Factice from Oil of *Putranjiva roxburghii*

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ABSTRACT: Preparation and characterization of factice by vulcanization of oil extracted from *Putranjiva roxburghii*, a fairly abundant plant of the tropical Indian subcontinent, is presented. This information serves as a processing aid for substituting commercially available factices. Mechanical and thermal studies of this new type of factice, blended with rubber, showed higher thermal stability and improved processing characteristics during extrusion and calendering operations compared to rubber without factice.

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New opportunities exist for quite a few unexplored vegetable-based products of commercial value in the Indian subcontinent. Factice, one of the oil-based products, is made by heating nonedible oil with sulfur. This rubber supplement (1) is widely used for mastication during production of tubing, automobile parts, window seals and cable coverings. Other uses of factice include preparation of some pressure-sensitive adhesives. *Putranjiva roxburghii* (Euphorbiacae) is found widely distributed in the eastern region of India and scattered all over the tropical Indian subcontinent. This species has not attracted much attention. Small bead-like seeds yield (by solvent extraction) an average of 43% oil, which has an iodine value of 85 and a saponification value of 183.2 mg KOH/g. Gas–liquid chromatography (GLC) indicated the presence of palmitic, stearic, oleic, linoleic, and arachidic acids. Compositional data are given in Table 1 along with soybean and sunflower oil. About 93% of total fatty acids is composed of C_{18}, and 85% is unsaturated. Other than for soapmaking, the oil could be used for the production of factice. This was attempted by vulcanization of the oil with sulfur, and the results are presented below.

TABLE 1
Typical Compositions of Long-Chain Fatty Acids in Soybean[a], Sunflower, and *Putranjiva roxburghii*

	Soybean	Sunflower	*Putranjiva roxburghii*
$C_{16:0}$	6.5	1.5	6
$C_{18:0}$	4.2	7.0	5.6
$C_{18:1}$	32	26.7	57.6
$C_{18:2}$	49.3	64.8	29.8
$C_{18:3}$	22	—	—
$C_{20:0}$	0.8	—	1.0

[a]Values are obtained from *Lubrication and Allied Oils* by Elliot A. Evans, Chapman and Hall Ltd., 1990.

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EXPERIMENTAL PROCEDURES

To reduce solvent costs, oil was pressed out initially to the extent of 25%. The remainder of the oil was recovered from the oilcake by Soxhlet extraction in 10–12 cycles with hexane. After recovery of the solvent, the oil was preserved in an atmosphere of nitrogen in sealed bottles. The overall total average yield of oil was 43%. In a prototype experiment, 7.0 g oil and 2.0 g powdered sulfur were mixed in a hard-glass sealed vessel and stirred mechanically, heated on an oil bath to 150°C for 2.5 h or until a brown gel was formed, which solidified on cooling but did not melt on warming and had rubber-like physical properties. The physical properties of the factice (2) were determined, including acetone extract (31.4%), free sulfur (2.8%), ash (0.04%), and durometer hardness (24%). All experiments were carried out in the presence of nitrogen or in an inert atmosphere to prevent aerial oxidation of the oil. The vulcanized sample was crushed to powder by rubbing with a glass rod. The product was then washed thoroughly with carbon disulfide (CS_2) (E. Merck, Bombay, India) to remove excess unreacted sulfur. The sample was dried at room temperature. A weighed amount of dried sample was then allowed to swell completely in *p*-xylene at room temperature for two days. The volume of the swollen sample, V_2, was determined. The swollen sample was lightly blotted with a filter paper to remove any adhering solvent and weighed in a stoppered weighing bottle. The total of cross-links was then calculated from the Florey Rehner Equation (3):

$$M_c = -\rho\ V_1 V_2^{1/3}/[KV^2L_2) + \ln(1 - V_2) + V_2] \qquad [1]$$

which takes the approximate form

$$M_c = -2\rho V_1/V_2^{5/3}(1 - K) \qquad [2]$$

where higher terms in the expression of expansion of $(1 - V_2)$ are neglected. In this equation, V_1 represents the molar volume of the solvent, ρ is the density of the polymer, M_c is the molecular weight of the chain between crosslinks, V_2 is the

TABLE 2
Mass (in grams) vs. Density (volume) Chart[a]

