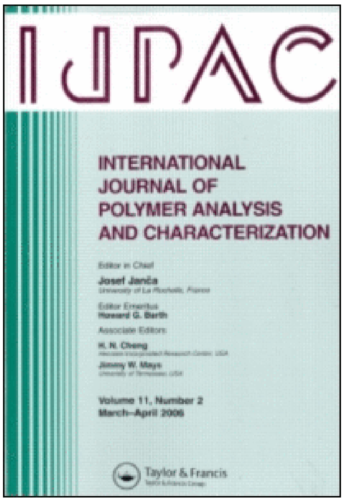

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Synthesis and Characterization of Castor Oil/Trimethylol Propane Polyol as Raw Materials for Polyurethanes Using Time-of-Flight Mass Spectroscopy

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Abstract: Recognizing the worldwide tendency towards biodegradable products, trimethylol propane (TMP) esters based on castor oil (CO) were synthesized, composition and properties were evaluated, and their potential as raw material for polyurethane preparation was assessed. The method of matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI TOF MS) and atmospheric pressure chemical ionization (APCI) under positive ion mode by the method of direct injection were used to determine the components of castor oil trimethylol alcoholysis product. Both the methods allowed unambiguous molecular mass determination of the intact ester molecules without any thermal degradation. The product was found to contain in the greatest amount monoricinoleate of TMP, diricinoleate of TMP, and triricinoleate of TMP and some quantity of triricinoleate of glycerol and unreacted trimethylol propane. APCI of the polyol was compared to that of castor oil. The MALDI TOF MS method described in this work is relatively simple, less time-consuming than the commonly used gas chromatographic method, and can be used to quantify various components of the polyol.

Keywords: Castor oil; Trimethylol propane; Polyol; MALDI MS

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INTRODUCTION

Castor oil (CO) is a naturally occurring monomer, which is triglyceride of ricinoleic acid containing three hydroxyl groups and three double bonds. Commercial castor oil consists of triglycerides that contain 90% ricinoleic acid residues and 10% nonfunctional acid residues, so that castor oil has effective hydroxyl functionality of 2.7.[1,2] The structure of castor oil is as shown in Figure 1.

The polyurethanes obtained from castor oil are typically water resistant and flexible due to the presence of a long fatty acid chain and lend themselves to thermosetting-type structures due to their tri-functional nature.[3–6] The long pendant chains of the fatty acids impart flexibility and hydrolysis resistance to the network, and the double bond present in the castor oil serves as a grafting center. Urethane polymers exhibit excellent abrasion resistance. They find applications as a polyol in the field of polyurethane foams;[7] Lyon et al.[8] and Lyon and Garrett[9] have described such polyols.

However, disadvantages in the use of castor oil include low hydroxyl number leading to inherently low modulus materials, a sluggish rate of curing of secondary hydroxyl groups,[10] and structural irregularity due to steric hindrances caused by the long pendant fatty acid chains during polyurethane formation, resulting in low tear strength.[11] Apart from this, the oils have low resistance to both oxidation and high-temperature treatment, and they readily undergo hydrolysis, particularly under the influence of natural hydrolases.[12]

To overcome these disadvantages, oil-based polyurethanes are mixed in the form of interpenetrating networks with other monomers like styrene, methacrylate, formaldehyde, etc.,[13,14] to improve their properties. They are also transesterified or alcoholyzed with polyhydroxy

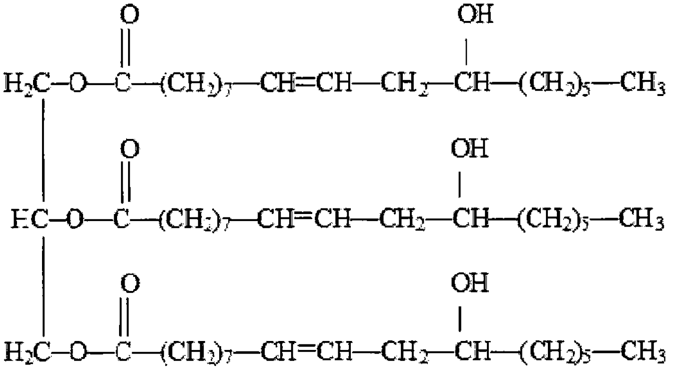

Figure 1. Castor oil structure.

