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STUDIES IN POLYURETHANE BASED SYNTHETIC POLYMERS

A THESIS SUBMITTED TO
UNIVERSITY OF POONA
FOR
THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
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POONA 8

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March 29th 1968

V. B. PHADKE
M.Sc.

STUDIES IN POLYURETHANE BASED SYNTHETIC POLYMERS: INTRODUCTION

SCOPE OF THE PRESENT INVESTIGATION

INTRODUCTION

Within the last 50 years there have been many additions of products in the chemical industry which are miracles of ingenuity, usefulness and versatality. Very few of these products have the virtues of Polyurethanes.

Polyurethanes were developed painstakingly and systematically to compete with the commercially successful nylon polymers.[1] The discovery, exploration and development of polyurethane polymers is attributed to Prof. Otto Bayer and his co-workers.

In the earlier development of polyurethanes the most spectacular applications of the polyurethanes were in the fields of adhesive and synthetic foam. It is reported that development work of polyurethanes started at the same time in Germany and in the U.S.A.

During the second World War, the Germans made extensive use of polyurethane adhesives in elastomer to metal bondings.[1] Initial development work on the polyurethanes was in the rigid foam field.[2,3] These were used in the aircraft industry. The commercial development of polyurethane flexible foams is reported to be during 1952-53.[4]

The discovery of polyester-urethane elastomer goes to the credit of Pinten[5] to prepare "I rubber" by reacting a diisocyanate with a polyester.

The first isocyanate was prepared in 1848 by Wurtz[6], and it is interesting to note that the first polyester resin[7] was prepared accidentally in the year 1847. Vulkollans[8] were the polyester based urethane elastomers having very outstanding physical properties. These were developed by Prof. Bayer and his co-workers in Germany.

Since then there have been many developments in polyurethane elastomers throughout the world. The main types of polyurethane elastomers are (i) millable, (ii) thermoplastic and (iii) Castable.

(i) Millable Elastomer

In the millable elastomer technique, the polymer is compounded along with the vulcanizing ingredients and the resultant mix is processed to a finished article. The millable elastomers are processed on the conventional rubber machinery and have, therefore, great commercial importance.

(ii) Thermoplastic Elastomer

These essentially look like millable gums and could be shaped into any desired article by heat and pressure.

(iii) Castable Elastomer

The castable technique involves the addition of liquid ingredients in one step and curing the resultant mass into a rubbery product.

Unlike other elastomers, polyurethane elastomers have the great advantage of making specific formulations needed for specific applications. For example, it is possible to change the properties of a polyurethane elastomer by chaning the molecular configurations, rather than by adding plasticizers, filler loading and type of cross linking agent etc. Thus 1,6 Hexamethylene diisocyanate can produce urethane elastomer having a little tensile strength, whereas 2,4 Toluene diisocyanate would produce tensile strength 2850 - 3550 PSI. 1,5 Naphthalene diisocyanate would have tensile strength 4000 - 5000 PSI, while 2,7 Fluorene diisocyanate would produce tensile strength 6200 PSI (Table I)[8]

Table - 1

Modification of undried Polyethylene Adipate with 30 % excess of diisocyanate, with water cure.

Diisocyanate	Tensile strength, PSI	Elongation, %	Tear strength, PSI*
1,6 Hexamethylene diisocyanate	Product was worthless, hardened immediately		
2,4 Toluene diisocyanate	2850 - 3550	730	1180
1,5 Naphthalene diisocyanate	4400	765	2370
2,7 Fluorene diisocyanate	6200	660	2020

*Measured on 4 cm plates, ring specimen, 1 mm notched.

Similarly polyethylene succinate can give tensile strength of about 3900 PSI; Polyethylene adipate can give a tensile strength of 5000 PSI; Polypropylene adipate can give tensile strength of 3100 PSI. The comparative properties of the polyester urethane elastomers are given in the Table II.[8]

Table - II

Urethane elastomers made from polyesters modified with 1,5 naphthalene diisocyanate.

Polyester Components		Tensile strength, PSI	Elongation, %	Tear strength, PSI
Glycol	Acid			
Ethylene	succinic	3900	625	1700
Ethylene	adipic	5000	640	2250
1,2 Propylene	adipic	3100	780	1300

For the sake of comparison, the properties of the polyurethane elastomers along with the properties of different commercially available elastomers are given in Table III.[9]

TABLE - III

Physical properties of different elastomers[9]

1	Poly-urethane 2	Natural Rubber 3	Synthe-tic iso-prene rubber 4	SBR 5	Neo prene 6	Nitrile 7	Butyl 8	EPR 9	Hypalan 10	Silicone 11
Specific gravity	1.07-1.17	0.91-0.93	0.91-0.93	0.93-0.94	1.23	0.97-1.00	0.92	-	1.1	0.95-0.98
Hardness, Shore A	60-80	30-100	30.100	40-100	49.95	40-50	40-70	60-70	45-95	45-60
Compression Set	Excellent	Fair to good	Fair to good	Fair to good	Fair to good	Good	Fair	-	Fair	excellent
Tensile strength, PSI	4000-8000	3000-4000	3000-4000	3500	4000	4000	3000	2000-3000	500-3500	500-600 2000 exception
Elongation, %	500-700	400-800	400-800	500-600	750-1000	500	600-1000	400-600	250-450	300-320
Tear resistance	Excellent	Good	Good	Poor	Good	Fair	Good	-	Fair	Fair

(Continued .....)

Table - III (Continued)

1	2	3	4	5	6	7	8	9	10	11
Abrasion resistance	Exce-llent	Good	Good	Good	Good	Good	Good	Good	Good	Fair
Resiliance	Exce. llent	Exce-llent	-	Fair	Good	Fair	Good	-	Good	Good
Permeability to gases	-do-	Fair	Fair	poor-fair	-do-	Fair-good	Exce-llent	-	-do-	Fair
Atmospheric oxygen and light aging	Exce-llent	poor	poor	poor	Good	poor	Exce-llent	Exce-llent	Exce-llent	Exce-llent
Ozone resistance	-do-	-do-	-do-	-do-	-do-	fair	fair-good	-do-	-do-	-do-
Acids & alkali resistance	poor-fair	fair to good	fair to good	fair to good	fair to good	-do-	exce-llent	-do-	-do-	good
Oil and fuel resistance	Exce-llent	poor	poor	poor	good	good	poor	Exce-llent	good	good

(continued ....)

(Table - III continued)

1	2	3	4	5	6	7	8	9	10	11
Polar solvent resistance	poor	Good but not halo-genated	Good but not halo-genated	Good but not halo-genated	poor	poor	Exce-llent	Exce-llent	good	poor
Non-polar solvent resistance	Exce-llent	poor	poor	poor	good	good	poor	-do-	-do-	fair-good
Cost /^{40}	0.74-1.85	-	0.195-0.2000	0.1330-0.2600	0.400-1.25	0.43-0.65	0.25-0.6500	0.20-0.30	0.45-0.500	2.500-4.01

Polyurethane elastomers have been suggested[10] for the following applications:-

Tyres:	Truck, Bus and Passenger treads.
Solid tyres:	Industrial trucks, Castor wheels.
Electrical:	Cables etc.
Foot wear:	Heals, soles etc.
Belts:	Conveyer, V belts etc.
Hoses:	For oil-wells, sand blasting equipments, air drills etc.
Coated fabrics:	Diaphragm, tarpaulins for low temperature, ultraviolet light and gases resistance coverings, tents etc.
Rolls:	Textile rolls, printing rolls, high pressure rolls etc.
Molded goods:	Automobile parts, oil seals, oil resistant washers, gaskets, O-rings, hydraulic buckets etc.

The above applications of polyurethane elastomers have induced the research workers of this laboratory to pay greater attention to these products and to undertake their development. It is expected that the knowledge acquired during this developmental work will be of immense help to the developing economy of our country.

PART I

SECTION I

AIM OF THE PRESENT INVESTIGATION

PART - I

SECTION - I

Aim of the present investigation

A complete systematic survey of polyurethane elastomers was made, and it is briefly summarised in Section II. It was observed that most of the conventional commercial millable urethane elastomers were based on polyesters derived from polyethylene polypropylene adipate.

In the present investigations, dibasic acids used in the studies were succinic acid, adipic acid, sebacic acid and hexadecamethylene dicarboxylic acid.

The glycol part used was the mixture of ethylene glycol and 1,2 propylene glycol in the proportion of 80:20. It may be noted here that polyesters derived from ethylene glycol- adipic acid and 1,2 propylene glycol - adipic acid, can be blended in the 80:20 proportion to give a mixed polyester which could be used to make millable urethane elastomers. But this process was not followed, as it was observed that the former process is much easier to operate.

It was observed that succinic acid polyester, sebacic acid polyester, hexadecamethylene dicarboxylic acid polyester produced polymers which were unsuitable for the preparation of urethane elastomers. However adipic acid polyesters gave polymers of elastomeric nature.

Since the hydroxyl number of a polyester is a measure of its molecular weight, it was decided to prepare adipate polyesters of different hydroxyl numbers. These polyesters of different hydroxyl numbers were used in the preparation of millable urethane elastomers in order to study the relationship between the hydroxyl number and the physical properties of the resultant elastomer.

Literature survey indicated that polyethylene polypropylene adipates were reacted invariably with 4,4' diphenyl methane diisocyanate to produce the urethane elastomers. Hence all the above mentioned different hydroxyl number polyesters were reacted with 4,4' diphenyl methane diisocyanate to produce hydroxy terminated urethane elastomers.

It is also reported that urea linkages impart some beneficial properties to millable elastomers.[11] Hence urethane-urea linkages possessing polymers were prepared by reacting polyethylene polypropylene adipate with slight excess of 4,4'diphenyl methane diisocyanate and chain extending the polymer with 4,4'methylene bis (2-chloroaniline).

The use of triallyl cyanurate in millable urethane elastomer (Urepan 640) has been reported by M/s Bayer to get better physical properties.[12] It was therefore decided to use triallyl cyanurate in those polymers which had physical properties nearer to the commercially available elastomers.

This study has produced an elastomer of the physical properties nearer to those of the millable commercial urethane elastomer. The properties are described in Table XXXV.

PART I

SECTION II

HISTORICAL DEVELOPMENT OF MILLABLE URETHANE ELASTOMERS

S E C T I O N - II

Historical Development of Millable Urethane Elastomers:

Early development in urethane elastomers was noticed in Germany and in England in 1940.

Vulcollans were the result of research and development by Prof. Bayer and his co-workers in Leverkusen, Germany.

Vulcaprene,[13] another type of urethane elastomer, was developed by Imperial Chemical Industry by about the same time i.e. 1940-42.

Since 1950 great strides have taken place in the preparation of urethane elastomer on commercial scale. The table IV mentions the name of manufacturers and the information along with the trade names of the different urethane elastomers, produced on commercial scale.

Polyurethane elastomer are now classified into three types: (i) Millable elastomer, (ii) Castable elastomer, (iii) Thermoplastic elastomer. Millable elastomers are solid in nature and processed on the conventional rubber machinery by the usual techniques. Castable elastomers are produced by mixing liquid ingredients in one step and curing them into the desired articles. Thermoplastic elastomers are those which are elastic in nature but obtained by the techniques of injection moulding, extrusion etc.

Table - IV

List of commercially available millable Polyurethane elastomers

Trade name	Description	Manufacturer
Urepan 600	Polydiethylene adipate - toluene diisocyanate	Farbenfabriken Bayer
Urepan 640	Polyester (adipic acid and mixed glycol) - 4,4' diphenyl methane diisocyanate	
Vulcaprene	Polyester amide - diisocyanate	Imperial Chemical Industry Ltd.
Genthane S	Polyethylene poly-propylene adipate -4'4 diphenyl methane diisocyanate.	General Tyre and Rubber Co.
Vibrathane	Polyethylene poly-propylene adipate -4,4' diphenyl methane diisocyanate and 1,6 Hexamethylene diamine.	U.S. Rubber Co.
Chemigum SL (Neothane)	Polyester diisocyanate	Goodyear Tyre and Rubber Co.
Cynaprene	Polyester diisocyanate	American cynamide Co.
Elastothane 455	Polyester diisocyanate	Thikol Chemical Corporation
Adiprene C	Polyether diisocyanate	E.I.du Pont De Nemours & Co.

Most of these elastomers are based on polyester - diisocyanate reaction. However polyether-diisocyanate reactions have also produced some millable commercial elastomers.

The mechanical properties of these urethane elastomers are surprisingly very high: They have hardness shore A 60 to Shore D 60; tensile strength 3000 to 9000 PSI; elongation 300 to 800; tear strength 300 to 1000 lbs/inch and very high abrasion resistance. All these combined properties make these elastomers ideal elastomers for engineering materials.

Chemistry:

The preparative steps involved in making these elastomers are (i) preparation of long chain diols such as polyester of about 2000 molecular weight. Polyester is prepared by thermally condensing slight excess of glycol with a dicarboxylic acid.

$$m\ HO - R - OH + n\ HOOC - R' - COOH \rightarrow HO - R - OCOR' \text{---} R\text{-}OH$$

Glycol Dibasic acid Polyester

(ii) Reaction of diol with diisocyanate to produce hydroxy/ isocyanate or terminated urethane polymer

$$\alpha\ HO \text{----} OH + \gamma\ OCN - R - NCO \longrightarrow HO \text{---} OCONH.RNHCO.O \text{---} OH$$

Diol(Polyester) Diisocyanate Hydroxy terminated urethane polymer

or

α HO - - - OH + γ OCN-R-NCO $\longrightarrow$ OCN-R-NH.CO ---OCONH-R-NCO

Isocyanate terminated polymer

(iii) Chain extension of isocyanate terminated polymer with (a) glyco, (b) diamine, (c) water etc.

(a) 2 OCN-R-NHCO.O ----- O.CO.NH-R-NCO + HO-R'-OH

Isocyanate terminate polymer ↓ Glycol

OCN - RNH.CO.O NH RNHCOO
R'
OCN - RNHCO.) NH RNHCOOO

Urethane

(b) 2 OCN - R - NHCO ---- O.CO.NH-R-NCO + $H_2N - R^2 - NH_2$

Isocyanate terminated polymer ↓ Diamine

OCN - R- NHCO.O --- O.CO.NH - R - NHCO NH
R^2
OCN - R- NHCO.O --- O.CO.NH - R -NHCONH

substituted urea

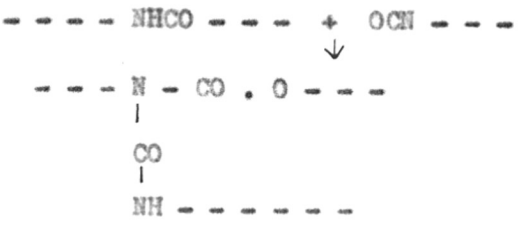
(c) 2 OCN - R - NHCOO --- O CO NH - R - NCO + HOH

Isocyanate terminated polymer ↓ water

OCN - R - NHCOO --- O.CO.NH R NH
$CO + CO_2$
OCN - R - NHCOO --- O CO.NH R NH

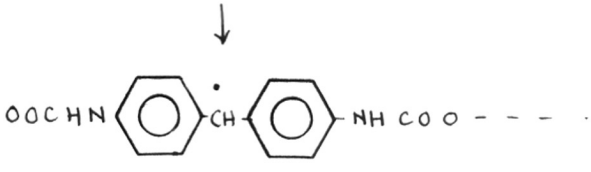
substituted urea

(iv) Curing or cross linking of isocyanate terminated polymers is achieved by heating

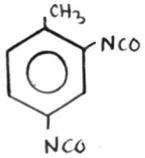


Allophanate cross linking

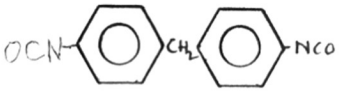
Millable polymer which possesses active hydrogen or unsaturation can be cured by use of peroxide and/or sulphur



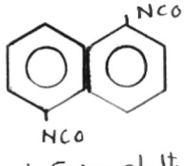
In most of these elastomer preparations the diisocyanate used are 2,4 toluene diisocyanate, 4,4'diphenyl methane diisocyanate, 1,5 naphthalene diisocyanate etc.



2,4 Toluene diisocyanate



4,4' diphenylmethane diisocyanate



1,5 naphthalene diisocyanate

VULKOLLAN

Vulkollans are a class of polyurethane elastomers developed by Prof. Otto Bayer and his collaborators in Germany.[8] Polyethylene adipate was reacted with 30 % excess of diisocyanate over the amount corresponding to the hydroxy number of the polyester, to produce isocyanate terminated prepolymer. The prepolymer was then reacted with water; the resultant crumb was rolled into sheet which was press-cured for 10 - 15 minutes at 150 - 170°C.

The diisocyanates were varied and the resultant properties of the elastomers (vulkollans) are described in Table V.[8]

From this study Prof. Bayer preferred to use 1,5 naphthalene diisocyanate for these elastomer preparations, because this diisocyanate had added advantage of low vapour pressure, less toxicity and good reactivity.

Prof. Bayer prepared a number of polyesters using different glycols and different diabasic acids. These polyesters were then reacted with 1,5 naphthalene diisocyanate and water. The properties of the resultant elastomers are tabulated in Table VI.

Prof. Bayer further prepared different polyester blends and reacted these with 1,5 naphthalene diisocyanate and water. The results of these elastomers are tabulated in Table VII.

TABLE - V

Modification of undried polyethylene adipate with 30% excess of diisocyanate with water cure[8]

Diisocyanate	Tensile strength, PSI	Elongation, %	Tear strength, PSI
1,6 Hexamethylene	Product was worthless, hardened immediately		
2,4 tolylene	2850 - 3550	730	1180
2,nitrodiphenyl 4,4' -	2650	743	1730
2-nitrodiphenyl methane 4,4' -	2800	629	1070
Diphenyl methane sulpone 4,4' -	3400	736	1540
Diphenyl sulfone 4,4'-	3000	331	1960
Naphthalene 1,4 -	4500	756	1900
Naphthalene 1,5 -	4400	765	2370
Naphthalene 2,7 -	5700	750	2320
2,7 fluorene	6200	660	2020
2,8 chrysene	4250	684	1900

*Measured on 4 cm plates (ring specimen, 1 mm notched)

Table - VI

Urethane elastomers made from linear polyester modified with 1,5 naphthalene diisocyanate

Polyester components		Polyester consistency	Tensile strength, PSI	Elongation, %	Tear strength, PSI	Remarks
Glycol	Acid					
Ethylene	Succinic	Wax	3900	625	1700	High permanent elongation, hardens leathery
Ethylene	Adipic	Wax	5000	640	640	Hardens slowly
Ethylene	Pimalic	Liquid	Not measured			
Ethylene	Sebacic	Wax	Not measured			Hardens on cooling, highly elastic only at high temperature
Ethylene	Decamethylene dicarboxylic	Wax	Not measured			-do-
Ethylene	Diglycolic	Thick resin	3800	570	2100	Leathery easily hydrolyzed.
Ethylene	Phthalic	Brittle	1500	261	1240	Requires plasticizers for processing
1,2 propylene	Succinic	Liquid	2250	670	1360	Leathery elastic at 17°C
1,2 propylene	Phthalic	Brittle	2550	-	-	-
2,3 Butylene	Adipic	liquid	2550	630	1300	Does not harden
1,6 Hexane	Adipic	Wax	3500	610	1730	Hardens
Hexahydroresorcinol	Succinic	Thick	1600	223	1160	Leathery

It was inferred from Table VII that polyethylene adipate based vulkollans have better physical properties and 1,2 propylene adipate have the lowest physical properties. The mixed polyester and blends produce vulkollans which had properties intermediate between these two types of vulkollans. The effect of molecular weight hydroxy number was also studied for polyethylene adipate in the preparation of vulkollans from 1,5 naphthalene diisocyanate and water. These results are described in Table VIII.

This study showed that the high molecular weight polyesters produced vulkollans having better mechanical properties, but the elastomer was reported to possess pronounced crystallization tendencies.

Glycol extended vulkollans:

So far the description has been by reaction of polyethylene adipate, 1,5 naphthalene diisocyanate and water to produce water extended vulkollans. It was then decided to study glycol in place of water as an extender, to avoid gaseous evolution. The properties of glycol extended vulkollans are described in the Table IX.

Diamine extended vulkollans:

Muller et al[14,15,16] had reported the use of diamine as chain extender in place of glycols. The reactivity of diamines

TABLE - VII

Modification of mixed esters and ester blends with 1,5 naphthalene diisocyanate and water

Polyester	Tensile strength, PSI	Elongation, %	Permanent elongation	Tear strength, PSI	Shore hard ness	Elasti- city	Harden- ing
Polyethyelen adipate	5000	640	6	2250	60	69	++
Mixed ester: Ethylene, propylene glycol 70:30, adipic acid	4000	725	15	1900	65	65	+
Blend Polyethylene adipate 70 Polypropylene adipate 30	4250	730	13	2050	67	63	+
Mixed ester Ethylene : Propylene glucol 50:50, adipic acid	3850	700	20	1550	71	70	-
Blend Polyethylene adipate (50) Polypropylene adipate (50)	3550	680	14	1650	66	70	-
Polypropylene adipate	3100	730	14	1300	69	76	-

TABLE - VIII

Modification of polyethylene adipates with 1,5-naphthalene diisocyanate

Polyester Properties		Gms NDI/100g of polyester	Mol.wt of the adduct	Tensile strength, PSI	300% modulus, PSI	Elongation, %	Tear strenghe, PSI	Elasticity	Shore hardeness
OH No.	Mol.Wt.								
24	4680	7.0	8920	5500	780	770	2250	-	59-63
32	3500	9.5	6600	5500	1040	710	2250	70	64-70
42	2670	12.5	5090	5400	1400	720	2300	61	71-76
52	2160	16.0	3895	4600	1700	726	2150	60	71-86
95	1180	30.5	2170	4700	2270	455	1200	63	83

with a diisocyanates was very fast, resulting into nonhomogeneous vulkollans. This difficulty of nonhomogeneous vulkollans was overcome by properly selecting the diamines and/or diisocyanates.

A qualitative method of testing appropriate reactivity of diamine and a diisocyanate has been suggested by Prof. Bayer, which is described below;

In a boiling methylene chloride solution a seminormal solution of both diamine and diisocyanate was added. If there is an immediate precipitate resulting from urea formation, both the components are unsuitable to produce diamine extended vulkollans. If slight turbidity is obtained, the two components may be suitable for the preparation of the vulkollan. Aliphatic diamines are reported to be faster than aromatic diamines when reacted with diisocyanate. Even the reactivity of the aromatic diamine may be controlled by substituting certain groups in the aromatic rings. The Table X describes the results of vulkollan obtained by reacting diamine.

Thus it was observed that substituting chloro group in ortho position to amino group produces less reactive aromatic amine.[17]

Diamine curing systems are more suitable, particularly for the production of castable elastomers. Some of the nonpourable compositions of polyurethanes using diamine chain extenders are described in Table XI.

TABLE - IX

Properties of glycol-extended vulkollans using 1,5 naphthalene diisocyanate.

Polyester OH No.50	Glycol extender	Tensile strength, PSI	Elongation, %	300 % modulus, PSI	Tear strength, PSI	Elasticity, %	Shore hardness
1	2	3	4	5	6	7	8
Polyethylene adipate	1,4 butane diol.2%	4800	700	1050	2100	59	84
70:30 Mixture**	1,4 butane diol.2%	4000	680	700	1750	57	75
Polypropylene adipate	1,4 butane diol.2%	3200	830	850	1050	43	76
Polyethylene adipate	1,4 cyclohexane diol. 2.2 %	5400	600	500	2500	59	67
70:30 Mixture**	1,4 cyclohexane diol. 2.2 %	4000	623	780	1600	58	75
Polypropylene adipate	1,4 cyclohexane diol. 2.2 %	2600	720	640	1350	70	70

** A 70-30 mixture of polyethylene adipate and polypropylene adipate

(Continued ....)

Table - IX (Continued ..)

1	2	3	4	5	6	7	8
Polyethylene adipate	Thiodiethylene glycol 2.2 %	3400	545	480	1750	69	62
Polypropylene adipate	Thiodiethylene glycol 2.2 %	2500	715	1200	1050	45	74
Polypropylene adipate	1,4 butyne diol. 2 %	4500	640	500	2250	70	60
Polypropylene adipate	Triethylene glycol 2.5 %	2200	925	310	530	41	68
Polypropylene adipate	Dimethyl propylene glycol 2.2 %	3100	780	350	590	41	62
Polypropylene adipate	Glycerin monophenyl-ether 2 %	2600	900	865	530	33	-
Polyethylene adipate	Hexahydro pyrocate-chol 2.5 %	5000	777	325	2100	52	57

TABLE - X

Properties of diamine-extended vulkollans

Castable combination			Tensile strength, PSI	Elongation, %	Tear strength, PSI	Rebound elasticity	300% Modulus, PSI	Shore hardness
Polyester	Diisocyanate	Diamine						
1	2	3	4	5	6	7	8	9
Polyethylene adipate	1,5 naphthalene diisocyanate 16 %	O-Dichloro benzidine 5.4 %	3010	271	2810	53	1510	80
Polypropylene adipate	"	"	1190	463	1020	40	940	77
70/30 Mixture*	"	"	3030	600	1490	50	1020	80
Polyethylene adipate	"	m-dichloro benzidine 5.4 %	2450	533	1920	45	340	59
70/30 Mixture*	Tolylene diisocyanate 13 %	o-dichloro benzidine 5.4 %	3870	630	2000	59	1490	76

*A 70-30 mixture of polyethylene adipate and polypropylene adipate

(Continued ...)

Table - X (Continued..)

1	2	3	4	5	6	7	8	9
Polyethylene adipate	Tolylene diisocyanate 13 %	Tolylene diamine 3 %	4070	720	2090	51	500	60
"	"	Dianisidine 6.5 %	3970	635	2630	37	460	58
"	"	Diamino phenatol 3.3 %	3030	602	1670	45	460	65
"	Hexamethylene diisocyanate 13 %	4,4'diamino-diphenyl methane 5 %	3900	680	3010	53	1170	90
"	"	Dianisidine 6.5 %	3150	650	1490	55	730	77
"	"	Tolylene diamine 3 %	3840	710	2090	57	570	69
Polypropylene adipate	"	"	1830	707	1600	54	370	70
70/30 Mixture*	"	"	3080	728	1370	51	360	65

*A 70-30 mixture of polyethylene adipate and polypropylene adipate

TABLE-- XI

Nonpourable combination with diamine extended vulkollans

			Tensile strength, PSI	Elongation, %	Tear strength, PSI	Rebound elasticity	300 % Modulus, PSI	shore Hardness
70/30 mixture*	1,5 naphthelene diisocyanate, 16 %	Tolylene diamine 2.64 %	4650	660	2400	57	1310	72
-do-	-do-	1,5 naphthelene diamine, 3.4 %	2860	430	2550	63	1620	69
-do-	-do-	Diamino-diphenyl methane 4.2 %	3920	590	2790	60	1520	72
-do-	-do-	Dichloro phenyl diamine, 3.8 %	1330	340	533	45	720	72

*A 70-30 mixture of polyethylene adipate and popypropylene adipate

Amino-alcohol extended vulkollans:

Amino-alcohol extended vulkollans can be obtained by using amino alcohols or a mixture of amine and glycols or diamines. The properties of such type of vulkollans are described in Table XII.

Table - XII

Properties of amino alcohol and diamine-glycol extended vulkollans*

Amino alcohol	Tensile strength, PSI	Elongation, %	300% Modulus, PSI	Tear strength, PSI	Elasticity, %	Shore hardness,
p-amino phenyl methyl carbinol 2.95 %	4500	650	935	1900	53	71
o-dichloro-benzidine 1.8 % and quinitol 1.66 %	3100	620	1080	1500	47	70

*Using 100 parts 70:30 mixture of polyethylene adipate and polypropylene adipate 16 parts of 1,5 naphthalene diisocyanate.

Storage stable vulkollans

In the preparation of above described vulkollans, excess of 1,5 naphthalene diisocyanate was used to produce isocyanate terminated polymers. These polymers when

press-cured under heat and pressure, cross-linked due to the presence of residual isocyanate groups. Such polymers were, however, unsuitable for storage. This difficulty was overcome by using diisocyanate in a slightly deficient amount than that needed for polyester. Since there was no free isocyanate groups left, they were storage stable polymers. These were produced into elastomeric articles by usual procedures.

Recently millable storage stable elastomers are produced under the trade name of Urepan by Farbenfabrikan Bayer A.G.

Urepan 600

Urepan 600 was produced by reacting polydiethylene adipate with toluene diisocyanate,[18] where the polymer chains are hydroxy groups terminated. Thus urepan 600 is chemically a storage stable polymer. Urepan 600 is cross-linked by 2,4 toluene diisocyanate dimer and hydroquinone dioxyethyl ether. A typical recipe and the physical properties of Urepan 600 are tabulated in Table XIII.

Urepan 640

Urepan 640 was produced by reacting a polyester (special mixture of glycols condensed with adipic acid) with deficient amount of 4,4' diphenyl methane diisocyanate,[12] so as to produce a hydroxy terminated urethane polymer. Thus

TABLE XIII[18]

Recipe and physical properties of Urepan 600

Recipe	A	B	C	D
Urepan 600	100.0	100.0	100.0	100.0
HAF black	20.0	-	-	20.0
Hydroquinone dioxyethyl ether	-	12.5	18.2	18.2
Dimeric tolyulene diisocyanate	10.0	30	40.0	40.0
Physical Properties				
Hardness, shore A	81	92	96	98
Hardness, shore D	-	41	57	64
Tensile strength, PSI	2844	4266	4266	4266
Elongation, %	700	500	350	280

TABLE XIV[12]

Recipe and physical properties of Urepan 640

Recipe	A	B
Urepan 640	100	100
HAF black	20	-
Highly reinforcing silica	-	20
Peroxide	3	3
Triallyl cyanurate	1	1
Physical properties		
Hardness, shore A	62	65
Tensile strength, PSI	4100	4000
Elongation, %	380	450

this polymer is also chemically storage stable. Urepan 640 can be cured with peroxide curing system. A typical recipe and physical properties are described in Table XIV.

Chemi gum SL (Neothane)

Seeger et al[19,20,21] of Goodyear Tyre and Rubber Co. developed chemigum SL. Chemigum SL was a reaction product of a linear polyester (adipic acid - ethylene and/or propylene glycol) with diisocyanate. These elastomers resembled pale crepe natural rubber. These elastomers were processed on rubber mixing mill or Banbury mixer with diisocyanate as cross-linking agent. Diisocyanate reported to be used in the preparation of storage stable elastomers are 4,4'xenylene diisocyanate, 1,5 naphthalene diisocyanate, 4,4'diphenyl methane diisocyanate and toluene diisocyanate.

In the preparation of storage stable urethane elastomers, it was observed that the ratio of NCO/OH was a critical factor. For this, Seeger proposed a formula: the ratio of NCO/OH group called R value, which is as follows:

$$R \text{ value} = \frac{\text{Moles of diisocyanate}}{\text{Moles of polyester}}$$

For the optimum storage and processing, an R value of 0.7 to 0.99 was reported to be most useful. Maximum molecular weight of the polymer could be obtained when R value was one. To produce storage stable polymer, R value should be lower

than one. When R value was greater than one, isocyanate terminated polymers were obtained, which, of course, were not storage stable polymers. The physical properties are described in Table XV.

TABLE - XV

Physical properties of vulcanized Chemigum SL[19]

Hardness, shore A	65
Tensile strength, PSI	5450
300 % Modulus, PSI	675
Elongation, %	750
Cured 15 minutes, at 140°C.	

Vulcaprene A

Vulcaprene A was prepared by reacting polyester amide and diisocyanate.[13] Vulcaprene A was developed in England by Imperial Chemical Industries. This elastomer is cross linked with variety of cross linking agents such as diisocyanate, triisocyanate, formaldehyde, paraformaldehyde, protein-formaldehyde combinations, polyvinyl formal, chromates and dichromates. Vulcaprene A showed excellent resistance to oil, solvents, gases etc. Vulcaprene was compatible with many polymers.

Genthane S:

Gruber et al[22] of General Tyre and Rubber Co. developed Genthane S. Genthane S was prepared by condensing polyester (adipic acid and 80:20 mixture of ethylene glycol and propylene glycol) and 4,4' diphenyl methane diisocyanate to produce hydroxy terminated storage stable polymer. Genthane S could be cured with peroxide cross-linking agents. A typical recipe of the compounding ingredients and the physical properties are given in the Table XVI.

