

WASTE *MORINGA OLEIFERA* GUM AS A MULTIFUNCTIONAL ADDITIVE FOR UNFILLED SBR COMPOUND

RIYA KOLEY,¹ RAJKUMAR KASILINGAM,² SUCHISMITA SAHOO,² SANTANU CHATTOPADHYAY,¹ ANIL K. BHOWMICK^{1,3,*}

¹RUBBER TECHNOLOGY CENTRE, INDIAN INSTITUTE OF TECHNOLOGY KHARAGPUR, KHARAGPUR-721302, WEST BENGAL, INDIA

²INDIAN RUBBER MANUFACTURERS RESEARCH ASSOCIATION, THANE WEST- 400604, MAHARASHTRA, INDIA

³DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING, THE UNIVERSITY OF HOUSTON, HOUSTON, TX 77204-4004

RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 94, No. 2, pp. 248–267 (2021)

ABSTRACT

A natural waste (gum) of the drumstick tree, *Moringa oleifera*, was used for the first time as a sustainable multifunctional additive in an SBR compound. Improved cure rate with lower optimum cure time was obtained by using the gum as an accelerator activator. Tack strength of the *M. oleifera* gum–SBR compound was superior to both the control and the compound containing commercial phenol–formaldehyde resin at 5 parts per hundred of rubber loading. At different loadings, the gum acted as a plasticizer for the rubber and augmented processing by reducing the viscosity of the compound. The glass transition temperature of the compounds decreased by 2 °C compared with the pristine SBR. *Moringa oleifera* gum at any loading reduced the die swell of SBR. This study has relevance because the rubber industry is looking for feasible sustainable additives as alternatives to existing petroleum-based compounding ingredients. [doi:10.5254/rct.21.79998]

INTRODUCTION

During the past few decades, the use of bio-derived natural materials has become the focus of various scientific research.¹ Fluctuating petroleum prices, depletion of petroleum storage, and increasing environmental awareness are the main driving forces for sustainability.^{2,3} In the polymer field, most of the work with sustainable material is centered on the synthesis of polymers from sustainable resources.^{4,5} Significant work has not been done on the synthesis of nature-based rubber compounding additives or on the direct use of natural materials as compounding ingredients.⁶ However, as an eco-friendly approach, rubber industries have commercially started to use recycled rubber with raw rubber while compounding. For example, Naskar et al. reported the effect of ground tire rubber on a NR-based compound.⁷ In addition, Nevatia et al. made thermoplastic elastomer by using waste scrap low-density polyethylene and reclaimed NR.⁸ The importance of natural waste is also increasing steadily,⁹ although its use in rubber compounding is occasional. The effect of *Euphorbia caducifolia haines* as a multifunctional additive (MFA) in rubber was studied by Bhattacharyya et al. and published in this journal.¹⁰ In our previous work, we reported on the synthesis of a drumstick tree, *Moringa oleifera*, gum-based phenol furfural tackifier resin for rubber compounding.⁶ Guhathakurta et al. presented the use of *Terminalia bellerica* gum as an MFA for NR and isobutylene-*co*-paramethyl styrene (BIMS)–based rubber compounds.¹¹

Rubber compounding is a very complex process, and the addition of a large number of compounding ingredients makes the process more critical.^{12,13} From a sustainability viewpoint, compounding ingredients should be eco-friendly, cost effective, and processable in the running manufacturing facility.

The term MFA was first suggested by Hepburn et al.^{14,15} as a compound with multitasking ability, but mainly used to reduce the number of compounding ingredients without sacrificing the required compound properties. Secondary amine salt surfactant shows easy processing with

*Corresponding author. Ph: +001-713-743-9241; email: anilbhowmick@gmail.com; akbhowmick@uh.edu

TABLE I
PHYSICAL PROPERTIES OF *MORINGA OLEIFERA* GUM

Property	Observation
Physical appearance	Brown-colored solid mass
Solubility of <i>M. oleifera</i> gum	Insoluble in all solvent, but partly soluble in hot water with 28% (w/w) solubility
Present functional groups (identified by Fourier transform infrared spectroscopy)	–CHO, –OH, –C=C– and the acidic carboxyl group
T_g , °C	18
Thermogravimetric analysis of gum	First peak at 85 °C: removal of moisture Second peak at 249 °C: loss of free and bound water in the <i>M. oleifera</i> gum $T_{max} = 301$ °C
Ash content at 650 °C, %	0.57

accelerated vulcanization, better filler dispersion, and improved physical properties.¹⁶ Amides having an amine bridge act as a processing aid and vulcanizing agent for chloroprene rubber.¹⁷ Ismail et al. studied the multifunctional effect of $\text{RNH}_2^+[(\text{CH}_2)_3\text{NH}^+][\text{R}'\text{COO}^-]_2$ on mechanical, curing, and other properties of the rubber compounds.¹⁸ Khanra et al. presented the accelerator and antioxidant properties of different MFAs on rubber compounds.¹⁹ Sheng et al. reported the multifunctional effect of carboxylic acid diamine salt on the bound rubber content of a filled rubber compound.²⁰ Because of the improved processability and curing property of rubber compounds containing natural oil, such as rice bran oil,²¹ linseed oil was also listed as a green MFA.^{22,23} However, we are interested in multifunctional additives from waste natural resources. Many unused natural resources are yet to be discovered. In the present work, for the first time, *M. oleifera* gum was used as MFA in unfilled SBR-based compound formulation.

The *M. oleifera* tree grows in tropical and subtropical regions such as South Africa, Latin America, Asia, Pacific Islands, India, Philippines, Ethiopia, and Sudan Caribbean.²⁴ It is a medicinal plant with various properties. Its leaves can be used as supplementary nutrients.²⁵ It can control blood sugar²⁶ and cholesterol²⁷ and reduce inflammation.²⁸ The carbohydrate, the major component in the gum, has been reported as a tablet binder.²⁹ Main constituents of the carbohydrate present in *M. oleifera* gum are arabinose, mannose, xylose, fructose, rhamnose, galactose, and a trace amount of glucuronic acid.⁶ Other natural compounds such as vanillin, terpenoids, tannins, flavonoids, organosulfur compounds, sitosterol, and octacosanoic acid are also present in the gum.³⁰ *Moringa oleifera* gum is partly soluble in hot water and insoluble in any other solvent. The detailed properties of the *M. oleifera* gum were reported in a previous work,⁶ and some of these properties are listed in Table I. A low tack and high double bond containing polymer make SBR the perfect choice for our work over NR. The tackifying property of *M. oleifera* gum would be more prominent in SBR.

The present work extensively explores the potency of a bio-waste, *M. oleifera* gum, as a sustainable MFA in an SBR-based compound. The applicability of the gum as an accelerator activator, processing aid, and tack promoter has been investigated by replacing the respective compounding ingredient by the gum in the formulation. Rheometric, tensile, dynamic mechanical, and processing properties were studied and compared with those of a control compound. Compared with the other chemicals that are currently being used for this purpose, *M. oleifera* gum can serve as a cost-effective alternative in the rubber industry.

EXPERIMENTAL

MATERIALS

SBR1502 (styrene content, 23.5%; Average molecular weight = 522 558 g mol⁻¹; glass transition temperature [T_g] = -49.6 °C; Mooney viscosity, ML_{1+4} @ 100 °C = 51) was supplied by Kumho Petrochemical, Seoul, South Korea. The compounding ingredients used were zinc oxide (ZnO; Merck Life Science Pvt. Ltd., Mumbai, India), stearic acid (C₁₈H₃₆O₂; Godrej Soap Limited, Mumbai, India), *N*-phenyl-*N'*-(1,3 dimethyl-butyl)-*p*-phenylenediamine (6PPD) (National Organic Chemicals Industries Ltd., Thane, India), sulfur (Loba Chemical Pvt. Ltd., Mumbai, India), and cyclohexyl benzothiazole sulfenamide (CBS) (National Organic Chemicals Industries Ltd.). *Moringa oleifera* gum was collected from trees in Burdwan, India, and characterized in our laboratory. POWERPLAST TR-0010, a clear amber viscous liquid phenol–formaldehyde (PF) resin with specific gravity of 0.97 and volatile content less than 1%, was obtained from PowerPlast Rubber Processing and Dry Bonding Chemicals section of Singh Plasticizer and Resins (I) Pvt. Ltd., New Delhi, India. In resin characterization by Fourier transform infrared spectroscopy, the obtained peaks from 2957 to 2850 cm⁻¹ and from 3295 to 3400 cm⁻¹ were for the stretching of C–H bond and stretching of present phenolic hydroxyl groups, respectively. For easy representation, POWERPLAST TR-0010 is further reported as PF resin herein. Toluene was purchased from Merck Life Science Pvt. Ltd. Cost of the stearic acid and PF resin were 2.5 and 6 times higher, respectively, than for *M. oleifera* gum. Hence, use of the low-cost *M. oleifera* gum as a rubber additive provides an additional cost–benefit advantage for the rubber compounds.

