

Elastomers from Castor Oil

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Synopsis

Castor oil has been used to prepare millable elastomers by using 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, and 1,5-naphthalene diisocyanate, respectively. These elastomers are vulcanized with sulfur and 4,4'-diphenylmethane diisocyanate separately by using the standard methods of rubber technology, and the properties of these vulcanizates are reported.

INTRODUCTION

Polyurethane elastomers are now broadly classified into three different types, namely: (1) cast elastomers, (2) millable elastomers, and (3) thermoplastics elastomers. The first two types of elastomers are the ones which have considerable commercial importance.

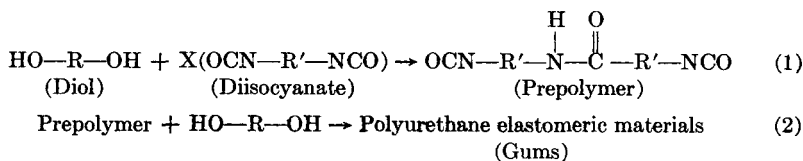
Polyurethane cast elastomers such as Adiprene L are obtained by mixing polyols with diisocyanates to give pourable liquid mixtures, which are cured on heating. This method of production does not enable the use of reinforcing fillers in these elastomers. They are thus comparatively expensive.

The millable elastomers such as Urepan, Genthane, Chemigum SL, and Vulcaprene A are the ones which can be processed on conventional rubber machinery, by well-known techniques without making any major changes in the present rubber technology. These can also be processed by incorporating reinforcing fillers, thereby reducing the cost of the article.

Castor oil and its derivatives have been reported in literature, being used in many polyurethane base formulations for various applications, but no detailed study regarding the use of castor oil for making polyurethane millable elastomers has come to our notice. It was therefore decided to study the preparation and evaluation of polyurethane millable elastomers based on castor oil.

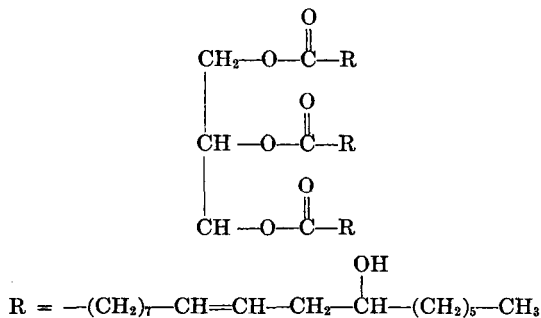
Chemistry of Polyurethane Elastomer Preparation

The polyurethane elastomers are prepared by reacting a long-chain diol having a molecular weight of about 2000 with an excess of diisocyanate to give an isocyanate-terminated prepolymer.¹ When a slight excess of low molecular weight polyol or a polyamine, termed a chain extender, is reacted with this prepolymer, an elastomeric material results.



These elastomeric materials, after incorporation of fillers and vulcanizing agents when processed by the usual rubber technological methods, produce articles of superior physical and chemical properties.

Castor oil is a naturally occurring vegetable oil having free secondary hydroxyl groups. About 90% of the fatty acid part of this glyceride consists of ricinoleic acid and the remaining 10% is oleic and linoleic acid.



The ricinoleic acid is utilized in the glyceride molecule to the extent of 77% for making the trihydroxyl glyceride, glyceryl tricinoleate, and 23% in making the dihydroxyl glyceride-glyceryl diricinoleate-monooleate or monolinoleate. Thus from the point of view of functionality, castor oil² is roughly 70% trifunctional and 30% difunctional.

Since difunctional polyols are needed in the preparation of polyurethane elastomers, the trifunctional part of castor oil has to be made difunctional. This has been achieved by reacting 0.7 equivalents of phenyl isocyanate with one mole (2.7 equivalents) of castor oil. It is assumed here that the major part of phenyl isocyanate reacts with one of the hydroxyl groups of glyceryl tricinoleate.

