Rubber Seed Oil: A Multipurpose Additive in NR and SBR Compounds

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ABSTRACT: Rubber seed oil was used as a multipurpose ingredient in natural rubber (NR) and styrene butadiene rubber (SBR) compounds. The study shows that the oil, when substituted for conventional plasticiser, imparts excellent mechanical properties to NR and SBR vulcanizates. Further, it also improves aging resistance, reduces cure time, increases abrasion resistance and flex resistance, and reduces blooming. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 487–492, 1999

Key words: rubber seed oil; multipurpose additive; natural rubber; styrene butadiene rubber; plasticizer; activator

INTRODUCTION

Vegetable oils, especially drying oils and their derivatives, have occasionally been used as additives in plastics and elastomers. Vulcanized vegetable oil (Factice) is used in elastomers for low-temperature flexibility and low hardness.[1] Epoxidized linseed oil is widely used in plastics and rubbers as a plasticizer[2,3] and heat stabilizer.[4] It is also used as a vulcanizing agent in carboxylated nitrile rubber (XNBR)–ionomer blends.[5] Other derivatives, such as linseed oil methyl ester diacetal[6] and linseed oil acetoxymethyl derivative,[7] are also used as plasticizers. Linseed oil as such is used as a multipurpose additive in NBR to improve its mechanical properties and processability and reduce cure time.[8] It is also used as plasticizer in poly(vinyl chloride) (PVC),[9] in heat-resistant neoprene rubber compounds,[10] and in some elastomer blends for cold resistance.[11] Soybean oil is used as a plasticizer in NR[12] and as a plasticizing agent in cold vulcanized rubber.[13] Blown soya bean oil is used as a plasticizer in ester gums,[14] castor oil as plasticizer in nitrocellulose,[15] in polystyrene film,[16] in rubbers containing acrylonitrile and styrene,[17] and in NR to enhance certain mechanical properties.[12]

This article reports the advantages of using rubber seed oil as a plasticizer and the fatty acid component of the activator in NR and styrene butadiene rubber (SBR).

EXPERIMENTAL

The following materials were used:

- NR: ISNR-5
- SBR: Synaprene 1502 [Mooney viscosity (ML 1 + 4, 100C)] − 50
- Rubber seed oil: commercial grade. All other ingredients used were commercial grade.

NR and SBR were compounded on a two-roll mixing mill (6″ × 12″) in accordance with ASTM D 15-627, according to the formulations given in Table I. In some formulations, vegetable oil is used as a substitute for aromatic oil and stearic acid. The optimum cure times of the compounds, t_{90} (time to reach 90% of the maximum torque),

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Table I Formulation

NR/SBR	100 phr
HAF	50 phr
Zinc oxide	5 phr
Stearic acid	2 phr
MBTS	1 phr
TMTD	0.2 phr
Sulphur	1.5 phr
Antioxidants	1.5 phr
Aromatic oil	6 phr

were determined using a Goettfert Elastograph Model 67.85. The compounds were vulcanized up to the optimum cure time in an electrically heated hydraulic press. Test specimens were punched out of the compression molded sheets, and the tensile properties were determined in accordance with ASTM D 412–80 using a Zwick Model 1445 universal testing machine. The results reported are the averages of at least five specimens. Tear strength was determined using angle test specimens. The aging resistance of the sample was determined by determining the retention in tensile properties after aging the sample in air at 100°C for 72 h. The crosslink density was determined by equilibrium swelling in respective solvents for 48 h at room temperature and calculated using the Flory–Rehner equation. The processability of the compound was studied using a Brabender Plasticorder. The compression set was measured in accordance with ASTM D 395 (1982, method B). Heat buildup of the vulcanizates was measured using a Goodrich Flexometer in accordance with ASTM D 623. Flex resistance was measured in accordance with ASTM D 430; resilience, in accordance with ASTM D 2632-88, and abrasion resistance, using a DIN abrader in accordance with DIN STD 53516.

RESULTS AND DISCUSSION

Figure 1 shows the flow behavior of compounds with different loadings of rubber seed oil in NR and SBR, obtained from the Brabender plasticorder, with (torque/rpm) representing viscosity and rpm representing shear rate. All of the compounds are pseudoplastic. The flow behavior of compounds with 6 phr aromatic oil in NR is between that of compounds with 6 and 8 phr rubber seed oil, but closer to the compound with 8 phr rubber seed oil. This shows that rubber seed oil is slightly less plasticizing in NR. This is probably due to the poor compatibility of polar vegetable oil in nonpolar NR. The behavior of rubber seed oil in SBR supports this view. Rubber seed oil is comparatively more compatible in slightly polar SBR, and the compounds with 6 phr aromatic oil and 6 phr rubber seed oil have comparable viscosities. It may be concluded that the processability of NR compounds in which rubber seed oil replaces aromatic oil is slightly decreased whereas it gives a comparable performance with aromatic oil in SBR.