COMPOUNDING

Compounding was carried out in a PLE-330 model plasticorder internal mixer (Brabender GmbH, Duisburg, Germany) with 65 mL capacity. The mixing was conducted at 120 °C at 60 rpm. Formulations for the different compounds are presented in Tables II–IV. SBR1502 was first sheared for 2 min followed by addition of ZnO, stearic acid, and 6PPD as listed in the tables. At 3 min, natural gum was added to the rubber and mixed for another 2 min. Next, the mix was passed through a laboratory-sized two-roll mill (0.15 × 0.33 m²; Farrell Bridge LTD, Rochdale, UK). After the maturation period, the rubber band was formed in the two-roll mill at room temperature, and the accelerator was mixed for 1.5 min followed by mixing of sulfur for the next 1.5 min. The sheeted final batch material was then left overnight for maturation.

For the peel test samples, SBR1502 was sheared for 2 min followed by the addition of *M. oleifera* gum and mixing for another 3 min.

CURE CHARACTERISTICS

The cure characteristics of the unfilled SBR compounds were investigated using an oscillating disk rheometer (model 100S; Monsanto, Akron, OH, USA) at 3° arc oscillation. The rheometric studies were carried out at 150 °C for 1 h following ASTM Standard D 5289-95. The optimum cure time (tc_{90}) of the compound was directly obtained from the rheometer software. The tc_{90} value was also calculated by following tangential method³¹ and by using Eq. 1:

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

Here, M_{90} is the torque corresponding to tc_{90} and M_H and M_L represent the maximum and minimum torque, respectively.

Similarly, the cure rate index (CRI) of the rubber compound was directly obtained from the rheometer software and also calculated using Eq. 2:

TABLE II
FORMULATION AND PROPERTIES OF MIXES CONTAINING *MORINGA OLEIFERA* GUM AS AN ACCELERATOR ACTIVATOR IN UNFILLED SBR

Ingredient, phr	SBRZS2	SBRZM2	SBRZM5	SBRZM10
SBR	100	100	100	100
ZnO	5	5	5	5
Stearic acid	2	0	0	0
<i>M. oleifera</i> gum	0	2	5	10
6PPD	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5
Sulfur	2	2	2	2
M_L , dN·m	10.67	11.26	11.57	10.27
M_H , dN·m	72.50	74.52	86.77	79.82
ts_2 , min	10.98	10.99	11.79	9.55
tc_{90} , min	26.87	20.76	19.32	16.48
CRI, min^{-1}	6.44	10.20	13.14	14.30
Tensile strength, MPa	2.28 ± 0.37	1.83 ± 0.16	1.76 ± 0.13	1.62 ± 0.10
Modulus at 100% elongation, MPa	1.26 ± 0.03	1.09 ± 0.04	1.18 ± 0.04	1.15 ± 0.02
Elongation at break, %	268 ± 49	239 ± 30	211 ± 17	197 ± 21
Swelling index	4.27	4.06	4.06	4.07
Crosslink density, mol/c.c.	3.9×10^{-4}	4.3×10^{-4}	4.5×10^{-4}	4.5×10^{-4}

$$\text{CRI} = [100 / (tc_{90} - ts_2)] \quad (2)$$

where scorch safety (ts_2) is the time required for 2 deci-Newton meter (dN·m) rise in the torque value from the M_L value.

To justify the values of the tc_{90} , CRI, and ts_2 from the rheometer curves (as SBR compound without natural gum exhibited slightly matching curve), we determined these parameters by all the three methods. The comparative rheograph data for the study of the gum as an accelerator activator, obtained by the three different methods discussed above, are presented in Table V. The formulation of these compounds is given in Table II. All the natural gum-containing compounds displayed almost the same values of the cure parameters (i.e., tc_{90} , CRI, ts_2) by the three methods, with a minimum error of <2%. Only the values of tc_{90} and CRI calculated by the tangential method for the control compound differed slightly from those of the software data. But these values, too, were within an error of 10%, which is acceptable in many rubber tests. The obtained ts_2 value from all three methods was the same, with an error of <1%. Hence, following the standard method of reporting, the software-obtained data are presented as the cure parameters of the compounds.

TABLE III
FORMULATION OF COMPOUNDS USING *MORINGA OLEIFERA* GUM AS A TACKIFIER

Ingredient, phr	SBRT0	SBRTM2.5	SBRTM5.0	SBRTM10.0	SBRTM15.0	SBRTPF5.0
SBR	100	100	100	100	100	100
<i>M. oleifera</i> gum	0.0	2.5	5.0	10.0	15.0	0.0
PF resin	0.0	0.0	0.0	0.0	0.0	5.0

TABLE IV
FORMULATION FOR RHEOLOGY STUDY OF COMPOUNDS

Ingredient, phr	SBRRM0	SBRRM2.5	SBRRM5.0	SBRRM10.0	SBRRM15.0	SBRRPF5.0
SBR	100	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
6PPD	1.5	1.5	1.5	1.5	1.5	1.5
<i>Moringa oleifera</i> gum	0.0	2.5	5.0	10.0	15.0	0.0
PF resin	0	0	0	0	0	5.0

MOLDING OF COMPOUNDS

For the tensile test, 1 mm thickness rubber sheet was molded in an electrically heated hydraulic press at 150 °C and 5 MPa for the tc_{90} obtained from oscillating disk rheometer.

For the peel test, the sheets were prepared by molding the compound at 150 °C and 5 MPa for 5 min. A 1 mm thick fabric was applied as backing on one side; the other side was backed with aluminum sheet.

TABLE V
COMPARISON OF OBTAINED CURE PROPERTIES FROM THREE DIFFERENT METHODS FOR COMPOUNDS CONTAINING STEARIC ACID AND *M. OLEIFERA* GUM AS AN ACCELERATOR ACTIVATOR

Method	SBRZS2	SBRZM2	SBRZM5	SBRZM10
tc_{90} obtained from rheometer software, min	26.87	20.76	19.32	16.48
tc_{90} calculated from rheometer data (Eq. 1), min	26.88	20.79	19.40	16.54
Error in calculated tc_{90} value from rheometer data over the software value, %	0.04	0.14	0.41	0.36
tc_{90} calculated using tangential method, min	25.18	20.83	19.45	16.62
Error in tc_{90} value calculated following tangential method over the software value, %	6.29	0.34	0.67	0.85
CRI obtained from rheometer software, min^{-1}	6.44	10.20	13.14	14.30
CRI calculated from rheometer data (Eq. 2), min^{-1}	6.31	10.17	13.16	14.25
Error in calculated CRI value from rheometer data over the software value, %	2.02	0.29	0.15	0.35
CRI calculated using tangential method, min^{-1}	7.07	10.13	13.07	14.08
Error in CRI value calculated following tangential method over the software value, %	9.78	0.69	0.53	1.54
ts_2 obtained from rheometer software, min	10.98	10.99	11.79	9.55
ts_2 calculated from rheometer data, min	11.04	10.96	11.80	9.52
Error in calculated ts_2 value from rheometer data over the software value, %	0.55	0.27	0.08	0.31
ts_2 calculated using tangential method, min	11.04	10.96	11.80	9.52
Error in ts_2 value calculated following tangential method over the software value, %	0.55	0.27	0.08	0.31

MEASUREMENT OF TENSILE PROPERTIES OF COMPOUNDS

Dumbbell-shaped ASTM Die-C tensile specimens were cut from the previously prepared rubber sheet. The tensile test was conducted at 25 °C and 500 mm/min following ASTM Standard D 412-98T in a Zwick/Roell Z010 universal testing machine (UTM) (Zwick Roell Group, Ulm, Germany). Tensile data were analyzed using testXpert II software, (Zwick Roell Group, Ulm, Germany) and the maximum stress of the stress–strain curve is reported as the tensile strength of the rubber compound. The reported values are the average of three test results.

MEASUREMENT OF PEEL STRENGTH

For 180° peel test, the samples (25.4 mm × 75 mm × 1 mm) were cut from the previously molded and conditioned rubber sheet. The Mylar sheet was removed just before the test, and two samples were placed over one another with a Mylar insert (25.4 mm × 55 mm) at one end. At 25 °C, a 2 kg load was applied to the sample for 2 min. The peel test was carried out in a Zwick/Roell Z010 UTM at 250 mm/min and 25 °C. The average of the separating forces of two samples was used for the peel strength calculation. The peel strength was calculated using Eq. 3:

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

where G_a is the peel strength (N/m), F (N) the average peel force, and w (m) is the width of the sample.

