

A Study on the Use of Coconut Oil as Plasticiser in Natural Rubber Compounds

RAJU, P.^{*,**}, NANDANAN, V.^{**} AND SUNIL, K.N. KUTTY^{*#}

Mechanical properties and thermal degradation characteristics of natural rubber compounds containing coconut oil were compared with that of a control compound containing naphthenic oil. Cure time was marginally lower in the case of coconut oil mixes, probably due to the presence of free fatty acids. Tensile strength, tear strength, resilience and abrasion resistance were better than the naphthenic oil-based compounds. Compression set and hardness were marginally inferior. The coconut oil mixes had a crosslink density comparable to that of the reference compound. Thermal studies showed that the temperature of initiation of degradation was increased by 10°C and the temperature at which the peak rate of degradation occurred was increased by 7°C. The peak rate of degradation was comparable to the control compound.

Key words: natural rubber; plasticiser; coconut oil; naphthenic oil; mechanical properties; thermal degradation; free fatty acids

Plasticisers are low molecular weight non-volatile substances that are added to a polymer to improve flexibility and processability. Even small quantities of plasticiser markedly reduces the glass transition temperature (T_g) of the polymer. This effect is due to the reduction in cohesive forces between polymer chains. Plasticiser molecules penetrate into the polymer matrix and act as a lubricant between polymer chains, thereby reducing the T_g .

Plasticisers also improve filler dispersion and help in controlling viscosity to desired levels. Generally used plasticisers include mineral oils, synthetic esters and some natural products such as wood rosin and animal glue¹.

Among these, the petroleum-based oils are quite extensively used in rubber compounds. The fast depletion of petroleum resources calls for exploration of alternatives materials. The vegetable oils are a potential substitute for mineral oils in this regard. The renewable nature of the source and the presence of other natural products such as tocopherol and free fatty acids can also be advantageous in rubber compounds.

Richtler² used vegetable oils, as a vulcanising agent in carboxylated nitrile rubber (X-NBR)-ionomer blends. Linseed oil was used as a multipurpose additive in NBR to improve its mechanical properties and processability as well as to reduce cure time³.

^{*}Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, Kerala, India

^{**}St. Paul's College, Kalamassery, Kerala, India

[#] Corresponding author (e-mail: sunil@cusat.ac.in)

Soyabean oil was used as a plasticiser in natural rubber (NR)⁴ and as a plasticising agent in cold vulcanised rubber⁵. Blown soyabean oil was used as a plasticiser in ester gums⁶. Castor oil has been used as plasticiser in nitrocellulose⁷, polystyrene films⁸ and in rubbers containing styrene⁹. Ghatge *et al.* prepared a millable and sulphur vulcanisable elastomer from castor oil¹⁰.

Substitution of dioctyl phthalate (DOP) with dehydrated castor oil in nitrile rubber compounds increased the plasticising effect without affecting the physico-chemical properties and ageing resistance¹¹.

Epoxidised rubber seed oil, rubber seed oil and its soap were used as a plasticiser in polyvinyl chloride (PVC)¹². The soaps were found to be effective in suppressing the initial degradation of PVC. Epoxidised rubber seed oil was also used as a leachable plasticiser for acrylonitrile butadiene rubber to improve the abrasion resistance of the vulcanisate¹³. It was also used as a secondary plasticiser for PVC¹⁴. Kuriakose *et al.* reported the use of rice bran oil as a multipurpose ingredient in the compounding of styrene butadiene rubber and found that the cure characteristics of the compound and the physical and mechanical properties of the vulcanisate were comparable to that of mixes containing conventional plasticiser¹⁵. Kundu¹⁶, reported the use of vegetable oil in general as a coupling agent for improvement of rubber-filler interaction in carbon black reinforced rubber¹⁶.

In the present study we have used coconut oil as the plasticiser in a typical natural rubber compound containing 45 p.h.r. of carbon black. The oil concentration was increased from 0 p.h.r. to 10 p.h.r. Mechanical properties and thermal characteristics of these compounds were compared with that of the control compound containing naphthenic oil.

EXPERIMENTAL

Materials

Natural rubber (ISNR 5) was obtained from the Rubber Research Institute of India, Kottayam. Zinc oxide and stearic acid were supplied by M/s Meta Zinc Ltd., Mumbai and Godrej Soaps (Pvt.) Ltd., Mumbai, respectively.

Mercaptobenzothiazole disulphides (MBTS) and tetramethyl thiuram disulphide (TMTD) were supplied by Bayer Chemicals, Mumbai and Polylefins Industries Ltd., Mumbai, respectively. Sulphur was supplied by Standard Chemical Company, Pvt. Ltd., Chennai. Carbon black (HAF N-330) used in the study was supplied by M/s Philips Carbon, Kolkata.

Naphthenic oil obtained from Hindustan Petroleum Ltd., Mumbai, had the following specifications: specific gravity – 0.98; aniline point – 78°C and a value of 0.87 for Viscosity Gravity Constant.

Coconut oil was of commercial grade and obtained from the local market. A major portion of the fatty acid present in coconut oil is lauric acid. The fatty acid composition is: caprylic acid – 9%; capric acid – 6%; lauric acid – 49%; myristic acid – 20%; palmitic acid – 8% and stearic acid – 3%.