Table - XVI

Recipe and physical properties of Genthane S

Recipe	A	B
Genthane S	100.0	100.0
Acrawax C	2.0	2.0
Carbon black	30.0	30.0
Dicumyl peroxide	30	-
Polymethylene polyphenylene isocyanate	-	5.0
Physical properties		
Hardness, shore A	60	72
Tensile strength, PSI	4400	3750
300 % Modulus, PSI	1925	1750
Elongation, %	500	550

Vibrathane:

Vibrathanes are a series of polyurethane elastomers developed by Urs of U.S. Rubber Company.[23] The elastomer[11] was obtained by reacting 1.0 mole of polyethylene polypropylene adipate (Hydroxy number 55.0, Acid No. 1.0) with 1.2 moles of 4,4' diphenyl methane diisocyanate and 0.2 mole of Hexamethylene diamine. The polymer was cured by peroxide curing agent. Urs pointed out that urea linkages accelerate the rate of curing. Thus curing was affected at 152°C for 45 minutes, 177°C, 3 minutes, 204°C, 2 minutes. A typical recipe and physical properties are given in the Table XVII.

Table - XVII

Recipe and physical properties of Vibrathane

Recipe		
	Vibrathane	100
	Stearic acid	0.25
	HAF	20.0
	Dicup 40C	4.0
	Cure time, minutes	45
	Cure temperature	152°C
Physical properties		
	Hardness, shore A	65
	300 % Modulus, PSI	2900
	Tensile strength, PSI	4200
	Elongation, %	400
	Tear strength, lbs/inch.	500

Elastothane 455

Swaab of Thikol Chemical Corporation described Elastothane 455 as sulfur curable urethane elastomer.[24,25] Elastothane 455 is a polyester based urethane elastomer. A typical recipe and physical properties are described in Table XVIII.

Table - XVIII

Recipe and physical properties of Elastothane 455.[24]

Recipe	
Elastothane 455	100.0
SAF black	30.0
MBT	2.0
MBTS	4.0
Activator ZC 456	1.0
Cadmium sterate	0.5
Sulphur	2.0
Physical properties	
Hardness, shore A	72
300 % Modulus, PSI	2700
Tensile strength, PSI	5100
Elongation, %	520
Tear strength, lb/inch	350

Adiprene C

Ogden of du Pont described Adiprene C as sulphur curable urethane elastomer.[10,26] Adiprene C is a polyether based urethane elastomer. A typical recipe and its properties are given in Table XIX.

TABLE - XIX

Recipe and physical properties of Adiprene C

Recipe	A	B
Adiprene C	100	100
EPC	30	30
MBT	1	-
MBTS	4	-
Activator RCD 2090	0.35	-
Sulphur	1.5	-
Di Cup 40 C	-	2.5
Physical properties:		
Hardness, shore A	71	69
300 % Modulus, PSI	2975	2975
Tensile strength, PSI	5000	4975
Elongation, %	450	450

Cynaprene:

In 1966 American Cynamide Company announced six polyurethane elastomers which are as follows.[27]

Cynaprene A8, A9, D-5, D-6, D-7, 4590

These are reaction products of polyester with toluene diisocyanate. The products have hardness shore, A 30 to shore D 82; 300 % Modulus, 150 to 4700 PSI; Tensile strength, 1700 to 9500 PSI; Elongation, % 250 - 800.

PART I

SECTION III

PRESENT INVESTIGATION AND RESULTS

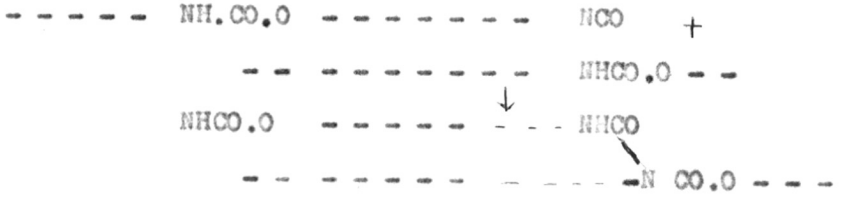
S E C T I O N - III

Present investigation and results.

In the preparation of millable polyurethane elastomer there are two types of polymeric materials (1) Having free isocyanate groups at the chain ends, (2) Having hydroxy, amino groups at the chain ends.

The former type of polymers are susceptible to the atmospheric moisture condition, while the latter do not change even on storage for longer time.

In the case of isocyanate terminated polymer, cross linking takes place in the storage time between isocyanate groups and active hydrogen centers of the polymer. This cross linking makes the processing of this type of millable elastomer very difficult on the conventional rubber machinery.



In the case of hydroxy/amino terminated millable polyurethane elastomer this difficulty does not arise. Therefore greater interest has been shown in the development of such millable polyurethane elastomers.

The following table describes the total number of polymers-elastomers attempted.

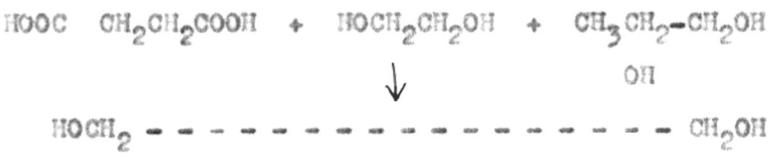
TABLE - XX

Name and nature of the different polymers-elastomers from polyesters

Name	Polyester, equivalent	MDI, equivalent	MOCA, equivalent	Remarks
A	Polyethylene polypropylene succinate 1.0	0.99	-	Millable polymer
B	Polyethylene polypropylene succinate 1.0	1.2	0.2	-do-
C	Polyethylene polypropylene adipate hydroxyl No.24, 1.0	0.99	-	Millable elastomer
D	-do- 1.0	1.2	0.2	-do-
E	Polyethylene polypropylene adipate hydroxyl No.46, 1.0	0.99	-	-do-
F	-do- 1.0	1.2	0.2	-do-
G	Polyethylene polypropylene adipate hydroxyl No.67, 1.0	0.99	-	Semisolid unworkable mass
H	-do- 1.0	1.2	0.2	Millable elastomer
I	Polyethylene polypropylene sebacate 1.0	0.91	-	Plastic polymer
J	Polyethylene polypropylene sebacate 1.0	1.2	0.2	-do-
K	Polyethylene polypropylene hexadecamethylene dicarboxylate 1.0	0.99	-	-do-
L	Polyethylene polypropylene hexadecamethylene dicarboxylate 1.0	1.2	0.2	-do-

Polyethylene polypropylene succinate (PEPS) based polyurethane polymer:

In the present investigation the polyester from succinic acid and 80:20 mixture of ethylene glycol and 1,2 propylene glycol has been prepared.



PEPS

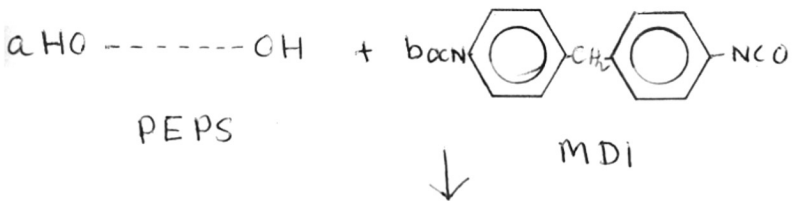
The details of the preparation of PEPS are described in Experimental Section V, Part 1.

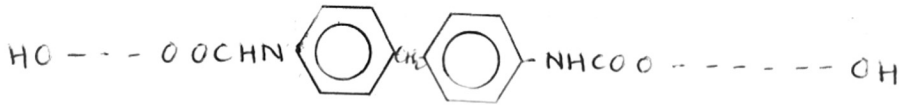
Polyethylene polypropylene succinate was a white waxy material having softening point 72 - 75°C

Polymers, A and B

Preparation of polymers, A and B

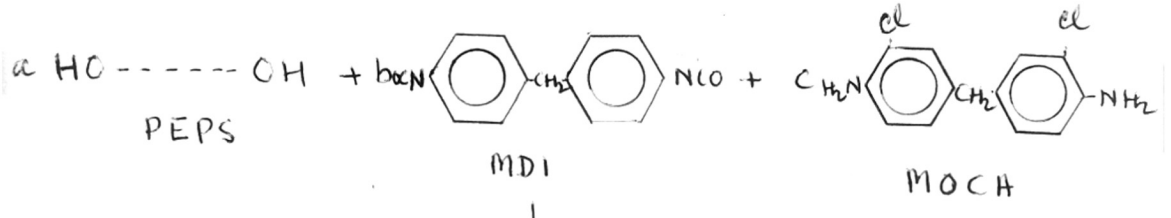
The polyethylene polypropylene succinate (PEPS) has been reacted with 4,4'diphenyl methane diidosycnate to produce storage stable gums of two types (i) hydroxy terminated polymer A was prepared by reacting 1 equivalent of polyester PEPS with 0.99 equivalent of 4,4'diphenyl methane diisocyanate.

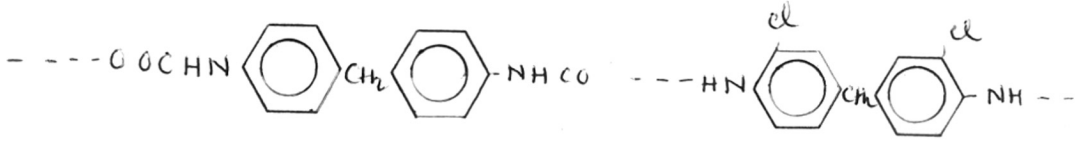




Polymer A

(ii) Amine extended polymer B was prepared by reacting 1 mole of polyester (PEPS) with 1.2 moles of 4,4'diphenyl methane diisocyanate (MDI) and 0.2 mole 4,4'methylene bis (2 - chloroaniline) (MOCA)





Polymer B

Physical properties of Polymers A and B

Both these polymers had a pale yellowish white colour and had about the same density. Polymer A softened at 72°C and polymer B softened at 145°C. Higher softening point of polymer B was probably because of the presence of urea groups and rigid aromatic rings. Both the polymers were soluble in dimethyl formamide and dimethyl sulphoxide.

Table - XXI

Physical properties of polymers A and B.

	Polymer A	Polymer B
Form	Pale yellowish white solid polymer	
Specific gravity	1.312	1.292
Softening point	72°C	145°C
Solubility	Dimethyl formamide and dimethyl sulphoxide	

Compounding and curing of polymers A and B

Both these polymers were easy to process on the laboratory rubber mixing mill. The compounding recipe is given in the table XXII.

These polymers were cured by diisocyanate and peroxide curing systems. The diisocyanate used for curing

Table - XXII

Compounding recipe of polymers A and B

	Polymer A		Polymer B	
	Peroxide cure	Diixocyanate cure	Peroxide cure	Diisocyanate cure
Polymer A	100	100	-	-
Polymer B	-	-	100	100
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
Dicup 40 C	5.0	-	5.0	-
MDI	-	10.0	-	10.0

reaction was 4,4'diphenyl methane diisocyanate (MDI). Buist et al has reported that the reactivity of 4,4'diphenyl methane diisocyanate (MDI), a diisocyanate of the diaryl methane type derived from aniline / o-toludine / formaldehyde condensate (methyl - MDI), 3,3'dimethyl diphenylene 4,4'diisocyanate (TODI) have satisfactory reactivity for diisocyanate curing. Since only MDI was available for our work, it was used for diisocyanate curings in all the diisocyanate curing experiments.

In the peroxide curing, stabilised dicumyl peroxide i.e. Dicup 40C was used as this was reported to be the best and safest peroxide curing agent.

The diisocyanate curing in the vulcanizates of polymers A and B was achieved at 115°C in 15 minutes. In practice diisocyanate cures are made at about 140°C in 15 minutes time, but in this particular case, curing system at 140°C temperature and at 10 and 15 minutes, serious blisters - scorchy phenomenon was observed in the test specimens.

Peroxide cure was achieved at 140°C, however there were no blisters in the test specimens.

Physical properties of the vulcanizates of polymers, A and B

The hardness shore A values of both diisocyanate and peroxide cures in polymers, A and B was 95 each. The specific gravity values in both of these curing systems were in the range of 1.39 - 1.44. Modulus, tensile strength and elongation % values were nearly similar in both the curing systems of polymers, A and polymer B. It was noted however, that in the case of tear strength, values of these polymers, the tear strength value for polymer A peroxide cure and polymer B is the diisocyanate cure were higher. These physical properties are tabulated in Table XXIII.

The vulcanizates of polymers A and polymer B were leathery. Hence no attempts were made to exploit these polymers for preparing useful articles.

Table - XXIII

Physical properties of vulcanizates of polymers A and B

Properties	Polymer A		Polymer B	
	Peroxide cure	Diisocyanate cure	Peroxide cure	Diisocyanate cure
Specific gravity	1.392	1.420	1.432	1.444
Hardness, shore A	95	95	95	95
100 % Modulus, PSI	1650	1500	1500	1500
300 % Modulus, PSI	2400	2700	2400	1900
Tensile strength, PSI	3500	4000	2800	2900
Elongation, %	450	400	450	450
Tear strength, lbs/inch	7300	3000	3300	4800
Cure time, in minutes, at 140°C	30	-	30	-
Cure time, in minutes, at 115°C	-	15	-	15

Polyethylene polypropylene adipate (PEPA) based urethane elastomers.

PEPA has been utilised in the manufacture of many commercial millable elastomers such as Genthane S, Urepan 640, Vibrathane etc. It was therefore decided to prepare the polyester in the present study. The PEPA was prepared in three different hydroxyl numbers, having a difference of about 20 units. Thus polyesters of 24, 46 and 67 hydroxyl number were prepared.

Polyethylene polypropylene adipate hydroxyl number 24 (PEPA - 26)

The details of the preparation of PEPA 26 are described in the experimental section V Part I.

$$HOOCCH_2CH_2CH_2CH_2COOH + HOCH_2CH_2OH + CH_3\underset{\underset{OH}{|}}{CH_2} - CH_2OH$$

Adipic acid ↓ Ethylene glycol 1,2 propylene glycol

$$HOCH_2CH_2OOC\ CH_2CH_2CH_2CH_2CO.O \text{ ---- } OOC\ \underset{\underset{CH_3}{|}}{CH_2}-CH_2O.OC\text{---}CH_2OH$$

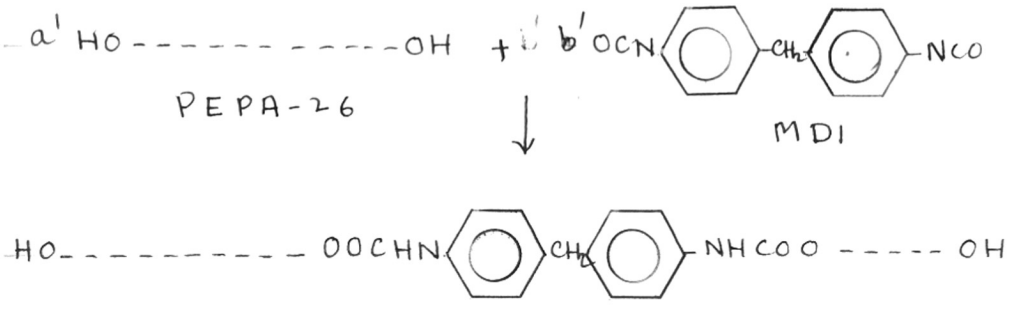
PEPA - 26

PEPA 26 was a soft white waxy material, and was having softening point 36-38°C hydroxyl number 24 and acid No.2.

Preparation of elastomers C and D

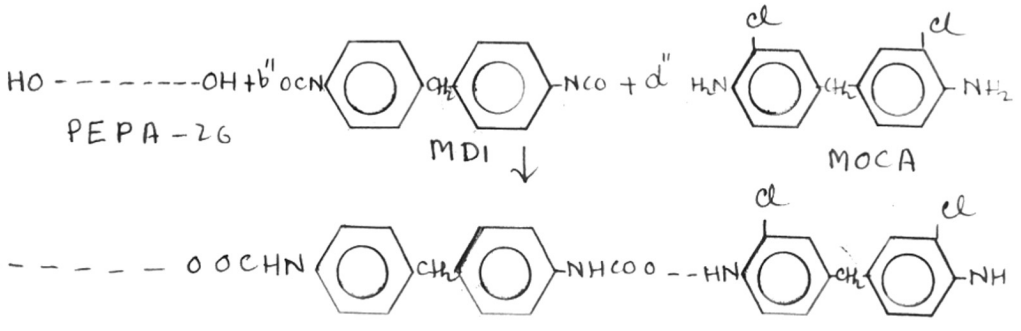
PEPA 26 was reacted with MDI to produce a storage stable millable elastomers of two types

(i) hydroxy terminated elastomer C was prepared by reacting 1 equivalent of PEPA 26 with 0.99 equivalent of MDI.



Elastomer C

(ii) Amine extended elastomer D was prepared by reacting 1.0 equivalent of PEPA-26 with 1.2 equivalent MDI and 0.2 equivalent MOCA.



Elastomer D

Physical properties of elastomers, C and D.

Both elastomers, C and D were pale yellowish white translucent soft solids. The softening point of elastomer C was 40°C and elastomer D was 52°C. The higher softening point of elastomer D was probably because of the presence of urea linkages and rigid aromatic rings of MOCA. Elastomer C was soluble in tetrahydrofuran, ketones, esters,

dimethyl formamide, dimethyl sulphoxide etc. while elastomer D was soluble in dimethyl formamide and dimethyl sulphoxide. The properties are briefly summarized in Table XXIV.

TABLE - XXIV

Physical properties of elastomers, C and D

	Elastomer C	Elastomer D
Form	Pale yellowish white, translucent soft solid	
Specific gravity	1.088	1.288
Softening point	40°C	52°C
Solubility	Tetrahydrofuran ketones, esters, dimethyl formamide, dimethyl sulphoxide.	Dimethyl formamide Dimethyl sulphoxide

Compounding and curing of elastomers, C and D

Inspite of the elastomers, C and D being soft in nature, they presented no difficulty in processing on the rubber mixing mill. The surface tack was excellent. The compounding recipe is given in the table XXV.

TABLE - XXV

Compounding recipe of elastomers, C and D

	Elastomer C		Elastomer D	
	Peroxide cure	Diisocyanate cure	Peroxide cure	Diisocyanate cure
Elastomer C	100.0	100.0	-	-
Elastomer D	-	-	100.0	100.0
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
Dicup 40C	5.0	-	5.0	-
MDI	-	10.0	-	10.0

The peroxide and diisocyanate cures were achieved at 140°C

Physical properties of the vulcanizates of elastomers, C and D

The vulcanizates from both elastomers C and D with peroxide and diisocyanate cures showed that the specific gravity values were in the range of 1.32 - 1.348. The hardness values for elastomers C and D peroxide cure was shore A 85, 65 respectively and in diisocyanate cure was shore A 65 and 75 respectively. The tensile strength and modulus values of elastomer C were higher. In general, the properties of the vulcanizates of elastomers C and D were rather poor as compared to other commercial polyurethane elastomers. The physical properties are given in Table XXVI.

Table - XXVI

Physical properties of the vulcanizates of elastomers, C and D

	Elastomer C		Elastomer D	
	Peroxide cure	Diisocyanate cure	Peroxide cure	Diisocyanate cure
Specific gravity	1.32	1.325	1.348	1.320
Hardness, Shore A	85	65	65	75
100 % Modulus, PSI	1160	460	200	378
300 % Modulus, PSI	1600	1200	780	600
Tensile Strength, PSI	450	1350	900	756
Elongation, %	450	375	350	450
Tear strength, lbs/inch	115	118	875	1640
Cure time, in minutes at 140°C	45	15	45	15

Polyethylene polypropylene adipate hydroxyl number 46 (PEPA - 46)

The details of the preparation of PEPA-46 are described in experimental section V Part I.

$$HOOC\,CH_2CH_2CH_2CH_2COOH + HOCH_2CH_2OH + 2CH_3\underset{\underset{OH}{|}}{CH}CH_2.CH_2OH$$

Adipic acid ↓ Ethylene glycol 1,2 propylene glycol

$$HOCH_2CH_2O.OCCH_2CH_2CH_2CH_2O.CO \qquad OOC,\underset{\underset{CH_3}{|}}{CH}CH_2OCO \qquad CH_2OH$$

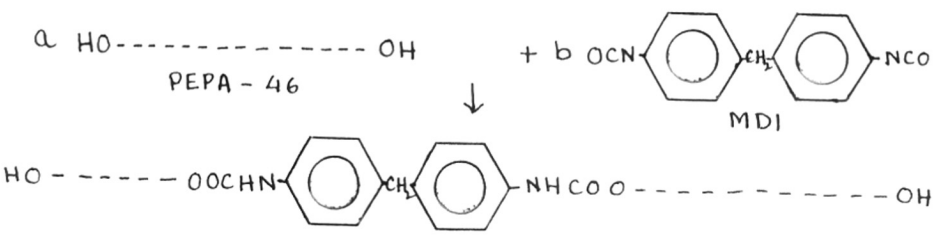
PEPA - 46

PEPA-46 was a white soft waxy solid and was having softening point 36-41°C, hydroxyl number 46.085 and acid number 2.

Preparation of elastomers, E and F

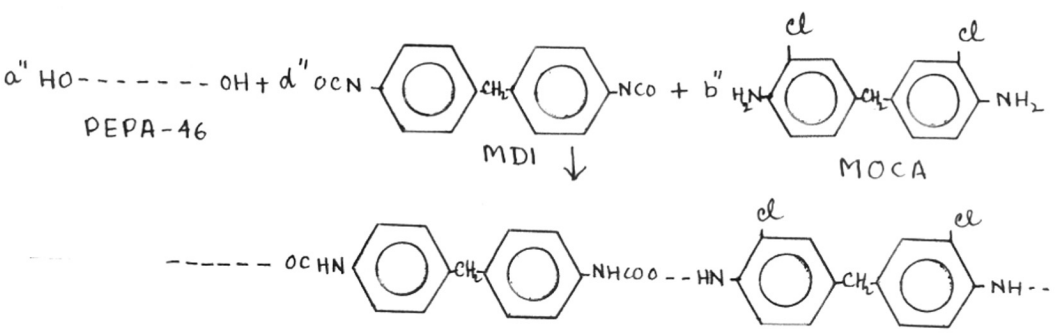
PEPA-46 was reacted with MDI to produce storage stable millable elastomers of two types:

(i) Hydroxy terminated elastomer E was prepared by reacting 1.0 equivalent PEPA-46 with 0.99 equivalent of MDI



Elastomer E

(ii) Amine extended elastomer F was prepared by reacting 1.0 equivalent of PEPA 46, with 1.2 equivalent MDI and 0.2 equivalent MOCA



Elastomer F

Physical properties of elastomers, E and F

Both elastomers E and F were pale yellowish white rubbery translucent solids. The specific gravity values of elastomers E and F were 1.177 and 1.288 respectively, softening points of polymer E and F were 100° and 157°C. The higher softening point of elastomer F was probably because of the presence of urea groups and aromatic rings of MOCA. Elastomer E like elastomer C was soluble in tetrahydrofuran, ketones, esters, dimethyl formamide, dimethyl sulphoxide etc., while elastomer F like elastomer D was soluble in dimethyl formamide and dimethyl sulphoxide. The properties are briefly given in the Table XXVII.

Table - XXVII

Physical properties of elastomers, E and F

	Elastomer E	Elastomer F
Form	Pale yellowish white, translucent rubber solid	
Specific gravity	1.177	1.288
Softening point	100°C	157°C
Solubility	Tetrahydrofuran ketones, esters, dimethyl formamide, dimethyl sulphoxide	Dimethyl formamide Dimethyl sulphoxide

Compounding and curing of elastomers, E and F:

Elastomers, E and F were tough and easy to process. Elastomer F was more tough than elastomer E and exhibited snapy behaviour similar to many synthetic elastomers. Both elastomers E and F had good surface tack. Compounding recipe is given in the table XXVIII.

TABLE - XXVIII

Compounding recipe of elastomers, E and F

	Elastomer E		Elastomer F	
	Peroxide cure	Diisocyanate cure	Peroxide cure	Diisocyanate cure
Elastomer E	100.0	100.0	-	-
Elastomer F	-	-	100.0	100.0
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
DiCup 40 C	5.0	-	5.0	-
MDI	-	10.0	-	10.0

Elastomers, E and F were cured with peroxide and diisocyanate curing systems. The peroxide used was DiCup 40 C while diisocyanate used was MDI and both were cured at 140°C

According to Bayer's technical literature that triallyl cyanurate in peroxide curing systems improves the physical properties. Therefore 1 % of triallyl cyanurate was used in the present investigations in peroxide curing system.

Physical properties of the vulcanizates of elastomers, E and F.

The specific gravity values of all the vulcanizates of elastomers, E and F were in the range of 1.339 - 1.361. Hardness values of peroxide cure, with and without coagent, was Shore A 45 each and diisocyanate cure was Shore A 70. 100 % Modulus values in peroxide cure, without coagent and with coagent in the case of vulcanizates of elastomer E were 100, 175; and that of the elastomer F were 170 and 240 PSI respectively. 100 % Modulus in diisocyanate cure in vulcanizates of elastomers, E and F were 900 and 700 PSI respectively. 300 % Modulus without coagent and with coagent in peroxide cure vulcanizates of elastomer, E were 550, 820 respectively; and that of the elastomer F were 800 and 1200 PSI respectively. 300 % Modulus in diisocyanate cure in vulcanizates of elastomers, E and F were 900 and 1600 PSI respectively. Tensile strength values without coagent and with coagent in peroxide cure in vulcanizate of elastomer E were 2700, 3400 respectively; and that of elastomer F were 2700 and 4500 PSI respectively. Tensile strength v alues in diisocyanate vulcanizates of elastomers, E and F were 3600 and 4000 PSI respectively. Tear strength values without coagent, and with coagent in peroxide cure in vulcanizates of elastomers, E and F were 1300 and 200 respectively; and that of the elastomer F were 1200 and 207.1 lbs/inch respectively. Tear strength values in case of elastomer, E and F in diisocyanate vulcanizates were 3800 and 4000 lbs/inch respectively. Abrasi n index values of elastomers, E and F, with coagent in peroxide - - -

TABLE - XXIX

Physical properties of the vulcanizates of elastomers, E and F

	Elastomer E			Elastomer F		
	Without coagent peroxide cure	With coagent peroxide cure	Diisocyanate cure	Without coagent peroxide cure	With coagent peroxide cure	Diisocyanate cure
Specific gravity	1.351	1.351	1.347	1.361	1.361	1.339
Hardness, shore A	45	45	70	45	45	70
100% Modulus, PSI	100	175	350	170	240	700
300% Modulus, PSI	550	820	900	800	1200	1600
Tensile strength, PSI	2700	3400	3600	2700	4500	4000
Elongation, %	550	600	600	550	600	550
Tear strength, lbs/inch	1300	200	380	1200	207.6	4000
Abrasion index, %	-	704.1	108	-	550	1550
Time in minutes, at 140°C	30	30	15	30	15	15

TABLE - XXX

Heat aging studies of elastomers, E, F and Adiprene C

Properties	Temp.	Elastomer E		Elastomer F		Adiprene C
		Peroxide cure	Diisocyanate cure	Peroxide cure	Diisocyanate cure	Diisocyanate cure
Hardness, Shore A	25	45	70	45	70	65
	75	50	60	55	80	70
	100	55	70	57	80	70
	150	55	70	50	75	85
300% Modulus, PSI	25	820	900	1200	1600	1600
	75	1000	900	1600	2200	1600
	100	1000	750	2100	2500	-
	150	-	-	-	-	-
Tensile strength, PSI	25	3400	3000	4500	4000	3750
	75	3200	3600	4400	4200	3300
	100	3200	1000	4000	4200	3300
	150	1500	600	1200	1000	600
Elongation, %	25	600	600	600	550	550
	75	550	660	450	550	400
	100	450	200	450	500	200
	150	255	225	250	175	30

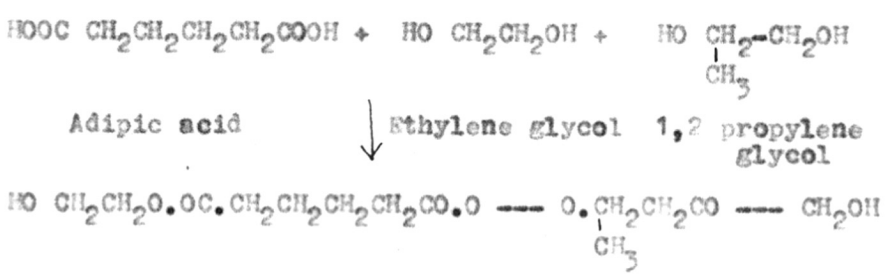
vulcanizates were 704 and 550 while the values for the diisocyanate vulcanizates were 108 and 1550 respectively. The physical properties are tabulated in Table XXIX.

Heat aging properties of vulcanizates of elastomers, E and F with coagent in peroxide cure and in diisocyanate cure were compared with vulcanizates of Adiprene C diisocyanate cure, at 25°, 75°, 100° and 150°C for 7 days in aging oven. The properties are summarised in Table XXX.

In these studies, all the vulcanizates showed that the hardness of all the specimens progressively increased at higher temperature. The tensile, elongation and modulus values of all these elastomers are retained at 100°C aging, excepting the values of elastomer E diisocyanate cure.

Polyethylene polypropylene adipate hydroxyl number 67 (PEPA - 66)

The details of the preparation of PEPA-66 are described in experimental section V, Part I.



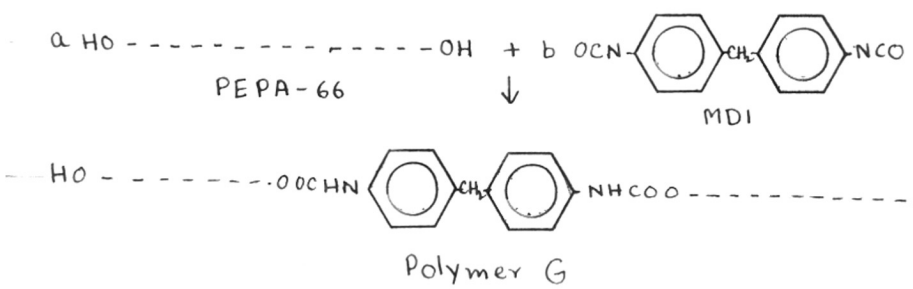
PEPA-66

PEPA 66 was a white soft waxy solid and was having softening point 36-42°C, hydroxyl number 67, acid number 2,

Preparation of Polymer G and elastomer H

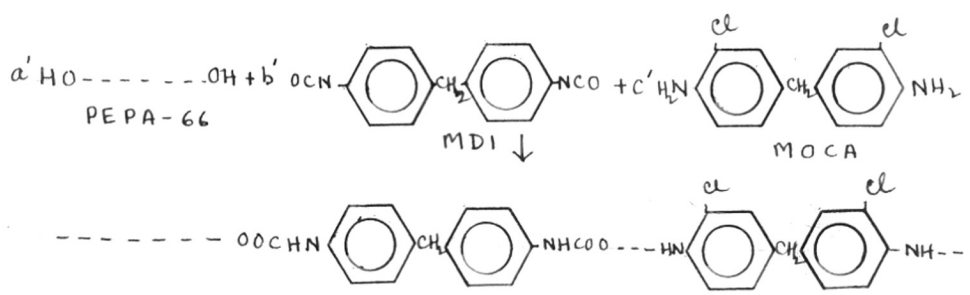
PEPA-66 was reacted with MDI to produce two types of storage stable products.

(i) Hydroxy terminated polymer G was prepared by reacting 1.0 equivalent PEPA-66 with 0.99 equivalent of MDI.



Polymer G

(ii) Amine extended elastomer H was prepared by reacting 1.0 equivalent of PEPA-66 with 1.2 equivalent of MDI and 0.2 equivalent of MOCA.



Elastomer H.

Physical properties of polymer G and elastomer H:

Polymer G was semi-solid material unsuitable for processing on the mixing mill; hence it was not processed further.

Elastomer H was a pale yellowish white translucent rubbery solid; specific graviety was 1.167; softening point was 100°C. Elastomer H was soluble in dimethyl formamide and dimethyl sulphoxide. The physical properties of polymer G and elastomer H are given in the Table XXXI.

TABLE - XXXI

Physical properties of polymer G and elastomer H.

	Polymer G	Elastomer H
Form	Semi-solid sticky gum	Pale yellowish white translucent rubber solid
Specific gravity	-	1.167
Softening point	30°C	100°C
Solubility	Ketones, esters, dimethyl formamide, dimethyl sulphoxide.	Dimethyl formamide Dimethyl sulphoxide.

