

# Rubbery Products From Castor Oil Tris(thioglycolate)—A New Polythiol\*

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## Synopsis

Castor oil tris(thioglycolate), a new trithiol, was synthesized from castor oil and thioglycolic acid. This thiol, which showed an inherent propensity to form a solid, insoluble film on exposure to air, was cured with lead peroxide and *p*-quinone dioxime, using various fillers. Mechanical properties of the cured products as well as their solvent resistance were determined.

## INTRODUCTION

The chemistry of organosulfur compounds—including organosulfur polymers—centers around thiols, probably because thiols exhibit a multitude of important chemical properties. Of these, the propensity for facile oxidation to disulfide structures with a wide variety of inorganic and organic oxidizing agents is of importance in industrial applications. Polymers obtained by oxidative cures are of more utility since the process of oxidation does not result in the introduction of oxidant fragments into the polymer backbone. Many polymers and high-molecular-weight compounds with —SH functionality having interesting applications not only in biology and medicine but also in the domain of commercial adhesives and coatings have been synthesized.

In the present study, castor oil tris(thioglycolate), COTT, was synthesized from castor oil and thioglycolic acid. COTT exhibits a strong tendency to form transparent, brittle, and insoluble solid film on exposure to air. COTT also formed solid products with lead peroxide, an inorganic oxidizing agent, and *p*-quinone dioxime, an organic oxidizing agent. This article describes our attempts to synthesize rubbery products from oxidative curing of COTT, which is monomeric in nature, and a study of the mechanical properties of the products so synthesized.

## EXPERIMENTAL

Thioglycolic acid (80%) (from Veb-labor Chemie Apolda, Germany) and commercial castor oil were used as received. Lead peroxide was used as C-5 paste prepared by mixing PbO<sub>2</sub> (50 parts), dioctyl phthalate (45 parts), and stearic acid (5 parts).

*p*-Quinone dioxime (GMF) and diphenyl guanidine (DPG) were used as received. Polysulfide—SH terminated polymers LP-32 or LP-2 (MW 4000) were from Thiokol Corp., New Jersey.

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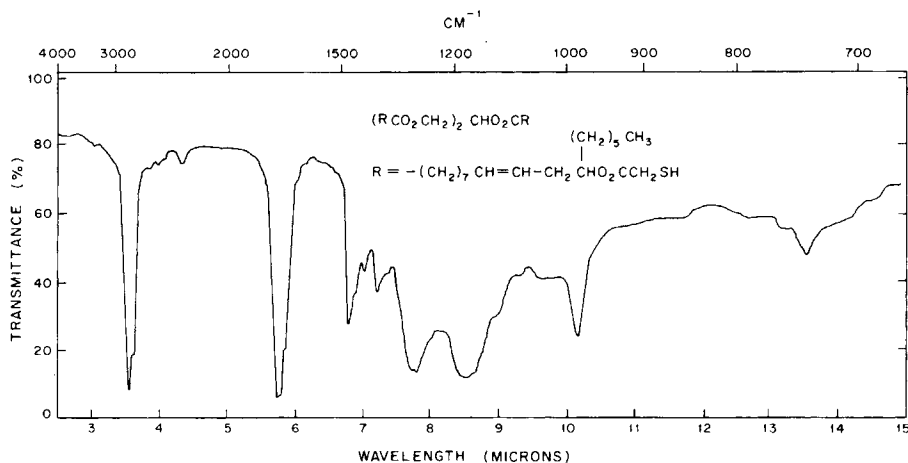


Fig. 1. Infrared spectrum of castor oil tris(thioglycolate).

### Synthesis of COTT

A toluene or xylene solution (400 ml) of castor oil (0.1 mole, 93.2 g) was heated with stirring in a three-necked flask equipped with a Dean-Stark azeotropic apparatus to 85–90°C; thioglycolic acid (0.35 mole, 32.0 g) was added, followed by *p*-toluenesulfonic acid (1.5% w/w of the polyol). The contents were refluxed with effective stirring to remove water azeotropically. After all the water had been removed, the refluxing was continued for a further 19 hr. The cooled reaction mixture was washed several times with the hot water and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the product dried under vacuum. Figure 1 shows the IR of COTT. Yield: 95%.  $\eta_D^{25}$  1.489.

