TNT-MOLECULARLY IMPRINTED MEMBRANES VIA PHASE INVERSION METHOD

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Abstract: *This paper aims to provide novel molecularly imprinted membranes with TNT as template (TNT-MIMs) prepared via wet phase inversion. Two PAN -co-acrylic acid matrix systems, obtained by free emulsion polymerization, were used to prepare copolymer solutions in dimethylformamide in order to establish the appropriate parameters for membrane preparation (rheological study). Additionally, experimental FT-IR spectroscopy has been conducted to validate both TNT imprinting and extraction. The TNT-MIMs can be further used as sensing receptors to prepare a versatile sensor.*

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1. Introduction

TNT (2,4,6-trinitrotoluene), a widely and inexpensive nitroaromatic explosive compound, is commonly used in military and terrorist activities. Its detection is newsworthy considering global environmental protection and national security issues [1,2]. Different techniques have been reported for TNT detection, such as fluorescence [3,4], luminescence spectroscopy [5], immunochemistry [6], ion mobility spectrometry [7,8] and Raman spectroscopy [9]. There are some limitations concerning the above mentioned techniques, hence it is crucial to discover new sensitive methods for TNT rapid detection based on state-of-the-art techniques i.e. molecular imprinting (MI). MI has become one of the most promising methods for preparing artificial receptors with tailor-made molecular recognition binding sites (known as molecularly imprinted polymers – MIPs). This technology consists in the polymerization of functional monomers in the presence of target molecules (called template), via reversible interactions. Template removal creates complementary cavities in shape, size and electronic entourage with template molecules being responsible for the recognition process [10].

Over the last decades, MI has been used to develop molecularly imprinted membranes (MIMs) used as separation tools and electrochemical sensing receptors. Phase inversion is regarded as an attractive technique in order to prepare MIMs [11] or imprinted pearls [12] due to its advantages including high efficiency, processing simplicity, operating at atmospheric pressure and temperature.

Herein, we report the preparation and characterization of novel TNT molecularly imprinted membranes obtained by phase inversion method using acrylonitrile (AN) and acrylic acid (AA) as functional monomers. The main objective referred to the evaluation of the imprinting effect (confirmed by FTIR spectroscopy) over the polymer matrix, in order to establish whether or not these precursor membranes can be further used as sensitive elements for TNT.

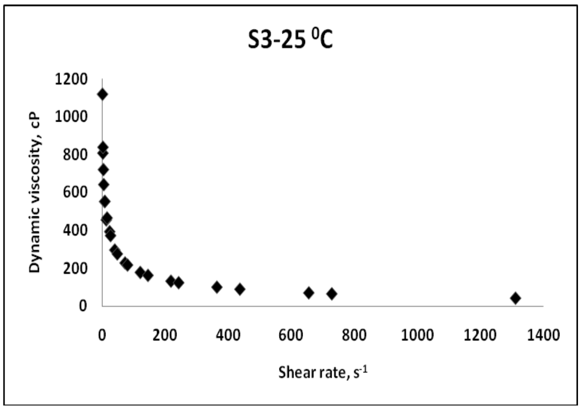
2. Experimental section

Two PAN-co-PAA systems, prepared by soap-free emulsion copolymerization, were intensively studied by our group using different weight ratios of AN: AA monomers according to a previously procedure described by some of us [12]. For this particular application two AN: AA ratios were developed, 80:20 and 85:15, noted hereafter as S3 and S4, respectively. The copolymers (8 wt. % relative to solvent) were dissolved in dimethylformamide

(DMF, solvent) at 80 °C for about 2 h. The imprinted precursor solutions were obtained by adding TNT (10 wt. % relative to copolymers) at room temperature. The non-imprinted and imprinted membranes were obtained by casting the above solutions using a glass plate and a dragging technique. Immediately, the membranes were generated using water coagulation baths. The membranes were maintained in the inversion media in order to stabilize their structures. TNT was extracted with ethanol, in an ultrasonic bath for 30 minutes at room temperature. Finally, the membranes were dried at 60 °C for 24 h, for analysis.