Compounding and curing of elastomer H.

Elastomer H was a tough polymer and easy to process. The compounding recipe is given in Table XXXII.

TABLE - XXXII

Compounding recipe of elastomer - H

	Peroxide cure	Diisocyanate cure
Elastomer H	100.0	100.0
Stearic acid	0.2	0.2
HAF	30.0	30.0
Dicup 40C	5.0	-
MDI	-	10.0

Elastomer H was cured with peroxide and diisocyanate curing systems. The peroxide used was dicup 40C while diisocyanate used was MDI and both were cured at 140°C.

Peroxide cured samples showed tiny bubbles in the test samples. All attempts to rectify this bubble phenomena failed. Hence obviously peroxide cured samples had poor physical properties, which are reported in Table XXXIII.

Physical properties of the vulcanizates of elastomer H

Specific gravity value in the diisocyanate vulcanizate of elastomer H was 1.342; hardness Shore A was 80; 100 % modulus was 630 PSI; 300 % modulus was 2100 PSI;

Tensile strength was 3800 PSI; Elongation, % was 400; tear strength was 8800 lbs/inch and abrasion index was 125.6 %. The physical properties are described in Table XXXIII.

TABLE - XXXIII

Physical properties of the vulcanizates of elastomer H

	Peroxide cure	Diisocyanate cure
Specific gravity	1.326	1.342
Hardness, shore A	50	80
100 % Modulus, PSI	160	630
300 % Modulus, PSI	360	2100
Tensile strength, PSI	540	3800
Elongation, %	450	400
Tear strength, lbs/inch	1000	8800
Abrasion index, %	-	125.6
Time of cure, in minutes at 140°C	30	15

Polyethylene polypropylene sebacate (PEPSe) based polyurethane polymer:

The details of the preparation of PEPSe is described in experimental section V Part I.

$$HOOC(CH_2)_8COOH + HOCH_2CH_2OH + CH_3CH_2CH_2OH \quad (OH \text{ on } CH_3CH_2CH_2OH)$$

Sebacic acid — Ethylene glycol — 1,2 propylene glycol

$$\downarrow$$

$$HOCH_2CH_2OC(CH_2)_8CO.O - - - - - - - - OH$$

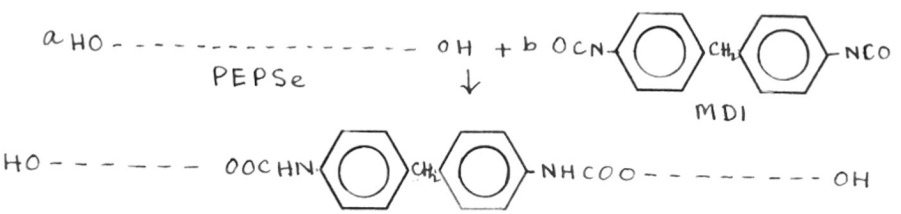
PEPSe

PEPSe was a brittle waxy material, and was having softening point 68 - 70°C, hydroxyl number 40.6, acid number 6.7

Preparation of Polymers, I and J

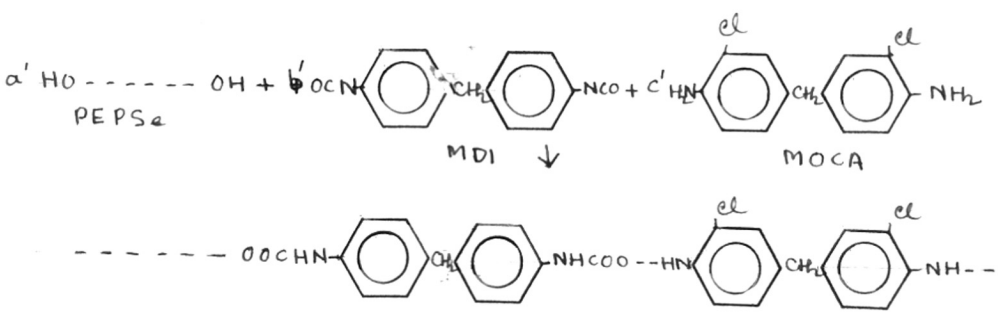
PEPSe was reacted with MDI to produce storage stable polymers of two types:

(i) hydroxy terminated polymer I was prepared by reacting 1.0 equivalent of PEPSe, with 0.99 equivalent of MDI



Polymer I

(ii) Amine extended polymer J was prepared by reacting 1.0 equivalent of PEPSe, with 1.2 equivalent MDI and 0.2 equivalent MOCA.



Polymer J

Physical properties of polymers, I and J

Both polymers, I and J were pale yellowish white hard solids. The softening point of polymer I was 38° - 40°C and that of polymer J was 50 - 52°C. The higher softening point of polymer J was probably because of the presence of urea linkages and rigid aromatic rings of MOCA. Polymer I was soluble in tetrahydrofuran, ketones, esters, dimethyl formamide, dimethyl sulphoxide etc. while polymer J was soluble in dimethyl formamide and dimethyl sulphoxide. The properties are briefly summarized in table No.XXXIV.

TABLE - XXXIV

Physical properties of Polymers I and J

	Polymer I	Polymer J
Form	Pale yellowish white polymer	
Specific gravity	1.212	1.325
Softening point	38 - 48°C	50 - 52°C
Solubility	Tetrahydrofuran, ketones, esters, dimethyl formamide, dimethyl sulphoxide.	Dimethyl formamide and dimethyl sulphoxide

Polymers I and J were plastic material unsuitable for processing on the rubber mixing mill; hence work was not processed further.

Polyethylene polypropylene hexadecamethylene dicarboxylate (PEPH) based polyurethane polymers.

The details of the preparation of PEPH is described in experimental section V, Part I.

$HOOC(CH_2)_{16}COOH$ + $HOCH_2CH_2OH$ + $CH_3CH(OH)CH_2OH$

1,16 Hexadecamethylene dicarboxylic acid — Ethylene glycol — 1,2 propylene glycol

$HOCH_2CH_2.O.OC(CH_2)_{16}CO.O$ - - - - - - - - - - OH

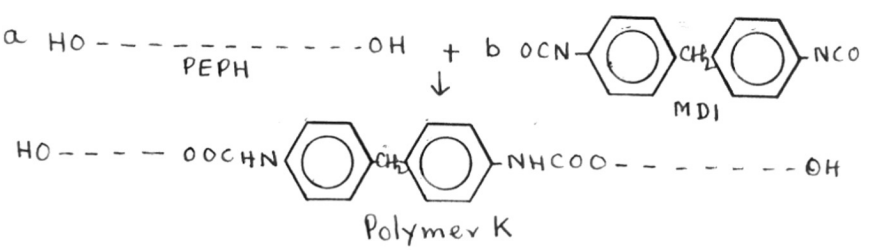
PEPH

PEPH was hard brittle solid, and was having softening point 92 - 96°C, hydroxyl number 20.2 and acid number 8.

Preparation of polymers, K and L:

Attemps were made to prepare polymers from PEPH and MDI of two types viz (i) hydroxy terminated and (ii) amine extended. Only in the former case i.e. polymer K was obtained, in the case of latter type a nonhomogeneous mixture was obtained.

Hydroxy terminated polymer K was prepared by reacting 1.0 equivalent of PEPH, with 0.99 equivalent of MDI.



Physical properties of polymer K

Polymer K was a pale yellowish white hard solid. The softening point was > 250°C. Polymer K was soluble in tetrahydrofuran, ketones, esters, dimethyl formamide, dimethyl sulphoxide. The properties are briefly summarized in Table XXXV.

TABLE - XXXV

Physical properties of Polymer K

Form	Pale yellowish white hard solid
Specific gravity	1.314
Softening point	> 250°C
Solubility	Tetrahydrofuran, ketones, esters, dimethyl formamide, dimethyl sulphoxide.

Polymer K was a plastic material unsuitable for processing on the rubber mixing mill; hence work was not processed further.

PART I

SECTION IV

DISCUSSION

SECTION - IV

DISCUSSION

Polyesters prepared from adipic acid, ethylene glycol and 1,2 propylene glycol gave elastomeric polymers with 4,4' diphenyl methane diisocyanate (MDI). Succinic acid, sebacic acid and hexadecamethylene dicarboxylic acid polyesters when used separately in the proportion mentioned in table XXXVI are unsuitable for producing polyurethane elastomeric polymers. Succinic acid polyesters gave leathery polymer while sebacic acid and hexadecamethylene dicarboxylic acid polyesters gave polymers which were more towards plastics. It can be said that when a polyester is reacted with MDI, the more the methylene groups between the two ester groups of the polyester chain, the greater the plastic nature of the resultant polyurethane polymer.

Bayer in his work on vulkollans[8] has studied the influence of molecular weight of polyesters on the physical properties of urethane elastomers. He has used polyethylene adipate and 1,5 naphthalene diisocyanate in his studies. Since the hydroxyl number is the measure of the molecular weight, he has varied hydroxyl number from 32 to 81. He found that the best physical properties were obtained when the hydroxyl number of the polyester was from 50 to 60, and acid number less than 1.

TABLE - XXXVI

Nature of the reaction products from different polyesters and MDI

Polyesters (1.0 equivalent)	Diisocyanate (0.99 equivalent)	Nature
Succinic acid	MDI	Leathery product
Adipic acid	MDI	Rubbery product
Sebacic acid	MDI	Hard plastic product
Hexadecamethylene dicarboxylic acid	MDI	Hard plastic product

(Glycol part in all cases was 80:20 mixture of ethylene glycol : 1,2 propylene glycol)

In the present studies polyesters were prepared from adipic acid and 80:20 mixture of ethylene glycol and 1,2 propylene glycol. The hydroxyl numbers used for the studies were 24, 46 and 67. These polyesters were reacted with MDI separately to produce millable elastomers, which were cured with peroxide and with diisocyanate. Polyester with 67 hydroxyl number when reacted with MDI only, gave a soft unworkable polymer (on the rubber mixing mill), whereas the other two hydroxyl number polyesters gave millable elastomers. The reason for obtaining soft polymer may be that under the experimental conditions, the molecular weight build up was low.

4,4'methylene bis (2 chloroaniline) extended millable elastomers were obtained from the polyesters of hydroxyl number 24, 46 and 67. These elastomers were comparatively tough than the corresponding unextended elastomers. The general compounding recipe for the two curing systems for polymers/elastomers from A to H are mentioned in detail in section III is given in Table XXXVII

TABLE - XXXVII

Compounding recipe for the two curing systems.

Ingredients	Peroxide cure	Diisocyanate cure
Polymer/elastomer	100.0	100.0
Stearic acid	0.2	0.2
HAF	30.0	30.0
Dicup 40C	5.0	-
MDI	-	10.0

The physical properties of the vulcanizates of Polymers - elastomers from A to H are described in Table XXXVIII.

TABLE - XXXVIII

Vulcanizate properties of the different elastomers from A to H with peroxide and diisocyanate cures

Polymers - elastomers	Tensile strength, PSI		300 % modulus, PSI		Elongation, %		Tear strength, lb/inch		Hardness, Shore A	
	P	I	P	I	P	I	P	I	P	I
A	3500	4000	2400	2700	450	400	7300	3000	95	95
B	2800	2900	2400	1900	450	450	3300	4800	95	95
C	2300	1350	1600	1200	450	375	115	118	85	65
D	900	756	780	600	350	450	875	1640	65	75
E	2700	3600	550	900	550	600	1300	3800	45	70
E+1 % coagent	3400	-	820	-	600	-	200	-	45	-
F	2700	4000	800	1600	550	550	1200	4000	45	70
F+1 % coagent	4500	-	1200	-	600	-	207	-	45	-
G	-	-	-	-	-	-	-	-	-	-
H	540	3800	360	2100	450	400	1000	8800	50	80

Elastomer E and Elastomer F show better physical properties. The use of triallyl cyanurate in 1 % on the weight of elastomers, E and F in peroxide cures showed that the values of tensile strength, 300 % modulus, tear strength and elongation % were increased considerably. These values are graphically given in Figure 1,2 and 3.

Vulcanizates of elastomer F with triallyl cyanurate, cured faster than without triallyl cyanurate. In elastomer F optimum tensile strength was obtained in 15 minutes in the case of vulcanization with triallyl cyanurate in peroxide cure, while without triallyl cyanurate optimum tensile strength was obtained in 30 minutes. In elastomer E optimum tensile strength with and without coagent were obtained in 30 minutes time. Elastomer F was a MOCA extended polyurethane elastomer while elastomer E was without the use of MOCA. The use of MOCA in the elastomer F preparation results into urea-urethane groups possessing elastomer. This elastomer vulcanizes faster with triallyl cyanurate; it may be so because of the presence of urea groups. This elastomer F also shows better physical properties. MOCA molecule can also impart fire resistance properties to the polymer due to the presence of chlorene groups.

The use of triallyl cyanurate has certainly imparted beneficial effect in reducing the time of vulcanization and improving the physical properties. This is more so where the elastomer has been obtained by the use of MOCA.

Vulcanizates of elastomers, E, F and adiprene C in diisocyanate cure and vulcanizates of elastomers, E and F with triallyl cyanurate, in peroxide cure, were subjected to hear aging studies. These results are shown graphically in figures 4, 5, 6 and 7.

On heat aging at 75°C, the elastomer E diisocyanate vulcanizate showed increase in tensile strength, while at 100° and 150°C heat aging the tensile strength values fell. On heat aging at 75° and 100°C elastomer F diisocyanate vulcanizate showed the tensile strength values to be of the unaged sample, while at 150°C the tensile strength fell.

On heat aging at 75°, 100° and 150°C, Adiprene C diisocyanate vulcanizate, showed continuous fall of tensile strength values.

The steady fall in tensile properties of Adiprene C may be attributed to the polyether backbone of the polymer.[41]

On heat aging at 75°, 100° and 150°C elastomer E diisocyanate vulcanizate showed continuou s fall in the 300% modulus values.

On heat aging at 75° and 100°C, elastomer F diisocyanate vulcanizate showed an increase in 300% Modulus values while at 150°C the modulus value fell sharply.

On heat aging at 75° and 100°C, elastomer E with coagent peroxide vulcanizates, showed very little fall in tensile stren th values but at 150°C the tensile value fell sharply.

On heat aging at 75° and 100°C, elastomer F with coagent peroxide vulcanizate retained the original tensile strength values but at 150°C heat aging, polymer F the tensile values fell.

On heat aging at 75° and 100°C elastomer E with coagent peroxide vulcanizates, showed an increase in 300% modulus values while at 150°C heat aging, the 300% modulus values fell.

On heat aging at 75° and 100°C elastomer F with coagent, peroxide vulcanizates, showed an increase in 300% modulus values while, at 150°C heat aging modulus values fell.

In the case of elongation all the three elastomers with different crosslinking agent showed fall in elongation values.

It is felt that the comparative retention of physical properties of elastomer F may be owing to the presence of urea groups, which are known to have heat aging/antioxidant properties.

The comparative physical properties of some of the commercially available urethane elastomers and elastomer F are given in Table XXXIX.

TABLE - XXXIX

Vulcanizate properties of the commercially available millable elastomers and elastomer F.

Properties	Chemigum SL	Genthane S		Vibrathane	Urepan 640	Elastomer F	
	Diisocyanate cure	Peroxide cure	Diisocyanate cure	Peroxide cure	Peroxide cure	Peroxide cure	Diisocyanate cure
Tensile strength, PSI	5450	4400	3750	4200	4124	4500	4000
300 % Modulu, PSI	1750	1925	1750	2900	-	1200	1600
Elongation, %	515	500	515	400	300	600	550
Hardness, Shore A	65	60	72	65	62	60	70

Conclusions

In a comparative study, it has been shown that polyurethane elastomers of good physical properties can be prepared from adipic acid, 80:20 mixture of ethylene glycol and 1,2 propylene glycol. Dibasic acid having lower or higher members, in the adipic acid homologus series are found to impart leathery or plastic properties when used for making polyester polyurethane elastomer. The polyester from adipic acid, 80:20 mixture of ethylene glycol and 1,2 propylene glycol of hydroxyl number 46 when reacted in proportions of 1.0 equivalent of polyester with 1.2 equivalent of MDI

and 0.2 equivalent of MOCA gave a urea-urethane elastomer. This elastomer can be cured with diisocyanate and peroxide curing systems. The resultant vulcanizates of this elastomer have comparable physical properties to that of the commercially available millable urethane elastomers.

Moulded products from polyester urethane-elastomer F.

PART I

SECTION V

EXPERIMENTAL

SECTION - V

EXPERIMENTAL

Preparation of polyethylene polypropylene succinate (PEPS)

In a one-litre, four necked flask equipped with a nitrogen gas inlet tube, a thermometer, a distillation condenser, a mercury seal stirrer were placed 472 g (4.0 moles) succinic acid, 218 g (3.52 moles), ethylene glycol, 66.88 g (0.88 mole), 1,2 propylene glycol. The reaction mixture was heated with a one-litre heating mantle. Nitrogen gas was flushed with efficient stirring.

The reaction mixture was heated at 160 - 170°C for 6 hous, 180 - 190°C for 15 hours and 200°C at 1mm of mercury pressure for six hours. The physical properties of PEPS are described in Table XL.

TABLE - XL

Physical properties of polyethylene polypropylene succinate (PEPS)

Form	Hard white waxy material.
Softening point	72 - 75°C
Acid number	2 - 3
Hydroxyl number	58.6

Preparation of polymer A:

In a 500 ml. three necked flask equipped with a thermometer, a mercury seal stirrer and a glass stopper, was placed 200 g of dried polyethylene polypropylene succinate. The reaction mixture was heated in an oil bath at about 100°C, 25.9 g of powdered 4,4'diphenyl methane diisocyanate was added and the mixture was stirred vigorously for about 10 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven. The physical properties of polymer A are described in table XXI, Section III, Part I.

Compounding of polymer A

Polymer A was easy to process. The polymer was placed on cold rubber mixing mill, immediately a band was formed. The compounding ingredients were added according to the order given in the compounding recipe in table XXII. The mix was cut thrice from either side and rolled six times through tight mill and sheeted out and moulded at 140°C in peroxide cure and 115°C in diisocyanate curing system in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412-64 T (1965).

Preparation of polymer B

In a 500 ml, 3 necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper, was placed 200 g of dried polyethylene polypropylene succinate. The

temperature of the reaction mixture was maintained at 110°C by means of an oil bath. 31.4 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck. Stirring was continued vigorously for 10 minutes, followed by the addition of 5.56 g finely powdered 4,4'methylene bis (ortho chloroaniline) (MOCA), stirred again vigorously for few minutes. The reaction mixture was poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven. The physical properties of polymer B are described in Table XXII, Section III, Part I.

Compounding of polymer B

Polymer B was easy to process. The polymer was placed on cold rubber mixing mill; immediately a band was formed. The compounding ingredients were added according to the order given in the compounding recipe in Table XXII. The mix was cut thrice from either side rolled six times through tight mill and sheeted out and moulded at 140°C in peroxide cure and 115°C in diisocyanate curing systems in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965)

Preparation of polyethylene polypropylene adipate hydroxyl number 24 (PEPA - 26)

In a one- litre four necked flask equipped with a nitrogen gas inlet tube, a thermometer, a distillation condenser, a mercury sealed stirrer were placed 438 g

(3.0 moles) adipic acid, 173.6 g (2.8 moles) ethylene glycol and 54.0 (0.7 mole) 1,2 propylene glycol. The reaction mixture was heated with one-litre heating mantle. The reaction system was flushed with nitrogen till the polyesterification was complete. The reaction mixture was heated at 160 - 170° for 6 hours, 180 - 190°C for 12 hours and 190 - 200°C at 1 mm of mercury pressure for 6 hours. The physical properties of PEPA 26 are described in Table XL1.

TABLE - XLI

Physical properties of PEPA - 26

Form	Soft white waxy material
Softening point	36 - 38°C
Acid number	2.0
Hydroxyl number	24

Preparation of elastomer C

In a 500 ml, 3 necked flask, equipped with a thermometer, a mercury seal stirrer, a ground glass stopper was placed 200 g of PEPA 26. The temperature of the polyester was brought to 100°C with the help of an oil bath. 10.76 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck. The reaction mixture was vigorously stirred for about 10 minutes. The reaction mixture was poured into

silicone waxed tray and further polymerized for about 24 hours at 100°C in an electric oven. The physical properties of elastomer C are given in Table XXIV.

Compounding of elastomer C

Elastomer C was quite a soft polymer having excellent surface tack. The elastomer C was placed on cold mixing mill, a band was immediately formed. The compounding ingredients were added according to the order given in the compounding recipe in Table XXV. The mix was cut thrice from either side rolled six times through tight mill and sheeted out and moulded at 140°C in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965).

Preparation of elastomer D

In a 500 ml, 3 necked flask, equipped with a thermometer, a mercury seal stirrer and a ground glass stopper, was placed 200 g of dry PEPA-26. The temperature of the polyester was brought to 110°C with the help of an oil bath. 13 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck. The reaction mixture was stirred vigorously for about 10 minutes followed by addition of 2.32 g of powdered 4,4'methylene bis (ortho chloro aniline) stirred vigorously for 2-5 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized

in an electric oven. The physical properties of elastomer D are described in Table XXIV.

Compounding of elastomer D

Elastomer D was a soft polymer having excellent surface tack. The elastomer D was placed on cold mixing mill, a band was immediately formed. The compounding ingredients were added according to the order described in the compounding recipe in Table XXV. The mix was cut thrice from either side, rolled six times through tight mill, sheeted out and moulded at 140°C in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965).

Preparation of polyethylene polypropylene adipate, hydroxyl number 46 (PEPA - 46)

In a one-litre, four necked flask equipped with a nitrogen gas inlet tube, a thermometer, a distillation condenser and a mercury seal stirrer were placed 438 g (3 moles) adipic acid, 173.6 g (2.8 moles) ethylene glycol, 54.9 g (0.7 mole) 1,2 propylene glycol. The reaction mixture was heated with a one litre capacity heating mantle. The nitrogen gas was flushed in the system till the polyesterification was complete.

The reaction mixture was heated at 160 - 170°C for six hours, 180 - 190°C for 26 hours and 190 - 200°C at 1 mm of

mercury pressure for six hours. The physical properties of PEPA 46 are described in Table XLII

TABLE - XLII

Physical properties of PEPA - 46

Form	hite waxy solid
Softening point	36 - 41°C
Acid number	2
Hydroxyl number	46.085

Preparation of elastomer E

In a 500 ml, three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper were placed 200 g of dry PEPA-46. The temperature of the PEPA-46 was brought to 100°C with the help of an oil bath, 20.34 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck and the mixture was stirred vigorously for about 10 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven. The physical properties of elastomer E are given in Table XXVII.

Compounding of elastomer E

Elastomer E was easy to process. The elastomer had good surface tack. The elastomer was placed on cold rubber

mixing mill, a band was immediately formed. The compounding ingredients were added according to the order given in the compounding recipe in Table XXVII. The mix was cut thrice from either side, rolled six times, through tight mill, sheeted out and moulded at 140°C in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965).

Preparation of elastomer F

In a 500 ml, three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper was placed 200 g of dry PEPA-46. The temperature of the PEPA-46 was brought at about 110°C by means of an oil bath, 24.66 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck and the reaction mixture was stirred vigorously for about 10 minutes followed by addition of 4.372 g of powdered methylene bis (ortho chloro aniline) stirred again vigorously for a few minutes. The reaction mixture was poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven. The physical properties of elastomer F are described in Table XXVII.

Compounding of elastomer F

Elastomer F was a tough polymer having excellent surface tack. Elastomer F was placed on cold rubber mixing

mill, a band was immediately formed. The compounding ingredients were added according to the order given in the compounding recipe in Table XXVIII. The mix was cut thrice from either side, rolled six times, through tight mill, sheeted out and cured at 140°C in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965).

Heat aging studies of elastomers, E and F.

The samples of elastomers, E and F cured with peroxide, with coagent and with diisocyanate were placed in Geer's oven at 75°C, 100°C and 150°C for seven days. For comparison an optimum cured Adiprene C diisocyanate cured samples were also simultaneously heat aged. The physical properties of aged sample were determined as usual, and are described in Table XXX.

Preparation of polyethylene polypropylene adipate hydroxyl number 67 (PEPA - 66)

In a 1-litre, four necked flask, equipped with a nitrogen gas inlet tube, a thermometer, a distillation condenser, a mercury seal stirrer were placed 438 g (3.0 moles) adipic acid 173.6 g (2.8 moles) ethylene glycol, 53.9 g (0.7 moles) 1,2 propylene glycol. The reaction mixture was heated with one-litre heating mantle. The nitrogen was flushed till the polyesterification was complete.

The reaction mixture was heated at 160 - 170°C for 3 hours, 180 - 190°C for 26 hours and at 200°C at 1 mm mercury pressure for six hours. The physical properties of PSPA-66 are given in Table XLIII

TABLE - XLIII

Physical properties of PSPA - 66

Form	White soft waxy solid
Softening point	36 - 42°C
Acid number	2
Hydroxyl number	67.6

Preparation of polymer G

In a 100 ml. three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper, was placed 50 g of dry PSPA 66. The temperature of the PSPA-66 was brought to 100°C with the help of an oil bath. 7.479 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck and vigorously stirred for 10 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized at 100°C for 24 hours in an electric oven. The physical properties of polymer G are described in Table XXXI.

Preparation of elastomer H

In a 500 ml three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper was placed 200 g of dry PEPA-66. The temperature of the PEPA-66 was brought to 110°C with the help of oil bath. 36.2 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck with vigorous stirring for about 10 minutes followed by addition of 6.42 g of finely powdered 4,4'methylene bis (ortho chloro aniline) MOCA. The reaction mixture was poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven. The physical properties of elastomer H are described in Table XXXI.

Compounding of elastomer H

Elastomer H was easy to process and had good surface tack. The polymer was placed on cold rubber mixing mill, a band was immediately formed. The compounding ingredients were added according to the recipe given in the table XXXII. The mix was cut thrice from either side, rolled six times, through tight mill, sheeted out and moulded at 140°C in standard moulds. The physical properties of the vulcanizates were determined according to ASTM D 412 - 64 T (1965).

Preparation of polyethylene polypropylene Sebacate (PEPSe):

In a one-litre four necked flask equipped with a nitrogen gas inlet tube, thermimeter, a distillation

condenser, a mercury sealed stirrer etc. were placed 202 g (1.0 mole) sebacic acid, 57.8 g (0.96 mole) ethylene glycol and 17.9 g (0.23 mole) 1,2 propylene glycol. The reaction mixture was heated with 1-ℓ heating mantle. The reaction system was flushed with nitrogen gas till the polyesterification was complete.

The reaction mixture was heated at 160 - 170°C for six hours, 180 - 190°C for 12 hours and 190 - 200°C at 1 mm of mercury pressure for 6 hours. The physical properties are described in Table XLIV.

TABLE - XLIV

Physical properties of PEPSe

Form	Brittle waxy material
Softening point	68 - 70°C
Acid number	6.7
Hydroxyl number	40.6

Preparation of polymer I

In a 250 ml, 3 necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper, etc. was placed 100 g of dry PEPSe. The temperature of the polyester was brought to 100°C with the help of an oil bath.

8.8 g of powdered 44' diphenyl methane diisocyanate was added through the side neck. The reaction mixture was vigorously stirred for 10 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized for about 24 hours at 100°C in an electric oven. The physical properties of the polymer I are given in table XXXIV, Section III.

Since polymer I was plastic and unsuitable for processing on the rubber mixing mill, it was not processed further.

Preparation of Polymer J:

In a 250 ml, 3 necked flask, equipped with a thermometer, a mercury seal stirrer and a ground glass stopper, etc. was placed 100 g of dry PEPSe. The temperature of the polyester was brought to 110°C with the help of an oil bath. 10.7 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck. The reaction mixture was stirred vigorously for about 10 minutes followed by addition of 1.9 g of powdered 4,4'methylene bis (ortho chloroaniline) stirred vigorously for 2-5 minutes. The reaction mixture was poured into silicone waxed tray and further polymerized in an electric oven for 24 hours at 100°C. The physical properties of polymer J are described in Table XXXIV, Section III.

Preparation of polyethylene polypropylene Hexadecamethylene dicarboxylate: (PEPH)

In a 1-l four necked flask equipped with a nitrogen gas inlet tube, a thermometer, a distillation condenser, a mercury seal stirrer etc., was placed 314 g (1.0 mole) 1,16 Hexadecamethylene dicarboxylic acid, 57.8 g (0.96 mole) ethylene glycol and 17.9 g (0.23 mole), 1,2 propylene glycol. The reaction mixture was heated with 1-l heating mantle. The reaction system was flushed with nitrogen gas till the polyesterification was complete. The reaction mixture was heated at 160 - 170°C for six hours, 200°C for 12 hours and 200°C at 1 mm of mercury pressure for six hours. Physical properties of the polyester are given in Table XLV.

TABLE - XLV

Physical properties of PEPH

Form	Brittle hard solid
Softening point	92 - 96°C
Acid number	8.0
Hydroxyl number	20.2

Preparation of polymer K:

In a 100 ml. 3 necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper etc., was

placed 33.2 g of dry PEPH. The temperature of the polyester was brought to 100°C with the help of an oil bath. 1.54 g of powdered 4,4' diphenyl methane diisocyanate was added through the side neck. The reaction mixture was vigorously stirred for 5 minutes. The reaction mixture was poured into a silicone waxed tray and further polymerized for about 24 hours at 100°C in an electric oven. The physical properties are given in table XXXV, Section III. Since the polymer K was plastic and unsuitable for processing on the rubber mixing mill, it was not processed further.

Preparation of Polymer L:

In a 50 ml, 3 necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper etc., was placed 10 g of dry PEPH. The temperature of the polyester was brought to 110°C with the help of an oil bath, 0.56 g of powdered 4,4'diphenyl methane diisocyanate were added through the side neck. The reaction mixture was stirred vigorously but the mass suddenly jelled. Hence no further work was undertaken to develop this polymer.

PART II

SECTION I

INTRODUCTION

PART - 2

SECTION - I

Introduction

Castor oil which is also known as Ricinus oil, is a naturally occurring trihydroxy glyceride. It is obtained from the seeds of the plant Ricinus Communis of Euphobiaceae family. Ricinus Communis is grown as a wild plant or a cultivated plant in tropical or subtropical regions such as India, Brazil, Algeria, U.S.A. etc.

Table - I

Production of Castor Oil in India

Year	Estimated quantity of Castor oil produced. '000 Tonnes
1961 - 62	38
1962 - 63	35
1963 - 64	36
1964 - 65	38
1965 - 66	25

The castor oil is obtained by cold expression or by solvent extraction of castor beans. Cold expressed oil is of low acid number while solvent extracted oil is of high acid number. The low acid number oil is usually preferred

for urethane work. Baker's castor oil Co. of U.S.A. which has carried out extensive work in the utilization of castor oil for polyurethane purposes, recommends the use of D.B. castor oil. This castor oil is similar to the cold expressed castor oil in acid number but has very low moixture content.

Table - II

Properties of Castor Oil

Oil	OH value	% Vollatile moisture	Acid number	Colour Gardner
D.B. (Urethane grade)	163	0.02	1	1 +
Castor oil No.1	163	0.2	2	1 +
Castor oil No.3	154	0.3	12	6

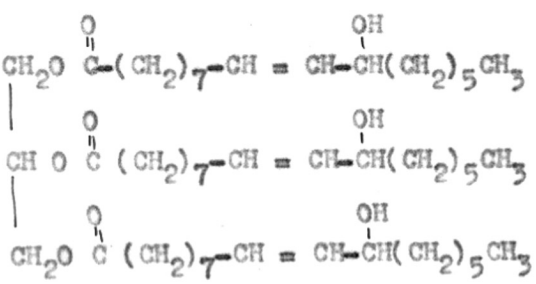
Castor oil is a viscous pale yellow liquid with characteristic unpleasant odour and taste. Chemically castor oil is a triglyceride of ricinoleic acid. The fatty acid component is 9/10 ricinoleic acid. The average fatty acid component is described in Table III.[28]

Castor oil can be considered as a mixture of 70 % glyceryl triricinoleate and 30 % glyceryl diricinoleate.[42]

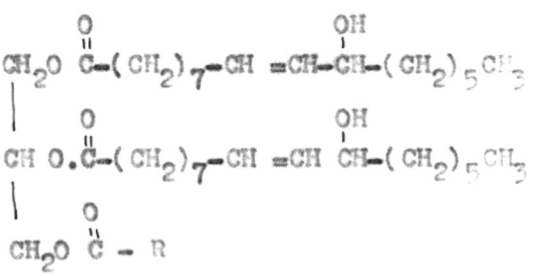
Table - III

Fatty acid components of Castor oil

Acid	Fatty acid components %
Ricinoleic acid	86
Oleic acid	8.5
Linoleic acid	3.5
Stearic acid	0.5
Dihydroxy stearic acid	1-2 %



70 % Glyceryl triricinoleate



30 % glyceryl diricinoleate.

