Effects of Hybrid Filler and Mixing Equipment on the Mechanical and Thermal Properties of NR/EPDM Rubber Blends

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Abstract: This research evaluated the effects of hybrid fillers and mixing equipment on natural rubber (NR) and ethylene propylene diene monomer (EPDM) properties with an 80/20 ratio. Silica (Si), carbon black (C), china clay (CC), and calcium carbonate (Ca) were used as hybrid fillers. Mixing techniques using two-roll mill and an internal mixer were compared. The study focused on cure characteristics, mechanical properties, and thermal stability. The study found that incorporating hybrid fillers significantly improved the curing process. Blends prepared by an internal mixer had more consistent mechanical properties such as modulus, tear strength, and hardness compared to those prepared by two-roll mill. Blends with Si and C (NE-SiC) showed significant enhancements in tensile and tear strength. Although adding multiple fillers did not accelerate curing, it enhanced the modulus, indicating a potential synergistic effect. The internal mixer method resulted in better elongation at break, except for the NE-SiC-CC.Ca blend, which had reduced flexibility. Thermal analysis revealed higher thermal stability for blends with hybrid fillers, decomposing at elevated temperatures with larger residues, particularly in NE-SiC-CC and NE-SiC-CC.Ca blends. These research findings highlight the critical role of filler types and mixing methods in optimizing the performance of NR/EPDM rubber blends.

Keywords: natural rubber; EPDM; rubber blends; hybrid filler; mechanical properties

INTRODUCTION

Blending rubber products to obtain new materials with a wide range of applications plays an important role in rubber product manufacturing because it can combine the attractive properties of the two components. It is also more effective than the synthesis of new polymer materials when considering the uncertainty of economic and preparation techniques. Polymerization of ethylene and propylene with a small amount of unconjugated diene usually gives good deterioration properties, oxidation in good weathering, and chemical resistance. Typically, the exterior properties of diene rubbers such as polybutadiene (BR), nitrile rubber (NBR) [1-4], styrene-butadiene rubber (SBR) [5], or natural rubber (NR) [6-7] could be greatly improved by incorporating low unsaturated rubber, such as ethylene propylene diene monomer (EPDM). Among the many high-diene rubbers, NR is a natural polymer with many interesting properties. It has excellent physical properties and good machinability characteristics but exhibits poor heat and UV radiation resistance. Therefore, mixing NR with EPDM is a useful approach to preparing new rubber materials with high resistance to aging. This mixture may provide a mixture of rubbers, which may be technologically significant. This is because it combines EPDM’s excellent outdoor properties with NR’s good resilience properties [4]. Botros [8] and Alakrach et al. [9] investigated the effect of different blend...
compositions of NR/EPDM on the swelling behavior of the blend in motor oil under compression strain. Some reports have appeared on improving the poor compatibility of EPDM with high diene content rubbers, such as the modification of EPDM with maleic anhydride (MA) [6-7,10], amino silane [11] as a compatibilizer for NR/EPDM, the functionalization of EPDM with mercapto groups as a compatibilizer in NBR/EPDM blends, and brominated EPDM blends with NR. All of these blends showed improved compatibility and rheological mechanical properties.

Fillers play a big role in changing the mechanical, thermal, and processing properties of rubber blends made of NR and EPDM. Common fillers like carbon black (C) [2,11], silica (Si) [12-13], clay [14], calcium carbonate (Ca), natural halloysite nanotubes [15], carbon nanotube [16], ZnO nanoparticles [18], rice husk fiber [3], and all mixed [19] are selected based on the desired outcome, such as enhanced tensile strength, wear resistance, or cost efficiency. The compatibility and dispersion of these fillers within the rubber matrix are crucial for optimizing the blend’s performance, impacting factors such as durability, heat resistance, and processing characteristics. Properly integrated, fillers can tailor NR/EPDM blends for specific applications, balancing the inherent qualities of elasticity and resilience of NR with the weathering resistance of EPDM. In addition to our knowledge, no study has been found that compares NR/EPDM blended compounds prepared by different mixing equipment.

