Sustainable Tertiary Accelerator of Sulfur Vulcanization of NR and SBR Rubbers From Natural Tree Extract

Nardeen A. Berto*, Auda J. Braihi, Mohammed H. Al-Maamori

Abstract

A novel natural, low cost and available accelerator for Styrene Butadiene Rubber (SBR) and Natural Rubber (NR) curing systems was prepared from waste agriculture. Dried powder of Conocarpus lancifolius leaf extract (CLLE) was added by (0.5, 1.0, 1.5 and 2.0) wt% for SBR and NR master batches individually containing benzothiazole accelerators (MBT, MBTS). (CLLE) was selected due to the presence of Flavonoids, Saponins and phenols within its structure, which promotes hydrogen bonding (H-bonds) as a secondary bonding, which in turn enhances the curing rate.

Results showed that CLLE has an ability to accelerate curing systems and its optimum concentration is 0.5 pphr for SBR and 1 pphr for NR. Its effects on NR curing system is higher than on SBR system, where with SBR, the optimum curing time (tc90) decreased only by 2.42%, while with NR, it decreased by 17.74% and the curing rate index (CRI), increased with SBR only by 5.9%, while increased by 24.83% with NR. Also, CLLE addition reduced the scorch time (ts2) of both two rubbers. The ts2 for SBR-based samples are always higher than those for NR-based samples. In addition to that, CLLE caused opposite effects on torques of SBR and NR, and had no effects on tensile strength, slight decreasing in hardness, increasing in modulus at 300% elongation and increasing in stresses and strains before failure. The addition of CLLE increased curing rates due to the active components (Flavonoids, Saponins and phenols), which encouraged using these elastomeric products for bio applications and act as a coupling agent for hydrophilic and hydrophobic polymers.

Keywords: Conocarpus lancifolius leaf extract (CLLE), Curing system, Rubber, Scorch time, Vulcanization accelerator.

Introduction

All facts in nowadays life contact with polymers (especially rubbers) in many fields including transports, housing, health, sport, food, water, clothing, more and more which improve the quality of our lives1,2. In elastomer technology, vulcanization is considered one of the oldest and most obvious significant process3.

Vulcanization can be expressed as a process of changing highly soluble rubber material to highly insoluble and elastic one, through series of complex reactions taking a place amidst the rubber, sulfur and auxiliary chemicals present. In macromolecules that contain double bonds, vulcanization with sulfur curing system is commonly used. Accelerated sulfur vulcanization is the most prevalent kind of vulcanization in case of using dyne-type rubbers which includes [natural rubber (NR), Styrene Butadiene Rubber (SBR), isoprene rubber (IR) and
butadiene rubber (BR)] because of its superior mechanical properties, regular cross-linking and stability \(^4^5\). Vulcanization process creates some crosslinks between the polymeric chains, which give three dimensional network structure that controls the enhanced insolubility and high elasticity of the vulcanizates \(^6\).

Vulcanization process has its own related characteristics, such as crosslink formation rate, the time passing before crosslinking starts and crosslinking final extent. To permit shaping, forming and flowing in the mold a sufficient delay or scorch resistance must exist, then crosslink formation should be rapid. When acceleration in vulcanization process occur, it makes improvement in both of rate and efficiencies\(^7\). Whereas accelerators are substances that are added to the vulcanizates during rubber compounding in small quantities to accelerate vulcanization process, also they are able to improve the service and physical properties of finished products\(^8^\)-\(^11\).

Accelerators can be classified functionally into two broad categories: single accelerator (primary accelerators) and mixed accelerator system (secondary accelerators)\(^12\). By comparing single and varied accelerator systems in rubber vulcanization, varied accelerators are well known nowadays to achieve greater chemical and physical properties to the vulcanizates due to the synergism in crosslink density which gives strong improvements in properties. So in the rubber industry binary accelerator systems are widely used\(^13^\)-\(^15\).

