

Reactive Ester Plasticizer for Elastomers

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Ester plasticizers are traditionally used to provide low temperature and improved processing of elastomers. New esters have been designed recently to improve the permanence of these materials when subjected to high heat and fluid extraction. Even though these new esters show marked improvements, they are still fugitive and can be extracted or volatilized out of the elastomer compounds in severe service conditions. Ideally, reactive esters, which provide non-extraction and low volatility while still providing low-temperature flexibility, are desired.

In this study, a reactive ester is compared to high-performance traditional esters in various elastomers. Heat aging, hydrocarbon fluid immersion (i.e.; oils and fluids) and hexane extraction tests show not only the permanence of the reactive esters but also that these esters provide the low-temperature flexibility required by many rubber applications.

Introduction

Plasticizers are polymer modifiers, as are all the other ingredients included in the formation of an elastomer compound. Plasticizers may be thought of according to their function in a compound or by their type. Some of those classifications might be internal, external, chemical, physical, esters, oils, primary, secondary, etc.

Internal plasticizers include flexible monomers (soft segments) incorporated regularly or irregularly between inflexible monomers (hard segments) of a polymer chain. Flexible polymers may be added to rigid polymers, for example, nitrile rubber to polyvinyl chloride (PVC), or grafted as side chains that reduce crystallinity and glass transition through the reduction of intermolecular forces. External plasticizers are materials that interact physically with the elastomer but are not chemically reacted with the polymer. Solvent and non-solvent are two distinct types of external plasticizers.

Common esters and polymeric polyesters are both external and physical plasticizers. Physical plasticizers may have some weak attraction to the polymer, such as through hydrogen bonding or Van der Waals forces, but as with external plasticizers, they do not chemically react with the elastomer. An exception to this can occur under the right conditions provided one of the reactants used to make the plasticizer, after the esterification reaction, retained a reactive group. A potential problem arises here, however, as materials reacted with the polymer molecules will make the polymer molecule larger and thus less flexible.

This paper is about a reactive ester that provides excellent permanence properties when exposed to high heat and extractable organic fluids. These properties, along with retention of flexibility and low temperature, are highly desirable in critical long-term rubber applications.

Experimental

The formulation used in our experimental investigation of Hydrogenated Nitrile Butadiene Rubber (HNBR) compound is as follows:

Formulation: Therban 3907 - 100.0, N-990 - 40.00, Naugard 445 - 1.0,
 PE-AC-617 - 1.0,
 Kadox 911C - 3.0, Maglite® DE - 3.0, ZMTI - 0.53, TAIC -
1.5,
 Plasticizer as noted - 10.00
Mill Addition: Peroxide as noted - 8.0

Test methods

Compounds for performance testing were mixed in a BR Banbury, except for curatives, which were added on a two-roll mill. Test specimens for compound performance properties were molded as follows: press temperature – 149°C, press time – 1.25 x t’c(90) min and at 5.75 MPa on the sheet surface. Specimens for original properties, low-temperature testing, air-oven aging and immersions were die cut from molded sheets.

<u>Mooney Viscometer -</u>	ASTM D1646-94, viscTECH+, large rotor, 1 min preheat
<u>Oscillating Disc Rheometer -</u>	ASTM D2084-93, RheoTECH Rheometer, round die, 3° arc, 30 s preheat. MH at central point of torque rise, rate – one lb., 2.5 cm / 5 min
<u>Original Properties -</u> Tensile, Elongation, Modulus	ASTM D412-92, Method A, Die C, Crosshead speed 51.0 cm/min
Hardness	ASTM D2240-91, 1s reading
Specific Gravity	ASTM D792-91
<u>Low-Temperature</u> Impact (Brittleness) Gehman	ASTM D2137-83 Method A ASTM D1053
<u>Air-Oven Aging</u>	ASTM D573-81
<u>Immersion</u>	ASTM D471-95
<u>Plasticizer Extraction</u>	ASTM D2124-95 (Soxhlet) CPH-05-06 (IR Scan)

Reactive Ester – Plasthall® RP-1020

For an ester to react with a polymer, a double bond must exist so a reaction can take place between the ester and the unsaturated polymer. Figure 1 shows the general structure of a reactive ester.

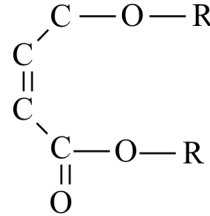


Figure 1. Unsaturated ester

In this study, one elastomer, HNBR, was evaluated at varying levels of the reactive ester.