The following are the characteristics of coconut oil:

- Viscosity gravity constant: 0.84
- Specific gravity: 0.91–0.92
- Iodine value: 6–11
- Saponification value: 248–265

Processing

The formulation of the mix is shown in Table 1. The samples were prepared using a

TABLE 1. COMPOUND FORMULATION (p.h.r.)

Ingredients	Mix number										
	C ₀	C ₂	C ₄	C ₆	C ₈	C ₁₀	N ₂	N ₄	N ₆	N ₈	N ₁₀
Natural Rubber	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Vulcanox HS®	1	1	1	1	1	1	1	1	1	1	1
Vulcanox 4020®	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	1	1	1	1	1	1	1	1	1	1	1
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
HAF	45	45	45	45	45	45	45	45	45	45	45
Coconut oil (C)	0	2	4	6	8	10	—	—	—	—	—
Naphthenic oil (N)	—	—	—	—	—	—	2	4	6	8	10
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

TABLE 2. THERMAL DEGRADATION CHARACTERISTICS OF MIXES C₄ AND N₄

Mix	Temperature of initiation (T _i)°C	Peak degradation temperature (T _{PD}) (°C)	Peak rate of decomposition (R _{PD}) (%/min)	Residue at 600°C (%)
C ₄	308	389	1.09	31.4
N ₄	298	382	1.17	29.6

laboratory sized two-roll mixing mill (16 cm × 33 cm) at a friction ratio of 1:1.25 as per *ASTM D 3184-89 (2001)* over a time period of 18 min. Cure characteristics at 150°C were determined using Goettfert Elastograph Model (67.85). Tensile and tear strength were measured according to *ASTM D 412* and *ASTM D 624*, respectively using a Shimadzu Universal Testing Machine, model AG 50 kN. The hardness (Shore A) of the samples was determined using Zwick 3114 hardness tester according to *ASTM D 2240-86*. Samples with dimensions of 12 mm diameter and 6 mm thickness were used. A load of 12.5 N was applied and the readings were taken 10 seconds after the indenter made a firm contact with the specimen.

The flex resistances of the vulcanisates were determined using a Wallace De Mattia flexing machine as per *ASTM D 430-57 T*. In

cases where the samples did not fail, the test was carried out continuously up to 5 million cycles. Abrasion resistance of the samples was measured using a DIN abrader based on *DIN 53516*. The results were expressed as volume loss per hour:

$$V = \frac{\Delta M \times 27.27}{\rho} \quad \dots 1$$

where,

V = Abrasion loss in cm³/h

ΔM = Mass loss and

ρ = Density of the sample.

Rebound resilience was determined by vertical rebound method according to *ASTM D 2832-88*.

Heat build up was tested using a Goodrich Flexometer as per *ASTM D 623-78* (Method A).

The samples were 25 mm in height and 19 mm in diameter. The oven temperature was maintained constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.05 kN.

Compression set at constant strain was measured according to *ASTM D 395-86* (Method B). Samples with 6.25 mm thickness and 18 mm diameter were compressed to constant strain (25%) and kept for 22 h in an air oven at 70°C. At the end of the test period the test specimens were taken out, kept at room temperature for 30 min and the final thickness was measured. The compression set in percentage was calculated as follows:

$$\text{Compression set (\%)} = \frac{T_i - T_f}{T_i - T_s} \times 100 \quad \dots 2$$

Where T_i and T_f are the initial and the final thickness of the specimen, respectively and T_s is the thickness of the spacers used.

Crosslink Density

Crosslink density of the vulcanisates was determined by an equilibrium swelling method using the Flory-Rehner equation^{17,18}. Samples of approximately 0.3 g were cut and kept to swell in toluene for equilibrium swelling. The outer portion of the swollen samples was then dried using a filter paper and weighed. It was then placed inside the oven at 60°C for 24 h to remove the solvent. The de-swollen weight was determined. The value¹⁹ of the interaction parameter (χ) taken was 0.42.

Thermal Analysis

Thermogravimetric analysis of the specimens was carried out on the Universal V4 2E, TA Instrument, with a heating rate of 10°C/min under nitrogen atmosphere. The following

characteristics were determined from the thermogravimetric curves: the temperature of onset of degradation; the temperature at peak rate of decomposition; the peak rate of degradation and the weight of residue remaining at 600°C.

Scanning Electron Microscopy (SEM)

SEM studies were carried out using Model No S 360, Cambridge Instruments, U.K. To study the failure mode, the broken surfaces of tensile and tear test specimens were carefully cut from the failed test specimens without touching the fractured surface and were sputter coated with gold. The orientation of the samples was kept constant in a particular mode of failure.

RESULTS AND DISCUSSION

The cure characteristics of the mixes are shown in *Figures 1–4*. The coconut oil mixes showed a lower cure time compared to the control mix (*Figure 1*). These mixes also showed a higher rate of cure reaction (*Figure 2*). The increased cure rate and lower cure time showed that coconut oil has an activating effect on the cure reaction. This may be due to the presence of free fatty acids in it. There was no appreciable variation in the scorch time between the mixes with increasing loading of oil (*Figure 3*).

Figure 4 shows that the torque development ($T_{\text{max-min}}$) was higher in the case of coconut oil at all oil loadings. The higher torque may be either due to higher crosslink density or better filler-matrix interaction resulting from better dispersion. *Figure 5* shows that the crosslink density of the mixes was almost the same for both the series of mixes. Hence the higher observed torque for the coconut oil mixes points to a better dispersion of the filler in the matrix.