alcohols thereby introducing reactive hydroxyl groups.[8,9,15–17] This process involves heating of oil with poly-hydroxy alcohols like glycerol, trimethylol propane, pentaerythritol, etc., at elevated temperatures and usually in the presence of basic catalysts like litharge (PbO), calcium hydroxide, calcium soaps, and sodium carbonate.[16,18,19] This is a random reaction and at equilibrium consists of different glycerides of varying functionality with respect to the hydroxyls and can be used to react with di-isocyanates for various applications.

Most of the literature published has illustrated the use of glycerol[14] for transesterification. However, glycerol, a component of the triglyceride molecule, is readily destructible at high temperatures. This disadvantageous property stems from the presence of hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule. This structural feature is conducive to the partial defragmentation of the molecule and the formation of unsaturated compounds. The compounds formed undergo polymerization, increasing the liquid's viscosity and resulting in the formation of precipitate particles. The problem can be solved by replacing glycerol with another polyhydric alcohol that does not contain β-hydrogen atoms, i.e., neopentyl glycol (NPG), trimethylol propane (TMP), or pentaerythritol. Although such alcohols also decompose at high temperatures, their thermal decomposition has a radical character and proceeds slowly.[20] Composition of these esters can be determined using gas chromatography[20,21] and matrix-assisted laser desorption ionization mass spectroscopy (MALDI MS).

MALDI MS is rapidly becoming a dominant analytical tool for the determination of molecular distribution of complex mixtures. At the onset, it was primarily used for the analysis of proteins and peptides, carbohydrates, and synthetic polymers. However, in recent publications, use of MALDI has been reported for determination of the fatty acid composition of palm kernel oil, palm oil, olive oil, soybean oil, and castor oil.[22–24]

The objective of the present work was to develop a fast and reliable method to detect and characterize the components of castor oil and TMP polyol and compare the characterization with that of castor oil using MALDI MS and LCMS.

EXPERIMENTAL SECTION

Materials Used

Castor oil was commercial grade purchased from the local market. It was dehydrated at 105°C in nitrogen atmosphere and characterized for hydroxyl value (148), acid value (2), and moisture content (0.379%). Trimethylol propane (Aldrich, Germany) was used as such and has hydroxyl value of 1255.98. HPLC grade dimethyl formamide was procured from Qualigens, India (HPLC grade).

Transesterification of Castor Oil

Polyol was synthesized from castor oil by reactions with trimethylol propane in a ratio of 1:3 in nitrogen atmosphere with catalyst litharge (0.1%). The reaction was carried out for approximately three hours in 1 L stainless steel jacketed reactor connected to a constant temperature bath/circulator through a solenoid valve and electronic relay supplied by Julabo Instruments (Germany; model-F-20VC/3, VC-5 and SC-12HT/10). The reaction temperature was 205 ± 0.1°C, and the completion of the reaction was checked by dissolving the sample in ethanol.

Characterization Using APCI

Polyol prepared from CO/TMP was analyzed using atmospheric pressure chemical ionization (APCI). It was carried out in a Thermo Quest Fannigan MAT LCQ model mass spectrometer. Samples were dissolved in methanol (HPLC grade) followed by filtration through 0.45 μm Millipore filter and were analyzed using APCI in positive mode by direct infusion without column. X-Caliber software was used, and the spectrum was taken in the range of 150–2000 m/z ratio.