SWELLING INDEX STUDY OF COMPOUNDS

The swelling index (SI) value of the compounds was obtained following the ASTM Standard D 3616 by using toluene as the solvent. Initial specimen weight was noted, and the sample was immersed in a toluene-filled covered glass bottle. The test was continued until the weight of the swollen specimen reached the equilibrium (after 48 h). Next, the test pieces were removed from the solvent and dried in an oven until they reached a constant weight. The SI was calculated using Eq. 4:

$$SI = \frac{\text{swelling weight}}{\text{original weight}} \quad (4)$$

The crosslink density was calculated using the Flory–Rehner equation, given as Eq. 5:

$$v_e = \frac{-[\ln(1 - V_r) + V_r + \chi V_r^2]}{\left[V_l \left(V_r^{1/3} - \frac{V_r}{2} \right) \right]} \quad (5)$$

where v_e is the effective number of chains in a real network per unit volume; V_r is the volume fraction of polymer in a swollen network in equilibrium with pure solvent; and χ presents the polymer–solvent interaction parameter, with a value of 0.378.³² V_l is the molecular volume of solvent.

DMA OF COMPOUNDS CONTAINING *M. OLEIFERA* GUM AND PF RESIN

The T_g values of the compounds containing natural gum and commercial PF resin were measured by temperature sweep test in an MCR102 modular compact rheometer (Anton Paar, Graz, Austria) in torsion mode. The standard test piece was cut from the previously molded sheet of 1 mm thickness. The test was carried out within the temperature range of –70 to 0 °C, keeping the frequency constant at 1 Hz and strain at 0.1%. The temperature ramp was set at 10 °C/min. Frequency sweep was conducted in parallel plate mode, keeping a 1 mm gap between two parallel

plates of 2 cm diameter. The frequency was varied within the range of 0.01 to 160 rad/s at 90, 100, and 110 °C, respectively.

DSC OF CONTROL COMPOUND AND COMPOUNDS CONTAINING *M. OLEIFERA* GUM

Effect of *M. oleifera* gum on the T_g of the SBR was also investigated by differential scanning calorimetry (DSC) with a DSC 200 F3 Maia differential scanning calorimeter (NETZSCH-Gerätebau GmbH, Selb, Germany) in a nitrogen atmosphere within the temperature range of –65 to 0 °C at 10 °C/min heating rate. To eliminate the previous thermal history of the compound, second heating data were considered for analysis in Proteus thermal analysis software (NETZSCH-Gerätebau GmbH). The midpoint temperature of the differential scanning calorimetry (DSC thermogram) was considered as the T_g of the compound.

RHEOLOGICAL PROPERTIES OF COMPOUNDS

Smart Rheo capillary rheometer (CEAST, Pianezza, Italy) with 20:1 length-to diameter (L/D) ratio was used to study the effect of natural resins and PF on melt flow property of SBR. The extrusion temperature was varied from 90 to 110 °C with a fixed preheating time of 3 min. Effect of shear was studied by varying the shear rate in the range of 200–1500 s⁻¹.

The apparent shear stress (τ_{app}), apparent shear rate ($\dot{\gamma}_{app}$), and apparent shear viscosity (η_{app}) are the main determining parameters of the material rheology. For capillary rheometer, the parameters were calculated using the following equations:

$$\tau_{app} = d_c \Delta P / 4l_c \quad (6)$$

$$\dot{\gamma} = 32Q / \pi d_c^3 \quad (7)$$

$$\eta_{app} = \tau_{app} / \dot{\gamma}_{app} \quad (8)$$

where pressure drop across the capillary length is ΔP and length and diameter of the capillary are l_c and d_c , respectively. The material volumetric flow rate in the capillary is presented as Q .

Flow behavior index (n) gives an idea about the velocity profile of the material in the capillary. For Newtonian flow, the velocity profile is parabolic in nature. As a result of shear thinning, the velocity profile of the polymer melts deviates to non-parabolic nature. The power law model was used to calculate the flow behavior index and consistency index (k) of the compound. The equation is as follows:

$$\tau_{app} = k \dot{\gamma}_{app}^n \quad (9)$$

As per definition, $\eta_{app} = \tau_{app} / \dot{\gamma}_{app}$

Hence,

$$\eta_{app} = k \dot{\gamma}_{app}^{n-1} \quad (10)$$

The logarithmic form of the equation is as follows:

$$\log \eta_{app} = \log k + (n - 1) \log \dot{\gamma}_{app} \quad (11)$$

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

Running die swell index of the compounds was directly recorded using a microprocessor-controlled laser beam scanner working by the following equation:

$$\text{Die swell index} = d_e/d_c \quad (12)$$

where d_e and d_c represent the extrudate diameter and the capillary die diameter, respectively. Reported die swell value is the average of the die swells obtained from the software attached to the capillary rheometer.

MORPHOLOGY STUDY OF *M. OLEIFERA* GUM-CONTAINING COMPOUNDS

Dispersion of the *M. oleifera* gum in the SBR-based compounds was investigated in a Merlin scanning electron microscope (Carl Zeiss, Wetzlar, Germany) with a field emission gun attachment. Accelerating voltage of the gun was 5 kV, and the cryo-fractured surface of the compound was studied for the analysis. Before the experiment, the samples were coated with gold.

RESULTS AND DISCUSSION

EFFECT OF *M. OLEIFERA* GUM AS AN ACCELERATOR ACTIVATOR

Natural gum is a mixture of compounds containing carbohydrate as the main component. Following the previous literature, leaves, stem, and oil of *M. oleifera* gum contain long-chain fatty acids (FAs).^{33,34} Plant exudate of *M. oleifera* gum also contains a small amount of glucuronic acid and long-chain FAs such as octacosanoic acid ($C_{28}H_{56}O_2$). For rubber compounding, ZnO is normally used as an accelerator activator with stearic acid as a co-activator. Hence, we have attempted to use *M. oleifera* gum in rubber compounding as a co-activator. Compounds with different parts per hundred of rubber (phr) of *M. oleifera* gum loading were prepared (Table II) to study its activation effect compared with stearic acid. Curing properties are graphically presented in Figure 1, and the details as obtained from the rheometer software are listed in Table II. Cure rate improved with an increase in the gum loading. Enhanced M_H also suggested better state of cure compared with the control compound containing stearic acid. Decreasing curing time can increase the production efficiency of the compound. Increase of curing rate suggested the higher reactivity of the complex with octacosanoic acid present in the gum compared with the stearic acid-containing complex. The reaction mechanism is presented in Scheme 1.^{35,36} Normally, ZnO forms a reactive complex by reaction with the accelerator. Further reaction of sulfur with the active complex formed a zinc per-thio sulfurating agent that functioned as an actual accelerator for the curing of rubber compounds. Usually, ZnO co-activator is the stearic acid, because it increases the Zn^{2+} accessibility of the accelerator by forming active zinc stearate complex.³⁵ Heideman et al. proposed that the reactivity of the complex increases with the decrease of its stability.³⁷ ZnO complex with other longer chain FAs will be less stable due to the lower acidity of the longer chain FAs and less stability of the polar ionic bond with Zn ion. Low bond strength and increase of steric hindrance escalated the reactivity of the complex. Hence, the presence of octacosanoic ($C_{28}H_{56}O_2$) acid made the *M. oleifera* gum a better co-activator than stearic acid. The long chain of the octacosanoic acid also improved the compatibility of the activator complex with the rubber matrix. The crosslink density of the compound increased with the increase of *M. oleifera* gum loading in the compound. At 10 phr loading, *M. oleifera* gum softened the compound, leading to a decrease of M_H during curing. As a result, the tensile strength and modulus decreased due to the softening effect of the *M. oleifera* gum. The tensile properties are presented in Table II, and the stress-strain graph is shown in Figure 2. The retention of the tensile strength of the compound was 71% even at 10 phr natural gum loading. Improved cure rate and cure time were obtained at 2 phr gum loading; hence, this gum can be used as an accelerator activator in rubber compounding. Bahera gum was also reported as an accelerator activator for vulcanization of NR and BIMS compounds.¹¹

