Chemoenzymatic Synthesis of Urethane Oil Based on Special Functional Group Oil

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ABSTRACT: A two-step chemoenzymatic synthesis of urethane oil, consisting of a lipase-catalyzed transesterification of castor oil with *n*-butanol and a reaction of the resulting precursor (partial esters) with different diisocyanates, was studied. The effect of the type of lipase, alcohol chain length, solvent, and temperature in the transesterification step was examined. Urethane oils were characterized by IR, ^{1}H-NMR, and GPC techniques. The film properties were also tested. The composition varies with time in the transesterification step. Conversions were faster and more complete using lipozyme, where yields to 75% could be achieved. Enzyme activity increases with increase in the log P value of the solvent. The degree of transesterification and composition of the precursor have influence on the molecular weight and film properties of urethane oils. A good correlation was observed between the scratch resistance and monoglyceride percentage of the precursor of the respective urethane oils. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1451–1458, 1998

Key words: castor oil; chemoenzymatic synthesis; lipase; partial esters; diisocyanate; urethane oil; characterization

INTRODUCTION

Vegetable oils play an important role in surface coatings because of their availability as a renewable source, variety, and versatility. During the last several years, the use of urethane materials in the surface coatings industry is well recognized.[1] These materials provide better gloss, excellent abrasion resistance, flexibility, hardness, solvent and chemical resistance, and resistance to degradation from weathering. Urethane oils (isocyanate-modified vegetable oils), the first urethane materials, find a special place among the many binders available for decorative paints and protective-coating formulations. Vegetable oils of different origin have frequently appeared in the literature as the oil components of urethane oils.[2,3] More recently, Erciyes et al. investigated urethane oils based on *Ecballium elaterium* and *P. mahaleb* seed oils.[4]

It has been reported that castor oil–diisocyanate coatings can be upgraded if the castor oil is first treated with low molecular weight polyols by typical alcoholysis, leading to shortening of the distance between hydroxyl functional groups in the molecules.[5] Urethane oils are chemically synthesized by reacting a diisocyanate with partial esters obtained from the transesterification of triglyceride oils (TG) with polyols. Partial esters are commonly synthesized by base-catalyzed transesterification at 220–230°C. The degree of transesterification and composition of the precursor (partial esters) have an important effect on the molecular weight and film properties of the final resin.[6] However, practically, the reaction does not go to completion. High temperature facilitates the reaction only at the cost of the randomization, loss of

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ingredients, and darkening of color. In light of these difficulties, in the present work, the recently developed biocatalytic approach was employed.[7,8]

EXPERIMENTAL

Chemicals

Castor oil and methoxymelamine were locally purchased and the purity of castor oil was checked on a gel permeation chromatograph prior to use. 2,4-Toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI) were obtained from Fluka AG. All reagent-grade primary alcohols were obtained from Aldrich and all the solvents, namely, tetrahydrofuran (THF), dichloromethane (DCM), diisopropyl ether (DIPE), toluene (TOL), and hexane (HEX) were of analytical grade.

Lipase

Lipozyme IM20 (LIPO; 41 IU g^{-1}), a commercially available lipase from the fungus *Mucor miehei* immobilized on macroporous anion-exchange resin was obtained from Novo-Nordisk Denmark. Lipase from hog pancreatic (HPL; 2.27 units/mg) was obtained from Fluka, Switzerland. A crude porcine pancreatic lipase (PPL; 35% protein) of activity 30–70 units/mg and *Candida cylindracea* lipase (CCL; 665 units/mg) were obtained from Sigma Chemical Co., Missouri, USA.

Two-step Chemoenzymatic Synthesis of Urethane Oil

A two-step chemoenzymatic synthesis of urethane oil, consisting of the lipase-catalyzed transesterification of castor oil with *n*-butanol[9] and the reaction of the resulting precursor (partial esters) with different diisocyanates to obtain urethane oil, was carried out in the laboratory.

