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Design of sensitive and selective sensing materials for ethanol detection

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ABSTRACT

Potential sensing materials for ethanol were selected using a directed approach that focussed on the chemical nature of the target analyte (ethanol) and design constraints of the application. Using this directed approach, one polymeric material, polyaniline (PANI), was chosen as the base case, which was subsequently modified by changing the functional groups on the PANI backbone. This resulted in three potential polymeric materials: PANI, poly (*o*-anisidine) (PoANI), and poly (2,5-dimethyl aniline) (P25DMA). These three polymers were then doped with different metal oxide nanoparticles: aluminum oxide (Al_2O_3), copper oxide (CuO), nickel oxide (NiO), titanium dioxide (TiO_2), and zinc oxide (ZnO). In total, twenty-six potential polymeric and nanocomposite sensing materials were evaluated for their sensitivity and selectivity to ethanol, with respect to methanol, acetone, and benzene, as typical interferents. Of these potential sensing materials, four polymeric nanocomposites had the required high sensitivity and selectivity towards ethanol for the application (transdermal ethanol detection).

KEYWORDS: gas sensors, polymeric sensing materials, polyaniline, dopants, ethanol detection

1. Introduction

Driving under the influence of alcohol is a major problem, despite strict laws for blood alcohol content (BAC) when driving [1]. The best way to reduce drinking and driving is to install an ignition interlock system into every vehicle, which is able to monitor a person's BAC while they drive [2]. This can be done with a transdermal (from the skin) ethanol sensor located in the steering wheel or with a wearable ethanol detection device that also monitors BAC through transdermal ethanol emission [3].

For this application, highly sensitive and selective sensing materials are required. The sensitivity of a sensor is related to the limit of detection (LoD), where the lower the LoD, the higher the sensitivity of the sensor. The selectivity is the ratio between the response of the target analyte (ethanol, in this case) and an interferent analyte. These are the two most important properties for sensing materials [4].

Polymeric sensing materials are ideal as sensing materials because they can be tailor-made to attract a specific gas analyte [5] and thus, have high selectivity. This can be done by modifying one or more side chains, adding a dopant (small amount of another material such as a metal oxide), or creating a copolymer [6]. Polymeric sensors work mainly at low temperatures (below 100 ºC) and are relatively inexpensive [7].

The addition of a metal or metal oxide nanoparticle dopant to a polymer, creating a polymer nanocomposite, can improve the sensitivity and/or selectivity of the polymeric sensing material. Furthermore, the addition of metal and metal oxide nanoparticles generally improves the thermal and mechanical properties of polymers [8] and the electrical properties of conductive polymers [9].

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By selecting appropriate polymers and metal or metal oxide dopants, it is possible to create polymeric sensing materials that have the sensitivity and sensitivity needed for a target application. This paper focuses on the steps for designing and evaluating potential polymeric sensing materials for ethanol detection, which can be used in a transdermal ethanol sensor to monitor a person's BAC.

2. Sensing material selection

Instead of using a trial-and-error approach, polymeric sensing materials can be selected through a directed approach that takes into consideration both the chemistry of the target analyte (ethanol) and the design constraints of the target application (transdermal sensor). This directed approach improves the efficiency and reduces the costs typically associated with the more common trial-and-error approach [10].

2.1. Sensing mechanisms for ethanol

The dominant sensing mechanisms with which ethanol will likely interact with a polymeric sensing material are determined based on the chemical nature of ethanol. Ethanol is a small (62.6 cm^3/mol), polar (1.69 D) molecule with a hydroxyl (-OH) group. This means that ethanol is able to hydrogen bond and therefore, a sensing material that is able to hydrogen bond would be ideal. This narrows down the polymeric materials to those containing N-H and O-H groups such as amines, alcohols, and carboxylic acids.

2.2. Design constraints

Design constraints encompass the required sensitivity and selectivity of the sensors, other sensing characteristics such as response and recovery times, the environmental conditions in which the sensors will be operated and stored, and the type of sensor onto which the sensing material will be used. Each constraint will limit further which polymeric materials can be used as an appropriate sensing material for the target application. A summary of the constraints for a transdermal ethanol sensor are listed in table 1.

Of these design constraints, the operational temperature and type of sensor affect the sensing material the most. The response and recovery times are more dependent on the type of sensor and the sensor electronics. The polymeric material must have a glass transition temperature well above the operational/storage temperatures. This is to ensure the polymer does not soften, which can affect the sensing properties. The minimum glass transition temperature will be set at 80 ºC to ensure the polymer stays in the glassy state.

The type of sensor also affects the sensing material. If a resistive sensor is being used in the application, a conductive sensing material is required. If a capacitive sensor is being used, a non-conductive sensing material may be better, or a sensing material that swells when it interacts with the analyte. In this example, since there is no predetermined type of sensor, there is some flexibility in the polymeric materials chosen.

2.3. Potential polymeric sensing materials

The requirements for a polymeric sensing material based on the sensing mechanisms and design constraints discussed in sections 2.1 and 2.2, respectively, are summarized in table 2. Any potential sensing material chosen must meet these minimum requirements. From here, the polymeric material can then be modified by changing some functional groups and/or by adding different dopants (such as metal oxide nanoparticles).

Polyaniline (PANI) contains an amine group (N-H) that is able to hydrogen bond to ethanol and has a glass transition temperature of 105 ºC [11]. In addition, PANI has the unique ability to be conductive or non-conductive, depending on whether it is doped with acid. When doped with acid, PANI is conductive [12].

Table 1. Summary of the design constraints for a transdermal ethanol sensor.