ANAL. for  $\text{C}_{63}\text{H}_{110}\text{O}_{12}\text{S}_3$ . Requires: C, 65.51; H, 9.53; S, 8.33. Found: C, 66.63; H, 9.79; S, 9.62.  $\text{SH}^1$ : Calcd: 8.595. Found: 8.475. Molecular weight (from —SH value)<sup>2</sup>: Calcd: 1154. Found: 1170.

### Curing of COTT

The curing recipes for  $\text{PbO}_2$  or GMF/DPG curing systems for different fillers are shown in Table I. COTT was weighed into a mixer and the filler was added with intermittent mixing in three portions at intervals of 10 min and thoroughly mixed. The curing agent was added and mixed well for a further 30 min and allowed to set in an oven at 70°C. The setting times are shown in Table II.

TABLE I  
Compounding Recipes for COTT

	Parts
COTT	100
Filler <sup>a</sup>	x
Curing agent <sup>b</sup>	y

<sup>a</sup> Carbon black, 30 parts;  $\text{TiO}_2$ , 50 parts; or  $\text{SiO}_2$ , 15 parts.

<sup>b</sup>  $\text{PbO}_2$  curing system: C-5 paste, 15 parts; stearic acid, 1.0 part; and sulfur, 0.25 part. GMF/DPG system: GMF, 10.5 parts; and DPG, 4.5 parts.

TABLE II  
Setting Times of Various Mixes at 70°C

Filler	Time, hr	
	PbO <sub>2</sub> system	GMF/DPG system
Carbon black	20	12
TiO <sub>2</sub>	16	72
SiO <sub>2</sub>	10	70

### Curing of Mixture of COTT and Thiol-Terminated Polysulfide Liquid Polymers

Separately weighed amounts of COTT and the polysulfide polymer were transferred into a mixer and mixed thoroughly with carbon black. The rest of the procedure was as described earlier for the curing of COTT.

Different mixing ratios and their setting times are shown in Table III.

### Testing

All the tack-free cured products were kept overnight before testing for their tensile properties. These tack-free products, after being crumbled on a laboratory rubber mixing two-roll mill, were pressed out at 160°C for 10 min in a silicone grease-pretreated metallic mold. Tensile strength, elongation, and hardness were determined at room temperature on dumbbell-shaped specimens according to ASTM designations D 412-68 and D 2240-68. These results are tabulated in Tables IV and V.

TABLE III  
Mixing Ratios of COTT and Polysulfide Liquid Polymer and their Setting Times at 70°C

System	COTT	LP-32	LP-2	Setting time, hr	
				PbO <sub>2</sub> cure	GMF/DPG cure
I	25	75	—	33	—
II	50	50	—	36	—
III	75	25	—	43	—
IV	50	50	—	—	8
V	50	—	50	—	8

TABLE IV  
Physical Properties of Cured Vulcanizates of COTT Pressed Out at 160°C for 10 Min

Filler	Tensile strength, MPa <sup>a</sup>		Relative extension, %		Shore A hardness	
	GMF/DPG		GMF/DPG		GMF/DPG	
	PbO <sub>2</sub> cure	cure	PbO <sub>2</sub> cure	cure	PbO <sub>2</sub> cure	cure
Carbon black	0.568	0.64	20	20	65	70
TiO <sub>2</sub>	— <sup>b</sup>	0.26	—	20	55	55
SiO <sub>2</sub>	—	0.38	—	10	50	50

<sup>a</sup> Mega-Pascal (see ref. 3).

<sup>b</sup> Too brittle for properties to be determined.