The objective of this work was to study the effects of hybrid fillers and mixing equipment on the properties of NR/EPDM rubber blends. Si, C, china clay (CC), and Ca were used as hybrid fillers. The two-roll mill and internal mixer were used to prepare NR/EPDM rubber blends. The mechanical properties containing tensile properties, hardness, compression set, tear strength, and thermal properties of the blends were described.

- EXPERIMENTAL SECTION

Materials

NR (STR 5L) was produced by the Rubber Plantation Organization (Nabon), Ministry of Agriculture and Cooperatives. EPDM rubber grade Vistalon 2504 has an ethylene content of 55.5% by weight and contains 3.8% by weight of ethylidene norbomene (ENB), manufactured by ExxonMobile chemical. Stearic acid (C₁₇H₃₅O₂), zinc oxide (ZnO), sulfur (S), N-tertiarybutyl-2-benzothiazole sulfenamide (C₁₁H₁₄N₂S₂, TBBS) and tetramethylthiuram disulfide (C₆H₁₂N₂S₄, TMTD) were commercial grade as used in the rubber industry.

Instrumentation

Yong Fong Machinery Co., Ltd. and Charoen Tas Co., Ltd. manufacture and supply the two main instruments used to prepare NR/EPDM rubber blends: a two-roll mill and an internal mixer. We applied the rheometer (TECH-PRO) to study the cure and vulcanization characteristics. The tensile properties were measured with an Instron model M350-10AT machine, and the thermal degradation properties of NR/EPDM rubber blends were looked at with a PerkinElmer TGA4000 analyzer.

Procedure

Preparation of NR/EPDM blends

There were two ways to prepare NR/EPDM rubber blends by using two different instruments, which are a two-roll mill rubber mixer and an internal mixer to mix rubber and chemicals. They were mentioned as Method 1 and 2, respectively. In Method 1, the first step entails masticating the NR for 3 min before adding an EPDM rubber, activator, fillers, accelerator, and vulcanizing agent in succession for a total of 15 min of mixing. In Method 2, mixing was carried out in an internal mixer. NR was first masticated in the mixer for 3 min. EPDM was then mixed, followed by the addition of activators (ZnO and stearic acid), fillers, and an accelerator. The completely vulcanized compound was prepared by adding sulfur using a laboratory-sized two-roll mill mixer for 5 min, details of which are shown in Fig. 1. Table 1 shows the blend formulation used in this study. The fillers containing Si, C, CC, and Ca were used as hybrid fillers. The cure and vulcanization characteristics, mechanical properties, and thermal properties of the blend compounds were carried out using the following procedures.
Fig 1. Block diagram of the preparation of NR/EPDM blends: Method 1 (two-roll mill mixer process) and Method 2 (internal mixer process)

Table 1. Formulation of blend compounds

<table>
<thead>
<tr>
<th>Components</th>
<th>NE-0</th>
<th>NE-SiC</th>
<th>NE-SiC-CC</th>
<th>NE-SiC-Ca</th>
<th>NE-SiC-CC.Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>STR 5L</td>
<td>80.0</td>
<td>80.0</td>
<td>80.0</td>
<td>80.0</td>
<td>80.0</td>
</tr>
<tr>
<td>EPDM</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>TBBS</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Silica</td>
<td>-</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>C-Black</td>
<td>-</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>-</td>
<td>-</td>
<td>40.0</td>
<td>-</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Cure characteristic. Cure characteristics were studied according to the ISO 3414 method for 30 min at 150 °C. The testing procedure was conducted according to the ISO 289-1 method.

Vulcanization process. The vulcanization process was carried out. All compounds were compression molded at 150 °C using a hydraulic hot press. The respective cure time, T₉₀, was determined by a rheometer. Rubber blends were conditioned for 24 h before testing.

Mechanical properties. Mechanical properties were evaluated by tensile, hardness, compression set and tear testing. Tensile properties (tensile strength, elongation at
break, and modulus) were determined according to ASTM D412 at a 500 mm/min crosshead speed. The hardness measurement of samples was done according to ASTM D2240 (shore A). The compression set measurement of samples was done according to ASTM D395 method B – compression test under constant deflection in air at 70 °C for 72 h. The tear properties of the samples were measured according to ASTM D624 type C (right angle). The maximum force required to cause a test piece to rupture is then divided by the thickness of the test piece.

