



## Synthesis And Evaluation Of Methyl 3,4,5-Trihydroxybenzoate And Methyl 3,4,5-Trihydroxybenzohydrazide As Additives For Natural Rubber Composites

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### Abstract

Methyl 3,4,5-trihydroxybenzoate (methyl gallate) was synthesized from 3,4,5-trihydroxybenzoic acid (gallic acid) by reaction with methanol in presence of sulphuric acid. Methyl gallate was then reacted with hydrazine monohydrate to give 3,4,5-trihydroxybenzohydrazide (galloyl hydrazide). The structure of methyl gallate and galloyl hydrazide was characterized with Fourier transforms infrared (FTIR) spectroscopy, mass spectrometry (MS), and field emission scanning electron microscope (FESEM). Gallic acid, methyl gallate, and galloyl hydrazide were mixed with natural rubber by concentrations 1-3phr (part per hundred parts of rubber), using the rubber two roll mill machine. Rheological characteristics and physico-mechanical properties of the prepared natural rubber composites were measured. Swelling in toluene and crosslink density were calculated. Also, the surface morphology was studied using FESEM. The results showed that galloyl hydrazide almost has superior properties over both methyl gallate and gallic acid. Consequently, galloyl hydrazide can be recommended as a good rubber additive as it shows the behavior of secondary accelerator in natural rubber composites. Also, it can be used as an antioxidant.

Keywords: Gallic acid; Methyl gallate; Galloyl hydrazide; Tensile strength; Swelling; Aging.

### 1. Introduction

Accelerators and antioxidants are traditional additives for rubber. They are low molecular weight organic compounds. These compounds are often incompatible with rubber, and also can bloom towards the rubber surface [1,2]. There are three different types for acceleration of sulfur vulcanizates based on the ratio of accelerator to sulfur. These types are efficient vulcanization, semi-efficient, and conventional. Conventional vulcanizates showed greater mechanical properties than efficient vulcanizates [3,4]. Viscosity, swelling and glass transition temperatures showed that sulphur vulcanization forms the highest degree of cross-linking and filler-matrix interactions [5]. The effect of different vulcanization accelerators like MBT, TMTD, and CBS on curing, mechanical and thermal properties was also studied [5-8]. The chemical structure of natural rubber is poly(cis-1,4isoprene). This characterizes natural rubber with high elasticity, resilience and damping behavior. Although natural rubber has these good properties, its oxidation

resistance is very poor. The mechanical properties of natural rubber at ambient condition are distinctive because of the high stereo-regular structure, which results from its high molecular weight [9]. The resistance of natural rubber to oxygen, ozone, ultra violet irradiation and heat is very poor and this is due to the great number of double bonds in its chemical structure [10]. Therefore, a lot of research work were carried out to protect natural rubber against degradation. Degradation of natural rubber is caused by different environmental aspects; such as humidity, high temperature, impurities, chemicals, irradiation, and mechanical stresses in the presence of oxygen. All these factors make the beneficial lifetime of several rubber products limited due to the oxidative reactions [11].

The free radicals, if present, attack the polymer chains, and as a result chain scission, crosslink creation, and crosslink rupture. The alterations in polymer properties with aging depend on the degree

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of such reactions [12]. Oxidative aging of natural rubber is an essential problem that faces scientists in both scientific and industrial fields [13]. When natural rubber is exposed to aging during service in the environmental conditions, a significant change in the physico-mechanical properties is observed [14]. Subsequently, it is essential to protect natural rubber from aging by adding materials that act as antioxidants [15]. Nevertheless, there are no universal antioxidants [16,17]. In addition, the efficiency of antioxidants greatly depends on their chemical structure [18]. M. N. Ismail, et al. prepared 4 pyridazine derivatives and examined them as antioxidants in natural rubber [19]. Pyridazines are good antioxidants in comparison with the antioxidant N-isopropyl-N-phenyl-p-phenylenediamine commercially used. E.M.A. Yakout, and S.H. El-Sabbagh designed novel uracil derivatives to be used as antioxidants in natural rubber [20]. It was found that the synthesized compounds showed good antioxidant activities compared with phenyl- $\beta$ -naphthyl amine, which is commercially used in industry. Byungwoo Moon, et al. studied the aging properties of natural rubber blends with butadiene rubber [21]. A.A. Yehia, et al. showed the good antioxidant efficiency of amino-phosphine compounds in natural rubber and styrene butadiene rubber [22]. Gallic acid is 3,4,5-trihydroxybenzoic acid [23].

