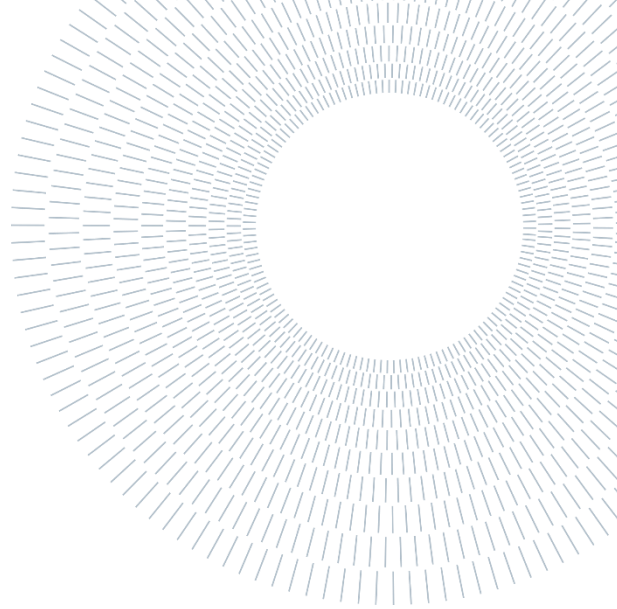




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EXECUTIVE SUMMARY OF THE THESIS

Soft materials for gas sensing: bijels as chemiresistors

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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1. Introduction

Volatile Organic Compounds, VOCs, are a wide variety of components characterized by a high volatility at ambient temperature. They are present in considerable amounts in indoor environments (furniture coatings, glues, and paints for buildings) and are supposed to be source of health issues, especially chronic, related to respiratory (e. g. formaldehyde), irritating (e. g. terpene oxidation products), cardiovascular (e. g. benzene, xylenes) neurological (e. g. formaldehyde) or carcinogenic (e. g. formaldehyde, acetaldehyde) effects [1]. For this reason, research is looking for sensors able to detect their presence in an effective way. The aim of this thesis is to develop a sensing material. The materials selected are called bijels, word that stands for bicontinuous interfacially jammed emulsions. They are characterized by the co-existence of two immiscible phases, hydrophobic and hydrophilic, stabilized by colloidal particles (solid particles with a polarization). Their structure is similar to channels of the two phases bounded by colloids, which are at the interface between them, contributing to minimize considerably the interfacial tension the phases involved [2]. The

materials selected for the production of the hydrophobic phases are ϵ -caprolactone (ϵ -CL) and ω -pentadecalactone (ω -PDL), due to their known capability to polymerize (by means of a Ring Opening Polymerization, ROP) and give bijels with addition of water (the hydrophilic phase) [3] [4]. In this work, the possibility to use them as chemiresistor has been addressed. Chemiresistors are sensing devices able to change their electrical resistance when they are in contact with a certain species. To increase the electrical conductivity of these sensors, graphene nanoplatelets and carbon nanotubes were added to the formulations, due to their known positive contribution to the electrical conductivity. [5]

2. Materials, instrumentation, and methods

This section is divided in materials employed (2.1), equipment involved in this thesis (2.2), and bijels preparation (2.3).

2.1. Materials

Graphene nanoplatelets (purity: 99%, size: 3 nm) and carbon nanotubes were bought from Nanografi Nanotechnology AS (Ankara, Turkey).

ϵ -caprolactone (ϵ -CL, $\geq 99\%$), ω -pentadecalactone (ω -PDL, $\geq 98\%$) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, $\geq 95\%$) were purchased by Sigma (Sigma-Aldrich Chemie GmbH, Deisenhofen, Germany). All reagents and solvents employed have been used without further purification. Solvents were of analytical laboratory grade. The reactions were carried under atmospheric air. Synthesized products (bijels materials) were stored at 4°C in dark, until their use (analytical purposes).

2.2. Analysis and bijels synthesis equipment

Analyses techniques performed in this work are SEM, DSC, and gas detection tests.

SEM (Scanning Electron Microscopy) were performed with Evo 50 EP Instrumentation (Zeiss, Jena, Germany), using gold sputtered samples at 10 kV.

