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Aliphatic amines vapours detection by quartz crystal microbalance sensor

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ABSTRACT

Polymerized castor oil based quartz crystal microbalance (QCM) sensors are fabricated for the detection of aliphatic amines vapours. The sensors are fabricated by solution dip-dry method followed by heating at 100 °C under argon atmosphere to get cross linked film on QCM surface. A series of sensors with various weight percentages of benzoyl peroxide added to the solution are fabricated for the optimization of the sensitivities of the polymeric films. It is found that the sensor fabricated with a solution having 1.40% (w/v) of benzoyl peroxide has high sensitivity for vapours of organic compounds and are very effective for aliphatic amines vapours. The adsorption of the vapours to the surface of the QCM sensor is determined by the frequency shift of QCM. The frequency shift linearly increases with the gas vapour concentrations from 5 to 250 ppm at room temperature. The sensitivity-values of methylamine, ethylamine, tert-butylamine, diethylamine, triethylamine and ammonia vapours are 0.917, 0.657, 0.655, 0.543, 0.407 and 0.397 Hz/ppm respectively. The structure of the polymeric film is studied by FTIR spectra. The surface morphologies of the QCM sensor before and after gas adsorption are characterized by AFM, which indicates mild swelling of the surface after adsorption and it is reversible.

1. Introduction

Castor oil is the triglyceride of fatty acids with ricinoleic acid (12-hydroxy-cis-9-octadecenoic acid) as the major constituent. Two reactive sites of castor oil are the double bond and the hydroxyl group of the unsaturated fatty acid and the acid is connected to the glycerol through the ester group. The structure of castor oil is given in Fig. 1.

The castor oil finds many bulk uses for industrial products. The oil is used to synthesize biodegradable cross linked polyurethane elastomers for the potential applications in soft-tissue engineering and elastomeric implants [1]. Its trihydroxyl structure helps in producing highly cross-linked polyurethane systems [2]. These triglycerides form epoxides, which can also be polymerized using chemical modification methods [3]. The triglyceride molecules are ester of fatty acid with glycerol. Many of which have sufficient amount of unsaturated fatty acid which are important for the production of cross-linked polymers. These triglycerides have been used in the synthesis of crosslinked polymers via two approaches (i) vinyl polymerization of internal double bonds and (ii) condensation polymerization of —OH groups in triglycerides using isocyanate or dibasic acid [4].

Castor oil is used in the synthesis of interpenetrating polymer networks of polyurethane, adhesive for metal-metal bonding, paint for surface coating, printing ink, etc. [5–7]. As the viscosity of castor oil is very high, it is also useful as a component in blending lubricants. Hydrogenated castor oil is used in cosmetics, hairdressing, ointments, preparation of hydrostearic acid and its derivatives. It is also used in the preparation of brake fluids, soaps, lubricants, paints, varnishes and motor oils for high speed automobile engines [8]. There are very few uses of castor oil as a fine chemical. We have attempted to prepare a cross linked polymer film of castor oil on quartz crystal microbalance (QCM) surface for the detection of organic vapours. It is noted that it is very effective for detection of aliphatic amines without having any acid groups in the polymer back bone.

From the literature, it is found that polyvinylpyrrolidone (PVP) coated QCM is used for the detection of ammonia, methylamine, ethylamine, n-propylamine, iso-propylamine and n-butylamine [9]. PANI and PANI–TiO_2 nano-composite coated QCM sensor is sensitive for the detection of trimethylamine and triethylamine

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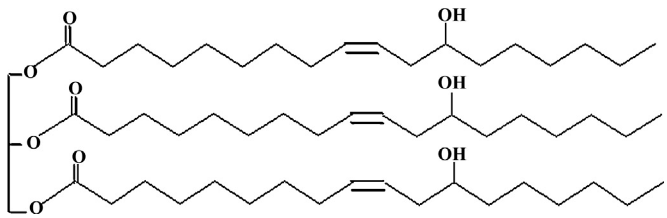

Fig. 1. The chemical structure of castor oil.

[10,11]. The QCM with thin PANI in the state of emeraldine base (PANI/EB) film is developed for the detection of methylamine, dimethylamine, trimethylamine and triethylamine vapours in air [12]. Synthetic polypeptides with conducting polymers on a quartz crystal microbalance sensor is used for the detection and identification of VOCs such as acetic acid, butyric acid, ammonia, dimethyl amine, benzene, chlorobenzene and their mixtures [13]. The TiO_2/PAA films are highly effective in capturing amine odours, and the ambient ammonia concentration [14]. In parallel efforts, many systems have been developed for detection of NH_3 using polyacrylic [15], electrospun PDPA/poly(methyl methacrylate) (PMMA) nanofibers [16], Graphene/PANI [17], copper biphenylbis(phosphonate) [18], Pd^{2+} doped ZnO nanotetrapods [19], Electron beam-evaporated Ta_2O_5 film, etc. [20].