It is found in several natural plants such as gallnuts, green tea, grapes, sumac, tea leaves, strawberries, oak bark, lemons, pineapples, and bananas. Gallic acid is natural antioxidant [24] with high biological activity as antiviral [25], antimicrobial [26], anticancer [27], and anti-inflammatory [28]. Consequently, it is widely used in food additives. Therefore, the aim of the present work is to prepare natural-based compounds (e.g. methyl gallate and galloyl hydrazide) and to evaluate their effects on the properties of natural rubber composites. The efficiency of such compounds would be evaluated in terms of the rheometric characteristics, physico-mechanical properties, swelling, crosslink density and aging properties of NR vulcanizates.

## 2. Materials and Experimental Techniques

### 2.1 Materials

The materials and additives used in this research are: gallic acid, and hydrazine monohydrate were

purchased from Sigma. Natural rubber (ribbed smoked sheets (RSS-1) with specific gravity 0.913, Mooney viscosity ML (1 + 4) of 60-90 at 100 °C and Tg at -75°C.) Other rubber ingredients were kindly obtained from local rubber industries and namely: stearic acid, zinc oxide (ZnO) as activators, naphthenic processing oil as plasticizer, N-cyclohexyl-2-benzothiazole sulphenamide (CBS) as accelerator, High abrasion furnace black (N330) as reinforcing filler and elemental sulfur as Curing agent.

### 2.2 Experimental Techniques

#### Preparation of rubber vulcanizates

Natural rubber composites were prepared using formulations in Table 1 according to ASTM D3182-07(2012) on a laboratory two roll mill of diameter 470 mm, width 300 mm, and speed of slow roll 24 rpm and gear ratio (1:1.4). The rubber composites were left over night. The mixing process was carried out on the mill according to the usual regime. Rheometric studies were carried out by the Moving Die Rheometer(MDR) of TA instruments, USA at 142 OC according to ASTM D2084. The NR composites were then molded into sheets having about 1 mm thickness by applying a constant force of 4 MPa using a compression molding heat press for the respective cure time obtained from the rheometer data for the selected molding temperature (142°C).

#### Physico-mechanical properties

The physico-mechanical properties (tensile strength, elongation and modulus) of the vulcanized rubber were determined with a Zwick 1425 testing machine (Germany) according to ASTM D 412. Dumbbell specimens of about 1 mm thickness were cut from the molded sheets with a Wallace steel die of constant width (4 mm). The thickness of the tested specimen was determined by a gauge calibrated in hundredths of a millimeter. The speed of the crosshead is 500 mm/min., five specimens were used, and the average was calculated in each case.

#### Equilibrium Swelling

The equilibrium swelling of the NR vulcanizates in toluene was carried out according to ASTM D 573-2007. The molecular weight between two successive crosslinks ( $M_c$ ) was determined by using the swelling data and applying Flory-Rehner equation:

$$\frac{1}{(2Mc)} = \frac{-1}{2\rho V_0} \times \left[ \frac{\ln(1 - V_R) + V_R + \mu V_R^2}{\left(V_R^{\frac{1}{3}} - \frac{1}{2} V_R\right)} \right]$$

Where  $\rho$  is density of rubber (0.913),  $V_0$  is the molar volume of the solvent (toluene  $V_0=106.3$  cm<sup>3</sup>/mole),  $V_R$  is the volume fraction of rubber in the swollen material (calculated as  $V_R = 1/(1 + Q_m)$ , where  $Q_m = Q$  (equilibrium swelling percent)/100, and the interaction parameter constant ( $\mu$ ) for natural rubber is 0.393.

#### Fourier transforms infrared (FTIR)

The Fourier transforms infrared (FTIR) was measured using Shimadzu 8400, Japan. The measurements were carried out in the spectral range from 400-4000 cm<sup>-1</sup>.

