New Castor Oil-Based Urethane Elastomers[1]

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ABSTRACT

Urethane elastomers with a wide range of properties were prepared by reaction of toluene diisocyanate, diphenylmethane diisocyanate or an aliphatic diisocyanate with a series of castor oil derivatives. The castor derivatives included amides prepared by reaction of castor oil with mono- or dialkanolamines, amides of ricinoleic acid with long chain di- and triamines, butanediol diricinoleate and the commercial products–castor oil itself and the monoricinoleates of propylene glycol and pentaerythritol. Elastomers were also prepared from commercial polyether diols for comparison. Properties evaluated include hardness, resilience, tear strength, stress-strain properties, compression set and resistance to water and oil. Particularly high tensile and tear strengths were obtained from the amides. Softer products with good properties were obtained from propylene glycol monoricinoleate and from mixtures of the amides with castor oil or butanediol diricinoleate. Improved products were obtained by the use of diphenylmethane diisocyanate in place of toluene diisocyanate.

INTRODUCTION

Castor oil and castor oil derivatives have been used with considerable success as intermediates for the preparation of urethane elastomers (1-6), which are made by the reaction of polyhydroxy compounds with polyisocyanates. The castor-based elastomers have desirable properties such as good moisture resistance, and shock absorbing and electrical insulating properties. They may be prepared with a considerable range of properties of value in such applications as potting, encapsulating and casting compounds.

This paper describes an attempt to prepare castor-based urethane elastomers with a wider range of properties and thus to extend the use of castor oil derivatives in these elastomers.

EXPERIMENTAL PROCEDURES

Materials

The polyols used are listed in Table I. The preparation of 1,4-butanediol diricinoleate was described previously (7).

Alkanolamides (8) of ricinoleic acid: A mixture of 1.2 mol alkanolamine (Table I) and 0.01-0.02 mol sodium methoxide was heated under N_2 to 125 C. Castor oil (0.2 mol) was added over a period of 1 hr. Stirring at 125 C was continued for 1.5-3 hr, except with diisopropanolamine, which required 12 hr. Completeness of reaction was estimated from disappearance of ester absorbance at 1735 cm^{-1} and increase of amide absorbance at 1620-1650 cm^{-1}. The product was dissolved in ether, washed with water, 10% HCl, and water until neutral; it was then dried over Na_2SO_4, filtered, and evaporated to dryness. Yields were in the range of 87-93%. Equivalent weights, based on OH number and acid number (<2.0), are listed in Table I.

Polyamides of ricinoleic acid: A purified ricinoleic acid (OH no. 182, acid no. 189) was obtained from crude castor acids by extracting the nonhydroxy acids five times with petroleum ether from a 45% solution of castor acids in 85% methanol. Amides were prepared (9) on a 0.1-0.4 mol scale by heating to reflux a di- or triamine (Table I) with a 10% excess of ricinoleic acid in the presence of 15% of xylene. Heating was continued for ca. 3.5 hr, at which time no more water could be collected in a Dean-Starke tube. The product, in ether solution, was washed with 5% NaOH, water, 5% HCl, water and half-saturated NaCl until neutral; it was then dried over Na_2SO_4 and evaporated to dryness. Yields of di- and triamides were 86%.

Prepolymers: Unless indicated otherwise, the elastomers

TABLE I

Polyols Used for Preparation of Elastomers

Abbreviation	Polyol	Equivalent wt
---	Castor oil[a]	340
PG Ric	Propylene glycol monoricinoleate[b]	187
Pe Ric	Pentaerythritol monoricinoleate[c]	155
BD Ric$_2$	1,4-Butanediol diricinoleate	338
BD	1,4-Butanediol[d]	45
B-1000	Polytetramethylene ether glycol[e]	510
P-1000	Polypropylene glycol[f]	508
TMP	Trimethylolpropane[g]	45
Ricinoleic acid amides of:		
EA Ric	Ethanolamine[d]	176
DEA Ric	Diethanolamine[h]	138
IPA Ric	Isopropanolamine[h]	182
DIPA Ric	Diisopropanolamine[h]	142
D230 Ric$_2$	Polyoxypropylenediamine[i]	432
T403 Ric$_3$	Polyoxypropylenetriamine[j]	390

[a] AA-Standard, Baker Castor Oil Co.
[b] Polycin 51, Baker Castor Oil Co.
[c] Flexricin 17, Baker Castor Oil Co.
[d] Eastman Kodak Co.
[e] Polymeg 1020, Quaker Oats Co.
[f] Niax Polyol PPG 1025, Union Carbide Corp.
[g] Celanese Corp.
[h] Aldrich Chemical Co.
[i] Jeffamine D-230, Jefferson Chemical Co.
[j] Jeffamine T-403, Jefferson Chemical Co.