Characterization Using MALDI MS

MALDI TOF measurements were performed with a Bruker Daltonics Ultraflex TOF/TOF MALDI Tandem TOF (time of flight) mass spectrometer. Acceleration voltage used was 25 kV with pulsed ion extraction (PIE). The positive ions were detected with reflectron mode (20 kV). The nitrogen laser (337 nm, 1-ns pulse width) operating at 4 Hz was used to produce laser desorption, and 125–225 single shot mass spectra were summed to give a complete spectrum. The sample was dissolved in dimethyl formamide (DMF) with a concentration of 10 mg/mL, and matrix material 2,5-dihydroxybenzoic acid (DHB, $M = 153\,g/mol$) was also dissolved in DMF. The sample solution and matrix solution were mixed in a ratio of 5:2 and electrolyte NaCl solution was added. Of these solutions, 0.5–1 μL was deposited onto a sample plate (stainless steel) and allowed to air dry.

RESULTS AND DISCUSSIONS

Figure 2 shows all the possible reaction products of CO and TMP transesterification reaction. The figure shows that the reaction products

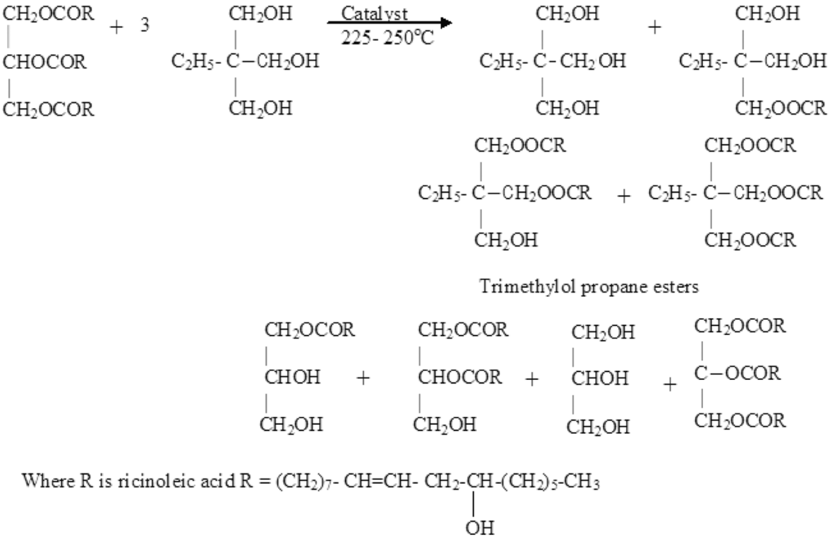

Figure 2. All the possible reaction products of transesterification of castor oil and trimethylol propane.

include esters of trimethylol propane and glycerol. As an exception, each of the reaction products contains three hydroxyl groups, as the ricinoleic acid (the major component of castor oil) has one hydroxyl group in its structure. Therefore all the components irrespective of their structure have functionality of 3.

Figure 3, shows mass spectra of the castor oil in methanol for the range 150–1500 m/z. Figures 4 and 5 show the mass spectra of CO/TMP polyol taken in methanol for the range 150–1500 m/z and the range 60–150 m/z respectively.

In the Figure 3 APCI/MS spectra of castor oil, the main peak appears at 932.8 m/z, representing triricinolein (RRR), the most abundant triacylglycerol of castor oil.[1,22,25] In addition to 932.8 m/z, triricinolein exhibited a dominating ion at 879.5 m/z. This ion could be rationalized as a loss of three water molecules from the extremely labile protonated molecular ion [M + H-3H_2O], where M refers to triricinolein. There is a low abundance of ion at 897.7 m/z, corresponding to the loss of just two water units. The water losses were derived in both cases from the hydroxylated fatty acid, 12 hydroxy-9-octadecenoic acid (ricinoleic acid). Although a solidated molecular ion at 955.4 m/z could be detected, its abundance was low, and even for this type of more stable molecular ion the loss of one water molecule was observed (935.3 m/z). Furthermore, two ions in the lower mass range, at 600.4 m/z and 599.3 m/z, were