#### Mass spectrometry

Mass spectrometry (MS) was measured using a Finigan SSQ 7000 mass spectrometer to determine the molecular weight of the prepared materials.

#### Field emission scanning electron microscope

The surface morphology of the prepared natural rubber composites was considered by FESEM model QUANTA FEG 250 ESEM.

#### 2.3 Synthesis of methyl 3,4,5-trihydroxybenzoate

Methyl 3,4,5-trihydroxybenzoate or methyl gallate was prepared according to the method mentioned in literature [29]. A mixture of gallic acid (1.7 g, 0.01 mole), methanol (10 mL, 0.25 mole) and concentrated sulphuric acid (2.7 mL, 0.05 mole) were refluxed for 4 hrs. The obtained precipitate was filtered off, washed with methanol and dried. Methyl gallate was then characterized with FTIR, MS, and FESEM.

#### 2.4 Synthesis of methyl 3,4,5-trihydroxybenzohydrazide

Methyl 3,4,5-trihydroxybenzohydrazide (galloyl hydrazide) was synthesized according to the procedure mentioned in literature [29]. Hydrazine monohydrate 15 mL was added to a solution of methyl gallate (1.84g, 0.01 mole) in ethanol. The mixture was refluxed for 8 hrs. Ethanol was evaporated and the solid product was obtained. The obtained galloyl hydrazide was characterized with FTIR, MS, and FESEM.

### 3. Results and discussion

#### 3.1 Synthesis of methyl 3,4,5-trihydroxybenzoate

As illustrated in Scheme 1, methyl gallate was prepared by the reaction of gallic acid with methanol. The formed methyl gallate was characterized with FTIR, MS, and FESEM.

FTIR spectrum of methyl gallate showed a broad sharp peak at 3430 cm<sup>-1</sup> which is attributed to the

stretching vibrations of phenolic -OH groups. The peak at 2925 cm<sup>-1</sup> is attributed to vibrations of unsaturated =CH stretching. The stretching vibration at 1747 cm<sup>-1</sup> is corresponding to the stretching of carbonyl group. The stretching vibration of phenyl C=C group appeared at 1621 cm<sup>-1</sup>.

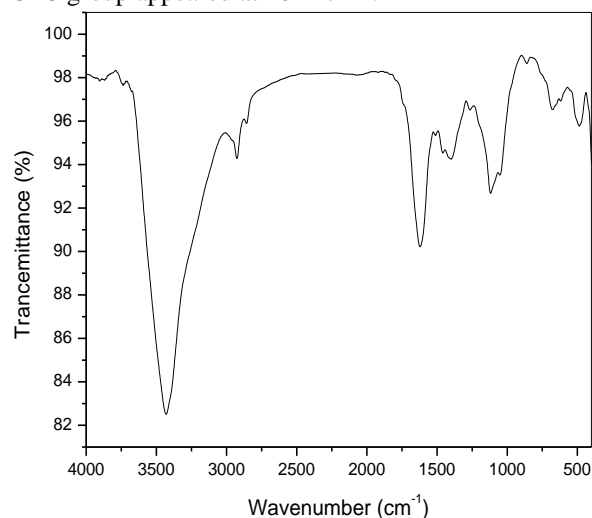


Fig. 1 FTIR of methyl gallate.

MS of methyl gallate shows molecular ion peak at 184, which represents the molecular weight of methyl gallate. All fragmentations indicate the correct structure of the obtained methyl gallate. The obtained fragmentations were as follows: ( $m/z$ , %): 184 ( $M^+$ , 19), 153 (40), 125 (15), 107 (8), 69 (97), 55 (100). FESEM image of methyl gallate was illustrated in Fig. 3. The image showed that the surface of methyl gallate is smooth, and contains some pores. Also, it has a paper like-structure. It may consist of sheets on top of each other.