Due to the world’s trend towards a sustainable environment and the use of green chemistry and the attempts to replace chemicals with natural materials (knowing that chemicals have a bad effect on the environment and humans), a natural alternative material was used in this work, where a plant extract of \textit{Conocarpus lancifolius} leaf (CLLE) was used as a mix accelerator with benzothiazol accelerators. The reason behind choosing this material is due to its abundance, local availability, its simply requirements to cultivate including efforts, cost or even water in addition to its fast growth\(^16\). Also, CLLE, contains Flavonoids, Saponins, and phenols as shown in Fig. 1. Flavonoids acts as an antioxidant because it has the ability to control the accumulation of reactive oxygen species (ROS) via scavenger ROS when they are formed\(^17\). Saponin component is an amphiphilic material, which contains both a glycone (very hydrophobic), and the sugar chains (very hydrophilic)\(^18\). On the other hand, phenol component gives the CLLE a polar nature, which facilities the formation of hydrogen bonds with the elastomeric matrix, thus enlacing the curing properties. The aim of this work is use a natural, low cost and available material prepared from waste agriculture as an accelerator for Styrene Butadiene Rubber (SBR) and Natural Rubber (NR) curing systems.

![Figure 1. Some of chemical components in the CLLE](image-url)
Materials and Methods

In addition to the *Conocarpus lancifolius* leaf CLLE material, other materials were used, such as Styrene Butadiene Rubber (SBR), Natural Rubber (NR), Zinc Oxide (ZnO), Stearic Acid (St.A), Sulfur (S), Carbon black (CB), 2-Mercaptobezothiaole (MBT) and mercaptobenzothiazole disulphide (MBTS). Later materials were supplied from Al-Diwaniya State Company for Tyre Industry (Iraq).

**Instrumentation**

Higher Precision Density Tester GP-1205 was used to measure the specific gravity. Oscillating Disc Rheometer (ODR) used to evaluate the vulcanization rheology parameters, such as minimum torque (ML), maximum torque (MH), scorch time ($t_{sc}$), optimum cure time ($t_{90}$) and cure time index (CRI). This test was proceeded at 180°C for 6 min. Shore A apparatus was used to measure the hardness according to ASTM D-1415. Tensile properties were measured according to ASTM D-638-II by employing a Universal Tensile Test machine type (WDW/5E). This test started by applying specified load of 5KN and the cross head speed was 5 mm/min.

**Methods**

**Leaf Preparation**

*Conocarpus leaves* were collected from local tree, cleaned by distilled water, shade dried and then powdered by an electrical mill.

**Master Batch Preparing**

CLLE was added by four amounts 0.5, 1.0, 1.5 and 2.0 (pphr) to the ten elastomeric master batch according to ASTM (D 3184) as shown in Table 1.

<table>
<thead>
<tr>
<th>Master Batch</th>
<th>SBR</th>
<th>NR</th>
<th>ZnO</th>
<th>St. A</th>
<th>CLLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>100</td>
<td>-</td>
<td>3.63</td>
<td>1.815</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>100</td>
<td>-</td>
<td>3.63</td>
<td>1.815</td>
<td>0.5</td>
</tr>
<tr>
<td>A3</td>
<td>100</td>
<td>-</td>
<td>3.63</td>
<td>1.815</td>
<td>1</td>
</tr>
<tr>
<td>A4</td>
<td>100</td>
<td>-</td>
<td>3.63</td>
<td>1.815</td>
<td>1.5</td>
</tr>
<tr>
<td>A5</td>
<td>100</td>
<td>-</td>
<td>3.63</td>
<td>1.815</td>
<td>2</td>
</tr>
<tr>
<td>B1</td>
<td></td>
<td>100</td>
<td>3.63</td>
<td>1.815</td>
<td>0</td>
</tr>
<tr>
<td>B2</td>
<td></td>
<td>100</td>
<td>3.63</td>
<td>1.815</td>
<td>0.5</td>
</tr>
<tr>
<td>B3</td>
<td></td>
<td>100</td>
<td>3.63</td>
<td>1.815</td>
<td>1</td>
</tr>
<tr>
<td>B4</td>
<td></td>
<td>100</td>
<td>3.63</td>
<td>1.815</td>
<td>1.5</td>
</tr>
<tr>
<td>B5</td>
<td></td>
<td>100</td>
<td>3.63</td>
<td>1.815</td>
<td>2</td>
</tr>
</tbody>
</table>