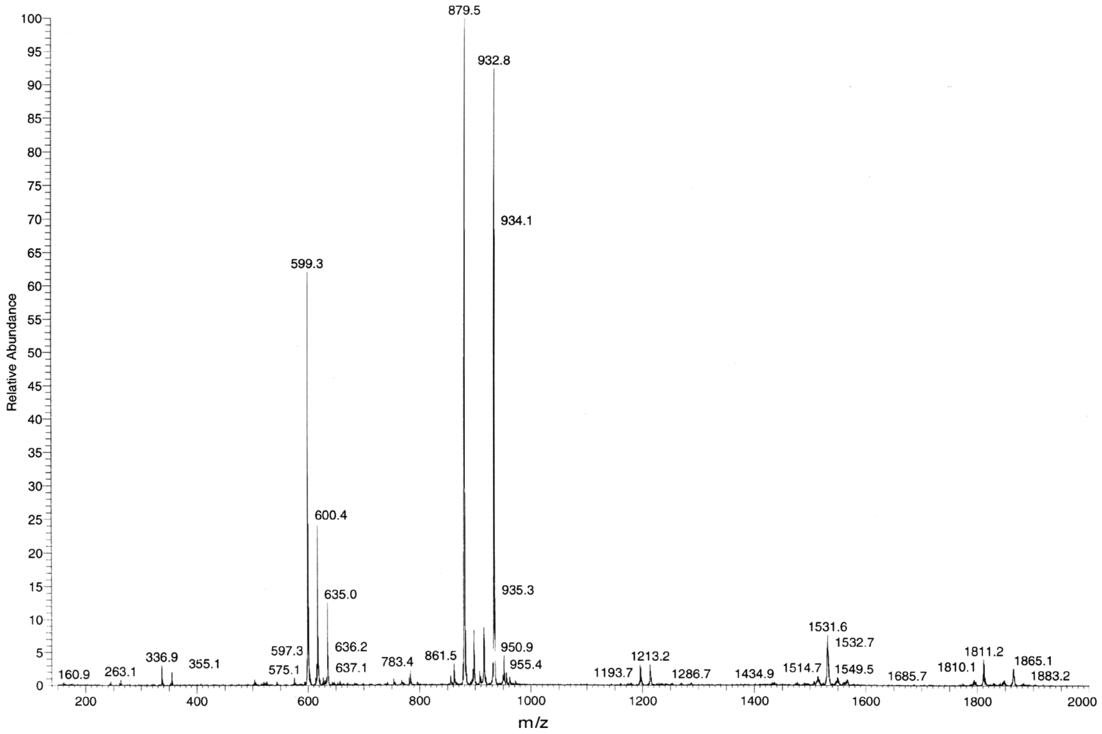

Figure 3. APCI mass spectra of castor oil taken in methanol for the range 150–2000 m/z.

