The compounding process ensures that each chemical compound exerts specific effects on the resulting latex film. The crosslinking junctions play a crucial role in regulating the mechanical properties of cross-linked rubber [4]. The conventional method, which utilizes sulfur bridges to link C-C bonds and form a three-dimensional rubber network, is the most prevalent crosslinking approach for enhancing the mechanical properties of natural rubber [5]. Peroxide vulcanization, on the other hand, involves utilizing organic peroxide to forge C-C bonds between macromolecular chains. Notably, peroxide vulcanization offers high thermal stability [6].

The latex dipping method is a widely employed technique for producing natural rubber latex films, particularly in the fabrication of rubber gloves. In this process, plate-shaped ceramic formers are conveyed through various stages including cleaning, drying, coagulant dipping, latex dipping, gelling, vulcanizing, beading, and stripping [7]. This technique, involving the use of a latex concentrate to produce dipped products, stands as the oldest and simplest method in latex technology [8]. Groves et al.'s research in 2022 indicated that the latex dipping process, where a plate-shaped ceramic former is immersed in a coagulant solution (typically calcium nitrate), has been in practice for nearly a century [9]. Among the three latex dipping processes (straight dipping, coagulant dipping, and heat-sensitive dipping), coagulant dipping predominates in latex film production [8]. Overall, the latex dipping process proves highly effective in current latex film production.

The objective of this study was to introduce peroxide-crosslinking using dicumyl peroxide as an accelerator-free alternative to conventional sulfur crosslinking in natural rubber formulation and to ascertain the suitable range of curing temperatures (100, 120 and 140 °C) for peroxide-crosslinking of accelerator-free natural rubber. The latex films formed were evaluated based on two standards, ASTM D3578: Standard specification for rubber examination and ASTM D412: Tensile properties for vulcanized rubber.

EXPERIMENTAL

Chemicals and Materials

High ammonia natural rubber latex (HA NRL) was provided by Sri Trang, Thailand. Zinc oxide, dicumyl peroxide, sulphur, potassium hydroxide, antioxidant, titanium dioxide, zinc diethyldithiocarbamate, calcium carbonate, calcium nitrate, calcium carbonate and the wetting agent used in this experiment were AR (Analytical Reagent) grade and purchased from Sigma Aldrich.

Characterization Methods

Preparation of Latex Compounds

The latex compounds were prepared in five different sets. The first set was the control set, where the compounding of latex was done with the use of the accelerator ZDEC. Set 1 was prepared without the use of an accelerator or peroxide, while Set 2, Set 3, and Set 4 were prepared without an accelerator but with three different amounts of dicumyl peroxide (1.5, 2 and 4 PHR). Different amounts of dicumyl peroxide were added to study its effects on latex crosslinking and film strength. Set 2 used 1.5 PHR, Set 3 used 2.0 PHR, and Set 4 used 4.0 PHR of dicumyl peroxide. The formulation of the latex compounds in each set are listed in Table 1 below. The chemicals shown in Table 1 were mixed and stirred for 48 hours at room temperature.

Table 1. Different Sets of Latex Compound Formulations.

Chemicals	Samples									
	Control Set		Set 1		Set 2		Set 3		Set 4	
	PHR	Weight (g)	PHR	Weight (g)	PHR	Weight (g)	PHR	Weight (g)	PHR	Weight (g)
HA NRL	100	650	100	650	100	650	100	650	100	650
KOH	0.6	23.4	0.6	23.4	0.6	23.4	0.6	23.4	0.6	23.4
ZnO	0.6	3.9	0.81	5.27	0.6	3.9	0.6	3.9	0.6	3.9
Sulphur	0.9	5.85	0.84	5.46	0.9	5.85	0.9	5.85	0.9	5.85
Dicumyl Peroxide	-	-	-	-	1.5	9.75	2.0	13.0	4.0	26.0
Antioxidant	0.7	5.46	2	15.6	0.7	5.46	0.7	5.46	0.7	5.46
TiO_2	0.02	0.08	0.31	1.727	0.02	0.08	0.02	0.08	0.02	0.08
ZDEC	2.0	15.99	-	-	-	-	-	-	-	-

Coagulant Solution Preparation

The coagulant solution was prepared by mixing calcium nitrate, calcium carbonate, the wetting agent and water, and stirring for 18-20 hours at room temperature.

