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SHORT COMMUNICATION

Fluorinated Epoxy Resins-based Sorbent Coating Materials for Quartz Piezoelectric Crystal Detector

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ABSTRACT

Fluorinated epoxy resins were synthesised and evaluated as sorbent coating materials for the detection of organophosphorus compounds using quartz piezoelectric crystal detector. These resins were prepared by reacting excess of epichlorohydrin with each of or in combination of fluorinated diols, ie, α, α, α', α' tetrakis (trifluoromethyl) 1,3 benzene dimethanol (TTFMBD), 4,4′ bis-2-hydroxy hexafluoro isopropyl) biphenyl (BHHFIBP), 4,4′ dihydroxyocta fluorodiphenyl (DHOFDP) and 2,2,3,3,4,4 hexafluoro 1,5 pentanediol (HFPD) in the presence of sodium hydroxide at reflux temperature. These polymers were extracted in organic solvents and dried. Each of these fluoroepoxy resins were coated over quartz piezoelectric crystal by solution-casting method and tested using dimethylmethyl phosphonate (DMMP) as model compound. Change in the frequency (ΔF) of quartz piezoelectric crystal oscillator was recorded. Sensitive and potential fluorinated epoxy resins, ie, diglycidylethers (DGE) of HFPD-TTFMBD (in the molar ratio 6:4) and DGE (HFPD-BHHFIBP in the molar ratio 4:6) were characterised by viscosity, number average molecular weight (Mn), epoxy equivalent, infrared spectroscopy, and thermal stability.

Keywords: Fluoroepoxy resins, sorbent coating material, detection, organophosphorus compounds, piezoelectric detector, fluoroepoxypolymers, coating material, crystal detector

1. INTRODUCTION

The use of piezoelectric device as a chemical vapour sensor typically requires the application of a sorbent coating material as a thin film on the surface of a quartz crystal. Ideally, this material will specifically and selectively sorb the vapours of interest to provide a sensitive sensor. Due to sorption of foreign substance on its surface, frequency of piezoelectric crystal is decreased. This variation in frequency (ΔF) of piezoelectric crystal may be calculated[1] using Sauerbrey's equation as

$$\Delta F = -2.3 \times 10^6 . F^2 (Ms/A)$$

where, ΔF is the basic frequency of the piezoelectric crystal, Ms is the mass (g) of sorbent coating material deposited on the crystal surface, and A is the area (cm^2) of the quartz piezoelectric crystal over which coating was applied.

In the initial stages, stationary phase material used in gas chromatography, inorganic metal salts, and complexes were used as sorbent coatings for the detection of toxic organophosphorus compounds[2-3]. These organophosphorus compounds have already been used as pesticides, insecticides, and chemical warfare agents. However, these coatings were found to be unstable. Polymers offer a number of advantages as sorbent materials for the detection of organic

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compounds. Polymers are stable and diffusion of absorbed vapours within the material is quite rapid, provided the glass-to-rubber transition temperature (T_g) is below the operating temperature of the sensor. Polymers suitable as sorbent materials for quartz piezoelectric crystal detector and capable of interacting with the target vapours have already been reported in the literature, particularly polymers like polyethylene maleate[4], fluoropolyol[5], polymers modified by incorporating hexafluoro-2-propanol (HFIP) and hexa-fluorobisphenol-A, respectively, eg, polystyrene, polyisoprene[6], and polysiloxane[7]. Among these polymers, fluoropolyol was found to be the most selective and sensitive material for the detection of organophosphorus compounds (chemical warfare agents) using surface acoustic wave (SAW) sensors. However, synthesis of fluoropolyol is very difficult since it involves use of hexafluoroacetone, which is a highly moisture-sensitive toxic gas at ambient temperature[8]. Therefore, an attempt was made to synthesise alternate fluoroepoxy polymers which are simple to prepare, cost-effective, and give response against organophosphorus compounds equivalent to fluoropolyol. This work, reports the synthesis, characterisation, and evaluation of fluorinated epoxy resins as sorbent materials for the detection of organophosphorus compounds using DMMP as model organophosphorus compound and quartz piezoelectric crystal detector.

2. EXPERIMENTAL PROCEDURE

Chemicals required for the present study, ie, TTFMBD, DHOFDP (Acros, UK), BHHFIBP, HFPD (Lancaster, UK). Epichlorohydrin, DMMP (Fluka, Switzerland) were procured from trade and used as received.

