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CHEMICAL MODIFICATION OF PVC FOR POLYMER MATRICES WITH SPECIAL PROPERTIES

Claudiu LĂZĂROAIE[1], Edina RUSEN[2], Bogdan MĂRCULESCU[3],
Teodora ZECHERU[4], Gheorghe HUBCĂ[5]

Studii recente au relevat faptul că îndeplinirea anumitor condiții în vederea utilizării PVC-ului este condiționată de alegerea unui raport optim între părțile hidrofilă şi hidrofobă ale suprafeței polimerului. Studiul prezent a avut drept scop creşterea procentului hidrofil prin modificări chimice. S-au obținut derivați de PVC care au fost caracterizați prin FT-IR, analiză elementală, UV şi GPC. S-a demonstrat faptul că modificările chimice de suprafață ale PVC-ului este metoda optimă în vederea schimbării naturii chimice a suprafeței pentru utilizarea în aplicații speciale.

Recent studies have highlighted that the fulfillment of important conditions for PVC use is considered by an optimum ratio between hydrophilic and hydrophobic parts of the polymer surface. The research was conducted with the purpose to increase the hydrophilic part by chemical modifications. PVC-derivatives were obtained, and they were characterized through FT-IR, elemental analysis, UV and GPC. It was demonstrated that chemical modification of PVC proves to be a facile method to change the surface chemical nature, in order to become suitable for the special required applications.

Keywords: Poly(vinyl chloride), surface modification, grafting

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most versatile polymers for general use, with application in various fields, including body protection or medicine. For some purposes, the only requirement is to be chemically and biologically pure, requirement easy to fulfill through a rigorously controlled processing, followed by sterilization and conservation in sterile environment.

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[1] Sci. Res. 3rd deg., NBC Defense and Ecology Scientific Research Center, Romania, claudiu@nbce.ro

[2] Lecturer, Faculty of Materials Science and Applied Chemistry, University POLITEHNICA of Bucharest, Romania

[3] Reader, Faculty of Materials Science and Applied Chemistry, University POLITEHNICA of Bucharest, Romania

[4] Sci. Res., NBC Defense and Ecology Scientific Research Center, Romania

[5] Prof., Faculty of Materials Science and Applied Chemistry, University POLITEHNICA of Bucharest, Romania

When talking about the applications involving the direct contact with the human body (organs, blood plasma, etc.), supplementary restrictions are to be considered and the biological compatibility is even more difficult to achieve. Biological compatibility is referring to the increase of organism's tolerance towards polymeric surface and, simultaneously, to the repulsive response of the same surface towards microbial deposits or living cell.

The substantial improvement of interfacial compatibility between PVC and liquid medium can be achieved by different surface treatments, simultaneously with strong reduction of adverse reaction induced by the contact of biological active liquids with additives from PVC formulation [1].

Surface modification of polymers has found recent application in the field of obtaining some contrast agents with high performance in ultrasound technique [2]. Membranes with surface attached lipids films are used in biophysics or in biosensor manufacture. Biological active films are obtained by chemical binding of Langmuir-Blodgett films, obtained from amphiphilic polymers, on the surface of synthetic polymers membranes [3].

The most used methods for composition modifications, strictly surface located (preserving the composition and mass properties), are presented in Table 1.

Table 1

General surface modification methods for polymers [4-10]

1. Physical methods	2. Chemical methods (reagents treatment)*	3. Physical-chemical methods (radiation use in the presence of reactive gases)**
Physical adsorption of Langmuir-Blodgett films	- Functionalization with gaseous reagents; - Functionalization with liquid reagents; - Vapour phase chemical grafting; - Liquid phase chemical grafting.	- Plasma discharge; - Corona discharge; - UV irradiation; - Laser ion beam; - Laser ion beam; - Electron beam; - γ irradiation.

*"Functionalization" means the attachment of organic functions on polymeric surface (halogenation, oxidation, nitration, sulfonation, amidation);

**"reactive gases" designate any substance in gaseous phase, from atmospheric gases (O_2, N_2) to monomers in vapor phase, when a group of mixed methods among columns 2 and 3, respectively photo- and radio-induced grafting, are considered.

