

Study on the Effect of Rare Earth Compounds Additives on the Properties of Natural Latex Films

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Abstract—Rubber is a material with significant influence worldwide, widely used in various fields. The main challenge for this industry is improving the existing drawbacks of natural rubber and creating diverse, high-performance products. This study aims to incorporate the rare earth compound strontium aluminate with natural rubber latex in the hope of producing products that can enhance some properties of rubber and exploit the phosphorescent capabilities of strontium aluminate for potential applications in research and the production of new products. Through measurements of 100% modulus (M100) and tensile strength at 500% elongation (M500), the results consistently demonstrate improved tensile strength. Simultaneously, aging and swelling tests show that incorporating strontium aluminate into natural rubber latex enhances the thermal and chemical resistance of the products. Additionally, the observation of products using scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA) of the NR/strontium aluminate sample yields promising results in demonstrating the positive effects of combining strontium aluminate and natural rubber latex.

Keywords— Noise reduction, Audio spectrum processing, Fruit quality determination.

I. INTRODUCTION

Currently, the development of new materials capable of meeting the growing demands of humans is receiving attention from scientists. Rubber, a material with significant global impact, is widely used in various fields[1]. Natural rubber, in particular, has been a traditional and indispensable material applied in various forms such as technical rubber in thin films, in industries, construction, and the medical field.

Recognizing the outstanding development potential of rare earth elements for various technologies in the modern era and considering Vietnam's rare earth reserves, it is essential to conduct research related to rare earth elements and the rubber processing and manufacturing industry. This opens up many opportunities to address issues and shortcomings of rubber, such as aging due to heat, improving mechanical properties for increased durability and applicability, replacing harmful substances in rubber formulations, etc. Additionally, incorporating the unique properties of rare earth elements, such as phosphorescence, into rubber can lead to the creation of new materials that bring significant benefits to society.

From the early years, the world began exploring the potential of rare earth elements in various aspects of life. This is evident in research related to natural rubber, as exemplified by Zhongkun Zou's study[2] on a rare earth complex

containing phenol and thioether groups that hindered styrenebutadiene rubber/synthetic silica nanocomposites with improved antioxidant properties. In 2016, Yongkun Zou and colleagues[3] focused on enhancing the mechanical properties styrene-butadiene rubber/silica nanocomposites of by modifying the interfacial region with a new rare earth complex. Yanping Wang and collaborators[4] investigated the mechanical properties of heat-treated modified natural rubber with cerium oxide in 2017, showing that CeO₂ could effectively be used as a reinforcing filler to improve the mechanical bonds of rubber, such as high wear resistance, high tear strength, and good heat aging resistance. In 2019, researchers from the Faculty of Materials Technology at Ho Chi Minh City University of Technology[5] conducted research on the influence of cerium oxide on the properties of natural rubber.

In this study, we will investigate the influence of the additive rare earth compound, specifically Strontium aluminate, on the properties of rubber membranes. Strontium aluminate possesses outstanding properties that can be applied to rubber, and its phosphorescent characteristic is one of the features that may bring about new breakthroughs in the rubber processing and manufacturing industry in the present and future.

II. MATERIALS AND METHODS

A. Materials

Natural rubber latex supplied by Duy Hang Company, Vietnam, with a total solid content (TSC) of 60% and pH of 8. Strontium aluminate powder (SrAl₂O₄:Eu²⁺) was purchased from Shandong Zhishang New Materials Co., Ltd (China), with particle sizes ranging from 15-95 μ m. The experiments utilized a sulfur vulcanization system, with accelerator and activator additives such as zinc oxide (ZnO), ZMBT, ZDEC. CaCO₃ powder was used as a filler, and in addition to this, PVA was employed as a dispersing agent, tween 80 as a surfactant, and KOH as a pH stabilizer. All these chemicals are industrial-grade and sourced from Vietnam.

B. Methods

The sample immersion film preparation process consists of three stages as follows:

First, the filler $CaCO_3$ and the substances in the vulcanization system such as S, ZMBT, ZDEC, ZnO in solid form will be put into a ball mill and add water to form

mixtures in solution form and then proceed to determine the TSC content to calculate the amount of substances forming a suitable compounding unit (shown in Table I). Next, NR latex is poured into a 500ml becher, ensuring pH stability \geq 7, adding water and KOH solution according to the calculated ratio and stirring for 30 minutes. pH values of the mixture are regularly checked during this process. The vulcanization system, consisting of S, ZnO, ZDEC, ZMBT, is added to the mixture, and continuous stirring is maintained for 24 hours to achieve homogeneity. pH is monitored continuously during this period to ensure a value of ≥ 8.5 . Then, CaCO₃ powder is added to the mixture and stirred for an additional 24 hours. The purpose is to ensure even dispersion of materials and to facilitate crosslinking formation between latex and the vulcanization system. The stirring system is turned off, and the mixture is allowed to stabilize for 2 hours.

