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Novel hybrid nanocarbons/poly(dimethylsiloxane) composites based chemiresistors for real time detection of hazardous aromatic hydrocarbons

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ABSTRACT

Hybrid nanocarbons have been reported to have synergetic advantages in several mechanical and electrical applications. However, little is understood how two geometrically different nanocarbons can affect the response of a chemiresistive sensor. The study reports development of poly(dimethylsiloxane) (PDMS)/carbon nanotube (CNT) and nanocarbon black based novel chemiresistive sensors through a solvent free route. These PDMS based sensors demonstrated high sensitivity and reversible response against benzene, toluene, ethyl benzene and xylene (BTEX) under dynamic flow as well as under static vapour conditions. It was found that the sensing response had a strong correlation with the BTEX-PDMS interaction parameters (χ_{12}). However, such dependence was not observed at 3 wt% loading of CNT, due to CNT induced changes in the diffusion behavior of BTEX. CNT loading affected detection of each analyte differently; though, the principle component analysis using an array of four chemiresistors with different CNT content demonstrated distinct pattern only for benzene. Intriguingly, the sensitivity and the temperature coefficient of resistance of chemiresistors decreased; whereas, the detection range increased considerably with addition of CNT.

1. Introduction

Rapid detection of volatile organic compounds (VOCs) is desired to maintain their concentration within permissible limit and avoid exposure associated health hazards [1,2]. Chronic exposure of VOCs such as benzene, toluene, ethyl benzene and xylene (BTEX) poses serious health concerns such as skin and sensory irritation, carcinogenesis, mutagenesis, central nervous system depression and respiratory system damage [3,4]. There are varied sources of BTEX exposure which include petroleum products, consumer products, synthetic rubber, plastics, leather industry, insecticides and paints. They are also reported in exhaust gases as a result of wood and fossil fuels' incomplete combustion [3,5]. Such a wide extent of exposure along with severity of health consequences put a pressing need for development of fast responsive BTEX detection systems [6–8].

Different approaches can be used to synthesize sensors for the detection of BTEX and other VOCs [9]. They generally rely on chemical field effects, surface plasmon resonance, chemiresistivity, surface acoustic wave sensing, micro-electromechnical sensing and quartz crystal microbalance [7,10–15]. Chemiresistive sensors have distinct advantages of cost, response time and possibility of an easy integration into a chemiresistive array [16,17]. Electrical conductivity and a responsive polymer phase are two essential requirements for the development of chemiresistive sensors. Different thermoplastic and elastomeric matrices have been explored for this application. Kumar et al. have recently reported chemiresistive properties of several conducting polymer composites against different analytes [17,18]. They have reported that poly(caprolactone)/carbon nanotube (CNT) conductive composites can be effectively used for sensing polar analytes namely toluene, THF and chloroform [18]. By using layer by layer assembly, they also explored the suitability of latex based process for development of chemiresistive sensors and demonstrated that such composites are highly useful in sensing polar VOCs [19]. In a very interesting work, Taher et al. have reported a chemiresistor sensor for formaldehyde field detection, using Poly(methyl methacrylate)/graphene composites [20]. These studies as well as several other reports on the intrinsic sensing characteristics of nanocarbons, underscore the

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high potential of conducting nanocarbons for the development of novel chemiresistive sensors [16,21]. As a result, there is an increasing interest in the development of nanocarbon based sensors with fast response time, high sensitivity, selectivity, portability and process ease; however, so far little attention has been paid to the use of hybrid fillers and solvent-free route for the synthesis of polymeric chemiresistors [9,21,22]. Interestingly, there are emerging evidences that suggest that the use of hybrid fillers can improve the sensing response of chemiresistors; for example, Kaniyoor et al. have recently reported that graphene nanoplatelets and CNT hybrids can enhance sensitivity for hydrogen detection along with excellent stability and repeatability [23], and blend of SWCNT bundle layers with indium-tin oxide nanoparticles are reported to yield threefold sensitivity increase by Rigoni et al. [24]. Though both these studies relied on intrinsic response of hybrid filers and not much work is reported on the hybrid nanocarbons/polymer nanocomposites based sensors, it is understood that hybrid fillers in a polymer matrix might provide unique opportunity of controlling the CNT network and inter-tube interconnections and thus could be a route of designing advanced chemiresistors with improved detection range, sensitivity and detection limit.

Percolation of filler in a polymer matrix demands high loadings of conducting fillers. With the advent of nanofiller, the amount typically required to develop conducting composites has come down, however, it is still a major impediment in terms of process efficacy, stable conductivity and reproducible response. Use of hybrid nanofillers is a one of the effective techniques that has been used to entail synergistic advantages in terms of enhanced conduction and mechanical properties. Prasad et al. have reported exceptional synergy between the use of nanocarbons [25]. Recently, we have reported advantages of hybrid fillers and selective percolation in terms of better electromechanical response, higher conductivity, mechanical properties and positive temperature coefficient behavior [26–29]. These along with several other studies demonstrate that hybrid fillers can yield synergistic advantage in conductivity, mechanical properties and other properties of interest [30–34]. However, as stated above, little is understood how two geometrically different nanofillers would affect the sensing response of a chemiresistive matrix. Further, little attention has been paid to utilize solvent free polymer processing technologies that are energy efficient and can be easily up-scaled [35].