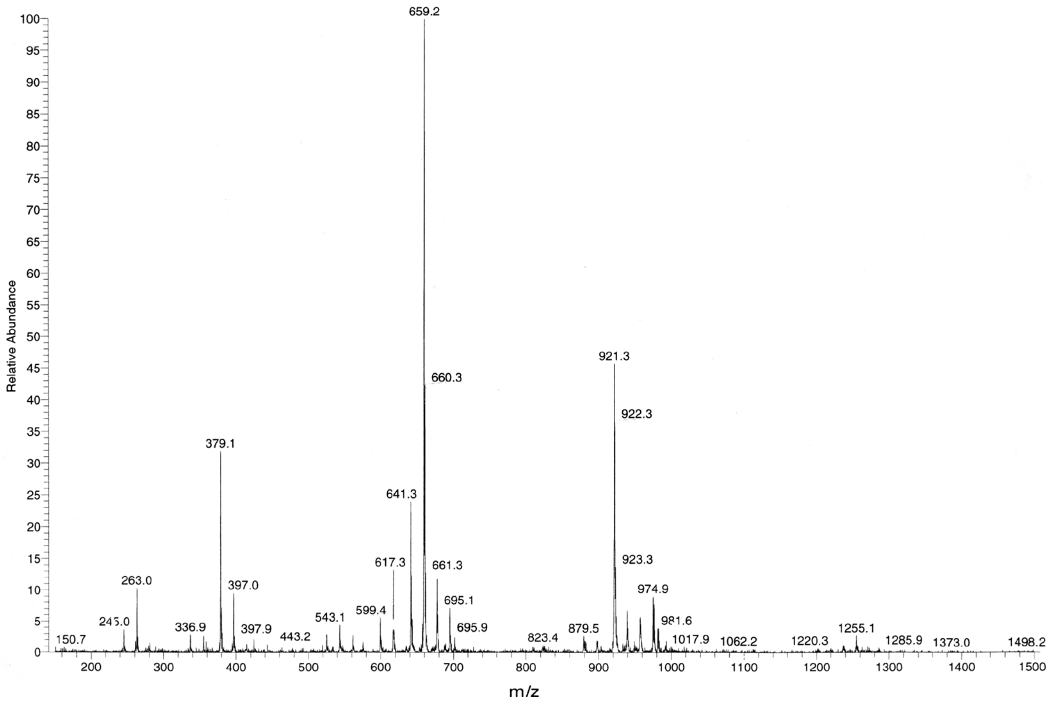

Figure 4. Mass spectra of the CO/TMP polyol taken in methanol for the range 150–2000 m/z.

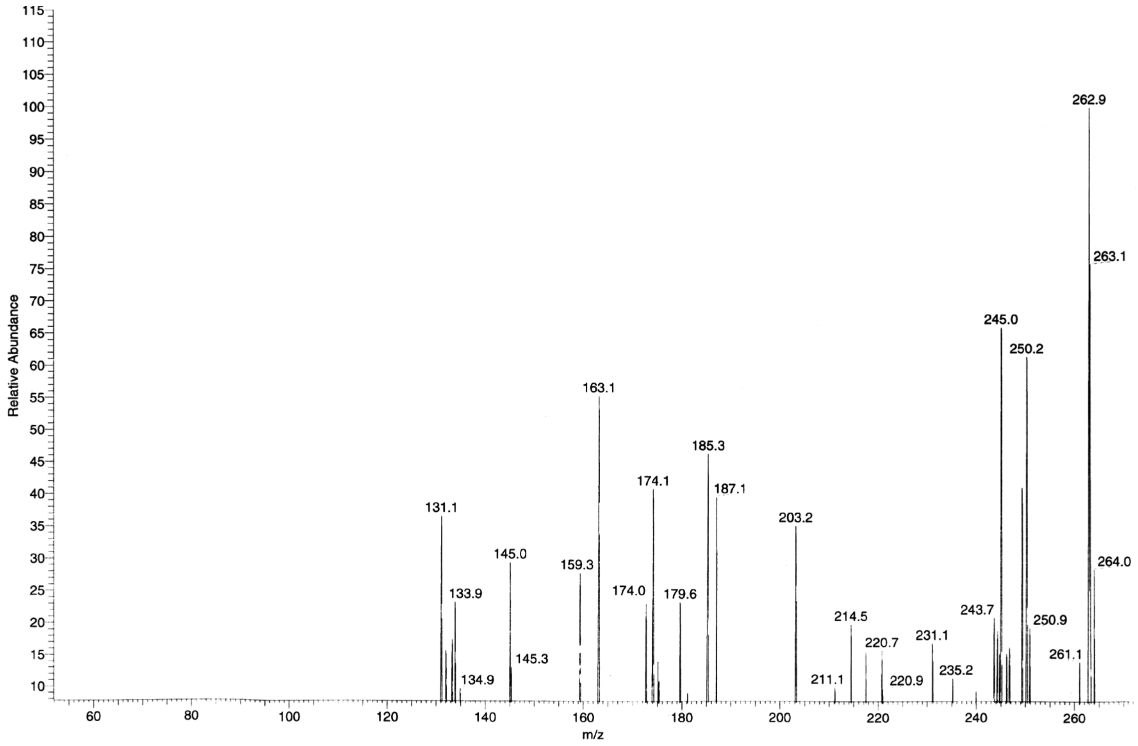

Figure 5. Mass spectra of the CO/TMP polyol by LCMS for the range 60–265 m/z.