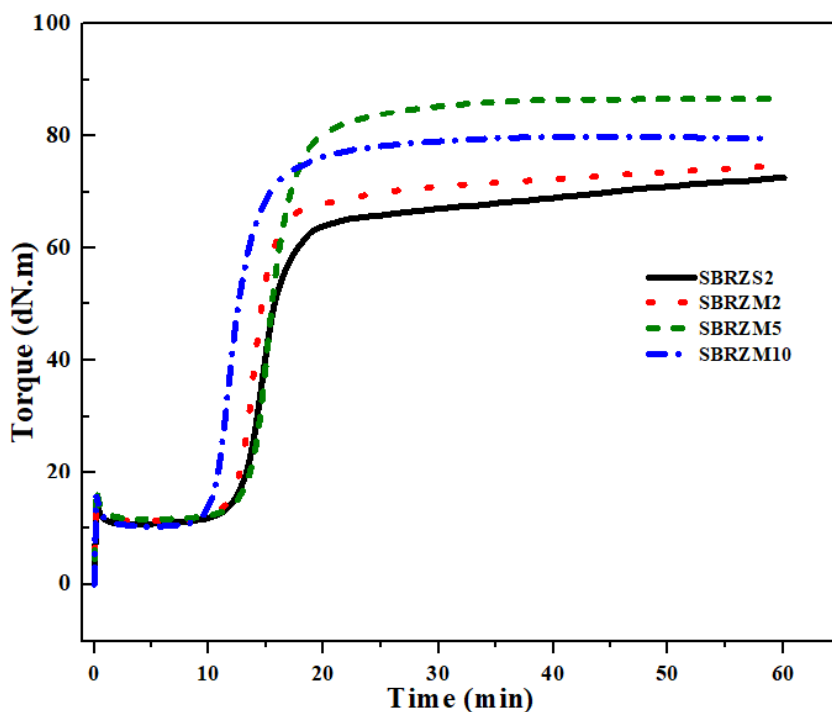
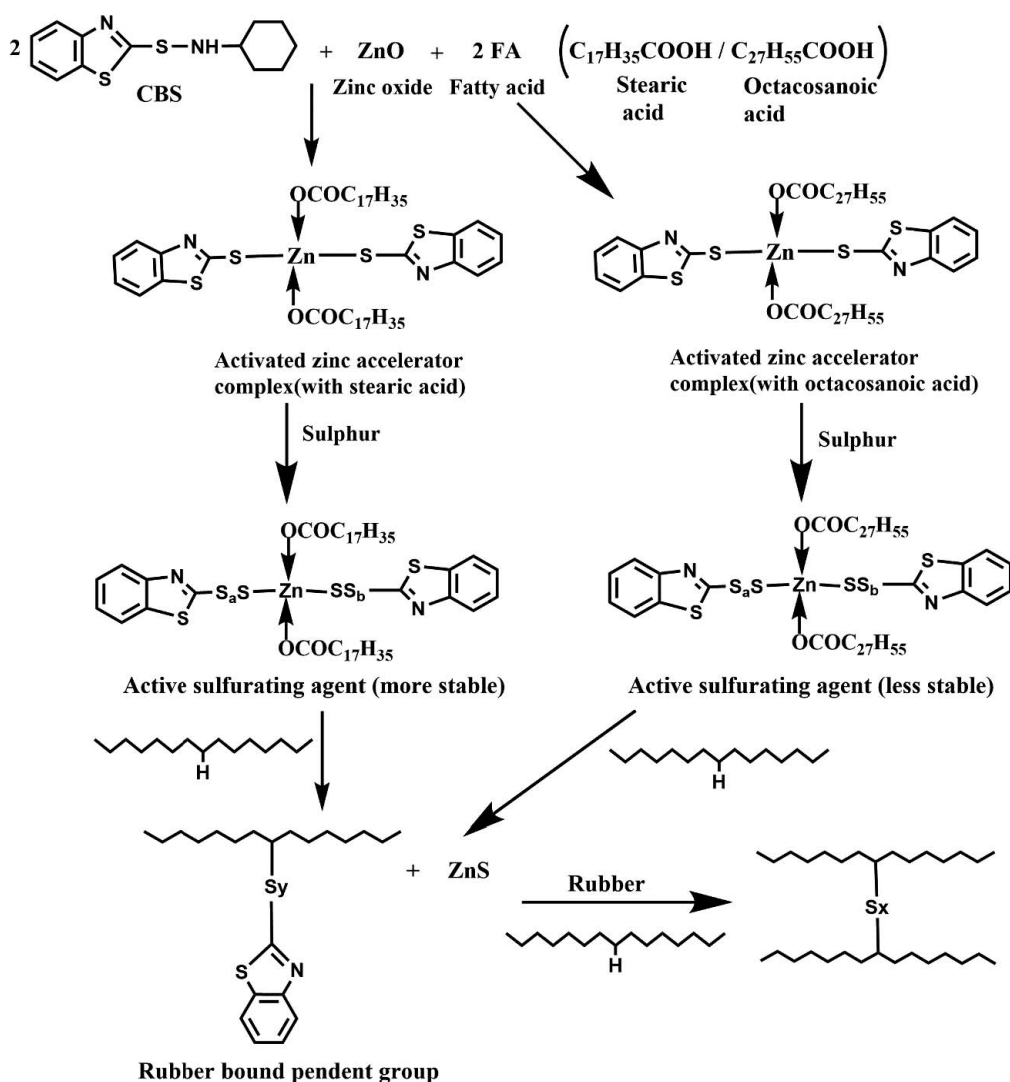


FIG. 1. — Curing behavior comparison of the compounds containing natural *Moringa oleifera* gum with the control compound.

EFFECT OF *M. OLEIFERA* GUM AS A TACKIFIER

The tackifying effect of the *M. oleifera* gum was studied by mixing the gum with SBR following the formulation presented in Table III. To avoid the interference of the other ingredients, only gum was mixed with the rubber. Effect on peel strength before aging and after aging (at 30 °C for 2 months) is presented in Figure 3a and Figure 3b, respectively. The peel strength of all the compounds before aging was higher than for the control compound. The results showed that the peel strength gradually increased with the addition of *M. oleifera* gum up to 5 phr and then decreased with the further addition of natural gum in the compound. Main controlling factors for the tack strength are molecular contact of the surface polymers, diffusion of the polymer chains at the interface, and cohesive strength. As per literature, natural gums increase the tack strength by reducing the viscosity of the compound.¹¹ The low molecular weight fraction of natural gum helps to flow by reducing the viscosity and interfacial diffusion of the chains improved.⁶ The same phenomenon was observed in our present work. The tack strength improved due to lowering of viscosity with the increase of *M. oleifera* gum loading, as discussed below. Maximum tack strength was observed at 5 phr natural gum loading. Decrease of tack strength at 10 and 15 phr loading may be ascribed to the fall in tensile strength, as shown for the SBR–*M. oleifera* gum compounds. Tack strength of the compounds up to 10 phr gum loading was even higher than that of the commercial PF resin-containing compound (Figure 3a). The hydrophilicity of natural gum made it easily wetting and tacky in nature. On the other hand, the presence of terpenoids improved the peel strength of the *M. oleifera* gum–SBR compounds just like natural rosin. Hence, the peel strength of the natural gum-containing material was better than that of the commercial resin–rubber compound. During



SCHEME 1. — Plausible reaction mechanism for sulfur crosslinking of rubber in presence of *Moringa oleifera* gum as an accelerator activator.

long-term aging of the compounds, *M. oleifera* gum at 5 phr loading provides equivalent tack strength to the phenolic resin, possibly due to easy migration of *M. oleifera* gum. Guhathakurta et al. also reported the surface migration of natural gum.¹¹

STUDY OF EFFECT OF *M. OLEIFERA* GUM ON T_g OF COMPOUNDS BY DSC AND DMA

The T_g of a rubber compound is an important property to decide the application of the material. Herein, natural gum resin was used as an additive with the doses of 2.5, 5, 10, and 15 phr only (Table IV). The T_g of the *M. oleifera* gum and SBR obtained from DSC was 18 and -49.6°C , respectively. The calculated T_g value for 2.5, 5, 10, and 15 phr gum-loaded SBR by using the Fox equation was -48.3 , -47.0 , -44.3 , and -41.5°C , respectively. For the compounds containing 5 and 10 phr *M.*

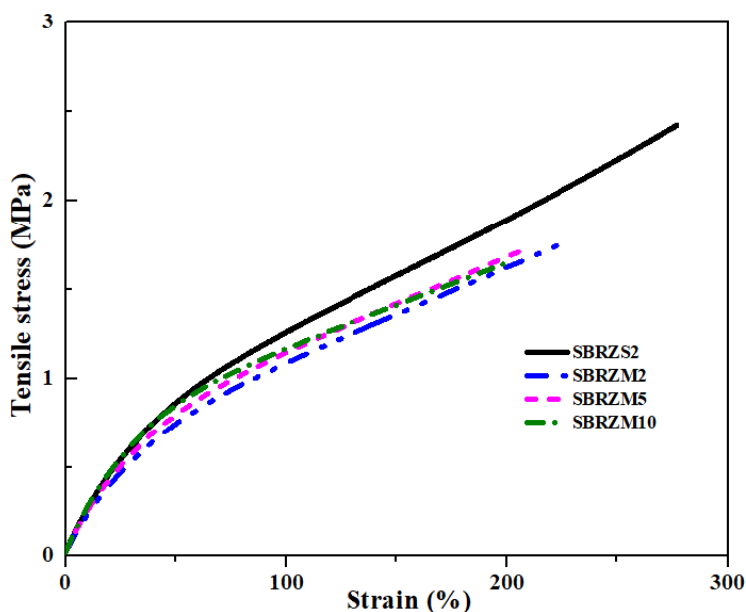


FIG. 2. — Stress–strain curve of both the compounds containing stearic acid and *Moringa oleifera* gum at different loadings.

