A Low Cost Processing Aid from Oil Refinery Waste for Compounding Rubber Blends

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ABSTRACT

Oily sludge accumulates in large quantities as waste in petroleum refineries. Disposal of this waste is a difficult problem in the overall waste treatment management programme of refineries. Since this sludge contains about 70 % hydrocarbons, it was thought worthwhile to try this as a substitute for processing oil in the compounding of rubber blends. The sludge was first purified and different mixes containing varying concentrations of the conventional processing aid namely aromatic oil and the refinery sludge were prepared. The processability of the mixes was studied in a Brabender Plasticorder. The cure characteristics of the mixes were evaluated and the vulcanizates were tested for various physical properties and cross-link density including ageing. The processing characteristics showed that rubber blends could be processed with sludge just like the other conventional processing oils. It was found that, on complete substitution of aromatic oil with sludge, the optimum cure time reduced significantly and the tensile properties exhibited some improvement. Since sludge is a waste material from oil refineries, posing disposal problem, which is a pollutant to environment due to open dumping, its utilization as processing oil in rubber compounding can be a simple practical method of disposal in a useful manner.

Key Words: refinery sludge, processing oil, rubber blends, sulphur vulcanization, carbon black, aromatic oil

INTRODUCTION

In petroleum refineries, oily sludge accumulates in large quantities as a dumped waste. It is a mixture of bituminous hydrocarbons [1] together with clay, sand, inorganic matter, heavy metals, water, etc. The origin of this oily sludge can be:

Cleaning of crude oil, asphalt, LSHS (low sulphur heavy stock), furnace oil and intermediate storage tanks, cleaning of heavy oil spillages, and cleaning of surge ponds in waste water treatment plant, etc.

Disposal of this waste is a problem in the overall

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waste treatment management programme of refineries.

The current methods of disposal are: landfill, land farming, incineration, and bioconversion. But these methods of disposal like landfill, land farming, incineration, etc. help only for the disposal of the sludge and not for its effective utilization.

Moreover, the methods like landfill and land farming have problems like ground-water contamination, whereas, the incineration method is highly expensive, as it requires the use of support fuel and the installation of expensive flue gas scrubbing or solid removal equipment to meet air pollution regulations. The success of bioconversion depends on the choice of: (a) the right type of micro-organism, (b) the right type of biosurfactant formation, (c) the right quantity of additives, (d) the correct incubation period and (e) the right temperature profile. Even a micro-variation in any of these parameters can upset the entire operation and can render the subsequent operations ineffective.

A survey has shown [2] that this sludge contains approximately 25 % water, 5 % inorganic sediments like sand, clay, etc. and the rest 70 % hydrocarbons. The asphaltene content [2] in the hydrocarbon fraction is 7.8 %. A study carried out by the present authors [3] with this sludge showed that 17 % of lighter oil fraction can be recovered. The properties of the recovered lighter oil fraction showed that it is good enough to be used as diesel fuel by blending with other appropriate streams of petroleum refineries. The residue left after the removal of lighter oils was converted into different grades of industrial bitumen by heat treatment at temperatures ranging from 200–250 °C with $AlCl_3$ catalyst for time period ranging from 2 to 3 h.

In another study carried out by the same authors [4, 5], it was found that purified refinery sludge could function as a substitute for processing oil both in natural rubber (NR) and in styrene butadiene rubber (SBR) compounding. On the evaluation of their cure characteristics, physical properties, ageing resistance, cross-link density etc., it was found that purified refinery sludge could substitute for the conventional processing oil without much affecting the cure properties of the mixes or tensile properties of the vulcanizates.

Based on the above encouraging results obtained when purified refinery sludge was used as a processing aid, we thought it worthwhile to investigate its utility in NR/SBR blend. This study was undertaken mainly because one type of rubber may not possess all the physical properties desired and so it is a usual phenomenon that two or more rubbers are blended together [6–10].

Springer [11] reports practical information regarding processing and vulcanization of NR-SBR blends. Mastication of NR is necessary prior to blending with SBR [12]. Shundo et al., [13] have compared the use of roll mill and Banbury mixer for the preparation of NR-SBR blends, and they have found that mill mixing furnishes more uniform compounds. In the vulcanization of this blend, NR phase takes a larger share of curatives leaving the SBR phase slightly under cross-linked [14].