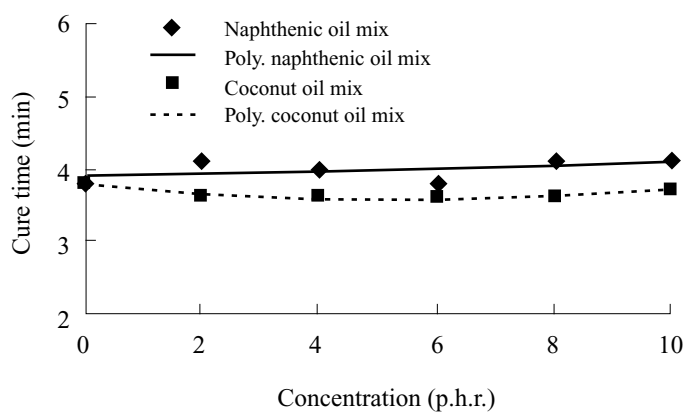


Figure 1. Variation of cure time (min) with plasticiser content.

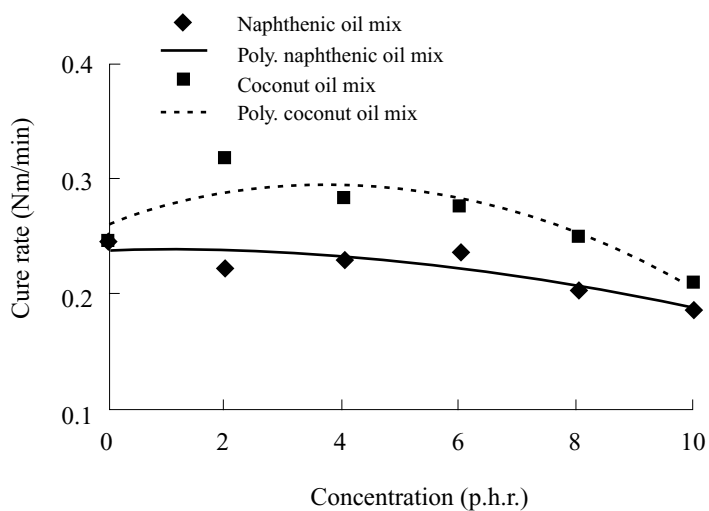


Figure 2. Variation of cure rate (Nm/min) with plasticiser content.

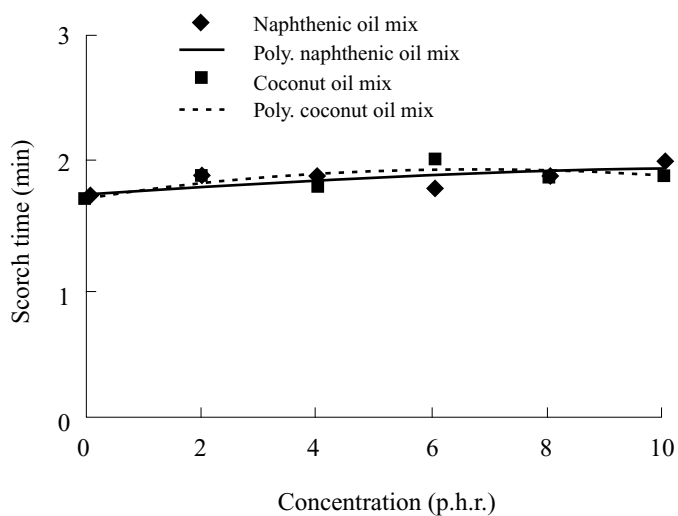


Figure 3. Variation of scorch time (min) with plasticiser content.

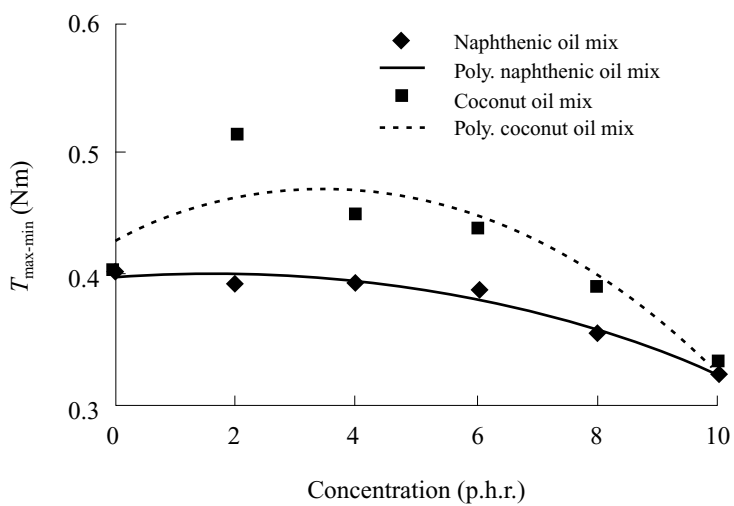


Figure 4. Variation of $T_{\max-\min}$ (Nm) with plasticiser content.

Figure 6 gives the variation of the tensile strength of the vulcanisates with oil loading. The maximum tensile strength was obtained in the 4 p.h.r. – 8 p.h.r. range. Better strength is obtained when the filler was dispersed homogeneously in the matrix. At lower oil loadings the filler dispersion was non-uniform and hence the strength was not fully developed. At loadings beyond 6 p.h.r., the oil is in excess of what was required and the plasticiser effect was more significant, resulting in better strength at intermediate oil loading.

