

# Plasticizing Effect of Acetylated Castor Oil on Castor Oil-Based, Moisture-Cured Polyurethane Film

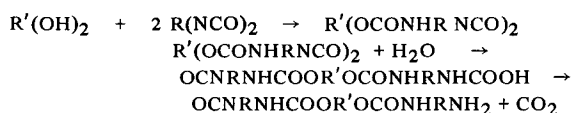
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## ABSTRACT

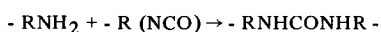
Moisture-cured polyurethane films have been prepared by reaction between toluene diisocyanate and castor oil or derivatives such as castor oil diethanol amide, castor oil monoglyceride, ethylene glycol monoricinoleate, and propylene glycol monoricinoleate. Effect of acetylated castor oil as an internal plasticizer on the resulting urethane films has been studied. Catalytic effect of 3-5% triethanol amine on curing of plasticized films has been noted. Plasticized polyurethane films show good tensile strength (105-550 kg/cm<sup>2</sup>) and elongation (15-215%) properties, having high melting point (210-272 C) and good resistance to solvents and chemicals.

## INTRODUCTION

The chemistry of the moisture-cured polyurethane involves the reaction of the diisocyanate with hydrogen donors, leaving excess NCO available to react with the atmospheric moisture. The curing reaction is believed to proceed according to the following equations:



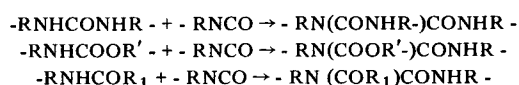
The amine immediately reacts with additional isocyanate to form a substituted urea.



If a polyester functions as a portion of the hydrogen donor system in a prepolymer, it is possible to obtain amide linkages in the final structure of the polymer because of the reaction of latent carboxyl groups of the polyester.



Such a reaction will lead to linear polymer chains. Cross-linking may occur at a relatively slow rate by reaction of free isocyanate groups with the active hydrogen in urea, urethane, and amide links.



Studies on moisture-curable polyurethane have been reported on earlier workers (1-3). Application of polyols derived from castor oil for the preparation of urethane coatings has been reported extensively by Metz et al. (4). Polyurethane films based on propylene glycol monoricinoleate have been reported by Heiss and others (5). Although plasticized polyurethane-based optical laminates have been reported in the patent literature (6), there has been only very limited study on the effect of plasticizer on polyurethane films.

In the present study, different castor oil-based polyols have been used for preparation of moisture-curable urethane films. Effect of plasticization with acetylated castor oil as an internal plasticizer on the resulting film properties has been studied. Effect of amine type accelerators for curing of such plasticized films and their effects on film properties has also been studied.

## MATERIALS AND METHODS

Chemically pure grade ethylene glycol (Pfizer), 1:2, propylene glycol (British Drug House); diethanol amine (BDH); acetic anhydride (BDH); glycerol and toluene diisocyanate (TDI), 80:20 (Bayer) have been used.

Castor oil (Indian-local source, properties as in Table I) has been used. Castor oil fatty acids are prepared by refluxing 200 g castor oil with 200 ml 25% ethanolic potassium hydroxide followed by acidification and extraction with ether. No further purification has been made.

Castor oil monoglyceride (7) and diethanol amide of castor oil (8) are prepared by the standard methods.

## Acetylated Castor Oil

Partially acetylated castor oil was prepared by dropwise addition of 88 g of acetic anhydride to 500 g of castor oil maintained at 105-110 C, heated for an additional 1½ hr, allowed to stand at room temperature for 20 hr, and heated