Batch (A) refers to SBR-base samples and batch (B) refers to NR-base samples. The amount of carbon black (CB) that used was 8, sulphur (S) amount was 3 and MBT, MBTS amounts were 0.31 for each.

**Results and Discussion**

In rubber industries specially vulcanization process, accelerators play a certain role because of their ability to enhance the rate of vulcanization. Moreover, in our days, mix accelerator systems are well known to obtain better acceleration in the vulcanization process.

**Cure Characteristics**

This work studied the effects of CLLE as a natural accelerator (in the presence of MBT and MBTS thiazole accelerators) upon the vulcanization system of SBR and NR, which examined at 165 °C, as shown in Table 2.
Table 2. Effects of CLLE on the curing parameters on the prepare master batch.

<table>
<thead>
<tr>
<th>Master Batches</th>
<th>ML*(lb.in)</th>
<th>MH*(lb.in)</th>
<th>t₂* (min)</th>
<th>t₉₀* (min)</th>
<th>CRI * (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>4.1</td>
<td>33.8</td>
<td>3.9</td>
<td>10.33</td>
<td>15.55</td>
</tr>
<tr>
<td>A1</td>
<td>3.6</td>
<td>31.4</td>
<td>3.78</td>
<td>10.08</td>
<td>15.87</td>
</tr>
<tr>
<td>A2</td>
<td>3.5</td>
<td>31.3</td>
<td>4.05</td>
<td>10.23</td>
<td>16.18</td>
</tr>
<tr>
<td>A3</td>
<td>3.6</td>
<td>30.0</td>
<td>3.82</td>
<td>10.17</td>
<td>15.74</td>
</tr>
<tr>
<td>A4</td>
<td>3.6</td>
<td>29.6</td>
<td>4.15</td>
<td>10.22</td>
<td>16.47</td>
</tr>
<tr>
<td>B0</td>
<td>5.6</td>
<td>62.8</td>
<td>2.0</td>
<td>9.3</td>
<td>13.69</td>
</tr>
<tr>
<td>B1</td>
<td>6.1</td>
<td>60.1</td>
<td>2.07</td>
<td>9.05</td>
<td>14.32</td>
</tr>
<tr>
<td>B2</td>
<td>7.4</td>
<td>55.4</td>
<td>1.8</td>
<td>7.65</td>
<td>17.09</td>
</tr>
<tr>
<td>B3</td>
<td>9.7</td>
<td>55.5</td>
<td>1.9</td>
<td>8.78</td>
<td>14.53</td>
</tr>
<tr>
<td>B4</td>
<td>6.7</td>
<td>63.4</td>
<td>1.93</td>
<td>9.47</td>
<td>13.26</td>
</tr>
</tbody>
</table>

ML*, MH* refers to minimum and maximum torque respectively, t₂ *is the time to reach a 2-unit increase in torque above minimum and t₉₀ * is defined as the time to achieve 90% cure, while CRI* represents cure rate index.

**Torques Results**

ML, represents indeed a measure of the stiffness and viscosity of un-vulcanized compound. This torque happened at the beginning of heating, whereas the rubber gets heated, the viscosity decreased and the torque falls. Therefore, it is the minimum obtained torque. This torque is 4.1 lb.in for un-vulcanized SBR and 5.6 lb.in for un-vulcanized NR. This is because that, aromatic styrene ring in SBR prevents its chain from getting close to each other; creating some voids among chains compared with the converging NR chains. The elastomeric converging chains restrict the mixer motion and rises the torque. Addition of CLLE decrease the ML of SBR and increase it for NR. The reason behind this opposite behavior is originated from the difference of the composition of the two rubbers; NR is composed from single monomer, while SBR is composed from two monomers with some phase separation between them. This addition deepened the phase separation between SBR's monomers, thus decreasing the ML, while with NR, CLLE particles occupy the voids among chains and increasing its ML.