Table I. Individual components identified in castor oil based on APCI-positive ion mode

LC fraction	$[M+H]^+$ or $[M+Na]^+$ observed	$[M+H]^+$ or $[M+Na]^+$ calculated	Δm (%)	Glyceride structure
1	955.4	956.75	0.141	$[M+Na]^+$
2	935.3	934.45	0.091	$[M+H]^+$
3	934.1	933.45	0.069	$[M]^+$
4	932.8	933.45	0.069	$[M]^+$
5	879.5	880.41	0.103	$[M+H\text{-}3H_2O]^+$
6	635.0	635.98	0.155	$[M\text{-}RCOOH]^+$
7	600.4	600.96	0.094	$[M+H\text{-}2H_2O\text{-}RCOOH]^+$
8	599.3	599.95	0.109	$[M\text{-}2H_2O\text{-}RCOOH]^+$

M denotes triricinolein (most abundant component of castor oil) molecule.

detected, these resulting from the loss of one ricinoleic acid molecule and subsequently one or two water molecules from the protonated diacylglycerol molecular ion. Table I illustrates the observed mass and calculated mass of all the components as identified by liquid chromatography mass spectroscopy (LCMS) for castor oil.

In the APCI/MS spectrum for CO/TMP polyol, for the range 150–1500 m/z, i.e., Figure 4, there are three high-intensity peaks: at 379.1 m/z, referring to monoricinoleate of TMP after removal of two molecules 659.2 m/z, for diricinoleate of TMP after removal of two water molecules, and 921.3 m/z, representing triricinoleate of TMP after removal of three water molecules. Medium intensity peaks at 695.1 m/z and 974.9 m/z represent intact molecules of diricinoleate and triricinoleate of trimethylol propane, respectively. A very low intensity peak at 981.6 m/z may be due to removal of one water molecule from triricinoleate of TMP and association of one Na^+ ion. A medium intensity peak at 641.3 m/z refers to diricinoleate of TMP after removal of three water molecules and the peak at 397.0 m/z refers to monoricinoleate of TMP after removal of one water molecule. The actual molecular weight is one less than the peak value of di- and triricinoleate of TMP. This may due to addition of H^+ during ionization of the sample. A medium-intensity peak at 617.3 m/z refers to diricinoleate of castor oil after removal of one water molecule, and a low-intensity peak at 879.5 m/z[25] refers to triricinoleate of glycerol after removal of three water molecules. A low-intensity peak at 599.4 m/z results from loss of one ricinoleic acid molecule and subsequently one or two water molecules from the protonated diricinoleate of glycerol.

In the spectra for CO/TMP polyol, for the range 60–265 m/z, i.e., Figure 5, a peak can be identified at 133.9 m/z, referring to unreacted

Table II. Individual components identified in CO/TMP polyol based on APCI-positive ion mode

LC fraction	$[M+H]^+$ observed	$[M+H]^+$ calculated	Δm (%)	Glyceride structure
1	974.9	975.53	0.064	$[T+H]^+$
2	921.3	921.49	0.020	$[T\text{-}3H_2O]^+$
3	879.5	880.41	0.103	$[M+H\text{-}3H_2O]^+$
4	695.1	696.09	0.145	$[DT+H]^+$
5	659.2	660.06	0.130	$[DT+H\text{–}2H_2O]^+$
6	641.3	642.04	0.116	$[T+H\text{-}2H_2O\text{-}RCOOH]^+$
7	617.3	617.97	0.109	$[M+H\text{-}H_2O\text{-}RCOOH]^+$
8	599.4	599.94	0.091	$[M+H\text{-}2H_2O\text{-}RCOOH]^+$
9	397.0	397.62	0.156	$[MT+H\text{–}H_2O]^+$
10	379.1	379.60	0.134	$[T+H\text{-}2RCOOH]^+$
11	263.0	263.44	0.167	$[RCOOH+H\text{-}2H_2O]^+$
12	262.9	263.44	0.204	$[RCOOH+H\text{-}2H_2O]^+$
13	245.0	245.43	0.175	$[RCOOH+H\text{-}3H_2O]^+$
14	133.9	134.17	0.201	TMP

T refers to triricinoleate of TMP, DT refers to diricinoleate of TMP, MT refers to monoricinoleate of TMP, and M refers to triricinoleate of glycerol.