Table 2 gives some of the most important applications of surface-modified synthetic polymers in different fields, focusing on the defense and protection field.

Researches carried out in the last decade have highlighted that the fulfillment of these conditions is decided by an optimum ratio between hydrophilic and hydrophobic parts of the polymer surface. Due to the fact that

PVC is intrinsically hydrophobic, researches were conducted in order to increase the hydrophilic part by chemical modifications.

Table 2

Special applications of surface-modified synthetic polymers [11-13]

Applicability	Uses	Materials	Objectives
Nuclear, Biological and Chemical (NBC) Defense	- polymer matrices; - polymer composites.	PVC, PE, PMMA, nanotubes	- molecule immobilization; - protection equipment.
Biosensors	- sensor membranes; - diagnostic biosensors.	PC, PP, cellulose, PS	- biomolecule immobilization.
Bioseparations	- separation membranes; - haemodialysis membranes.	PP, cellulose derivatives, PSF	- enhanced biocompatibility; - wettability enhancement.
Cardiovascular	- vascular grafts; - catheters.	PET, PTFE, PE, SiR, PVC, PU	- improved biocompatibility; - wettability enhancement; - reduced friction; - lubricious coatings; - antimicrobial coatings.
Ophthalmological	- contact lenses; - intraocular lenses; - artificial corneas.	PMMA, SiR, PMMA, SiR, PVA, PHEMA	- improved biocompatibility; - wettability enhancement; - antimicrobial coatings.
Orthopaedic	- joints; - ligaments.	UHMWPE, PET	- enhancement cell adhesion; - enhancement tissue in-growth.
Pharmacy	- devices for drug controlled release.	SiR, PGA, PLA	- reduction of molecule diffusion.
Tissue culturing	- tissue culture supports	PS, PET	- enhanced cell adhesion / growth; - wettability enhancement.

Abbreviation: PET (polyethylene terephtalate); PTFE (polytetrafluoroethylene), PE (polyethylene), SiR (silicone rubber), PVC (polyvinyl chloride), PU (polyurethane), PMMA (polymethyl methacrylate), UHMWPE (ultra high molecular weight polyethylene), PGA (polyglycolic acid), PLA (polylactic acid), PS (polystyrene), PC (polycarbonate), PP (polypropylene), PSF (polysulfone), PHEMA (polyhydroxyethyl methacrylate).

Generally, the effect found for surface parameters may be revealed both by radical chemical modifications of bulk polymer and by modification operated strictly at the surface level, without modifying the composition and properties of the bulk polymer. Several methods for localized chemical modifications were tested in this study. The following approach strategy was considered: polymer-analogue reactions were carried out on PVC suspension. The composition modification, even it is limited to surface coating, can be detected by common identification techniques, due to high specific surface.

2. Experimental

2.1. Raw materials and reagents

Table 3

Materials

Name	Symbol	Role	Origin/method of purification
Poly(vinyl chloride)	PVC	Polymeric support	OLTCHIM, obtained by suspension polymerization, Molecular weight=50,300, elemental analysis (0% N, 39.36% C, 4.83% H), (grains); d=0.063-0.09 mm
Ethylenediamine	EDA	Reagent	Merck, vacuum distillation, t=54.44 °C, p=50 mmHg
Hexamethylene diisocyanate	HMDIC	Reagent	Merck
Hexane	H	Reaction medium	Aldrich, deposited on molecular sieves of 4Å
Benzene	B	Reaction medium	Chimopar, distillation at t=80 °C
Polyethylene glycol (400 and 1500)	PEG 400 and PEG 1500	Reagents	Fluka
Acrylamide	AA	Reagent	Merck
2-phenyl-2-oxazoline	FO	Reagent	Merck
Carbon tetrachloride	CCl_4	Reaction medium	Chimopar, distillation at t=76.8 °C
Acetone	A	Reaction medium	Chimopar, distillation at t=56 °C
Sodium iodide	NaI	Reagent	Aldrich
Methanol	M	Precipitation medium	Chimopar, distillation at t=65 °C
Heptane	HEP	Reaction medium	Aldrich, anhydrised by deposition on molecular sieves of 4Å
Ethanol	E	Precipitation medium	Absolute Ethanol, Fischer

Other reagents, used for precipitations, washing or extractions, were used as received from Chimopar.

