

# Waste Natural Gum as a Multifunctional Additive in Rubber

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**ABSTRACT:** Bahera gum, extracted from the bark of *Terminalia bellerica*, is a waste material. The present study involves the use of this natural gum as a multifunctional additive in natural rubber (NR) and brominated isobutylene-co-paramethyl styrene (BIMS). Fourier transform infrared (FTIR) analysis was employed to study the functional groups present in the gum. It was found that fatty acids/esters in the gum act as accelerator activator and can replace stearic acid in rubber formulations. Polyphenols in the gum act as antioxidant and the action is comparable with the commercial antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline (TQ) in natural rubber. The gum improves the tack strength of the rubbers (21% at 2.5 phr loading for

NR and 54% at 10 phr loading for BIMS). The gum imparts plasticization effect which is reflected in the reduction in  $k$  and enhancement in  $n$  values, the exponents in the power law equation, with increasing gum concentration. The activation energy of flow is also reduced with the addition of the gum. Moreover, it decreases the elastic memory of the system which causes reduction in die swell. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4897–4907, 2006

**Key words:** natural gum; rubber; multifunctional additive; *Terminalia bellerica*; NR; BIMS

## INTRODUCTION

Utilization of waste material in rubber has been of commercial and environmental interests for many decades.<sup>1–2</sup> Various advancements in this field are concerned with the use of ground waste rubber in virgin polymer as an additive or as substitute for virgin polymers in thermoplastic elastomeric blend.<sup>3–7</sup> Compared to the literature published on the earlier studies, less attention has been paid to the replacement of compounding ingredients in rubber formulation. A simple, novel, and environment friendly approach in waste management is the utilization of a waste natural gum in virgin rubber.

The gum is extracted from the bark of *Terminalia bellerica* (local name Bahera). It is basically a waste material. This tree is mostly found in the tropical countries like India, Myanmar, Srilanka, and various other parts of East and South East Asia. In India, the tree is distributed in deciduous forests of West Bengal, Bihar, Madhya Pradesh, Maharashtra, Uttar Pradesh, and Himachal Pradesh. It is a medicinal plant that belongs to the family of Combretaceae. The chloroform extract of its fruit possesses antimutagenic, anticarcinogenic, anti-HIV, antimalaria, and antifungal activities.<sup>8,9</sup> Ace-

tone extract of *Terminalia bellerica* contains polyphenolic compounds, which can be used as effective chemopreventive agent.<sup>10</sup> The barks have been found to be rich in tannins and natural deposits of calcium oxalate. Composition of the bark as obtained from the literature<sup>11–13</sup> is as follows:

Calcium oxalate	12–20%
Tannins	3–16%
Mono/polysaccharides (mannitol, glucose, fructose, galactose, rhamnose, galloyl glucose, etc.)	20–30
Moisture	6–13%
Ash	18–30%

The tannins isolated from the bark are used as cheap dyeing material. It has been observed that tannin and oxalic acid contents vary within the samples of same species in various regions. Gallic acid, ellagic acid, ethyl gallate, galloyl glucose, mannitol, glucose, galactose, fructose, rhamnose, and several other triterpenoids and their glycosides are the other constituents that have been reported so far.<sup>14,15</sup>

The number and complexity of ingredients used in rubber compounds are very large with each ingredient having a particular function. Since the ingredients need to be dispersed uniformly throughout the rubber matrix, increasing their number creates

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crucial problem. Multifunctional additive (MFA) was introduced to simplify this situation where a single compounding ingredient possesses several functions simultaneously.<sup>16</sup>

The concept of MFA was introduced by Hepburn et al. in 1983. The MFAs studied were cationic surfactant having the structure of secondary amine salt. They impart a unique combination of properties to a rubber compound. They provide internal and external lubricating action during processing of uncured mix, accelerate the vulcanization reaction, function as crosslinker, or improve filler dispersion in rubber matrix, thus resulting in vulcanizates having good physical properties.<sup>17-20</sup> Furthermore, amine bridge amides were also found to function as multipurpose vulcanizing agents and processing aids in polychloroprene rubber.<sup>21</sup> Another class of new generation multifunctional additive introduced by M/S Bayer (now LANXESS), Germany, has been used mainly in tire tread compound to prevent reversion during service. Additionally, it increases the cure rate and can act as a crosslinking agent.<sup>22</sup>

The present article describes the research carried out to find the effect of the bahera gum as a multifunctional additive in natural rubber and a representative synthetic rubber, i.e., brominated isobutylene-*co*-paramethyl styrene (BIMS).

## EXPERIMENTAL

### Materials

NR (ISNR-5: supplied by Rubber Board, India (ML<sub>1+4</sub> (100°C) = 86), brominated isobutylene-*co*-paramethylstyrene (grade-BIMS-7745; paramethyl content, 7.7 wt %; bromine content, 1.2 wt %; ML<sub>1+8</sub> 125°C, 45; M<sub>n</sub>, 2 × 10<sup>5</sup> g/mol, supplied by Exxon Mobil Chemical Company, Baytown, TX, bahera gum (collected from the forests of West-Midnapore district in West Bengal, India; gums from the same species and same region were used for minimizing variations), zinc oxide (procured from E-Merck, Mumbai, India), stearic acid (supplied by Godrej Soaps, Mumbai, India), 2,2,4-trimethyl-1,2-dihydroquinoline (TQ), (obtained from ICI, Rishra, India), *N*-cyclohexylbenzothiazylsulfenamide (CBS) (supplied by ICI, Rishra, India), and sulfur (Jain Chemicals, Thane, India) were used.

### Characterization of bahera gum

Differential scanning calorimetric study of the bahera gum was carried out using a TA instruments (Luken's Drive, New Castle, DE) DSC model Q100. The scans were taken in the temperature range from 0 to 350°C with a programmed heating rate of 10°C/min.

The infrared spectra of the bahera gum was recorded with a Nicolet Nexus Fourier Transform Infrared Spectrophotometer (FTIR) in DRIFT mode using 45° KRS5 prisms at room temperature. The sample was scanned from 4000 to 700 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The spectra were taken after an average of 32 scans. The result was analyzed using OMNIC software, version 5.1, attached to the spectrophotometer.

### Preparation of the rubber compounds

The NR compounds were prepared by using an oil heated laboratory sized two roll mill (0.15 × 0.33 m<sup>2</sup>) supplied by Farrell Bridge, UK, following the ASTM procedure. The normal operating speed for the front roll was varied from 33.6 to 16.8 rpm, whereas the speed of the back roll was kept constant at 33.6 rpm.