Uses of Castor oil

The largest single use of castor oil is in the preparation of sebacic acid and capryl alcohol. Sebacic acid is used in the manufacture of 6, 10 nylons, sebacate plasticizers, sebacate polyesters etc.

The other notable use of castor oil is dehydrated castor oil for the manufacture of paints and varnishes.

Castor oil is also used in the preparation of undecylenic acid and heptaldehyde, which are used in the synthesis of 11 nylon and in perfumery, respectively.

Since castor oil has three secondary hydroxyl groups, it has been utilized in isocyanate reactions for adhesives,[29] coatings,[30] foams,[31,32,33,34] castable elastomers[35,36] etc. The Germans used isocyanate based adhesives for metal to metal, metal to rubber bondings etc. 4,4'diphenyl methane diisocyanate castor oil, based isocyanate terminated prepolymer has been used as adhesives for cements and other patching materials.

Excellent clear and pigmented coatings have been prepared from castor oil and toluene diisocyanate.

Blown castor oil has also been used for producing superior coatings for wood.

Castor oil has also been used in rigid and semi-rigid urethane foams. Castor oil has been used for many foam applications and the most recent one is heat protecting foam for the space-man.[43]

Castor oil has also been used in the preparation of castable elastomers. Notable work has been done by Patton et al of Baker's Castor Oil Co. and by Heiss of Mobay Chemical Co.

Patton prepared castable prepolymer from castor oil and castor oil derivatives (polycins).[36] The compositions of these prepolymers are described in Table IV.

Table - IV

Composition and properties of castor polyol prepolymers[36]

Composition pbw	Polycin U-prepolymers		
	Polycin U-56	Polycin U-63	Polycin U-75
DT Castor oil	62	-	-
Polycin 59	-	50.5	-
Polycin 60	-	-	52.5
TDI (80/20 Type)	38	49.5	47.5
	100.0	100.0	100.0
Colour	Light amber colour		
Viscocity (P/25°C)	275	400	390
NCO contents %	10	13.6	13.7
Equivalent wt/NCO gr	420	308	306
Density at 25°C lb/gall	8.9	9.15	9.20

T A B L E - V

Properties of castor-polyol / TDI elastomers[36]

Elastomer coding	Polycin U prepolymer		Polycin curing polyols		Pot life at room temp. viscosity (poises) time hour			Density (g/cm³)	Hardness, shore A	Low temperature brittle point °C	Physical properties					Electrical properties			
	No.	%	No.	%	0	1	3				Tensile strength, PSI	Elongation, %	Abrasion resistance Tabor H22 ≃ 1000	Linear shrinkage Liquid at 100°C Solid at 25°C	Water absorption, %	Dielectric constant	Dielectric strength volts/ mil	Power factor	Volume resistivity Ohm cm 10^{10}
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
4	U-56	73.5	12	26.5	200	590	–	1.085	97	-5	2170	70	0.14	–	–	6.3	500	3.4	640
2	U-56	71.5	52	28.5	91	210	540	1.080	80	-70	1275	150	0.23	–	1.1	4.6	265	8.0	0.38
3	U-56	66.0	53	34.0	5	130	320	1.062	52	-70	320	140	0.13	1.9	1.0	3.7 4.0*	155 700*	9.2	0.18 7.3*
1	U-56	68.5	51	31.5	5	130	280	1.065	45	-45	300	210	–	–	1.2	2.3	110	3.5	0.022
7	U-56	54.0	DB	46.0	45	86	200	1.042	55	<-80	170	70	0.05	1.6	0.8	44 4.8*	200 550*	2.5	0.75 130*
5	U-56	42.5	23	57.5	24	37	62	1.017	28	-55	30	60	0.25	–	0.8	–	–	–	–
14	U-63	65.0	52	35.0	48	200	600	1.102	93	-20	2750	175	0.53	2.4	1.4	5.8 3.2*	600 800*	25	470 1600*
15	"	59.0	53	41.0	40	92	340	1.083	48	-45	1050	270	0.40	2.5	1.2	5.0 3.5*	280 650*	– 8.8	1.3 62*
13	"	61.5	51	38.5	18	56	200	1.082	41	-20	875	400	0.19	–	1.4	–	–	–	–
19	U-75	65.5	52	34.5	66	180	520	1.099	87	-30	2500	120	0.43	–	–	5.4	650	3.8	130
20	"	60.0	53	40.0	34	120	620	1.082	49	-45	1275	210	0.28	2.1	1.2	5.7	760	8.2	110
18	"	62.0	51	38.0	28	90	370	1.082	38	-35	925	330	0.34	–	–	–	–	–	–

*10 mill film.

The above mentioned prepolymers were cured by adding castor polyols and heating at high temperature. The properties of these elastomers are given in the Table V.

Heiss prepared castor oil based elastomers by both one and two shot methods.[35]

In one shot method all the components are added at the same time and cured at high temperature in moulds, and these results are described in Table VI.

In the case of prepolymer system castor oil was reacted with excess of diisocyanate to form -NCO terminated prepolymer.[35] This prepolymer was liquid in nature and was converted into solid rubber by reacting it with a curing agent or chain extender. The composition and physical properties are tabulated in Table VII.

Flexricin 15	Ethylene glycol monoricinoleate
" 32	Monodehydrated castor oil
Niax Diol 2025	Polypropylene glycol M.W. 2025
Niax Diol 425	Polypropylene glycol M.W. 425
Catalyst C-16	tertiary amines.

The above description mentions some of the important applications of castor oil-isocyanate reaction products. However, nowhere the use of castor oil for millable polyurethane elastomers, has been reported.

TABLE - VI

TDI/castor oil polymers, direct one step method*[35]

Formulation pbw					Composition wt. %					Properties			
Sample No.	Castor oil	Flexricin 9	Mondur TD-80	NCO/OH	TDI	Aromatic Urethane	Urea	Wt branch point	Shore A-2	Tensile strength, PSI	Elongation, %	100 % Modulus
No.1	67	33	34.5	1.0	25.7	11.0	16.4	0.2	1900	47	940	270	180
No.2	57	43	35.5	1.0	26.2	11.3	17.2	0.2	2290	43	1280	300	160
No.3	57	43	38.9	1.1	28.0	12.0	16.8	0.2	-	55	2460	260	300
No.4	57	43	42.3	1.2	29.7	12.9	16.5	0.2	-	63	2170	220	540
No.5	49	51	38.6	1.0	27.9	12.0	18.4	0.2	2710	43	1370	330	170

* Cured 40 min. at 140°C, plus 2 hours at 100°C, 0.5 % C-16 catalyst.

Flexricin 9 = Propylene glycol monoricinoleate

Mondur TD 80 = Tolylene diisocyanate 80 % 2,4 & 20 % 2,6 isomers.

TABLE - VII

TDI/Castor oil polymers prepolymer method*

Sample	Formulation pbw			Composition wt %					Properties			
	Prepolymer	Chain extender	NCO/OH	TDI	Aromatic	Urethane	Urea	Mt / Branch point	Shore A-2	Tensile strength, PSI	Elongation, %	100% Modulus, PSI
1	Castor oil/ Mondur TDI-80	Flex 15	1.0	25.2	10.7	17.1	<0.2	2490	57	1210	240	240
2	Castor oil/ Mondur TDI-80	Flex 9	1.0	26.0	11.2	17.6	<0.2	2410	54	1750	270	240
3	Castor oil/ Mondur TDI-80	Flex 32	1.0	16.2	7.0	11.0	<0.2	3870	25	120	160	65
4.	Castor oil Mondur TDI-80	Niax Diol-2005	1.0	11.0	4.7	7.5	<0.2	4050	14	85	310	30
5.	Castor oil	Niax Diol 425	1.0	25.2	10.7	17.1	<0.2	2490	31	830	280	190

*Cured 40 minutes at 140°C, plus 2 hours at 100°C. 0.5 % C-10 catalyst.

After gaining the experience of millable polyester urethane elastomers, it was decided to prepare castor oil based millable urethane elastomers.

Since difunctional high molecular weight (from 1000 - 2000) polymer is required for the preparation of millable polyurethane elastomer, castor oil was made difunctional by blocking, one of the three hydroxyl groups with phenyl isicyanate.

The method for blocking or removing one of the hydroxyl group is acetylation, benzoylation, methylation, dehydration, urethane formation etc. Out of these methods only urethane formation i.e. reaction of castor oil with phenyl isocyanate was preferred as this method has the following advantages:-

(1) Easy to prepare.
(2) No need of high temperature heating etc.
(3) Time needed is comparatively short.
(4) No need to wash the resultant products free from acid, alkalies etc.

The difunctional castor oil was reacted with 2,4 toluene di-isocyanate and 4,4'diphenyl methane diisocyanate separately to produce millable polymers - elastomers.

These polymers - elastomers were utilized in the preparation of articles such as typewriter roller, hammer

head, oil seals, hydraulic bracket, impellers, heels, soles, conveyor belting etc.

Since castor oil in India is cheaper than polyester, it is natural to expect that these products may be cheaper for their commercial exploitation.

PART II

SECTION II

PRESENT INVESTIGATION AND RESULTS

S E C T I O N - II

Present investigation and results:

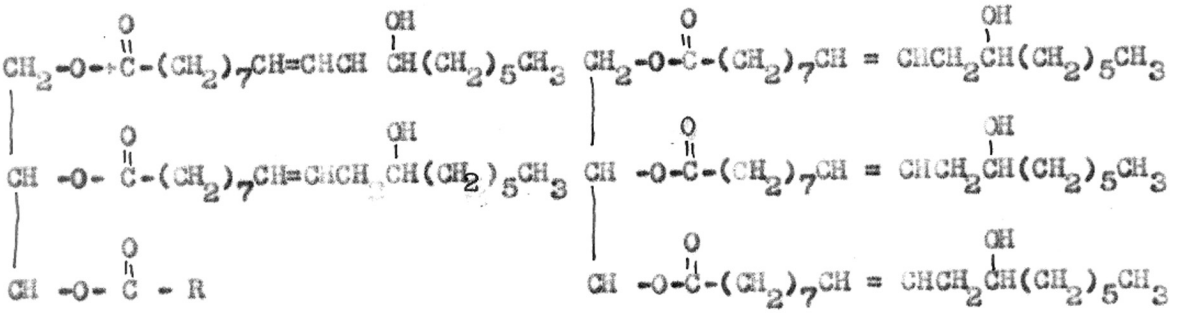
Castor oil is a naturally occurring triglyceride of whose predominant acid component is ricinoleic acid. Its molecular weight is reported to be roughly 1000. It is also reported that castor oil is roughly 70 % glyceryl triricinoleate and 30 % glyceryl diricinoleate. It could be made approximately 100 % difunctional by reaction with 0.7 equivalent of phenyl isocyanate with one mole (i.e. 2.7 equivalent) of castor oil, assuming that the major part of phenyl isocyanate would react with one of the hydroxyl groups of 70 % glyceryl triricinoleate.

This modified castor oil i.e. difunctional castor oil (DFCO) has been reacted with 2,4 toluene diisocyanate and 4,4'diphenyl methane diisocyanate separately and or chain extended with ethylene glycol and or water to produce polymers having hydroxyl groups terminated or isocyanate groups terminated urethane polymers. These polymers were then cured with (i) peroxide, (ii) sulphur, (iii) diisocyanate and (iv) radiation curing systems and the physical properties of the vulcanizates were studied.

Difunctional Castor Oil (DFCO)

The details of the preparation of DFCO are described in experimental section IV, Part II.

Medicinal castor oil (Swastic Oil Mills Ltd. Bombay, India) 2.7 equivalent was reacted with 0.7 equivalent of phenyl isocyanate resulting in difunctional castor oil (DFCO). DFCO was a brownish oily liquid with castor oil smell, hydroxyl number 118-119 and acid number less than 1.



30% Glyceryl diricinoleate 70 % glyceryl triricinoleate

The reaction is graphically represented as follows:

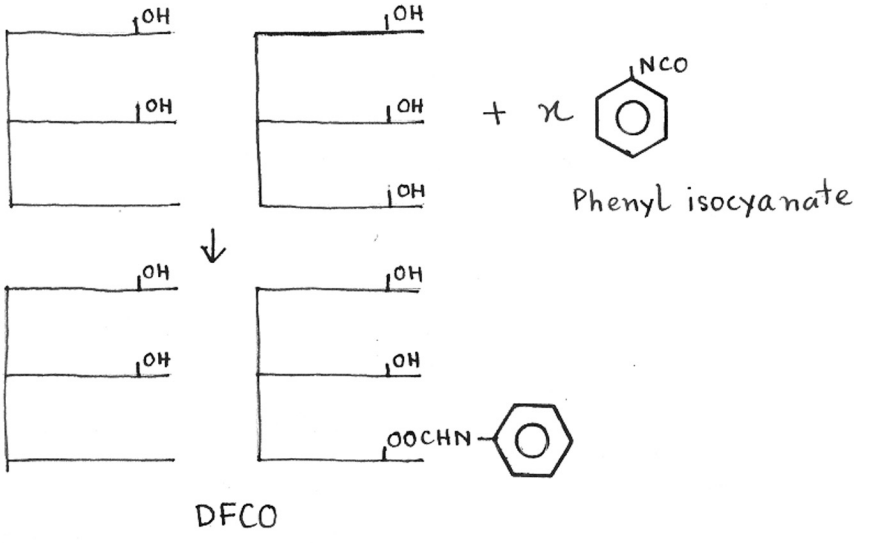


Table - VIII

Name and nature of the different polymers - elastomers from DFCO

S. No.	Polymer/ elasto-mer	Equivalent of					Nature
		DFCO	TDI	MDI	ETHY-LENE GLY-COL	ater	
1	M	1.0	0.99	-	-	-	Semisolid waxy material
2	N	1.0	-	0.99	-	-	Millable elastomer
3	O	1.0	2.0	-	1.01	-	Millable elastomer
4	P	1.0	-	2.0	1.01		Leather polymer
5	Q	1.0	3.0	-	1.0	-	Millable elastomer
6	R	1.0	-	3.0	1.0	-	Millable elastomer
7	S	1.0	3.0	-	-	1.0	Thermoplastic polymer

DFCO based Polyurethane elastomers / polymers

Polymer M

Preparation of polymer M

Polymer M was obtained by reacting 1.0 equivalent of DFCO with 0.99 equivalent of 2,4 toluene diisocyanate (TDI). This polymer is a hydroxy terminated polymer. Polymer M was a semisolid waxy polymer unsuitable to process

on the laboratory rubber mixing mill. Hence work was not pursued further. The physical properties of polymer M are described in Table IX

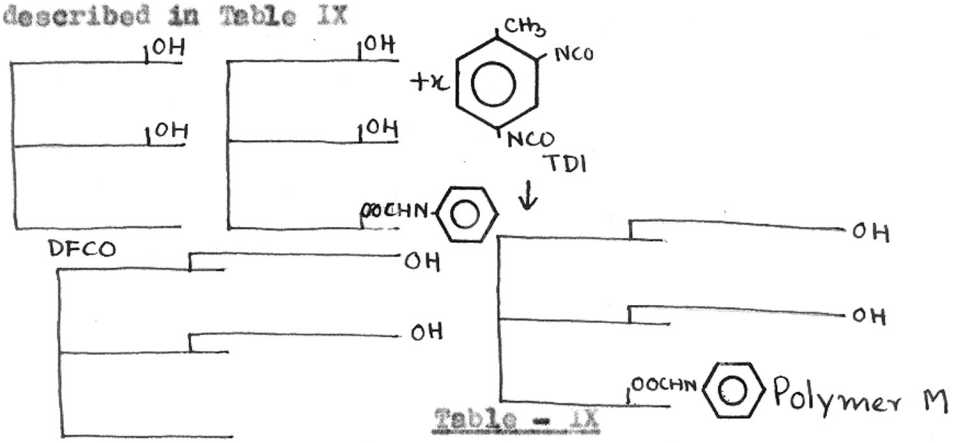


Table - IX

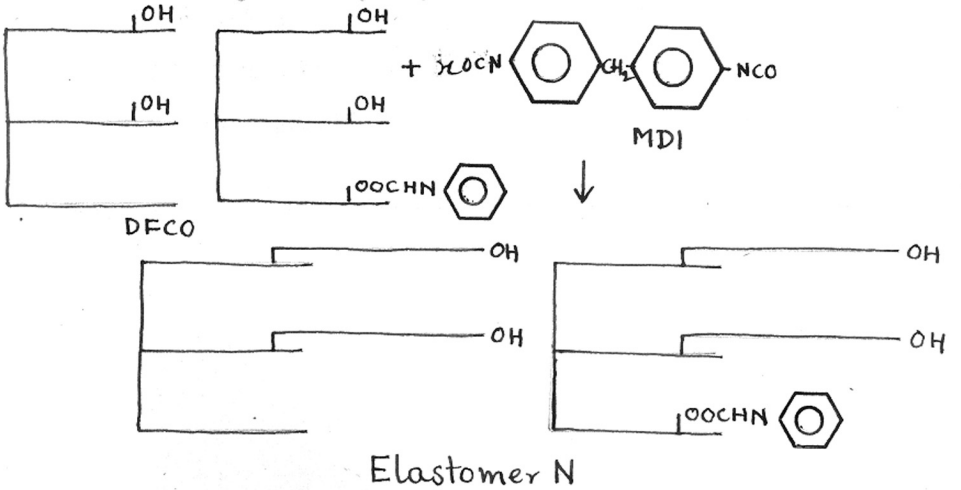
Physical properties of polymer M

Form	Brown coloured semisolid waxy material.
Odour	Castor oil smell
Specific gravity	1.01
Softening point	30°C

Elastomer N

Preparation of elastomer N

Hydroxy terminated elastomer N was obtained by reacting 1.0 equivalent of DFCO with 0.99 equivalent of 4,4'diphenyl methane diisocyanate (MDI)



Elastomer N

Physical properties of elastomer N

Elastomer N was a ~~red~~ brown coloured, transparent, soft rubbery solid, with characteristic castor oil smell. It's specific gravity was 1.099 and softening point was 220 - 230°C. The higher softening point of elastomer N than that of polymer M was probably due to the presence of aromatic rings of MDI. The physical properties are tabulated in Table X.

Table - X

Physical properties of elastomer N

Form	Brown coloured transparent soft rubber solid
Odour	Castor oil smell
Specific gravity	1.099
Softening point	220 - 230°C
Hardness, shore A	20
300 % Modulus, PSI	10.7
Tensile strength, PSI	10.7
Elongation, %	300
Tear strength, lbs/inch	45.6
Storage stability	Good

Compounding and curing of elastomer N

Elastomer N was easy to process on the rubber mixing mill. Surface tack was excellent. Elastomer N was cured with peroxide, sulphur, diisocyanate and radiation curing systems.

In the peroxide curing, stabilised dicumyl peroxide i.e. Dicup 40C, was used. In sulphur curing, rubber grade sulphur was used, in diisocyanate curing MDI was used and in radiation curing system, cobalt 60 was used as a source for radiation cure.

The compounding recipe of elastomer N are described in Table XI.

Table - XI

Compounding recipe of elastomer N

Ingredients	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Elastomer N	100.0	100.0	100.0	100.0
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
Dicup 40C	5.0	-	-	-
MBT	-	1.0	-	-
MBTS	-	4.0	-	-
RCD 2098	-	0.375	-	-
Sulphur	-	2.0	-	-
MDI	-	-	10.0	-

Physical properties of the vulcanizates of elastomer II:

Specific gravity values of peroxide, sulphur, diisocyanate and radiation cures were in the range of 1.170 - 1.215. The diisocyanate cure had the highest hardness i.e. shore A 65 followed by radiation cure shore A 50, sulphur cure shore A 45 and peroxide cure shore A 40. The sequence order as observed in the studies in shore hardness, was also observed in 100 % modulus studies, i.e. diisocyanate cure was 600 PSI, radiation cure was 285 PSI, sulphur cure was 260 PSI and peroxide cure 245 PSI. Tensile strength values were diisocyanate cure was 1100 PSI, peroxide cure was 820 PSI, sulphur cure was 600 PSI and radiation cure was 600 PSI. In the case of elongation % values were as follows: sulphur cure was 300 %, peroxide cure was 375 %, diisocyanate and radiation cure was 150 % each. The tear strength values were as follows: diisocyanate cure was 214 lbs/inch, peroxide cure was 180 lbs/inch, sulphur cure was 161 lbs/inch and radiation cure was 154 lbs/inch.

In general diisocyanate cure gave the best physical properties followed by peroxide, sulphur and radiation cures. The physical properties are described in Table XII.

Table - XII

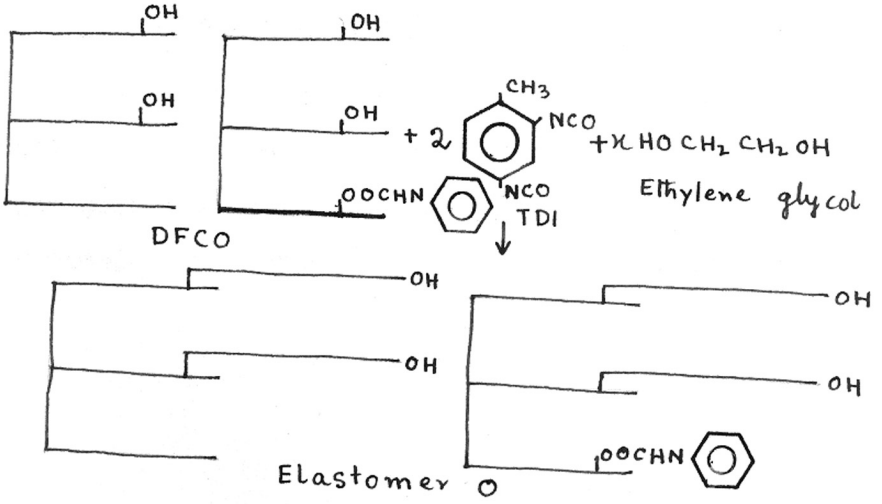
Physical properties of vulcanizates of elastomer N

	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Specific gravity	1.170	1.215	1.181	1.171
Hardness, shore A	40	45	60	50
100 % modulus, PSI	245	260	600	285
Tensile strength, PSI	820	800	1100	600
Elongation, %	275	300	150	150
Tear strength, lbs/inch	180	161	214	154
Cure time, in minutes, at 140°C	45	30	30	-
Cure time, in hours, at R.T.	-	-	-	100

Elastomer O

Preparation of elastomer O

Hydroxy terminated elastomer O was obtained by reacting 1.0 equivalent of DFCO, with 2.0 equivalent of 2,4 toluene diisocyanate (TDI) and 1.01 equivalent of ethylene glycol.



Physical properties of elastomer O

Elastomer O was a light brown, transparent elastomer with characteristic castor oil smell. Its specific gravity was 1.084 and softening point was 190°C. The physical properties of elastomer O are described in table XIII.

Table XIII

Physical properties of elastomer O

Form	Light brown transparent polymer
Odour	Castor oil smell
Specific gravity	1.084
Softening point	190°C
Hardness, shore A	45
100 % modulus, PSI	134
Tensile strength, PSI	750
Elongation, %	350
Storage stability	Good

Compounding and curing of elastomer O

Elastomer O was easy to process on the rubber mixing mill. Surface tack was excellent. Elastomer O was cured with peroxide sulphur, diisocyanate and radiation curing systems. The compounding recipe is described in Table XIV.

Table - XIV

Compounding recipe of elastomer O

Ingredients	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Elastomer O	100.0	100.0	100.0	100.0
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
Dicup 40 C	5.0	-	-	-
MBT	-	1.0	-	-
MBTS	-	4.0	-	-
RCD 2098	-	0.375	-	-
Sulfur	-	2.0	-	-
MDI	-	-	10.0	-

Physical properties of the vulcanizates of elastomer O.

Specific gravity values of peroxide, sulphur, diisocyanate and radiation cures were in the range of 1.218 - 1.229.

In the case of hardness the values were as follows - diisocyanate cure was highest i.e. shore A 75 followed by radiation cure was shore A 70, peroxide cure was shore A 50 and sulphur cure was shore A 40. The sequence order as observed in the studies in shore hardness was also observed in 100 % modulus. The modulus values obtained were as follows - diisocyanate cure was 1500 PSI, radiation cure

was 550 PSI, peroxide cure was 300 PSI and sulphur cure was 280 PSI. Tensile strength values were as follows - diisocyanate cure was 1500 PSI, radiation cure was 1300 PSI, sulphur cu re was 1100 PSI and peroxide cure was 950 PSI. Elongation % values were as follows - radiation cure was 300 %, peroxide cure and sulphur cure was 250 % each and diisocyanate cure was 100 %. In case of tear strength the values were as follows - peroxide cure was 270 lbs/inch, radiation cure was 269 lbs/inch, sulphur cure was 200 lbs/inch and diisocyanate cure was 190 lbs/inch.

The physical properties of vulcanizates are described in table XV.

Table - XV

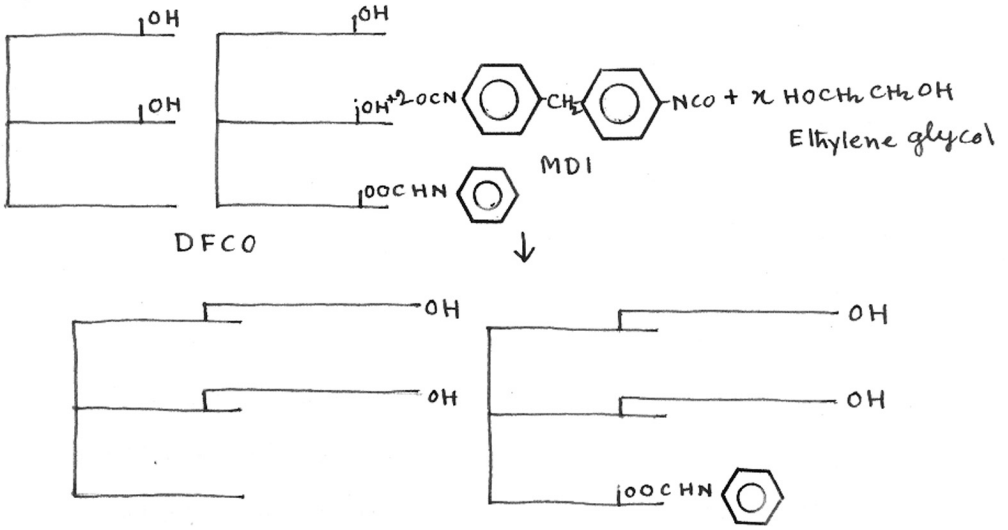
Physical properties of the vulcanizates of elastomer O

Properties	Peroxide cure	sulphur cure	diisocya-nate cure	Radiation cure
Specific gravity	1.229	1.228	1.224	1.218
Hardness, shore A	50	40	75	70
100 % modulus, PSI	300	280	1500	550
Tensile strength, PSI	950	1100	1500	1300
Elongation, %	250	250	100	300
Tear strength, lbs/inch	270	200	190	269
Cure time, in minutes, at 140°C	30	20	30	-
Cure time in hours at R.T.	-	-	-	100

Polymer P

Preparation of polymer P

Hydroxy terminated polymer P was obtained by reacting 1.0 equivalent of DFCO, with 2.0 equivalent of 4,4'diphenyl methane diisocyanate (MDI) and 1.01 equivalent of ethylene glycol.



Polymer P

Physical properties of Polymer P

Polymer P was a yellowish translucent hard leathery solid with characteristic castor oil smell. Its epecific gravity was 1.01 and softening point was 55 - 60°C. The physical properties are described in table XVI.

Table - XVI

Physical properties of polymer P

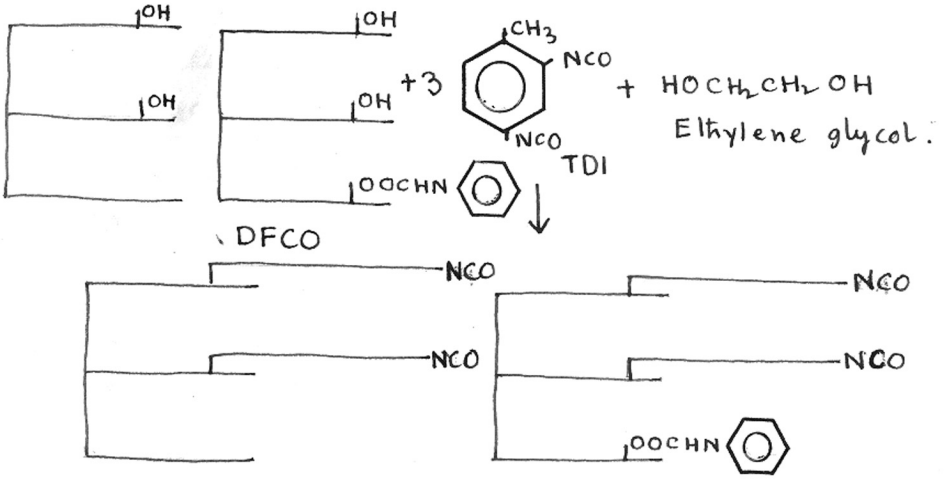
Form	Yellow translucent hard leathery solid.
Odour	Castor oil smell
Specific gravity	1.01
Softening point	55 - 60°C
Hardness, shore A	65
100 % modulus, PSI	622
Tensile strength, PSI	1400
Elongation, %	250
Tear strength, lbs/inch	344.2
Storage stability	Good

Polymer P was leathery and hence work was not pursued further.

Elastomer Q

Preparation of elastomer Q:

Isocyanate terminated elastomer Q was obtained by reacting 1.0 equivalent of DFCO, with 3.0 equivalent of 2,4 toluene diisocyanate (TDI) and 1.0 equivalent of ethylene glycol.



Elastomer Q

Physical properties of elastomer Q

Elastomer Q was a brownish yellow transparent solid having characteristic castor oil smell, its specific gravity was 1.08 and softening point was 200°C. Elastomer Q had 2.422 % free isocyanate groups, hence its storage stability was limited. The physical properties are described in Table XVII.

Table - XVII

Physical properties of elastomer Q

Form	Brownish yellow transparent solid.
Odour	Castor oil smell
Specific gravity	1.08
Softening point	200°C
Free NCO, %	2.422
Hardness, shore A	45
100 % modulus, PSI	370
Tensile strength, PSI	1000
Elongation, %	250
Storage stability	Limited

Compounding and curing of elastomer Q

Elastomer Q was easy to process on rubber mixing mill. The surface tack was good. Elastomer Q was cured with peroxide, sulphur, diisocyanate and radiation curing systems. The compounding recipe is given in Table XVIII.

The peroxide curing was done at 140°C while sulphur and diisocyanate curing were done at 121°C (above this temperature(121°C)severe blisters were developed in the test samples). On using RCD 2098, which is a recommended

accelerator in sulphur curings, severe blisters were observed. Hence it was not used in sulphur curing system.

Table - XVIII

Compounding recipe of elastomer Q

Ingredients	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Elastomer Q	100.0	100.0	100.0	100.0
Stearic acid	0.2	0.2	0.2	0.2
HAF	30.0	30.0	30.0	30.0
DBP	-	10.0	10.0	-
Dicup 40 C	5.0	-	-	-
MBT	-	1	-	-
MBTS	-	4	-	-
Sulphur	-	0.75	-	-
MDI	-	-	2.8	-

Physical properties of the vulcanizates of Elastomer Q

The specific gravity values of the vulcanizates in different curing systems were in the range of 1.20 - 1.24. The hardness shore A values of radiation and sulphur cure was 95 each, while diisocyanate and peroxide cures was 85 each. 100 % modulus values were as follows - radiation cure was 2800 PSI, peroxide and sulphur cure was 1900 PSI each and diisocyanate cure was 1400 PSI respectively. Tensile

strength values were as follows - radiation and sulphur cures was 2800 PSI each, diisocyanate cure was 2200 PSI and peroxide cure was 1900 PSI. Elongation % values were as follows - sulphur and diisocyanate cure was 150 % each, peroxide and radiation cure was 100 % each. Abrasion index in sulphur cure 50.9 %, diisocyanate cure was 40 % and peroxide cure was 36.21 %.