Figure 2 shows the cure curves of the compounds. As for flow curves, the cure characteristics of compound with 8 phr rubber seed oil in NR and 6 phr in SBR are very close to their respective compounds with 6 phr aromatic oil. Also note that the cure time of NR compound is affected considerably by rubber seed oil. Cure time is reduced at low phr, and slowly increases with increasing phr. But compounds with rubber seed oil have a 15–20% slower cure time than compounds with the same loading of aromatic oil. The higher cure rate at low concentration is due to the higher activity of unsaturated fatty acids compared to stearic acid. The gradual decrease in cure rate with increased oil concentration is due to the noncompat-

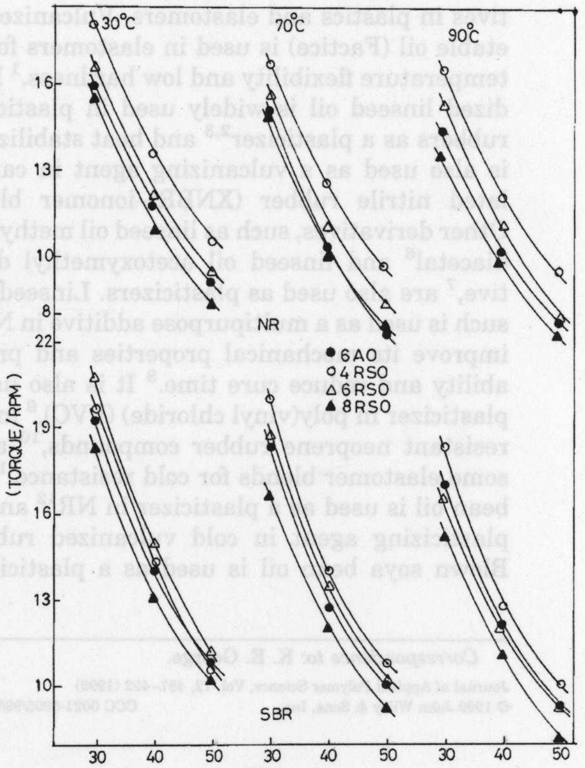

Figure 1 Flow curves of the compounds with different levels of rubber seed oil.

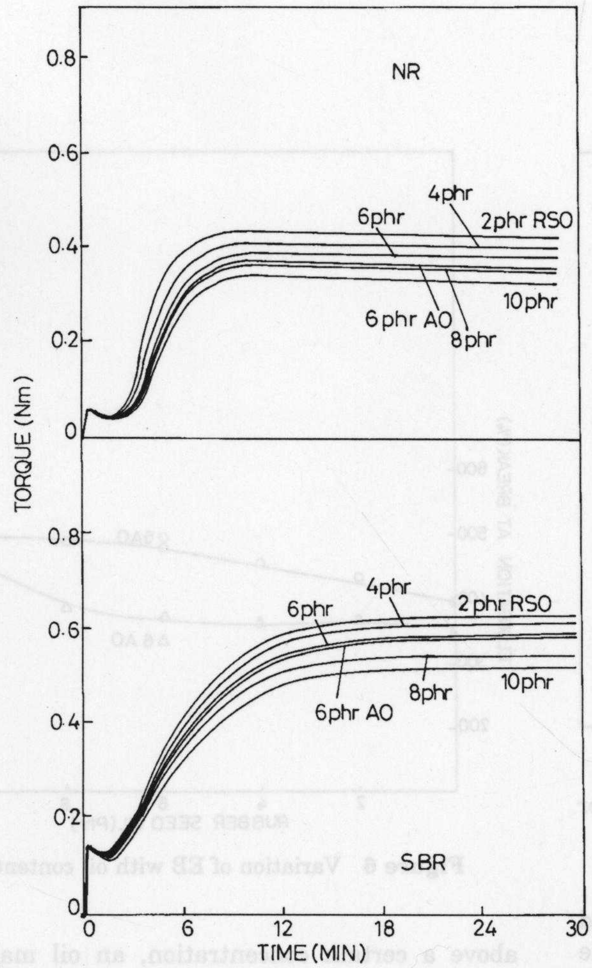

Figure 2 Cure curves of compounds with different levels of oil.

ibility of the oil, which outweighs the effect of unsaturated fatty acids.