The BIMS based compounds were prepared in a laboratory internal mixer (Brabender Plasticorder – model PLE 3300, capacity 65-mL) with a cam type rotor operating at 60 rpm at an initial temperature of 80°C and the temperature was maintained at (80 ± 5)°C by using a silicone oil bath. Mixing time in all cases was kept constant at 6 min to reach the steady state. For comparison, the neat elastomers were also subjected to the same mixing cycle. After mixing, the compounds were sheeted out on a two-roll mill, with the nip opening of about 1 mm and at roll temperature of 25°C. Formulations of various compounds are given in Tables I-III.

### Cure characteristics

The cure characteristics of the rubber compounds were studied using a Monsanto Moving Die Rheometer (model, MDR – 2000) and Oscillating Disk Rheometer (model, Monsanto Rheometer 100S) as per ASTM D5289-95. The rheometric studies were carried out at 150°C (for NR)/170°C (for BIMS) with an arc oscillation of 0.5° (MDR) and 3° (ODR). The optimum cure time of the compounds, *t*<sub>90</sub> obtained from the rheograph corresponding to an optimum torque, *M*<sub>90</sub>, is given by:

$$M_{90} = 0.9(M_H - M_L) + M_L \quad (1)$$

where *M*<sub>H</sub> and *M*<sub>L</sub> are the maximum and minimum torques, respectively.

Cure rate was calculated using the following equation:

$$\text{Cure rate} = 100 / (t_{90} - t_2) \quad (2)$$

where *t*<sub>2</sub> is the time corresponding to 2 unit rise in the torque above the minimum torque. The reproducibil-

**TABLE 1**  
Effect of Bahera Gum as Accelerator Activator in Natural Rubber and BIMS

	phr								
	$N_{ZS2}$	$N_{ZB1}$	$N_{ZB2}$	$N_{ZB5}$	$N_{ZB10}$	$B_{ZS1.5}$	$B_{ZB1.5}$	$B_{ZB3}$	$B_{ZB5}$
Ingredient									
NR	100	100	100	100	100				
BIMS						100	100	100	100
TQ	1.5	1.5	1.5	1.5	1.5				
ZnO	5	5	5	5	5	1.5	1.5	1.5	1.5
Stearic acid	2	–	–	–	–	1.5	–	–	–
Bahera	–	1	2	5	10	–	1.5	3	5
CBS	0.8	0.8	0.8	0.8	0.8	0.6	0.6	0.6	0.6
S	3	3	3	3	3	1	1	1	1
Curing parameters									
Minimum torque (dNm)	0.2	0.2	0.4	0.3	0.3	0.4	0.6	0.4	0.6
Maximum torque (dNm)	4.4	3.7	4.9	4.0	4.7	1.5	2.2	3.5	4.1
Scorch time ( $t_2$ min)	5.0	4.8	4.1	4.0	3.9	6.5	14.9	12.8	11.3
Optimum cure time ( $t_{90}$ min)	8.7	7.4	6.8	6.6	6.4	14.1	22.7	17.4	15.9
Cure rate ( $\text{min}^{-1}$ )	27	37.7	37.5	38.9	40.3	13.1	13.0	21.8	21.6

ity of the results was checked. Optimum cure time and scorch time had variations of  $\pm 1\%$  and  $\pm 2\%$  respectively.

### Molding

Test specimens were compression molded at  $150^\circ\text{C}$  (for NR)/ $170^\circ\text{C}$  (for BIMS) at 5 MPa pressure in an electrically heated hydraulic press. Optimum cure time  $t_{90}$  as obtained from MDR/ODR for each compound was taken as the molding time.

### Measurement of mechanical properties

The stress–strain properties were determined as per ASTM-D-412-98a (method A, Die C) standard. The measurements were done using a computerized Zwick Universal Testing Machine (model – 1445) at  $25^\circ\text{C}$ . A grip separation rate of 500 mm/min was used in all cases. Maximum deviations in the results of tensile strength, modulus, and elongation at break were  $\pm 5\%$ .

### Measurement of tack strength

For the measurement of tack strength, the rubbers were mixed with bahera gum in a two-roll mill at roll temperature of  $25^\circ\text{C}$ . Rubber sheets of  $2.5 \pm 0.05$  mm thickness were prepared by pressing at  $80^\circ\text{C}$  (for NR)/ $100^\circ\text{C}$  (for BIMS) for 3 (for NR)/5 (for BIMS) min between sheets of smooth aluminum foil at 5 MPa pressure in an electrically heated hydraulic press. One side of the rubber sheet was backed by cloth. Narrow strips (2 cm  $\times$  7 cm) were cut. Just before the test, the aluminum foil was removed and the strips were allowed to come into intimate contact quickly. A load of 2 kg was applied for 30 s in each case. After the desired contact time, the average force required to peel off the two strips was mea-

sured in a Zwick Universal Testing Machine (model-1445) at  $25^\circ\text{C}$ . A separation rate of 50 mm/min was used in all cases. The tack strength,  $G_a$  (N/m), was calculated using the following formula:

$$G_a = 2F/w \quad (3)$$

where,  $F$  is the average force (N) required for peeling and  $w$  is the width (m) of the sample. This test, extensively carried out from this laboratory, was reported in the literature and had error of  $\pm 5\%$  in this investigation.

### Viscosity measurement

The melt-flow properties of the rubber compounds (formulations given in Table V) were measured by means of a Monsanto Processability Tester, (MPT, model 83077) (barrel radius, 9.53 mm), which is a fully automated high-pressure capillary rheometer equipped with a laser beam scanner for the measurement of die swell. The capillary length to diameter ratio (30.0 : 1.0 mm) was 30 with an entrance angle of  $45^\circ$  and  $60^\circ$ . The preheat time for each sample was 5 min. The extrusion studies of the samples were carried out at 90, 100, 110, and  $120^\circ\text{C}$  at the shear rates ranging from 12–400  $\text{s}^{-1}$ .