The physical properties are tabulated in Table XIX.

Table - XIX

Physical properties of the vulcanizates of Elastomer 9

Properties	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Specific gravity	1.229	1.24	1.20	1.23
Hardness, shore A	85	95	85	95
100 % modulus, PSI	1900	1900	1400	2800
Tensile strength, PSI	1900	2800	2200	2800
Elongation, %	100	150	150	100
Tear strength, lbs/inch	740	190	180	635
Abrasion index, %	36.21	50.9	40.0	-
Cure time, in minutes, at 140°C	15	-	-	-
Cure time, in minutes, at 121°C	-	10	20	-
Cure time, in hours, at R.T.	-	-	-	50

Heat aging studies of peroxide, sulphur and diisocyanate vulcanizates of elastomer Q:

Dumbbell shaped test specimens of elastomer Q, of peroxide, sulphur and diisocyanate vulcanizates were placed in Geer's oven at 75°, 100° and 150°C for seven days. The physical properties are graphically shown in figure 23, 24, 25 and 26.

Peroxide cure vulcanizates

In the case of peroxide cure on heat aging the tensile strength which was initially 1900 PSI, increased to 2100 PSI at 75°C. The same tensile strength figure i.e. 2100 PSI, was also observed on aging at 100° and 150°C. 100 % modulus value which was initially 1900 PSI increased to 2100 PSI at 75°C. At 100° and 150°C however 100 % modulus figures fell sharply. Elongation % value which was 100 % at room temperature remained the same at 75°C. However it fell to 75 % at 100°C and 150°C. Hardness values observed were as follows - shore A 85, 90 and 95 at 75°, 100° and 150°C respectively.

Sulphur cure vulcanizates

In the case of sulphur cure, tensile strength value which was 2800 PSI at room temperature rose to 3400 PSI at 75°, 100° and 150°C aging temperatures. 100 % modulus value which was 1900 PSI rose to 3400 PSI at 75°C but at 100°C and 150°C it fell sharply. Elongation % value which was 150 % at room

temperature fell to 100 % at 75°C aging and to 75 % at 100° and 150° aging temperatures respectively. The hardness, shore A are value at these aging temperatures showed only a little change.

Diisocyanate vulcanizates

In the case of diisocyanate cured sample, the tensile strength value at 75°C aging was 2700 PSI but at 100° and 50°C was 2200 PSI, 100 % modulus value at 75°C was 2700 PSI but it fell sharply at 100°C and 150°C. Elongation % value was 150 % at 75°C aging while at 100°C and 150°C was only 75 %. The hardness values showed little change . The heat aging properties of elastomer Q are described in Table XX.

Blending studies of elastomer Q

Elastomer Q was blended with urethane rubber (Adiprene C) nitrile rubber (Perbunan N 3807), natural rubber (RMA - 1), chloroprene rubber(Neoprene WX) in 50:50 mixture. The ease of blending of these rubbers was found in the order of polyurethane > nitrile > natural rubber > neoprene. The compounding recipe is given in the Table XXI.

The specific gravity values of the vulcanizates of the blends were in the range of 1.210 - 1.243. Hardness shore A values were as follows - nitrile blend was 80; polyurethane blend was 75; natural rubber blend and neoprene

TABLE - XX

Heat aging studies of elastomer Q

Properties	Temp.°C	Peroxide cure	Sulphur cure	Diisocyanate cure
Hardness, Shore A	25	85	95	85
	75	85	95	80
	100	90	97.5	90
	150	95	95.0	92.5
100% Modulus, PSI	25	1900	1900	1400
	75	2100	3400	2700
	100	-	-	-
	150	-	-	-
Tensile strength, PSI	25	1900	2800	2200
	75	2100	3400	2700
	100	2100	3400	2200
	150	2000	3400	2200
Elongation, %	25	100	150	150
	75	100	100	100
	100	75	75	75
	150	75	75	75

TABLE - XXI

Compounding recipe of blends of elastomer Q with different rubbers

Ingredients	Urethane rubber	Nitrile rubber	Natural rubber	Neoprene rubber
Elastomer Q	100.0	100.0	100.0	100.0
Adiprene C	100.0	-	-	-
Perbunan N 3807	-	100.0	-	-
Natural rubber RMA-1	-	-	100.0	-
Neoprene WX	-	-	-	100.0
Stearic acid	1.2	1.2	0.4	0.5
Nonox D	-	-	2.0	2.0
Zinc oxide	-	4.0	5.0	5.0
MBT	2.0	2.0	2.0	-
MBTS	8.0	4.0	4.0	-
RCD 2098	0.7	0.375	0.375	-
Sulphur	3.5	3.0	3.5	-
Na-22	-	-	-	1
Magnesium oxide	-	-	-	4

blend was 70 each. The tensile strength values were as follows - polyurethane blend was 3000 PSI, nitrile blend was 2000 PSI, natural rubber blend was 1500 PSI and neoprene blend was 1300 PSI. 100 % modulues values were as follows - nitrile blend was 1350 PSI, natural rubber blend was 1290 PSI, polyurethane blend was 1000 PSI and neoprene blend was 720 PSI. Elongation % values were as follows - polyurethane blend was 400 %, neoprene blend was 250 %, nitrile blend was 200 % and natural rubber blend was 150 %. Tear strength values were as follows - polyurethane blend was 300 lbs/inch, neoprene blend and natural rubber blend was 250 lbs/inch each, nitrile blend was 240 lbs/inch. The physical properties of the blend are described in Table XXII.

TABLE - XXII

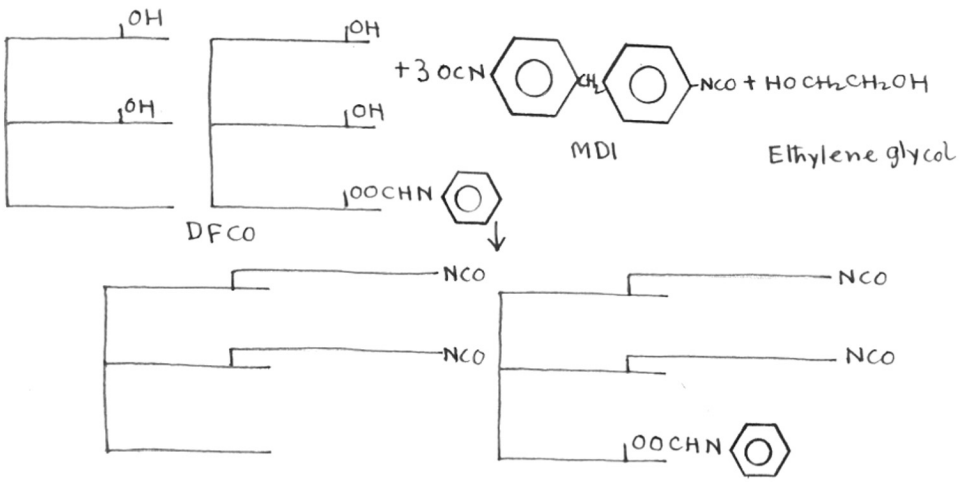
Physical properties of the blends of elastomer Q vulcanizates

Properties	Urethane blend	Nitrile blend	Natural rubber blend	Neoprene blend
Specific gravity	1.243	1.203	1.210	1.222
Hardness, shore A	75	80	70	70
100 % modulus, PSI	1000	1350	1290	720
Tensile strength, PSI	3000	2000	1500	1300
Elongation, %	400	200	250	250
Tear strength, lbs/inch	300	240	250	250

Elastomer R

Preparation of elastomer R

Isocyanate terminated elastomer R was obtained by reacting 1.0 equivalent DFCO, with 3.0 equivalent of 4,4'diphenyl methane diisocyanate (MDI) and 1.0 equivalent of ethylene glycol.



Elastomer R

Physical properties of elastomer R

Elastomer R was a brownish yellow tough solid having characteristic castor oil smell. Its specific gravity was 1.08, and it decomposes above 250°C. Elastomer R had 1.64 % free isocyanate groups and storage stability was only for a couple of days. The physical properties are given in Table XXIII.

TABLE - XXIII

Physical properties of elastomer R

Form	Brown hard polymer
Odour	Castor oil smell
Free isocyanate, %	1.64
Hardness, shore A	45
100 % modulus, PSI	398
Tensile strength, PSI	1200
Elongation, %	100
Storage stability	Couple of days.

Compounding and curing of elastomer R

Elastomer R was millable on the rubber mixing mill. The surface tack was poor. The compounding recipe is given in Table XXIV. It was cured with peroxide, sulphur, diisocyanate and radiation curing systems.

Peroxide curing was done at 140°C while sulphur and diisocyanate curing was done at 121°C.

Physical properties of the vulcanizates of elastomer R

The specific gravity values of the vulcanizates were in the range of 1.195 - 1.243. Hardness values were

TABLE - XXIV

Compounding recipe of elastomer R

	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Elastomer	100.0	100.0	100.0	100.0
Stearic acid	0.2	2.0	2.0	0.2
HAF	30.0	30.0	30.0	30.0
DBP	-	10.0	10.0	-
Dicup 40 C	5.0	-	-	-
MBT	-	1	-	-
MBTS	-	4	-	-
Sulphur	-	0.75	-	-
MDI	-	-	2.8	-

as follows - radiation and peroxide cure was shore A 90 each, while sulphur and diisocyanate cure was shore A 85 each. Tensile strength values were as follows - peroxide cure was 3500 PSI, diisocyanate cure was 2800 PSI, radiation cure was 1800 PSI and sulphur cure was 1500 PSI. 100% modulus values were as follows - peroxide cure was 3500 PSI, radiation cure was 1800 PSI, diisocyanate cure was 1500 PSI and sulphur cure was 1100 PSI. Tear strength values were as follows - peroxide cure was 1040 lbs/inch, radiation

cure was 1000 lbs/inch, diisocyanate cure was 172.2 lbs/inch and in sulphur cure was 105 lbs/inch. Abrasion index values were as follows - peroxide cure was 108.1 %, sulphur cure was 78.9 %, diisocyanate cure was 47 %.

Physical properties are described in Table XXV.

TABLE - XXV

Physical properties of the vulcanizates of elastomer - R

Properties	Peroxide cure	Sulphur cure	Diisocyanate cure	Radiation cure
Specific gravity	1.243	1.22	1.20	1.195
Hardness, Shore A	90	85	85	90
100 % Modulus, PSI	3500	1100	1500	1800
Tensile strength, PSI	3500	1500	2700	1800
Elongation, %	100	150	150	100
Tear strength, lbs/inch	1040	146.8	172	1000
Abrasion index, %	108.1	78.9	47.0	-
Cure time, in minutes, at 140°C	15	-	-	-
Cure time, in minutes, at 121°C	-	30	20	-
Cure time, in hours, at R.T.	-	-	-	50

PART II

SECTION III

DISCUSSION

S E C T I O N - III

D I S C U S S I O N

Polyurethane elastomers are characterized to possess better physical and chemical properties than the olefinic elastomers, because of the presence of more hydrogen bonding, Vander Walls forces etc. The difunctional castor oil (DFCO) used in the present investigation has pendulant long alkyl chains. The effect of these pendulant chains will be predominently to reduce the effectiveness of the inter molecular forces of attraction between the polymer chains. Similarly the rate of formation of high molecular weight polymers from difunctional castor oil diisocyanate reaction, may also be influenced by the secondary hydroxyl groups having adjacent long alkyl chains. These facts, therefore, appear to be responsible for low values of difunctional castor oil based polyurethane elastomers than the values obtained from polyester based polyurethane elastomers having no pendulant alkyl groups.

When the DFCO was reacted with 2,4 toluene diisocyanate in 1:0.99 equivalent proportion, a semisolid waxy polymer M was obtained. It appears that the molecular weight build up in this case was not very high, may be because, one of

the isocyanate groups (i.e. 2 position NCO)[37] of 2,4 toluene diisocyanate is less reactive and hydroxyl groups of DFCO are secondary in nature.

When TDI was replaced with 4,4'diphenyl methane diisocyanate, a diisocyanate having isocyanate groups with equal reactivity, in proportion of DFCO and MDI 1:0.99, a millable elastomer N was obtained. The softening point of elastomer N was higher than polymer M. This fact may be attributed to the nature as well as stearic constitution of MDI. However the properties of the vulcanizates in all the four i.e. peroxide, sulphur, diisocyanate and radiation curing systems of elastomer N were not very encouraging. The physical properties such as tensile strength, 100 % modulus, tear strength of elastomer N are plotted against time in minutes, and are graphically shown in the figures 8, 9 and 10.

It was therefore decided to react DFCO with diisocyanate (2,4 toluene diisocyanate and 4,4'diphenyl methane diisocyanate) in the proportion of 1:2 and then chain extending the resultant prepolymer thus formed with ethylene glycol. Thus DFCO:TDI:EG in proportion of 1:2:1.01 gave a millable elastomer O, while DFCO:MDI:EG in proportion of 1:2:1.01 gave a leathery polymer P. Amongst the properties of the vulcanizates from peroxide, sulphur, diisocyanate and radiation cures of elastomer O, reported in Table XXVI, curing with diisocyanate gave the best results. The physical

properties of elastomer O such as tensile strength, 100 modulus and tear strength are plotted against time in minutes and are graphically shown in figure 11, 12 and 13. These physical properties were found to be much lower than the physical properties of the reported common polyurethane elastomers. Table XXXIX, Part I.

Hence it was decided to increase the molar concentration of the diisocyanate in the preparation of DFCO elastomers. The proportion of DFCO:Diisocyanate:Ethylene glycol was therefore made 1:3:1. Thus DFCO:TDI:EG in the proportion of 1:3:1 gave a millable elastomer Q, while DFCO:MDI:EG in the proportion of 1:3:1 gave a millable elastomer R.

In the preparation of M, N, O and P polymers/elastomers the end groups of the polymer were hydroxy terminated. With the increase in concentration of diisocyanate in the preparation of elastomers, Q and R,the end groups of these elastomers were isocyanate terminated.

Elastomer Q was easy to process and was having good surface tack while elastomer R was also processable but with poor surface tack. This phenomenon may be attributed to the possibility of high molecular weight of elastomer R.

The vulcanizate properties of these elastomers are reported in Table XXV.

In the case of elastomer Q radiation and sulphur cures, higher figure for tensile strength were obtained. The physical properties of elastomer Q such as tensile strength, 100 % modulus and tear strength are graphically shown in figures 14 to 22.

Elastomer R gave highest tensile figure in peroxide cure amongst all the elastomers of DFCO. The physical properties of elastomer R such as tensile strength, 100 % modulus and tear strength are graphically shown in figs. 14 - 22.

The highest tensile values in peroxide cure in elastomer R may be due to the presence of higher percentage of MDI, which is a source of active methylene groups[38] in the polymer matrix, which may be susceptible to free radical attack. The same active methylene group may be supposed to remain active in the cross linking by sulphur, diisocyanate and radiation cures. It was therefore expected that the physical properties of all the four type cures of elastomer R should be higher. However only in the case of peroxide and diisocyanate cures , higher physical properties were obtained. It was also noticed that in the case of elastomer R tear strength values in peroxide and radiation cures were higher as compared to other two types of cures. The abrasion index for elastomer R in peroxide cure is also high. All these comparative properties of elastomer R may be because of higher percentage of MDI in the elastomer.

Even though elastomer R gave over all the best results, it was felt that studies in elastomer Q may be performed in more details, such as aging and blending with other rubbers, on the ground that elastomer Q was easy to prepare in large quantities and on considerations of cost.

Vulcanizates of elastomers Q in peroxide, sulphur and diisocyanate cures were subjected to heat aging at 25°, 75°, 100° and 150°C for seven days each. These results are graphically shown in the figures 23, 24, 25 and 26.

On heat aging peroxide, diisocyanate and sulphur vulcanizates showed increase in tensile strength at 75°C. On heat aging at 100° and 150°C, peroxide and sulphur vulcanizates had tensile values similar to the values obtained at 75°C heat aging. However diisocyanate vulcanizates at 100° and 150°C on heat aging showed the tensile strength values to be of the unaged sample.

Elastomer Q blended in all proportions with polyurethane (Adiprene C) and nitrile rubber (Perbanan N 3807) but with natural rubber and neoprene, the blending was poor.

Conclusions:

Comparative studies of polymers derived from (modified castor oil i.e.) DFCO - diisocyanate reaction to produce elastomeric materials are made. These studies indicate that castor oil elastomers can be utilized like other synthetic elastomers for making commercial products.

TABLE - XXVI

Physical properties of the vulcanizates of elastomers N, O, Q and R

Polymers	Properties								
	Specific gravity	Hardness, shore A	100% modulus, PSI	Tensile strength, PSI	Elongation, %	Tear strength, lbs/inch	Abrasion index, %	Cure time °C/mts.	Hours at R.T.
1	2	3	4	5	6	7	8	9	10
Elastomer N									
Peroxide	1.170	40	245	820	275	180	-	140°C/45	-
Sulphur	1.215	45	260	800	300	161	-	140°C/30	-
Diisocyanate	1.181	60	660	1100	150	214	-	140°C/30	-
Radiation	1.171	50	285	600	150	154	-	-	100
Elastomer O									
Peroxide	1.229	50	300	950	250	270	-	140°C/20	-
Sulphur	1.228	40	280	1100	250	200	-	140°C/20	-

(Continued ...)

Table - XXVI - continued

1	2	3	4	5	6	7	8	9	10
Elastomer O (contd)									
Diisocyanate	1.224	75	1500	1500	100	190	-	140°C /30	-
Radiation	1.218	70	550	1300	300	269	-	-	100
Elastomer Q									
Peroxide	1.225	85	1900	1900	100	740	36.21	140°C/15	-
Sulphur	1.24	95	1900	2800	150	190	50.9	121°C/10	-
Diisocyanate	1.20	85	1400	2200	150	180	40.0	121°C/20	-
Radiation	1.23	95	2800	2800	100	635	-	-	50
Elastomer R									
Peroxide	1.243	90	3500	3500	100	1040	103.1	140°C/15	-
Sulphur	1.222	85	1100	1500	150	146.8	78.9	121°C/30	-
Diisocyanate	1.20	85	1500	2700	150	172	47.0	121°C/20	-
Radiation	1.195	90	1800	1800	100	1000	-	-	50

Moulded products from DFCO based elastomers.

PART II

SECTION IV

EXPERIMENTAL

S E C T I O N - IV

E X P E R I M E N T A L

Preparation of Difunctional Castor oil (DFCO)

In a 2-litre three necked flask equipped with a mercury seal stirrer, a dropping funnel with an anhydrous calcium chloride guard tube, a thermometer, an oil bath etc. was placed 1 kg of dried castor oil. The temperature of castor oil was brought to 100°C followed by dropwise addition of 76 ml of phenyl isocyanate with efficient stirring for one hour. The flask was evacuated at 100°C/1 mm of mercury pressure for half an hour to remove any traces of volatile product. The reaction mixture was cooled and kept well stoppered. The physical properties of DFCO are described in Table XXVII.

TABLE - XXVII

Physical properties of DFCO

Form	Light brown oily liquid.
Odour	Castor oil smell
Specific gravity at 28°C	0.9792
Refractive index at 23°C	1.485
Acid number	1
Hydroxyl number	118 - 119

Preparation of polymer M

In a 100 ml three necked flask equipped with a thermometer, a mercury seal stirrer, a dropping funnel, an oil bath etc. was placed, 50 g of dried DFCO. The temperature of DFCO was brought to 100°C with the help of an oil bath. 2,4 Toluene diisocyanate, 9.057 g was added with vigorous stirring during 20 minutes. The reaction mixture was stirred for 30 minutes and it was then evacuated at 100°C, 2 mm of mercury pressure. The mixture was then poured into silicone waxed tray and further polymerized at 100°C in an electric oven for 24 hours. Polymer M was semisolid waxy material unsuitable for processing on the rubber mixing mill, hence it was not processed further.

Preparation of elastomer N

In a 250 ml three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper etc. was placed 100 g of dried DFCO. The temperature of DFCO was brought to 100°C with the help of an oil bath. 26.00 g of powdered 4,4'diphenyl methane diisocyanate was then added with brisk stirring. Viscosity of the reaction mixture increases very rapidly within about 5 minutes. The reaction mixture was poured into a silicone waxed tray and further polymerized at 100°C in electric oven for 24 hours.

Compounding of elastomer N

Elastomer N was soft rubbery solid and had good surface tack. A continuous band of polymer was formed immediately when placed on cold mixing mill. The ingredients were added according the order given in the compounding recipe in Table XI. The mix was cut thrice from either side and rolled through tight mill six times, and sheeted out. Peroxide, sulphur and diisocyanate were cured at 140°C in standard moulds.

The compounded stock for radiation cure was hot pressed in a standard mould and sheets were exposed to cobalt 60 source of radiation 7×10^{16} x 60 eV/hr/g in the "Gamma cell 200 Atomic Energy Commission of Canada" chamber.

The physical properties of the vulcanizates were determined according to A.S.T.M. 412-64 T (1965) and are described in Table XII.

Preparation of elastomer O

In a three-necked 500 ml flask, equipped with a thermometer, a mercury seal stirrer, a dropping funnel with anhydrous calcium chloride guard tube, an oil bath etc. was placed 200 g of dried DFCO. The temperature of the DFCO was brought to 100°C and 73.18 g of 2,4 toluene diisocyanate was added during 30 minutes. 13.17 g of ethylene glycol was then

added in 10 minutes with brksk stirring. The mixture was poured into silicone waxed tray and further polymerized in an electric oven at 100°C for 24 hours.

Compounding of elastomer O

Elastomer O was easy to process and had good surface tack. A continuous band of polymer was formed immediately when placed on cold rubber mixing mill. The ingredients were added according to the order given in the compounding recipe in Table XIV. The mix was cut thrice from either side rolled through a tight mill six times, and sheeted out. Peroxide, sulphur and diisocyanate stocks were cured at 140°C in standard moulds.

The compounded stock for radiation cure was hot pressed in standard mould and sheets were exposed to cobalt 60 source of radiation 7 x 10^{16} x 60 eV/hr/g in the 'Gamma Cell 220 Atomic Energy Commission of Canada' chamber.

The physical properties of the vulcanizates were determined according to A.S.T.M. D-412-64 T (1965), and are described in Table XV.

Preparation of Polymer P

In a 100 ml three necked flask equipped with a thermometer, a mercury seal stirrer, a ground glass stopper, an oil bath etc. was placed, 50 g of dried DFCO. The

temperature of DFCO was brought to 100°C with the help of an oil bath. 26.29 g of powdered MDI was added through the side neck with vigorous stirring. Viscosity of the reaction mixture increased very rapidly in about two minutes, 3.29 g of ethylene glycol was then added with stirring and poured into silicone waxed tray and further polymerized at 100°C in an electric oven for 24 hours. Since polymer P was leathery work was not pursued further.

Preparation of elastomer Q

In a one-litre three necked flask equipped with a thermometer, a mercury seal stirrer, a dropping funnel with an anhydrous calcium chloride guard tube, an oil bath etc. was placed 400 g of dried DFCO. The temperature of DFCO was brought to 100°C followed by addition of 219.60 g of 2,4 toluene diisocyante under stirring during 30 minutes. The temperature of the reaction mixture was maintained between 100 and 110°C. After the addition of 2,4 toluene diisocyanate, the reaction mixture was stirred for 15 minutes, ethylene glycol, 26 g, was then added with vigorous stirring. The reaction mixture was stirred for another 15 minutes and the flask was degassed under 1 mm of mercury pressure. The reaction mixture was poured into silicone waxed tray and further polymerized in an electric oven at 100°C for 24 hours.

Compounding of elastomer Q

Elastomer Q was easy to process and had good surface tack. A continuous band of polymer was formed immediately when placed on cold rubber mixing mill. The ingredients were added according to the order given in the compounding recipe in the Table XVIII. The mix was cut thrice from either side, rolled through a tight mill six times, and sheeted out. Peroxide stock cure was cured at 140°C, sulphur and diisocyanate stocks were cured at 121°C.

The compounded stock for radiation cure was hot pressed in a standard mould and sheets were exposed to cobalt 60 source of radiation 7 x 10^{16} x 60 eV/hr/g in the 'Gamma Cell 220 Atomic Energy Commission, Canada' chamber.

The physical properties of the vulcanizates were determined according to A.S.T.M. D 412-64 T (1965), and are described in Table XIX.

Heat aging studies of peroxide, sulphur, diisocyanate cured elastomer Q:

The peroxide, sulphur and diisocyanate cured elastomer Q were placed in Geer's oven at 75°, 100° and 150°C for seven days. The physical properties of the aged sample were tested according to the usual procedures. They are tabulated in the Table XX.

Blending of elastomer Q

Elastomer Q was compounded with urethane rubber—Adiprene C. Nitrile rubber-Perbunan N 3807, Chloroprene rubber-Neoprene WX and Natural rubber-RMA-1 in 50:50 proportions on rubber mixing mill.

The polymers were placed on cold rubber mixing mill. The ingredients were added according to the order given in the compounding recipe in Table XXI. The mix was cut thrice from either side, rolled through a tight mill six times, sheeted out and cured at 140°C in standard moulds.

The physical properties of the vulcanizates were determined in accordance to ASTM D 412-64 T (1965) and described in Table XXII.

Preparation of elastomer R

In a three-necked 250 ml flask, equipped with a thermometer, a mercury seal stirrer, a ground glass stopper, an oil bath etc. was placed 100 g of dried DFCO. The temperature of DFCO was brought to 100°C with the help of an oil bath. 78.87 g of powdered 4,4'diphenyl methane diisocyanate was added through the side neck under brisk stirring followed by the addition of 6.5 g of ethylene glycol. The reaction mixture was then poured into silicone waxed tray and further polymerized for 24 hours at 100°C in an electric oven.

Compounding of elastomer R:

Elastomer R was tough polymer but could be easily processed on the rubber mixing mill. The surface tack was poor. A continuous band of polymer was soon formed when placed on cold rubber mixing mill. The ingredients were added according to order given in the compounding recipe in Table XXIV. The mix was cut thrice from either side, rolled through tight mill six times and sheeted out. Peroxide cure was done at 140°C, sulphur and diisocyanate cures were done at 121°C in standard moulds.

The compounded stock for radiation cure was hot pressed in standard mould and sheets were exposed at cobalt 60 source of radiation 7 x 10^{16} x 60 eV/hr/g in "Gamma Cell 220 Atomic Energy Commission of Canada" chamber.

The physical properties of vulcanizates were determined according to ASTM D 412-64 T (1965) and are described in Table XXV.

S Y N O P S I S

Introduction

Polyurethane based synthetic polymers we e discovered by Prof. Otto Bayer and his associates in 1937 as a substitute for Dr. Carother's, of du Pont de Nemours, polyamide polymer (nylon). After the end of 2nd World War, the chemistry and technology of polyurethanes has developed to a considerable extent in the western countries and that these polymers have now become one of the most important industrial polymers

These polymers can be tailor made to any desired properties. Thus they have been used as synthetic fibres, foams, surface coatings, adhesives, rocket fuel binders, elastomers, etc.

The present studies describe the preparation of polyurethane millable elastomers from polyhydroxy compounds such as polyesters, castor oil derivative and diisocyanates such as 2,4 toluene diisocyanate and 4,4'diphenyl methane diisocyanate and the vulcanizate properties of these elastomers.

PART - I

Millable polyurethane elastomers from polyesters

Polyester based polyurethane elastomers are now commercially available from many manufacturers in western countries. No detailed information about their preparation

is available in the literature. Hence different polyesters were prepared from different dibasic acids and mixture of ethylene and 1,2 propylene glycols. These polyesters were then reacted with diisocyanates to prepare polymers. Only the adipic acid-ethylene, propylene glycol polyester gave the elastomeric products. These were then vulcanised with peroxide and diisocyanate curing agents and the properties of the vulcanizates were studied. These properties were found to be comparable to the commercial polyurethane elastomers. Useful articles such as trolly wheels, heels and soles, O-rings, hydraulic bucket of automobiles were prepared.

PART - II

Millable polyurethane elastomers from castor oil

Castor oil is a naturally occurring polyol. Castor oil has been used in polyurethane reactions for making coatings, adhesives and castable compounds. But systematic literature survey indicated that no attempts were made to prepare millable polyurethane elastomers from castor oil. Having gained experience in the preparation of millable polyester based urethane elastomers, it was decided to prepare millable elastomers from castor oil.

Trihydroxy part of castor oil was made dihydroxy by reacting with phenyl isocyanate to prepare difunction castor oil (DFCO). Difunctional castor oil was then reacted with different

diisocyanates in various proportions to prepare elastomers of different physical properties. These elastomers were vulcanized with peroxide, sulphur, diisocyanate and radiation. The properties of these were studied. Useful articles such as typewriter roller, heels, soles, trolly wheels, O-rings, V belts, etc. were prepared.

APPENDIX

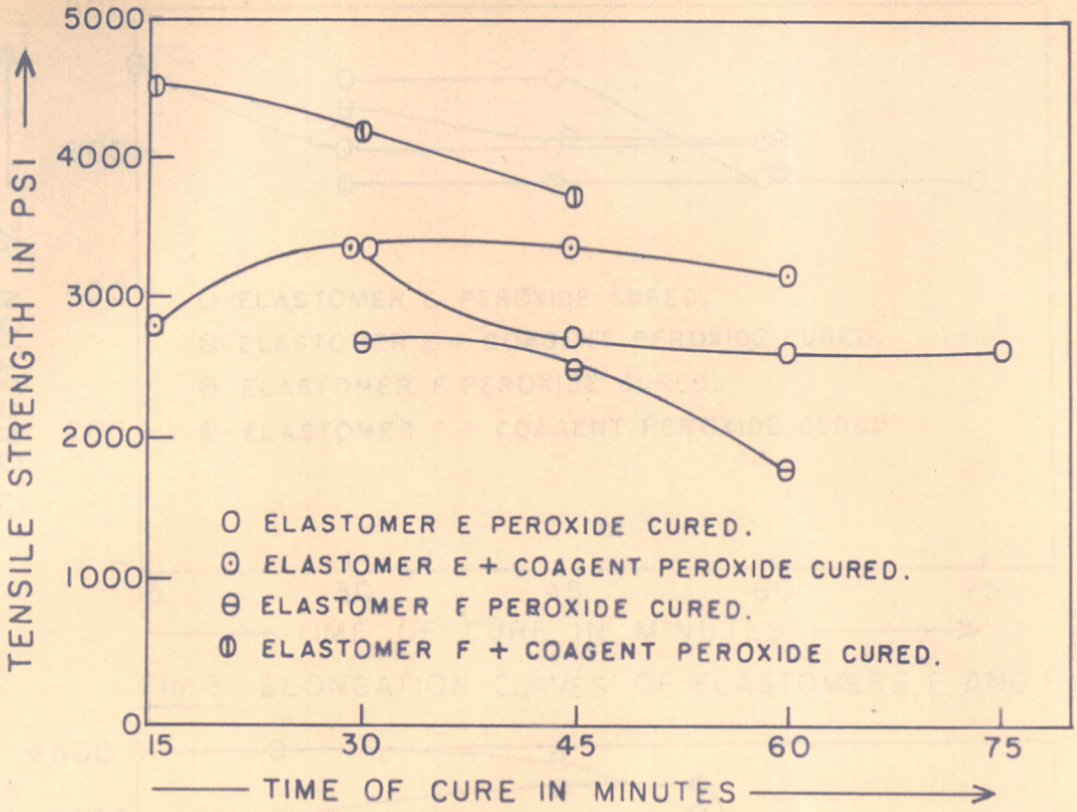


Fig. 1 TENSILE CURVES OF ELASTOMERS, E AND F.