HNBR

In our initial work using the reactive ester, the type of peroxide used had a major effect on the physical properties and the reactivity of the ester to the polymer. Table I lists the initial results of HNBR compounds that are cured with four different peroxides. The control compound for each comparison was tri-2-ethylhexyl trimellitate (TOTM). This ester, known for its very low volatility at high heat, is considered a standard for most HNBR applications. The four peroxides evaluated were as follows:

- Perkadox 14-40B-PD** - Di(tert-butylperoxyisopropyl) benzene
- Trigonox 101-45B-PD** - 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane
- Trigonox 17-40B-PD** - Butyl 4,4-di(tert-butylperoxy) valerate
- Trigonox 29-40B-PD** - 1,1-Di(tert-butylperoxy)-3,3,5-trimethylcyclohexane

Results

The results of air-oven aging after 14 days at 150°C indicate that reactive ester has its lowest weight loss using the 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane. The weight loss was -3.3 percent versus -5.4 percent for the TOTM compound. Both the reactive ester and the TOTM have similar molecular weights but considerably different neat volatilities. The weight loss of neat ester after heat aging is as follows:

	<u>RP-1020</u>	<u>TOTM</u>
<u>2 h at 155°C</u>		
Loss, %	-2.0	-0.05
<u>22 h at 155°C</u>		
Loss, %	-14.2	-6.3

Based on these results, all further evaluations and physical work were done only on the compounds' (3 and 4) cures with the 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane peroxide.

Plasticizer Extraction

To determine further evidence of the reactivity, HNBR compounds 3 and 4 were tested under Soxhlet extraction. The results are as follows:

<u>ASTM D2124</u>	<u>% extracted</u>
TOTM ^(a)	6.2
RP-1020 ^(a)	2.0

^(a)Products also identified by GC analysis.

The heat aging and Soxhlet extraction results show that about 60–70 percent of the RP-1020 did react in the polymer backbone. The amount of TOTM extracted is 6.2 percent, which also represents the amount mixed into the compound.

TABLE I

Formulation: Therban A3907 – 100.0, N-990 Carbon Black – 40.0, Naugard 445 - 1.0, PE-AC-617 – 1.0, Kadox 911C – 3.0, Maglite DE - 3.0, ZMTI – 0.53, TAIC – 1.50, Plasticizer - 10.0;
Mill Addition: Peroxide – 8.0

Plasticizer	1	2	3	4	5	6	7	8
	Plasthall® RP-1020	Plasthall® TOTM	Plasthall® RP-1020	Plasthall® TOTM	Plasthall® RP-1020	Plasthall® TOTM	Plasthall® RP-1020	Plasthall® TOTM
	Perkadox 14-40B- PD	→	Trigonox 101-45B- PD	→	Trigonox 17-40B- PD	→	Trigonox 29-40B- PD	→
Peroxide								
Viscosity and Curing Properties								
<u>Mooney Viscosity at 125°C (257°F)</u>								
Minimum Viscosity	35.9	36.6	35.6	37.5	37.6	38.3	40.4	43.5
t5, min	54.7	49.8	> 60	58.4	18.6	16.5	7.7	6.4
t10, min	> 60	> 60	> 60	> 60	28.0	22.0	10.1	8.0
t35, min	> 60	> 60	> 60	> 60	> 60	43.1	20.2	13.5
<u>Oscillating Disc Rheometer at 170°C (338°F)</u>								
M _L	7.6	8.4	8.0	8.6	9.3	9.5	10.7	11.9
M _H	40.5	46.7	33.5	58.4	26.4	40.1	23	33.4

t _{s2} , min	2.1	1.9	2.5	2.0	1.6	1.4	1.0	1.1
t' _c (90), min	21.8	7.8	10.7	12.7	5.0	5.2	2.5	2.7

Original Physical Properties

Stress at 300% Elongation, MPa	16.5	14.4	8.9	14.0	3.9	6.3	2.3	4.2
Tensile Ultimate, MPa	17.1	17.0	16.9	15.2	14.9	17.7	23.8	25.9
Elongation at Break, %	315	335	450	310	625	525	725	675
Hardness Duro A, pts.	60	58	59	60	57	57	53	57

Air Oven Aging, 7 d at 150°C (302°F)

Stress Change, %	67	73	90	79	82	146	174	84
Tensile Change, %	-7	-2	-12	4	5	3	-48	-41
Elongation Change, %	-21	-24	-27	-16	-16	-12	-12	-13
Hardness Change, pts.	6	8	7	7	8	6	12	7
Weight Change, %	-3.4	-3.4	-3.2	-4.0	-5.0	-3.2	-5.5	-3.7

Air Oven Aging, 14 d at 150°C (302°F)

Stress Change, %	76	100	94	91	97	179	205	116
Tensile Ultimate, MPa	14.8	16.3	14.7	15.9	13.8	15.6	10.3	13.2
Elongation Change, %	-14	-18	-18	-11	-12	-10	-20	-9
Hardness Change, pts.	8	10	7	9	9	9	13	8
Weight Change, %	-3.6	-4.9	-3.3	-5.4	-5.4	-4.7	-6.1	-4.4

Compounds 3 and 4 were tested for extraction properties by ASTM #1 Oil, IRM 903 Oil, distilled water and Fuel C.