TMP in the system. But no peak is visible at near 92 m/z, indicating that the presence of glycerol is completely ruled out. Table II illustrates the observed mass and calculated mass of all the components as identified by APCI for castor oil/ trimethylol propane polyol.

In the MALDI TOF mass spectrum for CO/TMP polyol, for the range 0–1000 m/z, i.e., Figure 6, there are three high-intensity peaks: 379.402 m/z, 421.447 m/z, 701.744 m/z. Peaks at 379.402 m/z and 421.447 m/z are for monoricinoleate of TMP. A peak at 379.402 m/z is after removal of two water molecules, and a peak at 421.447 m/z is due to sodiation and removal of one water molecule. A medium-intensity peak at 437.435 m/z is due to sodiated monoriciinoleate of TMP. A high-intensity peak at 701.744 m/z is due to sodiated diricinoleate of TMP after removal of one water molecule, and a medium-intensity peak at 717.730 m/z refers to sodiated diricinoleate of TMP. A low-intensity peak at 998.064 and 982.102 m/z refers to sodiated triricinoleate of TMP as such and after removal of one water molecule, respectively, and at 940.066 m/z refers to triricinoleate of TMP after removal of two water molecules.

A peak at 333.088 m/z may be due to sodiated methyl ricinoleate, commonly found in fatty acid methyl esters (FAMEs) from castor oil. A peak at 263.295 m/z is due to sodiated ricinoleic acid after removal