Chemical Characterization of Latex Compounds

The pH and swelling index values for every set were determined to observe the stability and crosslinking density of the latex compounds. A pH meter was used to measure the pH values of the latex compounds. For the swelling index, compounded latex was spread in a circle on a metal plate. The latex was then dried in the oven for 10 minutes at 100 °C. The dried latex was cut into a circle with a diameter of 5 cm and then dipped in toluene for 15 minutes. The change in diameter of the dried latex was recorded and the swelling index was calculated. Samples of each latex compound were taken for FTIR analysis to determine the changes in chemical structure of each formulation.

Latex Dipping

After both the latex compound and coagulant solution were prepared, the dipping process to form the latex film was performed. The ceramic plate former was washed and dried in the oven for 10 minutes at 100 ºC. The former was then dipped in the coagulant solution for 10 seconds before being placed in the oven at 100 ºC for 10 minutes. Then, it was dipped in the latex compound for 10 seconds and semi-dried in the oven. Next, the former coated with the latex compound was dipped in rinsing water at 60 ºC for 20 seconds. It was then dried in the oven for 25 minutes at 100 ºC, 120 ºC, and 140 ºC. Lastly, the former was cooled and coated with corn starch in order to strip off the latex.

Strength Characterization of Latex Film

The tensile properties of the films were determined using an Instron Universal tensile testing machine according to ASTM D412 and ASTM D3578. The tensile test was performed at 25 ºC with a crosshead speed of 500 mm/min. The tensile test data were used to calculate the tensile strength and elongation at break for every set.

RESULTS AND DISCUSSION

Chemical Characterization of Latex Compounds

Table 2 presents the pH and swelling index values measured for each set. Set 1 exhibited a pH value of 8.91, which was lower than that of the other sets as it was compounded without any accelerator or dicumyl peroxide. This lower pH could indicate a different ionization balance within the latex, potentially impacting the stability and homogeneity of the compound. Conversely, sets 2, 3 and 4 showed pH values of 9.67, 9.58 and 9.44, respectively, closely approximating the pH value of the raw HA NRL at 9.78. This suggests that the addition of dicumyl peroxide maintained the formulation's balance, contributing to consistent stability across these sets.

The swelling index values for Sets 2, 3, and 4 were 110 %, 104 %, and 100 %, respectively, all falling within the ideal range of 90-110 % for rubber compounds. This range is significant because it indicates an optimal balance between crosslink density and flexibility in natural rubber latex films. A swelling index within this ideal range suggests that the crosslink density is sufficient to impart desired mechanical properties while maintaining the necessary flexibility and durability of the latex film. Values above or below this range could indicate insufficient or excessive crosslinking, leading to weaker mechanical performance or reduced elasticity.

These results suggest that the crosslinking density of Set 2, utilizing 1.5 PHR of dicumyl peroxide, slightly exceeded the upper limit of the ideal range, indicating a potentially denser network structure. Conversely, Sets 3 and 4 demonstrated swelling index values within the optimal range, indicative of appropriately balanced crosslinking densities. This consistency in swelling index values across Sets 3 and 4 implies that the variations in dicumyl peroxide concentration did not significantly affect the crosslinking density within this range. These findings underscore the importance of careful consideration and optimization of dicumyl peroxide concentrations to achieve desired mechanical properties and performance characteristics in accelerator-free vulcanization processes.

Table 2. pH and swelling index values.