In the first step, a stoichiometric amount of castor oil (substrate) and *n*-butanol (nucleophile) and 0.5 g of enzyme were stirred in a round-bottom flask at ambient temperature (30°C). Samples were withdrawn at an interval of 1 h during the course of the reaction and analyzed by GPC in the LC mode for determination of the composition of the precursor. The first step was continued for approximately 8 h when the peak due to triglyceride decreased significantly.[10]

In the second step, the partial esters obtained in the transesterification step and 50 mL anhydrous chloroform were placed in two-necked round-bottom flask equipped with a reflux condenser, protected by a calcium chloride guard tube and dropping funnel. Diisocyante in 50 mL chloroform was introduced into the dropping funnel. The reaction mixture in the flask was continuously stirred on a magnetic stirrer and the diisocyanate solution was gradually added dropwise for 0.5 h and stirring continued. Ascertaining the completion of the reaction after 4 h, from the absence of the infrared band due to NCO at 2260–2280 cm^{-1}, the solvent was evaporated on a rotavapor to obtain urethane oil. Figure 1 shows the reaction scheme for the chemoenzymatic synthesis of urethane oil. The hydroxyl value was determined by the standard method.

IR Spectroscopy

A neat sample was used for recording the infrared spectra of urethane oil on a Perkin–Elmer 781 IR spectrophotometer. The sample was placed between two sodium chloride cells and IR spectra were scanned in the range of 4000 to 600 cm^{-1} using a medium scan rate. The following significant peaks were observed in the IR spectra:

3350 cm^{-1} (strong, —NH)
3300 cm^{-1} (broad, hydroxyl)
3010–3080 cm^{-1} (medium, aromatic)
2850–3000 cm^{-1} (strong, aliphatic)
1710–1740 cm^{-1} (strong, urethane and ester carbonyl)
1600–1625 cm^{-1} (weak, vinyl).

^{1}H-NMR Spectroscopy

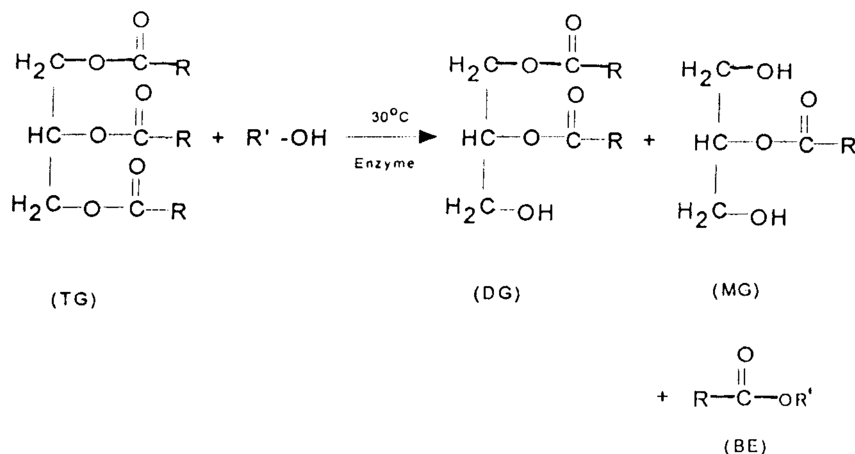
^{1}H-NMR spectra of representative samples were recorded using a Bruker AC 80 pulse Fourier transform NMR spectrophotometer. Samples were used in the form of a solution (10–15% w/v) in deuterated chloroform at ambient temperature. Tetramethylsilane (TMS) was used as the internal standard.

The ^{1}H-NMR spectra showed the following characteristic peaks:

δ 0.92 ppm (obscured triplet, $—CH_3$),
δ 1.29 ppm (broad singlet, $—CH_2$),
δ 2.06 ppm (broad singlet, $—CH_2—C=C$),

SCHEME

Step I



Step II

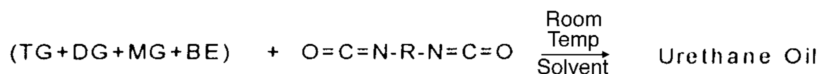


Figure 1 Reaction scheme for chemoenzymatic synthesis of urethane oil.