Hours	0	1	2	4	6	23
m_1	0.202	0.709	0.741	0.763	0.777	0.844
m_2	1.178	1.685	1.717	1.739	1.753	1.820
m_3	—	0.923	0.941	0.958	0.970	1.020
V_{cc}[b]	0.239	0.8798	0.897	0.902	0.9044	0.924

[a]The vulcanized sample, after crushing to powder by glass rod, was washed with carbon disulfide and evaporated to dryness. Soaked in alcohol–benzene (1:2) mixture for 6 days at room temperature (~35°C), changing the mixture every day. Sample was dried at room temperature. The weighed sample (m_1) was then allowed to swell completely in *p*-xylene in a finely calibrated small cylinder. The sample (m_2) was wrapped in a weighed filter paper and hung into *p*-xylene (m_3) by a weighed string from the open arm of a balance. Changes in weight and density (hence volume) were measured at time intervals.
[b]$V = (m_2 - m_3)/0.866$ where density of *p*-xylene = 0.866 (35°C); hence, density of factice at 35°C: $m_1/V_o = 0.202/0.239 = 0.845$.

volume fraction of the polymer in the swollen gel, and K is the interaction parameter, which has been shown by Sheley and Dyckes (4) to remain constant at 0.437. The reciprocal M_c gives the number of effective network chains, which when halved gives the number of crosslinks. The molecular weight of factice was determined by boiling point elevation in carbon tetrachloride with a trace of diethanolamine (5). For swelling, the change in mass and density (volume) was measured at certain intervals, as shown in Table 2 and its footnote. The change in volume and weight with time was determined.

Factice was mixed with natural rubber at ten parts per hundred parts of rubber (phr) in a two-roll mixing mill (size 10″ × 12″) by the following recipe: natural rubber, 100 parts; zinc oxide, 5 parts; stearic acid, 2.5 parts; factice, 10 parts; N-cyclohexyl-2-benzothizyl sulphenamide (CBS), 0.8 parts; sulfur, 2.0 parts by weight were mixed. After maturation of the compound, cure time was determined by a Monsanto (Akron, OH) Rheometer Model R-100S. Next, molding was performed in a molding press at 150°C. Tensile strength and elongation at break of the samples were determined at room temperature in a Zwick (Ulm, Germany) UTM-1445 at a testing speed of 500 mm/min according to ASTMD method 412-80 with dumbbell-shaped specimens (6). Thermogravimetric studies were carried out in a Stanton Redcroft (Surrey, United Kingdom) STA 625 thermal analyzer at a heating rate of 20°C/min. Differential scanning calorimetric studies of rubber compound containing factice were carried out in a Dupont (New Castle, DE) thermal analyzer (model number DSC 951) at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The iodine value of *Putranjiva* oil is 85.7 because it is dominated by monounsaturated fatty acids. This is also supported by GLC analysis, which shows the presence of 57% $C_{18:1}$. The free fatty acid value is 1.12. This shows that decomposition of the oil, either naturally or during the extraction process, has not taken place to a great extent, which is supported by the peroxide value of 18.35. Molecular weights, determined by boiling point elevation (4), showed an average molecular weight of 600 for the oil and (610)n for factice, where n < 2. Number of crosslinks was 1.642×10^{-4} (2), and the density of the factice was 0.845.

Tensile strength of the sample is drastically reduced from 21.5 to 3 MPa upon addition of 10 phr of factice. Elongation at break (percent) is also reduced from 1090 to 210%. This shows that only 10 phr of factice in natural rubber makes the strength properties deteriorate. It also indicates that the use of this factice as a plasticizer is likely to decrease hardness and improve processing of the vulcanizates.

Rheometric studies of the unvulcanized compound shows that the minimum viscosity decreases due to addition of factice compared to unvulcanized compound without factice (Table 3). Scorch time also decreases from 3 min to 1.5 min. This shows that scorch safety decreases during compounding due to addition of factice to natural rubber. Also the cure rate is drastically reduced from 100 to 18. The results indicate that addition of factice retards the cure rate. Factice facilitated the processing in extrusion and calendering operations. It also prevented deformation of compounds during curing at ambient pressure and improved the appearance of the vulcanizate. The above results imply that this factice imparts a desirable softness to natural rubber vulcanizates, and larger concentrations could be used in compounds designed for rubber erasers (7). The rheometer curves are shown in Figure 1. The compound can be used where extrudability and calenderability is to be improved (8).