Table II lists the data on both compounds. The reactive ester is showing only slight weight extraction (0.2 percent weight loss) versus TOTM (-5.3 percent weight loss) after ASTM Oil 1 aging. IRM 903 oil and distilled water extraction results show that reactive ester and TOTM compounds are absorbing these fluids. The reactive ester is acting very similar to a permanent polymeric ester in which very little ester is extracted, thus causing the polymer to increase in volume. Fuel C results are impressive for the RP-1020, again a strong indicator of reactivity to the polymer. The weight loss after dry out for RP-1020 is -0.8 percent versus TOTM at -5.1 percent. The volume change for the RP-1020 compound is 0.0 percent and the TOTM compound is -5.2 percent.

TABLE II

Formulation: Therban A3907 – 100.0, N-990 Carbon Black – 40.0, Naugard 445 - 1.0, PE-AC-617 – 1.0, Kadox 911-C – 3.0, Maglite® DE 3.0, ZMTI – 0.53, TAIC – 1.50, Plasticizer- 10.0;
Mill Addition: Peroxide – 8.0

Plasticizer	3 Plasthall® RP-1020	4 Plasthall® TOTM
Peroxide	Trigonox 101-45B-PD	—————>

Low Temperature Properties

Low-Temperature Impact – Brittleness

Brittle Point, as molded, all pass, °C	-42	-44
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Low Temperature – Gehman

As molded, Relative Modulus		
T10, °C	-23	-26
Apparent Modulus of Rigidity	121.4	133.5

ASTM 1 Oil, 168 h at 135°C (275°F)

Stress Change, %	-6	22
Tensile Change, %	-5	5
Elongation Change, %	-7	-6
Hardness Change, pts.	0	3
Volume Change, %	-0.2	-6.0
Weight Change, %	-0.2	-5.3

IRM 903 Oil, 168 h at 135°C (275°F)

Stress Change, %	4	22
Tensile Change, %	-41	-20
Elongation Change, %	-30	-24
Hardness Change, pts.	-6	0
Volume Change, %	18	6.5
Weight Change, %	15	5.5

Distilled Water, 70 h at 100°C

Stress Change, %	6	19
Tensile Change, %	1	11
Elongation Change, %	3	0
Hardness Change, pts.	1	1
Volume Change, %	6.1	3.6
Weight Change, %	5.6	3.4

Plasticizer	3 Plasthall® RP-1020	4 Plasthall® TOTM
Peroxide	Trigonox 101-45B-PD	—————>

ASTM Fuel C Immersion – 70 h at 23°C

Stress Change, %	-20	7
Tensile Change, %	-74	-76
Elongation Change, %	-53	-60
Hardness Change, pts.	-27	-14
Volume Change, %	68	32
Weight Change, %	49	35

ASTM Fuel C Dry Out – 22 h at 70°C

Hardness, Duro A, pts	59	62
Hardness Change, pts.	0	2
Volume Change, %	0.0	-5.2
Weight Change, %	-0.8	-5.1

DSC Results

Compounds 3 and 4, original and heat aged, were tested by differential scanning calorimeter. The glass transitions values are as follows:

	<u>T_g</u>
<u>TOTM</u> – original	-26.3
– heat aged, 7 d at 150°C	-21.3
<u>RP-1020</u> – original	-25.0
– heat aged, 7 d at 150°C	-21.4

The DSC results indicate that the reactive ester and TOTM are essentially equal at depressing glass transition. The low-temperature brittleness and Gehman values (Table II) also show that the two esters are essentially equal in depressing low temperature.

Summary

Our objective in this initial study was to determine if a reactive ester could provide flexibility and low-temperature properties to a cured elastomer and remain permanent or attached to the polymer after exposure to and extraction by organic fluids. Based on our results in HNBR, our conclusion is that approximately 60–70 percent of the reactive ester actually was bonded with the polymer. In addition, it is quite apparent that the choice and level of peroxide is critical in maximizing the reactivity of the ester to the elastomer. Further studies on other elastomers, such as EPDM and NBR, are in progress and will be reported at a later date.

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