2.2. Methods

a. Amination of PVC

The amination reaction of PVC for the PVC-NH_2 obtaining was performed in a three-neck reactor, provided with stirrer and nitrogen bubbler. Reaction (Fig. 1) was carried out for 1 h at 80 °C. Working protocol consisted in mixing 2 g of PVC and 20 ml EDA aqueous solution 80%, followed by polymer separation by filtration and washing with distilled water, for amine removal, and finally drying under vacuum up to constant mass.

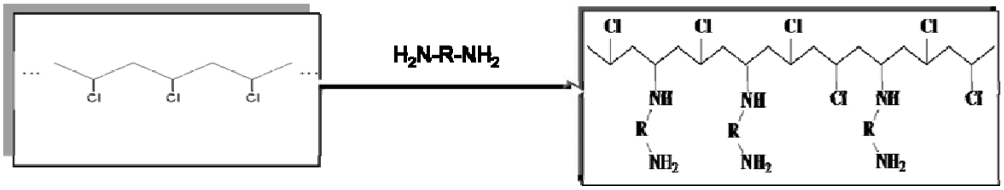


Fig. 1. Preparation of PVC-NH_2

b. Reaction of PVC-NH_2 with HMDIC

1 g of PVC-NH_2 was dosed in a reactor provided with stirrer and nitrogen bubbler. HEP (25 ml) was used as reaction medium, and 2 ml of HMDIC were added. Reaction was carried out at room temperature, for 1 h. When the reaction was completed (Fig. 2), the product was separated by filtration and by washing with HEP. After drying under vacuum, it was kept in a desiccator, in order to prevent uncontrolled hydrolysis reactions.

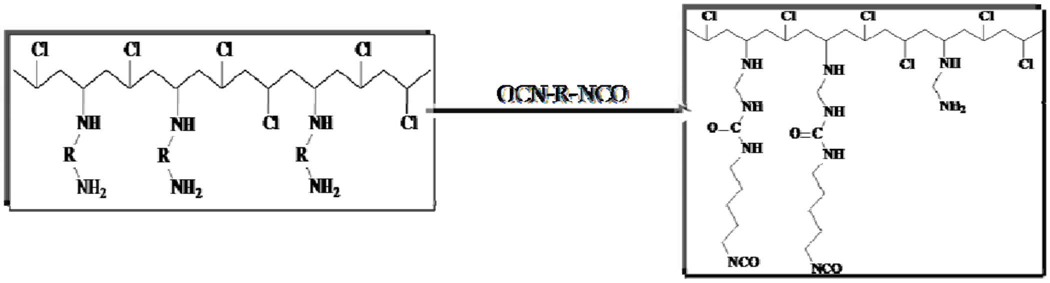


Fig. 2. Grafting reaction for the preparation of PVC-NH_2-HMDIC

c. Reaction of PVC-NH_2-HMDIC with PEG 400 and PEG 1500

0.37 g of PVC-NH_2-HMDIC was dosed in a reactor provided with stirrer and nitrogen bubbler. Reaction was carried out in benzene (10 ml), by adding subsequently PEG 400 (0.74 ml) and PEG 1500 (2.78 ml), respectively. The PEG-ilation (Fig. 3) was carried out at room temperature, for 15 min. The obtained product was separated by filtration, followed by washing with ethanol in order to remove any impurities, and it was dried under vacuum up to constant mass.

