A Study on the Use of Castor Oil as Plasticizer in Natural Rubber Compounds

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ABSTRACT

Mechanical properties and thermal degradation of natural rubber compounds containing castor oil were studied to evaluate its suitability as plasticizer. Naphthenic oil was used as a reference plasticizer. The cure time was marginally lower in the case of castor oil mixes, probably due to the presence of free fatty acids in it. The tear strength and modulus were better in the case of mixes containing castor oil, while most of the other mechanical properties were comparable to the mixes containing naphthenic oil. The heat build up and compression set were higher than that of the naphthenic oil mixes. Thermal studies showed an increase of 8 °C in the temperature of initiation of degradation and an increase of 6 °C in the temperature at which the peak rate of degradation occurred. The peak rate of degradation was comparable to that of the reference compound

INTRODUCTION

Plasticizers are low molecular weight non–volatile substances added to a polymer to improve flexibility and processability. Even small quantities of plasticizer markedly reduce the T_g of the polymer. This effect is due to the reduction in cohesive forces between polymer chains. Plasticizer molecules penetrate into the polymer matrix and act as lubricant between polymer chains, thereby reducing the glass transition temperature.

Plasticizers are also used to get better filler dispersion. They also help in controlling the viscosity to desired levels. Generally used plasticizers include

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mineral oils, synthetic esters and some of the natural products such as wood rosin and animal glue(1). Of these the petroleum-based oils are being used quite extensively in rubber compounds. The fast depleting petroleum resources call for exploration of alternative materials. The vegetable oils are 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 acid can be advantageous in rubber compounds.

H.J Richtler used vegetable oils, especially drying oils and their derivatives have occasionally been used as additives in plastics and elastomers. Vulcanized vegetable oil (factice) was used in elastomers for low temperature flexibility and low hardness(2). Epoxidized linseed oil was used as a vulcanizing agent in carboxylated nitrile rubber - ionomer blends(3). Linseed oil as such was used as a multipurpose additive in NBR to improve its mechanical properties and processability and to reduce cure time(4). Soya bean oil was used as a plasticizer in natural rubber (NR)(5) and as a plasticizing agent in cold vulcanized rubber(6). Blown soya bean oil was used as a plasticizer in ester gums(7).

Epoxidised rubber seed oil was reported to be used as less leachable plasticizer in NBR, which imparts better abrasion resistance to the vulcanizates(8). It was also used as a secondary plasticizer and heat stabiliser for PVC(9). Kuriakose *et al.* reported the use of rice bran oil as a multipurpose ingredient in the compounding of SBR, and found that the cure characteristics of the compound and the physical and mechanical properties of the vulcanizates were comparable with the mixes containing conventional plasticizer(10). Vegetable oils in general were used as coupling agent for improvement of filler-rubber interaction in carbon black reinforced rubber(11).

Castor oil has been used as a plasticizer in nitrocellulose(12) in polystyrene films(13), in rubber containing acrylonitrile and styrene(14). Lima *et al.* substituted dehydrated castor oil for DOP in NBR(15). They reported increased plasticizing efficiency without affecting the physiochemical properties and ageing resistance. Ashraf *et al.* reported the improvement of physical and mechanical properties of PMMA by blending with dehydrated castor oil(16).

In the present study we have used castor oil as plasticizer in a typical natural rubber compound containing 45 phr of carbon black. Mechanical properties and thermal characteristics of these compounds were compared with that of the control compound containing naphthenic oil.

EXPERIMENTAL

Raw Materials

Natural rubber (ISNR5) was obtained from 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.

Mercaptobenzthiazyldisulphide (MBTS) and tetramethylthiuramdisulphide (TMTD) were supplied by Bayer Chemicals, Mumbai and Polyolefins Industries Ltd., Mumbai, respectively. Sulfur 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, Viscosity Gravity Constant 0.87.

Castor oil used was of commercial grade obtained from local market. Castor oil is a colourless oil with a comparatively higher viscosity. A major portion of fatty acid present is recinoleic acid (12-hydroxyoctadeca-9-enoic acid), which gives the oil a higher viscosity. The fatty acid composition is palmitic 2%, stearic 2%, oleic 5%, linoleic 7%, linolenic 2% and recinoleic 82%.

Processing

Formulation of the mixes is given in Table 1.

Table 1. Formulation

	MIX NUMBER										
Ingredients	**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
Castor oil	0	2	4	6	8	10	-	-	-	-	-
Naphthenic oil	-	-	-	-	-	-	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

Mixes were prepared on a laboratory size two roll mixing mill (16 cm x 33 cm) at a friction ratio of 1:1.25 as per procedure given in ASTM D 3184 – 89 (2001) over a time period of 18 min.