Accelerated thermal aging test. Accelerated thermal aging test of the blends was carried out. Tensile, tear, and hardness specimens were aged at 70 °C for 72 h in an air-circulating aging oven. The tensile, elongation at break, tear and hardness properties of the aged samples were determined using ASTM D573.

Thermal gravimetric analysis. Thermal degradation of the NR/EPDM blends was studied by thermal gravimetric analysis (TGA) under nitrogen. A ramp mode TGA analysis was performed. The heating rate was applied at a 10 °C/min rate from 30 to 800 °C. The original state of the sample weight was around 4 mg. The TGA thermograms were evaluated to determine the temperatures at which decomposition begins.

■ RESULTS AND DISCUSSION

Cure Characteristics of NR/EPDM Blends

Fig. 2 shows a chart that compares the optimum cure times at 90% conversion for various NR, and EPDM blends with different fillers using two mixing methods: a two-roll mill and an internal mixer. The unfilled blend (NE-0) exhibits the highest cure time, suggesting fillers reduce cure time. NE-SiC (with Si and C) and later samples with CC (NE-SiC-CC) and Ca (NE-SiC-Ca) have shorter cure times, which shows that these fillers work well in the curing process [11]. The blend containing all fillers (NE-SiC-CC.Ca) doesn't significantly outperform the single-filler variants, suggesting no synergistic effect on cure time reduction. Across all variants, the two-roll mill method results in marginally longer cure times than the internal mixer, highlighting that while the mixing method influences cure time, the type of filler plays a more substantial role.

Mechanical Properties of NR/EPDM Blends

Fig. 3 shows the 100% modulus, which is the stress at 100% elongation, for different samples of NR and EPDM blend. This shows how different fillers and mixing methods change the material’s ability to resist deformation. The NE-SiC mix, which has Si and C added to it, has a much higher modulus than the NE-0 base sample, which is not filled. Adding CC to NE-SiC-CC and Ca to NE-SiC-Ca makes the mixtures stronger than the base, but the strength depends on the filler and how the mixtures are mixed. Notably, incorporating all fillers, the NE-SiC-CC.Ca sample exhibits one of the highest moduli, especially when mixed using an internal mixer, suggesting that the combination of fillers may have
Fig 3. Modulus of the NR/EPDM blends and composites with hybrid filler and mixing equipment

Fig 4. Tensile strength of the NR/EPDM blends and composites with hybrid filler and mixing equipment

Moreover, the internal mixer generally produces blends with slightly higher tensile strength than the two-roll mill, highlighting the influence of the mixing technique on the material properties. NE-0 is a rubber blend with lower tensile strength than a rubber blend with reinforcement fillers. Since NR and EPDM rubber are two types of rubber with different chemical structures, they are difficult to make compatible. EPDM rubber is a type of rubber that has few diene groups in its molecular structure. NR has many diene groups in its molecular structure [20]. Because of this difference, the compatibility between both rubbers decreased, and the tensile properties of rubber blends were low. Therefore, it is necessary to use reinforcing fillers to help improve the properties.
Elongation at break measures a material’s ductility, indicating how much it can stretch before it breaks. Fig. 5 demonstrates that the NE-SiC sample mixed using an internal mixer has the highest elongation at break, indicating that this combination of fillers and mixing technique produces the most ductile material. Generally, the internal mixer produces materials with higher elongation at break percentages than the two-roll mill across all samples. This might be due to the better dispersion of fillers and more uniform material properties achieved with the internal mixing process. The NE-SiC-CC.Ca sample has the least amount of elongation at break for both mixing methods. This could mean the fillers may make the material less flexible when mixed.