This difunctional castor oil is then reacted with diisocyanates to give isocyanate-terminated prepolymer. These prepolymers are then reacted with various chain extenders to give the elastomeric gums. The chain extenders are used in slight excess to get hydroxy-terminated storage-stable gums. These gums are, however, very soft and unsuitable for processing on the rubber mill. Therefore gums having free isocyanate groups are obtained by incorporating less of chain extenders.

This communication deals with the results of the elastomeric gums obtained by reacting one mole of difunctional castor oil with three moles of the diisocyanates and one mole of chain extenders.

EXPERIMENTAL

Table I gives the information on the various materials used in this study.

TABLE I
List of the Chemicals Used and Their Suppliers

Chemicals	Suppliers
Castor oil (medicinal grade)	Swastik Oil Mills, Bombay, India
Ethylene glycol	E. Merck A.G., Darmstadt, Germany
Diethylene glycol	
Dipropylene glycol	
2,4-Toluene diisocyanate (TDI)	National Aniline Div., Allied Chemical Corporation, USA
4,4'-Diphenylmethane diisocyanate (MDI)	Farbenfabriken Bayer A.G., Leverkusen, West Germany
1,5-Naphthalene diisocyanate (NDI)	
Trimethylol propane	Light & Co. Ltd., Bucks, England
Polyethylene glycol 1000	Union Carbide & Carbon Corp., USA

Preparation of Difunctional Castor Oil

Since these preparations involved toxic and reactive isocyanates, all the necessary precautions for their safe handling and carrying out their reactions under anhydrous conditions were taken in all the experimental work.

In a three-necked flask equipped with stirrer, dropping funnel, thermometer, oil bath, etc. was placed 1 kg. of dried castor oil. The temperature of castor oil was brought to 100°C. followed by the dropwise addition of 76 cc. phenyl isocyanate under stirring. The reaction mixture was cooled and kept well stoppered (hydroxyl number 118.95, acid number 1.11).

Preparation of the Elastomer Gum

In a three-necked flask equipped with stirrer, dropping funnel, thermometer, oil bath, etc., was placed dried difunctional castor oil. The temperature of the oil was brought to 100°C. and one-third the required diisocyanate was added in small portions, under stirring. The heating was continued for 1/2 hr. and the remaining two-thirds of the diisocyanate added. Heating was continued for another 1/2 hr. The equivalent quantity of the polyol of Table II was then added under stirring.

TABLE II
Composition of the Elastomeric Gums: Amounts of Polyols Added to 100 g.
Difunctional Castor Oil Plus 55.35 g. TDI

Glycol	Amount of polyol, g.
Ethylene glycol	6.57
Diethylene glycol	11.24
Dipropylene glycol	14.21
Trimethylol propane	9.46
Castor oil	74.96
Water	3.82

Heating was continued for another 15 min. The resultant mixture was then cast in stainless steel trays and cured for 15 hr. at 110°C. and 1 hr. at 150°C. Table III describes the composition of the elastomeric gums obtained by using difunctional castor oil, different diisocyanates, and ethylene glycol, and the method described above.

TABLE III
Composition of Elastomeric Gums Prepared with Different Diisocyanates

Difunctional castor oil, g.	Diisocyanate, g.			Ethylene glycol, g.
	TDI	MDI	NDI	
100	55.35	—	—	6.57
100	—	79.52	—	6.57
100	—	—	66.70	6.57

Compounding of the Elastomer

The elastomer was compounded on a laboratory-type 6 × 12 in. mixing mill. A continuous band of polymer was formed on the mill and the ingredients added according to the order given in the Table IV. After mixing all the ingredients, the elastomer was rolled through a tight mill six times, sheeted out, and molded at 250°F. in standard molds.

TABLE IV
Compounding Recipe for the Elastomers

Ingredients	Parts	
	Sulfur-cured	Diisocyanate-cured
Elastomeric gum	100.0	100.0
Stearic acid	2.0	2.0
HAF	30.0	30.0
DBP	10.0	10.0
MBT	1.0	—
MBTS	4.0	—
ZnO	5.0	—
Sulfur	0.75	—
4,4'-Diphenylmethane diisocyanate	—	2.8

Testing

Tensile strength, elongation, and modulus were determined in the manner described in A.S.T.M: D412-64T (1965).

