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Development of oil, freeze, high temperature resistant and flame retardant rubber compounds for high performance hydrolic hose

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Abstract

The high performance hydrolic rubber hose should resist to hydrolic oils and can run at temperature interval from –55 ^{0}C to 150 ^{0}C. In addition to these properties, for some areas such as mining should also be flame retardant. In this study, compound formulations having properties mentioned above were developped, mechanical properties, hydrolic oil and low, high temperature resistance performances were measured. Flame retardant tests were also been performed. Hoses were built using these newely developped compounds and then their burst tests were performed. The best performer compound for low temeperature performance hose was the one prepared with the blends of acrylonitrile butadiene (NBR), stirene-butadiene (SBR) and cis-butadiene (CBR) rubbers along with plasticizer diisononylphthalate (DINP). One of the compounds preapared with the blending of SBR, NBR rubbers, aluminium hydroxide $Al(OH)_3$, tricrezyl phoshate (TCP) and zinc borate was the best for the flame retardant hose. The best performer high temeperature resistant compound was preapred using MT N990 carbonblack and plasticizer paraplex G50 with blending of SBR 1502, NBR 2860 and NBR 3360 rubbers.

Key words: rubber compound, hose, low temperature resistance, flame retardant

1. INTRODUCTION

Hydrolic hose is designed to convey hydraulic fluid to hydrolic components such as valve, pump, actuator and reservoir and used in a wide range of hydraulic systems. It is often flexible, reinforced and usually constructed with several layers of reinforcements so that to withstand high pressure. They are capable of bending and flexing easily and must be capable of withstanding the vibrations and absorbing the shocks in the systems. There are high demand for hydraulic rubber hose in the market of construction, industrial and agriculture sectors. The another considerable factor driving the market is automotive industry.

A hydraulic hose is a type of hose made from synthetic rubber, or thermoplastic material. It is used to carry fluid which transmits force within the hydraulic machinery. These hoses are composed of a number of different layers, namely inner layer, reinforcement layer and outer layer that protects the hose from abrasion and outside conditions such as weather and other chemicals or oil. There are many other requirements, such as anti-static, flame-resistant and integral end-connections for hydraulic applications. Inner layer comes into dirtect contact with the fluid and made of synthetic rubber or thermoplastics. The crucial requirements of inner layer is that it must have flexibility and it must have the compatibility with a broad range of fluids. It must also resist to extreme temperatures. Reinforcement layer is a textile or wire cord that waraps the inner layer and provide the hose the necessary strength to resist both high internal pressure and external forces. It also prevent premature hose bursts. A hose designed for low working pressures uses textile fiber reinforcement; while ones designed for higher working pressures uses high-strength steel wire. Steel-reinforced hoses can be broken down in two categories; braided and spiral. In braided hose, wire wounds the inner layer and this type of hoses withstand to medium to high working pressures up to 400 bars. It is more flexible than the spiral hose and allows tighter band radius. The spiral hose has high tensile steel wire spiraled around the inner layer and successive layers laid at opposite angles in order to balance pressure. Spiral hoses are used for very high working pressures. Outer layer protects the inner layer and reinforcement layer from the cold, heat, abrassion and corrosion, ozon and UV light. Outer layer stripts is made from synthetic rubber and should not be allowed to rub against any other body.

Hydraulic hoses are clasified in terms of their sizes, pressure ratings, materials of construction and working temperature ranges. The important specifications of a hose include its inside diameter, wall thickness, minimum band radius and pressure ratings [1-2]. The demands for hoses are increasing, that is, the various requirements in high performance environments are being examined; such as very high pressure, extreme low and high temperatures, agressive fluids, abrasion resistance, service lifetime, offshore conditions. The standard hose is required to work at temperature interval from -40 ^{0}C to 100 ^{0}C. High performance hydraulic hose is ment that the hose is capable to withstand the following working conditions: very high inside working pressure up to 4000 bar (4000 MPa), very low temperature down to –55 ^{0}C and high temperature up to 150 ^{0}C. Aggressive fluids include some synthetic hydraulic fluids. Another important factor required for high performance hose is flame retardance property. For long service lifetime, hoses are been impulse tested to in excess of seven million cycles without failure [3]. Inner layer hose compound must have the compatibility with hydraulic oil which comes into direct contact. The compatibility depands on the chemical nature of fluid that is going to be used in a particular service. Aniline which is a polar aromatic liquid is used to measure the polarity of an oil or lubricant to be used in service. The temperature at which equal volumes of aniline and oil or lubricant are completely miscible is defined aniline point. The aniline point of a petrol-based fluid depends on its aromatic content. The higher the aromatic content the higher the aniline point [4]. The compatibilitty of inner layer compound is determined by degree of polarity of its rubber. The compatibility of rubbers having high polarity like nitrile rubber is better for fluid that of aniline point is low. The nitrile rubber swells less in oils having high aniline point. On the other hand, the swelling effect of the same oil is higher on compounds consist of low polarity rubbers such as natural rubber and stirene-butadiene rubber [5-6].