Fig. 6 demonstrates that samples mixed using the internal mixer typically have a higher hardness than samples mixed using the two-roll mill, with the NE-SiC/Ca sample showing the highest hardness value when mixed using the internal mixer. This suggests that the method of mixing significantly impacts the final material's hardness, with the internal mixer possibly providing better filler dispersion, leading to increased hardness. Additionally, the presence of fillers increases the hardness compared to the base NE-0 sample, with varying effects depending on the type of filler used. The NE-SiC sample has a higher hardness than NE-0 but is not as hard as the samples with additional fillers, indicating that the combination of fillers may contribute...
Fig. 7 depicts the compression set values for a series of rubber compounds, where a high value indicates less flexibility and a low value denotes greater resilience. The base compound without fillers, NE-0, demonstrates moderate resilience, particularly when mixed with an internal mixer, which yields a higher compression set than mixing by a two-roll mill. The NE-SiC sample, containing Si and C, exhibits lower resilience, especially with internal mixing. However, the NE-SiC-CC blend, which includes CC, shows higher compression set values, indicating decreased flexibility. The NE-SiC/Ca sample with Ca and the NE-SiC-CC.Ca sample with a mix of all the fillers are both as strong as the NE-SiC sample. Across all samples, two-roll mill mixing consistently results in a lower compression set, suggesting it is superior for enhancing the material's ability to recover from compression. Therefore, from the results of the experiment, it was found that the use of any filler in a blended rubber mixture between NR and EPDM will result in a higher setting value than a rubber blend that does not use fillers. This is because these fillers inhibit the movement of the rubber molecular chains, making it more difficult for the rubber molecules to recover when a force is applied. The experiment yielded results consistent with previous research by Sundaravadivel et al. [15].

Fig. 8 illustrates the tear strength of different rubber compound samples, measured in N/mm. Tear strength is a material's resistance to tearing, reflecting its durability when subjected to stress. For each sample, two bars represent two different mixing methods: mixing by a two-roll mill (diagonal stripes) and mixing by an internal mixer (crosshatch pattern). It is observed that the internal mixer generally produces a slightly higher tear strength for each sample compared to the two-roll mill, indicating that the mixing method plays a role in determining the material's resistance to tearing. The trend suggests that both the type of filler and the mixing method contribute to the overall tear strength of the rubber compound.

Table 2 displays the changes in mechanical properties of NR/EPDM rubber blends after thermal aging, comparing the outcomes based on the mixing method used. After age, the NE-0 sample loses some of its tensile strength and elongation at break for both mixing methods [7]. The internal mixer has a slightly bigger loss but gains a lot in tear strength and hardness compared to the two-roll mill. The NE-SiC blend experiences a decrease in tensile strength when mixed by the two-roll mill, but a marginal improvement in tensile strength and a small decrease in elongation at break when mixed by the internal mixer, which also provides a small increase in tear strength and a moderate increase in hardness [21]. The NE-SiC-CC blend sees an enhancement in tensile strength for both mixing methods, particularly with the internal mixer, and both
mixing methods yield an increase in tear strength and hardness, with the internal mixer associated with a slightly lesser increase in hardness. The NE-SiC-Ca sample loses some of its tensile strength and elongation at break. This happens more with the internal mixer. However, this method slightly lessens the loss of tear strength and makes the sample harder than the two-roll mill. Lastly, the NE-SiC-CC.Ca blend demonstrates a decrease in tensile strength and elongation at break with both mixers, with larger decreases seen with the internal mixer, while it shows a slight increase in tear strength with the internal mixer and a more significant increase in hardness with the two-roll mill. Across the board, the internal mixer typically shows greater preservation or enhancement of mechanical properties post-thermal aging, except for hardness, where the two-roll mill sometimes shows greater improvements.

Fig. 9 appears to be a TGA plot, demonstrating the thermal degradation behavior of various NR/EPDM rubber blend samples by showing their weight loss as temperature increases. Based on the provided Fig. 9, it is evident that NR remains stable until it reaches a temperature of 300 °C, whereas EPDM remains stable until it reaches a temperature of 400 °C, after which rapid degradation occurs. These results are consistent with the previous study by Anuar et al. [22]. The NE-0 sample, which lacks any fillers, starts to degrade at the lowest temperature, as indicated by its earlier weight loss onset.
Fig 9. TGA spectra of the NR/EPDM blends and composites with hybrid filler

Table 3. Thermal Degradation Stability of the NR/EPDM blends and composites with hybrid filler