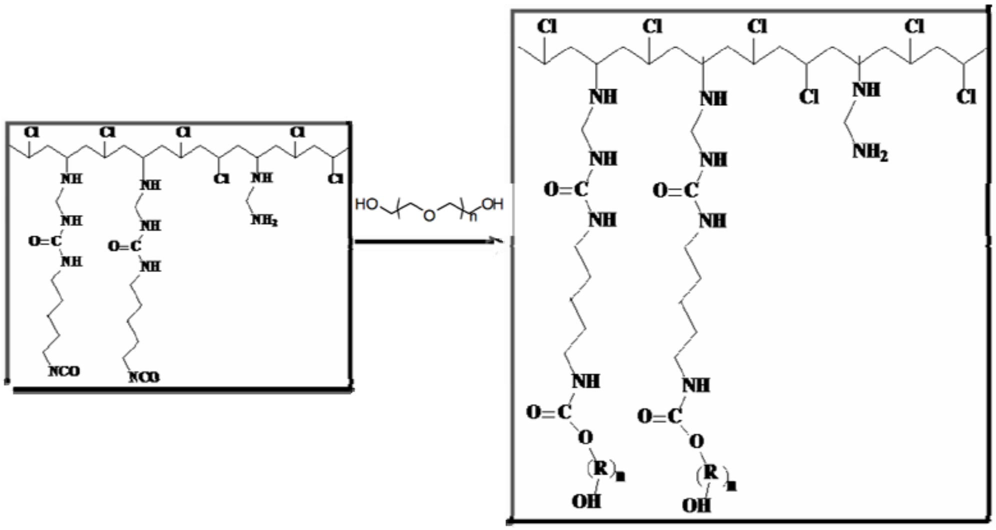


Fig. 3. PEG-ilation of PVC-NH_2-HMDIC

d. Reaction of PVC-NH_2 with AA

Michael reaction, Fig. 4, was performed in a single-neck flask for 3 h, under stirring, at room temperature. AA was in excess (AA/PVC-NH_2=3/1 molar, where AA used was 80% aqueous solution). When the reaction was completed, the product (Fig. 5) was separated by filtration, washed with distilled water in order to remove unreacted AA and then dried under vacuum up to constant mass.

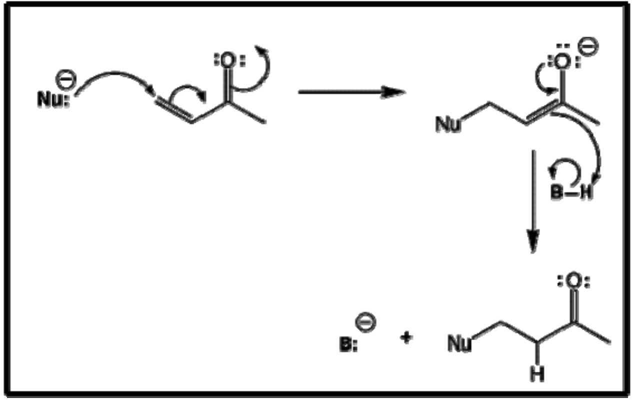


Fig. 4. Michael reaction

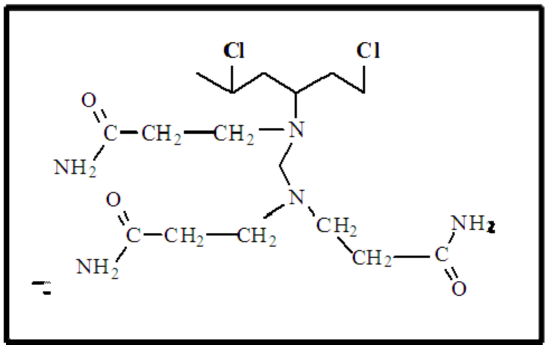
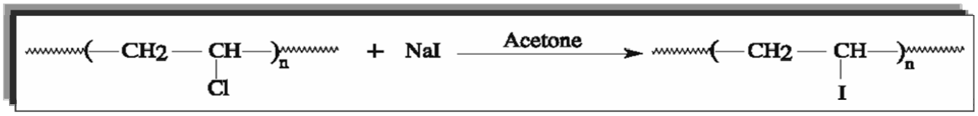


Fig. 5. Structure of the product resulted from PVC-NH_2 with AA reaction

e. Conant-Finkelstein reaction

1g PVC was suspended in 50 ml acetone, 2.4 g of NaI in 100 ml acetone were added to this solution, and then the reaction (Fig. 6) was carried out in a flask provided with stirrer, both at room temperature for 5 h, and at 50 ^{o}C for 1.5 h, in the view of modifying the iodination degree. After completing the reaction time, the modified polymer, PVC-I, was precipitated in a mixture of methanol/distilled water=2/1 (vol./vol.), separated and dried under vacuum up to constant mass.