Sensitivity/ Limit of detection	Selectivity	Response/ Recovery times	Operational/ Storage temperatures	Type of sensor
5 ppm	Minimum 5 for each interferent analyte	Below 1 second (for both)[1]	35 ºC / Up to 50 ºC	To be determined[2]

[1] *Note the response and recovery times, in general, are related to the sensor and not the sensing material.*

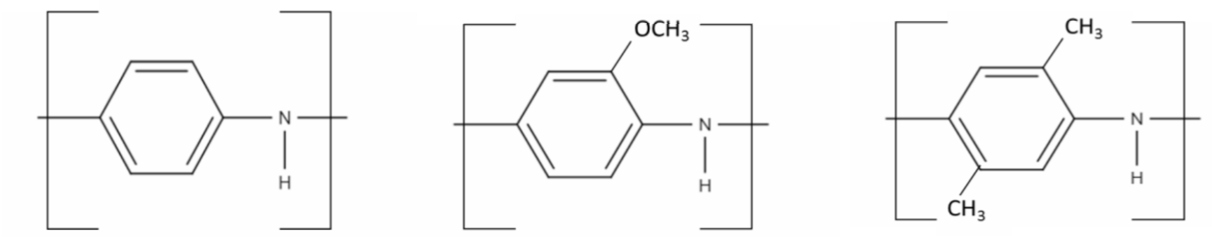
[2] *This will give some flexibility to the type of sensing material chosen.*

This ability to be conductive or non-conductive allows some flexibility in the type of sensor that PANI can be deposited on (i.e. resistive, conductive, and mass-based).

Two derivatives of PANI will also be investigated, poly (*o*-anisidine) (PoANI) and poly (2,5-dimethyl aniline) (P25DMA). PoANI contains a methoxy group (-OCH_3) off of the benzene ring and P25DMA contains two methyl groups off of the benzene group (see figure 1). PANI and its derivatives are environmentally stable [13] and the two derivatives, PoANI and P25DMA, are more readily processable owing to their functional groups that increase the interstitial spaces between the polymer chains [14]. This spacing may also improve the sorption of ethanol. PANI and its derivatives have previously been used as sensing materials for ethanol (see table 3).

Table 2. Summary of requirements for the polymeric sensing material.

Sensing mechanism	Functional groups	Glass transition temperature	Sensor constraints
Hydrogen bonding	N-H O-H	Above 80 ºC	None



(a) (b) (c)

Figure 1. Schematic of a) PANI, b) PoANI, and c) P25DMA.

Table 3. Polyaniline and its derivatives as sensing materials for ethanol.

Polymer	Dopant	Detection limit	Operational temperature	Response/ Recovery time	Reference
PANI	Ag 2.5 mol %	100 ppm	Room temperature	102 seconds/ 20 minutes	[15]
PANI	NiO 10 wt. %	1 ppm	21 ºC	-	[16]
PANI	Dinonylnaphthalene-sulfonic acid	764 ppm	Room temperature	5 minutes/ 2 minutes	[17]
PANI	TiO_2 10 wt. %	150 ppm	-	58 seconds/ 300 seconds	[18]
PoANI	-	3000 ppm	Room temperature	1 minute/ 4 minutes	[19]
PoANI	Polystyrene	3850 ppm	25 °C	30 minutes/ 30 minutes	[20]
P25DMA	-	-	Room temperature	1 minute/ 4 minutes	[19]
P25DMA	-	3 ppm	21 ºC	60 seconds/ 90 seconds	[21]

2.4. Potential dopants

Five potential metal oxide nanoparticle dopants were chosen that could be incorporated into the polymeric sensing materials to improve their sensing properties. These dopants were chosen based on their ability to coordinate well with the target analyte (ethanol). It should be noted that a metal or metal oxide may coordinate well with an analyte, but may not coordinate well with the polymer [22].

The five metal oxides chosen (in nanoparticle form) were nickel oxide (NiO), zinc oxide (ZnO), copper oxide (CuO), aluminum oxide (Al_2O_3), and titanium oxide (TiO_2). Information on several metal oxides as sensing materials for ethanol is summarized in table 4. Note that most of the sensors listed in table 4 are resistive sensors that sense ethanol after its oxidation and thus, operate at high temperatures (above 100 °C).

To reduce the number of materials evaluated, initially only two dopants were chosen, NiO and ZnO. These two dopants are commonly used as catalysts for the

Table 4. Metal oxides as sensing materials for ethanol.

Material	Dopant	Detection limit	Operational temperature	Response/ Recovery time[1]	Reference
NiO	-	5 ppm	300 ºC	-	[23]
NiO	-	10 ppm	Room Temperature	-	[24]
SnO_2	NiO (5 mol %)	5 ppm	300 ºC	2 seconds/ 3 seconds	[25]
ZnO	-	10 ppm	400 ºC	5 seconds/ 10 seconds	[26]
ZnO	NiO	0.3 ppm	450 ºC	~ 60 seconds/ ~60 seconds	[27]
ZnO	Ti (1.86 at %)	50 ppm	250 ºC	~ 200 seconds/ ~60 seconds	[28]
CuO	-	100 ppm	240 ºC	110 seconds/ 120 seconds	[29]
CuO	Pt	5 ppm	200 ºC	4 seconds/ 7 seconds	[30]
CuO	Au	5 ppm	200 ºC	4 seconds/ 7 seconds	[30]
γ-Al_2O_3	Dy^{3+} (1 mol %)	500 ppm	450 ºC	-	[31]
ZnO	Al_2O_3 (1 wt. %)	100 ppm	300 ºC	18 seconds/ 40 seconds	[32]
ZnO	Al_2O_3 (2 at. %)	1000 ppm	290 ºC	8 seconds/ 10 seconds	[33]
TiO_2	-	20 ppm	350 ºC	12 seconds/ 9 seconds	[34]
TiO_2	Ag	5 ppm	250 ºC	1 second/ 2 seconds	[35]
ZnO	TiO_2 (10 wt. %)	100 ppm	370 ºC	10 seconds/ 5 seconds	[36]

[1] *Note a "~" denotes an estimated time based on a graph showing the response and recovery of the sensor.*

oxidation of ethanol [37, 38] and thus, ethanol is able to coordinate well with these two dopants. Depending on the results obtained, the other three dopants, CuO, Al_2O_3, and TiO_2 can be (and were) evaluated at a subsequent stage.

2.5. Summary of potential polymeric sensing materials for ethanol

Based on the selection criteria presented in section 2, PANI was chosen as the basis. To potentially improve the sensitivity of PANI, two of its derivatives, PoANI and P25DMA were also selected, resulting in three potential polymeric sensing materials. Potential metal oxide nanoparticle dopants for ethanol were subsequently chosen, based on their affinity to ethanol, to improve the sensitivity and/or selectivity of the polymeric sensing material. This resulted in five potential metal oxide dopants.

