

**Liquid 1,2-Polybutadiene Resins as Additives
To EPDM and Other Elastomers
For The Oil Industry**

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Introduction

Liquid polyfunctional polymers and monomers have been used for many years to increase crosslinking in EPDM and EPM elastomer systems, and in many other elastomer systems as well.^{1,2,3} One of the better known materials for this purpose is trimethylolpropane trimethacrylate (TMPTMA). Liquid 1,2-polybutadienes have also been studied and used for this purpose.^{3,4,5} This paper is directed to applications in EPDM elastomers for oil field downhole use. It presents experimental data on the general property improvements to be expected from low concentrations of 1,2-polybutadienes in peroxide cured EPDM and EPM. Data is presented which shows that higher concentrations of 1,2-polybutadiene resins result in improved heat, chemical and oil resistance. Papers by A. R. Hirasuna and coworkers at L'Garde Inc. illustrating how 1,2-polybutadiene can be used in geothermal steam applications and discuss implications for the oil industry are referenced.^{9,12} This has led to new applications in severe environments such as deep oil wells.

Experimental

All compounds used in this study were prepared on a two-roll laboratory mill from a series of master batches. The compounds were mixed taking care that there were minimum variations in milling and temperature parameters. Tests were conducted with careful

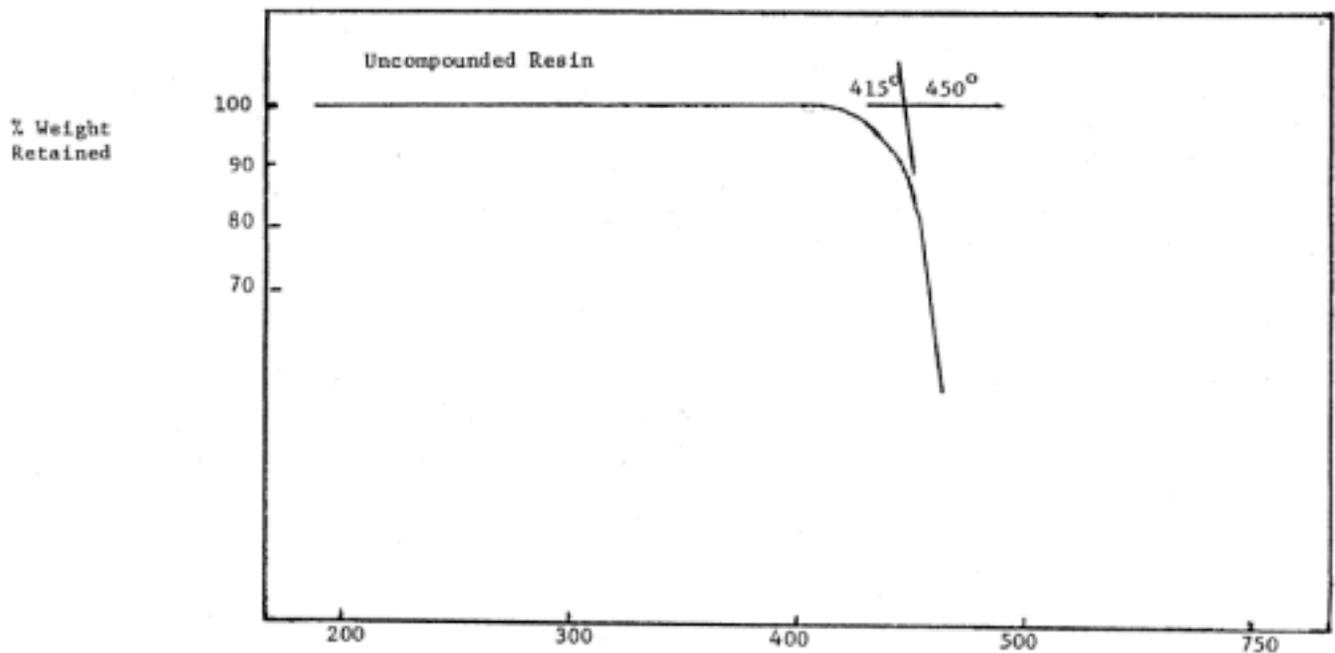
adherence to conditions specified by the various ASTM methods and these are listed for data wherever such data appears in the text. Nordel 1440 was selected as the principal EPDM to be studied. The initial study was designed to test physical properties obtained with various concentrations of 1,2-polybutadiene and to compare the properties so obtained with EPDM containing no polybutadiene and EPDM containing trimethylolpropane trimethacrylate. Cray Valley's Ricon® 153 was the 1,2-polybutadiene used. These materials were from production batches and were used without further purification. The 1, 2-polybutadiene used had an assay for vinyl content of 82 percent and molecular weight by Gel Permeation Chromatography ($M_n = 3140$). Master Batch A was made with the following composition by weight: Nordel 1440, 100.00 phr; SRF N-762 carbon black, 50.00 phr; ZnO, 5.00 phr; Agerite Resin D, 1.00 phr. Master Batch A was mixed on a two roll mill with catalyst, coagents and other additives as required. These compounds are shown in Table 1. The samples were cured 25 minutes at 160°C. The samples were processed and aged for 72 hours at 100°C. Aged physicals were determined with results shown in Table 1. Mooney viscosity and scorch by ASTM method D-1646 is presented in Table 2. Thermogravimetric data is presented in Figure 1 for peroxide cured specimens of 1,2-polybutadiene.