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TABLE II

Properties of Polyurethane Elastomers

Polyol[a]	Hardness shore A	Tensile, psi	Elongation, %	M_{100}, psi	Tear, lb/in.	Resilience, %	Compression set, %	Solvent uptake	
								H_2O, 1 day, 70 C, % wt increase	ASTM no.3 oil, 7 days, 70 C, % wt increase
					Castor oil, TDI prepolymer				
Ricinoleates									
Castor oil	59	476	140	359	22	7	2	0.5	25
PG Ric	69	1132	230	346	102	35	1	0.9	16
Pe Ric	96	2620	40	---	74	63	2	1.1	6
BD Ric_2	38	361	320	120	37	14	5	0.7	38
BD Ric_2/castor oil	51	341	160	233	24	12	---	0.7	33
BD Ric_2/Pe Ric	65	797	130	522	48	19	---	0.9	23
BD Ric_2/BD	55	1460	350	224	71	14	2	0.9	20
Polyethers									
B-1000	54	417	240	270	44	61	3	2.6	32
B-1000/castor oil	59	469	170	304	23	38	0	1.1	29
P-1000/castor oil	54	350	140	250	24	21	0	1.1	28
Ricinoleic amides									
EA Ric	98	3540	250	1455	284	59	4	1.5	6
EA Ric/castor oil	66	1360	220	387	85	23	1	0.9	16
EA Ric/BD Ric_2	51	984	350	236	62	11	3	1.1	22
DEA Ric	97	3080	170	1250	406	63	9	1.3	3
DEA Ric/castor oil	79	1840	170	740	97	33	---	0.9	14
DEA Ric/BD Ric_2	60	1400	290	366	66	16	---	0.9	20
IPA Ric	98	3460	230	1535	359	60	13	1.6	10
IPA Ric/castor oil	64	1425	220	404	85	25	2	0.8	16
IPA Ric/BD Ric_2	51	784	370	230	61	12	5	0.9	22
DIPA Ric	89	3440	160	1400	507	66	0	1.0	3
DIPA Ric/castor oil	81	2400	170	932	119	36	2	0.7	15
DIPA Ric/BD Ric_2	61	1712	250	416	84	21	---	0.7	20
D230 Ric_2	48	1040	460	132	65	14	5	1.6	14
D230 Ric_2/T403 Ric_3	62	1515	310	232	86	27	2	1.4	10
					Polyether (B-1000), TDI prepolymer				
B-1000	58	>1150	>600	314	123	70	15	2.1	33
3 (B-1000)/TMP	64	990	340	405	120	61	4	2.1	24
					Castor oil, TMDI prepolymer				
Castor oil	58	204	---	---	<20	33	---	0.7	32
DIPA Ric	66	1320	240	538	69	21	---	1.1	12
					Castor oil, MDI prepolymer				
Castor oil	65	1470	240	478	64	17	---	0.4	16
PG Ric	98	3090	190	1470	315	61	---	0.7	8
DIPA Ric/BD Ric_2	94	3440	190	1720	222	52	---	0.7	9

[a] Abbreviations in Table I. When two polyols are listed they are used at a 1:1 equivalent ratio unless indicated otherwise.

were prepared from a standard prepolymer containing ca. 15% free NCO. This prepolymer was prepared by heating a mixture of 55% castor oil and 45% toluene diisocyanate (TDI, Hylene TM, DuPont) under N_2 for 1 hr at 75 C. Storage stability was improved by addition of 0.04% benzoyl chloride. Other prepolymers with the same free isocyanate content were prepared similarly from 59% B-1000 (Table I) and 41% toluene diisocyanate; 40% castor oil and 60% 4,4′-diphenylmethane diisocyanate (MDI, Multrathane M, Mobay Chemical Co.); and 52% castor oil and 48% trimethylhexamethylenediisocyanate (TMDI, Hugo Stinnes Chemical Co.).

Elastomer Preparations

The polyol and prepolymer components were first degassed separately by heating in beakers in a 50 C vacuum oven for 30-60 min at 5 mm Hg. The polyol contained 0.02-0.10% of the catalyst dibutyltin dilaurate (Niax D-22, Union Carbide Corp.). The polyol and prepolymer components were then mixed, using a NCO/OH ratio of 1.05. The mixture was degassed again for 5-10 min and poured into pellet (0.50 x 1.129 in. diameter) and slab (3 x 6 x 0.075 in.) molds maintained at 100 C. When the polymer began to gel, the molds were closed and heated for 4 hr at 250-750 psi.