δ 2.18–2.27 ppm (CH$_3$—Ph in TDI)
δ 2.27–2.34 ppm (triplet, CH$_2$—C(=O)—)
δ 3.63 ppm (singlet, CH—OH)
δ 3.86 ppm (pH —CH$_2$— pH in MDI)
δ 4.06 ppm (2 doublets, CH$_2$—O—C(=O)—),
4.8–5.00 ppm (broad triplet, CH—O—C(=O)—),
δ 5.34 ppm (broad triplet, CH=CH)
δ 6.39 and 6.6 ppm (2 broad peaks, —OH and —NH)
δ 7.09 ppm (2 doublets, aromatic)
δ 7.76 ppm (singlet, aromatic).

Gel Permeation Chromatography

Gel permeation chromatography (GPC) experiments were carried out on a Waters Associates pump (730 data module) at ambient temperature. The detailed conditions and calibration chart for the GPC experiment are as follows:

Columns	μ-Styragel (10^3, 500, 100 Å)
Solvent	dry tetrahydrofuran
Flow rate	1.5 mL/min
Detector	refractive index
Sample size	100 μL
Standards	polystyrene (35, 8.5, 4, 2.9 $\times 10^3$)
Chart speed	0.80 cm/min
Accuracy	$\pm$6%.

Calibration Chart

Retention Time (min)	Molecular Weight ($\times 10^{-3}$)
10.77	35.0
12.32	8.5
13.07	4.0
13.70	2.9

Determination of Film Properties

Film properties such as scratch resistance, impact resistance, flexibility, and alkali and acid resistance were determined by standard methods.[11–14]

Glass plates of size 10 × 10 cm were taken and cleaned with xylene and subsequently with alcohol and water until wetted panels showed no water breaks when held in a vertical position. These plates were rinsed with acetone and allowed to dry in a dust-free chamber.

Twenty-four-gauge mild steel panels of two different sizes, namely, 15 × 10 cm and 20 × 10 cm, were first degreased in an alkali solution, washed thoroughly with water, and dried in an oven. Samples were thinned with xylene and the required amount of hexamethoxymelamine (crosslinking agent) was added. The film was cast onto the glass and mild steel panels by flowing along the length of the panel, the excess being drained out of the panel until a uniform film was obtained. The panels were baked at 150°C for 0.5 h in an oven. The resultant films of a dry film thickness of approximately 20–30 μ were ensured to be tack free and, subsequently, visually inspected for any film defects such as pinholes and haziness. For the flexibility and adhesion tests, the mild steel panels were used as a substrate, while the glass plates were used for the alkali- and acid-resistance tests.

RESULTS AND DISCUSSION

Triglyceride oils are natural products abundant in both plants and animals. While most of these oils contain only double-bond functionality, castor oil is one of the excellent agricultural sources of triol, having glycerol as a backbone and three hydroxyl groups, one on each acid residue. The dual character of castor oil to act as a polyol and as a curing agent leads to a unique morphology for network formation in a polymer molecule. After stirring the mixture of castor oil and lipase without the solvent and analyzing it by GPC in the LC mode, it was observed that the peak due to triglyceride remains unaltered, indicating that the hydroxyl group of ricinoleic acid is not showing any reactivity in lipase-catalyzed transesterification.

The monoglyceride was separated from the reaction mixture at the end of step I by column chromatography using a hexane : chloroform (95 : 5 v/v) solvent system. The ^{1}H-NMR spectrum of the isolated monoglyceride from step I shows the peak at δ 4.8–5.0 ppm due to CH attached to the ester linkage in the α position and confirms the exclusive formation of β-monoglyceride in step I, indicating the 1,3-positional specificity of lipase as expected and ruling out the possibility of randomization.[15] Hence, in step II, the reaction of diisocyanates with these partial esters formed in step I proceeds in a facile manner.