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation temperature (°C)</th>
<th>T max (°C) from TGA curves</th>
<th>Decomposition residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_d5</td>
<td>T_d10</td>
<td>T_d50</td>
</tr>
<tr>
<td>NE-0</td>
<td>309.25</td>
<td>341.10</td>
<td>397.34</td>
</tr>
<tr>
<td>NE-SiC</td>
<td>319.83</td>
<td>349.64</td>
<td>409.55</td>
</tr>
<tr>
<td>NE-SiC-CC</td>
<td>329.57</td>
<td>358.18</td>
<td>442.78</td>
</tr>
<tr>
<td>NE-SiC-Ca</td>
<td>333.79</td>
<td>358.23</td>
<td>440.87</td>
</tr>
<tr>
<td>NE-SiC-CC.Ca</td>
<td>331.22</td>
<td>360.33</td>
<td>449.28</td>
</tr>
</tbody>
</table>

The NE-SiC sample, incorporating Si and C fillers, shows a slight improvement in thermal resistance, degrading at a slightly higher temperature than the NE-0. Adding CC to the mix, as in the NE-SiC-CC sample, enhances thermal stability further, as evidenced by an even higher degradation onset temperature. The NE-SiC-Ca sample, containing Ca, follows the trend, suggesting that this filler also contributes to improved thermal stability. Lastly, the NE-SiC-CC.Ca sample, which combines all the fillers, exhibits the greatest resistance to thermal degradation, initiating weight loss at the highest temperature range of all samples [12]. This pattern illustrates that filler content in rubber blends can markedly influence their ability to withstand heat before beginning to break down.

Table 3 outlines the thermal degradation characteristics of various NR/EPDM rubber blends, indicating that hybrid fillers enhance thermal stability. For instance, the unfilled NE-0 blend exhibits the lowest thermal resistance, beginning degradation at 309.25 °C and leaving only a 5.058% residue post-decomposition. Blends with fillers like NE-SiC, NE-SiC-CC, NE-SiC-Ca, and NE-SiC-CC.Ca, on the other hand, have higher onset degradation temperatures (T_d5) and a lot more residues, which means they lose less material [22]. Specifically, NE-SiC-CC and NE-SiC-CC.Ca blends demonstrate the most significant improvement in thermal stability, with the former having the highest residue at 32.439% and the latter not far behind. The T max values agree with these results, showing that the second degradation step happens at higher temperatures than the first one. This shows that the materials break down in two stages, proving that fillers make materials more resistant to heat.
CONCLUSION

The properties of NR/EPDM rubber blend were successfully improved by adding hybrid fillers and using the performance mixing method. The hybrid fillers for the properties of NR/EPDM rubber blends used Si, C, CC, and Ca as fillers, providing the blends with faster cure and better mechanical properties. Additionally, the mixing options in the internal mixer generally produced slightly faster cure and more consistent mechanical properties, including higher modulus, tensile strength, elongation at break, and hardness with superior filler dispersion, leading to more uniform material properties. The NE-SiC inherited the greatest tensile strength, tear strength, and elongation at break in internal mixing case properties. Furthermore, the hybrid fillers increased the thermal stability of the NR/EPDM blends, with higher decomposition temperatures and larger residues, especially in NE-SiC-CC and NE-SiC-CC.Ca blends. The internal process consistently outperformed the two-roll mill method, producing higher mechanical properties and thermal stability blends. Post-thermal aging, the internal process enhanced the properties of the blends better than the two-roll mill, except in some cases of hardness improvement. These results highlight the critical role of filler types and mixing methods in optimizing the performance of NR/EPDM rubber blends for applications requiring high durability and thermal stability. Future research could explore hybrid techniques combining internal mixing and the two-roll mill to improve production efficiency. Additionally, using sustainable and bio-based fillers would also make NR/EPDM blends more eco-friendly. Customizing blends for specific industrial applications by adjusting fillers and mixing methods can provide valuable insights for meeting diverse needs.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Suwat Rattanapan conducted the experiment, Jutatip Artchomphoo and Diew Saijun conducted the formal analysis and testing, Kamonwan Booncharoen and Pasuta Sungsee conducted the literature review and validation, and Suwat Rattanapan and Jutatip Artchomphoo wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

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