The indispensable rubber of inner layer compound of a rubber hose is nitrile rubber (NBR) which is copolymer of acrylonitrile (ACN) and butadiene, due to its high polarity. Despite its excelent non-swelling behaviour in petroleum based oils, low temperature resistance is low, because it is brittle in the temeperatures below -40 ^{0}C. Rubber blending with the other polar and low glass transition temeprature (Tg) rubber is a way to overcome this drawback of nitrile rubber [7-8-9-10-11]. Rubber compounds are inherently flamable due to most of its ingredients such as rubber, carbonblack and chemicals. In order to improve fire resistance of a hose, outer layer compound must be formulated by adding some flame retardants such as aluminium hydroxide, phosphate esters, zinc borate and so on [12-13-14]. When a high performance hose compound is developped, besides flame retardance, low temperature and oil resistance, mechanical performance, abrasion resistance and durability requirements should be met.

In this study, novel high performance hose compounds were developped with blending high polarity acrylonitrile butadiene (NBR) and stirene-butadien (SBR) and cis-polybutadiene rubbers (BR). For flame retardance; aluminium hydroxide $Al(OH)_3$, zinc borate ($ZnBO_3$), and tricresyl phosphate (TCP) are used. Tensile properties, abrasion resistance and oil swelling properties, flame retandance of developped compounds were measured. Impuls tests which were indicator of indurance, low temeperature resistance, ozone resistance, flame resistance of hoses built from these compounds were performed.

2. MATERIALS AND METHODS

2.1. Materials

All materils used at this study were commercially available and were used without further purification. The Table 1 shows the list of materials and sources.

Table 1. Materials and suppliers

Material	Supplier
Acrylonitrile butadiene rubber (NBR 2860)	Polimeri Europa
Acrylonitrile butadiene rubber (NBR3380)	Polimeri Europa
Styrene-butadiene rubber (SBR)	Togliatti
Cis butadiene rubber (CBR 1203)	Voranesh
Plasticizer, tricresyl phosphate (TCP)	KLJ Organic Ltd
SRF N 772	Alexandria
FEFN 550 carbonblack	Alexandria
MTN 990 carbonblack	Alexandria
Ultrasil VN -3	Degussa
Kaolen	Ags (France)
Alüminium hydroxide	Europe Minerals (Holland)
Stearic acid	Pt Musim Mass
Zinc oxide	Metal Oksit
Rubber maker sulphur	Flexis
Accelerator, CBS	Flexis
Antiozonant 6 IPPD	Flexis
Antioxidant TMQ	Flexis
Zinc Borate	Metal Oksit

2.2. Compound mixing

Three groups of compound were mixed; low temperature resistant (LTR), flame retardant (FR) and high temperature resistant (HTR). LTR group of compounds were 11 formulations based on rubber ratios as shown on the Table 2 while DINP changes from13 Phr to 15, carbonblack from 97 to 115, Aluminium from 49 to 55 respectively.