Figures 7 and 8 show the SEM photomicrographs of the tensile broken surfaces of the mixes C_4 and N_4 , respectively, at $100\times$ magnification. For the naphthenic oil mix (N_4) the fracture surface was relatively clean with two crack paths propagating unhindered. For the coconut oil mix (Figure 7) the large number of cracks that were intersected, diverted and spread uniformly across the surface is in agreement with the observed higher tensile strength of the mix C_4 .

The tear strength values showed a significant increase in the case of coconut oil (Figure 9), especially at higher oil loadings. In the case of naphthenic oil, the tear strength remains constant at 60 N/mm whereas the coconut oil mixes showed an increase up to 90 N/mm at 4 p.h.r. – 6 p.h.r. loading range. This may also be due to improved filler dispersion.

Figures 10 and 11 compare the modulus and elongation at break of the vulcanisates. The modulus and the ultimate elongation of the coconut oil-mixes were comparable to that of the control mix. Figure 12 shows the variation of hardness with oil concentration. In both the cases the hardness was higher at intermediate oil concentrations, with the coconut oil mixes showing consistently lower hardness compared to the naphthenic oil mixes. The hardness being a surface property, any changes that affect the surface would affect

the observed hardness values. The coconut oil being relatively more polar, will tend to migrate to the surface making the surface softer compared to the bulk. This explains the lower hardness values of the coconut oil mixes even though the crosslink density and modulus are comparable.

Compression set values (Figure 13) showed a gradual reduction with oil loading having a minor tendency to increase at a higher oil content. At lower oil concentrations the filler dispersion was poor. At a higher oil content the plasticising effect and segmental mobility were very pronounced, leading to higher set values. At an intermediate oil content the elastic deformation is operational and hence the set values were lower.

Abrasion loss (Figure 14) and resilience (Figure 15) values of both the mixes were comparable at all oil loadings. The deformation of a viscoelastic matrix under impulsive loading conditions is more elastic and hence the system showed better resilience. Both the oils gave very good flex crack resistance (Table 3). None of the samples failed before 5×10^5 cycles.

The heat build up (Figure 16) was found to decrease with increasing oil content with the coconut oil mixes which showed higher heat generation at all oil contents. The preferential migration of the plasticiser to the surface leaves the bulk with a relatively lower oil content and hence the hysteresis loss was higher in the case of coconut oil mixes. This effect is not reflected in the case of resilience results as the test involves different modes of deformation and the conditions are not as severe as in the case of the heat build up test.

Figure 17a shows the thermogram of the control mix with naphthenic oil and Figure 17b, the thermogram of the coconut oil mix at 4 p.h.r. concentration. The improved thermal

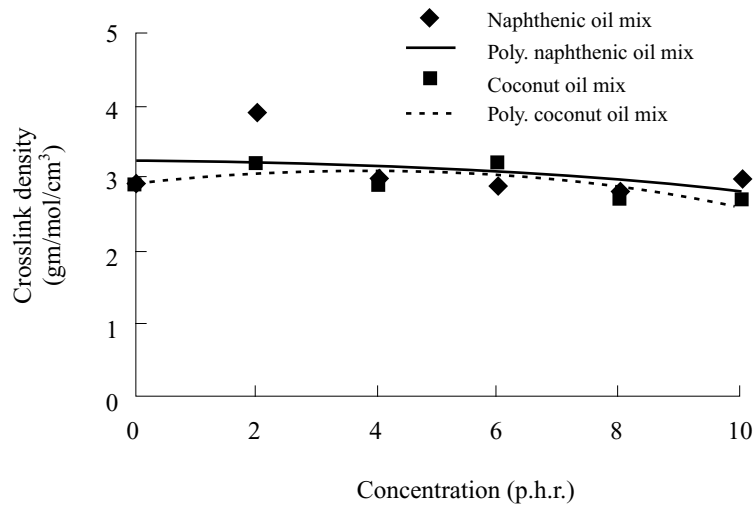


Figure 5. Variation of crosslink density (gm/mol/cm³) with plasticiser.

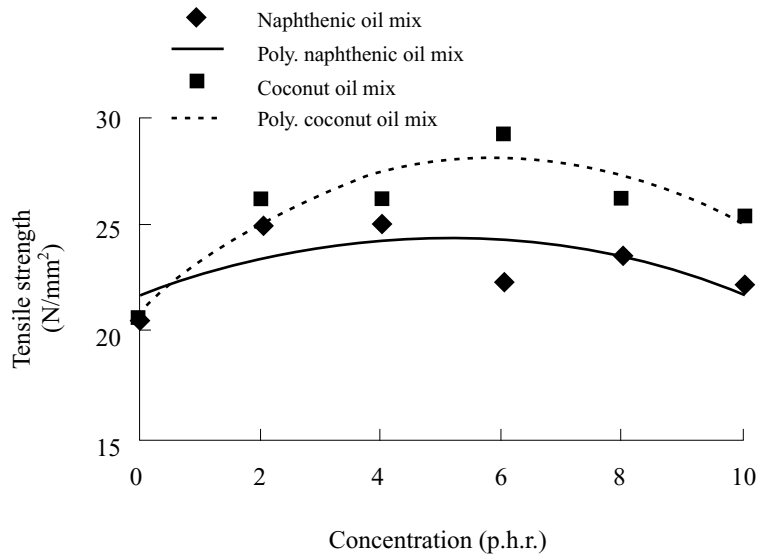


Figure 6. Variation of tensile strength (N/mm²) with plasticiser content.