Initially, two metal oxide dopants (NiO and ZnO) were incorporated into the three polymers and evaluated. NiO and ZnO were each incorporated at 10 wt. % and 20 wt. % into all three polymeric sensing materials. Based on the obtained results, three more metal oxide dopants (CuO, Al_2O_3, and TiO_2) were subsequently incorporated (at 5 wt. %, 10 wt. % and 20 wt. %.) into the best performing (highest sorption) polymer and also evaluated.

3. Materials and Methods

3.1. Material synthesis

The polymer nanocomposites were synthesized by mixing monomer (see below), ammonium persulfate (initiator), and if present, the dopants, in deionized water. Up to 0.41 mL of monomer was added to 20 mL of deionized water along with the metal oxide dopant (up to 20 wt. % of the total polymeric sample weight). The (doped) monomer solution was mixed using a sonicator for 30 minutes and then cooled to −1 ºC before adding a solution containing 1.0 g of ammonium persulfate (A.C.S. Reagent, Sigma-Aldrich, Oakville, Ontario, Canada) in 5 mL of deionized water. The resulting solution was shaken by hand for 1 minute to ensure thorough mixing, then left to polymerize for 6 hours. The polymer was filtered out using a Büchner funnel and Whatman #5 filter paper and washed with acetone, then left overnight to dry in air. The polymer nanocomposites were stored in atmospheric conditions in 20 mL scintillation vials [39].

Three different monomers were used: aniline (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada), *o*-anisidine (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada), and 2,5-dimethyl aniline (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada). In addition, five different metal oxide nanoparticles were used: copper (II) oxide (particle size <50 nm, Sigma-Aldrich, Oakville, Ontario, Canada), aluminum oxide (particle size < 50 nm, 10 wt. % dispersion in H_2O, Sigma-Aldrich, Oakville, Ontario, Canada), nickel (II) oxide (particle size < 50 nm, concentration of 99.8%, Sigma-Aldrich, Oakville, Ontario, Canada), titanium (IV) dioxide (particle size 21 nm, concentration of 99.5%, Sigma-Aldrich, Oakville, Ontario, Canada), and zinc oxide (ZnO) (particle size <100 nm, 50 wt.% in water, Sigma-Aldrich, Oakville, Ontario, Canada). All chemicals were used as received.

3.2. Gas sorption test system

A specially designed gas test system was used to evaluate the sorption capabilities of different potential sensing materials. The test system consisted of an analyte source (standard grade mixtures of a gas analyte in a balance of nitrogen) in gas cylinders, with the gas flow controlled by MKS RS-485 mass flow controllers (MFCs). The gas flowed through an MKS 640A pressure controller (PC) and an MKS 1179A flow meter (FM) to ensure the pressure remained above 15 psi and that the flow rate was maintained at 200 sccm, into a 100 mL round bottom flask, which contained the sample. An empty flask was used to establish the baseline. The gas flowed out of the round bottom flask and into a highly sensitive Varian 450 gas chromatograph (GC) with a photon discharge helium ionization detector (PDHID) capable of measuring down to the ppb range (see figure 2) [40].

3.3. Evaluation of potential sensing materials

Test samples of each polymer nanocomposite were prepared by adding 0.120 g of sample to a 100 mL round bottom flask with 5 mL of ethanol. The sample was swirled around the flask to coat the interior of the flask, and then placed in an oven at 50 ºC for 18 hours. The samples were cooled to room temperature (21 ºC) before being tested.

Prior to evaluation, each sample was purged with dry nitrogen (5.0 grade, Praxair, Mississauga, Ontario, Canada) for 60 minutes. This purge was conducted immediately before a sample was exposed to an analyte. Four gas analytes were used to evaluate

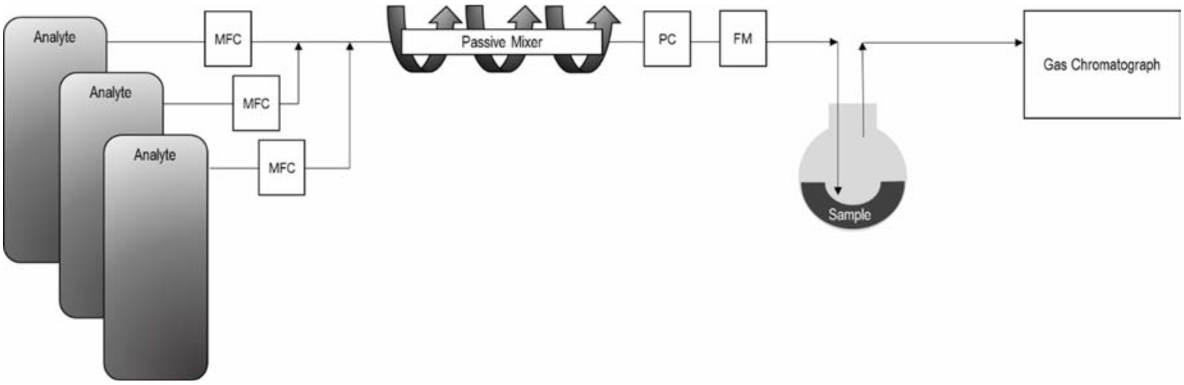


Figure 2. Experimental test set-up.

the effectiveness of these polymeric nanocomposites as sensing materials. These gas analytes were all approximately 5 ppm, standard grade mixtures in a balance of nitrogen (Praxair, California, USA): acetone (5.50 ppm), benzene (5.10 ppm), ethanol (5.00 ppm), and methanol (4.66 ppm).

The polymeric nanocomposites were evaluated (at room temperature) by exposing each polymeric nanocomposite to specific concentrations of different gas analytes (ethanol, methanol, acetone, benzene) individually. Approximately 5 ppm of each gas was used and the polymeric nanocomposites were exposed for at least 60 minutes to ensure equilibrium had been reached. The amount that did not sorb onto the polymeric nanocomposite was measured using the highly specialized GC. By subtracting this amount from the initial concentration exposed (from the standard grade gas tanks), the amount of gas analyte that sorbed onto the polymeric nanocomposite was ascertained. Three independent replicates were conducted for each polymeric nanocomposite for each gas tested.