Test Methods

Tensile strength, ultimate elongation and modulus (tensile stress) at 100% elongation were determined by ASTM method D 412-66; tear strength by ASTM method D 624-54, using die C; compression set by ASTM method 395-61, method B; and solvent resistance by ASTM method D 471-66, using weight gain after immersion in water and ASTM no. 3 oil at 70 C. Resilience was measured as the per cent rebound of a 0.625 in. diameter steel ball bearing in a Nopco Ball Rebound Tester (Custom Scientific Instruments, Inc.). Elastomer samples (0.50 x 1.129 in. diameter) were supported on a 2 in. thick hardwood block.

RESULTS AND DISCUSSION

Properties of elastomers prepared from castor oil and other esters of ricinoleic acid are listed at the top of Table II. For comparison, elastomers prepared from two commercial polyethers are included.

In general, in going from castor oil to its more highly hydroxylated derivatives (PG Ric and Pe Ric) or in combining $BDRic_2$ with more highly hydroxylated polyols (Pe Ric and BD), hardness, tensile strength, modulus and tear strength increased while elongation decreased. In this group, higher elongations and tear strengths were obtained with the more linear elastomers prepared from PGRic and $BDRic_2$/BD.

Elastomers prepared from polyethers and the standard castor oil-TDI prepolymer had stress strain properties and tear strengths similar to those of the elastomer prepared from castor oil. However elastomers prepared from polytetramethylene ether glycol (B-1000) and a B-1000/TDI prepolymer had considerably higher tensile strengths and elongations, and had higher tear strengths than the ricinoleate-based elastomers. A little trimethylolpropane was added with the B-1000 to obtain a crosslinked elastomer with low compression set.

The resilience of elastomers prepared from castor oil and from butanediol diricinoleate is very low. The harder elastomers from the monoricinoleates of propylene glycol and pentaerythritol have higher resiliences. In a comparable hardness range, B-1000-based elastomers are much more resilient than castor-based elastomers.

Solvent resistance was measured at 70 C in. water and ASTM no. 3 oil. The castor oil-based elastomer absorbed very little water, and the absorption was just a little higher when using the more highly hydroxylated monoricinoleates. On the other hand, oil absorption is greatly reduced when going from castor oil to the monoricinoleates. Compared with a castor oil-based elastomer, $BDRic_2$-based elastomers absorbed a little more water and about the same or somewhat more oil, depending on the copolyol. The polyether-based elastomers absorbed about the same amount of oil and about four times as much water as a castor oil-based elastomer. Water absorption was reduced by combining castor oil with the polyethers.

Properties of elastomers prepared from some amides of ricinoleic acid are listed in Table II. The amides of ethanolamine, diethanolamine, isopropanolamine and diisopropanolamine yielded hard, strong, high modulus elastomers with high tear strength and relatively high rebound resilience. In each case, the hardness, tensile strength, modulus, tear strength and resilience were reduced progressively by combining the amide with castor oil or butanediol diricinoleate. The more linear elastomers, containing $BDRic_2$, had the higher elongations.

Elastomers prepared from the amides alone have low oil absorptions and absorb about two to three times as much water as does a castor oil-based elastomer. Water absorption is reduced and oil absorption increased by combinations with castor oil or $BDRic_2$.

Except for higher elongations and lower moduli, elastomers prepared from the di- and triamides have properties similar to those of the monoamide-based elastomers with the same hardness.

The elastomers considered so far were made from prepolymers containing toluene diisocyanate (TDI). At the bottom of Table II are shown the properties of two sets of elastomers in which other diisocyanates were used. Two elastomers were made from a prepolymer prepared from castor oil and a commercial aliphatic diisocyanate, trimethylhexamethylenediisocyanate (TMDI). The castor oil-based elastomer was quite weak with a low tear strength. The amide based elastomer had a high tensile strength and moderate tear strength. Elastomers prepared from aliphatic diisocyanates are light in color and discolor less in sunlight than elastomers prepared from aromatic diisocyanates.

Three elastomers were prepared using diphenylmethane diisocyanate (MDI) in the prepolymer. This use of MDI in place of TDI increased the tensile and tear strengths of the castor oil-based elastomer about three-fold. Hard elastomers with much higher tensile and tear strengths were obtained, using the MDI prepolymer with propylene glycol monoricinoleate or a combination of butanediol diricinoleate and the amide of diisopropanolamine. The water and oil absorption of these elastomers was low.

These results demonstrate some of the versatility of the castor-based urethane elastomers and show how specific properties may be obtained by selection of appropriate isocyanates and castor-derived polyols.

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