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EVALUATION OF BIO- AND HEMO-COMPATIBILITY OF TWO PARTIALLY ALIPHATIC COPOLYIMIDES MODIFIED BY PLASMA AND CHEMICAL TREATMENT

Dumitru POPOVICI[1], Stelian VLAD[2], Iuliana STOICA[3], Dan Sorin VASILESCU[4]

The surface of two partially aliphatic copolyimides films was modified by radiofrequency He plasma treatment and chemical modification with alcoholic solution of diaminobenzoic acid. Modification that occurs at the films surface after chemical and plasma treatment were analysed by FT-IR spectroscopy and the modification of morphology, highlighted by atomic force microscopy, were discussed. Bio- and hemo-compatibility of pristine and modified films was evaluated using van Oss, Good and Chaudhury theory, by determine the contact angle of three test liquids with films surface and calculate the component of surface energy and work of spreading of main blood component.

Keywords: partially aliphatic copolyimide, plasma treatment, chemical modification, hemocompatibility, contact angle

1. Introduction

Originally developed for high-performance applications in aerospace, microelectronic or automotive industries [1-4], in recent years polyimides have begun to be used for various biomedical applications or for bio-MEMS systems [5-9]. Moreover, by micro-structuring of surfaces with various techniques, polyimide films have been successfully used for the controlled growth of osteoblast cells [10, 11]. Despite the excellent combination of properties, like thermal stability or mechanical and chemical strength, most aromatic polyimides are strongly coloured from yellow to dark brown, and are infusible or insoluble in common organic solvents, which make their processing by thermoforming techniques or casting from solution to be difficult or even impossible.

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[1] Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, and “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania, e-mail: dumitru.popovici@icmpp.ro

[2] “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

[3] “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania

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

In order to be used in biological or medical applications, polyimides should have a high optical transparency, to be thermally and mechanically stable, to have a low dielectric constant, the film surface energy at the interface of separation with the biological medium to be higher and, not the least, to be processed easily in complete imidized form. To get all these properties, it is necessary to modify the chemical structure of the structural unit of the polymer chain by introducing non-planar bulky groups, flexible bridges or bulky pendant groups. Introduction of these groups disrupts the linearity and prevents the formation of the intermolecular charge transfer complex – CTC [12, 13]. Moreover, the use of aliphatic or cycloaliphatic monomers leads to a substantial improvement of solubility, a decrease of glass transition temperature and, due to the interruption of conjugation along the polymer chain, significantly reduce the degree of staining of these materials, near to colourless [14, 15].

Due to the absence of polar functional groups, the surface energy of the polyimide film is low, leading to a low wetting capacity [16]. Through various surface modification techniques such as plasma treatment, high-energy coronary discharges or chemical functionalization, hydrophilicity, biocompatibility and other properties which are responsible for the biological response, can be improved [17-19]. A better understanding of the interactions with the biological environment at the interface separation can be evaluated by measuring the contact angle of the surface with various test liquids.

In this respect, the surface of two partially cycloaliphatic polyimide films have been modified by treatment with radio frequency plasma (cold plasma) and chemical functionalization. Bio- and hemo-compatibility were evaluated by measuring the contact angle of the modified films with various test liquids. Changes that occurred were highlighted by spectroscopic measurements.

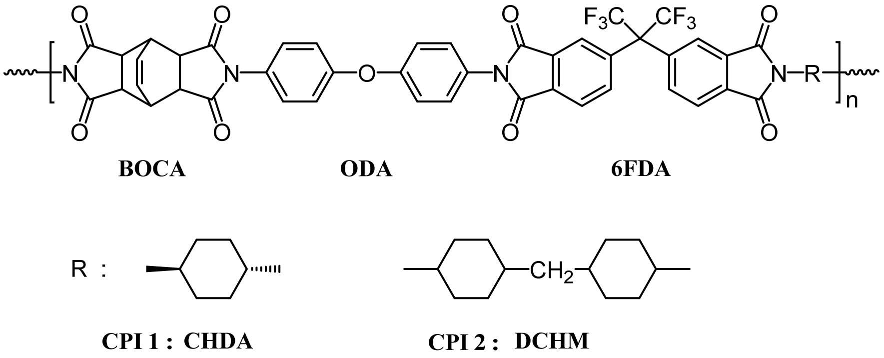
2. Experimental

The monomers used for synthesis were purchased from various commercial sources: bicyclo[2,2,2,]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA – Aldrich Germany) 4,4’-hexafluoroisopropyliden diphtalic anhydride (6FDA – Aldrich SUA), 4,4’-Oxydianiline (ODA – Merck Germany), trans-1,4-diaminocyclohexane (CHDA – Aldrich USA), 3,5-diaminobenzoic acid (DABA – Aldrich Germany). All reagents were of high purity and were used without further purifications. 4,4′-Methylene-bis-(cyclohexylamine) (DCHM – Aldrich USA) was purified by recrystallization from ethanol. 1-methyl-2-pyrolidone (NMP – Aldrich USA) was purified by distillation at low pressure and dried on 4 Å molecular sieves before use.