$$\sim\!\left(-CH_2-\underset{Cl}{\underset{|}{CH}}-\right)_n\!\sim \; + \; NaI \xrightarrow{Acetone} \sim\!\left(-CH_2-\underset{I}{\underset{|}{CH}}-\right)_n\!\sim$$

Fig. 6. PVC iodination.

f. Grafting reaction of FO on PVC-I

0.5 g of PVC-I were dispersed in CCl_4 (15 ml) and an excess of FO (2 ml) was added. FO grafting reaction, Fig. 7, was carried out in a reactor provided with stirrer and under nitrogen, at 70 ^{o}C, at various reaction times. The product obtained was separated by filtration and washed with CCl_4 (in order to separate the oxazoline grafted on PVC-I from FO homopolymers), then dried under vacuum up to constant mass.

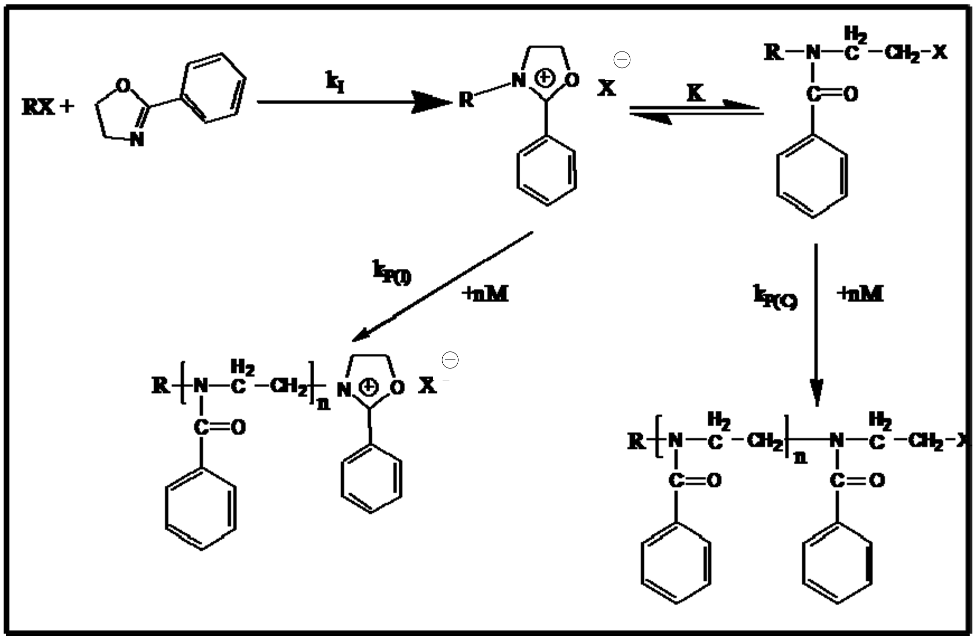


Fig. 7. FO grafting on PVC-I

3. Results and discussion

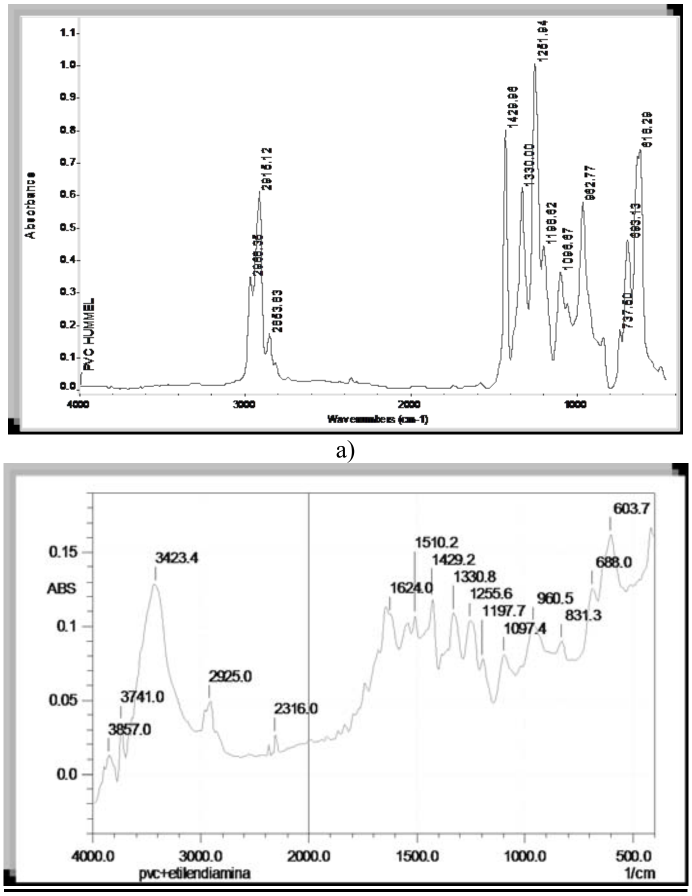
Qualitative analyses through FT-IR and elemental analysis (for the conversion determination) were performed, in order to highlight the modifications realized on the PVC surface.