This necessitates more active accelerator or binary accelerator system to obtain uniform curing. In rubber compounding, the process of incorporation of filler requires a lot of power/ energy and time. Uniform distribution and dispersion of the incorporated filler and other ingredients are the key factors, which determine the quality of the product ultimately. In order to make the compounding and processing of rubber easy without affecting the desired properties of the product, processing oils are incorporated. Because of the easy availability and good compatibility with most of the general-purpose rubbers, aromatic oil is the most commonly used processing aid.

We tried the refinery sludge as processing oil in 50–50 NR-SBR blends using carbon black as filler. Varying the amounts of sludge different formulations are tried and the results are compared with those obtained for the control mix containing aromatic oil.

The variation in processing characteristics brought about by the sludge was compared with that of aromatic oil using a Brabender plasticorder. The mixes were then cured to their optimum cure times and the cure characteristics and vulcanizate properties were compared.

The cross-link density values were also assessed to correlate them with the vulcanizate properties.

EXPERIMENTAL

Natural rubber conforming to ISNR-5 and Synaprene 1502(SBR) were used for the present study. Rest of the ingredients viz. zinc oxide, stearic acid, mercapto-benzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), carbon black (HAF N330), aromatic oil, sulphur, etc. used were all of rubber grade. The sludge used for the present study was obtained from Cochin Refineries Ltd., Kochi, India.

The purification of the sludge was affected by keeping the sludge at a temperature of 100 °C for a period of 4 h with constant stirring until it is fully dehydrated. The viscous oil left behind was then passed through strainers of various sizes to remove solid contaminants. The characteristics of the purified sludge so obtained are given in Table 1.

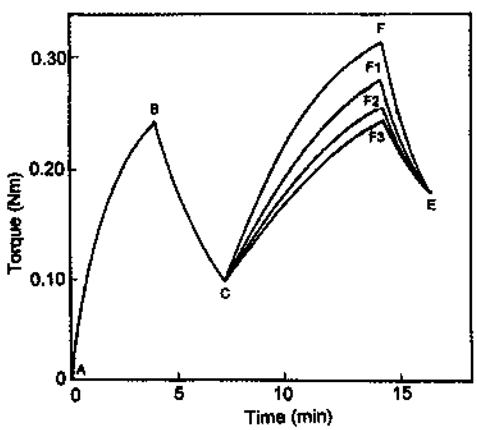
Different rubber mixes containing varying amounts of the conventional processing aid namely aromatic oil/sludge, were then prepared. The formulations of these mixes are given in Table 2. Mix A contains 5 parts of aromatic oil per-hundred-rubber (phr) and it is taken as the control. The mixes B to E contain varying percentages of aromatic oil and sludge while mix F contains 5 phr sludge as processing oil.

The processing characteristics of the different mixes were evaluated using a Brabender plasticorder (PL 3S). This torque rheometer gives a torque-time curve by measuring the torque generated during mastication. The processability of 50–50 NR/SBR blend with sludge was compared with that of aromatic oil. The rubber before feeding into the plasticorder was passed six times through a laboratory size two roll mixing mill at an opening of 0.8 mm so as to obtain a thin sheet. This was then cut into small strips and fed into the mixing chamber of the plasticorder, the mixing heads being set at 30 rpm and at 30 °C.

The total mixing time of 16 min had the following break up. Rubber mastication was completed within the first 4 minutes, activator and accelerator addition took 3 min, addition of carbon black mixed with sludge took 8 min and finally sulphur was added in the last one minute. The ingredients were added as per the formulation given in Table 2 except for the fact that the amounts of oil were varied. The same procedure was repeated for the control mixes containing aromatic oil. The torque curves obtained were recorded. An attempt was made to optimize the oil level by repeating the experiment using aromatic oil/sludge at 4, 5, 6, and 7 phr levels. It was found that the addition of aromatic oil/ sludge at 4 and 5 phr levels were not sufficient for proper mixing and comparatively higher torque values were obtained. But when these were added at 6 phr levels each, proper mixing occurred with maximum reduction in torque. There was no significant reduction in torque even when aromatic oil/sludge was added at 7

Table 1. Characteristics of purified refinery sludge.