oleifera gum, the experimentally obtained value of T_g from DSC was -49.9 and -50.6 °C, respectively (Figure 4a). This means that instead of shifting of T_g of SBR toward the higher temperature side as per the Fox equation, the glass–rubber transition temperature has gone toward the lower temperature, indicating plasticization of the rubber and an increased free volume of the SBR by the gum. To further confirm this relationship, dynamic mechanical analysis (DMA) was done. The results are presented in Figure 4b. It is known that the absolute value of the T_g obtained from DSC and DMA always differs from each other. The obtained T_g of the pristine SBR and that of the natural gum containing SBR compound from the DMA study was -37 and -39 °C, respectively. The T_g of the resin could not be obtained by the same method because of its powder nature having

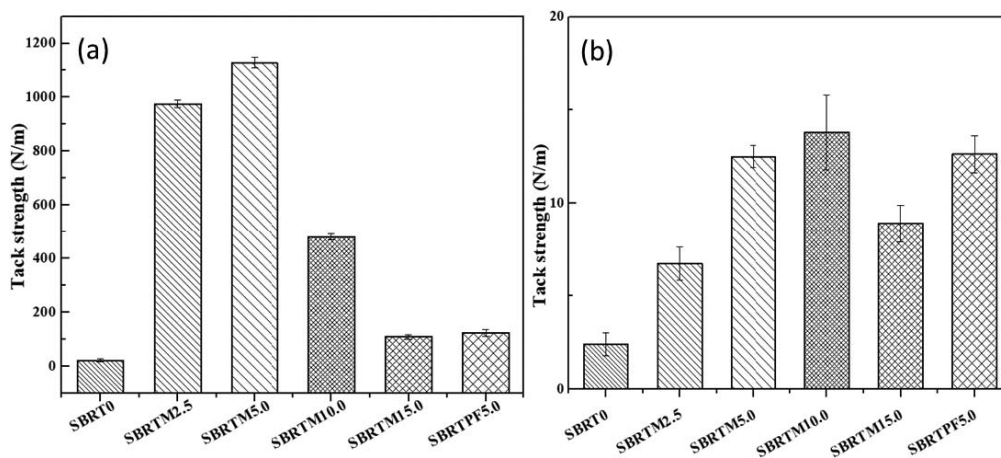


FIG. 3. — Comparison of peel tack properties of *Moringa oleifera* gum–containing compounds with pristine SBR and commercial PF resin–containing compounds (a) before aging and (b) after aging.

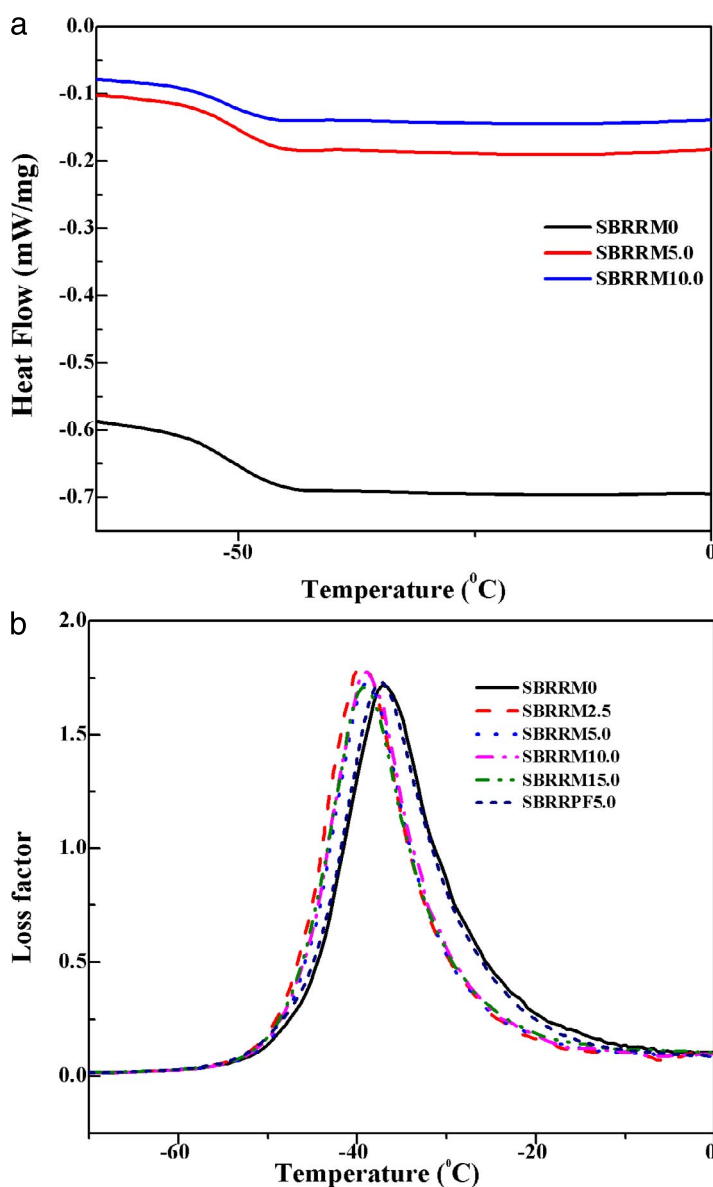


FIG. 4. — (a) Comparison of DSC of 5 and 10 phr gum-containing compound with control compound. (b) Dynamic mechanical analysis of the control compound, *Moringa oleifera* gum, and commercial PF resin containing compounds.

partial solubility in hot water only. Interestingly, the trend of the result was in good agreement with the T_g obtained from DSC (Figure 4a). In both the methods, the T_g was decreased with the addition of natural gum in the rubber. Hence, the natural gum-containing compounds do not follow the Fox equation. This is not the first time that such observation has been made. As per previous literature, plant resins such as rosin, chitosan, and bahera gum and extracts of *Diospyros peregrina* fruit can act as a plasticizer for polymers.^{11,38,39} Guhathakurta et al. reported the plasticization effect of bahera gum on NR-based compound.¹¹ Use of rosin and modified rosin plasticizer is very common for XSBR and other plastic materials such as polyvinyl chloride.^{38,40} As per literature, the T_g of

natural rubber ($-57\text{ }^{\circ}\text{C}$) showed slight low temperature shift of $\sim 3\text{ }^{\circ}\text{C}$ when *D. peregrina* fruit extract was added in the compound ($-60\text{ }^{\circ}\text{C}$).³⁹ The result of the present work shows a similar trend. Class and Chu reported that most of the discrepancies of the calculated T_g from the Fox equation and obtained T_g values from DMA were observed at low resin concentration of the rubber resin blend.⁴¹ Natural gum is an amorphous hemicellulose material formed by short chains of sugar units. The low molecular weight fraction of *M. oleifera* gum acted as a plasticizer for the SBR compounds. By this process, the components become technologically compatible^{42,43} and the T_g shifted to the low temperature. The higher tack of the compounds compared with the pristine rubber also supports the softening effect of the natural resin to the rubber.

EFFECT OF *M. OLEIFERA* GUM AS A PROCESSING AID FOR SBR-BASED COMPOUNDS

Frequency Sweep of Compounds. — The compounds were prepared by following the formulation given in Table IV. Commercial PF resin at 5 phr loading was also mixed in the same formulation for the comparison study. Storage modulus and the loss factor of the compounds were studied at 90, 100, and 110 $^{\circ}\text{C}$. The graphical presentation of the results at 100 $^{\circ}\text{C}$ is given in Figure 5a, b. At all the temperatures, loss factor increased and storage modulus decreased with the addition of gum to the compound. Here, the gum acted like a softener or processing aid for the rubber due to its lower molecular weight than the rubber and increased the flowability of the material by increasing the hydrodynamic volume of the polymer chain.

With the increase of angular frequency, the complex viscosity of all the compounds decreased. At higher frequency, the viscosity drop was more comparable with the control. The results are presented in Figure 5c. The compound with 5 phr natural gum content showed less viscosity than the compound with commercial PF resin. Gum materials are polysaccharides with crosslinked or hydrogen-bonded structure that can break more easily at high angular frequency and reduction of complex viscosity was more prominent.