For SBR, the change in oil concentration seems to have little effect on cure rate. This is probably due to the better compatibility of rubber seed oil in SBR (Table II).

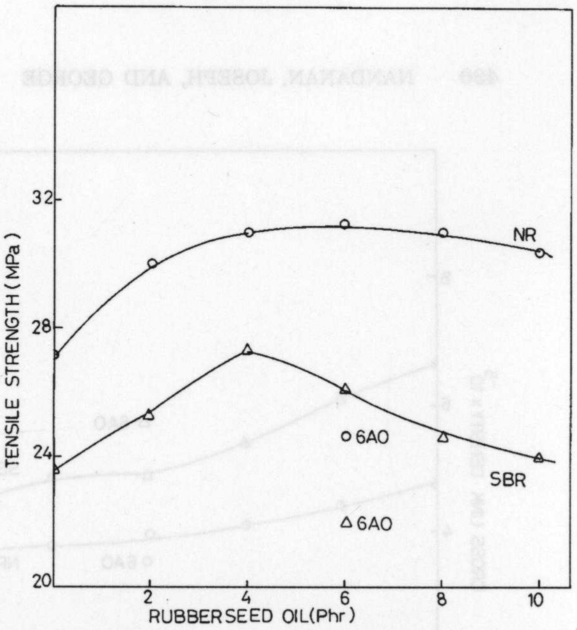

Figure 3 Variation of tensile strength with rubber seed oil content.

Figure 3 shows the variation in tensile strength at varying concentrations of rubber seed oil. A considerable increase in tensile strength occurs when aromatic oil is replaced with rubber seed oil. When vulcanizates with the conventional plasticizer show a gradual decrease in tensile strength with increase in their concentration, vulcanizates with rubber seed oil show a different behavior. The tensile strength of vulcanizates increases up to a concentration of about 8 phr and then starts to gradually decrease. Vulcanizates with rubber seed oil always show greater (25–30%) tensile strength when aromatic oil is replaced with the

Table II Cure Characteristics of Compounds

		NR		SBR	
Sample No.	Composition	Scorch Time (t_{10}) (min)	Cure Time (t_{90}) (min)	Scorch Time (t_{10}) (min)	Cure Time (t_{90}) (min)
1	6 phr aromatic oil	1.4	2.72	2.7	10.4
2	2 phr rubber seed oil	1.12	2.0	2.6	10.4
3	4 phr rubber seed oil	1.20	2.2	2.7	10.6
4	6 phr rubber seed oil	1.24	2.32	2.8	10.7
5	8 phr rubber seed oil	1.28	2.44	2.6	10.6
6	10 phr rubber seed oil	1.32	2.52	2.7	10.6

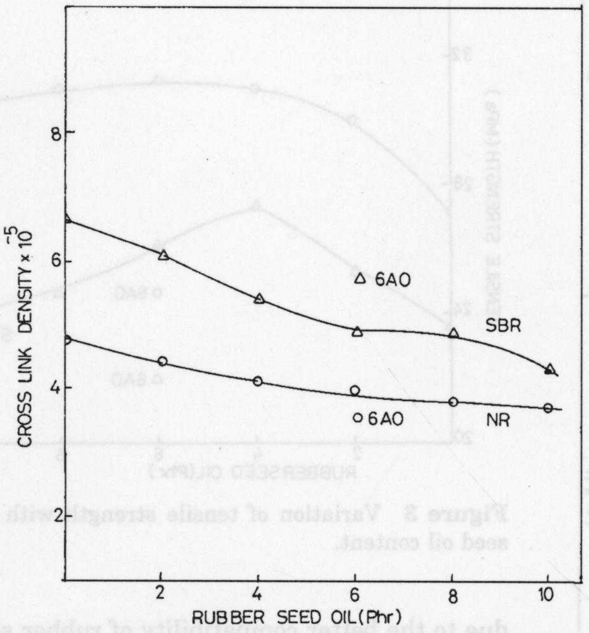

Figure 4 Variation of crosslink density with rubber seed oil content.