Properties	Values
Density at 15 °C (g /mL)	0.9573
Pour point (°C)	+ 42
Wax (% wt)	6.0
Asphaltenes (% wt)	7.8
Acidity (mg KOH/g)	4.3
Flash point (°C)	>200
Kinematic viscosity CS at 100 °C	30.33
Total sulphur (% wt)	3.43



AB-NR+SBR; BC- Activator & accelerator; CF- C.black + sludge (4 phr); CF1- C.black + sludge (5 phr); CF2- C.black + sludge (6 phr); CF3- C.black+ sludge (7 phr); FE, F1E, F2E, F3E - Sulphur.

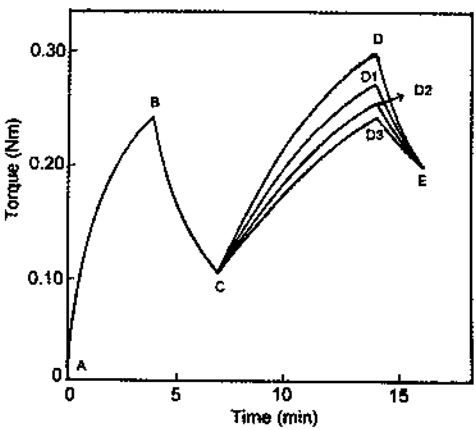
Figure 1. Brabender torque curves of mixes containing sluge.

Table 2. Formulation of the mixes.

Ingredients	A	B	C	D	E	F
NR	50	50	50	50	50	50
SBR	50	50	50	50	50	50
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Mercaptobenzthiazyl disulphide (MBTS)	1	1	1	1	1	1
Tetramethyl thiuram disulphide (TMTD)	0.5	0.5	0.5	0.5	0.5	0.5
N-1,3-dimethyl-*N'*-phenyl-*p*-phenylenediamine (Accinox HFN)	1	1	1	1	1	1
Carbon black (HAF N 330)	50	50	50	50	50	50
Aromatic oil	5	4	3	2	1	0
Sludge	0	1	2	3	4	5
Sulphur	2	2	2	2	2	2

phr levels. Hence, 6 phr of aromatic oil/ sludge can be taken as the optimum requirement (Figures 1, 2) in these carbon black filled NR / SBR blends.

Compounding was carried out in a laboratory size two-roll mill at a friction ratio of 1:1.1 as per ASTM D 3182-89. The blend was made initially and then the other additives followed in the usual order. Due to the higher shearing forces in the mixing mill compared to the plasticorder, it was found that



AB-NR+SBR; BC- Activator & accelerator; CD- C.black + aromatic oil (4 phr); CD1- C.black + aromatic oil (5 phr); CD2- C.black + aromatic oil (6 phr); CD3- C.black + aromatic oil (7 phr); DE, D1E, D2E, D3E-Sulphur.

Figure 2. Brabender torque curves of mixes containing aromatic oil.

aromatic oil/sludge at 5 phr level was enough for the proper incorporation of the filler during mill mixing compared to the plasticorder. The cure characteristics of the mixes were evaluated using Goettfert elastograph model 67.85 and the values obtained are given in Table 3.

The compounds were vulcanized up to their optimum cure time in an electrically heated laboratory type hydraulic press at 150 °C at a pressure of 140 kg/cm^2. The tensile properties of the vulcanizates were determined according to ASTM D –412-87 method A using dumb-bell specimens at 25 °C at a cross-head speed of 500 mm/min with a Zwick universal testing machine. Ageing resistance was determined as per ASTM D 573-88 by maintaining the samples at 100 °C for 48 h in an air oven and then measuring the retention in the tensile properties. The tensile properties evaluated are reported in Table 4. Tear resistance was tested as per ASTM D 624-86 using angular test pieces. Hardness of the vulcanizates was determined according to ASTM D 2240-86 and expressed in Shore-A units.

Compression set was determined as per ASTM D 395-89 (method B) and abrasion resistance was evaluated using DIN abrader (DIN 53516). All these results are reported in Table 5. The overall cross-link density of the vulcanizates was determined from the equilibrium swelling data as follows: samples of approximately 0.3 g were cut from the central portion of the vulcanizate and allowed to swell in toluene for

24 h. The outer portions of the swollen samples were dried using a filter paper and weighed.