TABLE I

Physico-Chemical Properties of Different Casor-Based Polyols

Polyols	Color	Viscosity (20 C poise)	Refractive index (25 C)	Density (g/cc)	Acid value	Hydroxyl value	Equivalent weight (based on OH value) (g)
Castor oil	R = 0 Y = 6	9.86	1.4760	0.9555 (d <sub>28</sub> <sup>28</sup> )	1.17	168	334
Castor oil monoglyceride	R = 0.6 Y = 12	9.64	1.4734	0.9811 (d <sub>31</sub> <sup>31</sup> )	1.78	338.5	165.8
Ethylene glycol monoricinoleate	R = 0.3 Y = 10	2.19	1.4699	0.9543 (d <sub>34</sub> <sup>34</sup> )	1.20	269.2	208.4
Propylene glycol monoricinoleate	R = 0.1 Y = 10	2.45	1.4674	0.9458 (d <sub>32</sub> <sup>32</sup> )	3.79	272.2	206.1
Diethanol amide of castor oil	R = 0.4 Y = 11	25.30	1.4834	0.9966 (d <sub>29</sub> <sup>29</sup> )	8.57	323.9	173.2
Acetylated castor oil	R = 0 Y = 8	3.94	1.4707	0.9610 (d <sub>32</sub> <sup>32</sup> )	0.88	85.2	658.6

TABLE II  
Properties of Unplasticized Moisture-Cured Polyurethane Films

Polyols	Weight ratio of polyol	Tensile strength (kg/cm <sup>2</sup> )	% Elongation at break	Melting point (C)	Appearance
Anhydrous castor oil	---	266	166	292	Transparent, very soft, elastic
Ethylene glycol monoricinoleate	---	401	0	255	Transparent, brittle
Propylene glycol monoricinoleate	---	---	---	268	Transparent, brittle
Monoglyceride of castor oil	---	625	25	272	Transparent, brittle
Castor oil/diethanol amide	1	684	40	265	Transparent, flexible, tough
Ethylene glycol monoricinoleate/diethanol amide	1.5	---	---	238	Transparent, flexible, very tough
Propylene glycol monoricinoleate/diethanol amide	1	---	---	240	Transparent, flexible, very tough

at 110 C until an acid number of 91-92 was reached (2½ hr). The crude acetylated castor oil was neutralized with 2N NaOH and extracted with ether. The emulsion formed was salted out with NaHSO<sub>4</sub>, washed with saturated aqueous Na<sub>2</sub>SO<sub>4</sub>, and then with water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, the ether was distilled off.

#### Ethylene Glycol and 1,2-Propylene Glycol Monoricinoleate

Esterification of castor oil fatty acids was conducted in a 500-ml three-necked flask, fitted with a stirrer, thermometer, and arrangement for bubbling N<sub>2</sub>. The reaction was carried out at 180-185 C for 6 hr in the presence of 0.2% potassium hydroxide as catalyst. Mole ratios of polyol/acid used were ethylene glycol/castor acids = 2.7 and propylene glycol/castor acids = 1.76. Products were extracted with ether, neutralized with aqueous sulfuric acid, and washed with water till free from glycols and acid. Finally, ether was distilled off.

#### Analytical Methods

*Color:* Lovibond tintometer, 10 mm cell.  
*Viscosity:* Oswald viscometer.  
*Refractive index:* AOCS method.  
*Density:* By specific gravity bottle.  
*Acid value and hydroxyl value:* AOCS methods.

#### Preparation of Urethane Derivatives

Water was at first removed from the polyol by refluxing in a Dean-Starke apparatus with xylene. For experiments with added plasticizer, the required amount of acetylated castor oil was added to the polyol prior to azeotropic drying. A calculated amount of solvent (xylene/ethyl acetate, 6:1), to make a 25% solution of the resulting urethane derivatives, was taken in a three-necked flask, and the required amount of toluene diisocyanate (two equivalents of TDI per equivalent of polyol) was added. The flask was fitted with a sealed stirrer, thermometer, and a dropping funnel through which was added the polyol/acetylated castor oil mixture during 1 hr. The flask was heated at 55-65 C for 4 hr, with good stirring. The product was cooled and kept for 24 hr to ensure the stabilization of the product.

#### Evaluation of Polyurethane Film

Films were cast on mercury. A small amount of dry acetone was poured over mercury. The pan was covered and allowed to stand for a few minutes. A 25% solution of the adduct was added to the layer of acetone. In case of

catalyzed films the catalyst (3-5% triethanol amine) was added to acetone. The pan was again covered and allowed to stand undisturbed at room temperature. Upon evaporation of the solvents, the adduct cured into a film in 1-4 days.