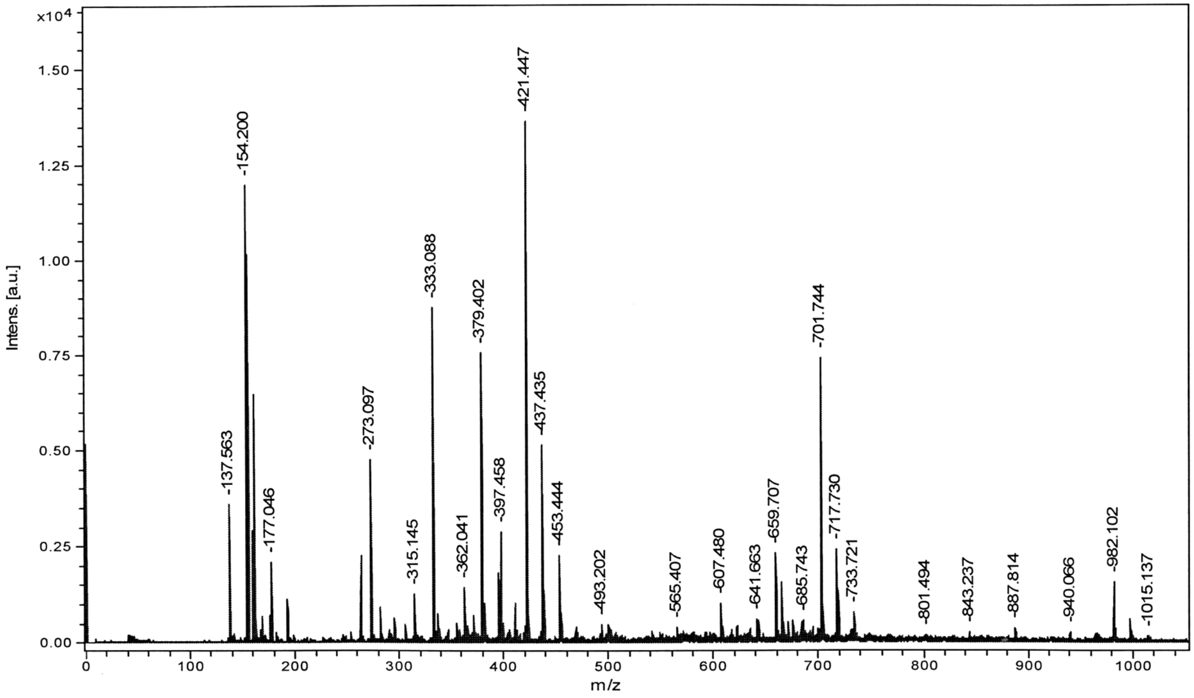

Figure 6. Mass spectra of the CO/TMP polyol by MALDI for the range 0–1000 m/z.

Table III. Individual components identified in CO/TMP polyol based on MALDI MS in positive ion mode

MALDI MS fraction	$[M+H]^+$ observed	$[M+H]^+$ calculated	Δm (%)	Glyceride structure
1	998.064	998.839	0.077	$[T+Na]^+$
2	982.100	980.823	0.130	$[T+Na\text{-}H_2O]^+$
3	940.066	939.508	0.059	$[T\text{-}2H_2O]^+$
4	717.730	718.382	0.090	$[DT+Na]^+$
5	701.744	700.366	0.196	$[DT+Na–H_2O]^+$
6	665.183	664.335	0.127	$[DT+Na–3H_2O]^+$
7	659.707	660.06	0.053	$[DT+H–2H_2O]^+$
8	641.663	642.04	0.058	$[T+H\text{-}2H_2O\text{-}RCOOH]^+$
9	622.429	623.016	0.094	$[T\text{-}3H_2O\text{-}RCOOH]^+$
10	622.429	622.232	0.031	$[M+Na\text{-}2H_2O\text{-}RCOOH]^+$
11	607.480	604.216	0.540	$[M+Na\text{-}3H_2O\text{-}RCOOH]^+$
12	437.435	437.929	0.112	$[MT+Na]^+$
13	421.447	419.912	0.365	$[MT+Na\text{-}H_2O]^+$
14	397.458	397.620	0.040	$[MT+H\text{-}H_2O]^+$
15	379.402	379.60	0.052	$[T+H\text{-}2RCOOH]^+$
16	333.088	335.795	0.859	$[RCOOCH_3+Na]^+$
17	315.145	317.779	0.829	$[RCOOCH_3\text{-}H_2O+Na]^+$
18	263.295	262.438	0.326	$[RCOOH\text{-}2H_2O]^+$
19	155.189	157.17	1.260	$[TMP+Na]^+$

T refers to triricinoleate of TMP, DT refers to diricinoleate of TMP, MT refers to monoricinoleate of TMP, and M refers to triricinoleate of glycerol.

of one water molecule. Table III lists all the components identified using MALDI MS spectra along with the observed mass and calculated mass.

In the two analyses, i.e., LCMS and MALDI MS, most of the peaks are common, indicating the presence of esters of trimethylol propane and glycerol. The intensity of the peaks varies because of the inherent difference in sample preparation. APCI gives a fair idea about the presence or absence of the different components but it cannot be used to quantify the different species present in the system. Therefore, MALDI was used to find the mass fraction of different components present in the system.

To calculate mass fractions of various components, total peak intensity was calculated for each component (by adding peak intensities of the same component shown at different m/z value, as identified in Table III). Mass fractions of various components present in the system as calculated using MALDI MS are: tri-ricinoleate of glycerol 2.98%, mono-ricinoleate of TMP 59.0%, di-ricinoleate of TMP 27.92%, tri-ricinoleate of TMP 4.96%, and unreacted TMP 5.13%. The hydroxyl value of polyol calculated from the above composition was 376.4 mg KOH/g, weight-average molecular weight was 521.05/mole, and moisture content using Karl Fisher titration was 0.81%.

CONCLUSION

This study has demonstrated that MALDI MS can be used to determine the composition and hydroxyl values of oil-based polyol if the components of the system are well identified and peaks can be assigned properly. This method can be used in conjunction with analytical techniques for greater reliability.

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