2.1 Synthesis of Fluoroepoxy Resins

Fluoroepoxy resins were synthesised by reacting excess of epichlorohydrin with each of or in combination with fluorinated diols, ie, TTFMBD, DHOFDP, BHHFIBP, and HFPD in the

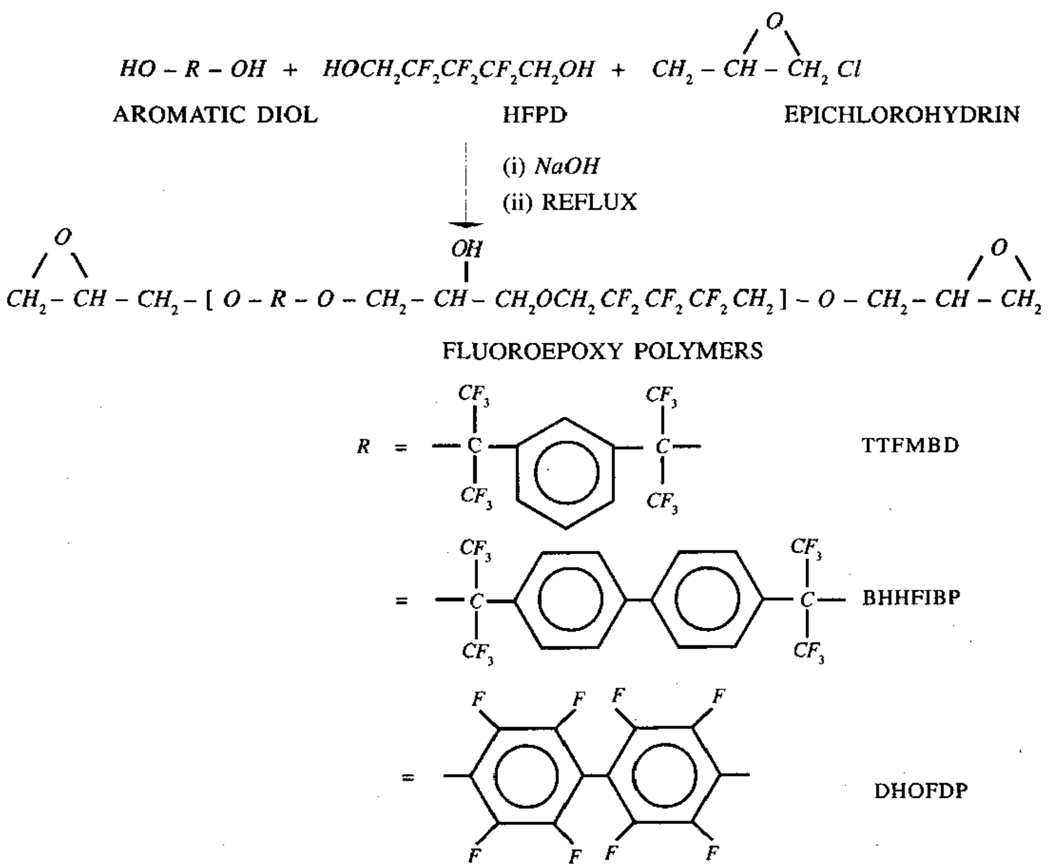

Figure 1. Synthesis of fluoroepoxy resins

presence of sodium hydroxide under reflux[9]. The reaction scheme is given in the Fig. 1. These polymers were extracted in organic solvents like benzene, acetone or DMF, etc and dried.

2.2 Characterisation

These fluoroepoxy resins were characterised by viscosity (at 30 °C in acetone), Mn (Knauer-Germany vapour pressure osmometer), IR (400-4000 cm^{-1} Nicolet-FTIR) and epoxy equivalent were determined (equivalent per 100 g) by reacting the resin in pyridine hydrochloride with alcoholic sodium hydroxide using phenolphthalein as indicator[9]. Thermal stability[10] was measured by determining per cent weight loss at 150 °C for 3 h.

2.3 Crystal Coating

The piezoelectric crystals used were AT-cut spherical quartz crystals of 7 mm diameter and 0.2 mm thickness with a basic resonant frequency of 10 MHz and were provided with circular gold electrodes on both the sides. Both surfaces of the crystal were coated with each polymer solution in acetone (10 mg/10 ml) using a microsyringe by solvent evaporation technique. The amount of coating was about 7.0 µg (after drying at 100 °C for 2 h and 1.0 mm mercury of vacuum) which was estimated from the frequency change after coating according to Sauerbrey's equation.