Parameter	Set 1	Set 2	Set 3	Set 4
pH	7.91	9.67	9.58	9.44
Swelling Index (%)	120	110	104	100

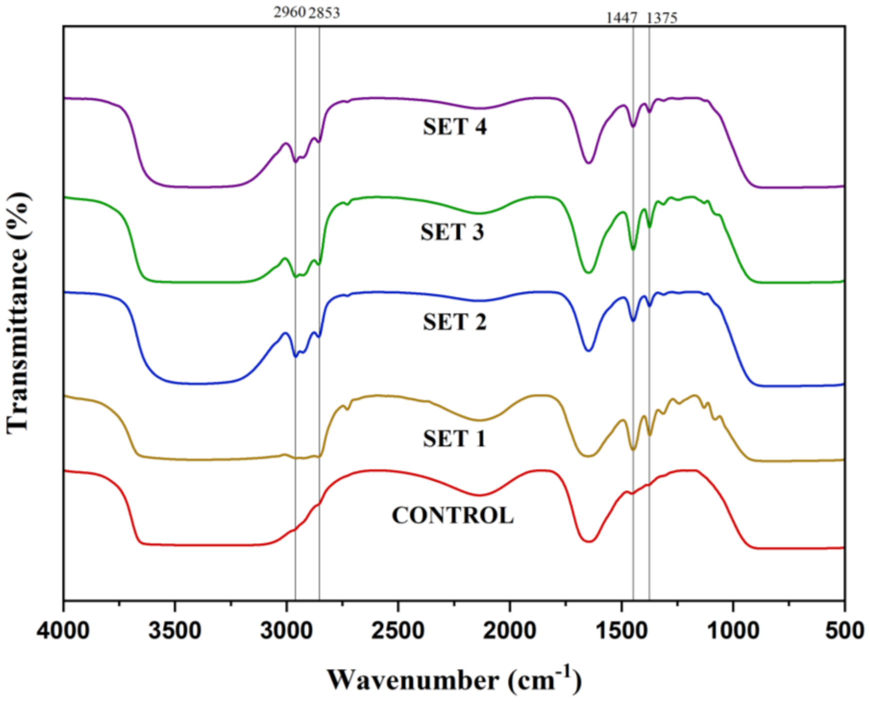

Figure 1. FTIR Spectra of Latex Compounds.

FTIR analysis was conducted to investigate both the occurrence of peroxide crosslinking in Sets 2, 3, and 4 (without accelerator), and the presence of the accelerator in the control set. Figure 1 presents the FTIR spectra for the control, Set 1, Set 2, Set 3, and Set 4. In the FTIR spectra of Sets 2, 3, and 4, distinctive peaks were observed, including C-H symmetric stretching vibrations for the methylene group at 2852 cm^{-1}, C-H symmetric stretching vibrations for the methyl group at 2960 cm^{-1}, and methyl C-H bending vibrations at 1447 cm^{-1}, alongside peaks corresponding to methylene groups at 1375 cm^{-1}. Particularly noteworthy was the presence of two distinct bands around 2964 cm^{-1} in the spectra of all rubber materials containing methyl groups. The first band arises from the asymmetrical stretching mode, where two C–H bonds of the methyl group extend while the third one contracts, while the second band results from symmetrical stretching, with all three C–H bonds extending and contracting in phase [10]. This chemical analysis offers valuable insights into the chemical composition and structural characteristics of the rubber compounds in each set, elucidating the mechanisms underlying peroxide crosslinking and accelerator presence [11].

Strength Characterization of Latex Films

Tensile Strength

Figure 2 illustrates the tensile strength of the latex films formulated with varying compositions at 100 °C, 120 °C, and 140 °C. The tensile strength of the control set exhibited an upward trend with increasing temperature, reaching a peak of 12.1 MPa when cured at 140 °C. Conversely, the tensile strength of the other sets generally decreased with higher curing temperatures. This trend aligns with previous reports indicating that lower vulcanization temperatures (less than 180 ^{o}C) require longer durations for optimal vulcanization, but yield improved vulcanizate properties [12]. Notably, Set 1 demonstrated the highest tensile strength among all sets at 100 °C, achieving a value of 10.5 MPa, despite lacking accelerator and peroxide. Among the sets containing dicumyl peroxide, Sets 2 and 4 approached similar tensile strengths to the control set at 100 °C. However, the tensile strength of Set 4, cured at 140 °C, fell to 1.4 MPa, the lowest value observed. This decline in tensile strength with increasing curing temperature can be attributed to the absence of accelerators and the presence of dicumyl peroxide in the latex formulation, which adversely affect the mechanical properties of the latex film under elevated curing temperatures. Elevated temperatures can lead to over-crosslinking or degradation of the rubber matrix, as excessive heat accelerates the breakdown of peroxide into free radicals, causing uneven crosslinking density and potentially degrading the polymer chains [13]. This can result in the compromised structural integrity and reduced tensile strength of the latex film.