Cure characteristics at 150 °C were determined by using Goettfert Elastograph Model 67.85.

Tensile and tear strengths were measured according to ASTM D 412 and ASTM D 624, respectively using 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 having dimensions of 12 mm diameter and a minimum thickness of 6 mm were used. A load of 12.5 N was applied and the readings were taken 10 s after the indentor made a firm contact with the specimen.

The flex resistances of the vulcanizates 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 continued 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.

$$V= \frac{\Delta M \times 27.27}{\rho} \qquad (1)$$

where V= abrasion loss in cm^3/hr, 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 kept constant at 50 °C. The stroke was adjusted to 4.45 mm and the load to 10.05 kg/cm^2.

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.

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

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.

Thermal Analysis

Thermogravimetric analysis of the specimens were carried out on TGA Q50, TA Instruments with a heating rate of 20 °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.

RESULTS AND DISCUSSION

Table 2 gives the cure characteristics of different mixes. Minimum torque (T_{min}) is found to remain constant for castor oil as in the case of naphthenic oil mixes. Maximum torque (T_{max}) is reduced gradually up to 8 phr and at 10 phr there is a significant reduction. The lower (T_{max}-T_{min}) indicates lower crosslink density at higher loading of castor oil. This behaviour is similar to that of mixes containing naphthenic oil (Mixes N_2–N_{10}). The lower extent of crosslink is also evident from the crosslink density values given in Table 3. Both the scorch time and cure time remain unaffected by the oil loadings. The cure time of the castor oil mixes is marginally lower than that of the mixes

Table 2. Cure characteristics of the mixes

Mix no.	Max. torque (Nm)	Min torque (Nm)	Cure time (t_{90}) (min)	Scorch time (t_{10}) (min)	Tmax-min (Nm)	Cure rate (Nm/min)
C_0	0.43	0.02	3.8	1.7	0.41	0.25
C_2	0.41	0.02	3.9	1.7	0.39	0.23
C_4	0.43	0.02	3.7	1.8	0.41	0.25
C_6	0.40	0.02	3.9	1.8	0.38	0.22
C_8	0.38	0.02	3.7	1.9	0.36	0.23
C_{10}	0.32	0.02	3.8	1.8	0.31	0.19
N_2	0.42	0.02	4.1	1.9	0.39	0.22
N_4	0.41	0.02	4.0	1.9	0.40	0.23
N_6	0.41	0.02	3.8	1.8	0.39	0.24
N_8	0.38	0.02	4.1	1.9	0.36	0.20
N_{10}	0.34	0.02	4.1	2.0	0.32	0.19

Table 3. The mechanical properties

Mix No	Hardness (Shore A)	Compression Set (%)	Resilience (%)	Abrasion loss (cm^3/hr)	Crosslink density x 10^5 (gm moles/cm^3)	Flex cracking (millons of cycles)	Heat build up (°C)
C_0	52	43	36	3.1	4.1	> 0.5	22
C_2	50	36	38	4.3	4.0	>0. 5	25
C_4	50	30	37	4.1	3.9	>0. 5	23
C_6	49	38	35	4.0	3.6	>0. 5	28
C_8	48	36	35	4.5	3.4	>0. 5	22
C_{10}	48	42	35	4.9	3.3	>0. 5	27
N_2	64	31	35	4.8	4.4	>0. 5	12
N_4	63	28	36	4.5	4.2	>0. 5	14
N_6	62	29	38	4.4	4.0	>0. 5	15
N_8	60	32	42	4.7	4.0	>0. 5	13
N_{10}	58	27	44	4.8	3.9	>0. 5	15

containing naphthenic oil. This in agreement with the higher cure rates of castor oil mixes. The improved rate of cure reaction may be attributed to the presence of natural fatty acids in the castor oil.

Figure 1 shows the variation in tensile strength of the vulcanizate with different loading of castor oil. Castor oil mixes show lower tensile strength at all oil loading. This may be attributed to relatively lower crosslink density and improper dispersion of filler in the presence of castor oil. Due to the difference in polarity of the NR and the castor oil the plasticization becomes less efficient, resulting in improper dispersion of filler. In a homogeneously dispersed matrix the crack propagation is very much hindered and hence the ultimate strength is higher. This is also evident from the SEM studies.