The swollen sample was placed inside the oven at 60 °C for 24 h to remove solvent. The deswollen weight was determined. The volume fraction of rubber, V_r, in the swollen network was then calculated as is well known from the literature [15]. From the value of V_r the total chemical cross-link density $½M_c$ was then calculated using the Flory-Rehner equation [16]. V_r in filled vulcanizates is calculated assuming that the filler does not swell. It is then converted to V_{r0} (the value V_r would have had in the absence of filler) according to Cunneen and Russel [17]:

$$\frac{V_{r0}}{V_r} = ae^{-z} + b$$

where: a and b are constants characteristic of the system and z is the weight fraction of the filler in the vulcanizate. The values for "a" and "b" for HAF black filled systems are; a=0.56 and b=0.44. The values of V_{r0} were then substituted in the Flory-Rehner equation in place of V_r to obtain the cross-link

Table 3. Cure characteristics of the mixes.

Mix No.	Optimum cure time t_{90} (min)	Scorch time t_{10} (min)	Induction time (h)	Cure rate index	Maximum torque (Nm)	Minimum torque (Nm)
A	7.3	2.3	1.2	20.0	0.50	0.03
B	8.5	2.2	1.6	15.9	0.56	0.03
C	8.8	2.6	1.6	16.1	0.43	0.02
D	7.8	2.6	1.6	19.2	0.61	0.04
E	6.7	2.2	1.8	22.2	0.66	0.04
F	5.5	1.9	1.6	27.8	0.73	0.05

Table 4. Tensile properties of the various vulcanizates.

Mix No.	Tensile strength (MPa)			Elongation at break (%)			Modulus 100% (MPa)		
	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)	Before ageing	After ageing	Retention (%)
A	18.70	11.17	59.73	442.5	198.5	44.85	4.29	7.21	168.07
B	18.78	11.18	59.53	440.2	198.4	45.06	4.48	7.32	163.39
C	18.80	11.28	60.00	431.3	196.0	45.46	4.50	7.50	166.67
D	18.98	11.30	59.54	420.9	195.4	46.42	4.55	7.59	166.81
E	19.06	11.38	59.71	418.9	190.1	45.38	4.62	7.86	170.13
F	19.02	11.36	59.72	419.0	190.3	45.41	4.60	7.82	170.00

Table 5. Other physical properties evaluated.

Mix No.	Tear strength (N/mm)	Hardness (Shore A)	Compression set (%)	Abrasion loss (cm^3/h)	Total cross-link density x10^5 (g mol/cm^3)
A	68.2	63	21.4	3.99	8.26
B	68.3	63	21.4	3.90	8.28
C	70.2	64	21.3	3.88	8.36
D	71.1	64	21.2	3.78	8.42
E	71.8	64	21.0	3.76	8.49
F	72.0	64	21.0	3.78	8.48

density ½M_c.

RESULTS AND DISCUSSION

Processability

The processing characteristics of purified refinery sludge were compared with those of aromatic oil in NR/SBR carbon black filled systems using the Brabender Plasticorder. From the different trials made, it was found that 6 phr of aromatic oil / sludge was the optimum level to be used in this plasticorder.

Mixes containing sludge showed slightly higher torque values than those containing aromatic oil (Figures 1 and 2). During mill mixing the optimum levels required in both cases was found to be only 5 phr. This can be attributed to the higher shearing forces encountered in the mixing mill compared to the plasticorder. Based on these processing characteristics and also on the cure and vulcanizate properties, reported in the subsequent sections, it is evident that refinery sludge can be effectively used as a processing aid in the various NR/SBR blends under review.

Cure Characteristics

The cure characteristics are given in Table 3. The cure curves of the compounds show no reversion tendency showing that the presence of SBR has given good reversion resistance to the blends. There is only little variation in the scorch time and induction time when sludge is incorporated in place of aromatic oil. It is noted that the introduction of sludge in the mix up to 40 % (mix C) has no acceleration effect on cure.

However, when sludge is used above this level substantial acceleration of cure is noted as indicated by the reduction of optimum cure time. Cure rate index also increases significantly on total substitution of aromatic oil with sludge. The maximum torque,

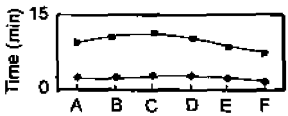


Figure 3. Optimum cure time (t_{90}) and scorch time (t_{10}) of vulcanizates.

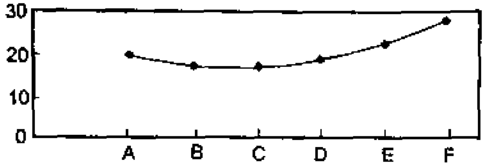


Figure 4. Cure rate index of vulcanizates.

increases steadily with the increase in concentration of sludge, with the exception of the mix C. The increaseed vulcanization rate obtained on total substitution by sludge may be attributed to the presence of sulphur and nitrogen compounds present in the residual portion of petroleum fraction.