4. Results and Discussion

4.1. Sensitivity

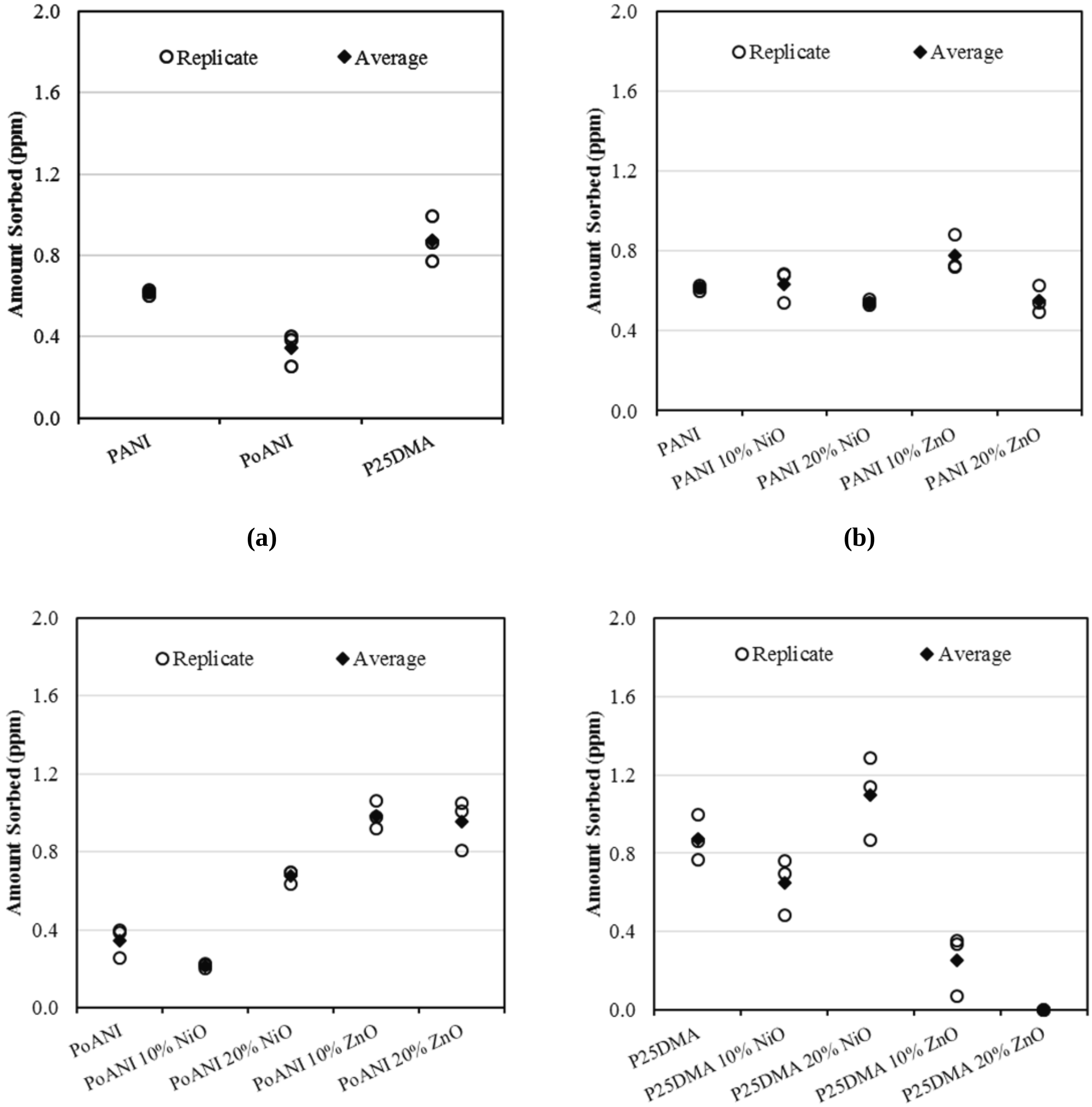
Evaluation of potential sensing materials was first done using the target analyte, ethanol, at the desired LoD of 5 ppm. The potential polymeric sensing materials were evaluated with respect to their ability to sorb ethanol when exposed to 5 ppm of ethanol in dry nitrogen. A material was considered sensitive if it was able to sorb at least 1 ppm of ethanol.

To perform this evaluation, PANI, PoANI, and P25DMA were exposed to 5 ppm ethanol and the amount of ethanol sorbed onto each polymer was measured (see figure 3). From figure 3a, it can be seen that P25DMA sorbed the most ethanol among the three polymers evaluated, and was the only polymer to sorb close to 1 ppm.

The addition of a methoxy group to PANI (e.g. PoANI) reduced the sensitivity to ethanol. This may be due to the amine in PoANI binding to the methoxy group and thus reducing the number of sensing sites available to ethanol. The two methyl side groups on P25DMA, on the other hand, improved the sorption of ethanol which was likely due to the reduced packing efficiency of P25DMA versus PANI. The methyl groups provided steric hindrance that created larger interstitial spaces within the polymer chains of P25DMA, compared to PANI, allowing ethanol to diffuse more easily into the P25DMA matrix.

These polymers were then doped with 10 wt. % and 20 wt. % NiO and ZnO nanoparticles (see figure 3b-c). Even when doped, PANI did not sorb more than 1 ppm of ethanol. PoANI doped with NiO did not perform well either, but PoANI doped with ZnO sorbed approximately 1 ppm. P25DMA did significantly improve with the addition of 20% NiO; however, the addition of ZnO resulted in poorer sorption (see figure 3d).

Given that P25DMA sorbed more ethanol than PANI and PoANI, only P25DMA was further doped with additional metal oxide dopants (CuO, Al_2O_3, and TiO_2). In addition, all five metal oxide nanoparticle dopants were evaluated at 5 wt. %, 10 wt. %, and 20 wt. %. This resulted in 15 doped P25DMA polymeric nanocomposites, which were all evaluated using 5 ppm ethanol (see figure 4).



(a) **(b)**

(c) **(d)**

Figure 3. Ethanol sorption for (a) undoped polymers, (b) undoped and doped PANI, (c) undoped and doped PoANI, and (d) undoped and doped P25DMA.

From figure 4, it can be seen that the addition of different metal oxide nanoparticles to a polymer matrix can significantly affect the sorption of ethanol. Therefore, metal coordination to the polymer composite also affects the design of a polymeric sensing material. Overall, the incorporation of NiO, Al_2O_3, and TiO_2 to P25DMA improved the sorption of ethanol.