The apparent shear stress ( $\tau_{\text{app}}$ ), apparent shear rate ( $\dot{\gamma}_{\text{app}}$ ), and apparent shear viscosity ( $\eta_{\text{app}}$ ) were calculated using the following equations:<sup>23</sup>

$$\tau_{\text{app}} = d_c \Delta P / 4l_c \quad (4)$$

$$\dot{\gamma}_{\text{app}} = 32Q / \pi d_c^3 \quad (5)$$

$$\eta_{\text{app}} = \tau_{\text{app}} / \dot{\gamma}_{\text{app}} \quad (6)$$

where  $\Delta P$  is the pressure drop across the length of the capillary,  $d_c$  and  $l_c$  are the diameter and length of

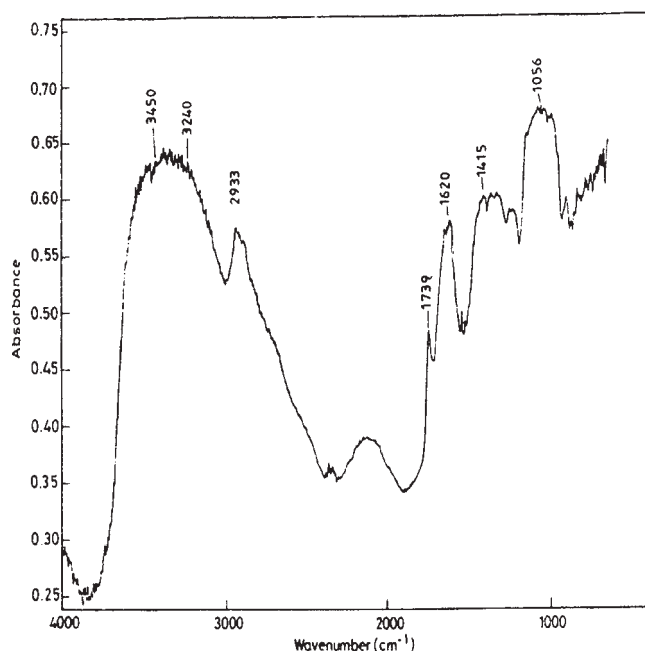


Figure 1 FTIR spectra of bahera gum.

the capillary respectively, and  $Q$  the volumetric flow rate of the material.

The flow behavior index ( $n$ ) and consistency index ( $k$ ), which indicate the pseudoplastic behavior and its dependence on the shear rate respectively, were calculated by using the Power Law model as indicated in the following equations:

$$\tau_{\text{app}} = k \dot{\gamma}_{\text{app}}^n \quad (7)$$

By definition  $\eta_{\text{app}} = \tau_{\text{app}}/\dot{\gamma}_{\text{app}}$ ; therefore;

$$\eta_{\text{app}} = k \dot{\gamma}_{\text{app}}^{n-1} \quad (8)$$

In the logarithmic form, eq. (8) may be written as,

$$\log \eta_{\text{app}} = \log k + (n - 1) \log \dot{\gamma}_{\text{app}} \quad (9)$$

The values  $n$  and  $k$ , were calculated from the slope and intercept of the linear plot of  $\log \eta_{\text{app}}$  versus  $\log \dot{\gamma}_{\text{app}}$ .

The running die swell at the exit of the capillary was calculated as the ratio of extrudate diameter,  $d_e$  to capillary diameter,  $d_c$ .

### Activation energy

Activation energy of viscous flow was derived from the Arrhenius-Frenkel-Eyring relation, which is valid for the power law fluids as given below:

$$\eta_{\dot{\gamma}} = B e^{E_{\dot{\gamma}}/RT} \quad (10)$$

where  $E_{\dot{\gamma}}$  is the activation energy of the flow at a particular shear rate,  $R$  the gas constant,  $T$  the tem-

perature in Kelvin,  $B$  the pre-exponential component, and  $\eta_{\dot{\gamma}}$  the viscosity in  $\text{Pa s}^n$  at that shear rate. The slope of the linear plot of  $\log$  viscosity versus reciprocal of temperature ( $1/T$ ) provides  $E_{\dot{\gamma}}/R$ , from which the activation energy was calculated.

## RESULTS AND DISCUSSION

### Characterization of bahera gum

Figure 1 shows FTIR spectra of the representative bahera gum sample. The strong broad band at  $3200\text{--}3600\text{ cm}^{-1}$  is attributed to the O—H stretching vibration for the absorbed moisture and hydrogen bonded hydroxyl groups present in the gum. The adjacent absorption band at  $2933\text{ cm}^{-1}$  is due to C—H stretching. The broad band around  $2300\text{ cm}^{-1}$  supports the presence of the O—H of carboxyl group. The band at  $1739\text{ cm}^{-1}$  is assigned to C=O stretching and strong absorption around  $1620\text{ cm}^{-1}$  is due to C=C stretching. Characteristic O—H in-plane deformation vibration gives rise to absorption band in the region of  $1415\text{ cm}^{-1}$ , which is overlapped with the C—H deformation vibration in the same region. Absorption due to C—O stretching and O—H bending vibrations appears around  $1056\text{ cm}^{-1}$ .

A typical DSC thermogram of bahera gum is shown in Figure 2. The distinct endotherm observed around  $123^\circ\text{C}$  corresponds to the melting of constituents of the gum. The sharp exotherm at  $\sim 255^\circ\text{C}$  may be due to some reaction in the gum matrix.

The IR and DSC results conform to the multiple ingredients present in the gum, as reported earlier by other workers.<sup>11–13</sup>