Figure 2 shows the kinetics of biocatalytic transesterification and the product distribution as a function of time for the model reaction of castor

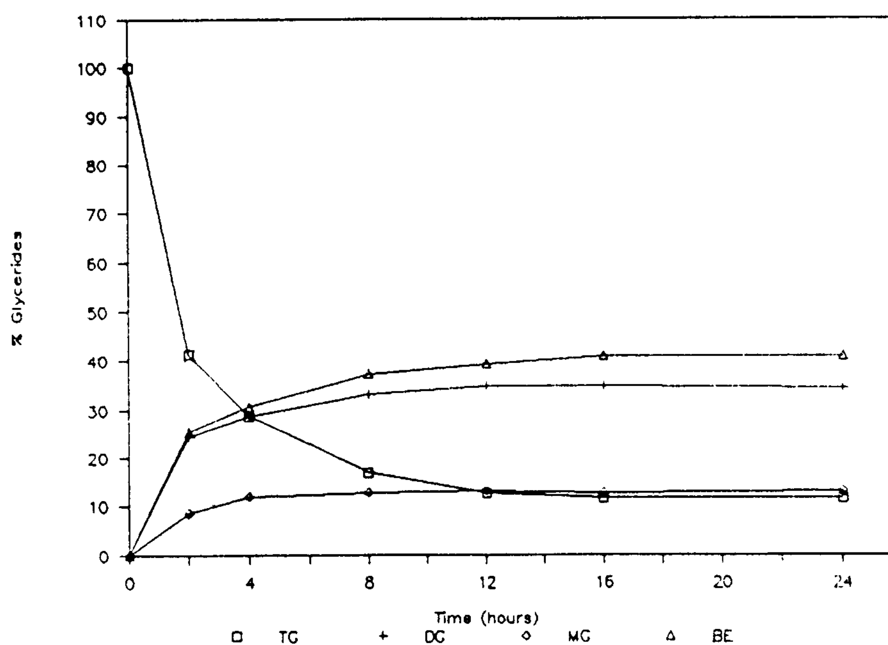


Figure 2 Kinetics of transesterification and product distribution as a function of time.

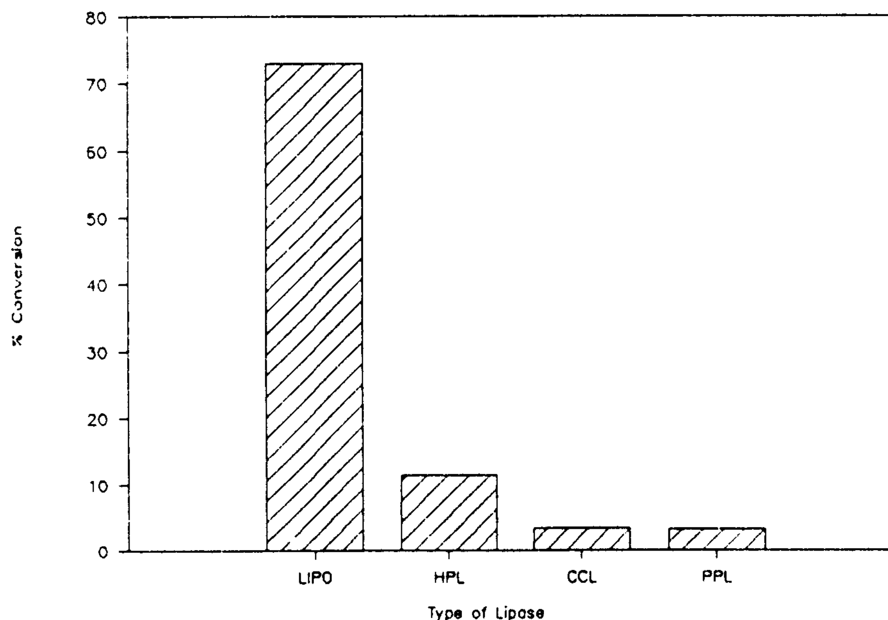


Figure 3 Effect of lipase on rate of transesterification.

oil and n-butanol in a 1 : 1 proportion at room temperature without the solvent over a period of 24 h using lipozyme as a biocatalyst. The products of the transesterification consist of monoglyceride (MG), diglyceride (DG), and butyl ester (BE). Figure 2 clearly shows that the decrease in the TG content with time is associated with a corresponding increase in the DG, MG, and BE content of the reaction mixture, as expected.