DSC (Differential Scanning Calorimetry) has been performed on a Mettler Toledo DSC Polymer machine calibrated with indium and zinc standards. The heating rate of the program selected was 20°C/min under nitrogen flow with minimum and maximum temperatures of -60 °C and 180 °C respectively.

Instruments employed to measure the electrical resistance of samples during VOC detection tests: AoKoZo Professional Digital Multimeter Model T28B and Voltcraft VC650BT Multimeter. In the resistance range measured in this project, AoKoZo T28B has an accuracy of 0.8 % + 5 digits, while VC650BT of 2 % + 5 digits.

Concerning bijels synthesis, the following equipment has been employed.

Bandelin Sonorex bath sonicator to solubilize carbon nanotubes in distilled water.

Agitators: Heidolph Multi Reax shaker with a 12-rack carousel for ϵ -CL-based bijels, Arex digital pro magnetic hot plate stirrer for ω -PDL-based bijels.

BenchTop Pro with Omnitronics - SP Scientific lyophilizer to lyophilize samples for SEM, DSC and gas detection tests.

2.3. Bijels preparation

2.3.1. Bijels from ϵ -CL

ϵ -CL polymerization occurs below 22 °C [3]. Here below steps to produce ϵ -CL bijels are described.

Reactants and reaction environment preparation.

Graphene nanoplatelets (constituted by non-polarized bonds) are soluble in the hydrophobic phase. The reactant to produce it, ϵ -CL, is hydrophobic too, so graphene nanoplatelets can be added to ϵ -CL and solubilized upon mixing (no sonication needed). Several graphene concentrations in ϵ -CL have been selected to produce bijel to compare them (especially in terms of their ability to detect VOCs). The selected concentrations of graphene in ϵ -CL are: 30, 40 and 50 mg/mL. In addition, few samples were produced with 20 mg/mL of carbon nanotubes solubilized in water (with sonication) instead of graphene solubilized in ϵ -CL. Reactants amounts to produce one bijel sample are presented in Table 1. Quantities of ethanol, TBD (polymerization initiator and catalyst, respectively), of hydrophobic phase (ϵ -CL+graphene), and hydrophilic one (distilled water) were selected according to [3] with the aim to obtain a bicontinuous structure stable in time.

Table 1 - Quantities of components needed to obtain an ϵ -CL-based bijel.

Component	Quantity	Unit of measure
ϵ -CL (+graphene)	500	μ L
Ethanol	55	μ L
TBD	12.5	mg
Distilled water (+carbon nanotubes)	375	μ L

The reaction environment selected is a syringe without the tip, to allow an easy use of the Heidolph shaker, and an easy way to remove the bijel once it has been produced (by pushing the material carefully outside from the syringe).

ϵ -CL (with graphene nanoplatelets) and ethanol addition in the syringe. Once this mixture is injected in the syringe, nothing happens. The catalyst, TBD, has not been already added. Without the catalyst the reaction rate is too low, so in the range of minutes no significant evolution occurs.

TBD addition. TBD, a solid white powder, is then added to the syringe. The reaction starts. It is recommended to control the time after this addition, but the most relevant aspect to be controlled is viscosity of the mixture, which

progressively increases. These bijels were previously produced using hydroxyapatite instead of graphene (or nanotubes) [3]. With these previous colloidal nanoparticles, the time needed to allow polymerization to occur sufficiently was about 10 minutes. With graphene nanoplatelets, this time is shorter, between 5 and 7 minutes. It is supposed so that graphene is involved as co-catalyst in the formation of polycaprolactone.

Mixing at 1000 rpm until viscosity significantly increases. The use of graphene introduces a difficulty in this step. With hydroxyapatite the solution appears as transparent before addition of TBD and becomes opaque when the polymerization produced a sufficiently high amount of polycaprolactone. So, it is possible to detect the time in which it is possible to move to the next step (which is injection of water) by looking at the syringe. With addition of graphene, the mixture becomes black, so it becomes not possible to rely on sight. The only parameter which can be observed is viscosity, detected moving the syringe. In this step, mixing has the role of homogenizing concentration in the reaction volume. Waiting not enough before water addition does not allow to produce enough polycaprolactone. Water suppresses the polymerization, and the mixture remains liquid. Waiting too much produces a too high degree of polymerization, and the formation of a bicontinuous gel becomes impossible. The hydrophobic phase will be segregated from the hydrophilic one.