TABLE I. Rubber formulation for finished product

Ingredient	Amount (phr)
Latex NR	100
KOH	0.1
S	1.2
ZnO	0.6
ZMBT	0.4
ZDEC	0.4
CaCO ₃	3.0
Aquanox	0.2

In the second stage, strontium aluminate powder is dispersed into a PVA and tween 80 solution. PVA is weighed according to calculated mass and added to distilled water at the required concentration. The PVA solution is stirred rapidly at room temperature for about 15 minutes to completely wet and disperse the solid, avoiding PVA particles settling at the bottom. Next, the PVA solution is heated to 90°C for 3 hours to obtain a homogeneous solution. Then, tween 80 and strontium aluminate are added and stirred for 1 hour to prevent unwanted gel formation during this process to obtain a homogeneous solution.

After stirring the PVA solution containing the strontium aluminate mixture, it is promptly added to the previously stirred latex mixture at high speed at room temperature for about 1 hour. This ensures even dispersion of the fluorescent polymer mixture in the latex solution.

This solution will be used to assess the impact of the strontium aluminate additive on the properties of natural rubber latex immersion films.

C. Evaluation Method

The evaluation values were obtained through the following standard tests, and these values represent the average of five measurements for each test as follows:

Tensile strength: Modules at 100%, 500% and tensile strengh are tested using a Testometric machine (Model M500-50CT), following ASTM D412:2004 standards, with a dumbbell-shaped sample.

The Brookfield method was employed to determine the viscosity of latex. It adheres to TCVN 4859:2007 standards (ISO 1652:2004). After synthesizing and stabilizing the

solution mixtures for the required duration, they were placed in a 100ml beaker for viscosity measurement.

Aging resistance testing of materials was conducted to determine the environmental durability and aging resistance of rubber materials. Test samples were prepared according to specified standards and placed in a drying cabinet at 70°C for 24 hours. After the designated time, the samples were taken out, allowed to stabilize for at least 4 hours at room temperature (but not exceeding 96 hours), and then the properties of the samples were measured following the aging test. The degree of aging (P) of the material was calculated using the formula:

$$P = \frac{A - O}{O} \times 100\%$$

where:

A: the tensile strength after aging.

O: the tensile strength before aging.

The volume swelling of the rubber compound is determined according to TCVN 2752:2008 standards (ISO 1817:2005). Toluene is used as the solvent. The mass of the sample is measured after 1, 3, 5, 24, 48, 72 hours, and so on until reaching saturation mass. The volume swelling is determined by the following formula:

$$\Delta G = \frac{G_2 - G_1}{G_1} \times 100\%$$

where:

 Δ G: volume swelling (%)

G₁: mass of the sample before immersion (g)

G₂: mass of the sample after immersion (g)

Samples with dimensions of $20\text{mm} \times 20\text{mm} \times 2\text{mm}$ are weighed before being immersed in the solvent. They are immersed in the solvent at various time intervals, and then taken out to determine the increase in mass.

The morphology of NR film and NR/strontium aluminate film at magnifications X100, X5000 has been examined using scanning electron microscopy (SEM) at an accelerating voltage of 10.0 kV. Before scanning, the samples are placed on a dish and fixed with double-sided carbon tape. Subsequently, the samples are coated with a thin layer of gold to prevent charging during the analysis.

Thermogravimetric Analysis (TGA) can determine the thermal stability of materials. The conditions for TGA analysis include:

- Sample holder: platinum
- Investigative atmosphere: Nitrogen gas
- Heating rate: 10°C/minute
- Analysis temperature: from room temperature to 600°C

III. RESULTS AND DISCUSSIONS

3.1. Investigation of PVA and Tween 80 concentrations

A. Impact on viscosity

The latex mixture is stirred according to the formulation, using a fixed amount of 1.5% tween 80 and 0.5 phr strontium aluminate. After stabilizing for 2 hours, viscosity parameters are tested. The investigation is carried out with samples having PVA concentrations of 1, 1.25, 1.5, 1.75, 2%. The results obtained are shown in Fig. 1.