Other cure characteristics of the blends show more of NR behaviour than of a synthetic rubber. This might be because a major share of the curatives has moved to the NR phase. The results obtained show that purified refinery sludge can be used as processing oil just like any other conventional processing aids in the rubber blends studied. The reduction in cure time on total substitution by sludge is a point of advantage (Figures 3 and 4).

Cross-link Density

The total cross-link density values of the different blends were evaluated and the results are given in Table 5. It is found that the cross-link density values increase from blend A to E, minimum being exhibited by blend A containing 5 phr aromatic oil. Tensile and tear strength also exhibited an increasing trend when aromatic oil was substituted with more quantities of purified sludge. This can be attributed to the better interaction between rubber and filler in those mixes. The mixes E and F containing 4 and 5 phr sludge gave almost identical cross-link density values showing that substitution of aromatic oil with sludge beyond 4 phr brings little effect.

Tensile and Other Physical Properties

Table 4 gives the tensile properties of the vulcanized samples. In these systems of under review it can be seen that there is an increase in modulus and tensile strength and a corresponding decrease in elongation at

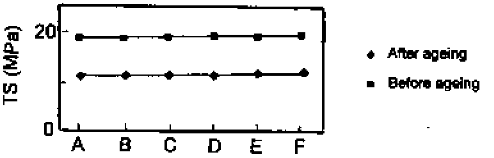


Figure 5. Tensile strength of vulcanizates.

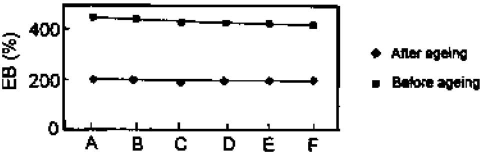


Figure 6. Elongation at break of vulcanizates.

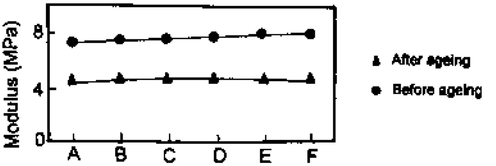


Figure 7. Modulus (100 %) of vulcanizates.

break from mix A to E. This is also in accordance with the change in the cross-link density values observed. Mixes E and F gave almost identical values for initial tensile strength. Heat ageing resistance of the vulcanizates give comparable results in tensile strength compared with that of the control mix (Figures 5–7).

The other physical properties evaluated are tear strength, compression set, hardness, and abrasion loss. These results are given in Table 5. Tear strength values are seen to increase from blend A to F,

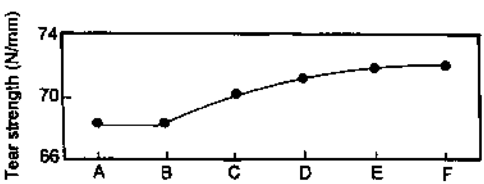


Figure 8. Tear strength of vulcanizates.

maximum being exhibited by mix F containing 5 phr sludge and the minimum by mix A containing 5 phr aromatic oil. The increase is found to be proportional to the sludge content of the mixes (Figure 8). Hardness, compression set and abrasion loss were found to be more or less same for blends containing aromatic oil and refinery sludge.

CONCLUSION

The results obtained in the above investigation show that the sludge obtained from petroleum refineries can be effectively used as a processing aid in the sulphur vulcanization of NR/SBR blends. Evaluations of the processing characteristics show that these blends can be processed with sludge just like the conventional processing oil namely aromatic oil. It is found that the use of sludge does not adversely affect either the cure characteristics of the mixes or the physical properties of the vulcanizates. The optimum cure time of the mixes was found to be reasonably reduced by the incorporation of sludge. Some improvement was also noticed in properties like tensile strength and tear strength in vulcanizates containing sludge compared to that of aromatic oil.

It is to be noted that this way of utilization of refinery sludge not only gives rise to a value added product but also helps to dispose this hazardous waste in a useful and eco-friendly manner. Again conventional processing oils currently used in rubber are becoming prohibitively costly ($ 560/t.) while sludge is a dumped waste of the refinery. The cost of purification amounts only $ 11.1/t. of which $ 6.0 is required for power and labour and the remaining $ 5.1 for steam. About 0.4 t. steam is required to purify one-ton sludge.

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