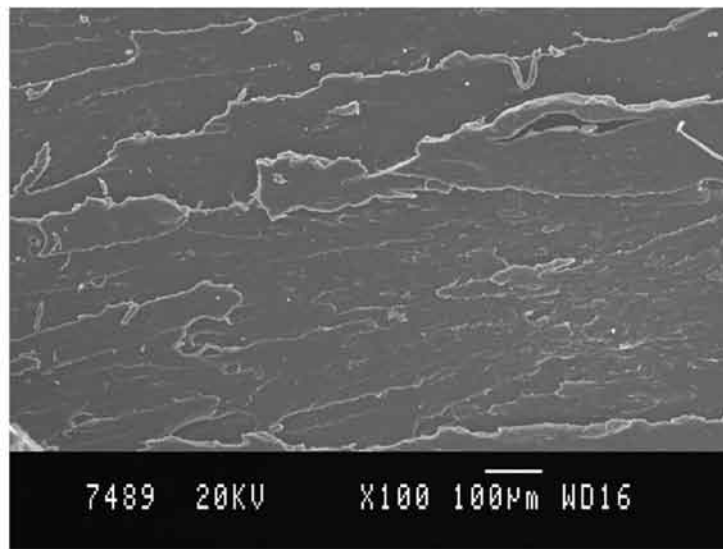


Figure 7. SEM photomicrograph of coconut oil mix at 4 p.h.r.

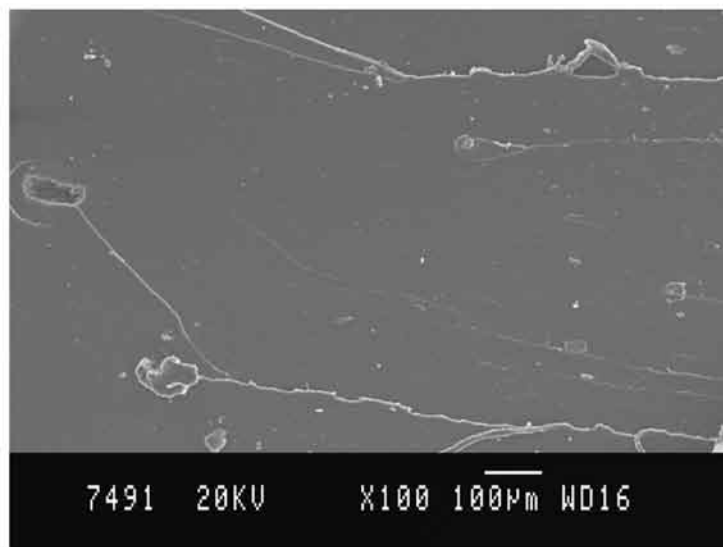


Figure 8. SEM photomicrograph of naphthenic oil mix at 4 p.h.r.

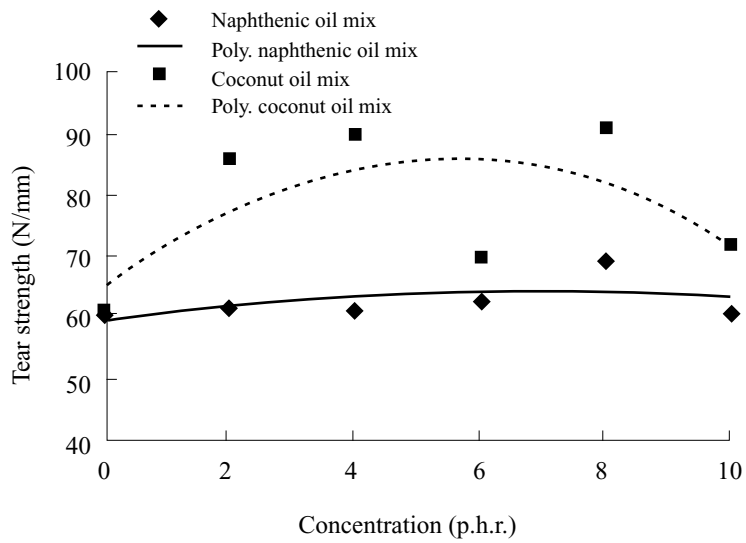


Figure 9. Variation of tear strength (N/mm) with plasticiser content.

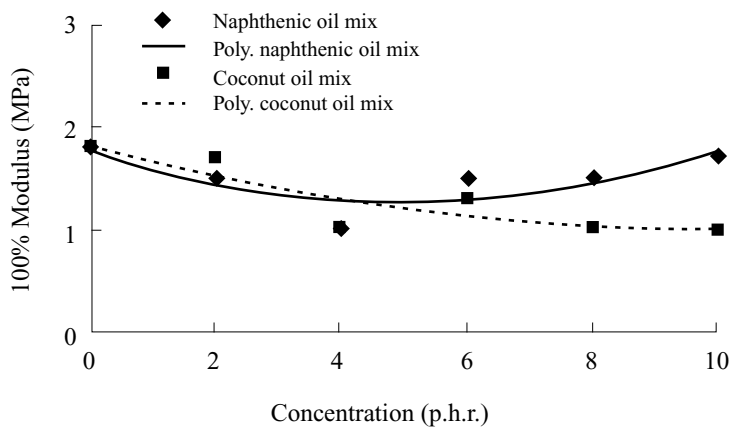


Figure 10. Variation of modulus at 100% elongation (MPa) with plasticiser content.