Capillary Rheology of Compounds. — Impact of the natural *M. oleifera* gum on melt viscosity of the SBR compounds was studied in a capillary rheometer by varying the shear rate at different temperatures, and the formulation of compounds is presented in Table IV. The gum loading was varied from 2.5 to 15 phr. Commercial PF resin was also mixed at 5 phr loading in the same formulation. All the compounds including pristine SBR and the compound containing commercial PF resin showed pseudoplastic behavior, and the apparent viscosity decreased with the increase of shear rate (Figure 6). There are two probable reasons for the pseudoplastic behavior of the material. Under the shear force, highly entangled rubber chains orient in a particular direction and viscosity of the compound reduces. At the very high shear rate, materials show nearly Newtonian behavior, as all the chains are almost oriented. On the other side, the presence of highly solvated materials and their shearing effect can reduce the viscosity. With the increase of natural gum loading in the compound, hydrodynamic volume increased, leading to the reduction of viscosity. Higher shearing temperature softened the gum and increased the flowable fraction of the compound. Comparative shear viscosity of the compounds containing the gum and pristine rubber at 100 $^{\circ}\text{C}$ presented in Figure 6 indicates the above-mentioned trend.

Change of flow behavior of the material with the addition of *M. oleifera* gum and increase of temperature were studied by using power law equation (Eq. 10). For shear thinning materials, n should be < 1 ; in all the cases, the values presented in Table VI were < 1 . Decrease of n value with increase of gum content suggested the shear thinning of the natural gum-containing compounds.⁴⁴ The k value represents the viscosity at the unit shearing rate, and k values for all the compounds decreased with the increase of temperature from 100 to 110 $^{\circ}\text{C}$. When the temperature increased from 90 to 100 $^{\circ}\text{C}$, the flow index value of the compound also decreased and became almost constant at 110 $^{\circ}\text{C}$. At 110 $^{\circ}\text{C}$, k value was higher for the PF resin-containing compound. Hence, the

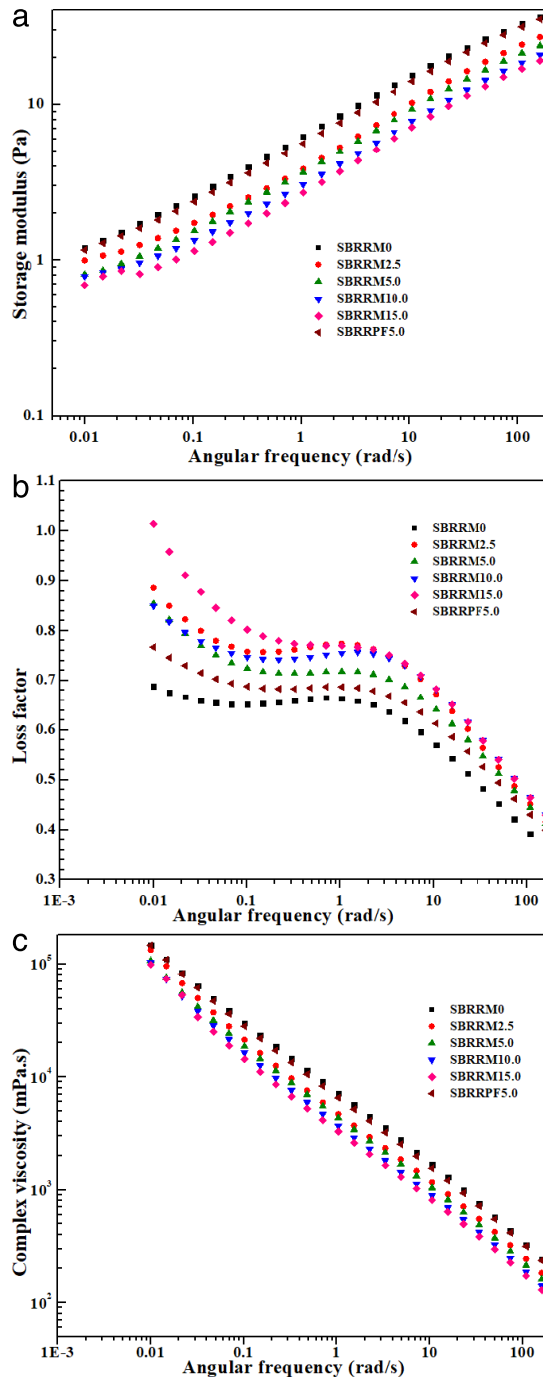


FIG. 5. — (a) Effect of the *Moringa oleifera* gum and commercial PF resin on storage modulus of the compounds at 100 °C. (b) Effect of different phr of *M. oleifera* gum and commercial PF resin on loss factor of the SBR-based compounds at 100 °C. (c) Effect of *M. oleifera* gum loading and commercial PF resin on complex viscosity of the compounds at 100 °C.

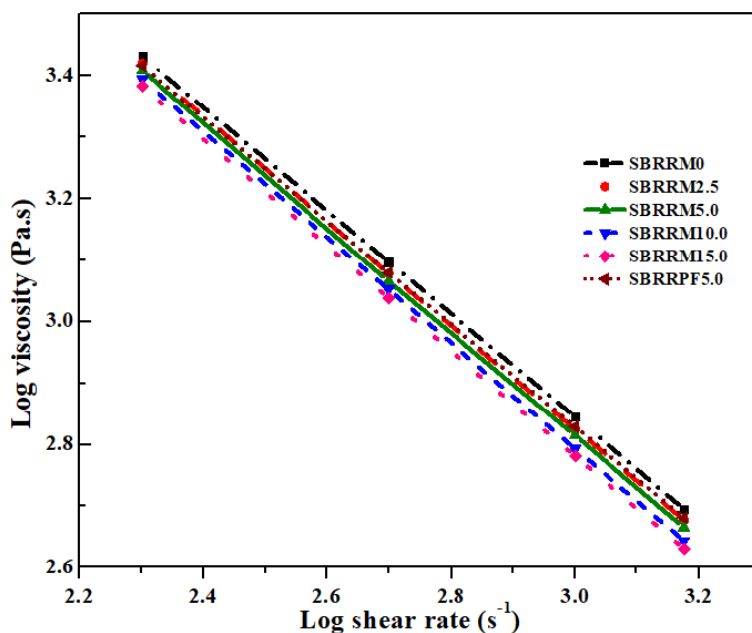


FIG. 6. — Effect of *Moringa oleifera* gum and commercial PF resin loading on shear viscosity of the SBR-based compounds at 100 °C.

natural waste gum imparted better flowability and processability to the compounds. Shear stress of the compounds also decreased with the addition of gum to the compound; the graphical representation of the same is given in Figure 7. This also confirmed the previous statement.

Die swell is one of the most important rheological properties for the rubber compound extrusion. As per literature, the perfectly smooth surface of the extrudate cannot be obtained for the unfilled gum rubbers.^{45,46} Normally, the addition of filler to the rubber solves the problem. For unfilled rubber extrudates, die swell changes with the change of temperature, L/D ratio of the capillary, shear rate, and presence of processing aid in the compound. The running die swell values of the SBR–*M. oleifera* gum compounds with different amounts of gum content was measured at 100 °C by using a die of 20:1 L/D ratio. The average values of the running die swell are graphically

TABLE VI
n AND k VALUES FOR SBR-*Moringa oleifera* GUM AND SBR-PF RESIN COMPOUNDS

Sample	Temperature, °C					
	90		100		110	
	n	$k \times 10^{-5}$	n	$k \times 10^{-5}$	n	$k \times 10^{-5}$
SBRRM0	0.20	2.19	0.16	2.34	0.16	2.09
SBRRM2.5	0.19	2.24	0.15	2.34	0.15	2.19
SBRRM5.0	0.19	2.45	0.15	2.29	0.16	2.00
SBRRM10.0	0.18	2.40	0.15	2.34	0.15	2.04
SBRRM15.0	0.17	2.29	0.14	2.26	0.15	2.00
SBRRPF5.0	0.18	2.29	0.16	2.24	0.14	2.45

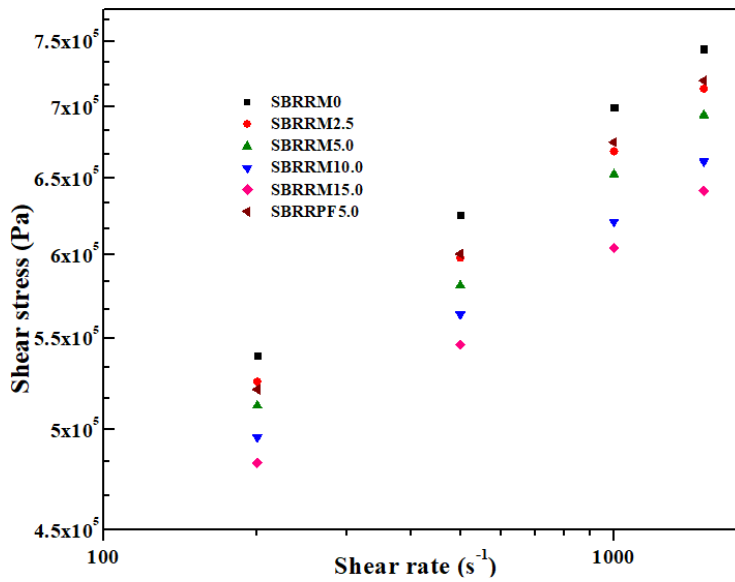


FIG. 7. — Effect of *Moringa oleifera* gum and commercial PF resin on shear stress of the compounds at 100 °C.