The polymers synthesis has been presented in previous works [20, 21]. The conditions of reactions and the molar ratio of the dianhydrides and the diamines being patent pending, cannot be presented in this paper. The general structure of ideal structural unit of partially aliphatic polyimides studied in this work is presented in Scheme 1.

Chemical modification was performed by immersion of dried copolyimides films in saturated solution of DABA in ethanol (0,87% w/v) for 6 hours, washed with ethanol and dried for 4 hours in a convection oven at 50 °C.

Plasma treatment was performed at low pressure in He cold plasma (radiofrequency plasma) for 6 minutes at 60W (EMITECH K105X - Empdirect, Huston, Texas).



Scheme 1. Chemical composition of ideal structural unit for CPI 1 and CPI 2

3. Polymer Synthesis

The partially aliphatic copolyimides were synthesized starting from two dianhydrides BOCA and 6FDA and a stoichiometric mixture of two diamines ODA/CHDA for CPI 1 and ODA/DCHM for CPI 2, by two steps polycondensation method.

The IR spectra for these copolyimides show the typical imide absorption bands at around 1,770 cm^{-1} (C=O asymmetrical stretching vibrations) 1,705 cm^{-1} (C=O symmetrical stretching vibrations) 1,370 and 722 cm^{-1} (C–N stretching and imide ring bending, respectively). The absorptions peaks at around 2,960, 2,926 and 2,875 cm^{-1} are assigned to the CH and CH_2 vibration of aliphatic units, while, the C–H linkage of aromatic rings shows a peak at about 3,062 cm^{-1}. The broad absorption bands at 3,700 – 3,500 cm^{-1}, characteristic to OH from carboxylic acid group and 3,450–3,350 cm^{-1}, characteristic of NH amidic group and the narrow absorption peak at 1,650–1,660 cm^{-1} due to C=O group in amide linkage disappeared, suggesting the completion imidization of the intermediate polyamidic acid into final polyimide structure and validates the synthesis of polymers.

4. Surface modification

In order to improve the wettability of the surface of polyimide films, two strategies were adopted.

In the first strategy, the polymeric film was treated in helium cold plasma for 6 minute, at 60W (CPI 1-p, CPI 2-p). We chose helium instead of air or nitrogen due to the neutral character of that gas. Following the films treatment in helium plasma at its surface functional groups as amide, amine, carboxyl, hydroxyl or ether have been formed, which due to their polar nature, increase wettability of the treated film. If it would be used air or nitrogen instead of He to generate the plasma, the ionic species formed in radiofrequency field would be more reactive and can lead to the destruction of polymer chains from the films surface [22-24].

In the second strategy, the polyimide film was treated with alcoholic solutions of 3,5-diaminobenzoic acid (DABA) for 6 hours (CPI 1-ch, CPI 2-ch). This treatment permitted to the diamine to attach along the macromolecular chain by breaking of some imide rings, with the formation of new polar groups as carboxyl and amide. Moreover, because DABA has two amine reactive functional groups, some intra or inter-chains crosslinking reactions may occurs, leading to a stabilization of the polymeric macromolecules at the film surface. Also the carboxyl group of DABA leads to an increases in the wettability of the polyimide film.

The changes results from the application of the two strategies were highlighted by IR spectroscopy – Fig. 1.