Table 1

		Formulation					
		100	100	100	100	100	100
Nordel 1440		100	100	100	100	100	100
SRF N-762		50	50	50	50	50	50
Zinc Oxide		5.0	5.0	5.0	5.0	5.0	5.0
Agerite Resin D		1.0	1.0	1.0	1.0	1.0	1.0
Ricon® 153		--	2.5	5.0	10.0	--	--
TMPTMA		--	--	--	--	--	2.5
Dicup 40C		7.0	7.0	7.0	7.0	7.0	7.0
Aged Physicals: Aged 72 hrs. @ 100°C							
		PBD	0	2½	5	10	--
		TMTM	--	--	--	--	2½
Tensile Mpa	D-573		14.3	13.9	14.1	12.5	13.?
Elongation %	D-573		440	370	310	250	410?
100% Modulus, Mpa	D-573		1.4	1.7	1.9	2.6	1.8?
200% Modulus, Mpa	D-573		3.4	5.0	6.4	8.8	4.8?
300% Modulus, Mpa	D-573		7.6	10.3	13.7	-	9.?
400% Modulus, Mpa	D-573		12.4	-	-	-	13.?
Hardness, Shore A	D-2240		60	63	63	65	63
Compression Set	D-395, Method B		22.0	14.5	18.6	12.8	14.?

Table 2

Mooney Viscosity: ML 1=4 at 121°C						
	PBD	0	2½	5	10	--
	TMPTM	--	--	--	--	2½
Initial Reading		74.3	73.9	73.8	64.5	75.7
4 Minute Reading		54.5	52.0	49.0	43.0	61.8
Mooney Scorch: MS at 121°C						
Time to 5 Point Rise, Mintes		69.0	71.0	59.0	60.0	26.5



Chemical resistance data was obtained at room temperature for mineral filled samples completely immersed in solutions specified in Table 3 and 4. It was sometimes necessary to weight the samples in order to keep them immersed in the test liquid. Following immersion, the test samples were washed with distilled water, blotted on absorbent paper and weighed to determine loss in weight. Samples were immediately tested for hardness and flexural strength

without conditioning to standard humidity conditions. Samples evaluated in boiling solvents were placed in gently boiling liquids, and not in the vapor space. They were weighed and tested like the room temperature specimens described above. Wherever possible the material attacked was designed to be the resin and not filler or additive. For example, samples containing silica were not tested in aqueous sodium hydroxide since the filler would be expected to undergo attack.

Table 3

Chemical resistance of 1,2 polybutadiene mineral filled molded specimens 80% filler: 20% resin. Exposure was 30 days at room temperature. There were no significant changes in flexural strength, flexural modulus or hardness with the following:

Toluene	Red fuming nitric acid
Methyl ethyl ketone	Conc. Nitric acid
Dimethyl sulfoxide	Conc. Hydrochloric acid
Carbon tetrachloride	Glacial acetic acid
Tetrahydrofuran	70% sulfuric acid
Chlorobenzene	Liquid bromine
Distilled water	Isopropanol
5% nitric acid	Formalin

Conc. nitric acid developed red color on the surface; conc. sulfuric acid darkened to black on surface and lost some physical strength; saturated chromic acid caused some darkening but little change in physical properties.