Differential scanning calorimetry shows that there are two transitions (Fig. 2) at −70 and −15°C, respectively, indicating the glass transition temperatures of the base natural rubber (T_g = −70°C) and of the factice compound (T_g = −15°C). There is also a melting peak around 110°C due to the melting point of the factice compound. Thermogravimetric studies highlight the higher degradation temperature for the factice compound compared to natural rubber, which degrades below 400°C (Fig. 3). Factice degrades at a higher temperature around 500°C. Incorporation of factice in natural rubber as a plasticizer clearly improves the thermal stability of the vulcanizate. This implies that processing operations, such as extrusion and calendering, can be performed at a considerable higher temperature with a natural rubber that contains this factice.

TABLE 3
Curing Parameters from Rheometer

Particulars	Compound without factice	Compound with factice
Initial viscosity $-L_o$ (dn • m)	8	3
Minimum viscosity $-L_i$(dn • m)	3	2
Scorch time (min)	3	1.5
Maximum cure $-L_f$ (dn • m)	47	37
Optimum cure time t_{90} (min)	4	7
Cure rate	100	18

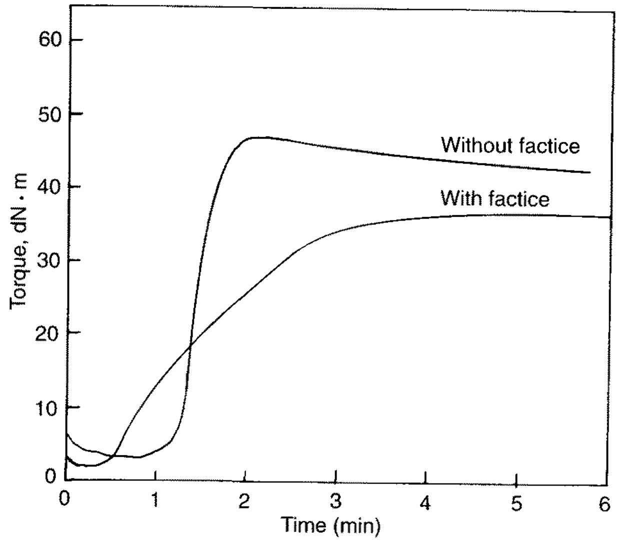

FIG. 1. Rheographs of natural rubber-based compounds with and without factice.

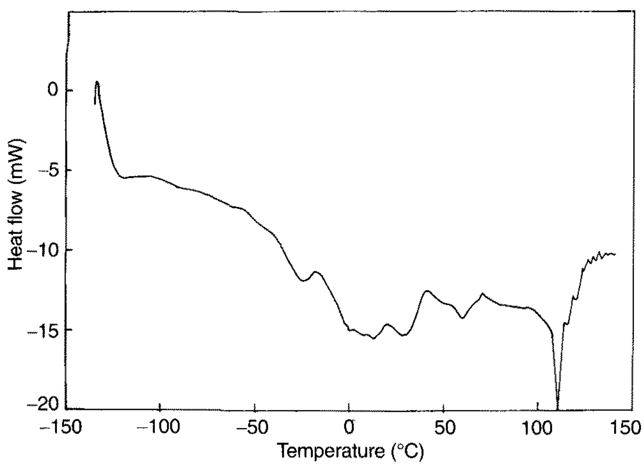

FIG. 2. Differential scanning calorimetry curve of the compound containing factice.

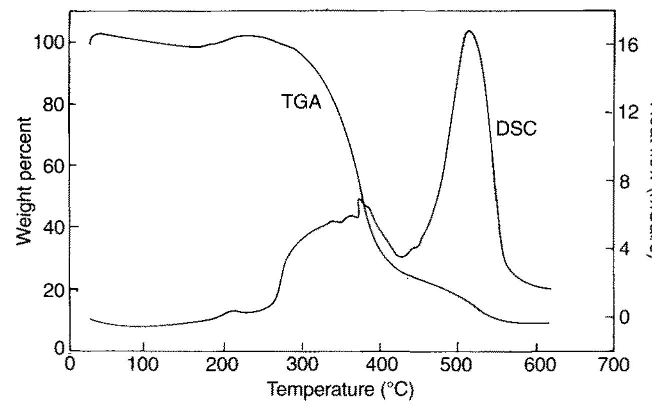

FIG. 3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of natural rubber compound containing factice.

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