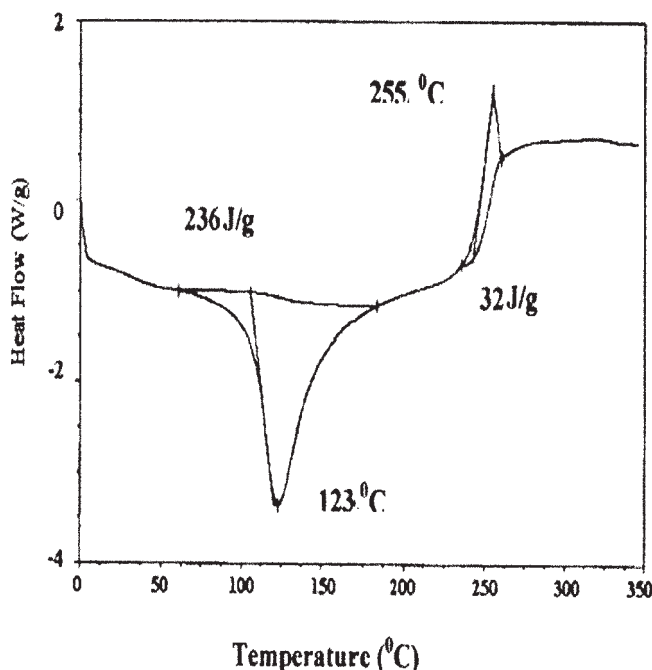
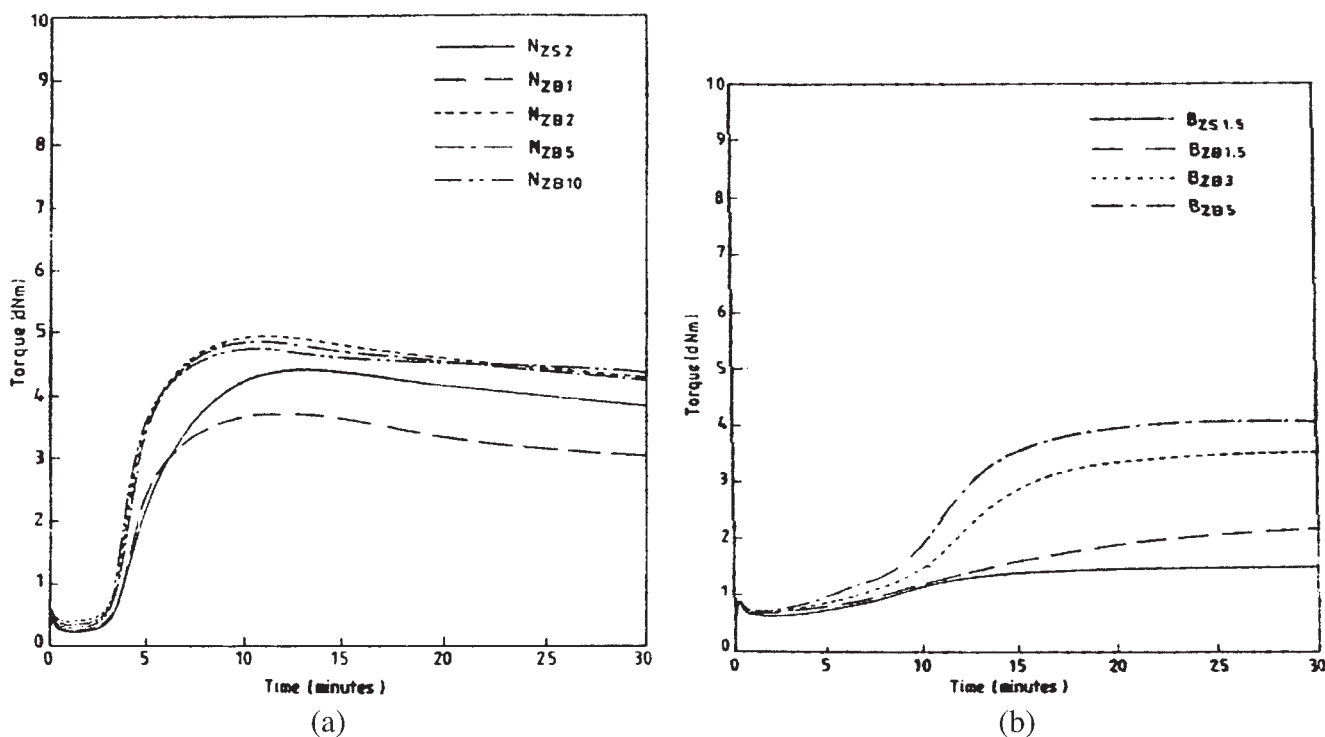


Figure 2 DSC thermogram of bahera gum.



**Figure 3** Curing behavior of compounds containing bahera gum at different loadings as an accelerator-activator. (a) Natural rubber at 150°C and (b) BIMS at 170°C.

#### Bahera gum as an accelerator-activator—comparison of cure and mechanical properties of gum vulcanizates with stearic acid

On the basis of the observed  $-\text{COOH}/\text{ester}$  group in the IR spectra of the bahera gum, it was decided to investigate the ability of the gum to function as accelerator-activator. Comparison was made with commercial activator, stearic acid. The experiment consisted of preparing rubber compounds in which the stearic acid was replaced by bahera gum (Table I). Cure characteristics and tensile properties of the rubber compounds are represented in Figures 3 and 4 respectively.

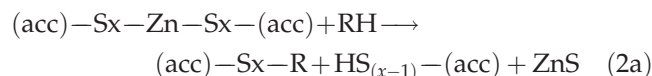
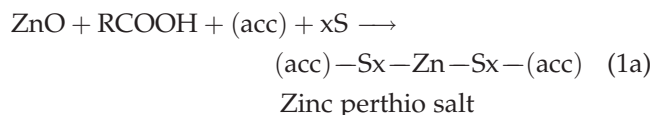
It is evident from the results that in NR based compounds, the rate of cure gradually improves with increasing gum loading, but there is a reduction in the scorch time ( $t_2$ ) as well as optimum cure time ( $t_{90}$ ).

Improvement in tensile strength and modulus with a slight decrease in elongation at break is observed when stearic acid is replaced by bahera gum in the same proportion in NR formulation (cf.  $N_{ZS2}$  and  $N_{ZB2}$ ). The compound containing gum in lesser amount (i.e.,  $N_{ZB1}$ ) still possesses higher modulus compared to the control ( $N_{ZS2}$ ), but this property falls on further increase in the gum dose.

For BIMS-based compounds, both the rate and state of cure as determined from the maximum torque improve with increasing dose of the gum. Additionally, the scorch safety of the compounds is higher compared to the control ( $B_{ZS1.5}$ ). The tensile properties versus gum loading [Fig. 4(b)] shows that

replacing stearic acid by bahera gum in the same proportion gives higher tensile strength, ultimate elongation, and modulus ( $B_{ZS1.5}$  and  $B_{ZB1.5}$ ). The strength and modulus increase with the gum loading, but the effect on tensile strength is less pronounced beyond 3 phr. Inclusion of the gum in place of stearic acid in higher dose shows detrimental effect on elongation at break, which may be attributed to the dilution and plasticization effect.

Activators are usually two component systems comprising of metal oxides and long chain fatty acids. Zinc oxide is the most commonly used inorganic activator and among fatty acids, stearic, palmitic, and lauric acids, etc., are important. Before the onset of the vulcanization, zinc oxide, fatty acid, sulfur, and accelerator (acc) react together to form a zinc perthio-salt,<sup>24,25</sup> which serves as actual accelerating agent. It reacts with the rubber hydrocarbon (RH) to form rubber-bound-sulfur-accelerator intermediate. The sequence of the reaction is as follows:



The acid reacts with ZnO to form  $\text{Zn}^{2+}$ , which then forms the complex salt.