For MH torque, the same behaviors occur with SBR-based samples, where it decreased linearly from 33.8 lb.in to 29.6 lb.in. In contrast, with NR-based samples, it decreased from 62.8 lb.in to 55.4 lb.in and the raised up to 63.4 lb.in. The later behavior is due to the physical interactions between CLLE and the NR-master batch. MH is a function of master batch stiffness and its decreasing with the CLLE is due to the chlorophyll action as a plasticizer.

**Scorch Time Results**

Scorch time is the time for viscosity (torque) to rise 2 units above ML. It is a measures of processing safety. Scorch is premature vulcanization in which the stock becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is the result of both the temperatures reached during processing and the amount of time the compound is exposed to elevated temperatures. Since scorching ruins the...
stock, it is important that vulcanization does not start until processing is complete.

Table 2 and Fig. 2, show the following findings:

1- The scorch times for SBR-based samples are always higher than those for NR-based samples, which indicates that the processing of SBR goods is safer than with NR and there is some delay time. This is because the free volumes which were available within the SBR structure. These voids delay the heat transfer compared with the dense NR structure.

2- Although, there is a fluctuation with both the two rubbers, but generally the CLLE addition causes reduction in the scorch times. This means that, CLLE accelerates the curing of both the two rubbers.

![Figure 2. Effect of CLLE on the optimum cure arte of (a) SBR-based samples, (b) NR-based samples](image)

**Figure 2. Effect of CLLE on the optimum cure arte of (a) SBR-based samples, (b) NR-based samples**

**Curing Time Results**

Both of tc90 and CRI give clear evidence about the curing state of the vulcanized compound. For example, tc90 represents the time at which 90% of cure has taken place, while the CRI determines the time the compound must be cured i.e. the cure time. CRI is the rate at which cross-linking and the development of stiffness (Modulus) of the compound occur after the scorch point. As the compound is heated beyond the scorch point, the properties of the compound changes from a soft plastic to a tough elastic material required for use. During the curing phase cross links are introduced which connect the long polymer chains of the rubber together. As more cross links are introduced, the polymer chains become more firmly connected and the stiffness (modulus) of the compound increases.

For both rubbers, tc90 decreased with the CLLE additions, which proved the acceleration effects of CLLE material on the curing system. With SBR, tc90 decreased only by 2.42% (from 10.33 min to 10.08 min at 0.5 wt% CLLE), while with NR, it decreased by 17.74% (from 9.3 min to 7.65 min at 1 wt% CLLE). That pointed to the higher effects of CLLE on NR compared with SBR, this is often due to the short induction period of NR that caused by its large degree of unsaturation molecular structure²¹.

For the CRI parameter, the same effects occurred, where with SBR it increased only by 5.9% (from 15.55 to 16.47 at 2 wt% CLLE), while with NR which have higher cross link rate²², it increased by 24.83% (from 13.69 to 17.09 at 1 wt% CLLE).

The reduction in curing time is very beneficial in the rubber industry because it leads to increase the rate of production. NR rubber shows much effecting comparing with SBR during addition of (CLLE) which definitely makes it better mix accelerators for NR.
Physical Properties:

The physical properties of SBR and NR master batch are shown in Table 3. These properties include specific gravity, hardness and some tensile properties, such as tensile strength, modulus at 300% elongation, strain and stress.