Table2. Rubber, carbonblack and oil ratios of LTR group of formulations in Phr

	NBR 860	NBR 3380	SBR 1502	CBR 1203	SRF77	Kaolen	DINP
Formulation			Phr*				
LTR1	48	40	12	0	97	49	13
LTR2	48	40	12	0	97	59	15
LTR3	48	40	12	0	115	55	15
LTR4	48	38	14	0	115	55	15
LTR5	48	40	12	0	115	55	16
LTR6	48	38	14	0	115	55	15
LTR7	48	34	18	0	115	55	15
LTR8	48	40	0	12	115	55	15
LTR9	48	38	0	14	115	55	15
LTR10	48	38	14	0	115	55	15
LTR11	48	37	15	0	115	55	17

*Phr: parts per hundreads rubber

Table 3. The formulation used for LTR group of compounds

Ingredient	Phr
Group LTR rubber (see table)	100
Carbonblack (see table)	
Kaolen (see table)	
Stearic acid	1
Softener	5.5
Resine	7.5
Zinc oxide	7.90
IPPD	1
TMQ	1
Sulfur	3.7
MBS	2.28

Compounds were mixed with two stages; masterbatch mixing was caried out using laboratory banbury mixer of 260 cm^3 capacity (Midgate, David Bridge) and final mix was done at laboratry mill. Setting of masterbatch mixing were 90 ^{0}C with temperature control unit, rotor speed at 40 rpm and ram pressure 3.5 kg/cm^2.

Table 4. Rubber, carbonblack and oil ratios of FR group of formulations

	SBR1 502	NBR 3380	CR	FEFN550	SILICA	$Al(OH)_3$	DINP	TCP
Formulation				Phr				
FR1	22	78	0	30	44	22	0	16
FR2	78	22	0	75		22	18	0
FR3	78	22	0	75		22	0	15
FR4	78	22	0	75		40	0	15
FR5	40	15	45	75		22	0	15
FR6	78	22	0	75		55	0	15
FR7	40	15	45	75		40	0	15
FR8	78	0	22	55	20	55	0	10

Table 5. Carbonblack and oil ratios of HR group of compounds

	SBR 1502	NBR 2860	NBR 3360	SRF N 772	MT N990	PARAPLEX G50
Formulation			Phr			
HR1	12	48	40	110		10
HR2	12	48	40		100	12

Table 6. The formulation used for Group HR compounds

Ingredient	phr
Group LTR rubber (see table)	100
Carbonblack (see table)	
Kaolen	60
Zinc Borate	11
Stearic acid	1
Softener	10.9
Resine	7.5
Zinc oxide	8.0
IPPD	1
TMQ	1
Sulfur	3.7
MBS	2.28

Rubbers, chemicals fillers were charged at start and carbonblack and and oil at 15th second. Maximum drop temperature was 105-115 ^{0}C. Sheeted out masterbatches at laborotory two roll mill were aged 6 hrs and then final stage mixing were done at two- roll mill by adding sulfur and accelerator. Hoses were built, impuls, britillness and flame tests were done at Bezek Hortum plant.

2.3. Physical properties

Steam heated hydrolic curing press with compressing molding was used for curing the green rubber compounds. The molding conditions were: 150 ^{0}C and 18 minutes. Alpha tensometer 2000 was used for tensile properties.

Hardness was measured with shore A durometer. ASTM 471 test procedure was employed for oil resistance. ASTM oil No 1, analytical and precision balance with density kit were used. Flame resistance tests were carried out according to ASTM D 5048 test method.

2.4. Hydraulic pressure impulse tests

High performance hydraulic hoses which are used on a fluid power operated equipments, such as heavy duty truck and erath- moving machines, provide a flexible connection between moving parts of hydraulic units. Such hoses include a polimeric inner tube on which successive layers of reinforcing material, mostly wire, are concentrically applied to contain the radial and axial pressures developped within the inner tube. High burst strength and long term fatigue resistance are required for many applications. Impulse test is used to measure the durability of a hose [15-16]. Hose tested according to ISO 6803:1994, should withstand the number of impulse cycles without failure and exibits no evidence of leakage during the subsquent cold-start evaluation.

Standard hose should withstand 250.000 cycles when tested using an oil temperature of 100 ^{0}C at 87 bar maximum continious working pressure. 150.000 cycles are required for 150 ^{0}C for high performance hoses.

Pressure – application apparatus, Bimal brand, I-701 model, capable of applying an internal pulsating pressure to test piece at a rate of 1 Hz+/-0,25 Hz using a hydraulic fluid circulating through the test hose, while the fluid is mainatained at the temeperatures 100 ^{0}C and 150 ^{0}C was used. 300 bar pressure was applied. The apparatus has graphical recorder, digital storage facility, capable of measuring the pressure cycle, The recorder has a natural frequency of more than 250 Hz. ISO VG 32 test fluid is used and circulated at arate sufficient to maintain a unifom fluid temperature within the hose assemblies. The connection of the hoses in the impuls test equipment is shown in Figure 1.