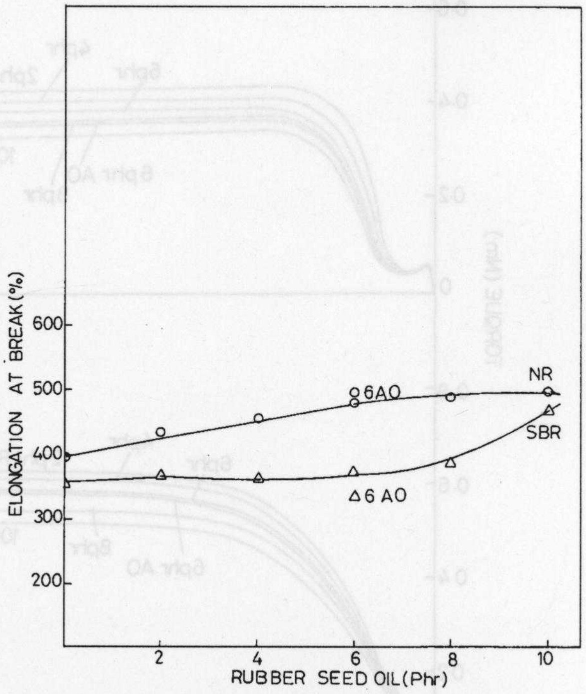

Figure 6 Variation of EB with oil content.

same loading of rubber seed oil in both NR and SBR. The main reason for the increased tensile strength may be the ability of unsaturated vegetable oils to covulcanize with the elastomer. But above a certain concentration, an oil may get crosslinked (factice formation) simultaneously with covulcanization, which reduces the strength of the vulcanizates. The variation in tensile

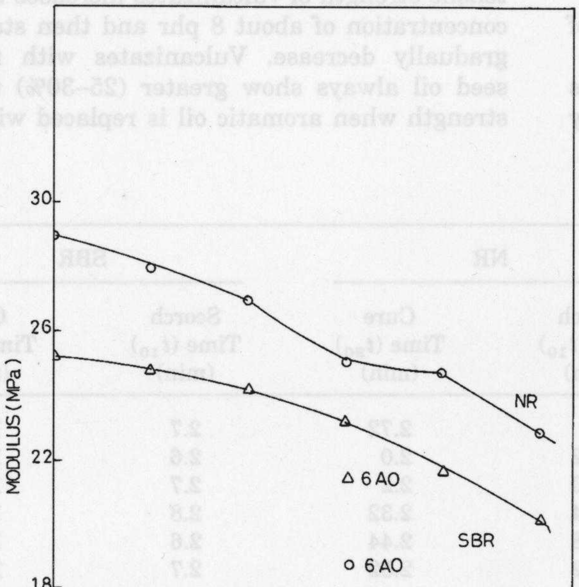

Figure 5 Variation of modulus with oil content.

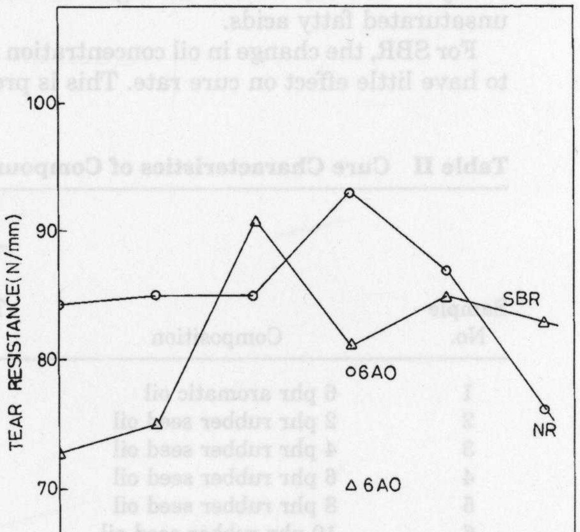

Figure 7 Variation of tear resistance with oil content.

Table III Tensile Properties of Aged and Unaged Samples

		Tensile Strength (MPa)			
		NR		SBR	
Sample No.	Composition	Unaged	Air Aged	Unaged	Air Aged
1	6 phr aromatic oil	24.5	12.71	21.8	15
2	2 phr rubber seed oil	30.3	22.3	25.4	17.9
3	4 phr rubber seed oil	31.0	24.9	27.25	23.6
4	6 phr rubber seed oil	31.1	26.3	26.2	21.8
5	8 phr rubber seed oil	31.4	25.3	25.1	20.1
6	10 phr rubber seed oil	29.4	21.2	24.0	18.9

strength can also be related to variation in crosslink density and better filler incorporations. The decrease in crosslink density with increased oil concentration is due to factice formation, as part of the sulphur is used for this (Fig. 4).

Figure 5 shows the variations of modulus with rubber seed oil content in NR and SBR. As expected, modulus varies directly with crosslink density, and inversely with elongation at break (Fig. 6). But in the case of NR, vulcanizates with rubber seed oil show higher modulus than those with the same loading of aromatic oil, whereas the variation in modulus is not pronounced in SBR.