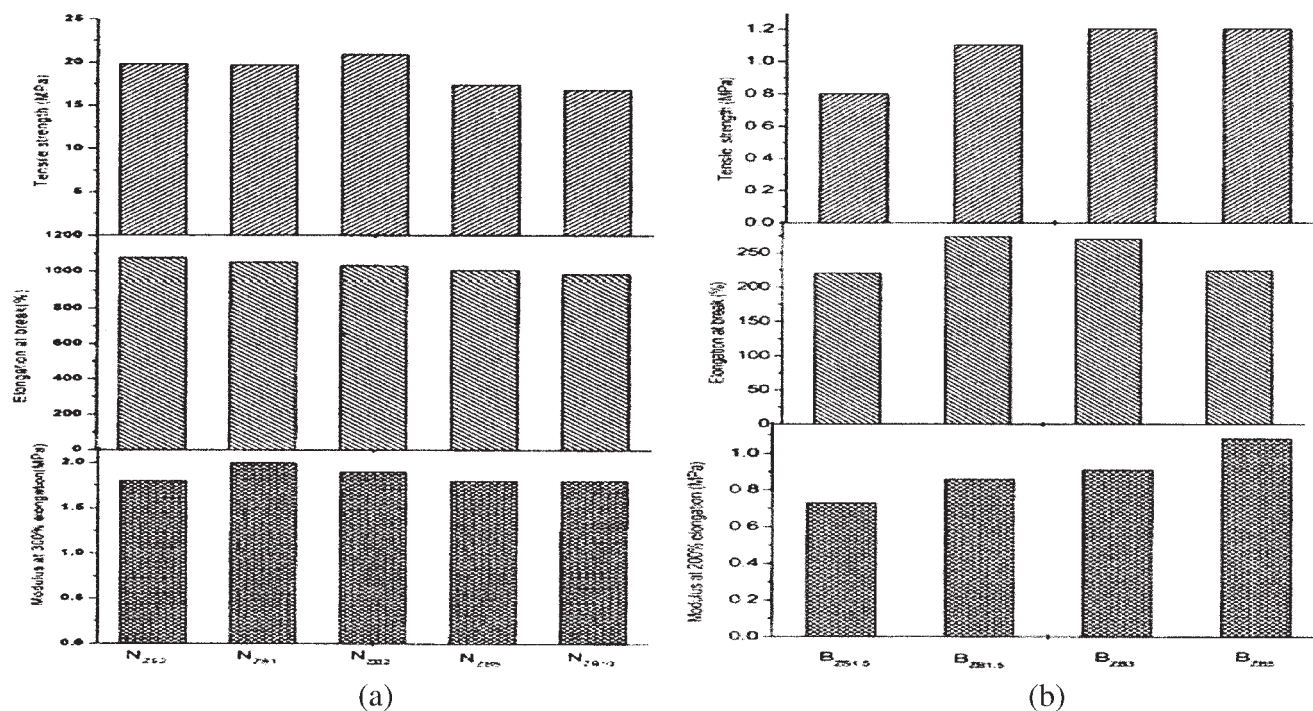
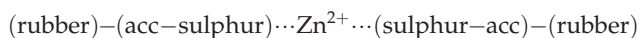


Figure 4 Tensile properties of vulcanizates containing bahera gum as activator. (a) NR and (b) BIMS.

The activators play multiple roles—besides accelerating the reaction between accelerator, sulfur and rubber, they also contribute to the gain in physical properties of the vulcanizates through the formation of strong secondary valence salt bridges of the type



Coran<sup>25</sup> described the role of zinc ion as a crosslink precursor in thiazole acceleration. Another function of the fatty acids is to make the complex more compatible in rubber, so that the reaction with the rubber is facilitated.

Good dispersibility of the fatty acid in the rubber matrix is of prime importance to achieve satisfactory activation. The enhancement of cure rate on replacement of stearic acid by bahera gum reflects that the fatty acid/ester present in it is more reactive than stearic acid, which may be attributed to the presence of oxalate. In polar BIMS matrix, better dispersibility

of the gum provides regular trend in the improvement of both rate and state of cure. Furthermore, it is interesting to note that optimum dose of the gum has been found to be  $\sim 2$  phr. Since the gum is a mixture of several constituents, this implies very small amount of the fatty acid/ester of the gum (less than 2 phr-normal dose of stearic acid in NR) is sufficient to produce the desired activation.

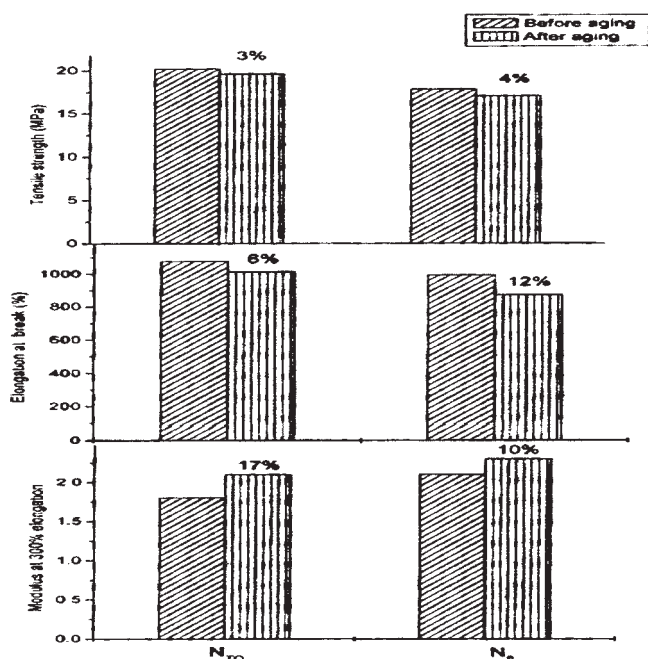
#### Bahera gum as an antioxidant—comparison of aging properties with a commercial antioxidant

In an earlier study on the bark of *Terminalia bellerica* species, the bark was found to be a potential source of tannins.<sup>11–13</sup> Tannins are basically polyphenolic compounds. In the present study, to explore the aging resistant property of the gum in NR matrix, compounds were designed according to the formulation given in Table II. The tensile properties were used to evaluate the aging resistance of the vulcanizates, and the results are illustrated in Figure 5. Comparison was made with a well-known commercial antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline (TQ) due to its better antioxidant activity than many polyphenols. It is known that in natural rubber there is deterioration of tensile strength and elongation at break upon aging. Replacing TQ by bahera gum ( $N_{TQ}$  and  $N_B$ ) offer better resistance to the change in modulus after aging at 70°C for 36 h and the change in tensile strength is comparable.