Comparative spectra and elemental analysis results are given below for each transformation (Figs. 8-11).

Analyzing the spectra from Fig. 8, the existence of primary amine groups (NH- 1580-1650 cm^{-1}) is certified, but the secondary amine groups cannot be ascertain due to overlapping, as follow: at 3300-3400 cm^{-1} and 3250-3300 cm^{-1} there are 2 characteristic straps from primary amine, at 3350-3310 cm $^{-1}$ there is 1 characteristic strap characteristic for secondary amine.

The substitution was confirmed by the results of elemental analysis: 1.77 % N, 36.06 % C, 4.65 % H, which correspond to a transformation degree of 5 % (molar).

Analogous reaction with HMDIC is highlighted both through spectroscopy (2300cm^{-1} NCO group, 1660 cm$^{-1,}$ $\nu_{C=O}$ from –NH-CO-NH-, respectively) and through elemental analysis (2.62% N, 40.40% C, 5.52% H), which corresponds to a 4.5% conversion.



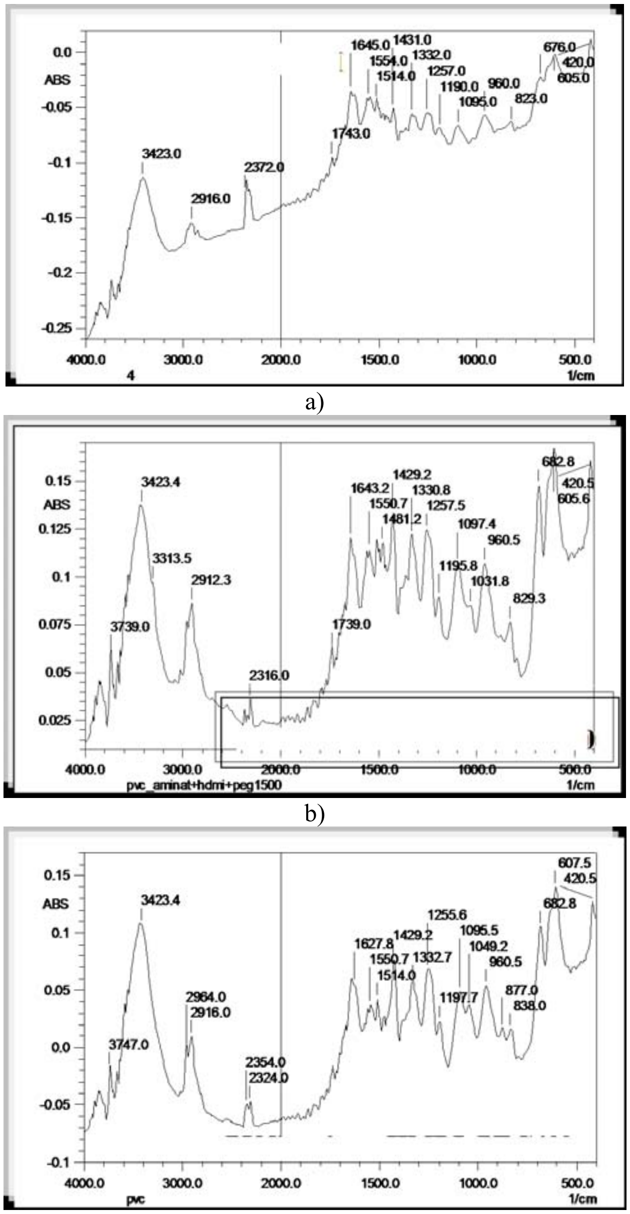
a)

b)