Table 3. Physical properties of the prepared master bath

<table>
<thead>
<tr>
<th>Master batch</th>
<th>CLLE (wt %)</th>
<th>Specific Gravity</th>
<th>Hardness Shore (A)</th>
<th>Tensile Strength (MPa)</th>
<th>Modulus at 300% elongation (MPa)</th>
<th>Strain</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0 %</td>
<td>0.97</td>
<td>62.67</td>
<td>1</td>
<td>1221</td>
<td>13.21</td>
<td>1.31</td>
</tr>
<tr>
<td>A1</td>
<td>0.5 %</td>
<td>0.96</td>
<td>63.96</td>
<td>1</td>
<td>1537</td>
<td>15.21</td>
<td>1.22</td>
</tr>
<tr>
<td>A2</td>
<td>1 %</td>
<td>0.96</td>
<td>62.10</td>
<td>2</td>
<td>1852</td>
<td>18.52</td>
<td>1.57</td>
</tr>
<tr>
<td>A3</td>
<td>1.5 %</td>
<td>0.97</td>
<td>61.36</td>
<td>1</td>
<td>1757</td>
<td>17.72</td>
<td>1.31</td>
</tr>
<tr>
<td>A4</td>
<td>2 %</td>
<td>0.97</td>
<td>61.20</td>
<td>1</td>
<td>1852</td>
<td>18.92</td>
<td>1.49</td>
</tr>
<tr>
<td>B0</td>
<td>0 %</td>
<td>0.95</td>
<td>51.3</td>
<td>2</td>
<td>2478.5</td>
<td>25.53</td>
<td>1.842</td>
</tr>
<tr>
<td>B1</td>
<td>0.5 %</td>
<td>0.94</td>
<td>48.8</td>
<td>2</td>
<td>2578.5</td>
<td>25.83</td>
<td>1.667</td>
</tr>
<tr>
<td>B2</td>
<td>1 %</td>
<td>0.95</td>
<td>51</td>
<td>2</td>
<td>2393.5</td>
<td>24.78</td>
<td>1.667</td>
</tr>
<tr>
<td>B3</td>
<td>1.5 %</td>
<td>0.94</td>
<td>52.1</td>
<td>2</td>
<td>2809.5</td>
<td>28.34</td>
<td>2.368</td>
</tr>
<tr>
<td>B4</td>
<td>2 %</td>
<td>0.94</td>
<td>50.6</td>
<td>2</td>
<td>2523.5</td>
<td>25.53</td>
<td>1.579</td>
</tr>
</tbody>
</table>

For both rubber types, the specific gravity decreased slightly with the CLLE addition, which indicates a benefit of this material; causing real change in the curing system without altering the internal structure.

From hardness results, one can obtain the following feedings:

1- The hardness of all SBR-based samples were always higher than those of NR-based samples. This is due to the presence of the bulky aromatic benzene ring in SBR. This ring provides SBR with some rigidity.

2- CLLE addition caused slight decreasing due to the plasticizing action of chlorophyll, which is present in the CLEE.

Tensile strength results showed that, generally, the CLLE addition do not affect this property and their values for NR-based samples were always higher than those for NR-based samples. That means, NR-samples bear loads higher than SBR. When combined this finding with the previous fact (NR cure system more affected than SBR system), the benefit are very clear from using CLLE as an accelerator.

The modulus at 300% elongation, generally increased with CLLE addition Fig. 3, which gives another advantage of using this material. This property increased by 51.67% with SBR and by 13.35 only with NR. These results coincide with strain and stress (before failure) results, where SBR can withstand 43.22% strain before failure, while NR withstand 11% only. SBR can bear stress up to 13.74% before failure, while NR bears only 0.526%.
The reason belongs to greater elasticity that showed by MBTS compounds where the crosslinks are longer compared to polysulfide and disulfide types, which are more flexible and elastic and hence promoting greater elongation to failure.

**Conclusion**

From the curing characteristics of the SBR and NR vulcanizates, it was clear that CLLE has ability to accelerate their curing systems. The optimum CLLE concentration was found to be 0.5 phr for SBR, 1 phr for NR.

CLLE addition causes opposite effects on torques of SBR and NR due to the differences of the two rubber compositions.