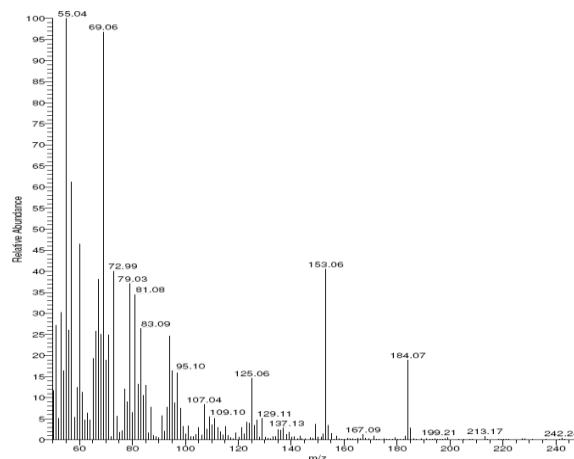


Fig. 2 Mass spectrum of methyl gallate.

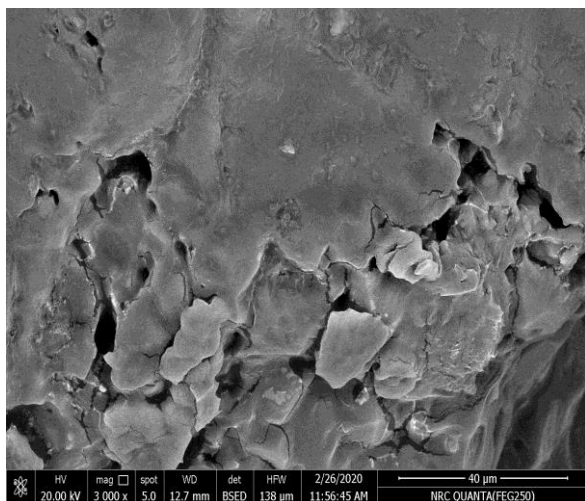
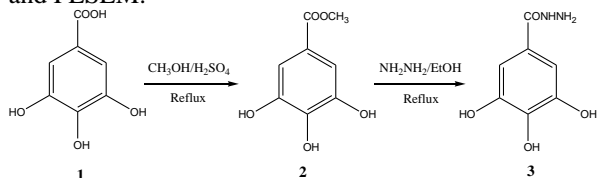


Fig. 3 FESEM of methyl gallate.

### 3.2 Synthesis of methyl 3,4,5-trihydroxybenzoate

As illustrated in Scheme 1, galloyl hydrazide was prepared in ethanol by hydrazine monohydrate. The obtained hydrazide was characterized by FTIR, MS, and FESEM.



Scheme 1 Synthesis of methyl gallate and galloyl hydrazide.

FTIR of galloyl hydrazide represented a peak at 3417  $\text{cm}^{-1}$  which is attributed to the stretching vibrations of hydroxyl groups. The stretching vibration at 1660  $\text{cm}^{-1}$  is corresponding to amide carbonyl vibration. The vibration at 1621  $\text{cm}^{-1}$  is due to C=C phenyl vibrations.



Fig. 4 FTIR of galloyl hydrazide.

MS of galloyl hydrazide illustrated molecular ion peak at 184 corresponding to the molecular weight of galloyl hydrazide and all fragmentations proved the

structure of the compound. Some fragmentations appeared at MS were as follows: (M/Z, %): 184 (M+, 51), 153 (100), 125 (31), 107 (10), 79 (50), 69 (27).

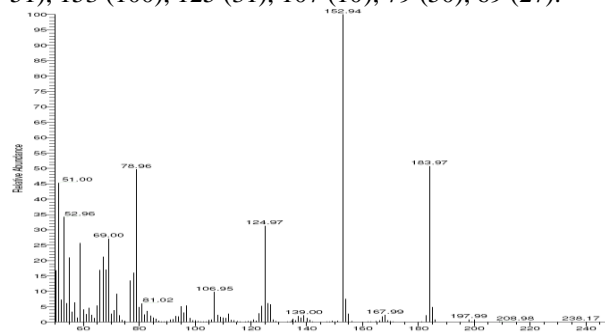


Fig. 5 Mass spectrum of galloyl hydrazide.