Fig. 8. FT-IR spectra of a) unmodified PVC and b) PVC-NH_2

Reaction of poly(ethylene oxide)s, Fig. 9, is easy to be remarked through the appearance of specific peaks at: 1690-1740 cm $^{-1}$ (characteristic peak of $\nu_{C=O}$ from RO-CO-N-), the amide II peak is found at δ_{NH}=1640 cm^{-1}, the ν_{NH} – at 3400-3500 cm^{-1}, and at 3450-3600 cm^{-1} is identified the ν_{OH} from polyalcohol.

The second method of modification used PVC-NH_2 as background, in a nucleophilic addition (Michael) of amine groups to acrylamide, which has a strong electrophilic double bond. The affinity of acrylic monomer's double bond to nucleophilic reagents is the driving force of their anionic polymerizations. Michael additions are rarely used as preparative methods in polymer synthesis. FT-IR spectrum demonstrated the chemical binding of propionamide fragments on PVC surface by the appearance of characteristic straps. Elemental analysis (1.09 % N, 39.26 % C, and 4.64 % H) indicated a 2 % conversion.



a)

b)

c)

Fig. 9. Comparative FT-IR spectra of: a) PVC-NH_2-HMDIC; b) PVC-NH_2-HMDIC + PEG 1500; c) PVC-NH_2-HMDIC + PEG 400

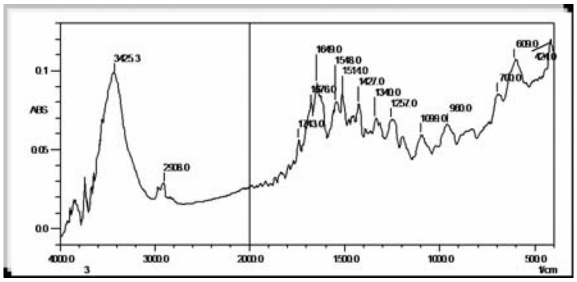


Fig. 10. FT-IR spectrum of PVC-NH_2 + AA

In order to polymerize FO as "***grafting from***", a PVC iodination surface was used. The reaction mechanism is presented below:

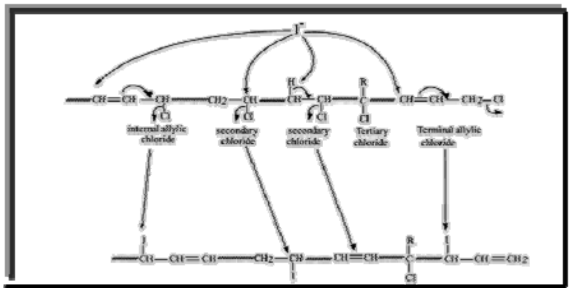


Fig. 11. General reaction of chloride-containing radicals

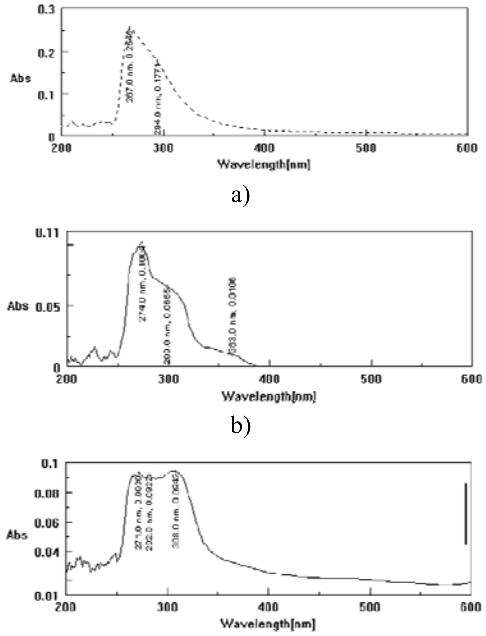
It can be easily seen from Fig. 11 the existence of a substitution-elimination competition, which is strongly dependent on temperature. This was the reason of performing the reaction both at room temperature and at 50 ^{o}C.