Figure 1. The connection of hoses in the impuls test cabinet

2.5. Low temperature test

ASTM D 380-94 test procedure was followed for low temperature test. The hoses were conditioned in a straight position for 72 hours at –40 ^{0}C for standard hose and –40 ^{0}C. For conditioning, Arctiko model, ULTF 320 series ultra low temperature freezer with temperature range -80/-40 ^{0}C was used. The hose was bent around a mandrel whose radius is equal to the minimum bend radius. The hose was examined for fracture or visible cracks.

2.6. Flame test

The flame test was carried out according to ASTP 5007 version: 2010-02-12 issued by Mine, Safety and Health Administration (MSHA)'s Standard Flame Test Procedure (STP) for Hose, and Other Materials: Title 30, Code of Federal Regulations, Part 18, Section 8.65.A flame test aparatus was used. The principal parts of the test apparatus are a cabinet with a transparent access door, air flow nozzle, fume exhaust system, specimen holder, Pittsburgh-Universal Bunsen burner, burner placement guide and a mirror. A hose part with15 cm of length was used. Hose was exposed to flame for one minute and then retracted. Duration of afterglow time was recorded by stopwatch.

2.7. Oil swelling test

For oil resistance, ASTM D 471- 06 test procedure was used for oil swelling behaviour. IRM 903 reference oil, analytical and precision balance with density kit, (Mettler Toledo AB204-S) were used to measure volume change.

The following equation was used to measure volume change of compound due to oil swelling.

$$\Delta V, \% = \frac{(m3-m4)-(m1-m2)}{m1-m2} x100$$

Where:

ΔV = change in volume
m1= initial mass of specimen in air, g,
m2= initial mass of specimen in water, g,
m3= mass of specimen in air after immersion, g,
m4= mass of specimen in water after immersion, g,

3. RESULTS AND DISCUSSION

3.1. Physical properties

Tensile stress, shore hardness, elongation at break, modulus 300 % of LTR, FR and HT group of compounds were reported in Table 7, Table 8 and Table 9 respectively.

Table 7. Tensile stress, shore hardness, elongation at break, modulus 300 % of LTR group of compounds

Formulation	Shore hardness	Tensile strength (Mpa)	Modulus 300 % (Mpa)	Elongation at break (100%)
LTR1	83.5	14.3	10.3	170.2
LTR2	83.0	14.1	10.2	171.5
LTR3	84.0	14.9	10.4	160.5
LTR4	84.5	14.9	10.5	162.0
LTR5	84.5	14.5	10.5	162.5
LTR6	84.0	14.3	10.5	160.4
LTR7	84.0	14.7	10.4	162.0
LTR8	84.5	14.7	10.4	162.0
LTR9	84.0	14.9	10.3	161.7
LTR10	84.0	14.9	10.5	161.7
LTR11	84.0	14.7	10.4	161.7

Table 8. Tensile stress, shore hardness, elongation at break, modulus 300 % of FR group of compounds

Formulation	Shore hardness	Tensile strength (Mpa)	Modulus 300 % (Mpa)	Elongation at break (100%)
FR1	84.5	14.8	10.5	160.2
FR2	83.5	14.3	10.3	161.5
FR3	84.0	14.1	10.2	166.5
FR4	84.5	14.7	10.5	162.0
FR5	83.5	14.5	10.3	162.8
FR6	84.5	14.3	10.5	166.4
FR7	84.0	14.7	10.4	162.0
FR8	83.5	14.4	10.2	168.0

Table 9. Tensile stress, shore hardness, elongation at break, modulus 300 % of FR group of compounds

Formulation	Shore hardness	Tensile strength (MPa)	Modulus 300% (MPa)	Elongation at break (100%)
HR1	85.5	15.1	10.9	162.2
HR2	85.0	14.8	10.6	164.5

3.2. Impuls test performance

Hydraulic pressure impuls test was performed for hose built from each group of compounds. Inside diameter of hose used for test was 9.5 mm. The test result was reported as a cycle.