Figure 1. The viscosity of the PVA samples

Increasing the PVA concentration results in an increase in the viscosity of the latex mixture. Specifically, at PVA concentrations ranging from 1 to 1.5%, the viscosity of the latex mixture increases from 100.33 cP to 111.33 cP. However, when using PVA solutions from 1.5 to 2%, the viscosity of the mixture increases from 111.33 cP to 488 cP, with a viscosity difference of 387.67 cP. The abrupt increase in viscosity with increasing PVA concentration may be attributed to the different solubilities of PVA and natural rubber latex.

It can be explained that as the PVA concentration increases, PVA surrounds the particles of natural rubber latex, hindering their movement in the liquid environment[6]. An increased amount of PVA means more latex particles are surrounded, leading to greater resistance forces and, consequently, an increase in the viscosity of the latex mixture in the direction of increasing PVA content.

The latex mixture is stirred according to the formulation and stabilized for 2 hours before viscosity testing. Using a PVA concentration of 1.25% and a fixed strontium aluminate content of 0.5 phr, the survey is conducted with varying tween 80 concentrations (0, 0.5, 1, 1.5, 2%). The results can be found in Fig. 2.



As the concentration of the surfactant (tween 80) increases, the viscosity of the mixture gradually decreases. Specifically, with no tween 80, the viscosity of the mixture is 126.667 cP. When the tween 80 concentration in the mixture is 2%, the viscosity significantly decreases to 49.33 cP. This can be explained by the ability of tween 80 to reduce the interfacial tension between the phases when blending the latex mixture with the PVA and strontium aluminate mixture. Tween 80, with its dual hydrophilic-lipophilic structure, can decrease the viscosity of the mixture, thereby enhancing the dispersibility of the components in the solution.

B. Impact on mechanical properties

The measured mechanical properties of the PVA concentration samples are presented in Fig. 3.



Figure 3. Modulus M100 and M500 of PVA samples

It can be observed that the stress at 100% and 500% elongation increases when the PVA concentration is increased from 1 to 1.75%, and this stress decreases as the PVA concentration continues to increase. The tensile stress at break shows a similar trend. The stability of natural rubber latex particles will be improved as the spatial barrier is provided by the PVA layer surrounding the natural rubber particles [7]. The PVA layer surrounding the latex particles provides additional stability for the latex particles, strontium aluminate particles, and additive particles. Although electrostatic repulsion may inefficiently push NR particles into contact with each other, the spatial barrier created by the PVA layer prevents the aggregation of NR particles, a cause of the coagulation process. Therefore, an increase in PVA content also contributed to the improvement of the mechanical properties of the post-curing sample. However, according to W. Wongthep [7], previous studies have revealed that the surface of natural rubber latex particles is not smooth but covered by a layer of phospholipid and protein mixture, and the PVA layer surrounding NR particles hinders the movement of the particle through the liquid environment by creating some friction as the liquid passes through the PVA layer surrounding NR particles. This indicates that an increase in PVA content reduces the mobility of molecular particles in the latex mixture, leading to their combination to form bonds

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between rubber and other substances in the mixture. This is also evidenced by the reduction in stress when the PVA concentration exceeds 1.75%. Based on the viscosity measurement results, the increase in viscosity when the PVA concentration increases from 1-1.5% also facilitates the dipping process.

The results of mechanical property measurements for samples with Tween 80 concentration are displayed in Fig. 4.



Figure 4. Modulus M100 and M500 of Tween 80 samples

The results show that the values of M_{100} and M_{500} for the samples remain relatively stable as the concentration of Tween 80 increases. Specifically, for the sample using 1% Tween 80, the M_{100} and M_{500} are 0.613 and 0.967 N/mm², respectively. In contrast, for the sample with 2% Tween 80, the M_{100} and M_{500} are 0.553 and 1.083 N/mm². This indicates that the increase in Tween 80 concentration does not significantly affect the mechanical properties of the film. The use of Tween 80 improves the dispersion ability of PVA and strontium aluminate particles in the latex rubber environment.

3.2. Investigation of Strontium Aluminate

The study was conducted with different concentrations of strontium aluminate: 0, 0.25, 0.5, 0.75, 1 phr. During the sample preparation, the concentration of PVA solution was maintained at 1.25%, and the Tween 80 concentration was 1.5%, with the remaining components following the formulation. The samples were allowed to stabilize for 2 hours before testing the viscosity parameters.