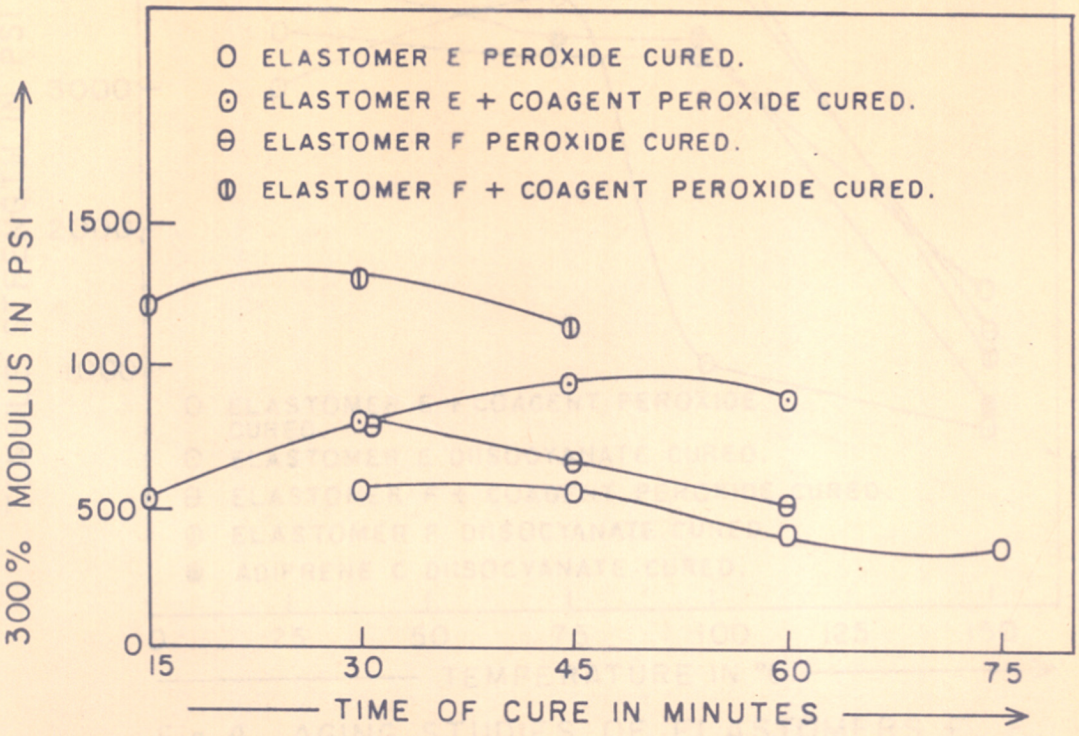


Fig. 2 MODULUS CURVES OF ELASTOMERS, E AND F.

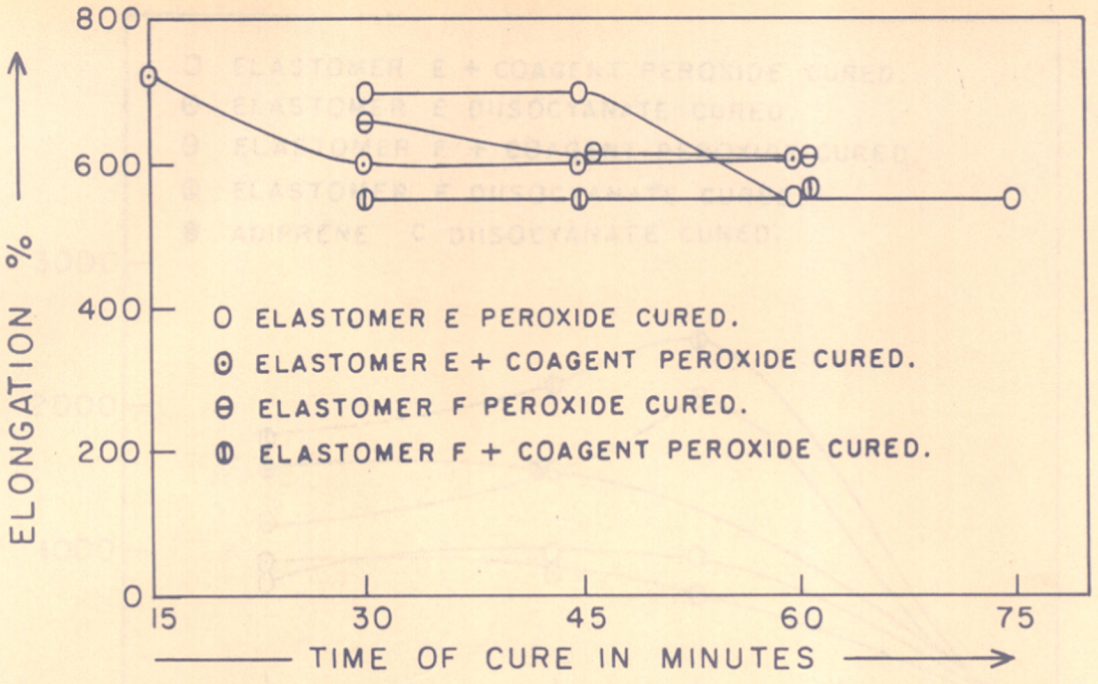


Fig. 3 ELONGATION CURVES OF ELASTOMERS, E AND F.

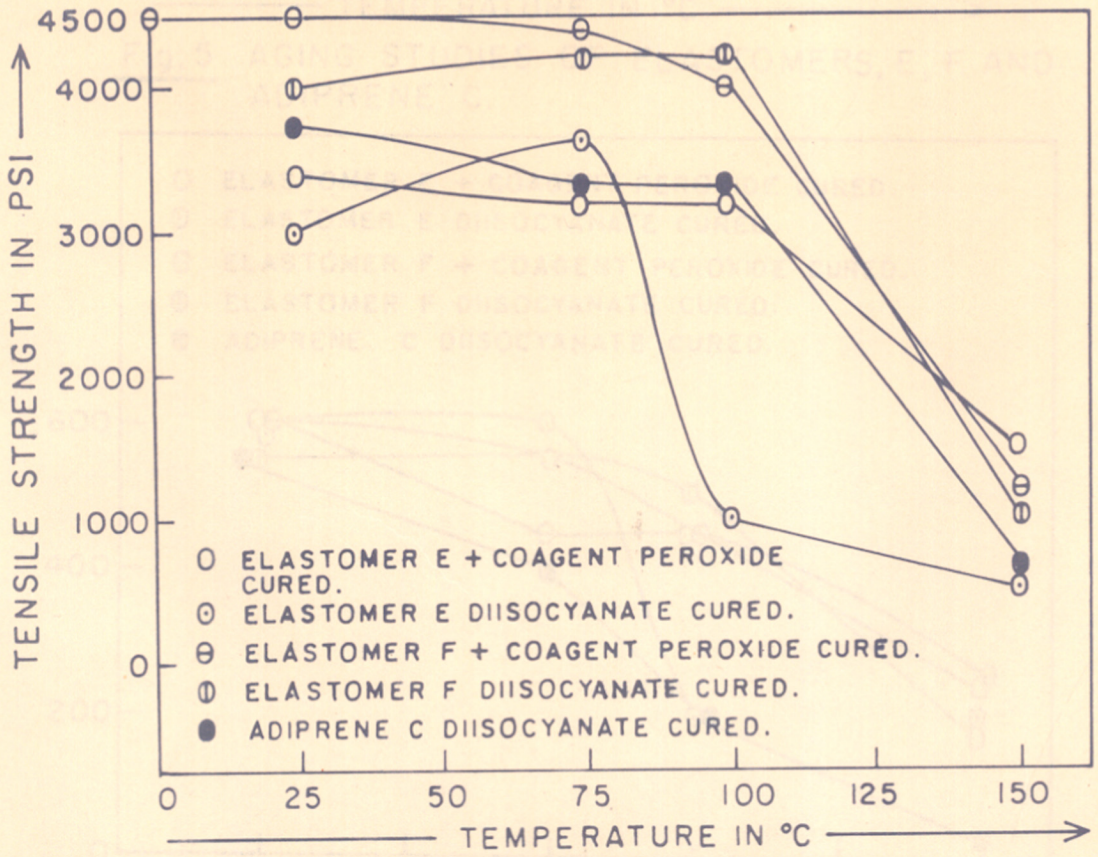


Fig. 4 AGING STUDIES OF ELASTOMERS, E, F AND ADIPRENE C.

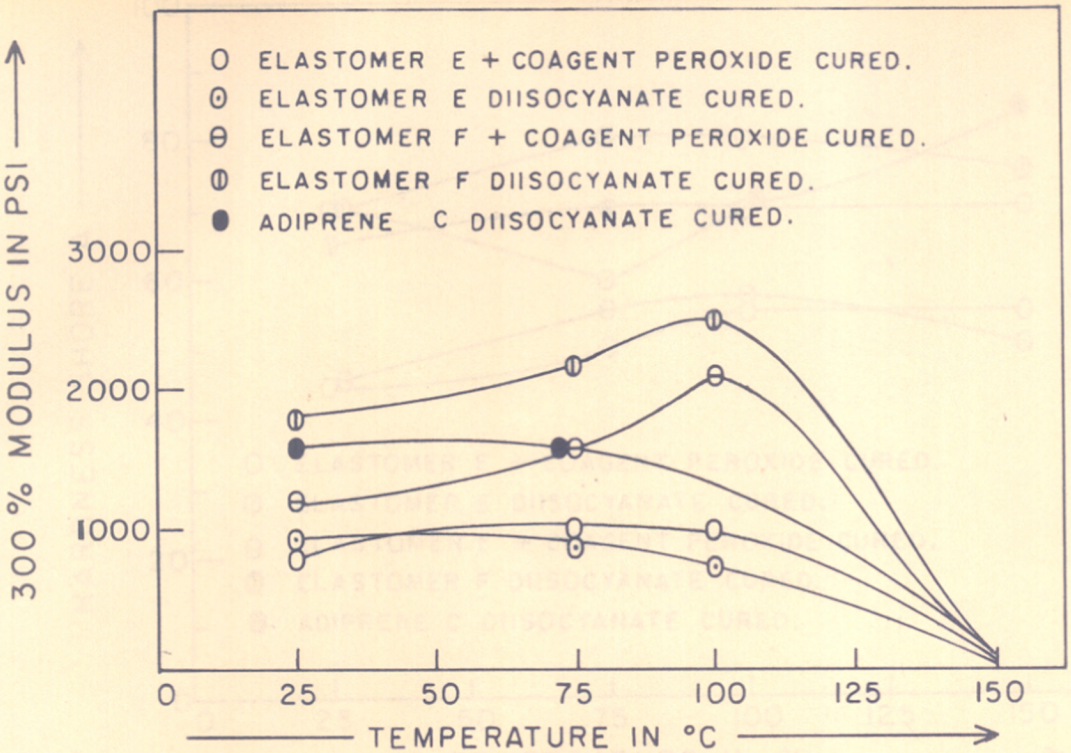


Fig. 5 AGING STUDIES OF ELASTOMERS, E, F AND ADIPRENE C.

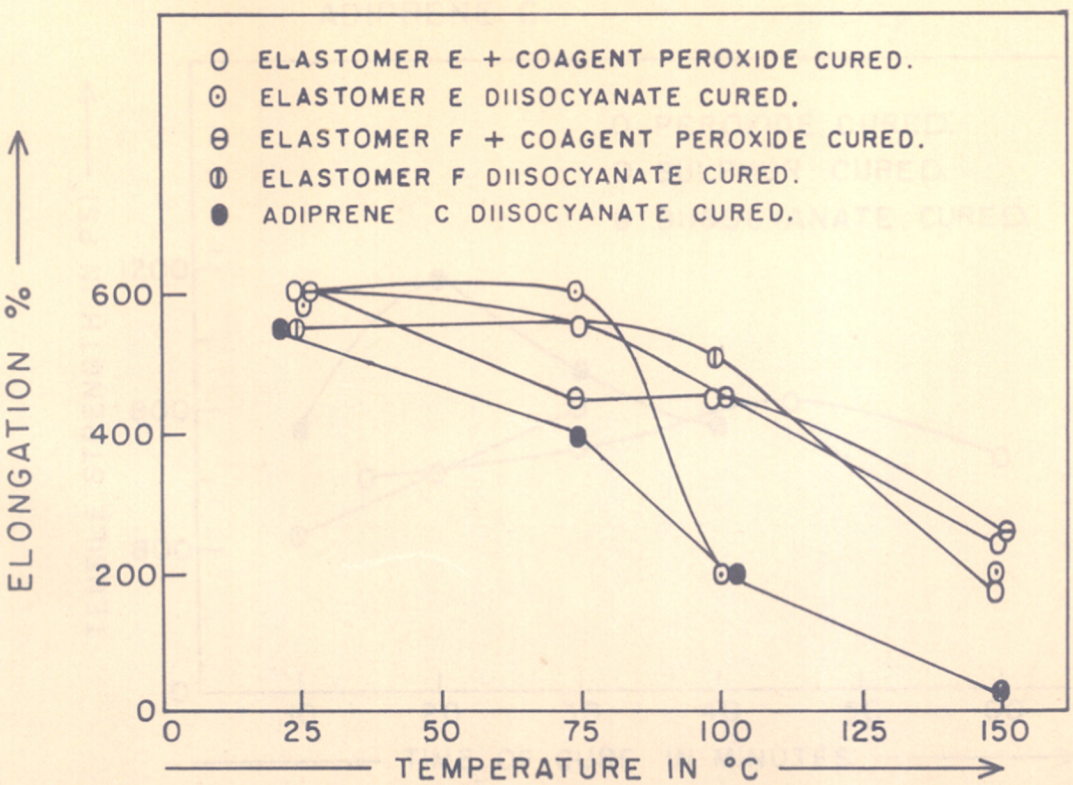


Fig. 6 AGING STUDIES OF ELASTOMERS, E, F AND ADIPRENE C.

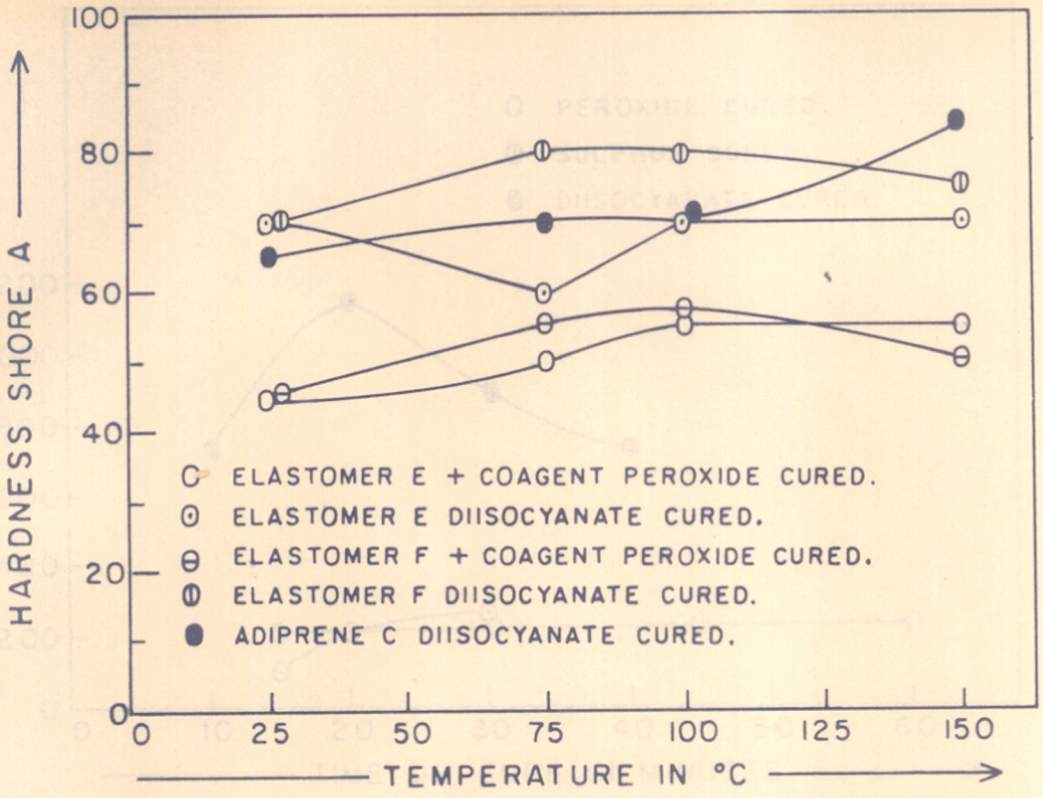


Fig. 7 AGING STUDIES OF ELASTOMERS, E, F AND ADIPRENE C.

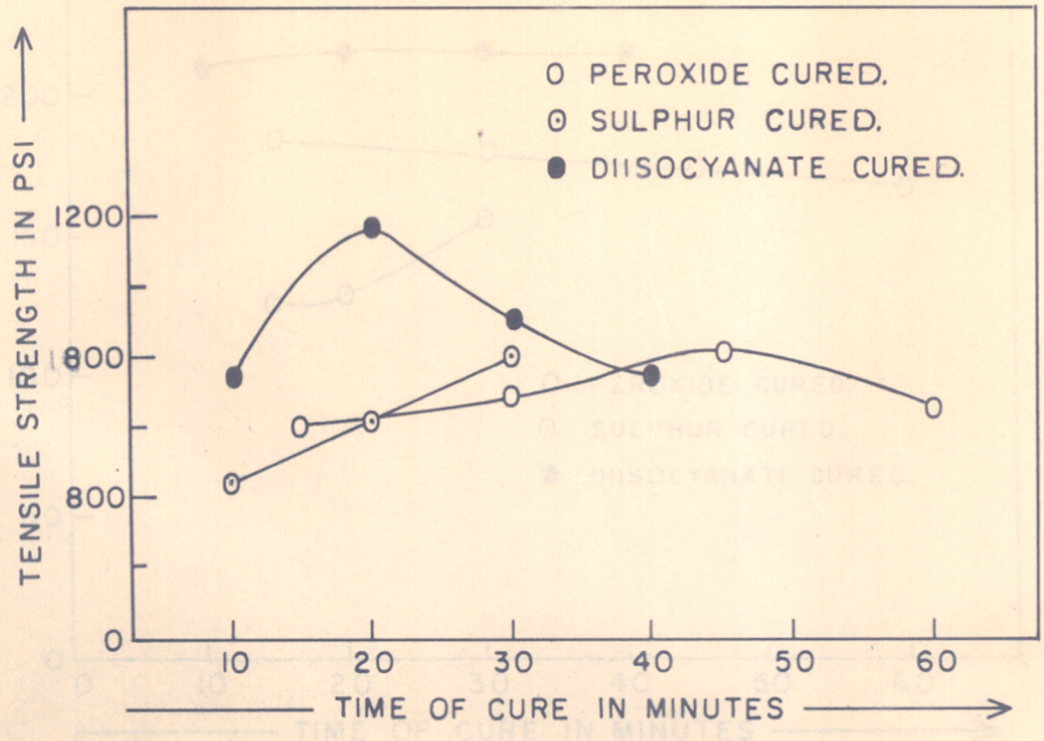


Fig. 8 TENSILE CURVE OF ELASTOMER N.

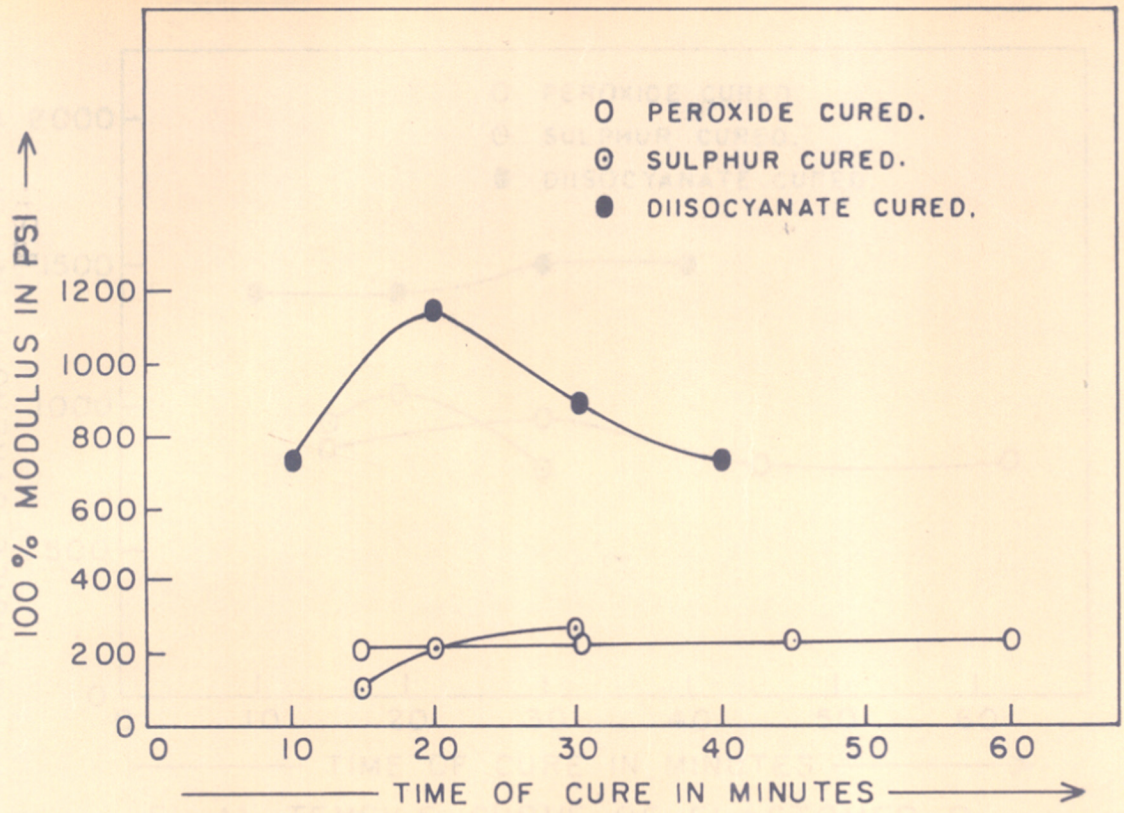


Fig. 9 MODULUS CURVE OF ELASTOMER N.

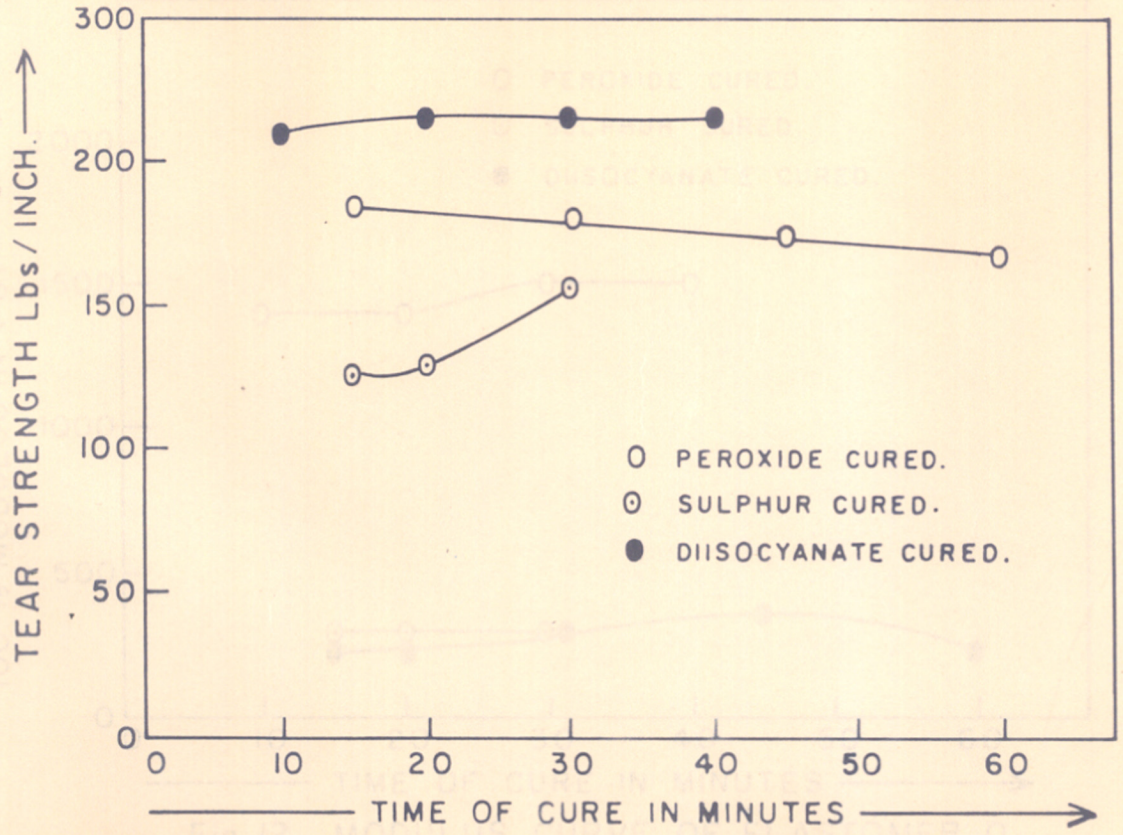


Fig. 10 TEAR CURVE OF ELASTOMER N.

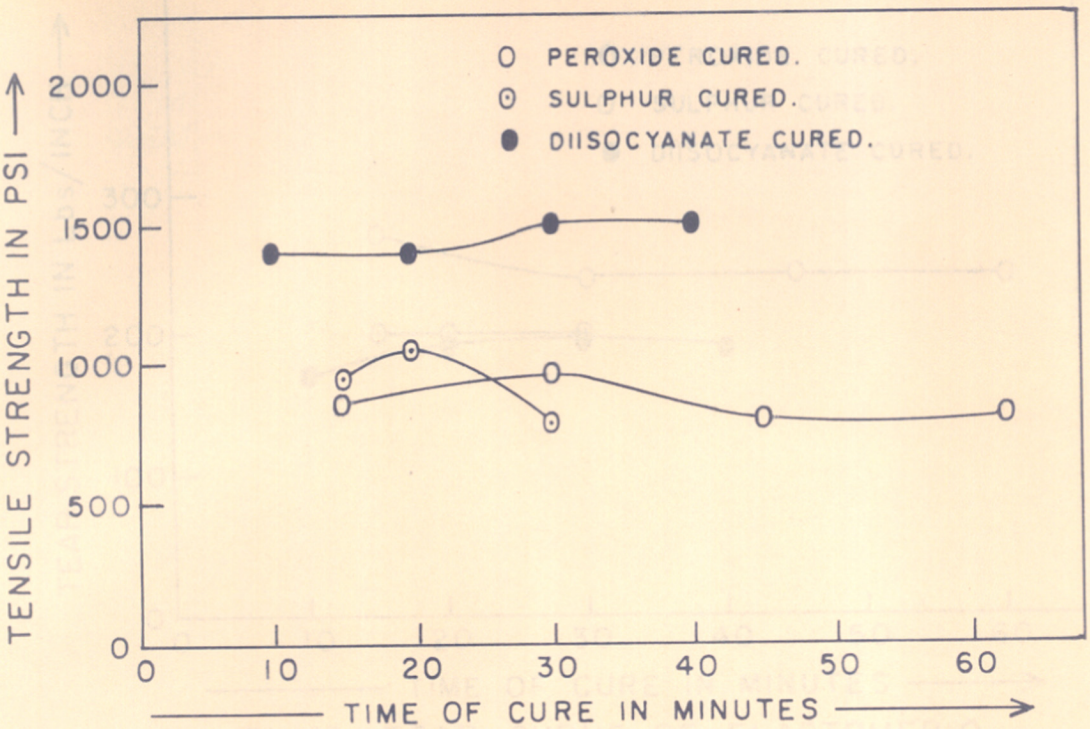


Fig. 11 TENSILE CURVE OF ELASTOMER O

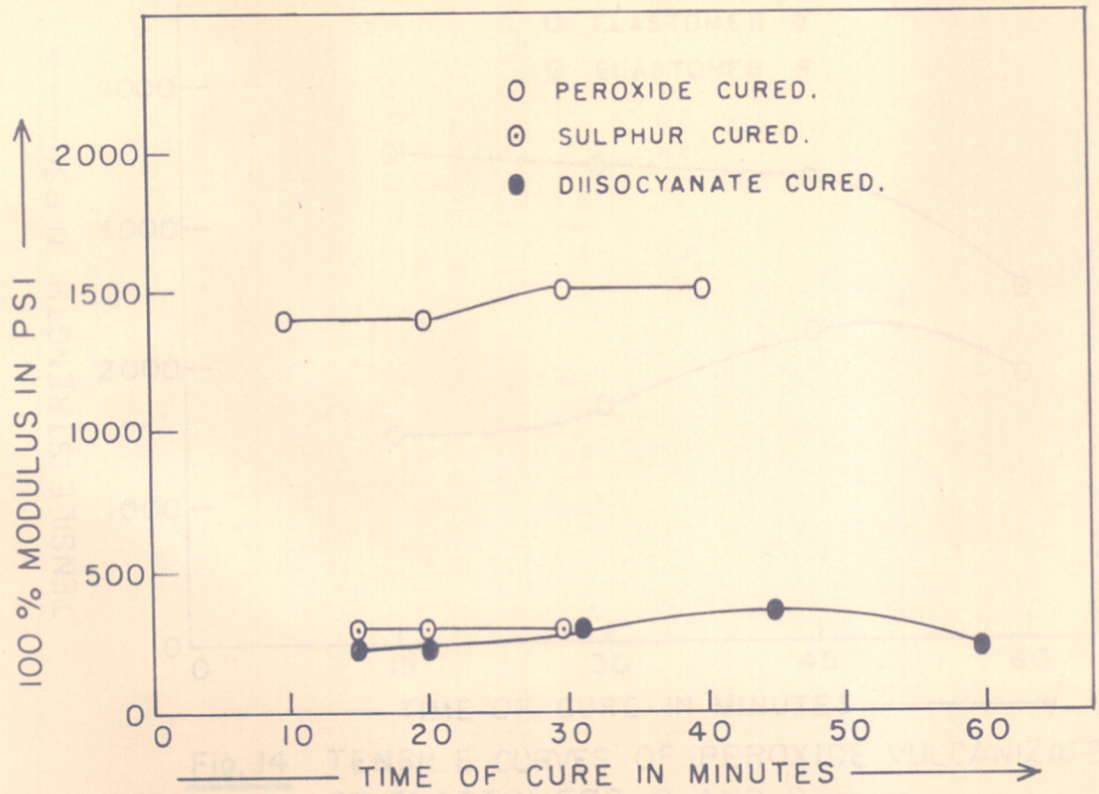


Fig. 12 MODULUS CURVE OF ELASTOMER O

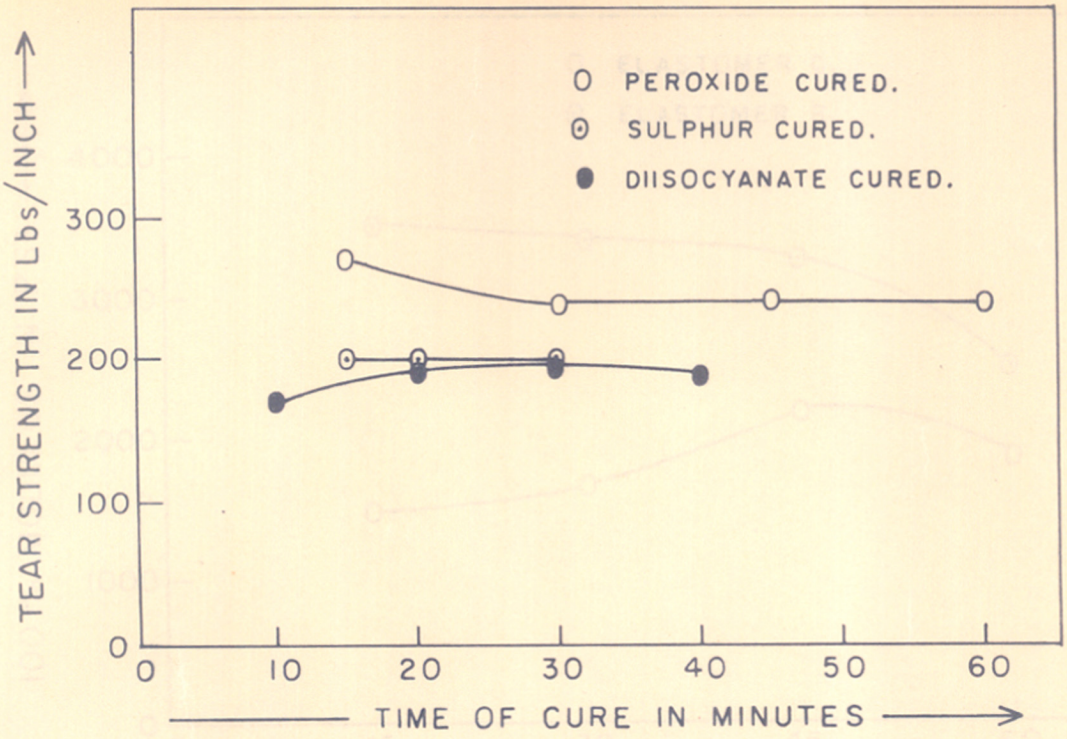


Fig. 13 TEAR CURVE OF ELASTOMER O.