It is established that during aging, oxygen attacks on the  $\alpha$ -methylene carbon atom of the unsaturated

TABLE II  
Compositions of the NR–Bahera Gum Mixes in the Study of Gum as Antioxidant

Ingredient	$N_{TQ}$	$N_B$
NR	100	100
TQ	1.5	–
ZnO	5.0	5.0
Stearic acid	2.0	2.0
Bahera	–	1.5
CBS	0.8	0.8
S	3.0	3.0



**Figure 5** Tensile properties of NR vulcanizates containing bahera gum as antioxidant.

rubber molecule, a hydrogen atom is abstracted and an oxidative chain reaction is initiated, which if unchecked, propagates autocatalytically.<sup>26</sup> Hydrogen donating antioxidants (AH) retard oxidation by competing with the polymer (RH) for peroxy radicals. Antioxidant inhibit the autocatalytic propagation either by (i) capturing the free radicals formed and/or (ii) ensuring that the peroxides and hydroperoxides produced decompose into harmless fragments without degrading the polymer chain.



In the study on the effect of gum as antioxidant, it is found that the aging resistance of the gum is comparable to that of TQ. This is because of the polyphenolic compounds present in the bahera gum. Additionally, TQ is expensive, carcinogenic, and causes staining of the product. On the contrary, bahera gum is cheap, ecofriendly, and nonstaining type.

#### Dual role of activation and aging resistance of bahera gum

The next study was to explore the possibility of using bahera gum as an accelerator-activator and antioxidant and for this purpose a natural rubber compound ( $N_{BB}$ ) was formulated in which both the

commercial activator (stearic acid) and antioxidant (TQ) was replaced by the natural gum. Table III summarizes the formulation, cure parameters, and tensile properties of the compounds. Cure parameters show cure acceleration; the rate increases from 27.0 to 54.7  $\text{min}^{-1}$ . Comparison was made with  $N_{ZS2}$  a compound containing both stearic acid (accelerator-activator) and TQ (antioxidant). In  $N_{BB}$ , the scorch time and the maximum torque are lower compared to the control, but the modulus values are higher with comparable tensile strength and elongation at break. On aging at 70°C for 36 h,  $N_{BB}$  shows no change in modulus and very little change in elongation at break. The percent decrease in tensile strength is comparable to  $N_{ZS2}$ . The results could be explained by the same mechanisms discussed in the earlier section.

#### Bahera gum as tackifier

Composition of the mixes used in this study are given in Table IV. No other ingredient was added, as the purpose of the study was to investigate the effect of bahera gum loading on tack strength. The influence of bahera gum on tack strength of NR and BIMS is demonstrated in Figures 6(a–b) respectively. In NR, addition of gum increases the tack strength (by 21%) with a dose of 2.5 phr, beyond which the tack strength reduces considerably. From the plot of tack strength versus gum concentration of the BIMS

**TABLE III**  
Dual Role of Activation and Aging Resistance of Bahera Gum in NR Matrix

	phr	
	$N_{ZS2}$	$N_{BB}$
Ingredients		
NR	100	100
TQ	1.5	–
ZnO	5.0	5.0
Stearic acid	2.0	–
Bahera	–	3.5
CBS	0.8	0.8
S	3.0	3.0
Curing parameters		
Minimum torque (dNm)	0.2	0.2
Maximum torque (dNm)	4.4	4.1
Scorch time ( $t_2$ ) (min)	5.0	4.3
Optimum cure time ( $t_{90}$ ) (min)	8.7	6.1
Cure rate ( $\text{min}^{-1}$ )	27.0	54.7
Tensile Properties		
Tensile strength (MPa)	20.2 (19.6)	21.1 (20.3)
Elongation at break (%)	1077 (1012)	994 (965)
$M_{100}$ (MPa)	0.7 (0.8)	0.9 (0.9)
$M_{200}$ (MPa)	1.2 (1.4)	1.5 (1.5)
$M_{300}$ (MPa)	1.8 (2.1)	2.1 (2.1)

The values within parentheses represent tensile properties after aging.

**TABLE IV**  
Compositions of the Rubber–Bahera Gum Mixes in the Study of Gum as Tackifier

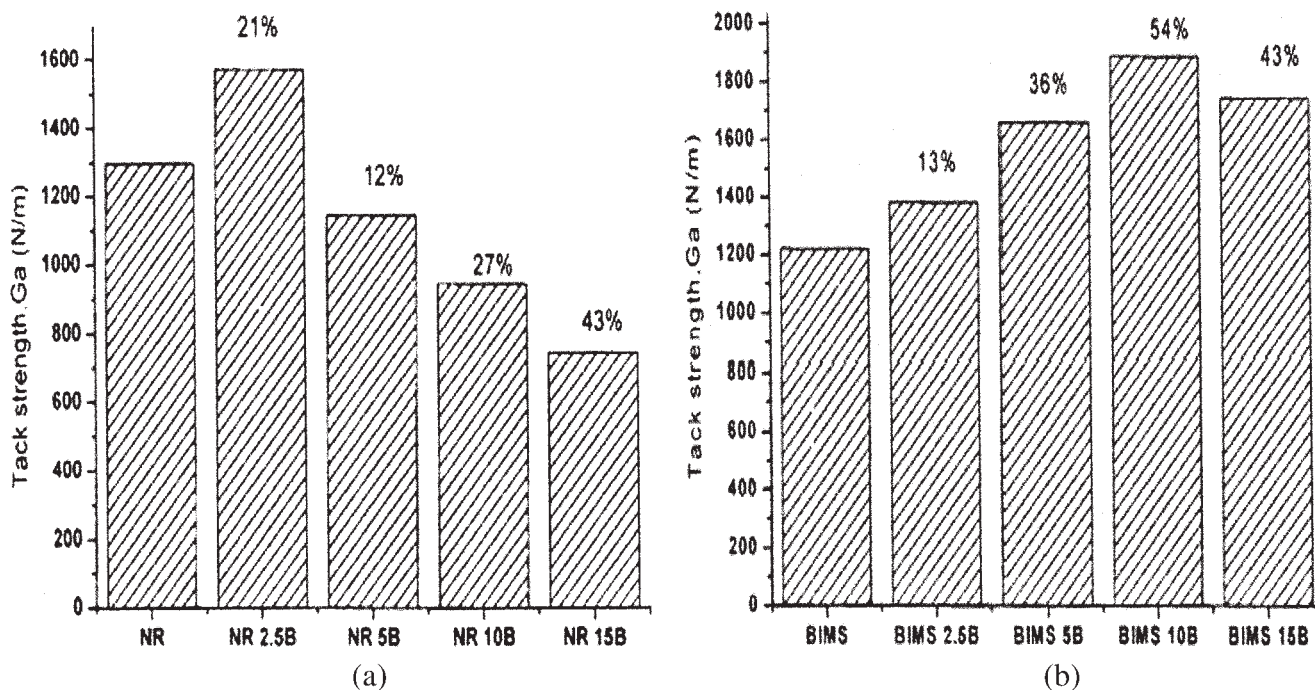
Sample no.	Bahera gum loading (phr)
Natural rubber based formulation	
NR	0
NR2.5B	2.5
NR5B	5.0
NR10B	10
NR15B	15
BIMS-based formulation	
BIMS	0
BIMS 2.5B	2.5
BIMS 5B	5.0
BIMS 10B	10
BIMS 15B	15