Figures 2a and 2b give the SEM photomicrographs of the broken surface of tensile test specimens containing 4 phr of castor oil and naphthenic oil, respectively. In the case of castor oil mix major crack paths are visible. This suggests that multiple cracks are initiated from different location and they propagate across the bulk, resulting in premature fracture. In the case of naphthenic oil mix, the crack pattern is different with no major crack paths. The presence of multiple minor cracks that do not propagate across the surface suggests a restricted crack propagation. This is in agreement with the observed higher tensile strength of the naphthenic oil mixes. The difference in the fracture modes may be arising from the difference in the crosslink densities of the two sets of mixes.

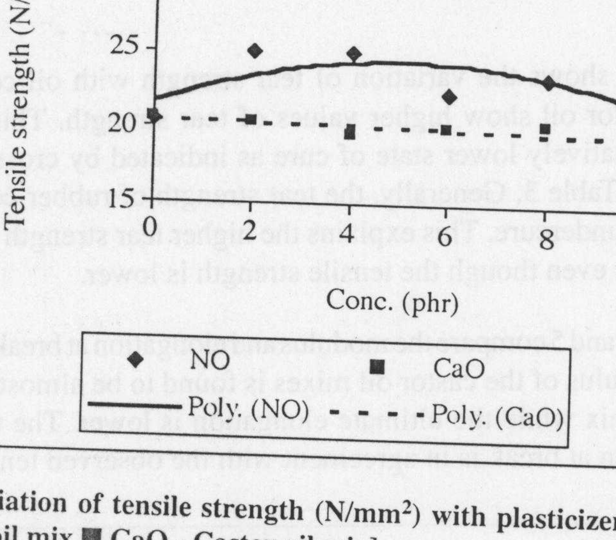
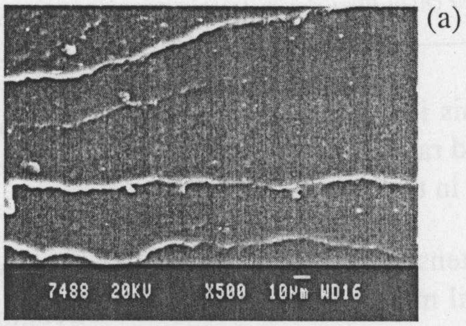


Figure 1. Variation of tensile strength (N/mm^2) with plasticizer content [◆NO -Naphthenic oil mix ■ CaO - Castor oil mix]



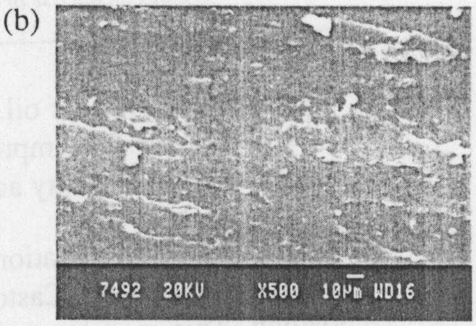


Figure 2a. SEM photomicrograph of castor oil mix at (4 phr) concentration

Figure 2b. SEM photomicrograph of naphthenic oil mix at (4 phr) concentration

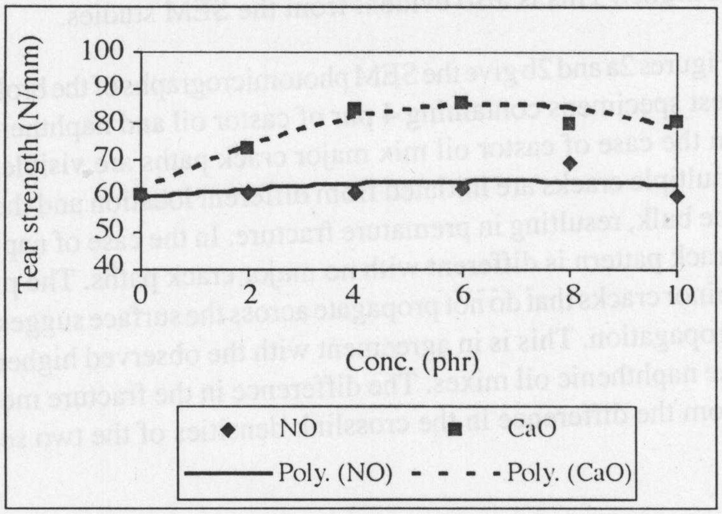


Figure 3. Variation of tear strength (N/mm) with plasticizer content [◆NO - Naphthenic oil mix ■ CaO - Castor oil mix]

Figure 3 shows the variation of tear strength with oil content. Compounds with castor oil show higher values of tear strength. This may be attributed to the relatively lower state of cure as indicated by crosslink density values given in Table 3. Generally, the tear strength of rubber compounds is higher at slight undercure. This explains the higher tear strength values of the castor oil mixes even though the tensile strength is lower.