2.4 Apparatus & Method of Measurement

Figure 2 shows the experimental setup of a quartz piezoelectric crystal detection system. The quartz piezoelectric crystal was housed in a glass cell. The input of this cell was connected to the vapour generator-(Graseby Analytical, UK) and output was connected to an exhaust. The vapour generator which was calibrated using instrument

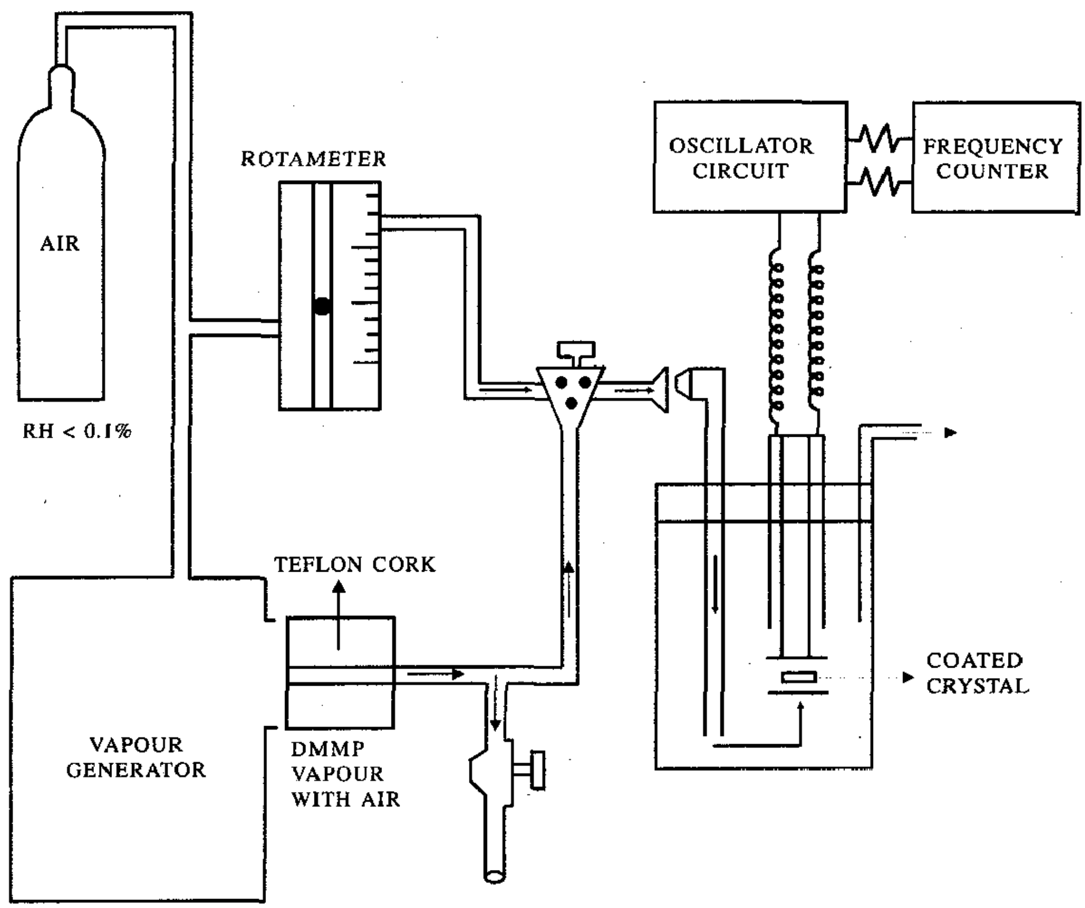

Figure 2. Test assembly for quartz piezoelectric crystal detector

AP2C-(Proengin-Etat Francais), provided vapours of DMMP of fixed concentration, followed by gas chromatography. The cell (housing the crystal) was fitted at the outlet nozzle of vapour generator and purged with zero air for about 5 min. The reading of the piezoelectric crystal oscillator frequency in the frequency counter was noted. This frequency was considered as baseline frequency. The piezoelectric crystal was exposed to DMMP vapours (concentration 17 mg/m^3). The frequency of the crystal started reducing and was recorded when stabilised as indicated by the frequency counter. The difference of this frequency from the baseline frequency was the frequency drift (ΔF in hertz), which was characteristic of sensing signal of the piezocrystal detector circuitory.

3. RESULTS & DISCUSSION

A total of 15 nos of fluoroepoxy resins were synthesised as given in the Fig. 1 and Table 1.

Table 1. Normalised vapours responses of fluoroepoxypolymers (Hz/3000 Hz/ 17 mg/m^3 of DMMP)

Epoxide/diglycidyl ether of diols	Feed composition m_2 (mole)	ΔF, Hz/3000 Hz
HFPD	—	8.0
TTFMBD=A	—	10.0
BHHFIBP=B	—	7.0
DHOFDP=C	—	9.0
HFPD + TTFMBD	0.2	11.0
HFPD + TTFMBD	0.4	25.0
HFPD + TTFMBD	0.6	18.0
HFPD + BHHFIBP	0.2	11.0
HFPD + BHHFIBP	0.4	—
HFPD + BHHFIBP	0.6	21.0
HFPD + DHOFDP	0.2	7.0
HFPD + DHOFDP	0.4	8.0
HFPD + DHOFDP	0.6	8.0
A+B+C with HFPD*	1.0	No response
A+B+C with HFPD**	1.0	No response

* Reaction in DMF (A+B+C : HFPD = 1:1)

