Chemical Modification of Poly(Vinyl Chloride) Using Aniline Characterization and Antimicrobial Evaluation

Ahmed Tabchouche[1*], Naoual Zobeidi[1], Abdellatif Rahmani[1], Khaled Mansouri[2], Abdelmalik Tahraoui[1]

[1] Faculté Des Sciences Appliquées, Laboratoire de Dynamique Interaction Et Réactivités Des Systèmes BP 511, Route de Ghardaïa, Université Ouargla, 30000, Ouargla, Algeria.

[2] Laboratoire. Mathematics and Applied Science, Ghardaïa University BP 455Ghardaïa, Algeria.

* Corresponding author: tabchouche.ahmed@gmail.com

nawalzoubeidi@gmail.com

dr.rahmani.univ.ouargla@gmail.com

khaledmansouri31@gmail.com

tahraoui.malik@gmail.com

Received: 12/05/2023; Accepted: 18/12/2023

Abstract

Polyvinyl chloride (PVC) modified with aniline was synthesized. The method is based on the nucleophilic substitution of a fraction of the chlorine atoms bound to the poly(vinyl chloride) backbone by aniline.

The chemical structure of the polymer-aniline matrix was analyzed using High-Resolution Nuclear Magnetic Resonance (HRMN), Carbon-13 Resonance Magnetic Resonance (CRMN), and Infrared (IR) spectroscopies, and its stability was studied by thermal analysis using TG and DSC.

The introduction of aniline groups into the PVC chains assists in giving new catalytic properties and high performance as a surfactant polymer.

The antimicrobial activity of the modified PVC was evaluated successfully against Gram-negative bacterial pathogens, such as Escherichia coli, and one Gram-positive bacterium, Staphylococcus aureus.

Keywords: aniline, PVC, chemical modification, antibacterial properties.

Tob Regul Sci.™ 2023;9(2):2595 - 2602

DOI: doi.org/10.18001/TRS.9.2.169

Introduction

Polymer composites remain one of the most excitingly developed materials in this century due to their ability not only to reduce costs but also to enhance properties such as mechanical, thermal, and barrier properties of the final polymer product [1,2].

The modification of surface properties in polymers has opened up numerous new application areas for these materials. The primary goal of surface treatment is to alter the outermost layer of a polymer by introducing functional groups onto the surface, thereby improving barrier properties, wettability, sealability, printability, dye uptake, resistance to glazing, and adhesion[3,4].

The modification of polymers has garnered increased attention to impart specific properties to the modified material, including physical aspects such as thermal stability and mechanical strength, as well as biological response.

Various ligands, such as polydentate amines, crown ethers, and bipyridine, have been bound primarily with polystyrene divinylbenzene copolymers[5,6].

Polyvinyl chloride (PVC) stands out as one of the most versatile polymers[7], attributed to its low production costs and excellent stability. Its significance extends to the advancement of macromolecular chemistry, and some PVC research focuses on industrial applications, covering polymerization, stabilization, bulk property modification, and the chemical and material recycling of PVC waste[8,9].

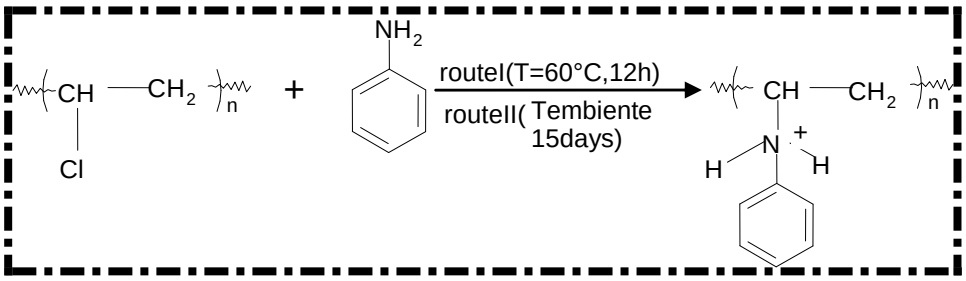
Recentlyit has been shownthat PVC can also be used as an interesting starting membrane material for electrodes containing active ionic species (iono phores). Generally large charged hydrophobic molecules of opposite charge to that of the investigated surfactant, and aplasticizer.