#### Film Properties

The tensile and elongation properties of the films 4-8 weeks old were determined using a stretching rate of 10 in/min for high tensile value specimens and 20 in/min for low tensile value specimens. The testing was done in a "Good-Brand" Tensile Tester. The melting points of the films were measured on a Fischer Johns melting point apparatus, using a heating rate of about 15-20 degrees per minute. Actually, it had been observed that the films went through a gradual softening process, and the melting point was taken as the point at which the films began to flow appreciably. Effect of solvent and chemicals was observed by immersion of strips of the film in the appropriate reagent for 200-250 hr at room temperature.

## RESULTS AND DISCUSSION

Table I lists the physico-chemical properties of the different polyols made from castor oil and those of acetylated castor oil used. Table II indicated the properties of the films made from castor oil, its derivatives, and different blends of castor-based polyols with toluene diisocyanate. It has been found that, in general, urethane films made from castor-based polyols are rigid. Some of them are very brittle, particularly films made from ethylene glycol monoricinoleate, propylene glycol monoricinoleate, and the monoglyceride of castor oil. Films made from castor oil as such exhibited some flexibility in character. These are elastic and have high elongation. This may be expected since unreacted castor oil present in the resin imparts some plasticizing action in the resulting film. Table III illustrates the plasticizing effect of acetylated castor oil on the polyurethane films. It is found that 10-25% incorporation of plasticizer in castor polyols gave the films highly desirable properties of good elasticity and flexibility. However, with 25% incorporation, the castor oil film loses somewhat its elastic behavior.

When partially acetylated castor oil is used as a plasticizer, the residual hydroxyl groups can also react with toluene diisocyanate and take part in the final structure of the polyurethane molecule, leaving polar acetylated group which impart desirable flexibility.

TABLE III  
Properties of Plasticized Polyurethane Films (Catalyzed and Uncatalyzed)

Sample no.	Components	Weight ratio of components	Uncatalyzed films (moisture cured)			Catalyzed films (3-5% triethanol amine)			Appearance
			Tensile strength (kg/cm <sup>2</sup> )	% Elongation at break	Melting point (°C)	Tensile strength (kg/cm <sup>2</sup> )	% Elongation at break	Melting point (°C)	
1.	Castor oil/acetylated castor oil	4:1	177	160	250	105	150	242	Transparent, soft, elastic
2.	- Do -	9:1	177	200	272	188	210	260	- Do -
3.	Propylene glycol monoricholeate/acetylated castor oil	9:1	350	145	253	348	145	235	Transparent, flexible, elastic
4.	Monoglyceride of castor oil/acetylated castor oil	9:1	550	140	264	545	130	248	Transparent, tough, elastic
5.	Ethylene glycol Monoricholeate/acetylated castor oil	4:1	218	160	220	146	160	210	Transparent, flexible, elastic
6.	Castor oil/monoglyceride/acetylated castor oil	2:2:1	255	140	260	139	215	250	- Do -
7 <sup>a</sup>	Castor oil/diethanol amide/acetylated castor oil	2:2:1	275	65	260				Transparent, flexible
8 <sup>a</sup>	Ethylene glycol monoricholeate/diethanol amide/acetylated castor oil	2:2:1	417	15	230				Transparent, flexible, tough
9 <sup>a</sup>	Propylene glycol monoricholeate/diethanol amide/acetylated castor oil	2:2:1	388	15	236				- Do -

<sup>a</sup> Additional catalytic effect on films (7, 8, and 9) has not been observed, since prepolymer composition contains tertiary nitrogen atoms which are expected to catalyze the curable reaction.

TABLE IV  
Effect of Solvents and Chemicals on Unplasticized Polyurethane Film<sup>a</sup>

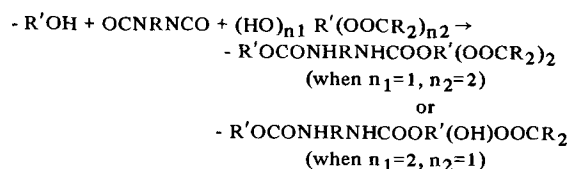
Polyols	Water	3% NaOH	10% HCl	Methanol	Hexane	Benzene	Acetone
Castor oil	E	E	E	F	G	F	P
Ethylene glycol monoricinoleate	E	E	E	F	E	F	P
Castor oil monoglyceride	E	E	E	F	E	F	P
Castor oil/diethanol amide (1:1)	E	E	E	P	E	F	P
Ethylene glycol monoricinoleate/diethanol amide (1.5:1)	E	E	E	G	E	G	G
Propylene glycol monoricinoleate/diethanol amide (1:1)	E	E	E	G	E	G	G