system, it is observed that tack strength increases with gum loading and attains maxima (increases by 54% compared to pure BIMS) at 10 phr. Beyond this level, the tack strength falls. It has been reported earlier that molecular contact, interdiffusion of polymer chains, and high cohesive strength are responsible for tack strength.<sup>27–30</sup> The enhancement in tack strength on addition of the gum may be attributed to the lowering of viscosity of both NR and BIMS (as discussed in the next section), which results in interfacial diffusion of polymer chains at the interface, thus giving rise to good interfacial bonding. Morphology of the rubber–resin mixture plays a crucial part. It has been shown in our early studies that the

bahera gum migrates to the surface of the natural rubber–resin mixture and there is a possibility of surface segregation of the gum tested.<sup>31</sup> It was also demonstrated that the storage modulus of the natural rubber–resin mixture at the temperature of peel testing increases with the content of the bahera gum. However, the  $\tan \delta$  peak height slowly decreases with an increase in the gum concentration indicating good interaction and the  $T_g$  of NR–bahera gum blends, calculated from the temperature corresponding to the maximum  $\tan \delta$  peak height, decreases. The higher value of optimum gum loading in BIMS implies that bahera gum with lot of polar functional groups has better compatibility with BIMS compared to NR.

#### Effect of bahera gum on the rheological properties of natural rubber and BIMS

The effects of shear rate and shear stress on viscosity of the rubber compounds containing bahera gum at different proportions (2.5, 10, and 15 phr) at different temperatures have been investigated (Table V). The viscosity decreases with the shear rate like neat natural rubber (not shown here), revealing the pseudoplastic or shear thinning nature of both the compounds. Viscosity versus shear stress plot for a representative natural rubber compound is shown in Figure 7. It is interesting to note that the compounds containing bahera gum show lower viscosity, compared to the control. The viscosity is reduced significantly at higher temperature. The reduction in vis-



**Figure 6** Tack strength of virgin rubber and rubber–gum mixes at different proportions (a) NR and (b) BIMS.

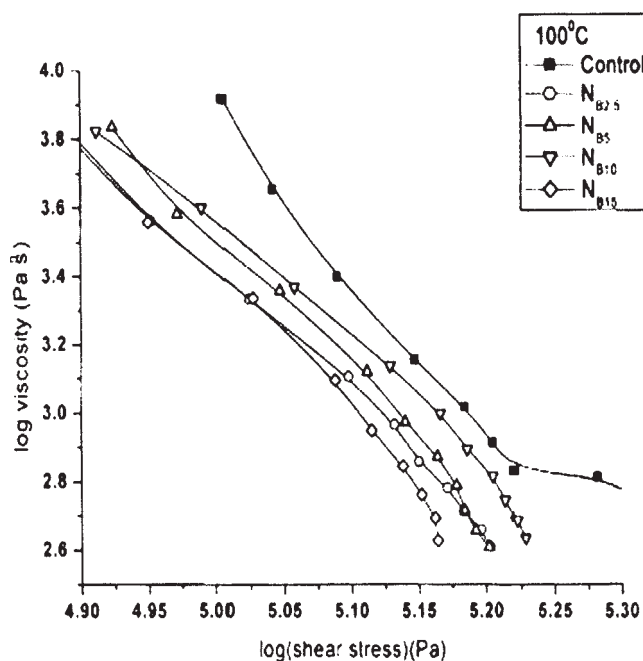


**TABLE V**  
Bahera Gum as Viscosity Modifier in Natural Rubber

Ingredient	phr				
	Control	$N_{B2.5}$	$N_{B5}$	$N_{B10}$	$N_{B15}$
NR	100	100	100	100	100
TQ	1.5	1.5	1.5	1.5	1.5
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
Bahera	—	2.5	5.0	10.0	15.0
CBS	0.8	0.8	0.8	0.8	0.8
S	3.0	3.0	3.0	3.0	3.0
Tensile properties					
Tensile strength (MPa)	17.2	17.1	14.9	14.7	13.4
Elongation at break (%)	908	926	902	903	909
$M_{100}$ (MPa)	0.9	0.9	0.9	0.8	0.8
$M_{200}$ (MPa)	1.5	1.5	1.4	1.4	1.2
$M_{300}$ (MPa)	2.3	2.2	2.1	2.0	1.8

cosity with the addition of bahera gum can be explained in terms of hydrodynamic effect of the gum, which increases the volume fraction of the flow medium and tends to lower the viscosity of the compound.<sup>32</sup>

It is observed that with increase in the gum loading, consistency index ( $k$ ) calculated from eq. (7) decreases, indicating a reduction in resistance towards flow (Table VI). The flow behavior index ( $n$ ) slightly increases, which means a decrease in the pseudoplastic behavior. Expectedly,  $n$  increases and  $k$  decreases on increasing the temperature.