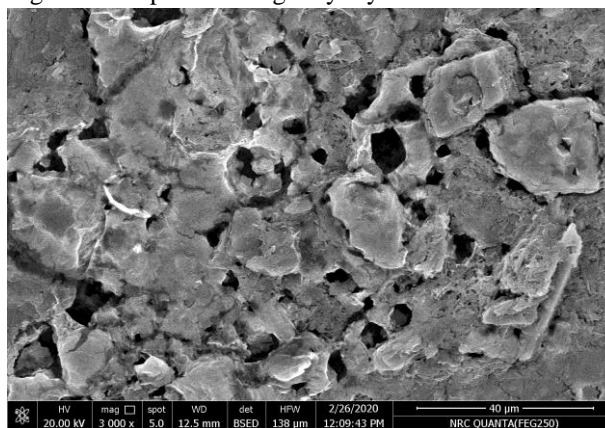


Fig. 6 FESEM of galloyl hydrazide.

### 3.3 Natural rubber formulations

Natural rubber and its ingredients (formulations) with and without the compounds used in this study; gallic acid (1), methyl gallate (2), and galloyl hydrazide (3) are given in Table 1. Natural rubber and its ingredients were mixed according to the normal regime.

### 3.4 Rheological characteristics

The rheological characteristics of the rubber composites containing the compounds under investigation are given in Table 1. It is worthy to mention that the values of the maximum torque for rubber composites containing gallic acid or methyl gallate was greatly decreased but in case of galloyl hydrazide such values are increased. This behavior may be attributed to the functional groups in the chemical structure of the prepared compounds. The rheological parameters namely maximum torque ( $S''$  max) can give a good idea about the stiffness (rigidity) of the rubber vulcanizates. On the other hand, the minimum torque ( $S'$  min) can give a good idea about the viscosity (softness) of the NR compounds.

Table 1: Formulations and rheometric characteristics of Natural rubber loaded with different concentrations of the prepared materials.

Rheometric characteristics					
S'' max, dNm	S' min, dNm	(S'' max-S' min) dNm	ts2, min.	tC90, min.	CRI (min-1)
3.17	1.51	1.66	1.54	25	4.21
Mechanical properties					
TS (MPa)	Elongation (%)		T(300), MPa		
3.5	822		1.3		

Base recipe (in phr): NR 100; ZnO 5; stearic acid 1.5; carbon black 50; process oil 7; CBS 1.2 and S 1.5.

Abbreviations: NR: natural rubber; GA: gallic acid; MG: methyl gallate; GH: galloyl hydrazide, ZnO: zinc oxide; phr is part per hundred parts of rubber; CBS (N-cyclohexyl-2-benzothiazole sulfenamide); S: sulfur. S''max: maximum torque, S' min: minimum torque, S'' max- S' min: difference between maximum and minimum torque, ts2: scorch time, tC90: optimum cure time, CRI: cure rate index.

It is clearly seen that the values of the optimum cure time tC90 and the scorch time (ts2) were increased with the incorporation of gallic acid or methyl gallate in comparison with NR blank mix. This increase goes hand in hand with the concentration of both gallic acid, and methyl gallate. This means that gallic acid and methyl gallate retard the vulcanization reaction. On the other hand, galloyl hydrazide accelerate the vulcanization reaction and this leads to decrease of the values of the optimum cure time tC90 and the scorch time (ts2).

Consequently, galloyl hydrazide can act as a secondary accelerator [20]. In order to confirm these findings, a rubber mix was prepared without the addition of CBS accelerator, but with a dose of 2 phr of galloyl hydrazide. The obtained data are represented in Table 2. This data proves that galloyl hydrazide can vulcanize the rubber, but with weak efficiency than CBS accelerator.

Table 2 Rheometric characteristics and mechanical properties of NR rubber mix containing 2 phr of galloyl hydrazide as an alternative of CBS accelerator.