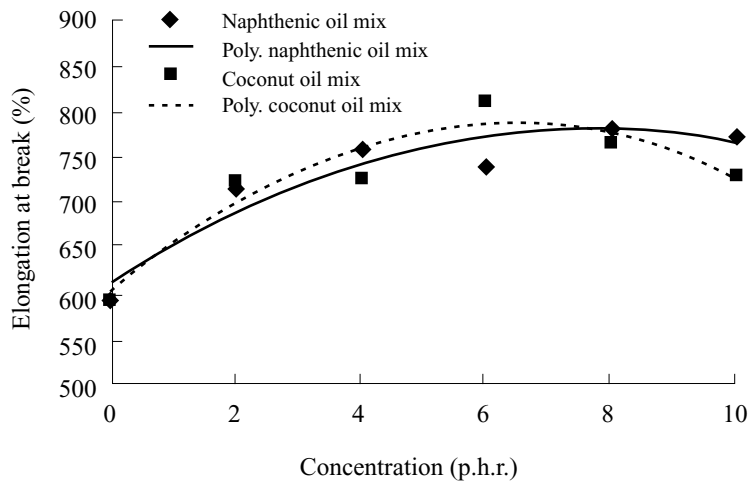


Figure 11. Variation of elongation at break (%) with plasticiser content.

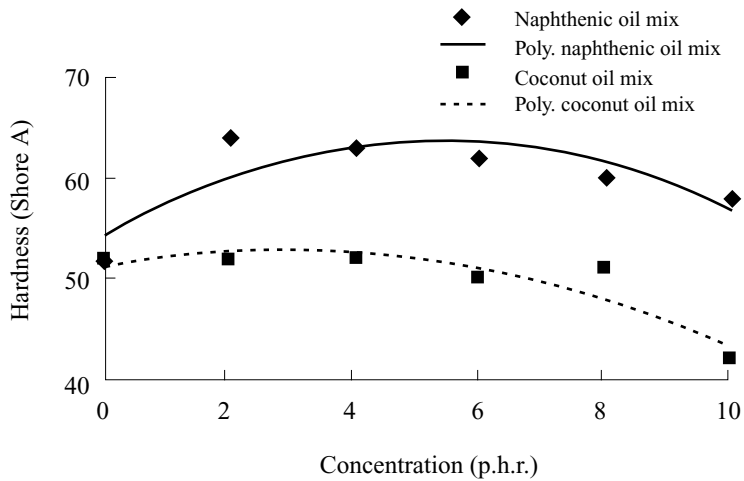


Figure 12. Variation of hardness (Shore A) with plasticiser content.

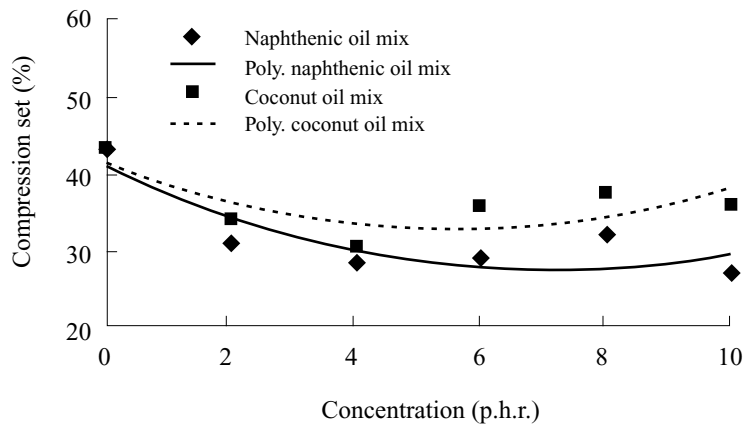


Figure 13. Variation of compression set (%) with plasticiser content.

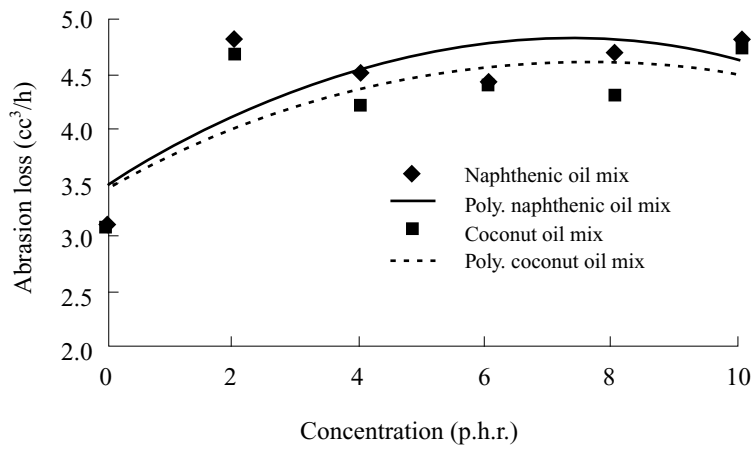


Figure 14. Variation of abrasion resistance (cc³/h) with plasticiser content.