** Reaction in *t*-amylalcohol

Table 2. Characteristics of fluoroepoxypolymers

Properties	DGE (HFPD-TTFMBD)	DGE (HFPD-BHHFIBP)
Relative viscosity	0.08	0.06
Colour	Light brown	Pale yellow
State	Liquid	Liquid
Average Mol wt	1760	1655
Weight loss at 150 °C 4.5 for 3 h	—	5.8
Epoxy equivalent (eq/100 g)	0.15	0.12
Response time	30 s	45 s
Recovery time	2-3 min	2-3 min
Stability	> 3 months	> 3 months

Each of these resins was coated over piezoelectric quartz crystal and exposed to DMMP vapours (concentration = 17 mg/m^3). Shift in frequency, ΔF was noted. Highest ΔF (25 Hz / 3000 Hz / 17 mg/m^3 of DMMP) was observed for [DGE (HFPD-TTFMBD)-I, in the molar ratio 6:4] indicating that it is the most sensitive and potential coating material for the detection of organophosphorus compounds using piezoelectric detector. Another fluoroepoxy resin, ie, [DGE (HFPD-B HHFIBP)-II, in the molar ratio 4:6] was the second best material as indicated by ΔF values (21 Hz/3000 Hz/17 mg/m^3). Fluoro-polymers have already been reported as useful materials for the detection of organophosphorus compounds using SAW sensors and for the use in sensor arrays. Sensitivity of these polymers for organophosphorus compounds may be ascribed due to hydrogen bonding interactions as reported in the literature[4-7]. These polymers have also been tested for minimum response time and this was found to be 30-45 s for DMMP (Table 2). Coating of these polymers applied to the piezoelectric crystal was stable and the crystal would detect DMMP for more than three months, and after that, the response started falling. It was also observed that if the chemical (to be detected) is taken off from the piezoelectric crystal detector, the oscillator is returned to its base frequency and it takes 2-3 minutes and this time is known as recovery time.

3.1 Characterisation

Fluoroepoxy resins are liquid at room temperature and pale yellow to light brown. Their relative viscosity in acetone at 30 °C is low (< 0.1) indicating oligomeric nature of these polymers. Average molecular weight of these polymers was found to be 1760 and 1655 for DGE (HFPD-TTFMBD)-I and DGE (HFPD-BHHFIBP)-II respectively, further supporting the oligomeric nature of these polymers. Epoxy equivalent of these polymers was found to be 0.15 and 0.12 equivalent/100 g of polymers for DGE (HFPD-TTFMBD)-I and DGE (HFPD-BHHFIBP)-II.

FTIR spectra of DGE(HFPD-TTFMBD)-I show peaks at 3396 cm^{-1} due to *-OH* group. Peaks at 2881 cm^{-1} and 2921 cm^{-1} may be due to *C-H* stretching. Aromatic $C = C$ stretching was also observed at 1456 cm^{-1} and 1652 cm^{-1}, indicating the presence of aromatic nuclei in these polymers. Further, peaks at 1222-1285 cm^{-1} indicate the presence of *C-F* bonds, whereas peaks at 1148 cm^{-1} show the presence of *C-O-C* group in these polymers.

Similarly, IR spectra of DGE (HFPD-BHHFIBP)-II show broad peaks between 1150-1193 cm^{-1} and 1221-1285 cm^{-1} due to the presence of *C-O-C* group and *C-F* bonds respectively in the polymer. Peaks at 3396 cm^{-1} and 2880-2930 cm^{-1} may be due to the presence of *-OH* group and due to *C-H* stretching. Presence of aromatic nuclei was also indicated by peaks at 1458 cm^{-1} and 1638 cm^{-1} due to $C = C$ stretching. Further, presence of epoxy group, *C-F*, *C-H*, and *C-O-C* peaks in FTIR spectra of fluoroepoxypolymers is in confirmity with the reported literature[9]. Thermal stability of these polymers was also determined and weight loss was 4-6 per cent at 150 °C for 3 h. Thermal stability may be attributed to the presence of aromatic unit in the epoxide structure[10].

4. CONCLUSION

Fluoroepoxypolymers DGE (HFPD-TTFMBD)-I and DGE (HFPD-BHHFIBP)-II were found to be potential coating materials for piezoelectric crystal detector for the detection of DMMP (organophosphorus compounds) as indicated by ΔF values (25 Hz and 21 Hz) using 10 MHz quartz piezoelectric crystal. The ΔF values achieved were 35 Hz when fluoropolyol was used as the coating material and sarin (actual organophosphorus compound) as target compound. Though ΔF values achieved were low but the advantages with these materials are their ease of preparation and low cost. Further, these materials are also used in the development of SAW devices and sensor arrays and ΔF values will increase manifold as given by Sauerbrey's equation, particularly when quartz crystals of higher frequency (100-400 MHz) were utilised.

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