3. Results and discussion

The two copolymer precursor solutions were rheological inspected in order to elucidate their behaviour when contacting the coagulation water bath. Figures 1 and 2 indicate the rheological behaviour of S3 and S4 solutions at 25°C and at 50°C. It can be observed that the solutions are characterized by a pseudo-plastic flow (described by a decrease of viscosity with the shear rate) and that the pseudo- plastic behaviour is more obvious at higher extents of AA (S4). S4 solution showed lower dynamic viscosity than S3 solution at the same shear rate due to higher content of AN, responsible for the intercatenar hydrogen bonds. The pseudo-plastic behaviour has a clear tendency to shift towards Newtonian (cvasi-Newtonian) behavior at higher shear rates. As expected, the incresease of temperature led to a decrease of dynamic viscosity, which is more pronounced in the case of S3 solution. Upon TNT addition (figure 3), it was noticed a similar flow behaviour as in the case of the non-imprinted precursor solutions (without TNT).



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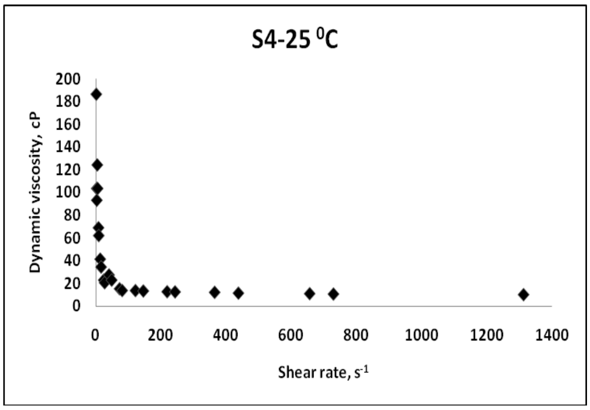

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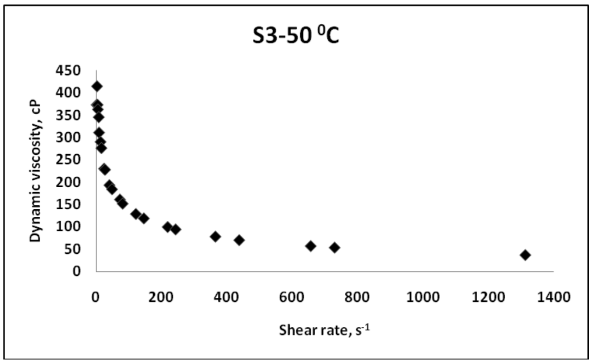
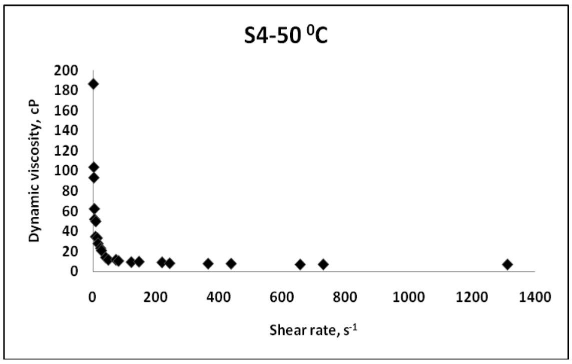


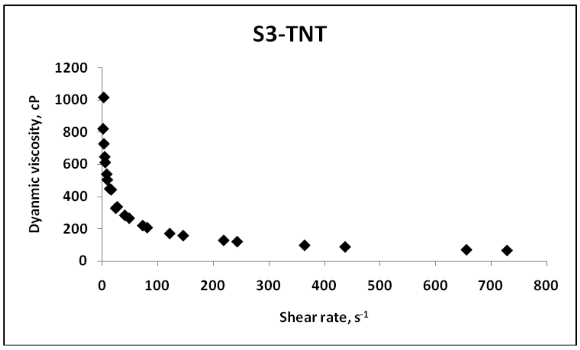
(b)