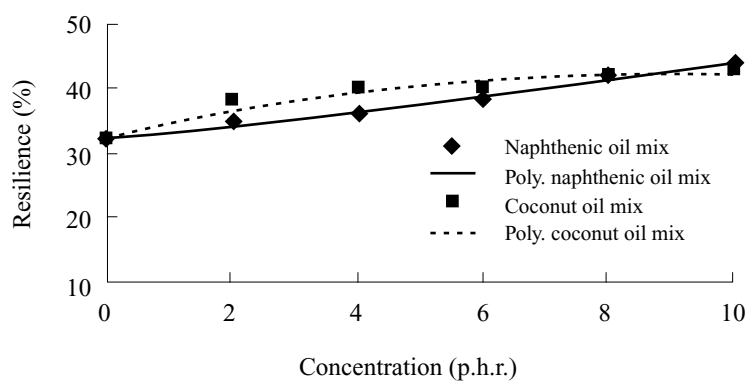


Figure 15. Variation of resilience (%) with plasticiser content.

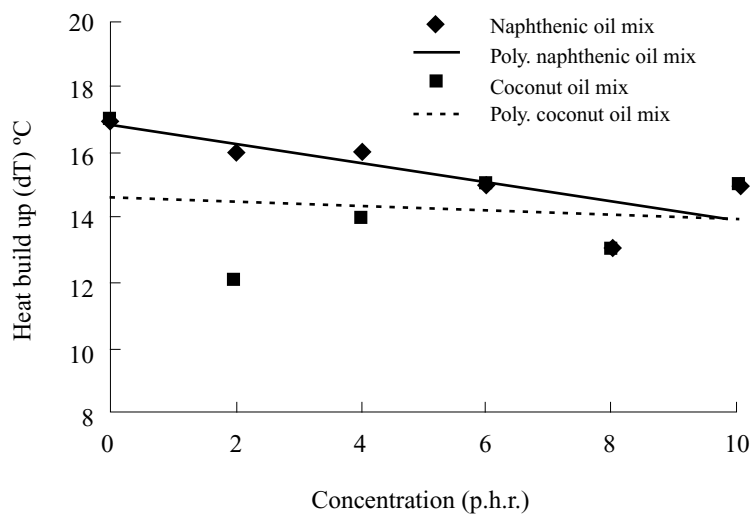


Figure 16. Variation of heat build up (dT) °C with plasticiser content.

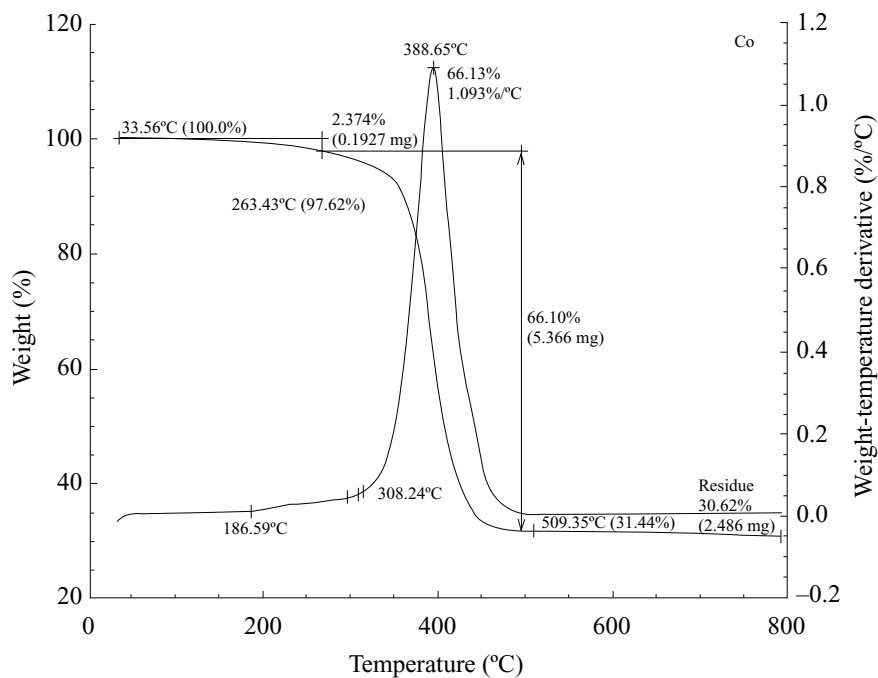


Figure 17a. Thermogravimetric curve of mix with (4 p.h.r.) coconut oil.