presented in Figure 8. With the increase of the shear rate, the die swell of the control compound and the compound with 2.5 phr gum also increased. More recoverable elastic energy gets stored in the compound at a high shear rate, and the die swell increased as the compound starts to release the energy after extrusion. At the low apparent shear rate, the recoverable stored energy was less and the obtained die swell was also low compared with the higher shear rate. Interestingly, the die swell values of all the natural gum-containing materials were lower than the pristine compound. The die swell was also reduced on shearing over the range of study. With the increase of the *M. oleifera* gum

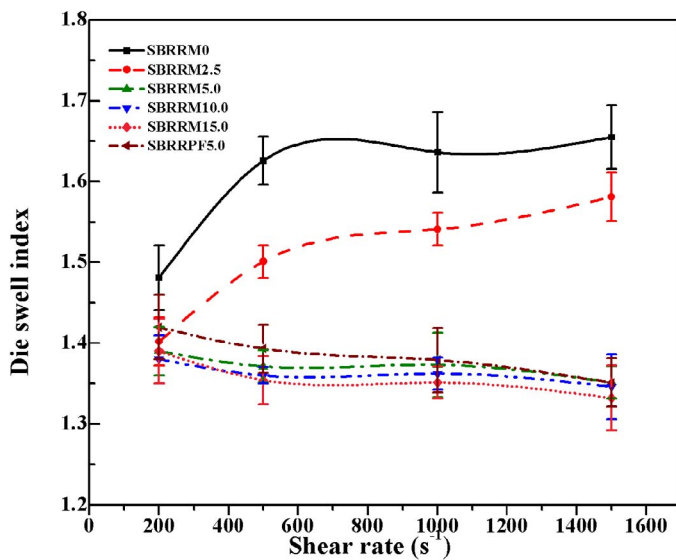


FIG. 8. — Effect of the commercial PF resin and *Moringa oleifera* gum on die swell of compounds at 100 °C.

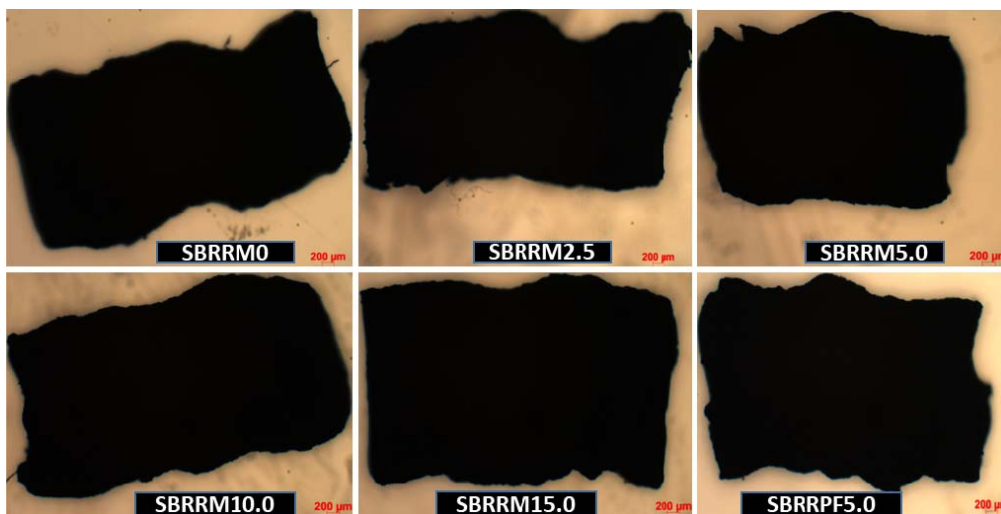


FIG. 9. — Optical microscopic images of the control compound, SBR-PF, and SBR-gum compound extrudates at 500 s^{-1} shear rate and $100 \text{ }^\circ\text{C}$.

loading, the die swell decreased and the values were even lower than the die swell of the commercial PF resin-containing compound. The images of the extrudate products after the equilibrium were recorded using an optical microscope at $100\times$ magnification (Figure 9). The surface of the *M. oleifera* gum-containing SBR compounds after equilibrium die swell experiments was relatively smoother than the pristine rubber (Figure 9). The appearance of the extrudates was also quite similar to that of the previously reported images of the unfilled rubber extrudates.^{45–47} Here, natural gum acted like a plasticizer and reduced the elastic energy storage by increasing flowability of the material. Hence, *M. oleifera* gum can be used as processing aid in rubber compounds.

MORPHOLOGY STUDY OF COMPOUNDS BY USING SEM

Dispersion of the *M. oleifera* gum in SBR was studied by scanning electron microscopy (SEM) analysis. The results are presented in Figure 10. For SBRTM2.5, SBRTM5.0, SBRTM10.0, and SBRTM15.0, the particles size was $150 \pm 33 \text{ nm}$, $390 \pm 44 \text{ nm}$, $436 \pm 10 \text{ nm}$, and $1.19 \pm 12 \mu\text{m}$, respectively. It was previously reported that the particle size of the resin having excellent tackifying property and acting as a processing aid for a rubber compound normally ranges from nanometers to a few micrometers.⁴⁸ The SEM results as presented in Figure 10 also support the previous literature. For all the compounds, the particle size of the dispersed natural gum was $<0.5 \mu\text{m}$, except the compound containing 15 phr *M. oleifera* gum (particle size of $1.19 \pm 12 \mu\text{m}$). With an increase of the resin amount, the particle size of any resin material increases due to the agglomeration of the resin particles. Hence, it was assumed that agglomeration of *M. oleifera* gum at 15 phr loading might be due to the higher concentration and immiscibility (thermodynamically). Normally, 5–7 phr resin is used as a processing aid in commercial tire tread formulation. The particle size of *M. oleifera* gum in the SBR-based compound was $436 \pm 10 \text{ nm}$ even at 10 phr loading, which serves successfully the purpose of using the resin as a processing aid in the rubber compound. Interestingly, Kumar et al. reported a particle size of 2–7 μm for compatible BIMS rubber–

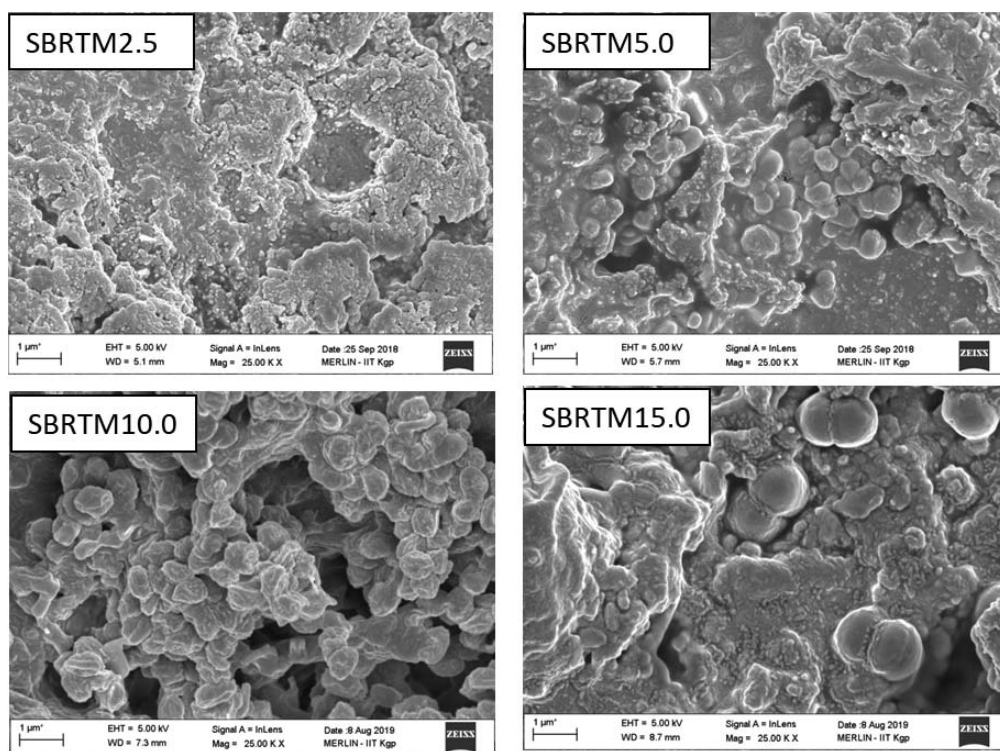


FIG. 10. — Morphology of the SBR–*Moringa oleifera* gum compounds.

hydrocarbon resin mixture.⁴⁸ The present observations are in line with the reported value in the literature.