Water (hydrophilic phase) addition. Water is added and the rpm are increased up to 1700 rpm for 30-40 s, providing energy to increase the interfacial area between hydrophobic and hydrophilic phases.

Mixing rate decreased to 1000 rpm. At this point, the rate is decreased to allow a partial re-arrangement of the phases. Stirring is still required to provide enough shear force to maintain a bicontinuous structure.

Waiting for 25 minutes and solid removal. The mixture becomes more and more viscous until a semi-solid behavior is obtained. Then, it is possible to push it outside from the syringe. A good bijel is obtained if there are no clear regions with different colors and the material retains all the water previously injected (or most of it).

2.3.2. Bijels from ω -PDL

ω -PDL is solid at room temperature (35 °C as melting temperature). So, it must be heated up to be used as a liquid. For this reason, the reaction set-up is different. Many steps are similar to ϵ -CL bijel production. However, since there are different thermal properties, the procedure to obtain bijels from ω -PDL has some peculiar aspects.

Reactants and reaction environment preparation. Graphene nanoplatelets are solubilized in ω -PDL while carbon nanotubes in distilled water. ω -PDL has to be heated up before to allow producing a liquid mixture. The graphene concentrations selected were 20, 30, 40 and 50 mg/mL (in ω -PDL), while carbon nanotubes were 20 and 30 mg/mL (in distilled water). It is difficult to obtain mixtures with larger concentrations of carbon nanotubes because their viscosity increases rapidly, making difficult to extract them from the place they are contained using syringes or pipettes. In Table 2 quantities of ω -PDL, initiator, catalyst (the same as for ϵ -CL), and distilled water are reported. Quantities are larger for all components except initiator and catalyst to produce more bijel samples (3 in the best situation) during a single reaction. Initiator and catalyst quantities were selected according to authors in [4].

Table 2 - Quantities of components needed to obtain an ω -PDL-based bijel.

Component	Quantity	Unit of measure
ω -PDL (+graphene)	1152	μ L
Ethanol	55	μ L
TBD	12.5	mg
Distilled water (+carbon nanotubes)	1000	μ L

A round-bottomed flask of 10 mL is then immersed in a water bath. The heating system has to be set on 80 °C as water bath temperature, as a compromise between reaction rate increase associated to a higher temperature and the need to reduce the progressive evaporation of water.

ω -PDL and ethanol addition. The first two components of Table 2 are injected in the round-bottomed flask. As in ϵ -CL, nothing happens before TBD addition. Once these components are added, it is possible to start stirring using a small

and thin stir bar. The stirring speed to be used is 750 rpm.

TBD addition. Once the catalyst is added polymerization rate becomes relevant. It is necessary to wait between 45 minutes and 1 hour 15 minutes for water addition. The speed increase of the polymerization has been observed also for ω -PDL compared to bijels produced without graphene [4]. Generally, with increasing graphene concentration usually the time needed for the polymerization is lower, so progressively closer to 45 minutes (typical for 50 mg/mL). It is possible to check the viscosity increase associated to polymerization, so the right moment to move to the next step, by taking a small amount of the mixture with a thin spatula.

Water addition. Water addition in this situation has the same effects of ϵ -CL bijels.

Mixing rate to 1100 rpm. As in the previous case, now mixing rate increases to increase the interfacial area of the two phases. After 30 s it is possible to return to 750 rpm.

Waiting for 30 minutes and product removal. Once 30 minutes are achieved, it is possible to take with a Pasteur pipette the liquid inside the flask and to push it inside three syringes without the tip. Solidification will occur in a very short time, but it is recommended to put some parafilm on it and to conserve it at 4°C for some hours. Then, it is possible to push the bijels outside from the syringes.

3. Results

In this section, the main results obtained in this work are reported. Sections refer to SEM (3.1), DSC (3.2), and gas detection tests (3.3) results.