The abrasion index was determined according to B.S. 903:Part 24, 1950, Section 24.3, using a Du Pont abrasion machine. The standard samples were prepared as per recipe suggested for A tire-tread type and compared with our samples at 30°C.

RESULTS

Table V describes the properties of the elastomeric gums obtained by reacting the prepolymer of difunctional castor oil-2,4-toluene diisocyanate, with various polyols. The elastomeric gums obtained by the use of ethylene glycol, trimethylol propane, and water have overall better properties. Of these, only the ethylene glycol-extended elastomer was processed on the

TABLE V
Physical Properties of the Elastomeric Gums from Difunctional Castor Oil, 2,4-TDI and Polyols

Chain extender (polyol)	Specific gravity	Dur-ometer Shore A hardness	Tensile strength, psi	Tensile elongation, %	100% Modulus, psi
Ethylene glycol	1.08	45	1000	250	370
Diethylene glycol	1.10	40	900	275	250
Dipropylene glycol	1.10	40	750	275	210
Trimethylol propane	1.10	65	1020	175	650
Castor oil	1.13	50	725	250	360
Water	1.14	75	1080	150	750

rubber mill. The compounding recipe for this polymer for vulcanization with sulfur and 4,4'-diphenylmethane diisocyanate is described in Table IV and the physical properties of the resultant elastomeric materials (elastomer X) are given in Table VI.

The difunctional castor oil was then reacted separately with 4,4'-diphenylmethane diisocyanate and 1,5-naphthalene diisocyanate and the resultant prepolymers were then chain-extended by reacting with ethylene glycol. The elastomeric gums thus obtained were then separately vulcanized with sulfur and 4,4'-diphenylmethane diisocyanate by standard methods by using the compounding recipe of Table IV. The physical properties of these elastomeric materials (elastomer Y and elastomer Z) are given in Table VII.

DISCUSSION

The properties of elastomers are the result of a combination of chain flexibility, chain entanglement, hydrogen bonding, van der Waals forces, crosslinking, etc. Because of the presence of more hydrogen bonding and van der Waals forces, the polyurethane elastomers have many "better" properties in comparison to the elastomers derived from olefinic compounds. The difunctional castor oil molecule used for evaluation here is a polyester of roughly 1000 molecular weight, having pendant long alkyl chains. The effect of these pendant chains will be predominantly to reduce the effectiveness of the intermolecular forces between the polymer chains. Similarly the elastomer chain of the difunctional castor oil-diisocyanate pre-

TABLE VI
Physical Properties of Elastomer X

	Cure, min. at 250°F.	Specific gravity	Durometer		Tensile strength, psi	Tensile elongation, %	100% Modulus, psi	Abrasion index, %
			Shore A hardness	Shore D hardness				
Unvulcanized gum	—	1.08	45	—	1000	250	370	—
Sulfur vulcanizate	10	1.24	95	—	2800	150	1900	50.9
Disocyanate vulcanizate	20	1.20	85	—	2200	150	1400	40.0

TABLE VII
Physical Properties of Elastomers X, Y, and Z

	Cure, min. at 250°C.	Specific gravity	Durometer		Tensile strength, psi	Tensile elongation, %	100% Modulus, psi	Abrasion index, %
			Shore A hardness	Shore D hardness				
Sulfur vulcanizates								
Elastomer X	10	1.24	95	—	2800	150	1900	50.9
Elastomer Y	30	1.22	85	—	1500	150	1100	78.9
Elastomer Z	30	1.25	90	—	2000	100	2000	84.5
Diisocyanate vulcanizates								
Elastomer X	20	1.20	85	—	2200	150	1400	40.0
Elastomer Y	20	1.20	85	—	2800	150	1500	47.0
Elastomer Z	30	1.22	95	—	2000	100	2000	42.0