### 3.5 Physico-mechanical properties

Mechanical properties of NR vulcanizates containing the prepared compounds are determined at room temperature and are presented in Table 3. It is clearly seen that, the incorporation of gallic acid or methyl gallate has decreased the tensile strength, and modulus at 300% elongation; in other words, the incorporation of 1 phr of gallic acid decreases the tensile strength from 12 MPa for the NR blank vulcanizates to 5.3 MPa for gallic acid, and to 10.5 MPa for methylgallate. Further addition of gallic acid or methyl gallate leads to more decrease in the mechanical properties. The decrease in tensile strength by addition of gallic acid, and methyl gallate

may be attributed to the aggregation of these compounds, which reduces the interfacial area between natural rubber and these compounds resulting in stress concentration weak points in the NR matrix, and consequently low tensile strength. On the other hand, galloyl hydrazide has the opposite behavior i.e. the TS has been greatly improved and it is increased as galloyl hydrazide concentration increased and reached to 27.1 MPa at using 3 phr of galloyl hydrazide. So, galloyl hydrazide improves the properties of NR vulcanizates. The increase in tensile strength by addition of galloyl hydrazide may be due to the strong bonding between the natural rubber matrix and galloyl hydrazide, which increased the stress transfer efficiency of the compound.

Also, it is observed from Table 3 that incorporating galloyl hydrazide increases elongation and this may be attributed to the high viscoelastic plasticity behavior of natural rubber. Moreover, the modulus at 300% elongation increased with adding galloyl hydrazide to natural rubber vulcanizates. This indicates the ability of this compound to impart stiffness to the natural rubber matrix, while modulus decreased in the presence of gallic acid and methyl gallate. This reduction may be due to the weak bonding, bad impeding, and poor interaction between the rubber matrix and these compounds.

### 3.6 Swelling

To confirm these findings, the swelling of NR vulcanizates containing gallic acid, methyl gallate and galloyl hydrazide was carried out in toluene at room temperature for 24 hours. The swelling data are presented in Table 4. These data showed that the swelling values for vulcanizates containing gallic acid or methyl gallate have increased, if compared with that for the NR blank vulcanizates. The increase in swelling values goes hand in hand with the increase of the doses of both gallic acid and methyl gallate. On the other hand, the swelling values for galloyl hydrazide are in the same level or slightly less than that for NR blank vulcanizates

Table 3 Physico-mechanical properties of NR mixes containing the prepared additives

Sample	NR0	GA1	GA2	GA3	MG1	MG2	MG3	GH1	GH2	GH3
Ingredients (phr)										
GA	----	1	2	3	----	----	----	----	----	----
MG	----	----	----	----	1	2	3	----	----	----
GH	----	----	----	----	----	----	----	1	2	3
Rheometric characteristics at 142°C										
S" max, dNm	8.16	5.12	3.72	2	7.05	4.35	2.49	9.38	8.63	8.52
S' min, dNm	0.43	0.32	0.47	0.46	0.65	0.67	0.76	1	0.95	1.26
(S" max- S' min)dNm	7.73	4.80	3.25	1.54	6.40	3.68	1.73	8.38	7.68	7.26
ts2, min.	1.5	2.4	3	2.7	2.7	3	3.6	1.5	1	0.7
tC90, min.	7.15	9.30	12.2	12.5	8.98	16.1	24.36	5.60	5.21	4.43
CRI (min-1)	17.7	14.5	10.9	10.2	15.9	7.62	4.81	24.39	23.75	26.8

TS: tensile strength, T(300): modulus at 300% elongation

Table 4 Crosslink density of NR vulcanizates containing different concentrations of the prepared additives(gallic acid, methyl gallate and galloyl hydrazide).

Code	Conc.	Qm	VR	Molecular weight between crosslinks Mc (g/mol)	v x 105 (crosslinking density) (mol/cc)
NR0	----	3.17	0.2398	4103.77	12.184
GA1	1phr	3.94	0.20243	6112.99	8.179
GA2	2phr	5.9143	0.14463	12892.81	3.878
GA3	3phr	7.384	0.1193	19347.54	2.584
MG1	1phr	3.65	0.2151	5312.56	9.412
MG2	2phr	5.202	0.1612	10186.96	4.908
MG3	3phr	8.404	0.10634	24489.34	2.0417
GH1	1phr	2.992	0.2505	3693.0241	13.539
GH2	2phr	3.0297	0.24816	3778.30	13.234
GH3	3phr	3.099	0.24396	3937.47	12.699

Utilizing the swelling data and the application of Flory-Rehner equation [30], it is possible to calculate the molecular weight between two successive crosslinks (Mc) and the crosslink density (v) according to the following equation:

$$v = 1/(2Mc)$$

The calculated data are in Table 4, which showed that Mc increases by addition of gallic acid or methyl gallate, hence a decrease in the crosslink density was resulted. On the other hand, Mc in rubber vulcanizates containing galloyl hydrazide decreases and hence the crosslink density increases. It is worthy to say that these findings confirm and comply very well with the rheometric and physico-mechanical characteristics.