3.1. Scanning Electron Microscopy

SEM tests allowed to appreciate the formation of the bicontinuous structure. as it possible to see in Figure 1, obtained from an ϵ -CL-based bijel. This sample is characterized by the presence of multiple channels distributed uniformly which were occupied by water before lyophilization.

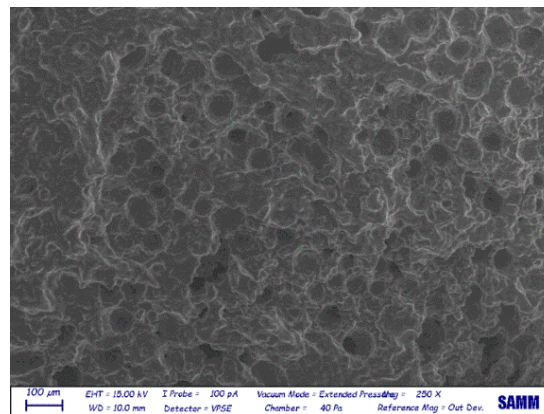


Figure 1 – 250 X SEM image of STR 46: ϵ -CL monomer with 40 mg/mL of graphene nanoplatelets.

The other two figures, Figure 2 and Figure 3, display results from two samples ω -PDL-based.

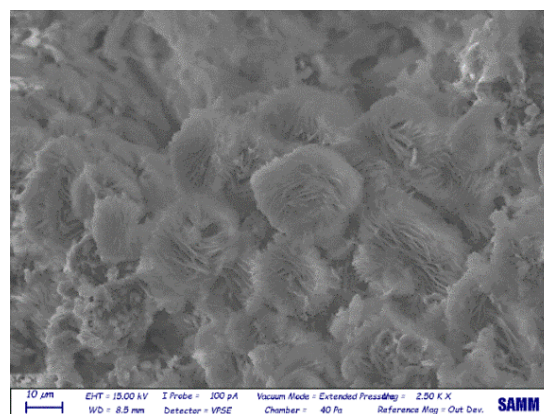


Figure 2 - 2500 X SEM image of STR 21: ω -PDL monomer with 30 mg/mL of graphene nanoplatelets.

Images show the presence of globular structures (Figure 2) and sponge-like structures (Figure 3) which are typical of bijels produced with ω -PDL.

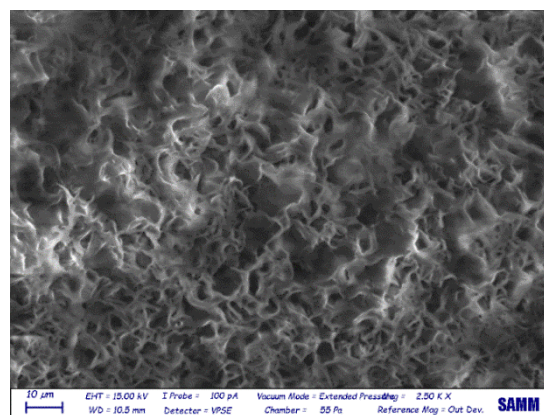


Figure 3- 2500 X SEM image of STR 71: ω -PDL monomer with 40 mg/mL of graphene nanoplatelets.

These results showed the possibility to obtain bicontinuous structures using graphene nanoplatelets (but also with carbon nanotubes) particles.

3.2. Differential Scanning Calorimetry

DSC allowed to detect thermal properties of bijels, especially their melting and crystallization temperatures (T_m and T_c). They can be measured from the minimum and maximum peaks (which are associated to a specific scanned temperature, refer to section 2.2 for the program selected).

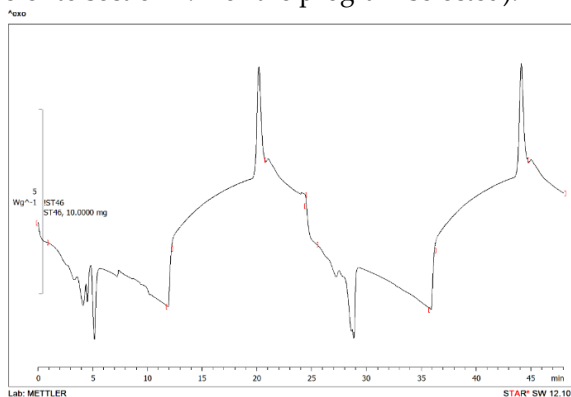


Figure 4 - DSC test of STR 46: ϵ -CL monomer with 40 mg/mL of graphene nanoplatelets.