Melt compounding and shear compounding do not involve any solvent or toxic chemicals. These approaches can be effectively employed to develop conducting polymer composites. However, the percolation threshold in compounding techniques is much higher than in-situ polymerization or in sonication assisted solvent/emulsion dispersion. Innovative strategies such as hybrid fillers, functionalization or selective percolation can be used to achieve desired electrical conductivity at lower loading of filler as well as to improve desired functionality. Carbon nanotubes and conducting nano carbon black (NCB) are among the most promising materials for the development of conducting composites [9,18,28,36,37]. Poly(dimethylsiloxane) (PDMS) is an elastomeric matrix widely used for electronic and biomedical applications [38–40]. It can be easily processed and has good temperature & chemical resistance and elasticity. Karuwan et al. used PDMS and CNTs to develop a slow injection based microfluidic device [41] whereas, Kang et al. used poly(dimethylsiloxane) (PDMS) mold for CNT-network devices to develop DNA sensors. However, there is little research on the chemiresistive response of PDMS/nanocarbon nanocomposites particularly via a solvent free route [42].

This study reports development of PDMS based novel chemiresistive matrices using CNT/NCB hybrid fillers and shear compounding. The sensing response of these chemiresistors was tested against BTEX and the effect of CNT addition on sensing characteristics was investigated. An attempt has also been made to understand polymer-BTEX interaction, BTEX diffusion, positive temperature coefficient behavior and morphology.

2. Material and methods

2.1. Materials

Poly(dimethylsiloxane) was procured from M/s DJ silicone, China (Hardness = 60; density = 1.13 ± 0.05 g/cc) containing vulcanizator 2,5-dimethyl-2,5-bis(tert-butyl peroxy) hexane (0.65%). Nano carbon black (NCB) (size 50 nm, surface area 70 m^2/g, density 1.8 g/cc) was procured from M/s TA Corporation, MUMBAI, India. Carbon nanotube (Multiple walled, OD: 8–20 nm; Length: 1–2 um SSA: 130–180 m^2/g) was purchased from Otto Chemie Pvt Ltd, Mumbai India. Benzene, xylene, toluene and ethyl benzene used were of Analytical grade (purity > 99.9%) and was procured from M/s SD Fine chemicals, Mumbai.

2.2. Sample preparation

Conducting PDMS/NCB composites were prepared by putting 0.30 weight fraction of NCB in PDMS (M0) through shear compounding the mixture in Brabender Plasticordar (mixing time 20 min) and then 0.01(M1), 0.02 (M2) and 0.03 (M3) weight fractions of CNT were added (mixing time 10 min). The quantity of the components was carefully chosen considering the bulk density to assure proper filling of the mixing chamber (40 cc, 80% of the maximum capacity). The homogeneous mix obtained was cut into small pieces and compressed into sheets of size 12 × 12 cm^2 of 100 micron thickness using compression-molding machine at 150 kg/cm^2 for 30 min at 120 °C. Chemiresistors were crosslinked by exposing to gamma radiation in a gamma chamber for 100 kGy of absorbed dose. Irradiation was carried out under aerated condition using a gamma chamber (GC-5000) having Co-60 gamma source supplied by M/s BRIT, India. The dose rate of gamma chamber was ascertained to be 1.0 kGy/h using Fricke dosimetry prior to irradiation of the samples.

2.3. Mechanical characteristics, diffusion behaviour and Field Emission Scanning Electron Microscopy

For tensile strength measurements, at least five dumbbell shaped specimens were cut from composite sheets using a sharp edged steel die of standard dimensions. The thickness of the samples were determined to the nearest of 0.1 mm. The tensile strength and elongation at break were measured using a universal testing machine supplied by M/s Hemetek, MUMBAI, India at crosshead speed of 100 mm/min at room temperature. For sorption studies, radiation cross-linked composites were Soxhlet extracted for 12 h to extract any sol content using xylene as a solvent. The insoluble gel part was then dried initially under room conditions and later under vacuum at 40 °C. The dried composites so obtained was cut into uniform square pieces (1 cm × 1 cm) using a sharp edged die and used for swelling studies. Pre-weighed samples were placed in a 200-mesh stainless steel compartment and immersed in excess of solvent at the desired temperature. The swollen samples were periodically removed, blotted free of surface solvent using laboratory tissue paper, weighed on an analytical balance (accuracy 0.00001 g) from M/s AND, India, in stopper bottles and returned to the swelling medium. Measurements were taken until the samples reached constant weight (equilibrium swelling).

Field Emission Scanning Electron Microscopy (FE-SEM) studies