NiO and TiO_2 incorporate well into P25DMA, whereas ZnO and Al_2O_3 do not (see table 6) [22]. CuO does not incorporate at all into P25DMA (see again table 6) [41]. When a metal oxide coordinates with a polymer, the polymer chains often have to change their conformation to coordinate, thus creating “kinks” in the polymer chain [42]. These kinks affect the morphology of

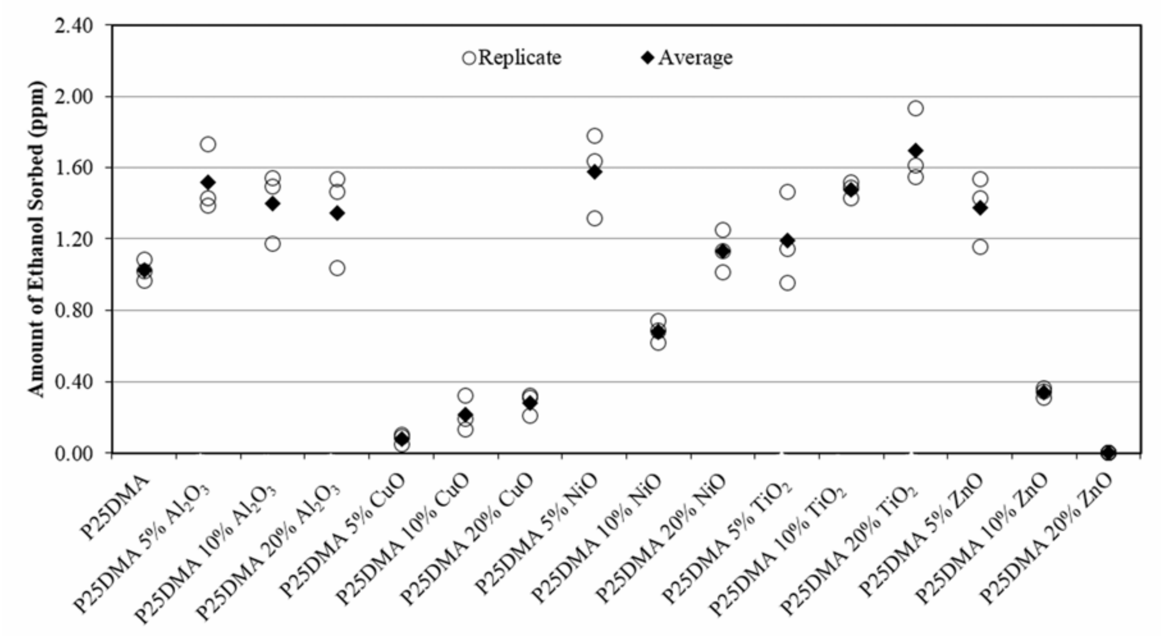


Figure 4. Ethanol sorption for P25DMA and P25DMA doped with five different metal oxide nanoparticles.

the polymer and may affect the sorption of analytes. It is important that the polymer and metal oxide dopant coordinate well. Note that there is a trade-off between the improved sorption provided by the coordination of the metal oxide dopant to the target analyte and the added kinks along the polymer chain, which may reduce the sorption of an analyte.

This trade-off is most noticeable in figure 4 for ZnO and TiO_2. As more ZnO is added to P25DMA, the increased number of kinks leads to the "destruction" of the polymer and ultimately the absence of ethanol sorption for P25DMA 20% ZnO. This "destruction" occurs because ZnO and P25DMA do not coordinate well. However, P25DMA and TiO_2 do coordinate well. As more TiO_2 is incorporated into P25DMA, the added kinks result is larger interstitial spaces into which ethanol can more easily diffuse and coordinate with the added TiO_2.

The polymeric nanocomposites which sorbed more than 1 ppm of ethanol were then selected for further evaluation. This resulted in eight different polymer composites (P25DMA 5% Al_2O_3, P25DMA 5% NiO, P25DMA 20% NiO, P25DMA 5% TiO_2, P25DMA 10% TiO_2, P25DMA 20% TiO_2, and P25DMA 5% ZnO (see figure 4), and PoANI 20% ZnO (see figure 3c)). Note that because P25DMA doped with Al_2O_3 at all three concentrations resulted in the same amount of sorption of ethanol, only the lowest amount of Al_2O_3 was evaluated for selectivity. Similarly, only PoANI 20% ZnO was chosen, despite both PoANI 10% ZnO and PoANI 20% ZnO sorbing more than 1 ppm ethanol.

4.2. Selectivity

Selectivity is the ratio between the response (sorption) of the target analyte to the response (sorption) of an interferent. A selectivity greater than 5 is considered good and a selectivity below 1 is very poor. If the selectivity is below 1, the interferent responded (sorbed) more than the target analyte.

The eight most promising materials from the previous sensitivity evaluation stage were further ranked with respect to their selectivity in the presence of three interferent gases (methanol, acetone, and benzene). Each of these three analytes is a common interferent for ethanol. In addition, these three interferents represent three different classes of volatile organic compounds (VOCs) in their own right. The selectivity of each of the sensing materials is shown in figure 5 and tabulated in table 5.

All of these eight sensing materials were more selective to ethanol than to the three interferents since they all sorbed more ethanol than any of the three interferents. The most selective sensing materials in table 5 are bolded. The two most selective sensing materials are P25DMA 5% Al_2O_3 and P25DMA 5% TiO_2, whereas the least selective sensing material was P25DMA 20% NiO. However, if acetone was more of a concern than methanol as an interferent, then P25DMA 10% TiO_2 and P25DMA 5% ZnO would be good sensing materials since they had the highest selectivity towards ethanol, with respect to acetone.

The addition of more NiO or TiO_2 resulted in poorer selectivity. It is likely that the increased amount of metal oxide incorporation resulted in larger interstitial spaces, which allowed all analytes to diffuse more easily into the polymeric matrix. Therefore, more of each analyte could sorb onto the polymeric material. It is important to realize that the diffusion (and sorption) for each analyte is different and thus, the sorption may improve much more for one analyte than another. This was the case here, hence resulting in poorer selectivity as the concentration of NiO and TiO_2 was increased.

4.3. Most promising materials

Based on the sensitivity and selectivity evaluation, the most promising sensing materials for ethanol detection are P25DMA 5% Al_2O_3 and P25DMA 5% TiO_2, with the next two most promising being P25DMA 10% TiO_2 and P25DMA 5% ZnO. While these four sensing materials did not have the highest sensitivity (i.e. they did not sorb the most ethanol as per figure 4), they did exhibit the best selectivity.