Figure 4 shows DSC tests of an ϵ -CL-bijel with 40 mg/mL of graphene nanoplatelets. It is possible to deduce $T_m = 40$ °C and a $T_c = 20$ °C from the peaks position. All ϵ -CL samples tested showed a low melting temperature, between 28 and 40 °C. These values may produce an issue related to their possible application, due to their melting during their use.

ω -PDL-based bijels showed better thermal stability, close to the following values for each sample: $T_m = 80$ °C and a $T_c = 60$ °C.

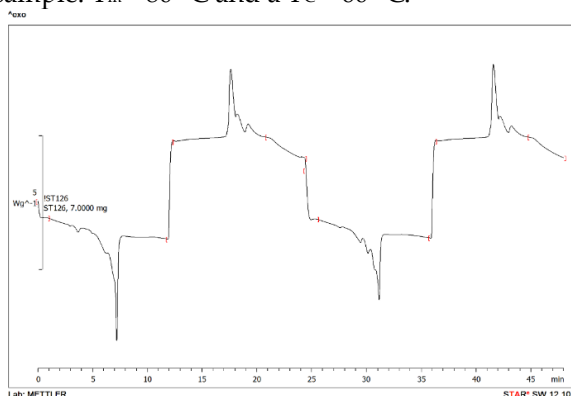


Figure 5 – DSC test of STR 126: ω -PDL monomer with 50 mg/mL of graphene nanoplatelets.

3.3. Gas detection tests

Gas detection tests have been made by alternatively exposing samples to air and an environment rich in acetone, the species selected to be representative of VOCs, present in large quantities compared to other VOCs [1]. Both lyophilized and not lyophilized samples were tested. Some not lyophilized samples of both ϵ -CL and ω -PDL monomers showed a significant response. It is possible to observe, in the selected figures below, Figure 6 and Figure 7, that when samples are exposed to acetone their electrical conductivity increases. Resistance difference percentage is defined as follows (Equation 1):

$$R_{\%}(t) = \frac{R_t - R_0}{R_0} \quad (1)$$

Equation 1 - Resistance difference percentage.

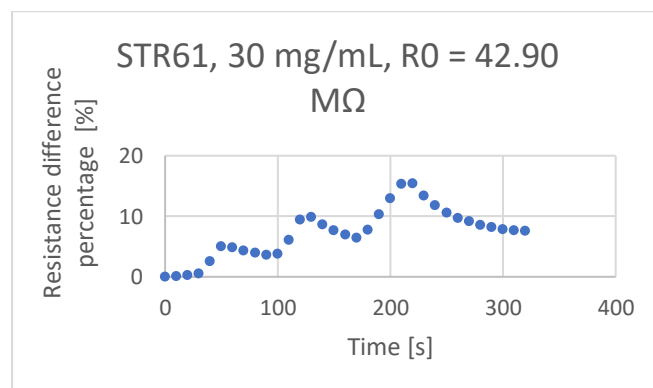


Figure 6 - STR 61 (ϵ -CL, 30 mg/mL of graphene nanoplatelets) response. Contact with acetone environment from 30 s to 50 s, from 100 s to 120 s, and from 170 s to 200 s.

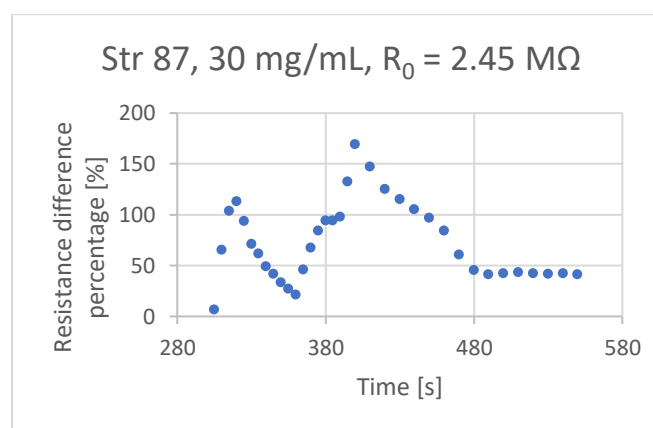


Figure 7- STR 87 (ω -PDL, 30 mg/mL of graphene nanoplatelets) response. Contact with acetone

environment from 270 s to 300 s, from 360 s to 390 s, and from 450 s to 480 s.