### 3.7 Thermal oxidative aging

A trial was carried out to see if galloyl hydrazide could protect rubber products from thermal degradation. Thus, samples from NR vulcanizates containing 2 phr of galloyl hydrazide were subjected to thermal oxidative aging at 90 OC for one and three days. The effect of aging on the physico-mechanical properties was studied as illustrated in Table 5. After aging for one day, the tensile strength of natural

rubber (NR0) became 8.8 MPa, while that of NR containing galloyl hydrazide 2 phr (GH2) became 12.1 MPa. After aging for three days, the tensile strength of NR0 became 4.8 MPa, while that of GH2 became 9.5 MPa. Moreover, the retained value of tensile strength after aging at 90 oC for one and three days was measured and given in Table 5. It was revealed that galloyl hydrazide can be used as a promising antioxidant in natural rubber mixes.

### 3.8 Field emission scanning electron microscope (FESEM) investigations

FESEM exhibits the simplest investigative procedure, since it detects surface features. The internal structure of the NR vulcanizates was investigated by viewing the surfaces formed at ambient temperature.

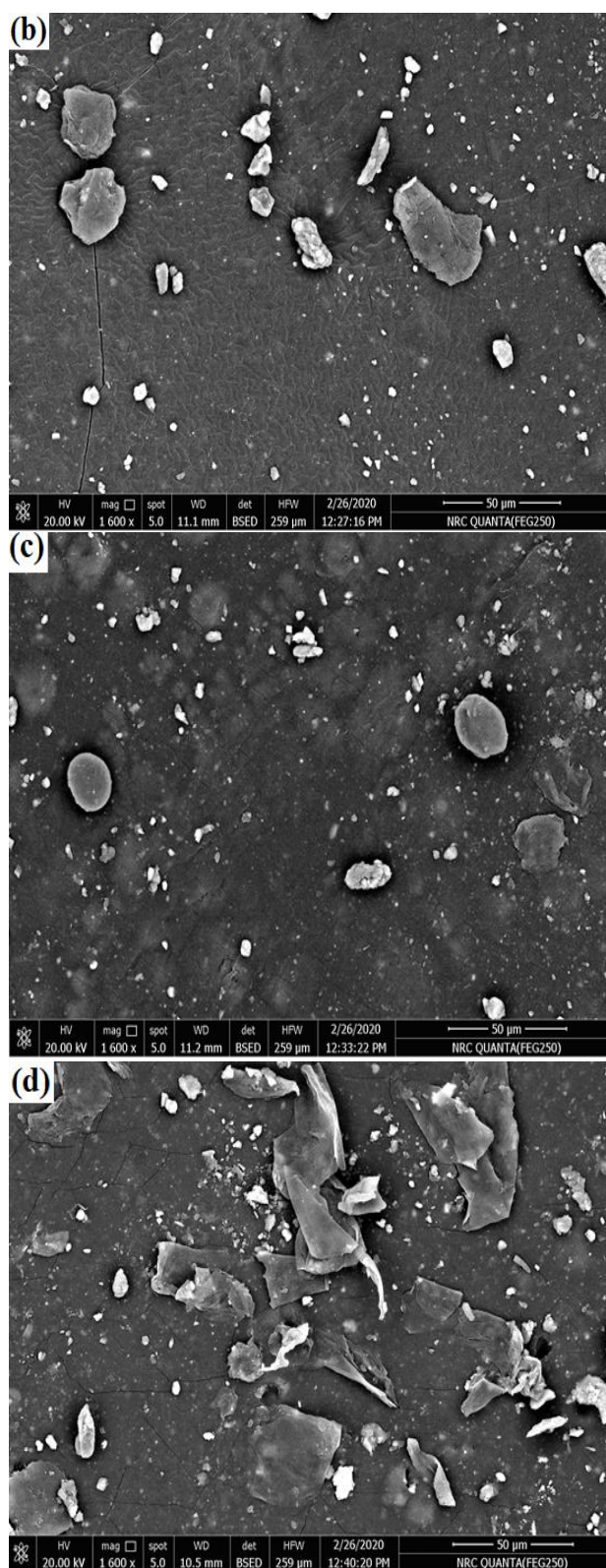
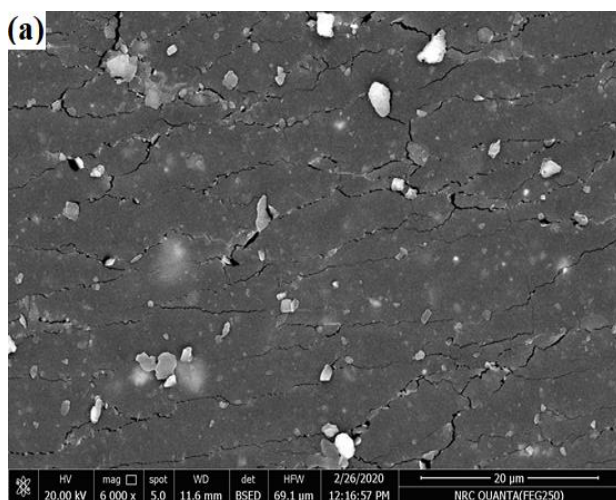
FESEM micrograph in Fig. 7(a) shows the morphology of NR0 vulcanizate, where there is irregular distribution of cavities all over the surface. On the other hand, NR vulcanizates containing 1phr of gallic acid (GA1) or natural rubber containing 1 phr of methyl gallate (MG1), the micrograph shows small transparent domains resembling spherulite structure (Figs. 7(b,c)).