It was assumed that the surfactant may form an immobile complex with the ionophore; therefore, the membrane in its conditioned state can be used for the construction of electrodes with a Nernstian response in the function of the equilibrium surfactant activity.

Transformation reactions of PVC have been studiedin both wet and dry processes with various

conditions[10]: organic media, aqueous solutions, aqueous suspensions,swollen states, phase transfer catalyzes (phase transfer catalysis),melt, solvent/non-solvent systems, irradiation, microwaveplasma, and ultrasound means. In the melt systems, thestudies were carried out as functions of the processingfactors, such as temperature, shear, resilience time, andscrew configuration. Processing conditions may include roll-milling, compression molding, and extrusion. In the wet process (solution), however, the nature of the nucleophile is not the only parameter that affects the transformation extent, but also, and to a greater degree, the nature of the solvent, the temperature, and the duration of the reaction.

In this work, two different strategieswere used to prepare a new graft copolymer conductive PVC-aniline.



Schema.1Mechanism for dechlorination of PVC with aniline

Experimental Section

Materials. PVC 4000 M (Mw=65,400) used in this study was produced at Skikda, Algeria.

PVC([ɳ] dl/g) =0.44a , Tg(˚C) = 81. Aniline (Aldrich) was distilled under vacuum before use. Tetrahydrofuran (THF) andethanol (Fluka) were used without further purification.

Modification of poly(vinyl chloride) by aniline

The modification was achieved in two different techniques, first,the modification was performed by dissolving in a 250 mL flask 2gof PVC in 100 mL of THF. The mixture was stirred and heatedat 60˚C for 12h under N2 atmosphere.

The obtained solution was cooled to room temperature, filtered , and the resulting product, PVC-aniline, was precipitated into excess ethanol and purified from the THF solution by reprecipitation in ethanol

The second synthesis technique is simpler and economical. In this method, 2g of PVC was dissolved in 100 mL of THF. The aniline was added to the copolymer solution. The mixture was stirred and left for 2 weeks at room temperature. After a 2-week reaction period, the reaction vessel was opened. The resulting polymer film was precipitated into excess ethanol and purified from the THF solution by reprecipitation in ethanol. Finally, the polymer was dried in a vacuum until it reached constant mass.

Methods

1H NMR spectra were obtained on a 400 MHz Bruker AVIII 400machine, using C5D5N as the solvent. Infrared spectra were recorded on a Perkin–ElmerSpectrum One FTIR spectrometer. Calorimetric measurementswere carried out on a Shimadzu DSC-50 thermal analyzer under N2flow using a heating rate of 20 °C/min. Thermal stability studieswere carried out on a Shimadzu TGA-50 thermobalance under N2flow with a heating rate of 10 °C/min.

In vitro antibacterial activity

The antibacterial properties of the modified PVC were assessed using the agar disk diffusion method with disks of 6 mm in diameter. For this purpose, selected microorganisms, namely Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, and Pseudomonas aeruginosa, were utilized as model bacteria.

The surfaces of agar plates were uniformly inoculated by swabbing with a bacteria suspension (106–107 cfu/mL). After a 24-hour incubation at 37°C, the dimensions of the inhibition zones were measured in four directions, and the average values were used to calculate the area of the circular inhibition zone.