Figures 4 and 5 compare the modulus and elongation at break of the vulcanizates. The modulus of the castor oil mixes is found to be almost equal to that of the control mix while the ultimate elongation is lower. The trend in the case of elongation at break is in agreement with the observed tensile values.

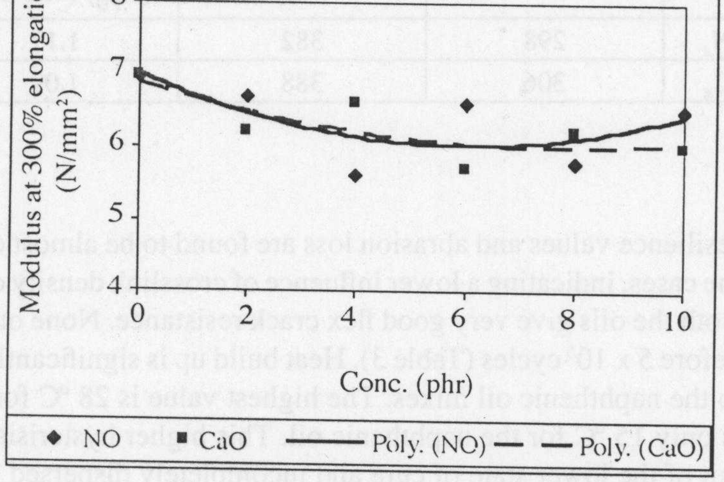


Figure 4. Variation of modulus at 300% elongation (N/mm^2)with plasticizer content [◆NO - Naphthenic oil mix ■ CaO - Castor oil mix]

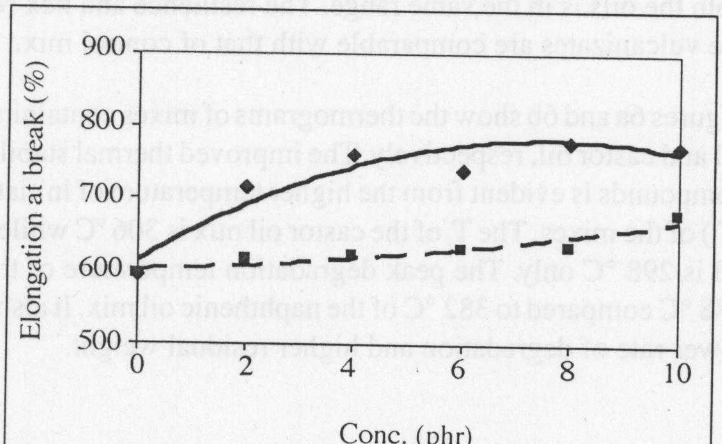


Figure 5. Variation of elongation at break (%)with plasticizer content [◆NO - Naphthenic oil mix]

Table 3 compares the hardness, compression set, resilience, abrasion loss, flex crack resistance, cross link density and heat build up of the vulcanizates with that of control mix containing naphthenic oil. The castor oil mixes are found to have lower hardness and higher compression set values compared to the mixes containing naphthenic oil. This again may be arising from the lower crosslink density of castor oil mixes and improper filler dispersion. The

Table 4. Degradation characteristics of mixes

Mix	Temperature of initiation (Ti)	Peak degradation temperature (T_{PD}) (°C)	Peak rate of decomposition (R_{PD}) (% / min)	Residue at 600 °C (%)
N_4	298	382	1.17	29.6
C_4	306	388	1.09	31.6

resilience values and abrasion loss are found to be almost comparable in both the cases, indicating a lower influence of crosslink density on these properties. Both the oils give very good flex crack resistance. None of the samples failed before 5 x 10^5 cycles (Table 3). Heat build up is significantly higher compared to the naphthenic oil mixes. The highest value is 28 ºC for castor oil while it is only 15 ºC for the naphthenic oil. This higher hysterisis loss may be a fall out of the lower state of cure and incompletely dispersed filler aggregates of these mixes. The break down of the filler structure during cyclic loading is a major source of energy loss. The observed higher compression set of these mixes is agreement with the higher heat build up values. The abrasion loss of both the oils is in the same range. The resilience and flex resistance values of the vulcanizates are comparable with that of control mix.