Table 5 Thermal oxidative aging of NR rubber vulcanizates containing 2 phr of galloyl hydrazide at 90 oC for one and three days

NR0	12	2065	1.2
GA1	5.3	1806	0.7
GA2	2.8	1188	0.7
GA3	2.1	1060	0.5
MG1	10.5	1834	1.5
MG2	3.1	1161	0.8
MG3	2.2	1101	0.6
GH1	17.9	2426	1.3
GH2	17.1	1978	1.4
GH3	27.1	1957	2.6

R.T.S: retained tensile strength, R.E: retained elongation, R. T(300): retained modulus at 300 % elongation.

Also, the surface is more homogeneous (smooth) than vulcanizates free of the prepared compounds (NR0). When using galloyl hydrazide (GH1) in the obtained vulcanizate, the shapes of GH1 appeared in the FESEM micrographs to be platy as can be seen in Fig. 7(d). This platelet shapes help in slippage of natural rubber chains from the surface of galloyl hydrazide particles leading to improved elasticity. This elasticity is attributed to the plasticizing and the conformational effects on the rubber at galloyl hydrazide matrix interface. Indicating that the galloyl hydrazide particles are in stacked condition and rubber chains are diffused inside the compound. From the above results, it is concluded that, increasing elongation by addition of galloyl hydrazide into natural rubber (Table 3) and also the appearance of plates from FESEM micrograph proves that this compound promote the plasticity and the flexibility. This means that, the distance between chains of rubber increases leading to increase the elasticity, beside the presence of processing oil as plasticizer in rubber formulation.



Figs. 7(a-d): (a): Natural rubber; (b): Natural rubber containing 1 phr of gallic acid; (c): Natural rubber containing 1 phr of methyl gallate; (d) Natural rubber containing 1 phr of galloyl hydrazide.

#### 4. Conclusions

Based on the obtained results, it can be concluded that methyl gallate and galloyl hydrazide were synthesized successfully and characterized by FTIR, MS, and FESEM techniques. Gallic acid, methyl gallate and galloyl hydrazide were evaluated in natural rubber composites and it was found that gallic acid, and methyl gallate retard the vulcanization reaction, while galloyl hydrazide accelerates this reaction. However, galloyl hydrazide can weakly vulcanize rubber without using CBS and can be used as a secondary accelerator. On the other hand, it behaves as an efficient antioxidant for NR vulcanizates.

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