CONCLUSIONS

For the first time, natural waste of the drumstick tree, *Moringa oleifera*, was used as an MFA in rubber compounding. It performed well as an accelerator activator and could replace stearic acid at the same phr in the rubber compound, with reduction of cure time. Tensile strength reduced marginally compared with that of the control compound. The 180° peel strength of all the compounds containing the gum was much higher than that of the pristine SBR and the commercial PF resin-containing compound. DMA and capillary rheology studies revealed the enhanced flow property and processability of the *M. oleifera* gum-containing compound compared with the pristine compound. Die swell was also less than that of the control compound. Hence, this work presents a new and economic natural MFA, *M. oleifera*, for the rubber industry.

ACKNOWLEDGEMENTS

We thank the Department of Heavy Industry, New Delhi; the Ministry of Human Resource Development, New Delhi, and the Indian Rubber Manufacturers Research Association, Mumbai, for funding the project to Prof. Anil K. Bhowmick. We also thank IIT Kharagpur for providing the research facilities.

REFERENCES

- ¹P. Sarkar and A. K. Bhowmick, *J. Appl. Polym. Sci.* **135**, 45701 (2018).
- ²Z. F. M. Aris, R. M. Bouldin, M. G. H. Pelletier, P. Gaines, B. Budhlall, and R. Nagarajan, *Carbohydr. Polym.* **155**, 432 (2017).
- ³G. W. Huber, S. Iborra, and A. Corma, *Chem. Rev.* **106**, 4044 (2006).
- ⁴P. Sahu and A. K. Bhowmick, *Ind. Eng. Chem. Res.* **58**, 20946 (2019).
- ⁵P. Sahu, P. Sarkar, and A. K. Bhowmick, *ACS Sustainable Chem. Eng.* **5**, 7659 (2017).
- ⁶R. Koley, R. Kasilingam, S. Sahoo, S. Chattopadhyay, and A. K. Bhowmick, *Ind. Eng. Chem. Res.* **58**, 18519 (2019).
- ⁷A. K. Naskar, S. K. De, P. K. Pramanik, R. Mukhopadhyay, and A. K. Bhowmick, *RUBBER CHEM. TECHNOL.* **73**, 902 (2000).
- ⁸P. Nevatia, T. S. Banerjee, B. Dutta, A. Jha, A. K. Naskar, and A. K. Bhowmick, *J. Appl. Polym. Sci.* **83**, 2035 (2002).
- ⁹S. Ravichandran, R. M. Bouldin, J. Kumar, and R. Nagarajan, *J. Cleaner Prod.* **19**, 454 (2011).
- ¹⁰S. K. Bhattacharyya, B. S. Parmar, R. Mukhopadhyay, and A. Bandyopadhyay, *RUBBER CHEM. TECHNOL.* **90**, 429 (2017).
- ¹¹S. Guhathakurta, S. Anandhan, N. K. Singha, R. N. Chattopadhyay, and A. K. Bhowmick, *J. Appl. Polym. Sci.* **102**, 4897 (2006).
- ¹²S. K. Bhattacharyya, B. S. Parmar, R. Mukhopadhyay, and A. Bandyopadhyay, *RUBBER CHEM. TECHNOL.* **88**, 421 (2015).
- ¹³C. Hepburn, M. H. Halim, and M. S. Madhi, *Kautschuk Gummi Kunststoffe* **43**, 794 (1990).
- ¹⁴C. Hepburn and M. S. Mahdi, *Plast. Rubber Process. Appl.* **6**, 257 (1986).
- ¹⁵S. Saha, N. K. Singha, R. N. Chattopadhyay, A. Ganguly, and A. K. Bhowmick, *J. Adhes. Sci. Technol.* **19**, 1349 (2005).
- ¹⁶G. Heideman, J. W. M. Noordermeer, and R. N. Datta, *RUBBER CHEM. TECHNOL.* **79**, 561 (2006).
- ¹⁷H. Ismail, P. K. Freakley, and E. Sheng, *Eur. Polym. J.* **31**, 1049 (1995).
- ¹⁸H. Ismail, C. L. Ho, and C. C. Lim, *Polym. Plast. Technol. Eng.* **40**, 505 (2001).
- ¹⁹T. K. Khanra, B. Adhikari, and S. Maiti, *RUBBER CHEM. TECHNOL.* **66**, 30 (1993).
- ²⁰E. Sheng, L. Sutherland, R. H. Bradley, and P. K. Freakley, *Eur. Polym. J.* **32**, 35 (1996).
- ²¹A. P. Kuriakose and G. Rajendran, *J. Mater. Sci.* **30**, 2257 (1995).
- ²²V. Nandan, R. Joseph, and D. J. Francis, *J. Elast. Plast.* **28**, 326 (1996).
- ²³Z. S. Petrović, M. Ionescu, J. Milić, and J. R. Halladay, *RUBBER CHEM. TECHNOL.* **86**, 233, 2013.
- ²⁴M. Daba, *J. Earth Sci. Clim. Change* **7**, 366 (2016).
- ²⁵S. J. Stohs and M. J. Hartman, *Phytother Res.* **29**, 796 (2015).
- ²⁶F. William, S. Lakshminarayanan, and H. Chegu, *Int. J. Food Sci. Nutr.* **44**, 191 (1993).
- ²⁷K. Mehta, R. Balaraman, A. H. Amin, P. A. Bafna, and O. D. Gulati, *J. Ethnopharmacol.* **86**, 191 (2003).
- ²⁸S. G. Mahajan and A. A. Mehta, *J. Ethnopharmacol.* **130**, 183 (2010).
- ²⁹D. S. Panda, N. S. K. Choudhury, M. Yedukondalu, S. Si, and R. Gupta, *Indian J. Pharm. Sci.* **70**, 614 (2008).
- ³⁰K. Chaudhary and S. Chaurasia, *Eur. J. Pharm. Med. Res.* **4**, 646 (2017).
- ³¹S. K. Chakraborty and S. K. De, *Polymer* **24**, 1055 (1983).
- ³²A. I. Dzulkiifi, C. M. S. Said, C. C. Han, and A. F. Mohd, *Adv. Mat. Res.* **1134**, 75 (2015).
- ³³A. Pandey, R. D. Pandey, P. Tripathi, P. P. Gupta, J. Haider, S. Bhatt, and A. V. Singh, *Med Aromat. Plants* **1**, 1 (2012).
- ³⁴A. Leone, A. Spada, A. Battezzati, A. Schiraldi, J. Aristil, and S. Bertoli, *Int. J. Mol. Sci.* **17**, 2141 (2016).
- ³⁵F. Grasland, L. Chazeau, J. M. Chenal, and R. Schach, *Polym. Degrad. Stab.* **161**, 74 (2019).
- ³⁶A. V. Chapman, and M. Porter, "Sulphur Vulcanization Chemistry" in *Natural Rubber Science and Technology*, A. D. Roberts, Ed., Oxford University Press, Oxford, 1988.
- ³⁷G. Heideman, J. W. M. Noordermeer, and R. N. Datta, *RUBBER CHEM. TECHNOL.* **78**, 245 (2005).
- ³⁸X. Niu, Y. Liu, Y. Song, J. Han, and H. Pan, *Carbohydr. Polym.* **183**, 102 (2018).
- ³⁹K. M. Z. Hossain, N. Sharif, N. C. Dafader, M. E. Haque, and A. M. S. Chowdhury, *ISRN Polym. Sci.* **621352**, 1 (2013).

- ⁴⁰M. P. Arrieta, M. D. Samper, M. Jiménez-López, M. Aldas, and J. López, *Ind. Crops Prod.* **99**, 196 (2017).
- ⁴¹J. B. Class and S. G. Chu, *Appl. Polym. Sci.* **30**, 825 (1985).
- ⁴²A. Y. Coran and R. Patel, *RUBBER CHEM. TECHNOL.* **56**, 1045 (1983).
- ⁴³A. K. Bhowmick and H. L. Stephens, *Handbook of Elastomers*, 2nd ed., CRC Press, Taylor & Francis Group, Boca Raton, FL, 2000.
- ⁴⁴N. Sombatsompop, M. C. Tan, and A. K. Wood, *Polym. Eng. Sci.* **37**, 270 (1997).
- ⁴⁵S. C. Einhorn and S. B. Turetzky, *J. Appl. Polym. Sci.* **8**, 1257 (1963).
- ⁴⁶M. A. Kader, A. K. Bhattacharyya, and A. K. Bhowmick, *Polym. Polym. Compos.* **9**, 263 (2001).
- ⁴⁷W. Chookeaw, Y. Sukniyom, S. Patcharaphun, and N. Sombatsompop, *Adv. Mat. Res.* **747**, 627 (2013).
- ⁴⁸K. D. Kumar, A. K. Bhowmick, and A. H. Tsou, *J. Adhes.* **84**, 764 (2008).

[Received January 2020, Revised September 2020]