

Thiol Modification of Difunctional Castor Oil and Its Utility as Room Temperature Setting Elastomeric Material*

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Synopsis

Difunctional castor oil has been reacted with thioglycolic acid for the synthesis of castor oil dithioglycolate (CODT). Elastomeric products have been obtained from CODT alone and in combination with liquid polysulfide polymer LP-33 by oxidative cure with manganese dioxide. Semireinforced (SRF) carbon black has been used as a filler. CODT has also been evaluated as a flexibilizer for liquid epoxy resin (Synpol 200).

INTRODUCTION

The petroleum oil crisis has created uncertainties concerning the availability and price of monomers on which synthetic rubbers are based. The emphasis is now concentrated all over the world on the use of renewable resources for industrial needs. Castor oil, an agricultural product, serves as an industrial raw material for the manufacture of a number of complex derivatives.^{1,2} The hydroxyl group, double bonds, and ester linkages in castor oil provide reaction sites for the preparation of many useful industrial products.

Thiol-terminated polymers are widely used as adhesives, sealants, coatings, rocket propellants, etc. The distinctive nature of these polymers is their capacity for vulcanizing at room temperature with an addition of suitable curing agent. Rubbery products from castor oil tri(thioglycolate)³ possess certain drawbacks such as very low elongation, high crosslink density, etc. These drawbacks may be due to presence of three —SH groups in its molecule.

In the present study castor oil dithioglycolate (CODT) has been synthesized from difunctional castor oil and thioglycolic acid. Elastomeric products have been prepared from CODT alone and in combination with liquid polysulfide polymer LP-33. It has also been evaluated as a flexibilizer for liquid epoxy resin (Synpol 200). The physical properties of all these products have been studied.

EXPERIMENTAL

Difunctional castor oil has been prepared by the method reported in the literature⁴ from commercial grade castor oil.

Phenyl isocyanate (from Fluka A. G., Germany), thioglycolic acid 80% (from Veb-labor Chemie Apolda, Germany), manganese dioxide (from M/s. Hindustan Mineral Products, Bombay, India), liquid polysulfide polymer LP-33 (from

* NCL Communication No. 3294.

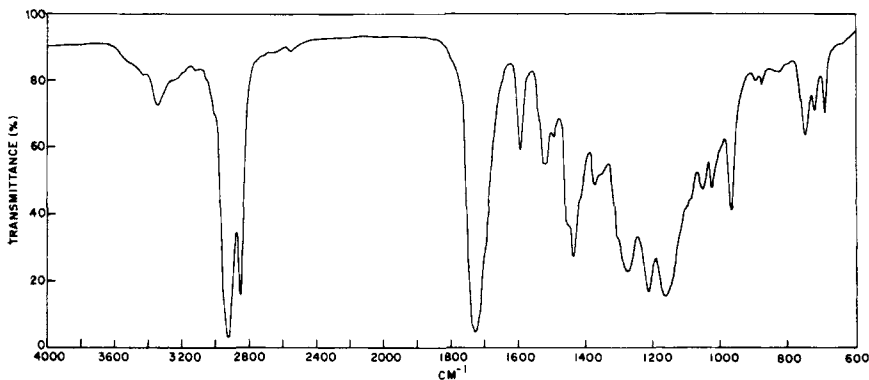


Fig. 1. IR spectrum of castor oil dithioglycolate.

Thiokol Corporation, New Jersey), and epoxy resin synpol 200 (from synthetic and polymer Industries, Gujrath, India) have been used as received.

All other chemicals used were commercial grade.

Synthesis of Castor Oil Dithioglycolate (CODT). A 1-L three-necked round bottom flask equipped with a mechanical stirrer, a thermowell, and a Dean-Stark azeotropic apparatus was charged with 400-mL toluene and 105.1 g (0.1M) of difunctional castor oil. The reaction flask was heated to 85–90°C with constant stirring and then 28.75 g (0.25M) of thioglycolic acid was added dropwise during 15 min time. The acid addition was followed by the addition of *p*-toluenesulfonic acid (1.5% w/w of polyol). The contents were refluxed with continuous stirring to remove water azeotropically. After all the water had been removed, the refluxing was continued further for 25 h. The cooled reaction mixture was washed several times with hot water and then dried over anhydrous sodium sulfate. After filtration the solvent was removed under reduced pressure and finally the product was dried under high vacuum. Figure 1 shows the IR spectrum of castor oil dithioglycolate.

Yield: 90%, η_D^{25} 1.493, Brookfield viscosity at 25°C (P): 17–18.

ANAL. Required for $C_{68}H_{113}O_{12}S_2N$: C, 68.00%; H, 9.27%; N, 1.33%; S, 5.30%. Found: C, 67.33%; H, 9.44%; N, 1.04%; S, 6.02%.

SH⁵: Calcd: 5.50%. Found: 4.90%.