The variation in tear resistance is similar to that for tensile strength and modulus variation in both NR and SBR and can be explained on similar lines (Fig. 7). The antioxidant nature of rubber seed oil is proven by the aging studies of the vulcanizates. Though rubber seed oil has little effect on aging resistance of SBR it improves aging resistance in NR. Tensile strengths of the aged and unaged samples are compared in Table III.

Table IV shows the compression set of vulcanizates with different loadings of rubber seed oil. The compression set is not much affected by rubber seed oil in NR. But a gradual decrease in the compression set occurs with increased oil content in SBR.

Other major properties that may be of interest in NR and SBR are their abrasion resistance, demattia flex resistance, heat buildup, and resilience, as these rubbers are generally used in tire tread and side wall compounds. Table V shows the abrasion loss for NR vulcanizates with different loadings of rubber seed oil. Abrasion resistance gradually increases with rubber seed oil concentration. Note that volume loss decreases by 13.5% when 6 phr aromatic oil is replaced with an equal amount of rubber seed oil. This may be due to better filler distribution.

Flex resistance is considerably increased when aromatic oil is replaced with rubber seed oil in NR and SBR (Table VI). Even at very low concentrations of rubber seed oil, flex resistance is considerably high. This can be explained by the free volume theory of plasticization. The comparatively small molecules of glycerides get entrapped between long chain rubber molecules and covulcanize with it, causing increased free volume between adjacent rubber molecules. This causes more flexibility in the vulcanizate.

Heat buildup is not much affected by rubber seed oil in NR, but in SBR it increases slightly

Table IV Compression Set of Vulcanizates

		Set (%)	
Sample	Composition	NR	SBR
1	6 phr aromatic oil	47.5	44.3
2	2 phr rubber seed oil	46.8	39.1
3	4 phr rubber seed oil	46.7	37.3
4	6 phr rubber seed oil	44.7	29.5
5	8 phr rubber seed oil	48.1	27.2
6	10 phr rubber seed oil	50.3	25.6

Table V Abrasion Loss of NR Vulcanizates

Sample No.	Composition	Loss in Volume (%)
1	6 phr aromatic oil	3.947
2	2 phr rubber seed oil	3.669
3	4 phr rubber seed oil	3.484
4	6 phr rubber seed oil	3.4358
5	8 phr rubber seed oil	3.2328
6	10 phr rubber seed oil	3.0444

Table VI Demattia Flex Resistance of Vulcanizates

Sample No.	Composition	Flex (Cycles) NR	Flex (Cycles) SBR
1	6 phr aromatic oil	1,12,500	41,000
2	2 phr rubber seed oil	1,35,000	49,000
3	4 phr rubber seed oil	1,46,000	56,000
4	6 phr rubber seed oil	1,68,000	1,12,500
5	8 phr rubber seed oil	1,92,000	1,16,500
6	10 phr rubber seed oil	2,82,000	1,33,500

with increased oil content (Table VII). Resilience of the vulcanizate is improved by the incorporation of rubber seed oil in both NR and SBR (Table VIII).

CONCLUSIONS

Rubber seed oil gives appreciable increase in properties like tensile strength, tear resistance, abrasion resistance, and demattia flex resistance in both NR and SBR vulcanizates. The viscosity of compounds with rubber seed oil is slightly higher than compounds with aromatic oil for NR, whereas it is almost equal for SBR, when compared with their respective compounds with aromatic oil. Cure rate and aging resistance are increased for both NR and SBR compounds. Sulphur blooming is reduced, and resilience is increased. The optimum concentration of rubber seed oil, in the range of 5–7 phr, can advantageously replace 6 phr aromatic oil and 2 phr stearic acid in conventional NR and SBR vulcanizates. Further, the cost of the compound can be reduced by substituting rubber seed oil for aromatic oil and stearic acid.

Table VII Heat Buildup of Vulcanizates

Sample	Composition	Rise in Temperature (F°) NR	Rise in Temperature (F°) SBR
1	6 phr aromatic oil	77	92
2	2 phr rubber seed oil	80	95
3	4 phr rubber seed oil	78	99
4	6 phr rubber seed oil	74	100
5	8 phr rubber seed oil	77	103
6	10 phr rubber seed oil	81	105

Table VIII Resilience of Vulcanizates

Sample No.	Composition	Resilience NR	Resilience SBR
1	6 phr aromatic oil	37	40
2	2 phr rubber seed oil	45	45
3	4 phr rubber seed oil	44	48
4	6 phr rubber seed oil	45	45
5	8 phr rubber seed oil	46	45
6	10 phr rubber seed oil	42	43

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