In our previous study, we have polymerized the linseed oil using benzoyl peroxide as the initiator for the detection of volatile organic compounds such as o-xylene, p-cresol, benzene and toluene [21], though the sensitivity of sensors towards organic amines are found to be poor. Incidentally, with polymer film prepared from castor oil presented in this study, the sensitivity is very high for the detection of organic amines. The presence of —OH group in the triglycerides chain of the castor oil possibly has introduced this remarkable property of detection of amines without having any acid group in the chain. This shows that a small change of structure of triglycerides may introduce a new class of the detection system.

Here in this paper, we report the performance of QCM sensors with polymerized castor oil for the detection of organic vapours. The polymerization process is optimized for best detection by using different percentage of benzoyl peroxide in the solution. The shifts of frequencies of the QCM sensors with different concentrations of vapours are measured. The sensitivity and selectivity of the sensors are determined from the least square parameters of the calibrated curve.

2. Experimental

2.1. Reagents and materials

Castor oil was purchased from Sigma-Aldrich. The benzoyl peroxide, chloroform, methylamine, ethylamine, tert-butylamine, diethylamine, triethylamine and ammonia were purchased from E.Merck, India. All the chemicals were used without any further purification. The 10 MHz AT-cut quartz crystal microbalance crystals with silver electrodes on both sides were purchased from the local market. A laboratory made setup was used for the frequency measurement of the quartz crystal.

2.2. Coating of QCM surface

The quartz crystals were rinsed with ethanol followed by deionised water before using for fabrication. The polymerization of castor oil was carried out by using benzoyl peroxide as initiator and chloroform was used as solvent. A series of solution were prepared with concentrations of 0.50, 0.80, 1.00, 1.40, 1.80 and 2.20 (w/v%) of benzoyl peroxide with castor oil. The compositions of the solutions prepared for coating are given in Table 1. The QCM wafers were manually dipped in the solution. The sensors were numbered as CB 1, CB 2, CB 3, CB 4, CB 5, and CB 6. The sensors were prepared with approximately 5-6 kHz thickness loading. The thin film on the surface of the QCM wafers was formed after the evaporation of the organic solvent. Then the films were dried at room temperature followed by drying in hot air oven at 100 °C for 2 h in the presence of argon. A free radical polymerization reaction takes place on the surface of the QCM.

Table 1
Chemical composition of precursor solutions.

Sample ID	Castor oil (v/v%)	Benzoyl peroxide (w/v%)	Chloroform (v/v%)
CB 1	4.70	0.50	94.80
CB 2	4.75	0.80	94.45
CB 3	4.80	1.00	94.20
CB 4	4.85	1.40	93.75
CB 5	4.90	1.80	93.30
CB 6	4.95	2.20	92.85

Table 2
Analytical characteristic parameters of polymerized castor oil fabricated sensors to the volatile organic vapours.

Sl no.	Volatile organic vapours	Standard deviation (S.D.)	Relative standard deviation (R.S.D)%
1	Methylamine	3.42	0.39
2	Ethylamine	5.99	0.90
3	Tert-butylamine	3.46	0.61
4	Diethylamine	3.62	0.76
5	Triethylamine	3.50	1.23
6	Ammonia	5.34	3.19
7	Dichloromethane	5.03	4.21
8	Chloroform	7.14	6.62
9	o-Xylene	5.06	5.61
10	Ethanol	5.44	6.50
11	Toluene	3.50	6.41
12	Benzene	4.20	9.22
13	Acetone	3.72	8.48
14	p-Cresol	2.82	47.14
15	m-Cresol	2.54	48.56

2.3. Experimental procedure

The fabricated sensors were placed in a sealed Teflon chamber of 100 ml volume. The different concentrations of the organic vapours were injected into the sensor chamber through glass syringe. The constant force of the injected vapour into the sensor chamber was

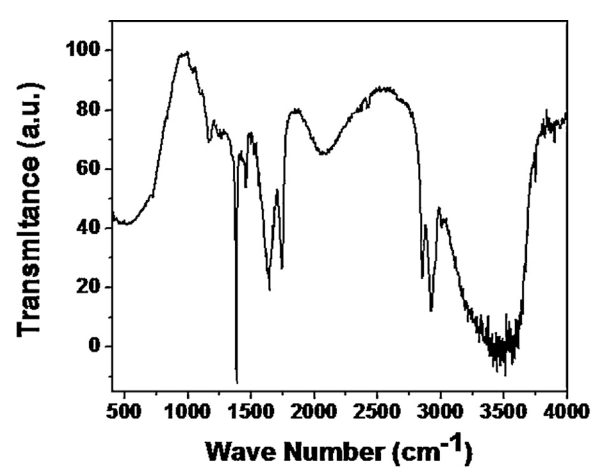

Fig. 2. FT-IR spectra of polymerized castor oil film.