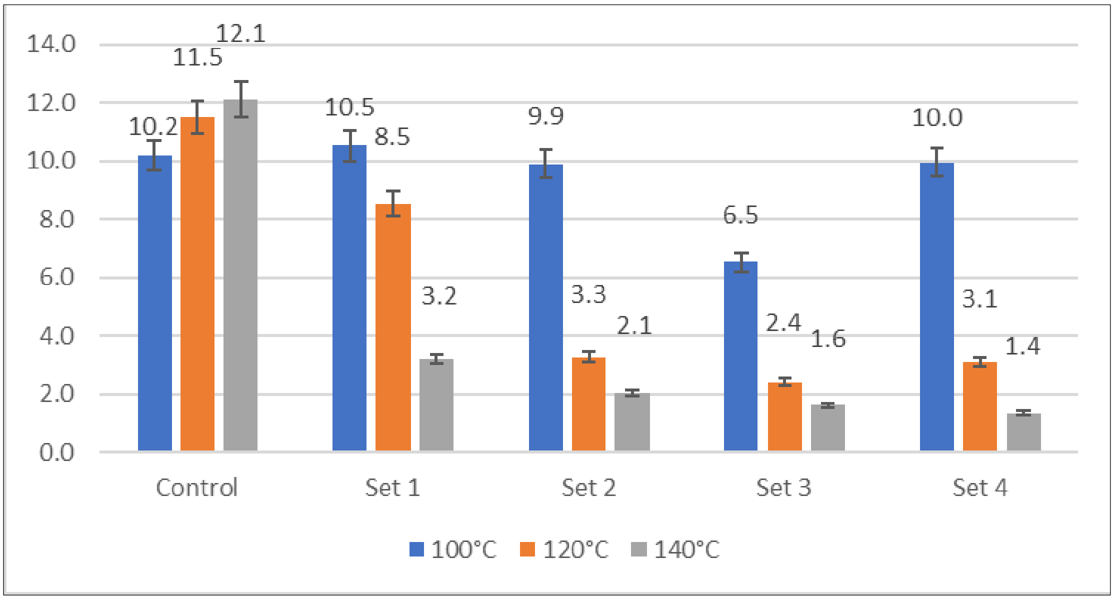

Figure 2. Tensile Strength (MPa) of Latex Films at 100 °C, 120 °C, and 140 °C.

Elongation at Break

The elongation at break (%) results of the latex films cured at various temperatures are depicted in Figure 3. Analysis of these results reveal a consistent decrease in elongation at higher temperatures, which is particularly evident for Sets 2, 3, and 4 at 140 °C. This decline can be attributed to overcuring at elevated temperatures, resulting in reduced stretchability of the latex films. Compared to the control set, which exhibited an elongation at break of 641.6 %, the latex films produced via peroxide vulcanization demonstrated lower elongation at break values. However, films cured at 100 °C and 120 °C using peroxide vulcanization still attained acceptable elongation at break levels. Notably, the elongation pattern of Set 1, lacking accelerator or peroxide, exhibited distinct variations at different curing temperatures. These findings underscore the influence of curing temperature and formulation composition on the elongation characteristics of the latex films, highlighting the need for precise control and optimization in film production processes.