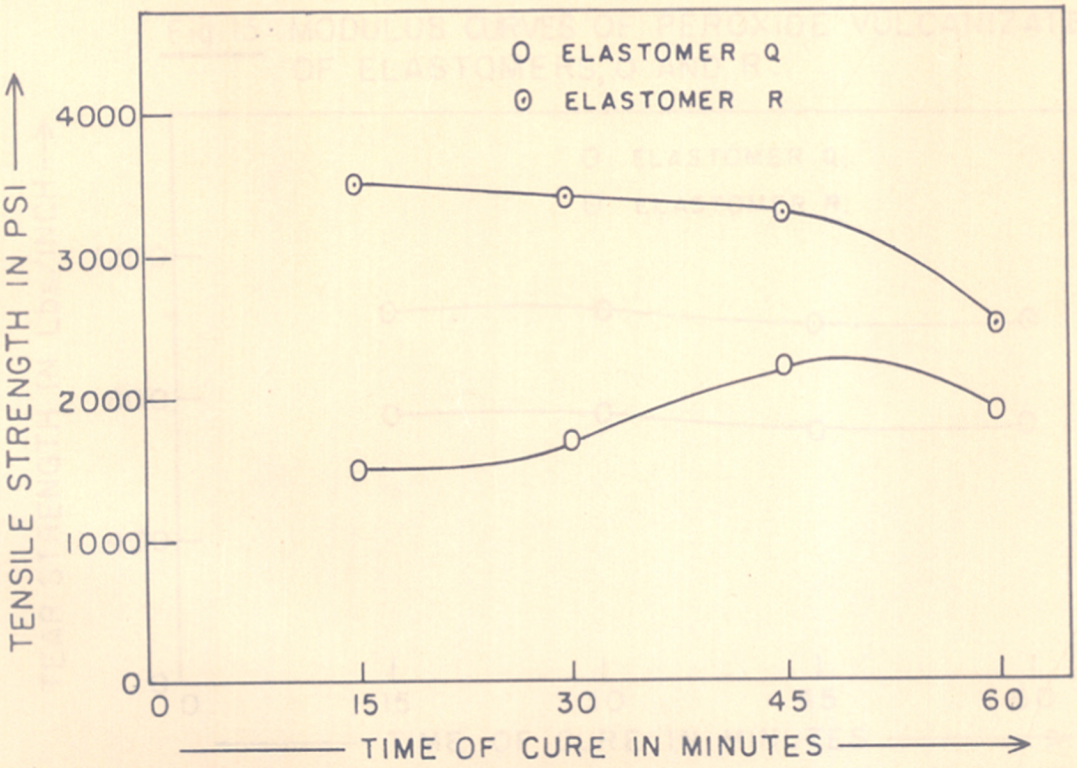


Fig. 14 TENSILE CURVES OF PEROXIDE VULCANIZATES OF ELASTOMERS, Q AND R.

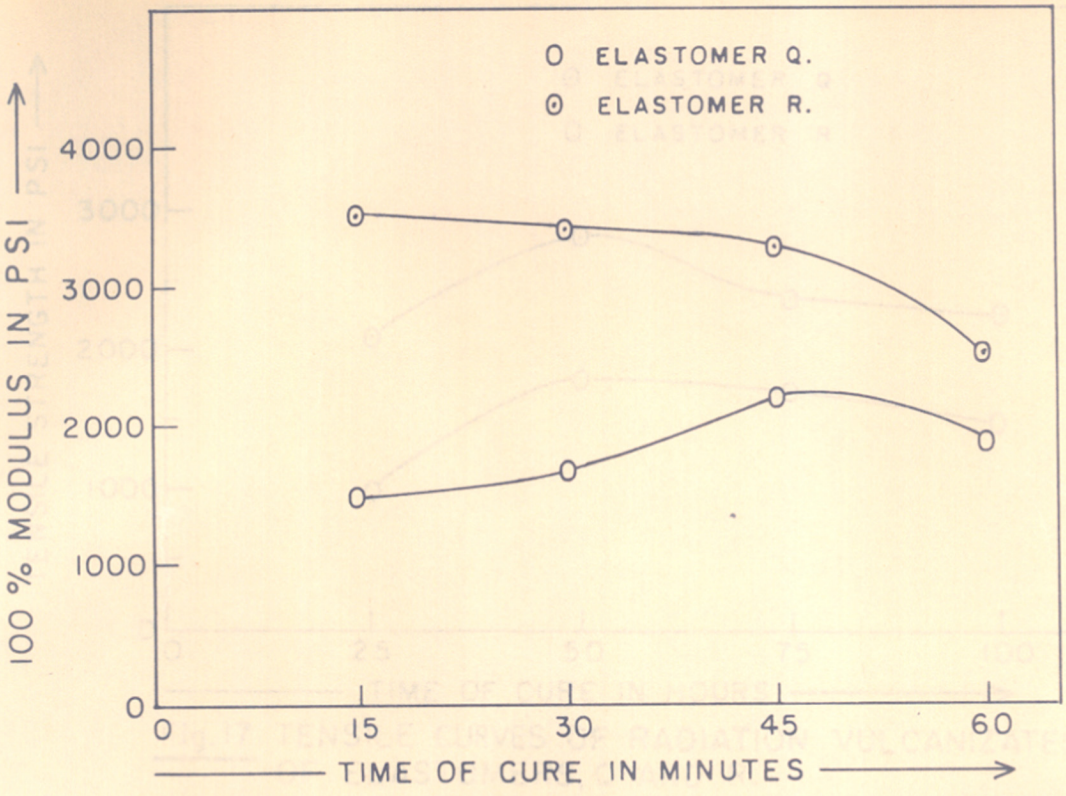


Fig.15 MODULUS CURVES OF PEROXIDE VULCANIZATES OF ELASTOMERS, Q AND R.

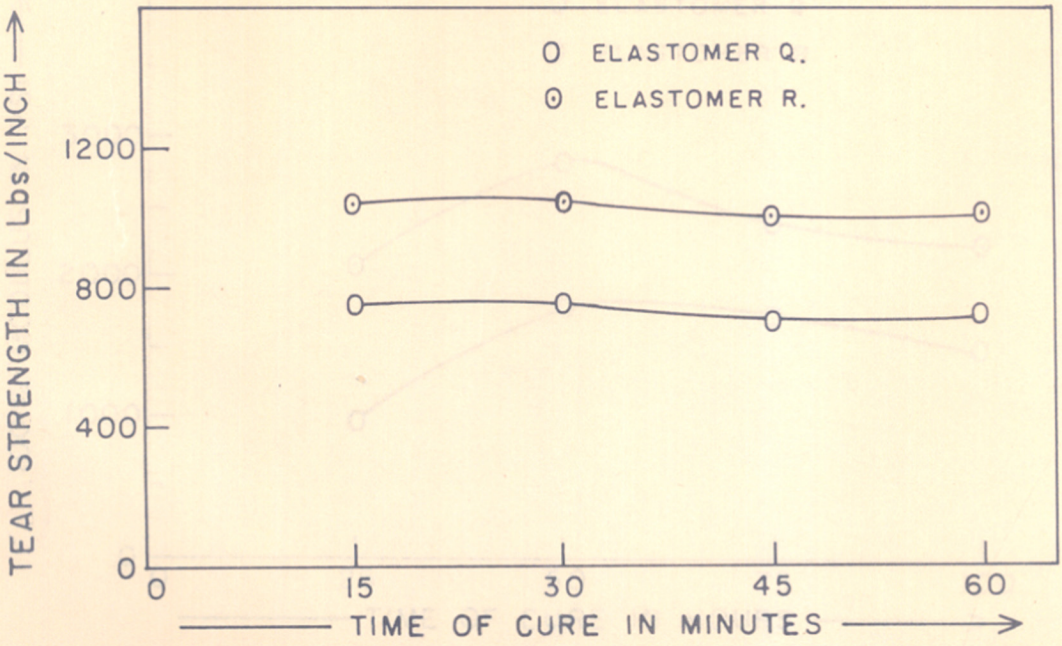


Fig.16 TEAR CURVES OF PEROXIDE VULCANIZATES OF ELASTOMERS, Q AND R.

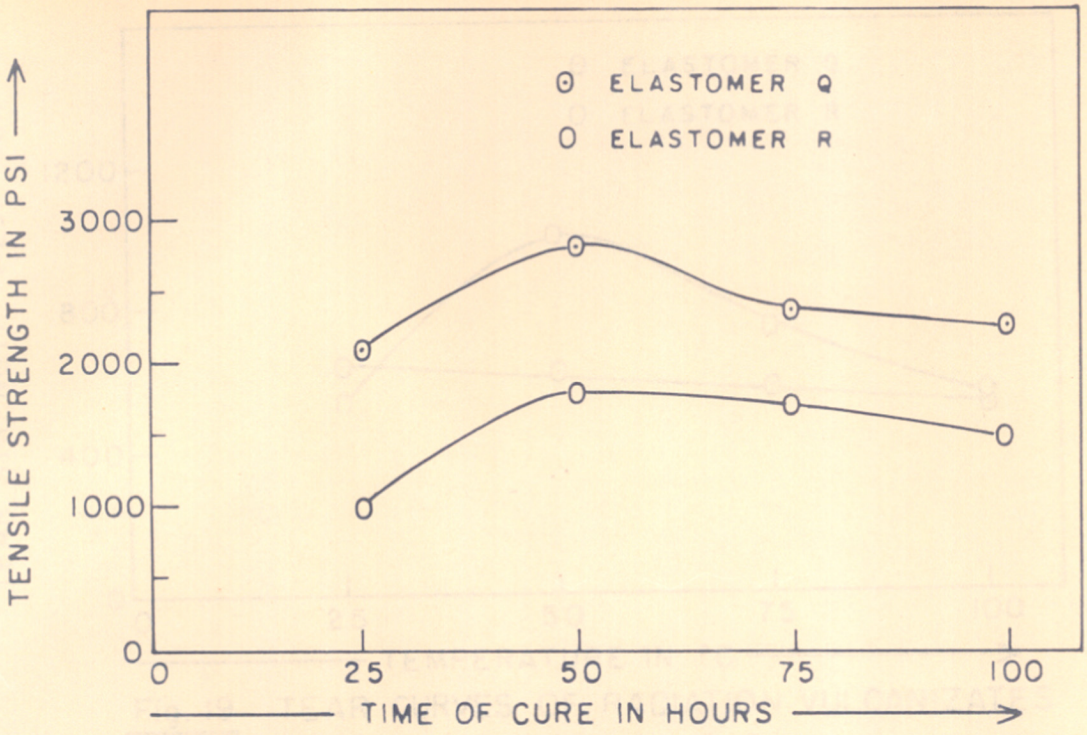


Fig. 17 TENSILE CURVES OF RADIATION VULCANIZATES OF ELASTOMERS, Q AND R.

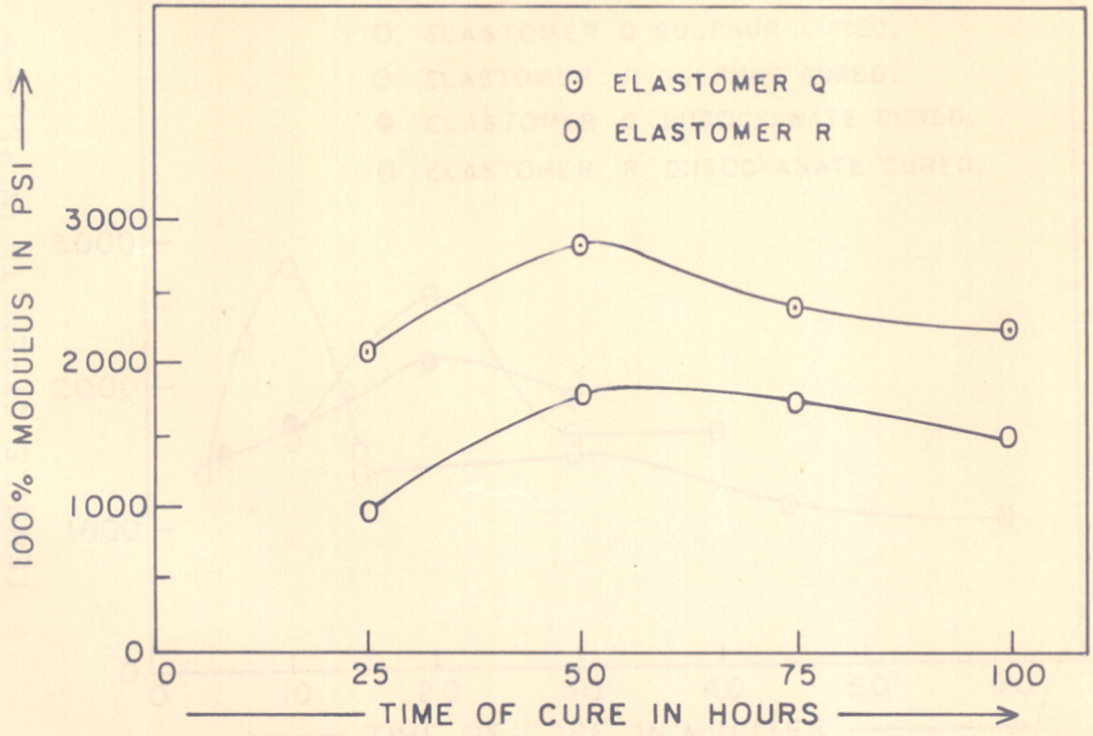


Fig. 18 MODULUS CURVES OF RADIATION VULCANIZATES OF ELASTOMERS, Q AND R.

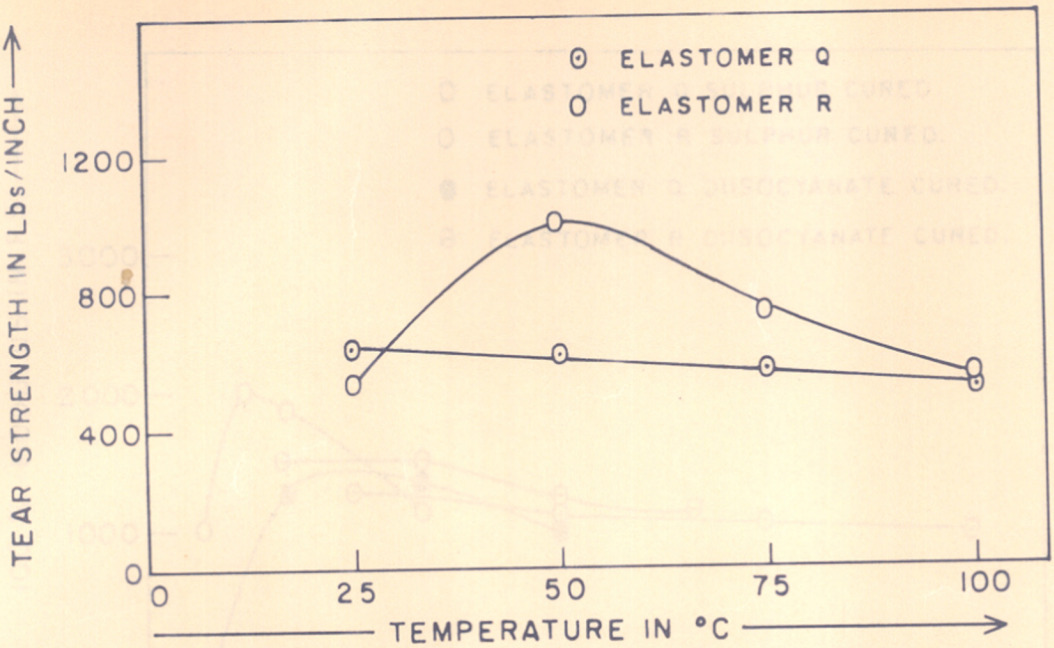


Fig. 19 TEAR CURVES OF RADIATION VULCANIZATES OF ELASTOMERS, Q AND R.

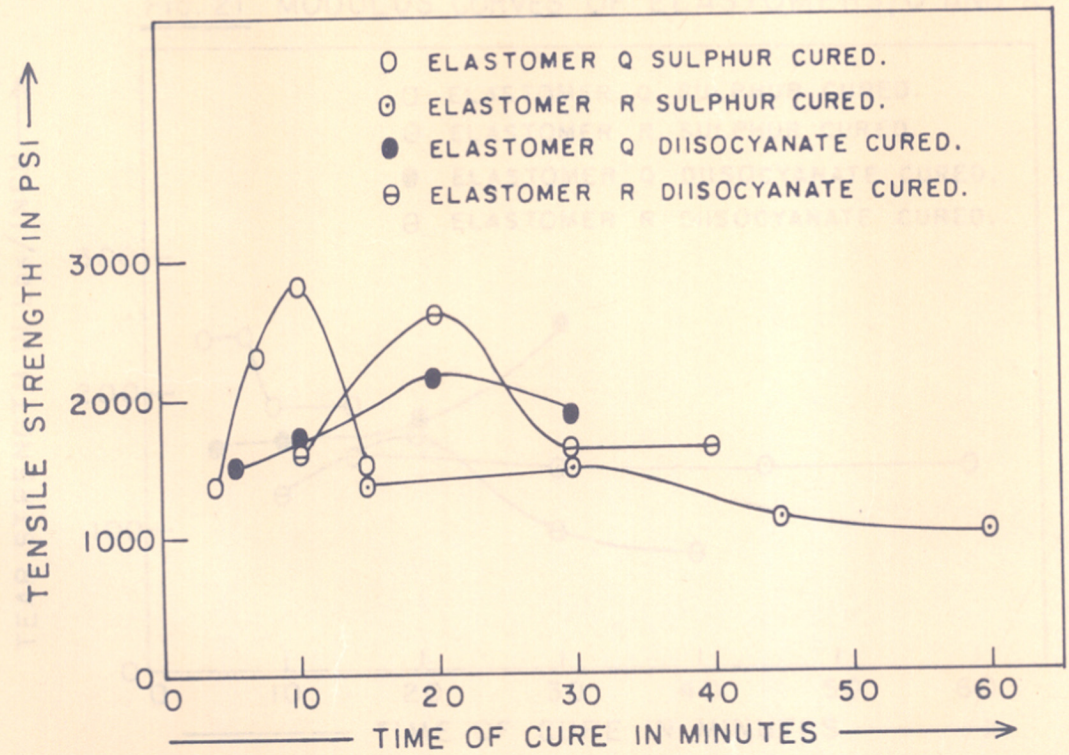


Fig.20 TENSILE CURVES OF ELASTOMERS, Q AND R.

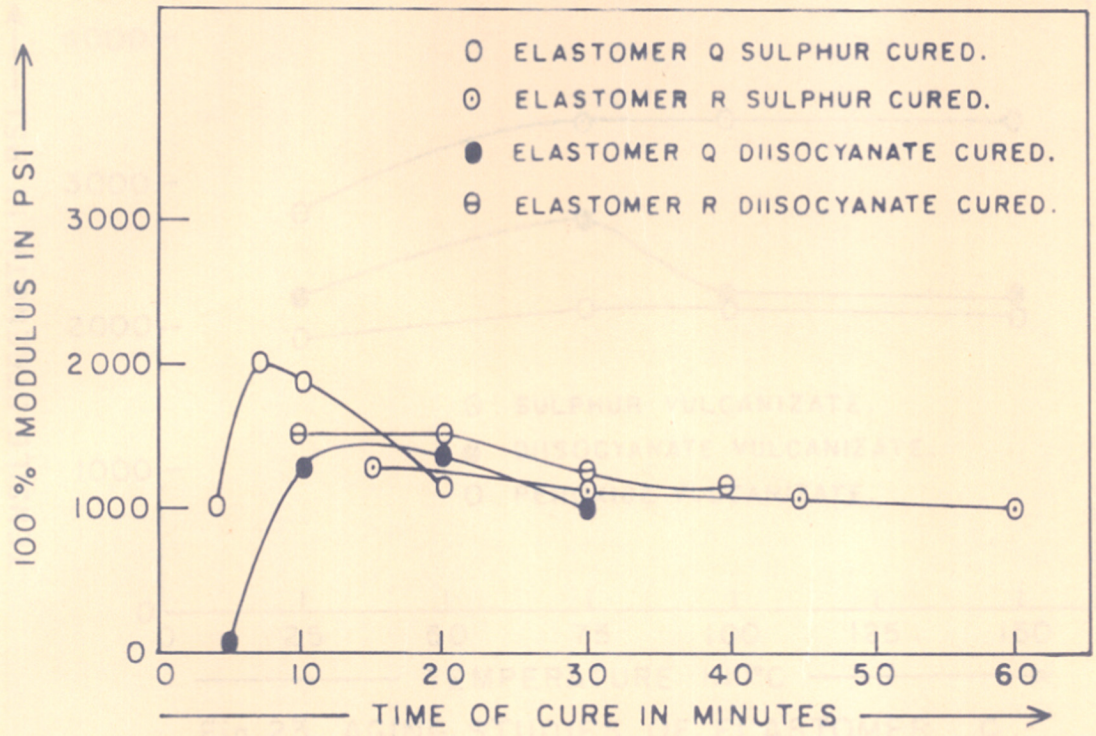


Fig. 21 MODULUS CURVES OF ELASTOMERS; Q AND R.

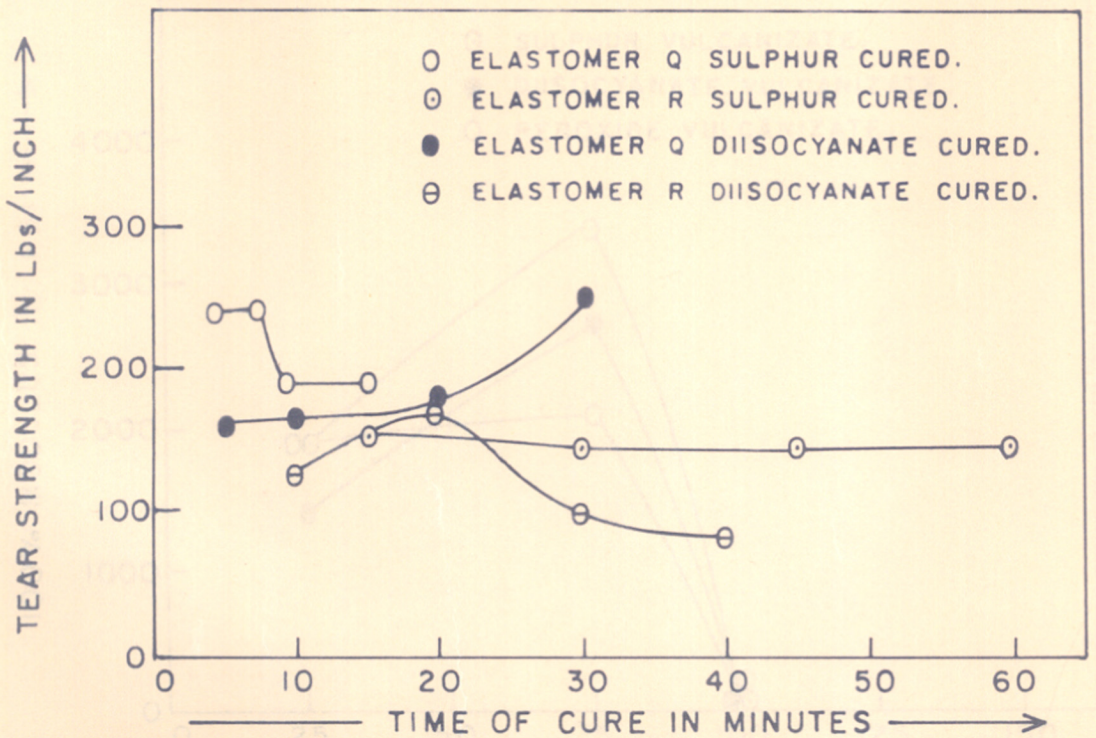


Fig. 22 TEAR CURVES OF ELASTOMERS, Q AND R.

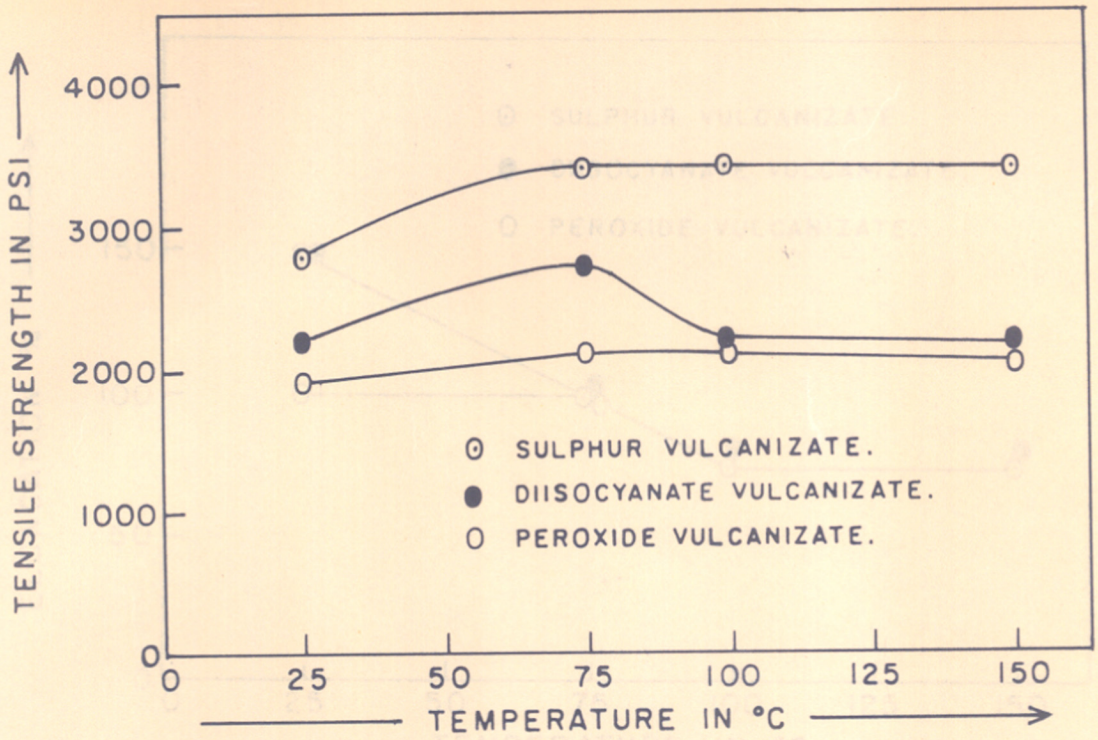


Fig.23 AGING STUDIES OF ELASTOMER Q.

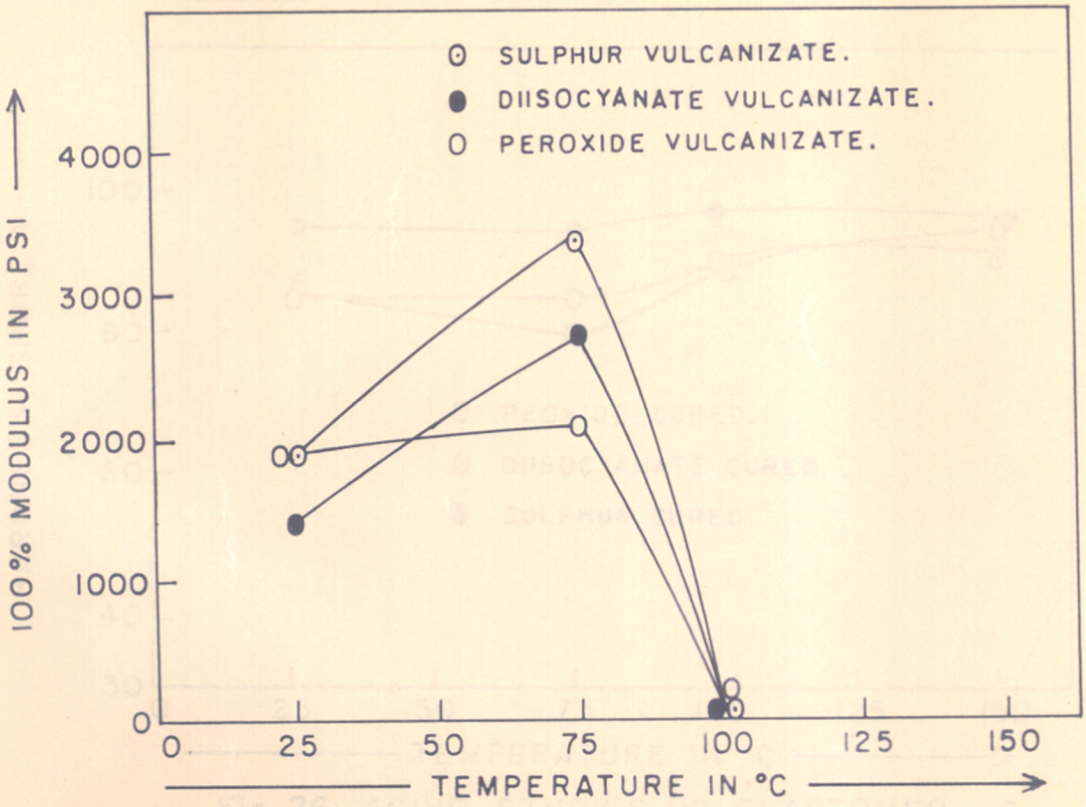


Fig.24 AGING STUDIES OF ELASTOMER Q.

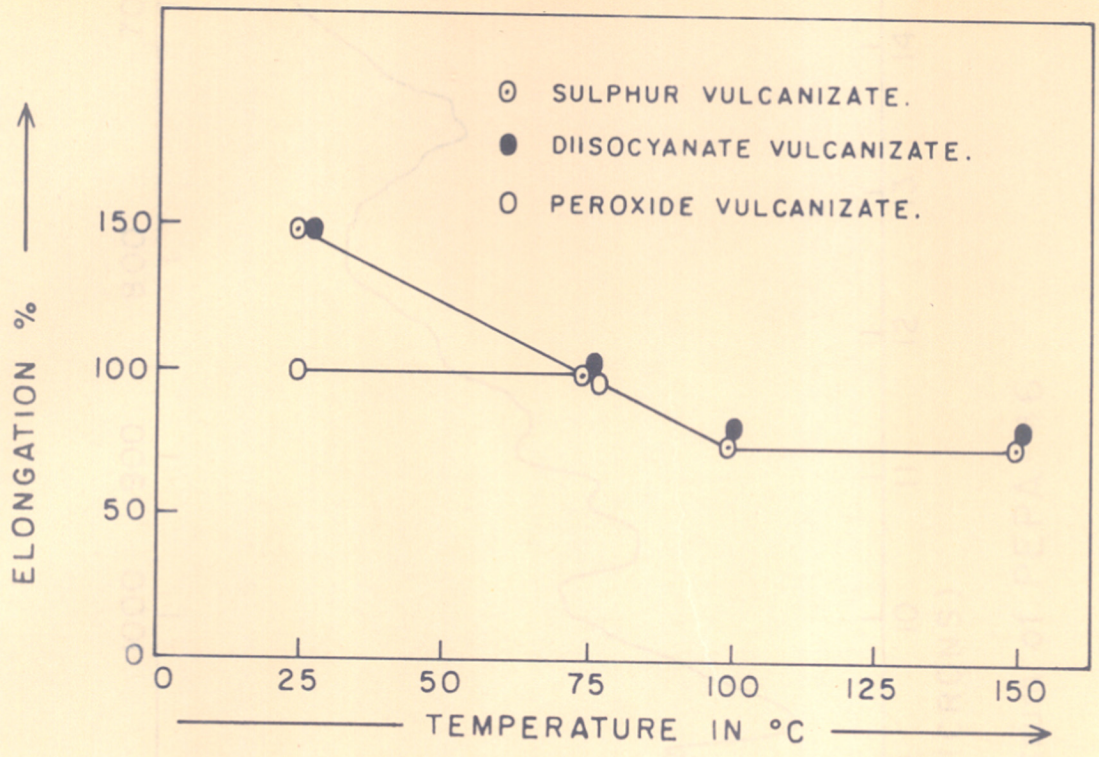


Fig. 25 AGING STUDIES OF ELASTOMER Q.