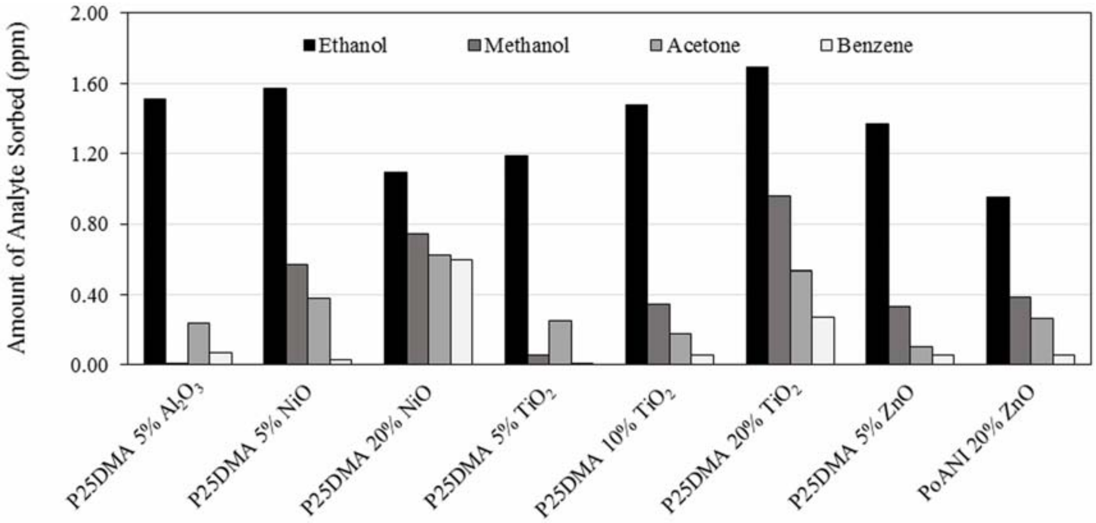


Figure 5. Selectivity of the most sensitive polymeric materials to ethanol.

Table 5. Selectivity towards ethanol.

Sensing material	Selectivity to ethanol		
	Methanol	Acetone	Benzene
P25DMA 5% Al_2O_3	**151.50**	**6.27**	**22.17**
P25DMA 5% NiO	2.78	4.14	55.59
P25DMA 20% NiO	1.47	1.76	1.84
P25DMA 5% TiO_2	**19.78**	**4.72**	**178.00**
P25DMA 10% TiO_2	**4.28**	**8.20**	**26.85**
P25DMA 20% TiO_2	1.77	3.18	6.28
P25DMA 5% ZnO	**4.14**	**13.27**	**23.51**
PoANI 20% ZnO	2.44	3.56	17.27

Note that if sensitivity is satisfied, the best sensing materials are those with the highest selectivity.

The next step would be to deposit the most promising sensing materials onto a sensor for further evaluation. By using this targeted approach, the number of potential sensing materials for ethanol has been drastically lowered down to 4 polymeric materials to be further evaluated versus the almost 50 initial combinations suggested (3 polymers doped with 5 metal oxide dopants at 3 different concentrations). This shows clearly the benefits of this approach versus the very time-consuming (and rather arbitrary) trial-and-error approach.

4.4. Other observations

From the data collected above, other comparisons and analyses can be made about polymeric nanocomposites and polymeric sensors. The modified PANI backbone enabled the comparison of different functional groups on a similar backbone. The incorporation of metal oxide nanoparticles into P25DMA provided insight into how metal oxides can affect the sorption of analytes. In addition, an aging study was conducted to evaluate whether PANI degraded over time, under no special storage conditions.

4.4.1. Effect of polymer functional groups

Three different PANI derivatives, PANI, PoANI, and P25DMA, were compared using ethanol to determine the effect of functional groups on sorption and sensing properties (see figure 1). The amount of ethanol sorbed onto each polymeric material (see figure 3a) was analyzed using analysis of variance (ANOVA), along with the Bonferroni t-test and Fisher's least significant difference (LSD).

It was found that P25DMA and PoANI sorbed statistically significantly different (at a 95% confidence level) amounts of ethanol; PoANI sorbed significantly less ethanol than P25DMA (see figure 3a). Since P25DMA and PoANI have different functional groups off the same backbone and sorb significantly different amounts of ethanol, it can be suggested that the functional groups, and by extension other side chains, do affect the sorption properties of a polymeric sensing material. Therefore, it is important to consider how the functional groups on a polymer will interact with the analytes.

This means that by modifying the functional groups (or side chains) on a polymer, the polymer can be tailored to sorb a target analyte or groups of analytes. This also means that changing the functional groups on a polymer to improve processability may significantly affect the sensing properties of the polymer.

4.4.2. Incorporation of metal oxide nanoparticles into polymer matrices

When adding dopants to a polymer, it is important that the dopant incorporates well into the polymer matrix. However, this is not always the case [22]. In terms of sensing properties, poor incorporation of a dopant can result in poorer sorption. Furthermore, the addition of a metal oxide during synthesis may inhibit the actual polymerization, as was the case for P25DMA and ZnO.

The actual amount of metal oxide dopant that was incorporated into P25DMA was measured using energy dispersive X-rays (EDX, Ametek EDAX, New Jersey, USA). Note that the dopant at the appropriate concentration (5%, 10%, and 20%) was added during synthesis of the polymer (e.g. 5 wt. % Al_2O_3 to 95% P25DMA). These measurements were used to confirm if the amount of metal oxide dopant (e.g. 5 wt. %) added during synthesis was actually incorporated into the polymer nanocomposite (see table 6).

A significantly higher amount of ZnO was observed when 20 wt. % was used during synthesis. According to EDX, double the amount of ZnO was incorporated than initially present, which means much less polymer (P25DMA) was polymerized when so much ZnO was present. This means that less 2,5-dimethyl aniline monomer was able to polymerize in the presence of ZnO, resulting in a lower conversion to P25DMA (in other words, it appears that the presence of ZnO effectively inhibits the polymerization of 2,5-dimethyl aniline). Hence, a smaller amount of P25DMA is produced. This reduced amount of P25DMA would explain the 47 wt. % of ZnO observed within the P25DMA 20% ZnO sample.