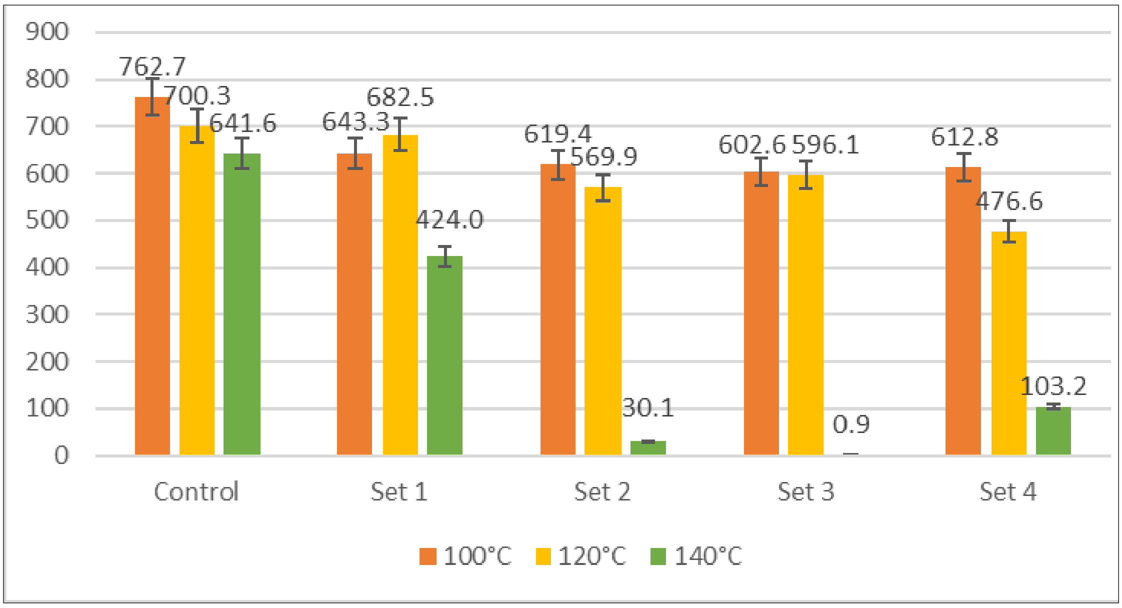

Figure 3. Elongation at Break (%) of Latex Films at 100 °C, 120 °C, and 140 °C.

The drying temperature employed during the formation of a natural rubber (NR) latex film holds considerable significance, as it significantly influences the resulting mechanical properties of the film. Prior research underscores the pivotal role of drying temperature in modulating the crosslinking process, thereby exerting a profound impact on the mechanical characteristics of the films [14]. Thin-walled products generated through immersion in NR latex typically undergo vulcanization within a temperature range of 100 to 150 °C, which notably falls below the customary temperature thresholds utilized for vulcanizing solid rubber products [15]. Nevertheless, findings from a study conducted by Harahap et al. revealed a positive correlation between higher drying temperatures and elevated tensile modulus values, compared to lower drying temperatures [16]. These revelations highlight the complex relationship that results between drying temperature and mechanical properties, indicating the need for careful optimization to produce appropriate film qualities.

In seeking alternatives to accelerators, peroxides offer a promising solution for the vulcanization of natural rubber latex films. Future studies could explore various organic peroxides and additives such as 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane (DHBP) under diverse curing conditions to optimize vulcanization efficiency and the mechanical properties of accelerator-free natural rubber latex films.

CONCLUSION

Peroxide-crosslinking of accelerator-free natural rubber latex demonstrated significant promise in producing latex films comparable to those obtained through conventional vulcanization methods. This study revealed that films produced using dicumyl peroxide at specific conditions exhibited comparable tensile strength to conventionally vulcanized films. The optimal curing temperature for peroxide-crosslinking, particularly with dicumyl peroxide, was identified as 100 °C, highlighting its potential in enhancing the film's mechanical properties. A consistent pattern was also observed across dicumyl peroxide-treated films, wherein tensile strength decreased with rising temperatures. These findings contribute valuable insights into advancing peroxide-crosslinking techniques as viable alternatives in latex film production, with implications for optimizing processing parameters to achieve desired mechanical attributes.

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