Figures 6a and 6b show the thermograms of mixes containing 4 phr naphthenic oil and castor oil, respectively. The improved thermal stability of the castor oil compounds is evident from the higher temperature of initiation of degradation (T_i) of the mixes. The T_i of the castor oil mix is 306 ºC while that of naphthenic oil is 298 °C only. The peak degradation temperature of the castor oil mix is 388 °C compared to 382 °C of the naphthenic oil mix. It also shows a relatively lower rate of degradation and higher residual weight.

CONCLUSION

The study shows that castor oil is a potential substitute for naphthenic oil as plasticizer in natural rubber compounds even though all properties are not equivalent. The castor oil improves the modulus, tear strength and thermal stability of the natural rubber vulcanizates. The resilience and abrasion loss are comparable to that of the naphthenic oil mixes. The heat build up and compression set are, however higher than that of the naphthenic oil mixes. The optimum loading of castor oil is 2 to 4 phr for 45 phr HAF black loaded natural rubber samples.

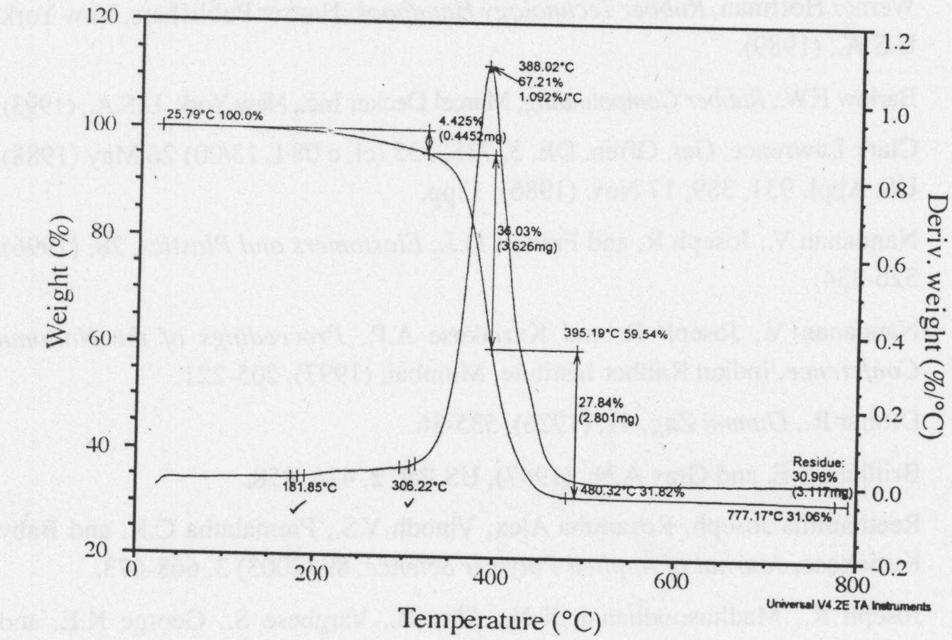


Figure 6a. Thermogravimetric curve of mix with (4 phr) castor oil

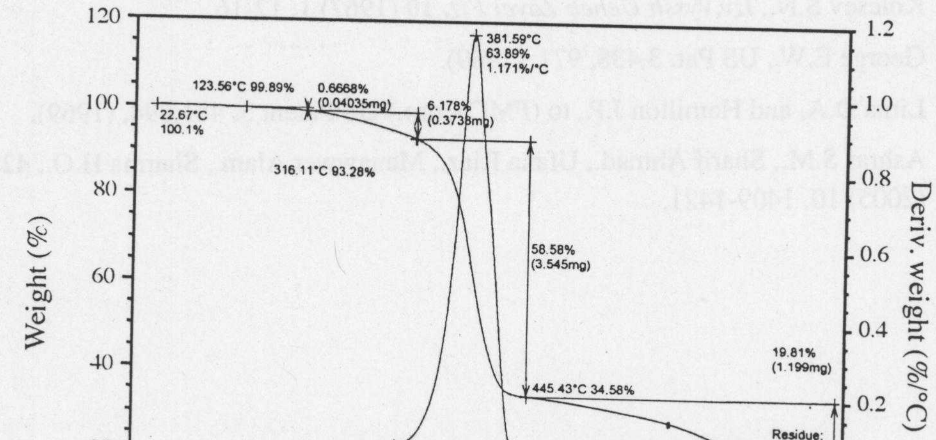


Figure 6b. Thermogravimetric curve of mix with (4 phr) naphthenic oil

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