Results and discussion

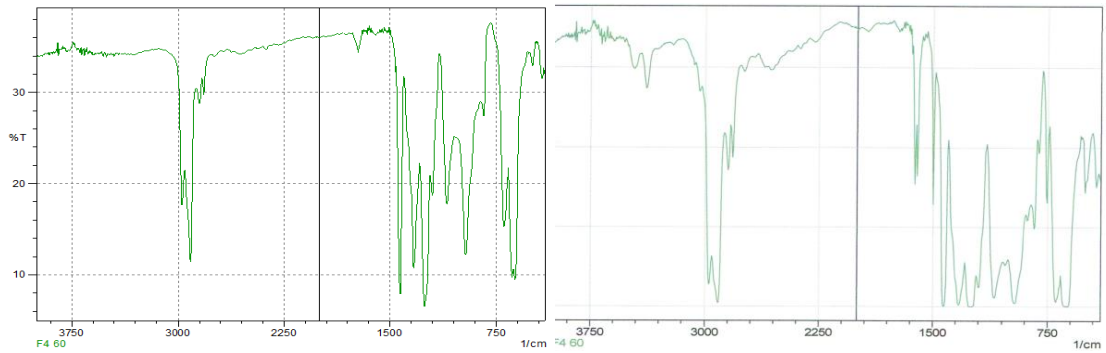


Fig .1. FT- IR spectra of (right) PVC, (left) modified PVC.

All of these spectra were obtained from KBr pellets. In comparaison with fig .1 (left) showsthe new peaks at 3450-3375 cm^{-1} due to N-H stretch and 1650-1500 cm-1 due to c=c stretch. This result implies some chlorine groups in PVC chain were substitued with aniline groups.

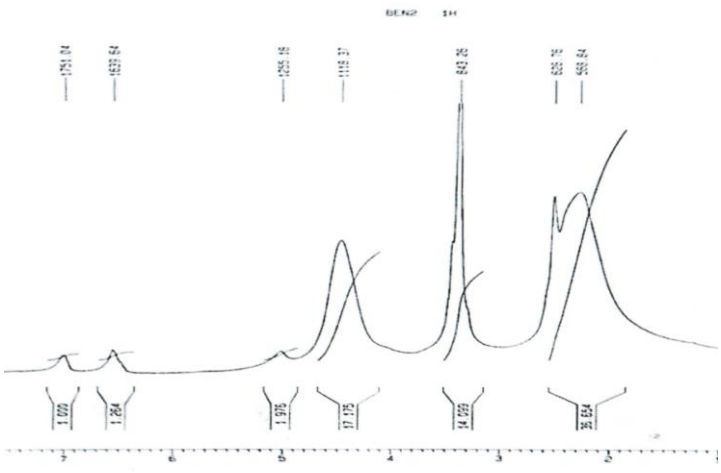


Fig.2. shows 1HMR spectrum of modified PVC.

The occurrence of the peaks at δ =6.5 and 7.0 in Fig. 2 and that at 3450-3375 cm^{-1} and 1650-1500 cm^{-1} in Fig. 1(left) indicate that aniline groups have been bound to PVC.