Comparing the amount of metal oxide dopants incorporated into the P25DMA matrix (see table 6) with the sorption of ethanol (see figures 4 and 5), it appears that the coordination of the metal oxide has an effect on the sorption properties; however, there is no correlation between the amount incorporated and the resulting sorption of an analyte. This is because sorption of an analyte is affected by many aspects, including the morphology of the

Table 6. Weight percent of metal in each polymer nanocomposite at different concentrations.

Polymeric nanocomposite	**Weight percent of each metal (M)**				
	Al	**Cu**	**Ni**	**Ti**	**Zn**
P25DMA 5% MO_x	0.61	0.16	5.58	3.68	0.34
P25DMA 10% MO_x	0.57	0.07	8.11	12.37	0.86
P25DMA 20% MO_x	0.49	0.11	19.14	17.09	46.89

polymer nanocomposite, interstitial spacing, and the ability to coordinate with the polymer and/or the metal oxide dopant.

In the case of P25DMA doped with Al_2O_3, only a small amount of Al_2O_3 was incorporated into the P25DMA matrix, even with the increasing amount of Al_2O_3 available during synthesis. Despite this small amount of Al_2O_3 incorporation, the sorption of ethanol onto P25DMA doped with Al_2O_3 was significantly better than the undoped P25DMA (see table 6 and figure 4).

By comparison, CuO effectively did not incorporate into P25DMA and significantly reduced the sorption of ethanol when compared to the undoped P25DMA. This is likely due to the CuO affecting the morphology of the P25DMA as it polymerizes [22]. Similarly, the increased amount of ZnO also affected the polymerization of 2,5-dimethyl aniline.

Both NiO and TiO_2 incorporated well into the P25DMA matrix, but their sorption trends were not similar. As more NiO was added, the sorption of ethanol initially increases (P25DMA 5% NiO), then drops (P25DMA 10% NiO), and then increases again (P25DMA 20% NiO). This is in contrast to the increased amount of TiO_2 resulting in increased ethanol sorption (see figure 4). This is because different sensing mechanisms are competing and, for the case of P25DMA doped with NiO, the dominant sensing mechanism changes as more NiO is incorporated [10].

It should be noted that the incorporation of metal oxides does significantly affect the sorption of analytes. However, since there is no correlation between the amount of metal oxide incorporated and the sorption of an analyte, it is important to do some screening experiments on new polymer nanocomposites for a target analyte to evaluate which polymer-dopant nanocomposites are worth pursuing for a specific target analyte and application.

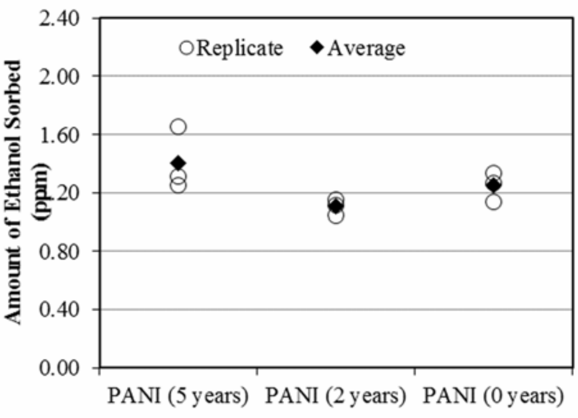


Figure 6. Amount of ethanol sorbed onto varying ages of PANI (five, two, and zero years old).

4.4.3. Sample stability

The environmental stability of polyaniline (PANI) was evaluated to determine if storage at atmospheric conditions (atmospheric pressure and room temperature, 21 ºC) caused any degradation. Three samples that were five years old, two years old, and freshly made (zero years old) were evaluated based on the amount of ethanol sorbed. The older samples (five and two years old) had been stored for their respective "ages" in 20 mL scintillation vials at atmospheric pressure and room temperature (21 ºC).

Each sample was exposed to 10 ppm of ethanol and the amount of ethanol sorbed onto each polymer sample was measured (see figure 6). The amount of ethanol sorbed by each sample was compared using ANOVA and determined that there was no statistically significant difference among the amounts of ethanol these polymer samples sorbed.

Since there was no significant difference between the three PANI samples, the indication was that PANI did not significantly degrade when stored at room temperature (21 ºC) in atmospheric conditions (i.e. no special storage considerations were used).

Therefore, PANI is environmentally stable and storage up to five years will not affect the analyte sorption of PANI. This may or may not apply to other backbones; however, the comparison results are encouraging for the aniline-based sensing materials (PANI, PoANI, and P25DMA). Similar comparative investigations can be conducted for other polymeric sensing materials, if these experimental investigations are designed properly and for the long term.

5. Conclusion

A targeted approach was used to design polymeric sensing materials for a specific analyte and application. Using this approach, three polymers and five metal oxide dopants were evaluated for sensitivity and selectivity. Beginning with screening experiments, the three polymers were evaluated with two metal oxides (NiO and ZnO). It was found that P25DMA sorbed significantly more ethanol than the other two polymers. Further evaluation of the other three dopants was subsequently conducted on P25DMA. This targeted approach, combined with an experimental design that used screening experiments to reduce the number of total experiments and thus reduce the cost associated with evaluating sensing materials, produced four very promising sensing materials for ethanol (from a list of about 50 tentative polymers, this approach reduced the number to three more promising polymers, which were then doped using different metal oxides).

These four polymeric nanocomposites were shown to have the necessary sensitivity and selectivity to ethanol. The two most promising polymers, which had the best selectivity, were P25DMA 5% Al_2O_3 and P25DMA 5% TiO_2. The next most promising polymeric nanocomposites, which had lower overall selectivity, but higher selectivity to ethanol with respect to acetone, were P25DMA 5% ZnO and P25DMA 10% TiO_2.

In addition to finding sensitive and selective sensing materials for ethanol, some other comparisons were also observed and analyzed. By comparing the response of ethanol to PANI and its derivatives, it was seen that changing the functional groups on a polymer backbone can significantly affect the sorption, and thus the sensing properties of a polymeric sensing material. Also, the incorporation of metal oxide nanoparticles also significantly affects the sorption; however, there is no correlation between the amount of metal oxide incorporated into the polymer and the amount of analyte that is sorbed.