Other samples showed a less impressive but still relevant response. Graphene nanoplatelets showed more often a significant response than carbon nanotubes. Best responses, shown in the above figures, are associated to low or intermediate values of graphene nanoplatelets.

4. Conclusions

In this work, production of bijel-based materials to be employed as chemiresistors has been addressed. These materials showed a response when exposed to acetone, a species representative of VOCs, components characterized by a high volatility present in indoor environments, considered as source of potential health risks [1].

Bijels, bicontinuous structures characterized by the co-presence of a hydrophobic and hydrophilic phase, were produced with two formulations, using ϵ -CL or ω -PDL as monomers for the hydrophobic phase, due to their known capability to produce bijels [3] [4]. Graphene nanoplatelets or carbon nanotubes were added to the formulations to increase their electrical conductivity [5].

SEM results showed the successful production of bijels structures. ϵ -CL samples showed a network of channels having diameters between 30 and 50 μm , while ω -PDL samples showed globular structures of 10 μm in some cases and porous, sponge-like structures of the same scale. Since graphene nanoplatelets and carbon nanotubes are neutral molecules, it is supposed that bijel formation has been favored by two possibilities: some unreacted monomers moved to the interface between hydrophobic and hydrophilic phases, or the presence of graphene or nanotubes in the reacting mixture promoted their conversion to polar species, able to stabilize the interface between the two phases involved.

DSC tests allowed to estimate melting and crystallization temperatures, T_m and T_c . Concerning ϵ -CL, two samples showed T_m of 28 and 30 $^{\circ}\text{C}$ (for samples with 50 and 30 mg/mL or graphene nanoplatelets respectively), which limits possible applications of this material for sensing. ω -PDL samples showed homogeneous thermal properties among all the graphene or nanotubes concentrations (80 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$ as T_m and T_c). ω -PDL samples showed a remarkably better stability than ϵ -CL, allowing to imagine a possible indoor use of devices made by ω -PDL bijels.

Gas sensing tests were made to find if the bijels produced were able to detect the presence of VOCs. Many samples of both bijels produced a sharp increase in their electrical conductivity: for ϵ -CL, samples with 30 and 40 mg/mL, while for ω -PDL a sample with 40 mg/mL. In both cases for samples with graphene nanoplatelets. In both cases for samples with graphene nanoplatelets. ϵ -CL-bijels showed more often a response, as the best one, obtained with STR 61, an ϵ -CL-based bijel with 30 mg/mL as graphene nanoplatelets concentration. Since significant responses were obtained with intermediate or lower concentrations it is supposed an optimal quantity of these nanoparticles gives a positive increase in their electrical conductivity. The behavior of these materials may be associated to a physical adsorption of acetone onto their surface, according to recent studies on similar formulations. If this is the situation, further studies may consider determining a correlation between surface area and response of these materials.

References

- [1] Halios et al., "Chemicals in European residences – Part I: A review of emissions, concentrations," *Science of the Total Environment*, p. 839 156201, 2022.
- [2] M. E. Cates and P. S. Clegg, "Bijels: a new class of soft materials," *Soft Matter*, 4, p. 2132–2138, 2008.
- [3] G. Massobrio, Organic-inorganic bijel-like structures as controlled drug delivery systems. Master's thesis, 2021.
- [4] A. Partenope, Bicontinuous structures formed by monomer/water interface stabilization with colloidal nanoparticles. Mater's thesis, 2021.
- [5] F. Pinelli, T. Nespoli, A. Fiorati, S. Farè, L. Magagnin and F. Rossi, "Graphene nanoplatelets can improve the performances of graphene oxide – polyaniline composite gas sensing aerogels," *Carbon Trends* 5, no. 100123, 2021.

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