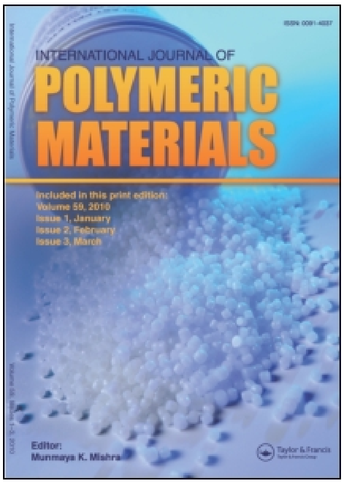

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Castor Oil Based Prepolymers and Thermoplastic Urethane Polymers

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Castor Oil Based Prepolymers and Thermoplastic Urethane Polymers

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Castor oil has been treated with 0.7 mole equivalent of phenyl isocyanate to obtain approximately bifunctional hydroxy adduct. This adduct was further reacted with commercial diisocyanates such as 2,4-toluene diisocyanate (TDI), 4,4′-diphenyl methane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI) to prepare isocyanate capped prepolymers. These prepolymers were characterized by Brookfield viscosity and isocyanate content and were extended through aliphatic glycols like 1,2-ethylene glycol, 1,2-propylene glycol, and 1,4-butylene glycol in dimethyl formamide to offer thermoplastic polyurethanes. These polymers were characterized by softening point, solubility and by inherent viscosity.

INTRODUCTION

The petroleum oil crisis has created uncertainties regarding the availability and price of monomers on which synthetic polymers are based. Hence attempts are being made all over the world on the use of renewable resources for industrial needs.

Castor oil is an agricultural product which serves as a raw material for the manufacture of variety of products.[1–3] The chemical

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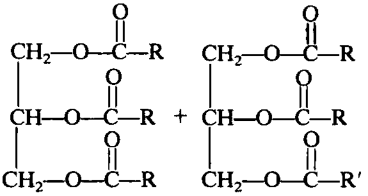
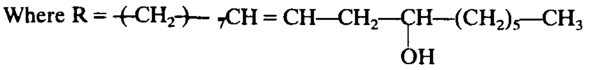
structure of castor oil is:





Where $\mathrm{R} = -(\mathrm{CH_2})_7-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}}-(\mathrm{CH_2})_5-\mathrm{CH_3}$

R′ = other fatty acids

A literature survey reveals that castor oil is a approximately 70% glyceryl triricinoleate and 30% glyceryl diricinoleate because other fatty acid components are in minor percentages. It has a 2.7 hydroxyl functionality which has been used in isocyanate reactions for making polyurethane adhesives,[4] coatings,[5] foams,[6–10], castables[11,12] and milliables.[13] These polymers are characterized by their low temperature flexibility, excellent hydrolytical stability and shock absorbing and electrical insulating properties.

This paper deals with the preparation of castor oil based isocyanate capped prepolymers and thermoplastic polyurethanes there from.

EXPERIMENTAL

Materials

Castor oil—commercial available castor oil was dried under reduced pressure before use. Phenyl isocyanate was obtained from Fluka, A.G. (Switzerland) and used as such.

2,4-Toluene diisocyanate (TDI), 4,4′-diphenyl methane diisocyanate (MDI), and 1,6-hexamethylene diisocyanate (HDI) were obtained from Bayer A.G. (West Germany) and were purified by vacuum distillation. Isophorone diisocyanate (IPDI), was obtained from Veba Chemie (West Germany) and used as received.

1,2-Ethylene glycol (EG), 1,2-propylene glycol (PG), and 1,4-butylene glycol (BG) were obtained from Koch light laboratories (England), and were purified by distillation.

N,*N*-Dimethylformamide (DMF) was obtained from S.D. Chemicals (Bombay), India, dried over P_2O_5 and distilled under reduced pressure before use. All other solvents used were of commercial grades.

Measurements

1) Brookfield viscosities of prepolymers were measured with Brookfield viscometer.

2) Hydroxyl number was determined by acetylation procedure.[14]

3) Acid number and isocyanate contents were determined by the procedure given in literature.[15]

4) Solubility of polymers was checked with 5% concentration in various solvents.

5) Softening points of polymers were determined in small test tube on a melting point apparatus.

6) Inherent viscosities of polymers were measured with 0.5% concentration in dimethylformamide at 30°C using modified suspended type Ubbelohde viscometer.

PREPARATIONS

Preparation of difunctional castor oil adduct (DFCO)

In a 2 litre four neck round bottom flask equipped with a mechanical stirrer, a dropping funnel with guard tube, a thermowell and nitrogen atmosphere was placed 1 kg dried castor oil. The temperature was raised to 100°C followed by dropwise addition of 76 ml phenyl isocyanate with efficient stirring for one hour. The flask was evacuated at 100°C/1 mm of Hg for half hour to remove traces of volatile products. The reaction product was cooled to room temperature and properties were measured.

Preparation of isocyanate capped prepolymers from DFCO (a typical procedure)

In a 1 litre four neck round bottom flask equipped with a mechanical stirrer, a dropping funnel with guard tube, a thermowell and nitrogen atmosphere was placed 208.8 g (1.2 mole) of toluene diisocyanate (TDI). The temperature was raised to 70°C and 209.2 g (0.2 mole) of difunctional castor oil (DFCO) was added dropwise. After the completion of addition of DFCO reaction was continued for three hours at same temperature.

Preparation of thermoplastic polyurethanes from castor prepolymers

In a 500 ml four neck round bottom flask equipped with a mechanical stirrer, thermowell, dropping funnel with guard tube and nitrogen atmosphere were placed 41.9 g of prepolymer of DFCO-TDI and 100 ml dry DMF. To this solution was added 9.0 g of dry 1,4-butylene glycol and 0.2 g triethylamine in 20 ml DMF at room temperature. The reaction was further continued at same temperature for one hour, at 50°C for two hours and 120°C for three hours. The reaction mixture cooled and precipitated into water. The precipitated polymer was filtered, washed with methyl alcohol and dried under vacuum at 70°C for several hours.