Finally, some comparative age/degradation studies were conducted on the sorption of PANI. Three samples, which had been stored in atmospheric conditions (i.e. no special treatment) showed that no degradation had occurred over the 5 years of storage. Therefore, a product containing PANI as a sensing material (and by extension its derivatives PoANI and P25DMA) would have a long shelf life since PANI does not degrade or show a reduction in its sensing properties, even after 5 years in storage.

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CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest in the work presented.

REFERENCES

1. Solomon, R., Cardy, J., Noble, I. and Wulkan, R. 2012, MADD.
2. Sullivan, A. 2015, Richmond J. Law Technol., 21, 4.
3. Chen, W. T., Stewart, K. M. E., Yang, C. K. and Mansour, R. R. 2015, IEEE T Microw Theory, 63, 4157.
4. Watson, J., Ihokura, K. and Coles, G. S. V. 1993, Meas Sci. Technol., 4, 711.
5. Talwar, V., Singh, O. and Singh, R. C. 2014, Sens. Act. B, 191, 276.
6. Rochat, S. and Swager, T. M. 2013, ACS Appl. Mater. Ins., 5, 4488.
7. Mabrook, M. and Hawkins, P. 2001, Sens. Act. B, 75, 197.
8. Chen, X., Sun, J. and Shen, J. 2009, Langmuir, 25, 3316.
9. Dirksen, J. A., Duval, K. and Ring, T. A. 2001, Sens. Act. B, 80, 106.

10. Stewart, K. M. E. and Penlidis, A. 2016, Polym. Advan. Technol., 133, doi:10.1002/pat.3893.
11. Wei, Y., Jang, G.-W., Hsueh, K. F., Scherr, E. M., MacDiarmid, A. G. and Epstein, A. J. 1992, Polymer, 33, 314.
12. Kukla, A. L., Shirshov, Y. M. and Piletsky, S. A. 1996, Sens. Act. B, 37, 135.
13. Valentini, L., Bavastrello, V., Stura, E., Armentano, I., Nicolini, C. and Kenny, J. M. 2004, Chem. Phys. Lett., 383, 617.
14. Bavastrello, V., Stura, E., Carrara, S., Erokhin, V. and Nicolini, C. 2004, Sens. Act. B, 98, 247.
15. Choudhury, A. 2009, Sens. Act. B, 138, 318.
16. Stewart, K. M. E., McManus, N. T., Abdel-Rahman, E. and Penlidis, A. 2012, J. Macromol. Sci. A, 49, 1.
17. Svetlicic, V., Schmidt, A. J. and Miller, L. L. 1998, Chem. Mater., 10, 3305.
18. Zheng, J., Li, G., Ma, X., Wang, Y., Wu, G. and Cheng, Y. 2008, Sens. Act. B, 133, 374.
19. Athawale, A. A. and Kulkarni, M. V. 2000, Sens. Act. B, 67, 173.
20. Aussawasathien, D., Sahasithiwat, S., Sahasithiwat, L. and Teerawattananon, C. 2011, Sens. Act. B, 151, 341.
21. Stewart, K. M. E., Chen, W. T., Mansour, R. R. and Penlidis, A. 2015, J. Appl. Polym. Sci., 132, doi: 10.1002/app.42259.
22. Stewart, K. M. E. and Penlidis, A. 2016, J. Macromol. Sci. A Pure and Applied Chemistry, 53, doi: 10.1080/10601325.2016.1212308
23. Kaur, N., Comini, E., Zappa, D., Poli, N. and Sberveglieri, G. 2016, Nanotechnology, 27, 205701.
24. Li, Z. 2016, Microelectron Int., 33, 68.
25. Liu, L., Li, S., Wang, L., Guo, C., Dong, Q. and Li, W. 2011, J. Am. Ceram. Soc., 94, 771.
26. Singh, R. C., Singh, O., Singh, M. P. and Chandi, P. S. 2008, Sens. Act. B, 135, 352.
27. Na, C. W., Woo, H.-S. and Lee, J.-H. 2012, RSC Advances, 2, 414.
28. Hsu, C.-L., Gao, Y.-D., Chen, Y.-S. and Hsueh, T.-J. 2014, Sens. Act. B, 192, 550.
29. Raksa, P., Gardchareon, A., Chairuangsri, T., Mangkorntong, P., Mangkorntong, N. and Choopun, S. 2009, Ceram. Int., 35, 649.
30. Gou, X., Wang, G., Yang, J., Park, J. and Wexler, D. 2008, J. Mater. Chem., 18, 965.
31. Okabayashi, T., Fujimoto, T., Yamamoto, I., Utsunomiya, K., Wada, T., Yamashita, Y., Yamashita, N. and Nakagawa, M. 2000, Sens. Act. B, 64, 54.
32. Patil, D. R., Patil, L. A. and Amalnerkar, D. P. 2007, Bull. Mater. Sci., 30, 553.
33. Yang, Z., Huang, Y., Chen, G., Guo, Z., Cheng, S. and Huang, S. 2009, Sens. Act. B, 140, 549.
34. Wang, C., Yin, L., Zhang, L., Qi, Y., Lun, N. and Liu, N. 2010, Langmuir, 26, 12841.
35. Hu, P., Du, G., Zhou, W., Cui, J., Lin, J., Liu, H., Liu, D., Wang, J. and Chen, S. 2010, Appl. Mater. Inf., 2, 3263.
36. Zhu, B. L., Xie, C. S., Wang, W. Y., Huang, K. J. and Hu, J. H. 2004, Mater. Lett., 58, 624.
37. Liberatori, J. W. C., Ribeiro, R. U., Zanchet, D., Noronha, F. B. and Beuno, J. M. C. 2007, Appl. Catal. A-Gen., 327, 197.
38. Xu, J., Pan, Q., Shun, Y. and Tian, Z. 2000, Sens. Act. B, 66, 277.
39. Stewart, K. M. E., McManus, N. T., Abdel-Rahman, E. and Penlidis, A. 2012, J. Macromol. Sci. A, 49, 1.
40. Stewart, K. M. E. and Penlidis, A. 2013, Macromol. Sy., 324, 11.
41. Stewart, K. M. E. 2016, PhD Thesis, Dept. of Chem. Eng., University of Waterloo
42. Han, J., Song, G. and Guo, R. 2006, J. Polym. Sci. A, 44, 4229.