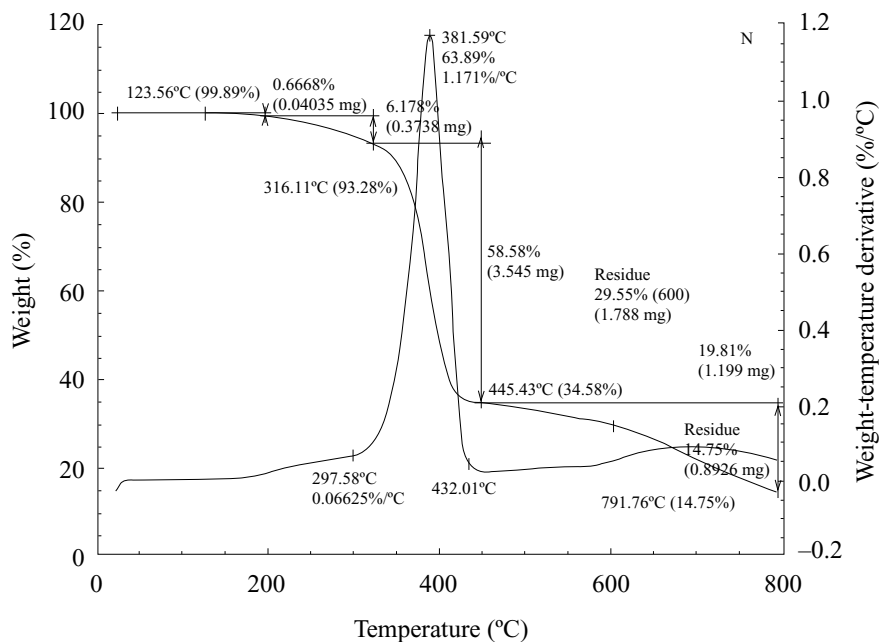


Figure 17b. Thermogravimetric curve of mix with (4 p.h.r.) naphthenic oil.

TABLE 3. FLEX CRACKING RESISTANCE OF THE VULCANISATES

Mix number	Flex cracking resistance (millions of cycles)
C ₀	>0.5
C ₂	>0.5
C ₄	>0.5
C ₆	>0.5
C ₈	>0.5
C ₁₀	>0.5
N ₂	>0.5
N ₄	>0.5
N ₆	>0.5
N ₈	>0.5
N ₁₀	>0.5

stability of the coconut oil compounds is evident from the higher temperature of initiation of degradation (T_i) of the mixes. The T_i of the coconut oil mix was 308°C while that of naphthenic oil was 298°C. Improvement in thermal stability was also evident from the higher temperature of initiation (by 10°C) and a higher peak degradation temperature (higher by 7°C). It also showed a lower rate of degradation and higher residue weight.

CONCLUSION

The study showed that coconut oil was a potential substitute for naphthenic oil as a plasticiser in NR compounds even though all properties were not equivalent. Coconut oil showed advantages in properties like cure time, tensile strength, tear strength, abrasion loss and resilience. The heat build up and compression set were however higher than the naphthenic oil mixes compounds. The optimum loading of coconut oil was in the 4 p.h.r. to 8 p.h.r. range for 45 p.h.r. HAF black-filled NR. Coconut oil also imparted better thermal stability to the natural rubber compounds.

Date of receipt: June 2006

Date of acceptance: January 2007

REFERENCES

1. WERNER HOFFMAN (1989) *Rubber Technology Handbook*. New York, U.S.A.: Hanser Publishers.
2. RICHTLER, H.J. 1983 *Challenges to a Mature Industry*. Dusseldorf: Henkel KGaA.
3. NANDANAN, V., JOSEPH, R. AND FRANCIS, D.J. (1996) *Elastomers and Plastic*, **28**, 326–334.
4. NANDANAN, V., JOSEPH, R. AND KURIAKOSE, A.P. (1997) *Proceedings of the National Conference, Indian Rubber Institute, Mumbai*, 205–221.
5. DITMAR, R. AND GUMMI ZUG (1926) **41**, 535–536.
6. BRILLHART, S.E. AND GRAY, A.N. (1947) *US Patent*, 2, 426, 858.
7. KRAUS, A. AND FARBE, U. LACK (1936) 243–244, 257–258, 268–270.
8. KOLESEV, S.N. (1967) *Izv. Vyssh Ueheb Zavel Fiz.*, **10(1)**, 12–16.
9. GEORGE, E.W. (1969) *US Patent*, **3**, 438, 971.
10. GHATGE, N.D. AND PHADKE, V.B. (1967) *Elastomers from Castor Oil. J. appl. Polym. Sci.*, **11(5)**, 629–638.
11. FAGADE, N.B., BANERJEE, M.S. AND MILLUS, W. (1981) *Elastomerics*, **113(7)**, 35–40.
12. OKIEIMEN, FELIX, E. AND EBHOAYE JUSTINE. (1993) *Polym. Prepr. (Am. Chem. Soc. Div. Poly. Chem.)*, **34(2)**, 227–228.
13. REETHAMMA JOSEPH, ROSAMMA ALEX AND VINODH, V.S. *et al.* (2003) Studies on Epoxidised Rubber Seed Oil as Plasticizer for Acrylonitrile Butadiene Rubber. *J. appl. Polym. Sci.*, **89(3)**, 668–673.

14. JOSEPH, R. MADHUSOODHANAN, K.N., ALEX, R., VARGHESE, S., GEORGE, K.E. AND KURIAKOSE, B. (2004) *Plastics, Rubber and Composites*, **33(5)**, 217–222.
15. KURIAKOSE, A.P. AND RAJENDRAN, G. (1995) Use of Rice-bran Oil in the Compounding of SBR. *J. Material Science*, **30(9)**, 2257–2262.
16. KUNDU, P.P. (2000) Improvement of Filler-rubber Interaction by the Coupling Action of Vegetable Oil in Carbon Black Reinforced Rubber. *J. appl. Polym. Sci.*, **75**, 735–739.
17. FLOREY, P.J. AND REHNER, J. (1943) *J. Chem. Phys.*, **11**, 512.
18. FLOREY, P.J. (1950) *J. Chem., Phys.*, **18**, 108.
19. SHEELAN, C.J. AND BASIO, A.L. (1966) Polymer / Solvent Interaction Parameters. *Rubb. Chem. Technol.*, **39(1)**, 144.