Fig. 5 shows that when the concentration of strontium aluminate increases in the mixture, the viscosity of the mixture also increases, but not significantly. Specifically, the viscosity of the mixture increases from 90.667 cP to 121.333 cP, corresponding to strontium aluminate concentrations of 0 and 0.75 phr. It can be said that adding strontium aluminate to the compound does not significantly affect the viscosity of the mixture, partly because the added amount of the compound is not substantial. However, the increase in viscosity indicates that there has been interaction between strontium aluminate and the latex mixture. When the concentration of strontium aluminate in the mixture increases to 1 phr, the viscosity

abruptly increases to 486.667 cP. This is due to the positively charged strontium aluminate particles, while the latex mixture carries a negative charge. When the concentration of strontium aluminate increases, the amount of PVA is not sufficient to encapsulate all the strontium aluminate particles, causing them to come into contact with the latex more. This leads to the phenomenon of physical coagulation, causing the mixture to coagulate and resulting in a sudden increase in viscosity. Excessive viscosity and coagulation difficulties can pose challenges in creating samples in the future.



Figure 5. Viscosity of the Strontium aluminate samples

The mechanical property results of the Strontium Aluminate study are shown in Fig. 6 and Fig. 7.



Figure 6. Modulus M100 and M500 of Strontium aluminate samples

It is obvious that the stress at 100% and 500% tends to increase as concentration increases. For the film without strontium aluminate, the stress at 100% and 500% reaches values of 0.520 (N/mm2) and 1.033 (N/mm²), respectively. In contrast, the film containing 0.5 phr of strontium aluminate has M100 and M500 values of 0.620 and 1.157 (N/mm²). The stress values at 100% and 500% continue to increase as the concentration of strontium aluminate increases to 1 phr. This indicates that strontium aluminate contributes to strengthening the molecular chains due to the enhancing effect of the



interaction between strontium aluminate particles and the polymer. As a result, the stress values at 100% and 500% increase with the increasing concentration of strontium aluminate.



Figure 7. Modulus at break of Strontium aluminate samples

As the strontium aluminate content increases, overall, the tensile strength of the membrane increases. In particular, tensile strength increases significantly when the strontium aluminate content increases from 0 to 0.25 phr. For example, in samples without strontium aluminate, the tensile strength is 18.787 (N/mm²), while in samples with 0.25 phr of strontium aluminate, the tensile strength is 21.519 (N/mm²).

According to Z. N. Ain and colleagues, the increase in initial tensile strength when the filler content increases is due to the reinforcing effect of fine fillers creating a large amount of bonding between the filler and polymer in the rubber matrix [8]. Although the strontium aluminate content used in the mixture is not much, it can be considered as part of the filler in the latex mixture. The increase in tensile strength indicates that there is a bond between rubber and strontium aluminate. When force is applied to samples without fillers, the force will mainly act directly on the bonds between the rubber chains, making them easier to break. However, with samples containing added strontium aluminate, when force is applied, it will not immediately attack the bonds between rubber chains, but instead, the bonds between strontium aluminate particles and rubber will be attacked first. The graph shows that tensile strength increases when the strontium aluminate content increases from 0 to 0.25 phr. However, after that, tensile strength decreases and hardly changes, not increasing even though additional strontium aluminate is added. The decrease may start from regions not filled by latex due to uneven dispersion of strontium aluminate particles. These voids act as initial crack sites, leading to the concentration of local stress during deformation. After decreasing, tensile strength hardly changes, which may indicate that a bond has formed between the latex mixture and strontium aluminate. Although it decreases, it remains stable without an increase even when the strontium aluminate content increases to 1 phr. This demonstrates that the amount of bonding has reached an optimal value, so even with an increase in strontium

aluminate, the number of bonds does not increase but reaches a saturated value.

3.3. Evaluation of Morphology, Structure, Thermal Properties, Heat Resistance, and Chemical Resistance of NR/Strontium Aluminate Material

A. Heat aging resistance

The results of testing the heat aging resistance of the material are presented in Fig. 8.



When strontium aluminate is present in the material, it alters the material's aging coefficient. The lowest value is observed when the sample does not contain strontium aluminate, and it tends to increase as the strontium aluminate content reaches 0.75 phr, decreasing when the content exceeds the optimal limit. The explanation is that at 1 phr of strontium aluminate, particles agglomerate on the surface, creating voids and defects that make the material susceptible to environmental factors, reducing its environmental resistance.