Table 4

Chemical resistance of 1,2-polybutadiene mineral filled molded specimens at elevated temperatures: 20% resin: 80% filler. Tested one week at refluxing temperature.

Solvent	Reflux Temperature °C	% Weight Change	% Flex Strength Change	Hardness Change
Tap Water	100	+0.25	-10	-2
Toluene	115	+2.5	-70	-1.5
Kerosene	145	+4	-35	-2
DMSO	189	+1.5	+15	+12
Glacial Acetic Acid	118	+2.0	-30	+5
96% H ₂ SO ₄	200	+5	-50	-9
20% H ₂ SO ₄	100	+2	+5	+1
10% NaOH ₍₁₎	100	+2	-2	+1

(1) Coke filled specimen; silica filled sample was attacked severely when tested.

Results and Discussion

Oil wells are operating in more difficult environments than ever before. Wells are being drilled deeper, dramatically increasing temperature and pressure conditions which the downhole elastomer must

withstand. In addition, harsh chemicals and steam are being injected into the well for various purposes. Elastomers currently in use are no longer doing an adequate job in these more difficult environments. These older elastomers react to brine and oil at 260°C as shown in Table 5.

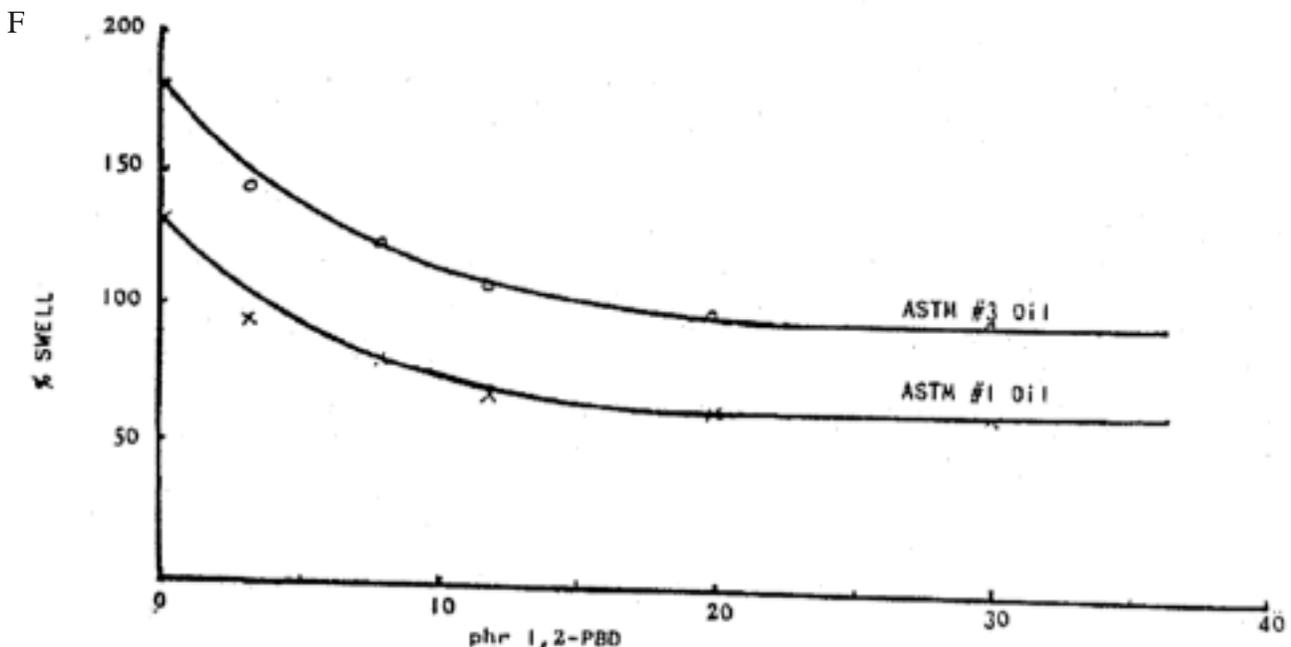
Table 5

1. Butyl (IIR)-softens, undergoes reversion
2. Nitrile (NBR)-hardens and becomes nonelastic. Embrittles on aging in presence of H₂S.
3. Epichlorohydrin (CO)-softens, hydrolyzes, extrudes.
4. EPDM-softens, swells, resists chemical attack.
5. Fluoroelastics (FKM)-embrittles on aging, loses HF.
6. Polyacrylics (ACM)-not resistant to hot water and steam at 260°C.⁹
7. Chloroprene (CR)-hydrolyzed.
8. Silicone (VMQ)-has good physicals, but swells in hydrocarbons and is destroyed in 260°C brine⁹
9. Fluorosilicones (FVMQ)-destroyed by 260°C brine, has excellent physicals at 260°C and is resistant to hydrocarbons. Possibly has selected downwell uses.⁹