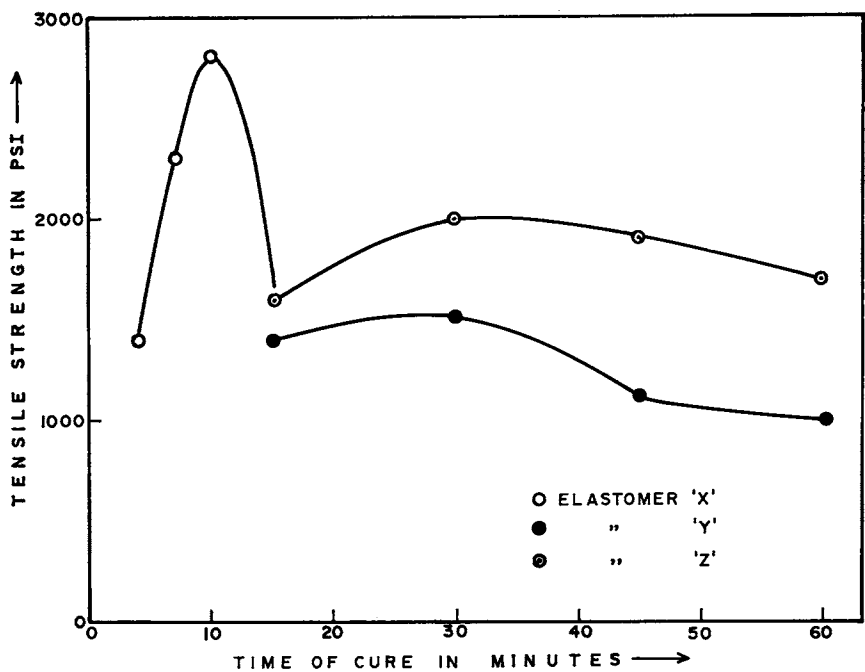


Fig. 1. Tensile curve of elastomers obtained by using sulfur: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

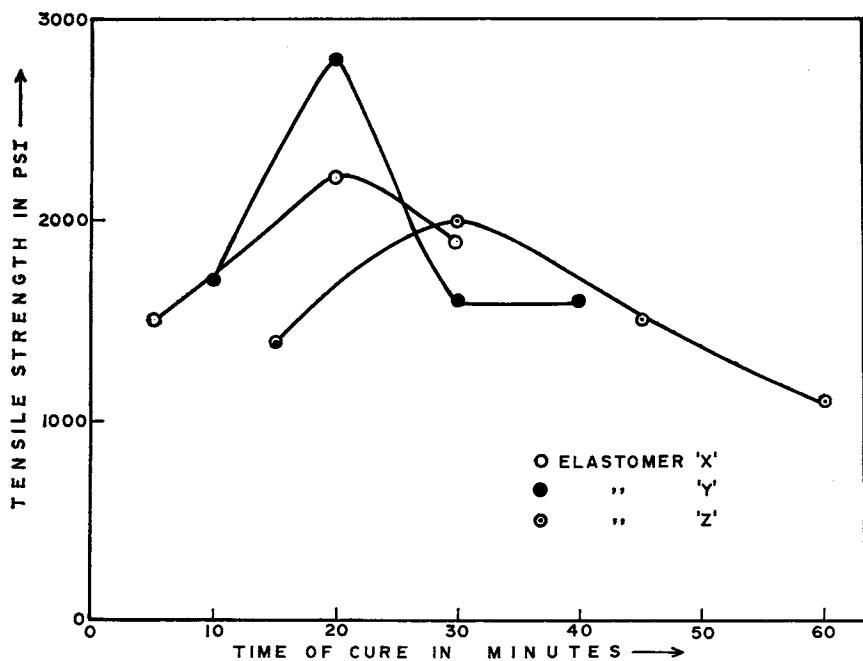


Fig. 2. Tensile curve of elastomer obtained by using diisocyanate: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