RESULTS AND DISCUSSION

The trifunctional part of castor oil has been made approximately difunctional by assuming that major part of phenyl isocyanate would react with one of the hydroxyl group of 70% glyceryl triricinoleate. Some important properties of this adduct in comparison with castor oil are given in Table I. The increase in Brookfield viscosity and decrease in the hydroxyl number confirm the formation of adduct. The formation of urethane linkages is also characterized by IR spectrum showing absorptions at 3280 due to —NH— and 1750 cm^{-1} due to C=O alongwith strong absorption band at 2270 cm^{-1} due to isocyanate group.

The difunctional castor oil is further reacted with 5 mole excess diisocyanates to obtain four isocyanate capped prepolymers. Prepolymer reactions were carried out in nitrogen atmosphere and in extremely dry conditions. Certain properties of these prepolymers such as Brookfield viscosity and isocyanate content are given in Table II. The prepolymer derived from HDI has lowest Brookfield

TABLE I

Properties of difunctional castor oil (DFCO)

No.	Property	Castor oil	DFCO
1	Appearance	Viscous	Viscous
2	Colour	Yellow	Brown
3	Sp. gravity, g/cc	0.9666	0.9725
4	Refractive index n_D^{25}	1.474	1.483
5	Acid number	1.35	1.67
6	Viscosity* in CPS	575.0	900.0
7	Hydroxyl value	166.6	118.0

* Brookfield viscosity at 25°C.

TABLE II

Properties of isocyanate capped prepolymers

Sr.		Prepolymer from DFCO and			
no.	Property	TDI	MDI	HDI	IPDI
1	Appearance	Viscous	Viscous	Viscous	Viscous
2	Colour	Brown	Dark brown	Yellow	Yellowish brown
3	Viscosity*	1575	1637	220	1600
4	Isocyanate content				
	Theoretical %	20.18	16.50	20.20	18.06
	Experimental %	19.96	15.93	20.01	17.52

* Brookfield viscosity at 25°C in CPS.

TABLE III

Inherent viscosities and softening points of polyurethanes

Sr. no.	Polymer composition DFCO +	n_{inh}* dl/g	Softening point in °C	Abbreviation
1	TDI + BG	0.09	60–70	PU_1
2	TDI + PG	0.12	85–90	PU_2
3	TDI + EG	0.10	40–50	PU_3
4	MDI + BG	0.40	165–175	PU_4
5	MDI + PG	0.15	150–155	PU_5
6	MDI + EG	0.16	165–170	PU_6
7	HDI + BG	—	150–155	PU_7
8	HDI + PG	0.29	110–115	PU_8
9	HDI + EG	0.66	100–105	PU_9
10	IPDI + BG	0.17	95–100	PU_{10}
11	IPDI + PG	0.08	85–90	PU_{11}
12	IPDI + EG	0.17	100–105	PU_{12}

* 0.5% in dimethylformamide at 30°C.

TABLE IV

Solubilities of polyurethanes

Sr. no.	Solvent	PU_1	PU_2	PU_3	PU_4	PU_5	PU_6	PU_7	PU_8	PU_9	PU_{10}	PU_{11}	PU_{12}
1	Benzene	±	±	±	−	−	−	−	±	−	±	±	±
2	Ethanol	±	±	±	−	−	−	−	±	−	±	±	±
3	Ethyl acetate	±	±	±	−	−	−	−	±	−	±	±	±
4	Acetone	++	++	++	+	+	+	±	+	±	+	+	+
5	Methyl ethyl ketone	++	++	++	+	+	+	±	+	±	+	+	+
6	Chloroform	++	++	++	+	+	+	±	+	±	±	±	±
7	Tetrahydrofuran	++	++	++	++	++	++	+	++	+	++	++	++
8	Dimethylformamide	++	++	++	++	++	++	++	++	++	++	++	++
9	Dimethylacetamide	++	++	++	++	++	++	++	++	++	++	++	++
10	Dimethylsulfoxide	++	++	++	++	++	++	++	++	++	++	++	++
11	*N*-Methylpyrollidone	++	++	++	++	++	++	++	++	++	++	++	++

− = Insoluble
+ = Soluble in hot
± = Swells
++ = Soluble

viscosity and can be attributable to aliphatic nature of diisocyanate. The experimentally determined isocyanate contents are in good agreement with theoretical values indicate the absence of dimer, trimer, and allophanate formation during prepolymerization reactions.

These prepolymers were further extended with three aliphatic glycols in 40% DMF solution to produce twelve thermoplastic polyurethanes. Here solution polymerization was selected because bulk polymerization of these prepolymers gives cross linked and insoluble polymers. During polymerization viscosity of reaction goes on increasing. Polymers were purified by precipitation method. Softening points and inherent viscosities of polymers are tabulated in Table III. Polymer obtained from MDI and HDI have comparatively high molecular weights and that is due to symmetric structure and equal reactivities of isocyanate groups. Overall low molecular weight formation is observed and that can be attributed to the presence of bulky sidechain in difunctional castor adduct.

Solubility of polymers has been tested in various solvents and is summarized in Table IV. Polymers derived from TDI and IPDI have solubility in common solvents such as acetone, chloroform, methyl ethyl ketone, and tetrahydrofuran while polymers derived from MDI and HDI are having solubility only in polar solvents like dimethylformamide (DMF), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and *N*-methylpyrollidone (NMP). This fact can be attributed to the symmetry loss present in TDI and IPDI structures.

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