Figure 1. *Rheological behaviour of S3 sample (a) at 25 °C and (b) at 50°C*



(b)

Figure 2. *Rheological behaviour S4 sample (a) at 25 °C and (b) at 50°C*



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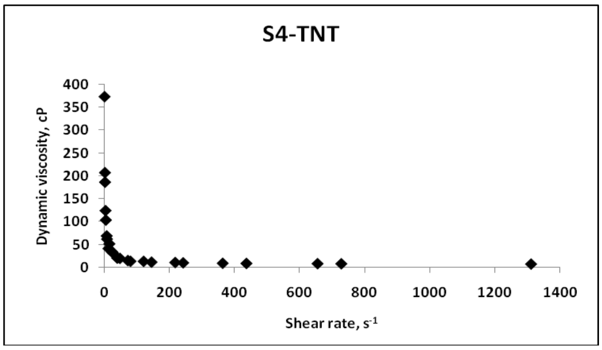
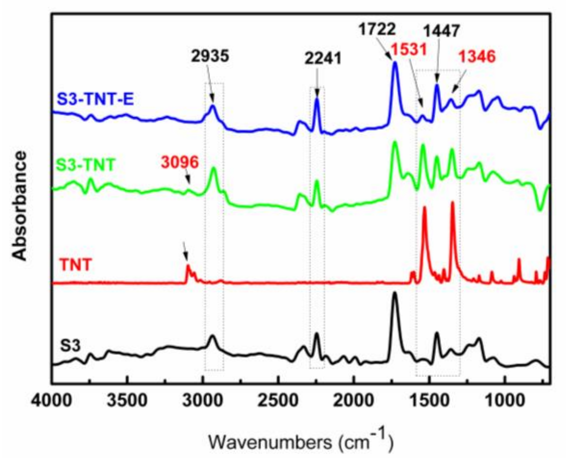


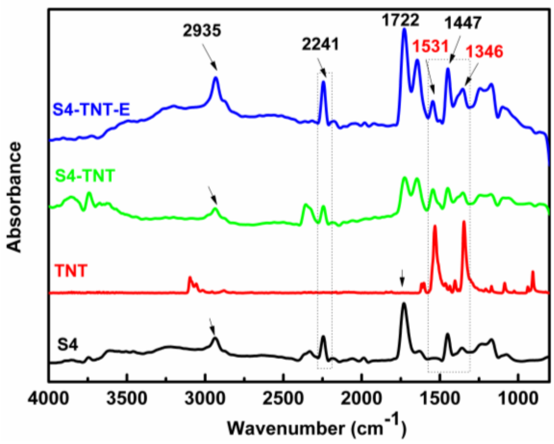
(b)

Figure 3. *Rheological behaviour of imprinted precursor solution at 25 °C for S3, (a) and S4, (b) samples*

As figure 4 revealed, FT-IR investigations highlighted the presence of characteristic S3 and S4 polymer bands and of those affected by the TNT-imprinting process. Characteristic bands of copolymer i.e. $\nu_{-C\equiv N}$ band (corresponding to AN monomer) and characteristic vibrations of the carboxyl functionality (a.k.a. ν_{-OH} and $\nu_{-C=O}$ bands associated with AA presence) appeared at 2241 cm^{-1} and at 1722 cm^{-1} wavelength, respectively. Also, comparing the TNT spectra, with the imprinted ones, sample-TNT, the appearance of a peak at 3096 cm^{-1}, corresponding to nitroaromatic specific bands, confirmed the presence of TNT in the imprinted membranes. This specific band completely disapears after ethanol extraction (sample-TNT-E), suggesting a proper extraction.



(a)



(b)

Figure 4. *FTIR spectra of precursor copolymer powder (S) and membrane of S-TNT and S-TNT-E compared to TNT alone for the S3 (a) and S4 (b) series*

4. Conclusions

In the present study, novel molecular imprinted membranes with TNT based on acrylic monomers, were successfully prepared via the wet phase inversion techniques. Furthermore, this particular inversion phase method provides a simple route to obtain imprinted membranes promising to the sensor research field.

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