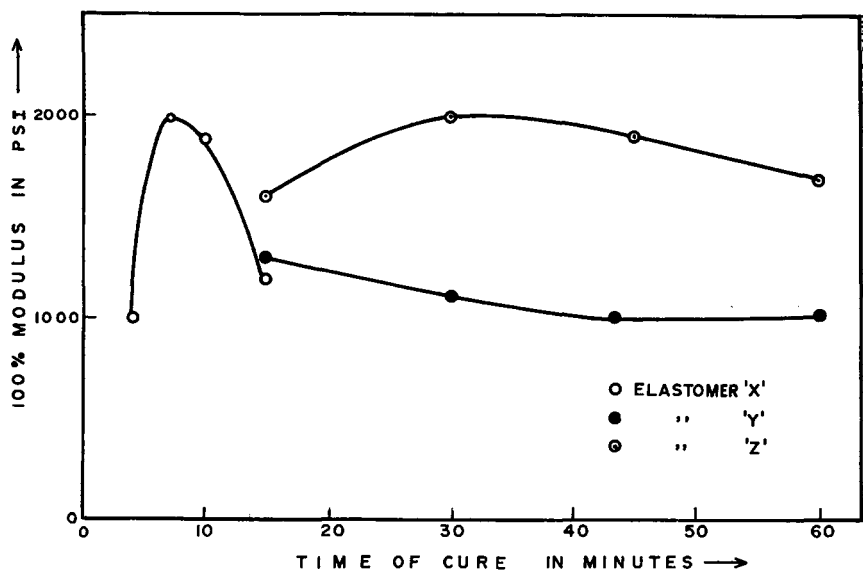


Fig. 3. Modulus curve of elastomers obtained by using sulfur: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

polymer may not be sufficiently long, as the molecular weight build-up may be influenced by the secondary hydroxyl groups having adjacent alkyl chains. It is therefore evident that the tensile strength of the castor oil-based polyurethane elastomers is much lower than that of the polyester-based polyurethane elastomers derived from polyester chains having no pendant alkyl groups.

It has been reported that in the preparation of polyester polyurethane elastomers, the replacement of 2,4-toluene diisocyanate with 4,4'-diphenylmethane diisocyanate and 1,5-naphthalene diisocyanate,³ leads to elastomers having better tensile strength, moduli, and tear strength. Thus, 4,4'-diphenylmethane diisocyanate and 1,5-naphthalene diisocyanate have been separately reacted with difunctional castor oil and elastomers Y and Z, respectively, prepared. However, the change in the physical properties of these elastomers X, Y, and Z is not very marked, indicating that the pendant alkyl chains play a marked effect in restricting the increase in tensile strengths, moduli, and tear strengths.

Figure 1 shows the rate of cure of sulfur-vulcanized elastomers. In the case of elastomer X, it is observed that the optimum cure is obtained in 10 min., whereas in the case of elastomers Y and Z, the optimum cures are obtained only in 30 min. Figure 2 shows the rate of cure of elastomers X, Y, and Z with 4,4'-diphenylmethane diisocyanate as the crosslinking agent. Elastomer Y has the maximum tensile strength, followed by the elastomer X and elastomer Z.

The tensile strength of the three elastomers, X, Y, and Z, vulcanized by sulfur and diisocyanate are summarized in Table VII. In the sulfur vul-