B. Chemical resistance

The chemical resistance test results are illustrated in Fig. 9.

The swelling ratio in toluene increases with the strontium aluminate content in the mixture. After 96 hours, the swelling ratios for samples with 0, 0.25, 0.5, 0.75, 1 phr ST are 400%, 440%, 450%, 463.64%, and 512.5%, respectively, compared to the initial sample. The results show that after 1 hour, the samples are almost saturated. Samples without strontium aluminate have lower swelling ratios than those with strontium aluminate. Notably, there is a significant difference between samples with 0.75 and 1 phr. The ST particles and the latex rubber matrix reduce solvent penetration, resulting in a lower swelling index of the membrane. However, factors such as the formation of voids/pores, the type of filler, and the filler amount also affect solvent absorption [9]. The results indicate that as the amount of strontium aluminate increases, the swelling index also increases, and the latex membrane with 1 phr strontium aluminate has the highest swelling index, more than 25% higher than the control membrane (0 phr). This slight increase is attributed to the formation of voids/pores,

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providing pathways for solvent infiltration, thereby enhancing solvent absorption capacity.



C. Surface observation results using SEM

At 100x magnification (Fig. 10), both samples, with and without strontium aluminate, show scattered particles on the surface. Sample (a) appears smoother with fewer imperfections, while sample (b) is less smooth, showing more scattered particles. However, at 100x magnification, the internal structure of the membrane is not clear. Therefore, observations were made at a higher magnification.



Figure 10. SEM of samples at 100x magnification (a) samples without strontium aluminate, (b) samples with 0.5 phr strontium aluminate

At 5000x magnification, a clear difference between the standard sample without strontium aluminate and the sample with strontium aluminate is visible. In Fig. 11(c), it is easy to observe that the particles agglomerate and distribute extensively on the sample surface. This can be explained by the fact that rubber has an amorphous structure, causing large voids between rubber chains, and the surface contracts to form particles. Alternatively, this phenomenon may be due to ZnO having a specific gravity of 5.61 g/cm³, higher than the specific gravity of rubber, causing it to settle and not disperse in the latex mixture, resulting in agglomerated particles on the membrane surface[10]. Meanwhile, in Fig. 11(d), although there are still aggregated particles on the surface, the quantity is evidently less, and the distribution is sparser. This demonstrates that the sample with added strontium aluminate helps disperse the components in the mixture better. The strontium aluminate particles also act as a structured positioning in the rubber chains, reducing the occurrence of "particle agglomeration."



Figure 11. SEM of samples at 5000x magnification: (c) samples without strontium aluminate, (d) samples with 0.5 phr strontium aluminate

D. TGA analysis

The TGA analysis results reveal the temperature range for the initiation and completion of material decomposition, along with the peak temperature of the most intense decomposition. The summarized outcomes are presented in Table II.

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TABLE I. IGA results					
Sample	Temperature at initiation of decomposition	Temperature at completion of decomposition	Peak temperature		
0 phr	279.15	383.91	479.95	87.86	
0.5 phr	266.33	376.14	509.85	86.07	
1 nhr	292.76	381 77	195 62	88 52	

The results indicate that the decomposition rate of the sample without strontium aluminate is faster than that of samples with strontium aluminate. The start temperature of the decomposition of the sample containing 1 phr strontium aluminate is 292.76°C, while for the sample without strontium aluminate, it is 279.15°C, demonstrating that adding strontium aluminate increases the starting temperature of the material's thermal decomposition. The temperature range of the thermal decomposition process for 0.5 phr and 1 phr strontium aluminate is longer than for 0 phr, indicating that the use of strontium aluminate enhances the material's heat resistance, and the longer decomposition time suggests that more time is needed to break the bonds formed between latex and strontium aluminate, increasing both the start temperature and the temperature range of the decomposition process.

IV. CONCLUSSIONS

Through the research process and analysis of the collected data, the following conclusions can be drawn. The optimal PVA concentration for single-phase formation is in the range of 1.25-1.75%. The optimal Tween 80 concentration for single-phase formation is in the range of 0.5-1.5%. Adding strontium aluminate to the latex mixture enhances the mechanical properties of the membrane. The appropriate strontium aluminate content for single-phase formation is in the range of 0.25-0.75 phr. Aging evaluation, swelling measurement, SEM imaging, and TGA analysis all support the feasibility of combining strontium aluminate with natural rubber latex.

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