Effect of Type of Lipase

Lipases from different sources were employed for the model reaction of 6-h duration. Among the lipases tested, conversions were faster and more complete using lipozyme, where yields to 75% could be achieved. The yields obtained using PPL and CCL were limited only to 4%, whereas for HPL, it could reach 10% (Fig. 3).

Effect of Alcohol Chain Length

As reported earlier,[16] in the present work, the effect of the alcohol chain length of various primary alcohols with different carbon numbers ranging from $n = 3$ to $n = 6$ on the lipase activity was examined using the same model reaction for 6 h (Table I). The substrate affinity of lipase increased from n-propanol and reached a maximum to n-butanol and decreased substantially further up to n-hexanol.

Effect of Solvent

In general, the catalytic activity of enzymes diminishes as the polarity of solvent increases.[17] The logarithm of the partition coefficient (log P) of a given solvent between a standard octanol–water two-phase system was introduced as a

Table I Effect of Alcohol Chain Length on the Transesterification of Castor Oil and Different Alcohols at 30°C

Time (h)	Triglyceride Percentage			
	n-Propanol	n-Butanol	n-Pentanol	n-Hexanol
0	100.0	100.0	100.0	100.0
1	86.8	73.7	87.9	88.2
2	73.7	47.4	75.9	76.5
4	44.1	30.0	39.4	66.6
6	35.3	26.8	34.7	50.7

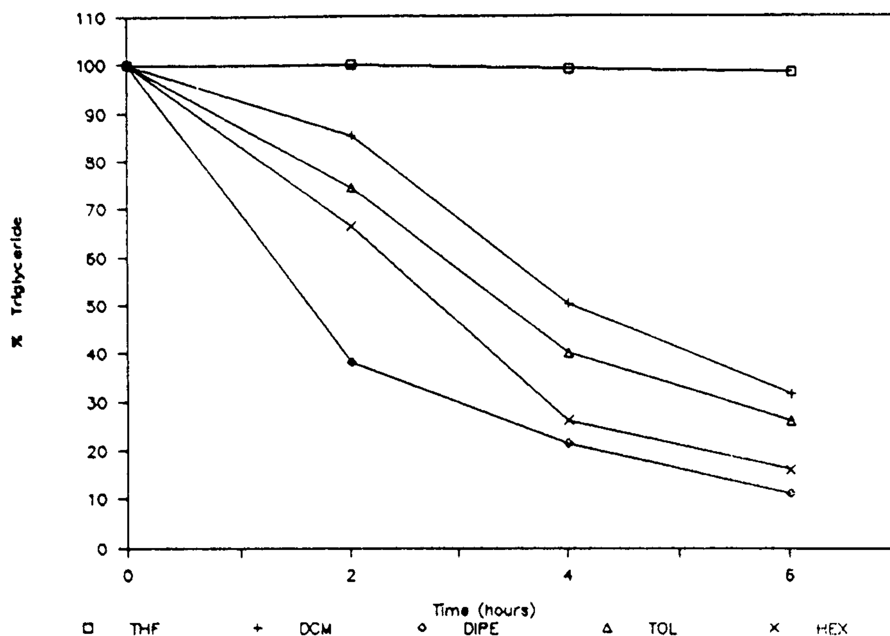


Figure 4 Effect of solvent on rate of transesterification.

quantitative measure of solvent polarity.[18] Generally, enzyme activity is relatively low in hydrophilic solvents having log $P < 2$, is moderate in solvents having a log P between 2 and 4, and is high in hydrophobic solvents having log $P > 4$.

In the present work, the polarity of the solvent played the most crucial role on the course of the model transesterification reaction of 6-h duration. It was observed that enzyme activity increases with an increasing log P value of the solvent, with diisopropyl ether being the exception (Fig. 4).

Higher rates were observed with hydrophobic solvents such as hexane having log $P > 2$, while low conversions resulted in solvents such as tetrahydrofuran with log $P < 2$. Diisopropyl ether was found to be the best suitable solvent.