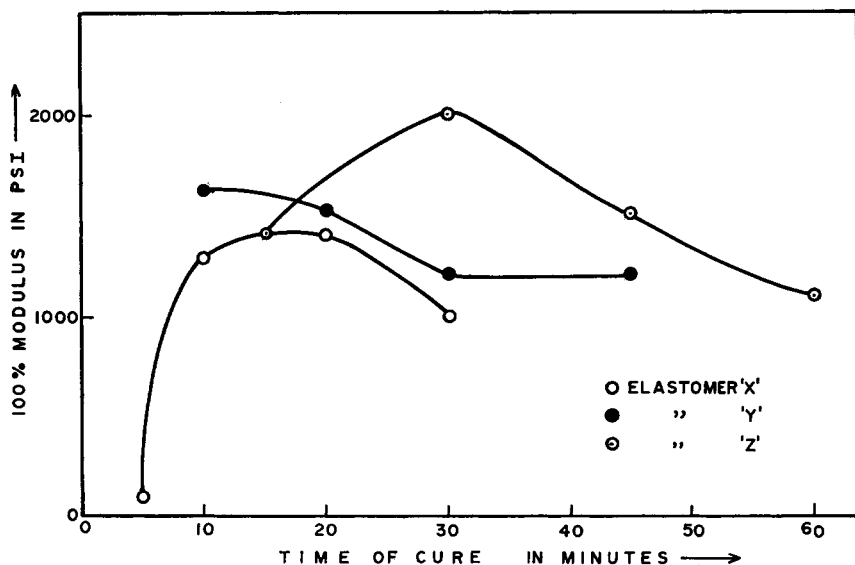


Fig. 4. Modulus curve of elastomers obtained by using diisocyanate: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

canization of the elastomers, the TDI-based elastomer X has the highest tensile strength. In the diisocyanate vulcanization of the elastomers, the MDI-based elastomer Y has the highest tensile strength. Excepting elastomer Y in sulfur vulcanization, all the tensile strength values of these castor elastomers are about 2000 or above. It appears that these values are about half of the tensile values reported for commercially available polyurethane elastomers.⁴ Elongation at break in case of X and Y is only 150%, and in case of Z only 100%. Thus elastomer Z is stiffer in both sulfur and diisocyanate vulcanization. The abrasion index for sulfur-cured elastomers is highest in the case of elastomer Z. It would appear that the presence of the sulfur vulcanizing ingredient⁵ improves the abrasion resistance compared to the case with diisocyanate-vulcanized elastomers. Figures 3 and 4 show the change in moduli with respect to time for sulfur- and diisocyanate-vulcanized elastomers.

CONCLUSION

It is possible to prepare elastomers by reacting castor oil with isocyanates by standard methods. These elastomers can be processed on standard rubber mills by known techniques. These could be used as substituents for rubber if the cost of isocyanate is not too high.

References

1. O. Bayer and E. Müller, *Angew. Chem.*, **72**, 934 (1960).
2. J. H. Sanders and K. C. Frisch, *Polyurethanes, Chemistry and Technology*, Vol. I, Interscience, New York, 1962, p. 50.

3. O. Bayer, E. Müller, S. Petersen, H. F. Piepenbrink, and E. Windemuth, *Rubber Chem. Technol.*, **23**, 812 (1950).

4. N. D. Ghatge and V. B. Phadke, *Rubber News*, **5**, No. 2, 22 (1965).

5. C. C. Davis and J. T. Blake, *Chemistry and Technology of Rubber*, Reinhold, New York, 1937, p. 427.

Résumé

A partir d'huile de ricin on a pu obtenir des élastomères prêtant au calandrage en utilisant un diisocyanate de 2,4-toluène, un diisocyanate de 4,4'-diphénylméthane et un diisocyanate de 1,5-naphthalène. On a vulcanisé ces élastomères avec le soufre et le diisocyanate de 4,4'-diphénylméthane en utilisant les méthodes technologiques habituelles des caoutchoucs. On rapporte les propriétés de ces composés.

Zusammenfassung

Rizinusöl wurde mit 2,4-Toluoldiisocyanat, 4,4'-Diphenylmethandiisocyanat und 1,5-Naphthalindiisocyanat zu walzbaren Elastomeren umgesetzt. Diese Elastomeren werden mit Schwefel und 4,4'-Diphenylmethandiisocyanat getrennt nach den kautschuktechnologischen Methoden vulkanisiert. Die Eigenschaften der Vulkanisate werden beschrieben.

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