<sup>a</sup>E = excellent resistance, little or no change; G = good resistance, slight swelling of surface; F = fair, considerable swelling and loss of strength; P = poor vigorous attack on film.

TABLE V  
Effect of Solvents and Chemicals on Plasticized Polyurethane Films<sup>a</sup>

Sample no.	Nature of films	Water	3% NaOH	10% HCl	Methanol	Hexane	Benzene	Acetone
1.	U	E	E	E	G	G	F	P
	C	E	E	G	G	F	F	P
2.	U	E	E	E	G	G	F	P
	C	E	E	G	G	F	F	P
3.	U	E	E	E	G	E	F	P
	C	E	E	E	G	E	F	P
4.	U	F	B	F	F	G	G	P
	C	F	B	F	F	G	G	P
5.	U	E	E	E	F	E	F	P
	C	E	E	E	F	E	F	P
6.	U	G	G	E	G	G	G	P
	C	E	E	E	G	E	G	P
7.	U	E	E	E	G	E	G	F
8.	U	E	E	E	G	E	E	F
9.	U	E	E	E	G	E	E	F

<sup>a</sup>U = uncatalyzed film; C = catalyzed film; B = brittle in character; other symbols same as in Table IV.



A set of experiments was also performed to determine the effect of a curing agent (catalyst) like triethanol amine on the physical behavior of the films. While it was observed that without being catalyzed the films took a long time to cure, sometimes as high as 3-4 days for unplasticized films and 48 hr for plasticized films, with triethanol amine (3-5%), cure time was considerably reduced to as low as 24 hr. The effect of curing agent on the physical behavior of the films is given in Table III. It is observed that the use of catalyst in most of the cases considerably reduces the tensile strength. Melting point of the films is also considerably reduced. This may be explained by assuming that the use of amine-curing agent during drying gave less time for molecular reorientation and packing of the molecules thereby reducing the film strength. Triethanol amine having three hydroxyl groups per molecule may also alter the polymer structure because of its reactivity with free NCO groups of the prepolymer.

The cured films were not affected by solvent tested, but were swelled and weakened by some, such as acetone and dimethyl formamide. The films were resistant to water, 10% hydrochloric acid, hexane, and benzene. The films

were slightly affected by acetone, methanol, and alkali. Solvent and chemical resistance properties of the films are summarized in Tables IV and V. It has been observed that the use of diethanol amide improves somewhat the chemical and solvent resistance properties of the films. No significant difference in solvent and chemical resistance properties has been observed between catalyzed and uncatalyzed or between plasticized and unplasticized films.

#### ACKNOWLEDGMENT

ACCI Ltd., Calcutta helped in evaluating film properties. One of the authors (KKS) obtained a UGC Fellowship.

#### REFERENCES

- Doyle, N.E., "The Development and Use of Polyurethane Products," McGraw Hill Book Company, New York, 1971.
- Bailey, M.E., SPE J. 14(2):41 (1958).
- "Symposium on Polyurethane Coatings," Ind. Eng. Chem., 51:1381 (1959).
- Metz, H.M., A. Ehrlich, M.K. Smith, T.G. Patton, Paint Oil Chem. Rev. 121:6 (1958).
- Heiss, H.L., J.H. Sounders, M.R. Morris, B.R. Davis, and E.E. Hardy, Ind. Eng. Chem., 46:1498 (1954).
- Katz, I., and F.L. Thomas (to Bjorkston Research Laboratories, Inc.) U.A. Patent 2,864,780 (Dec. 16, 1958).
- Raychoudhury, R.B., JAOCS 37:483 (1960).
- Lyon, C.K., and V.H. Garrett, Ibid. 50:112 (1973).

[Received April 18, 1978]