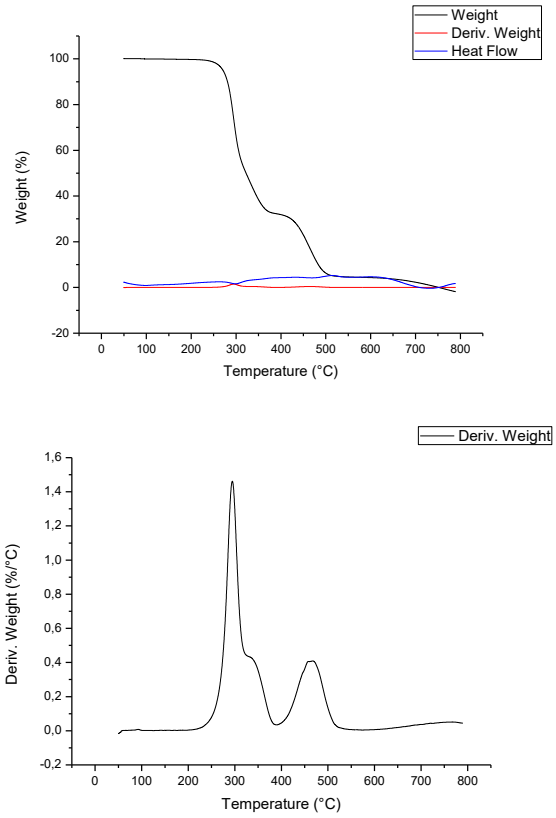


Fig.3. TGA thermograms of PVC

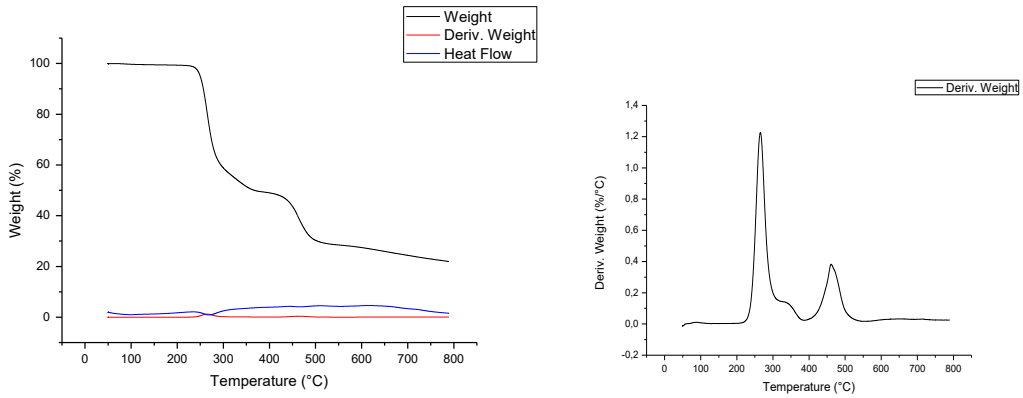


Fig.4. TGA thermograms of modified PVC

The TGA thermograms of PVC and modified PVC are presented in Fig. 3 and 4. In the case of PVC, the weight loss initiates at 265 °C. Between 265 and 360 °C, a rapid weight loss occurs, and PVC loses 60% of its weight, attributed to dehydrochlorination. The dehydrochlorination reaction concludes around 400 °C [11]. The weight loss above 400 °C can be attributed to polymer decomposition.

However, For the modified PVC film, a 6.2% weight loss occurs at about 247 °C, attributed to the expulsion of loosely bound water molecules from the polymer chain. Between 247 and 375 °C, a slower weight loss than in the case of PVC occurs, reaching about 54%. This is mainly attributed to dopant loss and the beginning of chain degradation. Above this temperature range, the polymer exhibits a very slow weight loss process assigned to main chain degradation. The composite shows lower weight losses compared to raw PVC, confirming its higher thermal stability. The relatively stable thermal degradation behavior of the copolymer above 375 °C might be due to the grafted branch polymer.

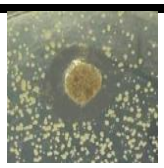
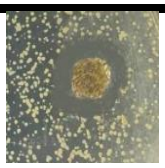
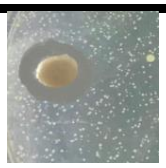
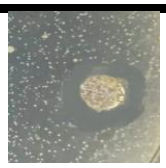
Two DTG peaks are found at 298.6 °C and 443.5 °C, corresponding to dehydrochlorination and depolymerization. The DTG curve of PVC depicts that the maximum degradation occurs at the temperature of 298.6 °C with a rate of 1.048 mg/min. Fig. 4 shows the TG, DTA, and DTG curves of PVC and modified PVC.Top of Form.

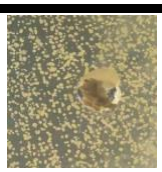
In vitro antibacterial activity

The results of the antibacterial activity studies, conducted using the agar diffusion test method, are presented in the respective figures (Table 1). The data is illustrated in the form of dependencies, showing the diameter of the growth inhibition zone against the concentration of antibiotics in the polymer film. As previously mentioned, our experiment focused on the antibacterial action of the polymer/antibiotic films against both Gram-positive (S. aureus) and Gram-negative (Escherichia coli, Pseudomonas aeruginosa, and Salmonella) bacterial strains. Notably, other tested bacterial strains are not inhibited in this case.

Conversely, the modified PVC systems demonstrate significant inhibition of the growth of all studied bacterial strains (Table 2). The investigated films exhibit the highest effectiveness against Staphylococcus aureus, followed by Gram-negative strains Escherichia coli, Klebsiella pneumoniae, and Pseudomonas aeruginosa, respectively. However, representatives of the Gram-negative strains sustain approximately half as large inhibition zones as the Gram-positive Staphylococcus aureus.

Table 3 Antimicrobial activity of modified PVC against human bacterial pathogens.