TABLE V  
Physical Properties of Cured Vulcanizates of COTT-Polysulfide Liquid Polymer Pressed Out at 160°C for 10 Min

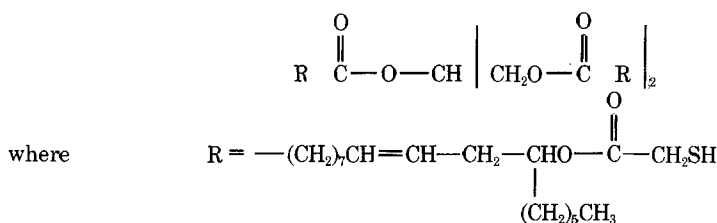
System	Tensile strength, MPa	Relative extension, %	Shore A hardness
I	1.28	110	45
II	0.68	30	53
III	0.66	20	55
IV	1.51	80	60
V	1.72	50	65

### Solvent Resistance

Solvent resistance of PbO<sub>2</sub>-cured COTT and systems I-III was determined as percent weight increase after 30 days of immersion at room temperature in different organic solvents and water according to ASTM designation D 471-64B. These results are recorded in Table VI.

### DISCUSSION

Esters containing at least three thiol groups prepared by the reaction of polyhydric alcohols with mercaptocarboxylic acids are known to form films on exposure to air which are insoluble in organic solvents.<sup>4</sup> COTT also exhibited a strong propensity to form a transparent and brittle film on exposure to air, even on storage in closed glass flasks, and this film was found to be insoluble in organic solvents. Hence, we attempted to cure COTT with the oxidizing agents employed usually for the curing of thiol-terminated polymers. We employed lead peroxide and *p*-quinone dioxime (GMF) for this purpose. The structure of COTT can be written, neglecting the double bond configuration, as



From the above structure, the following conclusions seem evident:

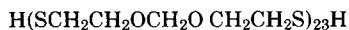
- (1) COTT is monomeric in nature.
- (2) COTT contains three —SH groups in its molecule. Thus, it will be extensively crosslinked in the cured state. Consequently, elongation will be low and hardness will be increased.
- (3) The R group in the molecule contains 16 carbons, and the —(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub> group present therein may be considered to be pendent enforcing less compact packing of chains resulting in low modulus and strength.

The tensile strengths of both PbO<sub>2</sub>- and GMF-cured COTT vulcanizates, shown in Table IV, seem to be in agreement with the above. However, the brittle nature of the silica- and titanium dioxide-filled, lead peroxide-cured vulcanizates of COTT might probably be due to the relatively poor reinforcing action of these fillers.

TABLE VI  
Solvent Resistance of Vulcanizates at Room Temperature Determined as Percent Weight Increase

Solvent	COTT (PbO <sub>2</sub> cured)	I	II	III
Benzene	97.3	153.0	161.0	183.0
Toluene	97.25	122.5	131.3	142.0
Xylene	95.1	107.5	127.4	130.5
Ethyl acetate	59.3	48.4	66.5	67.0
CCl <sub>4</sub>	146.0	176.0	184.0	193.0
Methanol	7.0	7.3	6.0	5.0
Isopropanol	5.0	7.6	6.0	2.0
Water	4.6	4.9	8.5	6.0

The above three phenomena, we thought, could be better understood by admixing COTT with other thiol-containing polymers with relatively high molecular weight, low crosslink density, and flexible structure. For this purpose we chose the following two polymers: LP-32, MW 4000, 0.5% crosslink; and LP-2, MW 4000, 2.0% crosslink. The polymers having the structure



with the crosslinks provided by 1,2,3-trichloropropane show high strength, elongation, and low shore A hardness when cured individually. By gradually increasing the LP-32/COTT ratio, a corresponding increase in tensile strength and elongation can be expected. This is supported by the results in Table V. On the basis of the better curing properties of GMF, relatively better improvements may be expected by employing the GMF curing system. The LP-32/COTT system should result in better strength and extension, while the LP-2/COTT combination might be expected to show comparatively more strength and hardness but low extension. These are fully supported by the results recorded in Table IV.

### References

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