Table II Effect of Temperature on the Transesterification of Castor Oil and *n*-Butanol

Time (h)	Triglyceride Percentage at Different Temperatures				
	20°C	25°C	30°C	40°C	50°C
0	100.0	100.0	100.0	100.0	100.0
1	86.1	83.7	73.7	70.6	67.9
2	72.3	67.5	47.4	41.4	35.7
4	64.2	51.3	30.0	28.1	26.4
6	59.9	44.2	26.9	24.3	22.5

Effect of Temperature

All chemical reactions are affected by temperature, and enzyme-catalyzed reactions provide no exception. The model reaction was carried out for 6 h at five different temperatures, namely, 20, 25, 30, 40, and 50°C (Table II). As expected, it was observed that the rate of the reaction increases with increase in temperature, resulting in the proportionate increase in the diglyceride and monoglyceride content.

IR Spectroscopy

The IR spectra of urethane oils show a characteristic broad band at 3300 cm^{-1}, indicating the presence of residual hydroxyl groups at the end of the second step. The presence of a medium band due to aromatic —CH stretching at 3010–3080 cm^{-1} and a weak band due to urethane carbonyl at 1710–1740 cm^{-1} confirm the formation of urethane linkage. The presence of a shoulder band at 3350 cm^{-1} due to —NH stretching further confirms the formation of urethane linkage of urethane oil samples. The absence of a band at 2260–2280 cm^{-1} due to the isocyanate group ruled out

Table III Characterization and Film Properties of Urethane Oils

Sample No.	Diisocyanate (0.5 mole)	Precursor Composition in Step I				Molecular Weight (M_w)	OH Value (mg KOH/g)	Scratch Resistance (g)
		TG (%)	DG (%)	MG (%)	BE (%)			
1	TDI	12.32	33.86	12.94	40.88	2886	130	400
2	MDI	12.32	33.86	12.94	40.88	2506	156	500
3	TDI	9.57	16.22	23.83	50.38	2143	142	600
4	MDI	9.57	16.22	23.83	50.38	2140	177	700
5	TDI	0	2.6	42.2	55.2	1827	170	700
6	MDI	0	2.6	42.2	55.2	1701	198	800

the presence of diisocyanate impurities in the urethane oils.

^{1}H-NMR Spectroscopy

The ^{1}H-NMR spectra of urethane oils showed that the unsaturation of the oil part exhibited at δ 5.34 ppm remains unaffected due to the mild conditions used for the enzymatic transesterification step. The presence of a peak at δ 3.63 ppm due to —CH attached to the hydroxyl group ensures that most of the hydroxyl groups of the recinoleic acid part of the castor oil remain unchanged, leading to a conclusion that the more reactive primary hydroxyl groups of mono- and diglyceride must have reacted preferentially over the secondary hydroxyl group of castor oil. All other peaks of the oil part appear at their respective positions as detailed in the Experimental section.

Table III gives the details of characterization of urethane oils resulting from the reactions of TDI and MDI with a precursor of different compositions obtained by the transesterification of castor oil and n-butanol in 1 : 1, 1 : 2, and 1 : 3 mol ratios each over a period of 24 h (Step I). It is clearly evident that the hydroxyl value of urethane oil increases with increase in the MG % in the precursor, as expected. The urethane oils show a decrease in molecular weight with increase in the MG %. A glance at the hydroxyl values shows that MDI is less rective than is TDI; nevertheless, the MDI-based urethane oils show better scratch resistance. The urethane oils show good film properties such as applicability, flexibility, and impact resistance. Acid resistance is found to be good, whereas alkali resistance is found to be moderate for all the urethane oil samples.

CONCLUSIONS

Better control of the composition could be achieved using enzymatic transesterification. The degree of transesterification and the composition of the precursor are the controlling factors for the molecular weight and film properties of urethane oils. Urethane oils of a desired molecular weight with improved film properties could be synthesized using this approach. A chemoenzymatic approach will provide better applications because of the kind of stereoregularity imparted to urethane oil which is not observed otherwise in conventionally prepared urethane oils.

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