Compounding and Testing. Initial mixing of component I for all the systems from Tables I and II was carried out in a pug mixer and finally on the three roll paint mill till a creamy consistency was obtained. The curing paste (component II) for systems A, B, and C consists of (1) manganese dioxide, 50 parts, (2) dibutyl

TABLE I
Mixing Ratios of CODT, CODT-Liquid Polysulfide Polymer (LP-33)

System	Component I			Component II	Component III
	CODT (g)	LP-33 (g)	Carbon Black (SRF) (g)	Curing paste (g)	Diphenyl guanadine (DPG) (g)
A	100	—	30	19.00	0.40
	100	—	50	19.00	0.40
B	75	25	30	19.50	0.40
	75	25	50	19.50	0.40
C	50	50	30	20.00	0.40
	50	50	50	20.00	0.40

TABLE II
Mixing Ratios of Epoxy Resin, CODT-Epoxy Resin

System	Component I		Component II
	Epoxy resin (Synpol 200) (g)	CODT (g)	Diethylene triamine (g)
D	100	—	10
E	100	25	10
F	100	50	10
G	100	75	10
H	100	100	10

phthalate, 45 parts, and (3) stearic acid, 3 parts. This paste was also prepared on a paint mill till a pasty consistency is obtained.

Number of mixes were prepared (for different systems) by mixing components I, II, and III (Table I) and components I and II (Table II) in glass or porcelain dishes. The potlife or viability of the systems has been given in Tables III and IV. For determination of physical properties samples were prepared by applying the thoroughly mixed material on an aluminium sheet coated with paraffin wax. A π -shaped template of thickness 2 mm and with internal dimensions 11 × 3 cm is placed on an aluminium sheet already coated with paraffin wax. Then the material is filled in the template by the help of a spatula to the top surface of the template and leveled in the direction of length. Afterward, the template is removed, and the aluminium plate is kept at room temperature for 24 h; then it is thermostated at 70°C for 24 h (for systems A, B, and C only). For other systems, namely, D–H, the curing was done at room temperature for 7 days. After the respective curing period, dumbbell-shaped specimens were cut from the cured samples and tested for tensile strength, elongation, and hardness according to ASTM designations D412-68 and D2240-68. The results are shown in Tables III and IV.

DISCUSSION

Availability of reactive liquid materials which could be converted into elastomeric products appear attractive in a present energy crisis situation. Polythiols are easily converted into polymeric structures which are crosslinked. Generally the crosslinking is effected with a wide variety of inorganic and organic oxidizing agents.

TABLE III
Physical Properties of Cured Vulcanizates of CODT and CODT-LP-33 Polymer after Curing at Room Temperature for 24 h + 24 h at 70°C

System	Carbon black (%)	Tensile strength (MPa)	Elongation (%)	Residual elongation (%)	Shore hardness, Shore A	Pot life (h)
A	30	1.05	100	5	35	4
	50	1.12	120	5	40	3
B	30	1.00	140	2	30	2
	50	1.10	180	2	35	1.50
C	30	1.30	250	4	30	1
	50	1.40	210	4	30	0.75

TABLE IV
The Effect of CODT on the Physical Properties of Liquid Epoxy Resin Sheets Cured for 7 Days at Room Temperature

System	Tensile strength (MPa)	Elongation (%)	Shore hardness, Shore D	Pot life (h)
D	17.80	0	90	0.5
E	18.70	10	88	4
F	18.00	20	87	2
G	6.30	30	85	2
H	3.80	50	80	1

We have employed manganese dioxide for the curing of CODT and CODT-liquid polysulfide polymer combinations. Although the oxidative cured products of CODT exhibit better tensile strength and elongation (Table III), the tensile strength values are lower than the values usually obtained from the cured products of difunctional thiol-terminated polymer. When CODT is mixed with the commercially available thiol-terminated polymer (LP-33) with gradually increasing LP-33/CODT ratio, a corresponding increase in tensile strength and elongation has been observed. This observation indicates that the low tensile strength of CODT could be due to the presence of long alkyl chain in its molecule which might be reducing the effectiveness of the intermolecular forces between the chains. Thus the higher loading of reinforcing carbon black filler also shows the marginal effect on its tensile strength. The lower elongation of CODT products might be due to its more crosslink structure.

Thiol-terminated polymers readily react with epoxy resins under basic conditions to form a block copolymer. These block copolymers have significantly higher impact resistance and more flexibility than epoxy resin alone.^{6,7} To explore the possibility of use of CODT as a flexibilizer/modifier for liquid epoxy resin (synpol 200 having epoxy equivalent 190), different formulations have been prepared (Table II). The effect of CODT on the physical properties of liquid epoxy resin has been shown in Table IV. It is interesting to note the increase in tensile strength of epoxy resin by adding up to 50% CODT. Although the elongation increases beyond 50% CODT in the formulation the sharp drop in tensile strength is observed. The effect of increased tensile strength and elongation up to 50% addition of CODT in synpol 200 epoxy resin indicate that these combinations may find uses as flexible epoxy adhesives, coatings, as water-proofing materials, potting, laminates, etc.

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Received June 9, 1983

Accepted July 28, 1983