The nominal rate pressure rise was equal to that shown below equation:

R= f(10p-k)
Where;
R= rate of pressure rise in MPa/s
f= frequency in Hz
p= nominal impulse tets pressure in MPa
k=5 MPa
Cycle rate was uniform at (0,2-1,0) Hz

Impuls test was maintained until any burst or oil likage is observed. If any likeage has not been observed, test was stopped. Table 10 and Table11 show the impuls test performance of hoses based on corresponding compounds. Hose was labeled as H at the begining of compound code

Table 10. Impuls test results of hoses built from LTR group of compunds as cycle

Hose	Cycle	Passed/failed
H-LTR1	255.000	passed
H-LTR2	300.00	passed
H-LTR3	175.000	failed
H-LTR4	225.000	failed
H-LTR5	315.000	passed
H-LTR6	305.000	passed
H-LTR7	300.000	passed
H-LTR8	277.000	passed
H-LTR9	283.000	passed
H-LTR10	187.000	failed
H-LTR11	279.000	passed

It was seen from the tablet tat most of the hoses passed the impuls test.

Table 11. Impuls test results of hoses built from FR and HR group of compunds as cycle

Hose	Cycle	Passe/failed
H-FR1	113.000	failed
H-FR2	287.000	passed
H-FR3	198.000	failed
H-FR4	227.000	failed
H-FR5	298.000	passed
H-FR6	127.000	failed
H-FR7	297.000	passed
H-FR8	276.000	passed
H-HR1	191.000	failed
H-HR-2	263.000	passed

3.3. Low temeperature performance

Table 12 shows the brittleness temperature of hoses built from coresponding compound formulations.

Table 12. Brittleness temeprature of H-LTR group of hoses

Hose	Brittleness temeperature ^0C	Passed/failed
H-LTR1	42	failed
H-LTR2	45	failed
H-LTR3	44	failed
H-LTR4	48	failed
H-LTR5	48	failed
H-LTR6	50	failed
H-LTR7	50	failed
H-LTR8	53	failed
H-LTR9	55	passed
H-LTR10	53	failed
H-LTR11	55	passed

3.4. Flame test performance

Afterglow time of hoses was shown at Table13

Table 13. Afterglow time of hoses of H-FR group of compounds

Hose	Afterglow time in second
H-FR1	127
H-FR2	148
H-FR3	97
H-FR4	122
H-FR5	109
H-FR6	53
H-FR7	41
H-FR8	27

3.5. Change in volume test performance

Change in volume of inner layer compound developped for LTR group showed that most of them were below 24 % which is required for the hydraulic hoses. Volume changes of inner layer compounds can be seen at Table 14.

Table 14. Volume change in refernece oil as %

Hose	Change %	Passed/failed
H-LTR1	18.4	passed
H-LTR2	17.3	passed
H-LTR3	19.8	passed
H-LTR4	22.4	passed
H-LTR5	17.6	passed
H-LTR6	21.8	passed
H-LTR7	24.2	passed
H-LTR8	15.1	passed
H-LTR9	14.0	passed
H-LTR10	17.6	passed
H-LTR11	13.6	passed

4. CONCLUSIONS

Three groups of compounds were prepared; ultra low temeperature resistant, flame retardant and heat resistant. 11 compound formulations for ultra low temeperature resistant, 9 formulations for flame resistant and 2 formulations for heat resistant, 22 in total were developped and tested. Hoses were built from each compound mixed based on each formulations. At the end of the hose brittleness and flame tests, it was decided what formulation was the best for each cathegory. Impuls test performance was essential for all cathegory of hoses.

The blend of 48 phr of NBR 2860, 37 phr of NBR 3380 and 15 phr of SBR 1502 with 17 phr of DINP plasticizer was the best for ultra low temperature resistant hose compound that withstand till -55^{0}C without rapture and that of volume change was under 24% which is standard. The blend of 78 phr of SBR 1502 and 22 phr of CR rubber with 55 phr of $Al(OH)_3$, 11 phr of $ZnBO_3$ and 10 phr of Tricrezyl phosphate (TCP) was the best for flame retardant hose compound that of afterglow time was 27 seconds. The formulations having 48 phr of NBR 2860, 40 phr of NBR 3360,12 phr of SBR 1502, MT N990 carbonblack and paraplex G50 plasticizer for the heat resistant hose compound. It withstood till 150 ^{0}C during the impuls test.

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