Both PVC (used during the experiment) and analogous compounds molecular masses were determined through GPC (Permeable Gel Chromatography, Waters 510, with THF as solvent). Molecular mass of iodinated compounds, resulted from chromatographic analysis, was 65,600 when iodination was performed at room temperature during 5 h (corresponding to a degree of transformation of 20 %) and 74,500 when iodination was performed at 50 ^{o}C, for 1.5 h (corresponding to a 33 % conversion).

Maintaining constant the ratio between PVC-I and FO, it was expected that the length and the graft number, respectively, on the PVC surface to be different. First step consisted in a preliminary UV investigation (Fig. 12), in order to evaluate the possibility to achieve these analogous reactions.

UV spectra mark the sequence PVC – PVC-I – grafted PVC.

Meanwhile, results of GPC chromatography on these products are more relevant (Fig. 13). The shift towards higher molecular masses as a result of iodination and grafting is obvious and it measures an increase of the adsorption bands. As a consequence, the amplitude of chemical transformations located on surface is much higher that the amplitude suggested by the average resulted from homogenous solution subjected to determination.



a)

b)

c)

Fig. 12. UV spectra of: a) PVC; b) PVC-I; c) PVC-I-grafted oxazoline

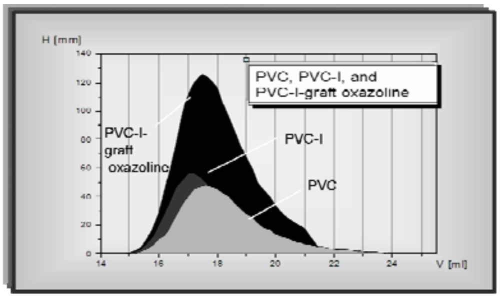


Fig. 13. Comparative GPC chromatography on PVC, PVC-I, and PVC-I-graft oxazoline

Analyzing the values presented in Table 4, it can be seen the increase of molecular mass of PVC grafted with FO (PVC-1-grafted FO), in comparison to PVC-I, which is easy to explain by the FO units attached to polymeric chain. From the difference of these two values can be obtained the average number of oxazolinic monomer attached units, which may be related to the number of active positions (average number of iodinated monomer units).

Table 4

Molecular masses of chemically modified polymers

Molecular mass		
PVC – 50,300	PVC-I 5 h, room temperature 65,600	PVC-I-graft FO I - 24 h, 70 °C, CCl_4 95,000
	PVC-I 1.5 h, 50 °C 74,500	PVC-I-graft FO II - 3.5 h, 70 °C, CCl_4 84,500 III - 11 h, 70 °C, CCl_4 113,000

For the first case (65,600-95,000 molecular masses), 196 oxazolinic units/167 iodinated units can be obtained, for the second case (74,500-84,500 molecular masses), 67 oxazolinic units/265 iodinated units, and for the third case (84,500-113,000 molecular masses) - 256 oxazolinic units/265 iodinated units.

The conclusions drawn are:

- 1st case, an average of 1-2 oxazolinic units/active position;
- 2nd case, an average of 1 oxazolinic unit/active position, without binding every active centre;
- 3rd case, an average of 1 oxazolinic unit/active position.

It is difficult to evaluate if the mass increase simultaneously with reaction time is due to:

- Appearance of other active centers and subsequently FO addition (a) or
- Lengthening of already initiated grafts (b).

The most probable hypothesis is the second one (b), due to cationic ring-opening polymerization.

Through the increase of the separation sensibility and selectivity, the oxazolinic polymers resulted from chain transfer with the impurities from reaction mass can be observed the presence in the polymer crust. Practically, their presence is not disturbing, as long as they are strongly fixed in the grafted chains and they have the same properties.

4. Conclusions

Chemical modification of PVC proves to be a facile method to change the surface chemical nature, in order to be suitable for desired special properties, such as polymer matrices for further use in polymeric composites in the field of nuclear, biological and chemical (NBC) defense, or other biochemical and biomedical application.

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