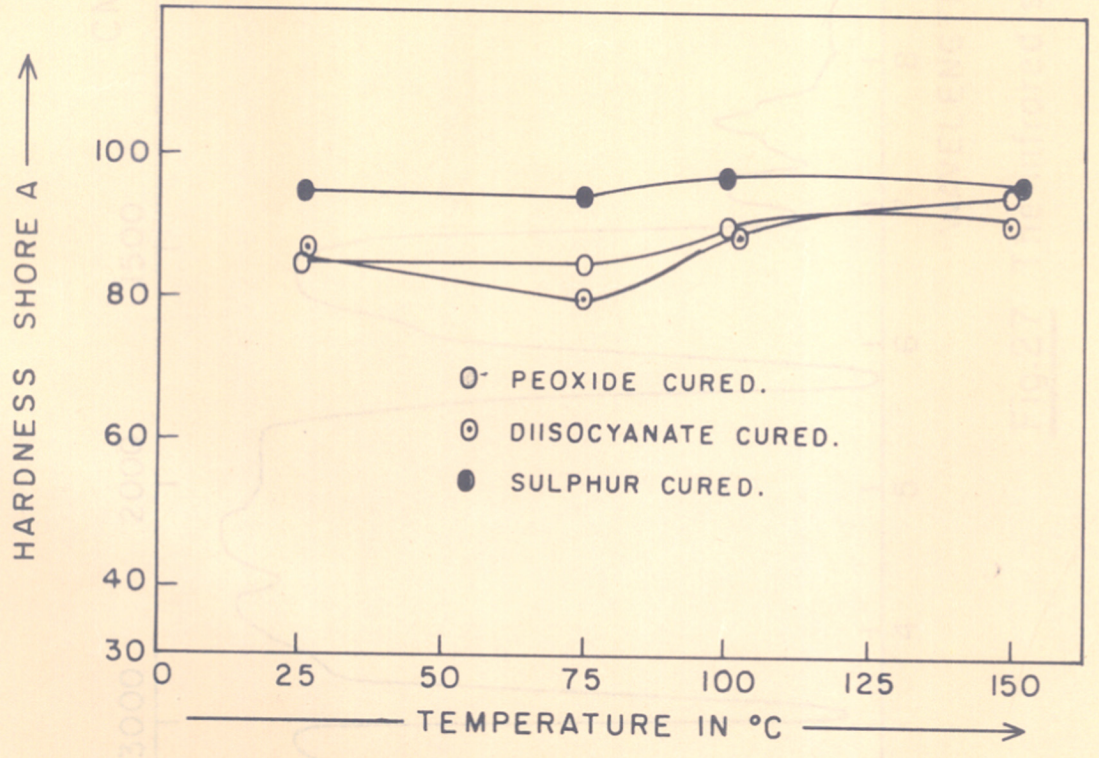


Fig. 26 AGING STUDIES OF ELASTOMER Q.

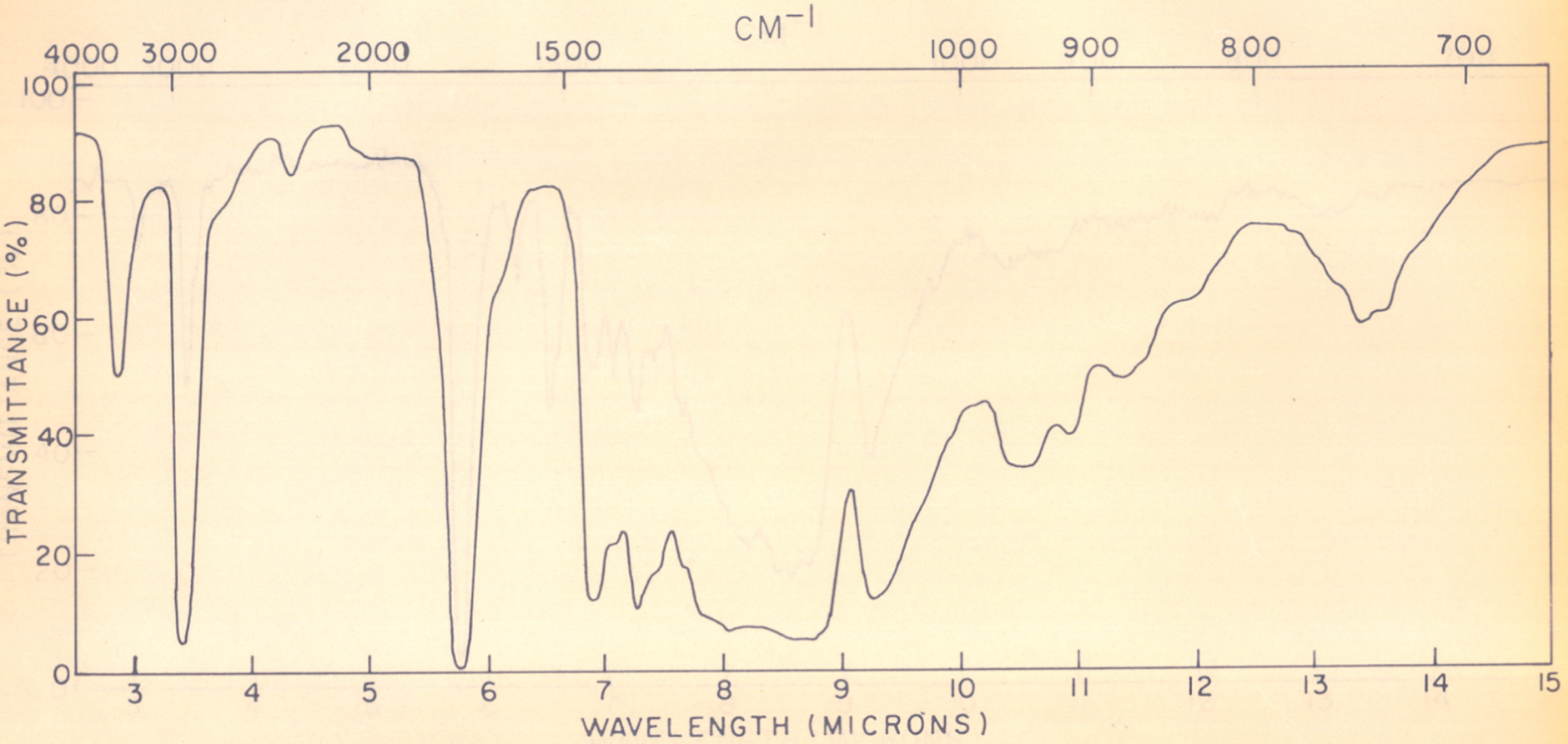


Fig.27 The infrared spectrum of PEPA-46

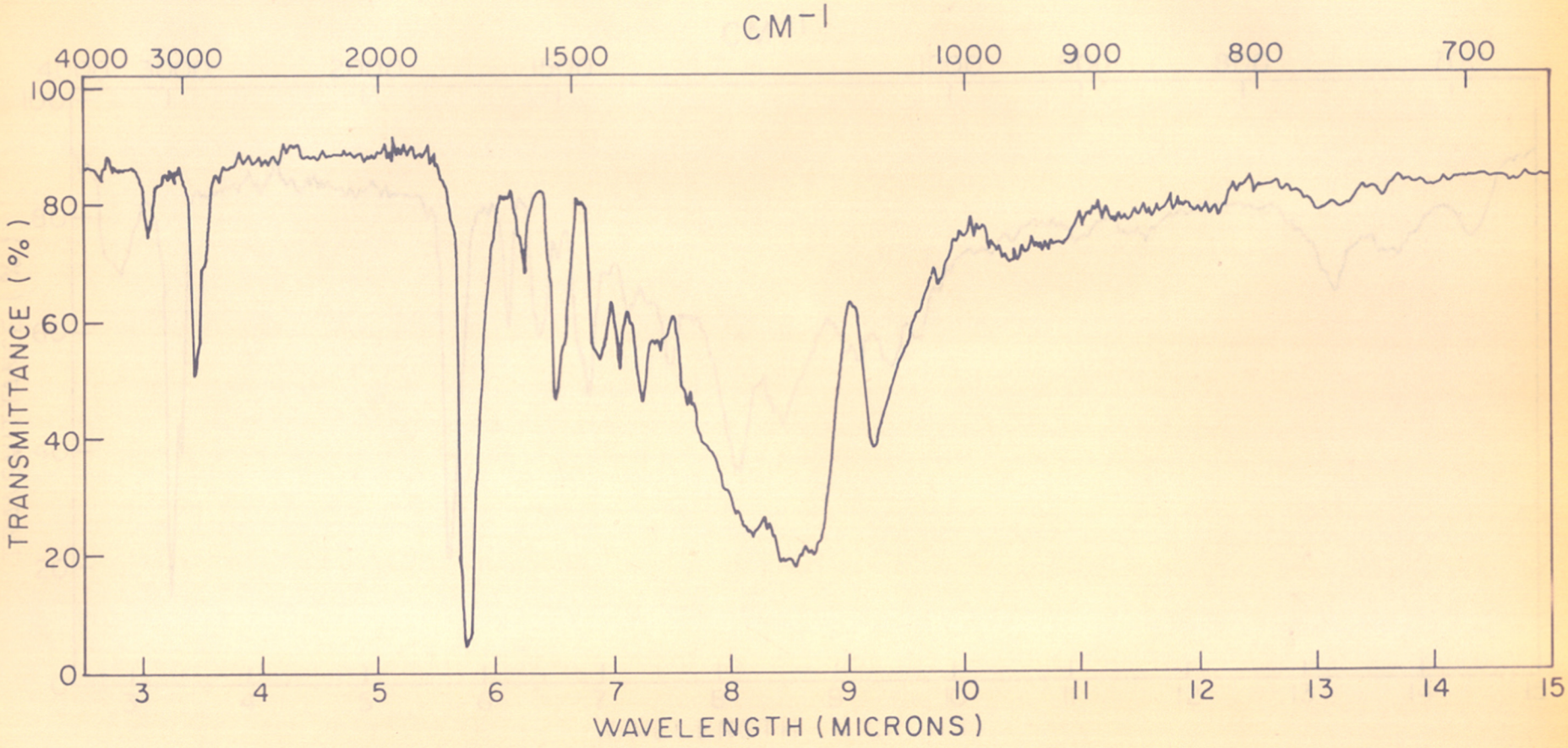


Fig.28 The infrared spectrum of elastomer F.

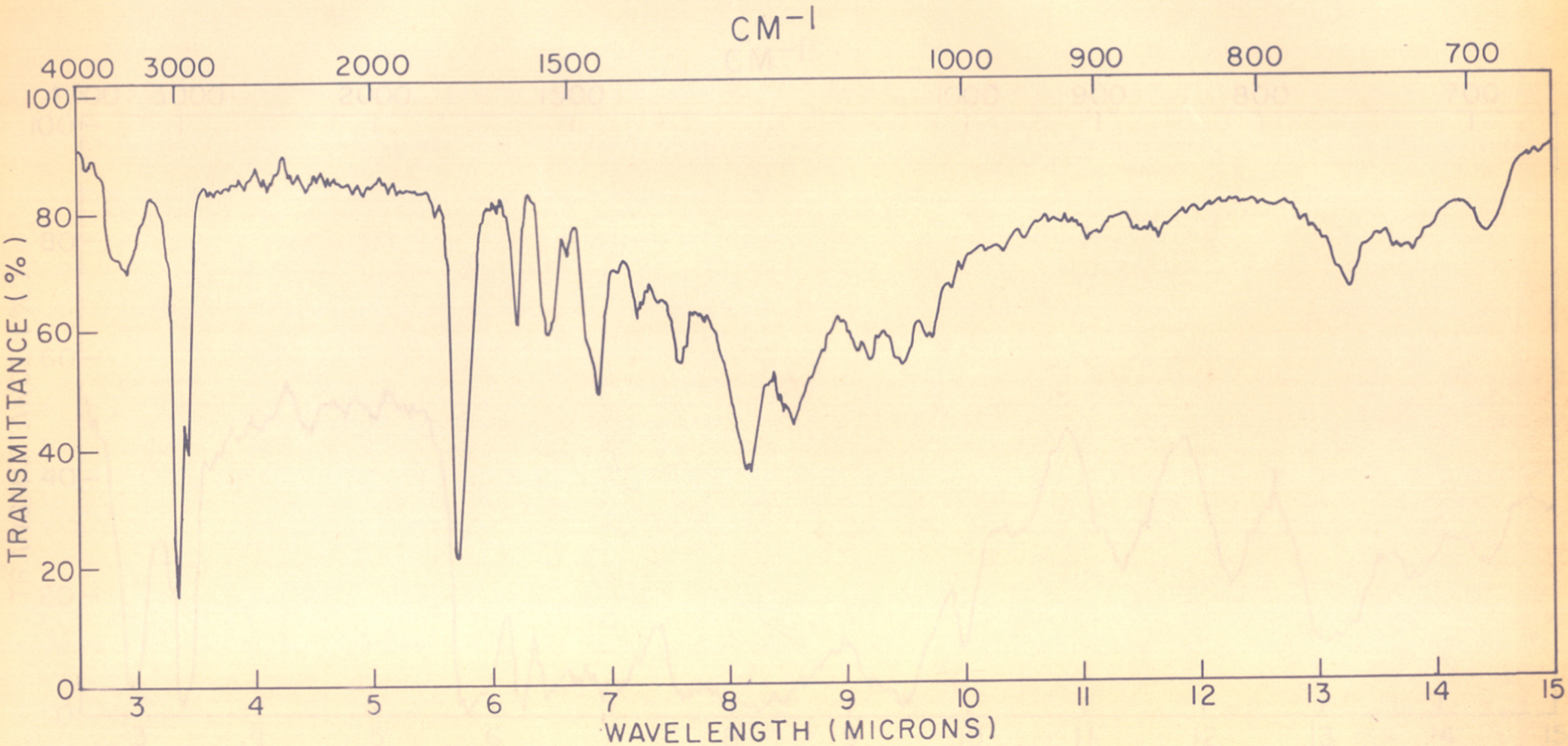


Fig.29 The infrared spectrum of DFCO

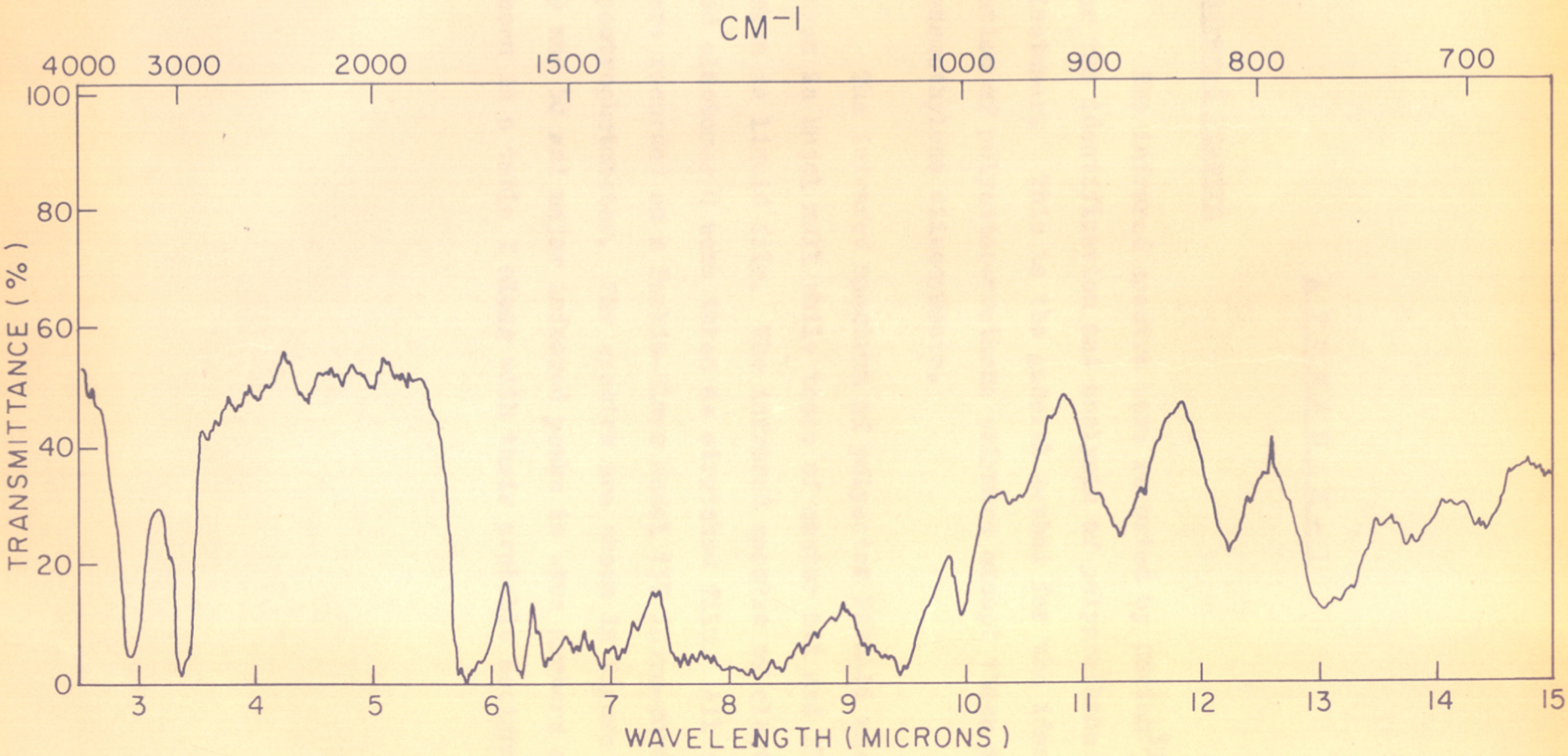


Fig.30 The infrared spectrum of elastomer Q.

A P P E N D I X - I

Infrared Spectra

The infrared spectra were reported by Corish[39] for the identification and analysis of polyurethane elastomer. This is the general method for the identification of polyester-urethane polymers except those from hexamethylene diisocyanate.

The infrared spectrum of polyester PEPA-46 was taken in Nujol mull while those of castor oil and DFCO were taken in liquid film. The infrared spectra of elastomer F and elastomer Q were taken as stretched film. All spectra were recorded on a Perkin-Elmer Model 137 infra-cord spectrophotometer. The spectra are shown in figure 27, 28, 29 and 30 and major infrared peaks in wave numbers are shown in a table I along with their probable assignments.

TABLE No. I

Major peaks observed in the infrared spectra of PEPA-46, elastomer F, DFCO and elastomer Q

Sample	Wave number cm^{-1}	Probable assignment
PEPA-46	3450 m	ν OH
	1739 vs	ν C = O ester
	1449 vs	Nujol
	1176 vs. b	ν C - O (ester)
	1075 vs	δ OH Primary OH
Elastomer F	3280 w	ν NH
	2899 m	νCH_2, CH_3
	1739 vs	ν C - O ester
	1600 w	Aromatic
	1538 m	Amide (secondary)
	1515 m	Aromatic
	1471 m	δ CH_2, δ CH_3
	1418 m	δ CH_2 adjacent to C=O
	1379 m	δ CH_3
	1220 s	ν C - O (ester)
DFCO	3450 w	ν OH
	2985 vs	νCH_2, CH_3
	1754 s	ν C = O (ester)
	1613 m	Aromatic

(Continued ...)

Table No.I (continued)

Sample	Wave number cm^{-1}		Probable assignment
DFCO (contd)	1538	m	Amide (secondary)
	1449	m	δ CH_2, CH_3
	1389		
	1220		ν C - O (ester)
	1163		
Elastomer Q	3390	s	ν NH
	2941	s	ν CH_2, CH_3
	1724	vs	ν C = O (ester)
	1600	s	Aromatic
	1550	s	Amide (secondary)
	1450	s	δ CH_2, CH_3
	1380	s	
	1176		ν C - O (ester)

A P P E N D I X - II

Suggested Compounds for specific products

Typewriter Roller

Elastomer Q	100.0
Perbunan N 3807	20.0
Stearic acid	0.2
HAF	30.0
Dicup 40C	5.0

Cure : 15 minutes at 140°C

Hardness, shore A	90
100 % Modulus, PSI	1200
Tensile strength, PSI	2000
Elongation, %	150
Tear strength, lbs/inch	250

Hammer head

Elastomer Q	100.0
Stearic acid	0.2
HAF	30.0
MBT	1.0
MBTS	4.0
S	1.0

Cure : 10 minutes at 121°C

Hardness, shore A	95
100 % Modulus, PSI	1900
Tensile strength, PSI	2800
Elongation, %	150
Tear strength, lbs/inch	265

Shoe heels and soles

Elastomer R	100.0
Stearic acid	0.2
HAF	30.0
Dicup 40C	5.0
Cure : 20 minutes at 140°C	
Hardness, shore A	90
100 % Modulus, PSI	3500
Tensile strength, PSI	3500
Elongation, %	100
Tear strength, lbs/inch	1040
Abrasion index, %	108

Shoe heels and soles

Elastomer F	100.0
Stearic acid	0.2
HAF	30.0
MDI	10.0
Cure : 15 minutes at 140°C	
Hardness, shore A	70
300 % Modulus, PSI	1600
Tensile strength, PSI	4000
Elongation, %	550
Tear strength, lbs/inch	4000
Abrasion index	1550

Trolly wheel

Elastomer F	100.0
High styrene GRS	30.0
HAF	30.0
Stearic acid	1.0
Dicup 40C	5.0
Cure : 20 minutes at 140°C	
Hardness, Shore A	85
300 % Modulus, PSI	1200
Tensile strength, PSI	3750
Elongation, %	400
Abrasion index, %	700

Hydraulic bucket, O-ring etc.

Elastomer F	100.0
Stearic acid	0.2
HAF	40.0
Dicup 40C	5.0
Triallyl cyanurate	1.0
Cure : 15 minutes at 140°C	
Hardness Shore A	45
300 % Modulus, PSI	1200
Tensile strength, PSI	4500
Elongation, %	600
Tear strength, lbs/inch	207.6
Abrasion index, %	550

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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

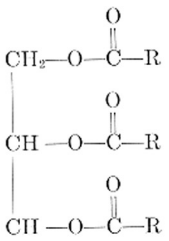
The polyurethane elastomers are prepared by reacting a long-chain diol having a molecular weight of about 2000 with an excess of diisocyanate to give an isocyanate-terminated prepolymer.[1] When a slight excess of low molecular weight polyol or a polyamine, termed a chain extender, is reacted with this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

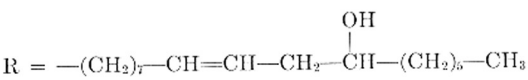
$$\underset{\text{(Diol)}}{HO{-}R{-}OH} + \underset{\text{(Diisocyanate)}}{X(OCN{-}R'{-}NCO)} \rightarrow \underset{\text{(Prepolymer)}}{OCN{-}R'{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}R'{-}NCO} \quad (1)$$

$$\text{Prepolymer} + HO{-}R{-}OH \rightarrow \underset{\text{(Gums)}}{\text{Polyurethane elastomeric materials}} \quad (2)$$

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 triricinoleate, and 23% in making the dihydroxyl glyceride–glyceryl diricinoleate–monooleate or monolinoleate. Thus from the point of view of functionality, castor oil[2] 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 triricinoleate.

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.,
Diethylene glycol	Darmstadt,
Dipropylene glycol	Germany
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	Durometer 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 Shore A hardness	Tensile strength, psi	Tensile elongation, %	100% Modulus, psi	Abrasion index, %
Unvulcanized gum	—	1.08	45	1000	250	370	—
Sulfur vulcanizate	10	1.24	95	2800	150	1900	50.9
Diisocyanate 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 Shore A hardness	Tensile strength, psi	Tensile elongation, %	100% Modulus, psi	Abrasion index, %
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

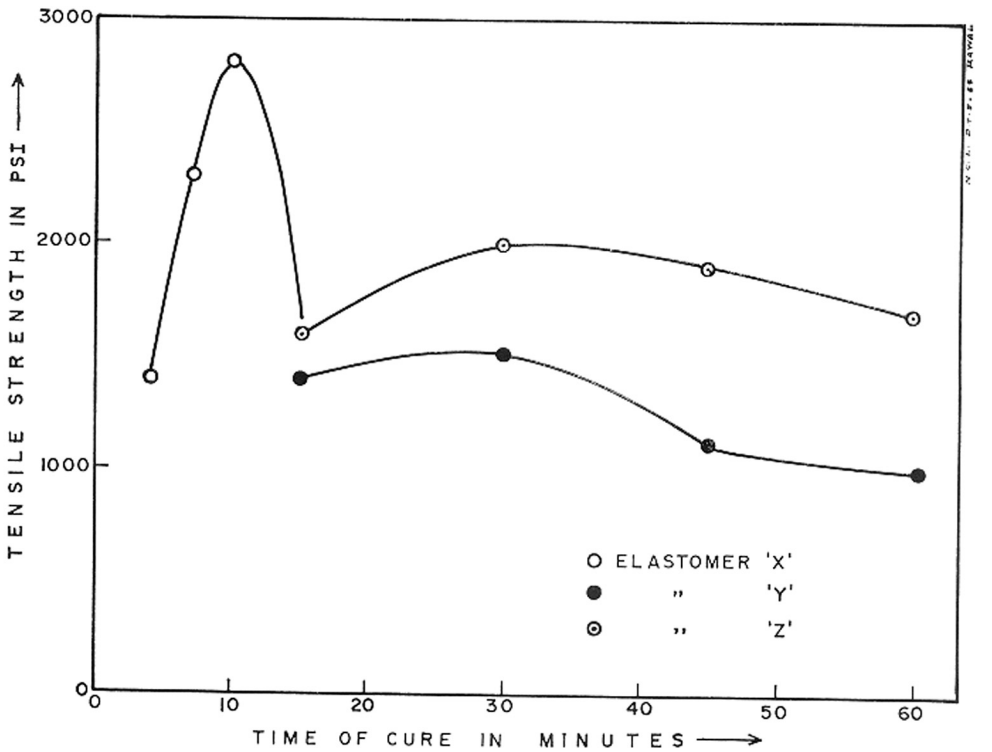


Fig. 1. Tensile curve of elastomers obtained by using sulfur: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

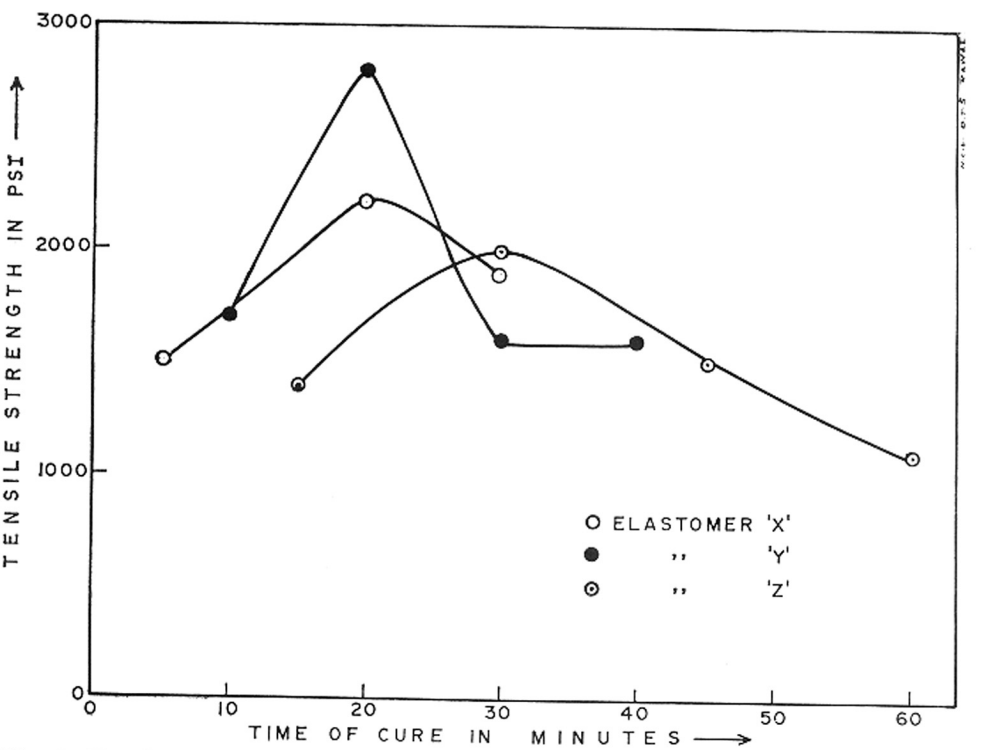


Fig. 2. Tensile curve of elastomer obtained by using diisocyanate: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

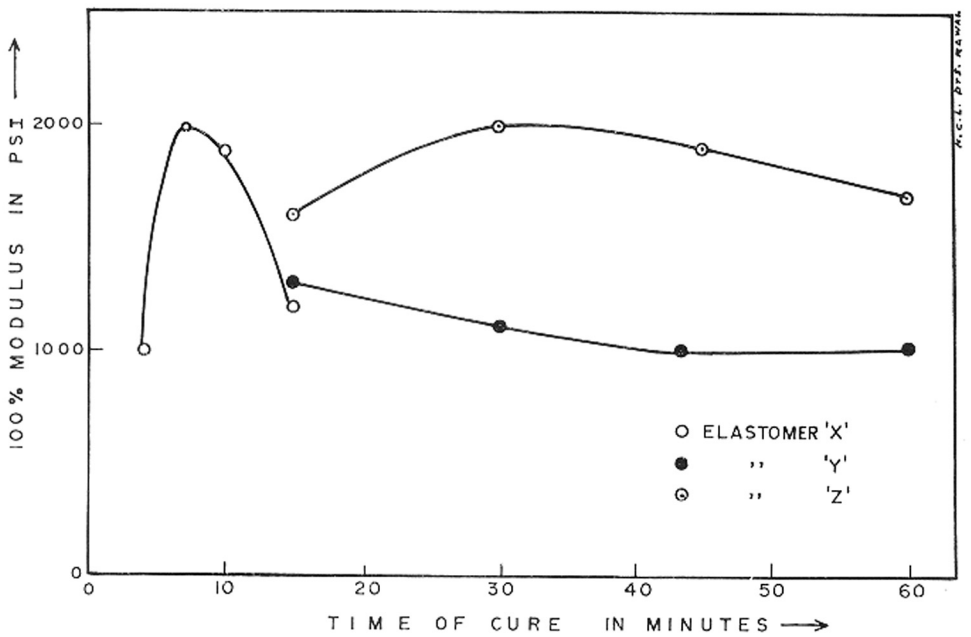


Fig. 3. Modulus curve of elastomers obtained by using sulfur: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

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-

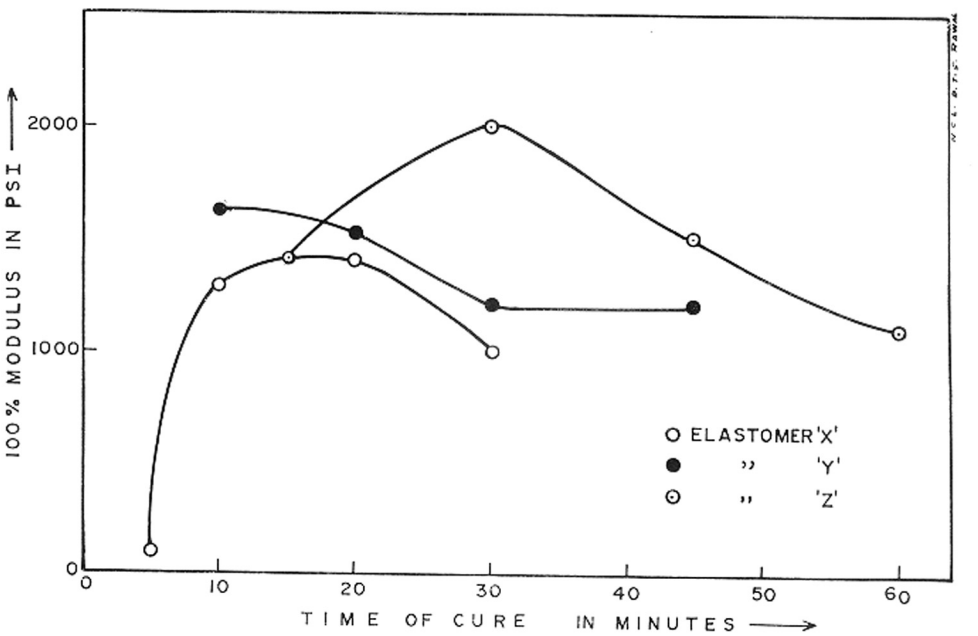


Fig. 4. Modulus curve of elastomers obtained by using diisocyanate: (O) elastomer X; (●) elastomer Y; (⊙) elastomer Z.

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 ingredient[5] 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.

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Résumé

A partir d'huile de ricin on a pu obtenir des élastomères prétant au calandrage en utilisant un diisocyante 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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