**Figure 7** Log viscosity as a function of log shear stress at 100°C for NR compounds.

**TABLE VI**  
Flow Behavior Index ( $n$ ) and Consistency Index ( $k$  Pa s <sup>$n$</sup> ) for NR–Bahera Gum System

System	Temperature (°C)					
	90		100		110	
	$k$ (10 <sup>-4</sup> )	$n$	$k$ (10 <sup>-4</sup> )	$n$	$k$ (10 <sup>-4</sup> )	$n$
Control	5.78	0.19	5.63	0.20	3.73	0.24
$N_{B2.5}$	5.62	0.19	5.37	0.20	3.58	0.24
$N_{B5}$	5.49	0.20	5.24	0.21	3.57	0.24
$N_{B10}$	5.37	0.20	4.95	0.21	3.56	0.25
$N_{B15}$	5.14	0.21	4.95	0.22	3.52	0.25

Activation energy at different shear rates was calculated using eq. (10) from the data of viscosity at different temperatures. The activation energy values lie in between 3.75 and 5.75 kJ/mol. These are a function of shear rates and content of bahera gum. Activation energy decreases with shear rate. With increase in gum dose, the activation energy gradually decreases compared to the control. This is due to the plasticization effect imparted by the gum, which causes increase in free volume of the matrix and thus reduces the energy required for the deformation.

The variation of die swell with rate of shear and gum loading is illustrated in Figure 8. It is evident from the graphs that the gum rubber shows maximum die swell in the range of shear rate studied. It is also seen that the die swell increases with shear rate. In BIMS matrix, the curves show three regions: (a) low shear region where the die swell decreases slightly with shear rate in both control and BIMS-gum compounds, (b) intermediate shear region where there is a sharp increase in die swell, and (c) high shear region where the rate of increase in die swell is considerably reduced. The reduction in die swell with increased gum loading for both the rubbers may be attributed to the plasticization effect imparted by the gum in rubber matrix and a decrease in the elastic memory of the system.

## CONCLUSIONS

A new class of MFA of natural origin has been discovered, which is basically a waste gum extracted from the bark of *Terminalia bellerica* (local name Bahera). This natural gum imparts a good combination of properties in NR and BIMS rubber. The conclusions drawn from the systematic study are summarized below:

Bahera gum can serve as an accelerator-activator and can replace stearic acid in rubber formulation. NR and BIMS compounds containing bahera gum in the same proportion as stearic acid give higher

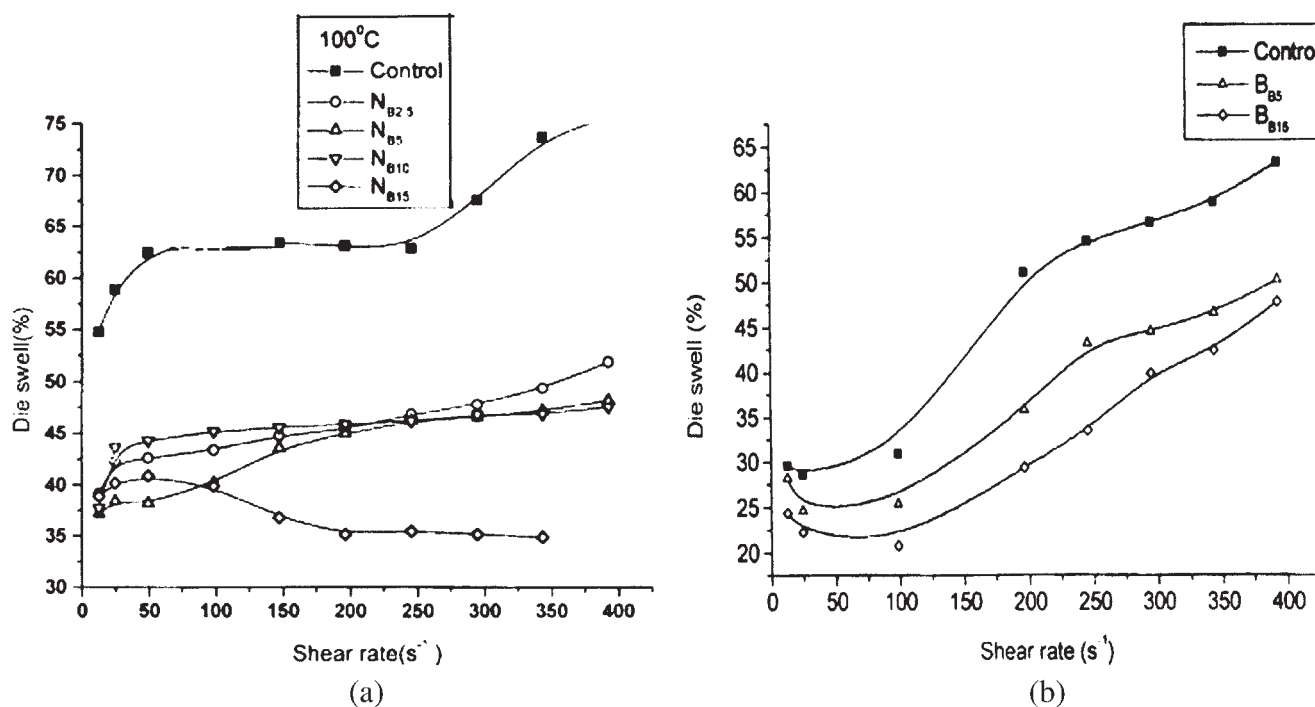


Figure 8 Dependence of die swell on shear rate for (a) NR compounds at 100°C and (b) BIMS compounds at 90°C.

tensile strength, modulus and for BIMS, better scorch safety too.

The gum can act as antioxidant in NR matrix. The change in tensile strength and elongation at break are comparable to TQ. It offers better resistance to aging considering modulus. Moreover, TQ is carcinogenic and causes staining of the product. Bahera gum is ecofriendly and cheaper.

The tack behavior of the uncrosslinked rubber-bahera gum system has been examined using 180° peel geometry. Addition of the gum in rubber increases the tack strength. The optimum dose of the gum for the maximum improvement (54% for BIMS versus 21% for NR) is 10 phr for BIMS compared to 2.5 phr for NR

The viscosity of all the systems studied, decreases with shear rate and shear stress indicating the pseudoplastic or shear thinning nature. Addition of the gum reduces the viscosity as well as die swell of the compounds. A prominent decrease in the activation energy is also observed with increasing loading of the gum.

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