Bacteria Strains				
	E. coli	***S. aureus***	***K. pneumoniae***	***P. aeruginosa***
Modified PVC				

PVC				

Conclusions

In conclusion, poly(vinyl chloride) (PVC) modified through the incorporation of aniline was prepared and characterized. The synthesis of the functionalized polymer is based on the nucleophilic substitution of a fraction of the chlorine atoms bound to the poly(vinyl chloride)backbone by aniline. The introduction of aniline resulted in significant changes in the material's chemical structure and thermal stability

The modified PVC exhibited enhanced antimicrobial activity compared to unmodified PVC, suggesting the potential utility of the modified material in applications where microbial resistance is desirable.

Bibliography

[1] SABA, N. et JAWAID, M. A review on thermomechanical properties of polymers and fibers reinforced polymer composites. Journal of industrial and engineering chemistry, 2018, vol. 67, p. 1-11, doi.org/10.1016/j.jiec.2018.06.018

[2] HSISSOU, Rachid, SEGHIRI, Rajaa, BENZEKRI, Zakaria, et al. Polymer composite materials: A comprehensive review. Composite structures, 2021, vol. 262, p. 113640,doi.org/10.1016/j.compstruct.2021.113640

[3] D'SOUZA, Anisha A. et SHEGOKAR, Ranjita. Polyethylene glycol (PEG): a versatile polymer for pharmaceutical applications. Expert opinion on drug delivery, 2016, vol. 13, no 9, p. 1257-1275,doi.org/10.1080/17425247.2016.1182485

[4] ZHANG, Yongqi, MAN, Jia, WANG, Jiali, et al. Surface modification of polyvinyl chloride with sodium alginate/carboxymethyl chitosan and heparin for realizing the anticoagulation. International Journal of Biological Macromolecules, 2023 Nov 2;254(Pt 3):127653, doi.org/10.1016/j.ijbiomac.2023.127653

[5] LEADBEATER, Nicholas E. et MARCO, Maria. Preparation of polymer-supported ligands and metal complexes for use in catalysis. Chemical Reviews, 2002, vol. 102, no 10, p. 3217-3274,doi.org/10.1021/cr010361c

[6] DZHARDIMALIEVA, Gulzhian I. et UFLYAND, Igor E. Synthetic Methodologies for Chelating Polymer Ligands: Recent Advances and Future Development. ChemistrySelect, 2018, vol. 3, no 46, p. 13234-13270, doi.org/10.1002/slct.201802516

[7] SINGH, Ritu et PANT, Deepak. Polyvinyl chloride degradation by hybrid (chemical and biological) modification. Polymer Degradation and Stability, 2016, vol. 123, p. 80-87,doi.org/10.1016/j.polymdegradstab.2015.11.012

[8] RAMESH, S., WINIE, Tan, et AROF, A. K. Investigation of mechanical properties of polyvinyl chloride–polyethylene oxide (PVC–PEO) based polymer electrolytes for lithium polymer cells. European polymer journal, 2007, vol. 43, no 5, p. 1963-1968, doi.org/10.1016/j.eurpolymj.2007.02.006

[9] MILIUTE-PLEPIENE, Jurate, FRÅNE, Anna, et ALMASI, Alexandra Maria. Overview of polyvinyl chloride (PVC) waste management practices in the Nordic countries. Cleaner Engineering and Technology, 2021, vol. 4, p. 100246, doi.org/10.1016/j.clet.2021.100246

[10] LI, Tian, ZHAO, Peitao, LEI, Meng, et al. Understanding hydrothermal dechlorination of PVC by focusing on the operating conditions and hydrochar characteristics. Applied Sciences, 2017, vol. 7, no 3, p. 256, doi.org/10.3390/app7030256

[11] CRUZ, Patrick Pimenta R., DA SILVA, Leonardo Cerqueira, FIUZA-JR, Raildo A., et al. Thermal dehydrochlorination of pure PVC polymer: Part I—thermal degradation kinetics by thermogravimetric analysis. Journal of Applied Polymer Science, 2021, vol. 138, no 25, p. 50598, doi.org/10.1002/app.50598