A study was undertaken to determine the effect of 1,2-polybutadiene resins on the physical properties of peroxide EPDM and EPM. Nordel 1440 was selected as the principal EPDM elastomer for study. Similar data was available for several other EPDM materials, i.e. Vistalon 404³, Nordel 1040^{4,8}, Nordel 1660⁹ and unpublished data on Royalene 521, Epcar 5465 and Nordel 1070. This information shows that peroxide-cured with 1,2-polybutadienes consistently improves physical properties of EPDM and EPM and that the magnitude of the effect is greater the higher

the 1,2 content of the resin.⁴ Liquid polybutadiene with 1,2 microstructure below 40% are non-extractible plasticizers but do not affect other properties greatly. Physical property enhancement of 1,2-polybutadiene with TMPTMA is compared. It can be seen from data in Table 1 that amounts of 1,2-polybutadiene as low as 2.5 phr have significant effects on compression set and hardness. The effects compare quite favorably with TMPTMA; the compression set values are quite close and tensile strength values favor the polybutadiene. Experimental evidence is given in Figure 2 to show that 1,2-polybutadienes reduce

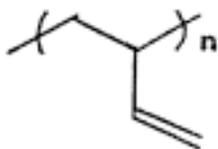
volume swell of EPDM with hydrocarbon oils.



Heat, Hydrocarbon and Chemical Resistant EPDM Formulations

EPDM and EPM have hydrocarbon backbone structures with no unsaturation to serve as a point of chemical attack. These resins are known to have excellent resistance to ozone, oxygen, heat and light.¹⁰ They are, however, severely swollen by hydrocarbons and some aqueous systems.¹¹ This is undoubtedly due to the fact that EPDM and EPM have relatively few crosslink sites and therefore have relatively open structures. Solvents are thus able to solvate the material readily.

1,2-polybutadienes having high 1,2 assay also have very few unsaturated sites in the polymer backbone, but unlike EPDM, have extremely high crosslinking potential. This can be seen from the structure.



This structure has a pendant vinyl group on every other chain carbon and in addition has the necessary hydrogens to participate in vulcanization reactions. When liquid 1,2-polybutadienes are cured with peroxide catalysts, the resulting product is a hard, glassy, brittle solid. Such materials are very heat, corrosion and hydrocarbon resistant. Figure 1 is a thermogravimetric trace of a peroxide cured 1,2-polybutadiene showing that there is little loss in weight when heated in a nitrogen atmosphere until a temperature of 425°C is attained, where a sharp break appears in the curve corresponding to thermal “cracking” of the polymer into carbon and gaseous hydrocarbon products. Table IV shows chemical resistance data from treatment of a carbon and/or silica filled molding formulation containing 1,2-polybutadiene for 7 days under conditions shown. There is good resistance to chemical attack for a wide range of corrosive chemicals including a representative spectrum of hydrocarbons. Therefore, it is not surprising that 1,2-polybutadienes significantly improve resistance of EPDM and EPM materials to solvent (Figure 2) and chemical attack. In a parallel way, 1,2-polybutadienes

have also proven to be useful additives, coagents and processing aids for polyethylene, polypropylene, CPE, EVA, BR and silicone rubber. An example of an application which has benefited from these properties was described by A.R. Hirasuna.^{9,12} The work on this subject was done on a compound containing 20 phr of 1,2-polybutadiene used to make packers and O-rings for geothermal brine wells. This compound passed rather strenuous tests at 260°C submerged in a synthetic geothermal brine containing enough H₂S to destroy unsaturated rubbers. This data is summarized in Table 6 where it can be seen that the physical properties of the composition were little changed by 22 hours of aging at 260°C immersed in synthetic geothermal brine. This has proven to be an exceptionally severe environment for elastomers. When this work was started no commercial or experimental elastomers known could withstand these conditions. Hirasuna and co-workers developed several elastomers which could with-stand these conditions. These materials are fully described in their published papers^{9,12} and the performance is outlined in Table 7. The 1,2-polybutadiene crosslinked EPDM (Compound #267) appeared to be the best material. It was chemically aged in geothermal brine at 315°C for 22 hours as a further test of its high temperature properties. This data is given in Table 8. At this very high temperature, there was some softening and loss of tensile strength, but considering these severe conditions, the material might very well perform useful work functions where no other elastomer can survive. Under these conditions, the fluoroelastomers embrittled and became useless.