CLLE addition reduced the scorch times of both two rubbers. The scorch times for SBR-based samples are always higher than those for NR-based samples.

CLLE have higher effects on NR curing system compared with SBR system. With SBR, tc90 decreased only by 2.42%, while with NR, it decreased by 17.74% and CRI parameter, increased with SBR only by 5.9%, while increased by 24.83% with NR.

CLLE addition caused no effects on tensile strength, slight decreasing in hardness, increasing in modulus at 300% elongation and increasing in stresses and strains before failure.

Due to containing CLLE of Flavonoids, Saponins and phenols, these components give antioxidant, amphiphilic and polarity actions to the elastomeric systems. These actions encourage using these elastomeric products for bio applications, possibility to act as coupling agents between hydrophilic and hydrophobic polymers, besides increasing the curing properties is due to the high polarity.

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**Authors’ Declaration**

- **Conflicts of Interest:** None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- **Ethical Clearance:** The project was approved by the local ethical committee in University of Babylon.
Authors’ Contribution Statement

All the authors contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript as follows:

A. J. B.: interpret, analyze and drafting the data. M. H. Al.: revision and proofreading.

N. A. B.: designed the idea, analyze and interpret the data. A. A. H.: collected the data.

References

معجل ثالثي مستدام لفلكنة الكبريت لمطاطي ال NR و ال SBR من مستخلص اوراق شجرة ناردين عدنان برتو،عودة جبار بريهي،محمد حمزة المعموري
قسم هندسة البوليمرات والصناعات الكيميائية، كلية هندسة المواد، جامعة بابل، بابل، العراق.

الخلاصة
تم تحضير معجل جديد، طبيعي، رخيص، ومتاح يستخدم في أنظمة فلكنة مطاط طبيعي NR و مطاط الستايرين بيوتادايين SBR. وقد تم تحضير هذا المعجل عن المخلفات الزراعية. حيث تم إضافة مسحوق مجفف لمستخلص من اوراق شجرة الكينوكاربس Conocarpus lancifolius (CLLE) بالنسب المئوية التالية: 0.5, 1.0, 1.5, 2.0 (wt%) إلى العجينة الرئيسية لمطاطي ال NR و ال SBR، والتي تحتوي على معجلات البنزوثايوزول (MBT, MBTS) كراطبة ثانوية، (H-bond) الترابط الهيدروجيني والذي يعزز الترابطابل وانتقلية الفلكة (curing systems) الاختلافات بين معجلات بنزوثايوزول. تأثير هذا المستخلص على نظام معالجة انظمة الفلكنة يمكن covariance بقيم الاختلافات (CLLE) التي من حيث انخفاض الأحماض المجلط في USP المطاطي من مطاط ال SBR، حيث انخفاض زمن الانضاج الامثل Tc90(B) بمقدار (2.42 %) في حين انخفاض الامتصاص CRI (2.0) % في حين انخفاض الامتصاص CRI (2.5) % فقط. بالإضافة إلى ذلك فان الامتصاص CRI (2.1) % في حين انخفاض الامتصاص CRI (2.0) %، وكانت قيم ال SBR لم تتأثر على قيمة مقادير الشد وكان هناك انخفاض طفيف في قيمة المطاطي عند (30%) زيادة في قيم الاستطالة عند (30%) زيادة في قيم الاستطالة عند (30%) نسبة التأثير. والانفعال قبل الفشل أدت إضافة المستخلص (CLLE) إلى زيادة معدلات المعالجة بسبب احتوائها على مكونات نشطة (الفلافونويد والسابونين والفينولات)، والتي شجعت على استخدام هذه المنتجات الموجهة للتطبيقات الحيوية وتعمل كعامل اقتران للبوليمرات المحبة للماء والطارئة للماء. 

الكلمات المفتاحية: مستخلص اوراق الكونوكاربس Conocarpus lancifolius (CLLE), نظما فلكنة, مطاط NR و SBR, زمن الانضاج, معجلات الفلكة.