One of the consequences of adding very high levels of 1,2-polybutadiene to an EPDM formulation is that a hard material results. The compound discussed above had a Shore A hardness of 92. In this case, a hard, non-extrudable compound is desirable since a major failure mode of packer assemblies is extrusion between the casing and back-up plate under the driving force of the very high heat and pressure encountered in oil wells. These new materials may find applications in deep oil wells, geothermal and process steam, under-the-hood and underfloor automotive products, solar collectors, and other stressful applications.

Table 6

L'Garde compound #267 physical properties before and after 22 hours aging in synthetic brine at 260°C (500°F). Brine composition:

H₂S –300 ppm; NaCl –25,000 ppm; CO₂ –1000 ppm; H₂O remainder

	Before	After CA	% Retention
Extrusion, PSIA	17.9	17.7	99
Hardness, Shore A	92	92	100
Elongation %	141	138	98
Tensile, PSI	1610	1554	97
Swell %	-	.46	-
Wt. Gain %	-	-	2.29

Formulation L'Garde Compound #267 from 4,2,1 Page 60

Component

Nordel 1660 (DuPont)	100 phr
Hypalon 20 (DuPont)	5
Statex 160 (N110, SAF) (Cities Service)	75
Cyanox 2246 (American Cyanamid)	0.5
Di-Cup R (Harwick Chemical Corp.)	3.5
Thermoguard S (M & T Chemicals, Inc.)	5
Polybutadiene #6081 (Polysciences, Inc.)	20

Press Cure:

350°F/60 minutes

Post Cure:

N₂ atmosphere

350°F preheat

50°F/hr. Step-up to 550° Started at insertion.

550°F for 5 hours.

Polybutadiene #6081 was Hystyl B-3000 polybutadiene resin.

Table 7

Slide 10 Summary of extended time packer seal SIM tests

T = 260°C (500°F); 50 mil Diametral gap

Compound	Trade Name	Run Time Hrs	Diff. Press., PSI	Comments Relative to 22 Hr. Run
255-1X-2	Fluoroelastomer (FKM) Viton	94	4030	Extrusion at both ends, some breakage at chamfer
267-11-8	EPDM Nordel 1660	94	4240	Slight more extrusion
266-11-3	Nordel/Viton	46	5220	Slightly more extrusion at both ends
275-11-1	Nordel/Viton	46	3310	Very slightly more permanent deterioration
291-11-2	AFLAS	46	3530	Very slightly more extrusion

Table taken from L'Garde paper 3.1.2. Page 25

Table 8

Retention of properties after 22 hours. Chemical aging in synthetic geothermal brine at 315°C (600°F).

	Before Aging	After Aging	% Retention
Extrusion PSIA	17.9	10.2	57
Hardness, Shore A	91	77	85
Elongation %	116	210	181
Tensile, PSI	1257	817	65
Swell %	--	.6 (with) 1.2 (thickness)	--
% Wt. Gain	--	3.2	--

Data is taken from L'Garde paper 3.1.3. Page 28.

Conclusions

The data presented in this paper clearly shows that 1,2-polybutadienes are effective co-agents for EPDM and EPM. These non-toxic and non-odorous resins are now readily available. When used with peroxide vulcanization catalysts, property enhancement results at low levels of 1,2-polybutadiene. There are additional benefits in that the resin serves as a non-extractible plasticizer which improves handling characteristics and decreases energy consumption. When cured using additive levels of 20-30 phr, hard but highly heat and hydrocarbon resistant materials are obtained.

These materials have been tested in geothermal and oil well environments and have performed in these carefully designed tests at temperatures up to 315°C. This is performance much beyond the usual limits for elastomers. Undoubtedly, 1,2-polybutadiene crosslinked EPDM has an important future in geothermal and oil well applications.

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