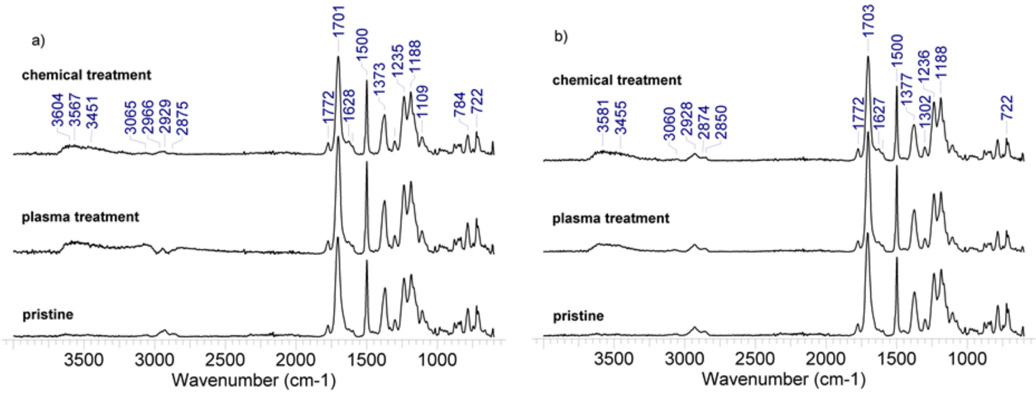


Fig. 1. Infrared spectra for copolyimide films CPI 1 (a) and CPI 2 (b) before and after surface modifications

The appearance of the characteristic bands for N-H bond of amide group in the range 3,450 – 3,350 cm^{-1} and O-H bond of the carboxyl groups in the region of 3,700-3,500 cm^{-1} demonstrate that the polar functional groups have been appeared on the surface of the modified polyimide films. Moreover, at 1,625 cm^{-1} can be observed vibrational characteristic peak for amide group, which is more intense for chemical treated films. The vibrational peak from 1,600 cm^{-1}, characteristic for tri-substituted aromatic ring, does not suffer major change in intensity after plasma treatment. In contrast, for chemically treated polyimide films, it can be observed an intensification of this peak, which demonstrates that DABA is grafted at the surfaces of polymeric films by chemical bonds.

5. Biocompatibility

Bio and hemo-compatibility of a polymeric material can be assessed based on the free energy surface - SFE, which is directly correlated with surface wettability. Starting from the general equation of Young, van Oss, Good and Chaudhury have developed a series of equations that correlates surface tension components with their chemical nature. According to this theory, the polar component of the surface tension is determined by acid-base interactions, (electron-acceptor and electron-donor type), and disperse component is described by London-van der Waals forces (Equations 1 – 3),

$$1+\cos\theta=\frac{2}{\gamma_{lv}}\cdot\left(\sqrt{\gamma_{sv}^{d}\cdot\gamma_{lv}^{d}}+\sqrt{\gamma_{sv}^{+}\cdot\gamma_{lv}^{-}}+\sqrt{\gamma_{sv}^{-}\cdot\gamma_{lv}^{+}}\right)\tag{1}$$

$$\gamma_{sv}^{p}=2\cdot\sqrt{\gamma_{sv}^{+}\cdot\gamma_{sv}^{-}}\tag{2}$$

$$\gamma_{sv}^{d/p}=\gamma_{sv}^{d}+\gamma_{sv}^{p}\tag{3}$$

where the superscript terms are: *d* – disperse component; *p* – polar component obtaining from γ_{sv} electron-donor and $\gamma_{sv}{}^{+}$ electron-acceptor interactions.

The literature indicates that to solve this equation it is necessary to measure the contact angles of the three test liquids, one of which just contain non-polar component [25]. The most common system used to determine the liquid surface tension using the theory of van Oss, Good and Chaudhury is water and ethylene glycol as polar liquid and methylene iodide – CH_2I_2 as nonpolar liquid. Contributions of polar and disperse component of this liquids have been presented previously, according with literature [15, 26-33]. In Table 1 are presented contact angles of pristine and modified surface of copolyimide films.

From Table 1, can be observed that after plasma or chemical treatments, the contact angle with water greatly decrease, due to the occurrence of polar groups on the surface. When the films are treated in plasma, at the surface the polar groups occurs mainly due to breaking of the imide cycles and emergence of polar type groups, like carboxyl, amide or hydroxyl [34]. In case of the chemical treatment, amine groups also break some imide cycles and forming of new amide and carboxyl groups [35, 36]. Increasing the contact angle with ethylene glycol after surface modification can ascribe to the increasing of electron-donor type concentration of carboxylic groups at the film surface.

Table 1

Contact angle and surface tension component of untreated (CPI 1 and CPI 2), plasma treated (CPI 1-p and CPI 2-p) and chemical treatment (CPI 1-ch and CPI 2-ch) copoyimides films

Semple	**Contact angle**			γ_{sv}^{d} (mN/m)	γ_{sv}^{p} (mN/m)	γ_{sv}^{-} (mN/m)	γ_{sv}^{+} (mN/m)	$\gamma_{sv}^{d/p}$ (mN/m)
	Water	Ethylene glycol	CH_2I_2					
CPI 1	84	44	51	34.87	2.55	3.27	0.49	37.42
CPI 1-p	33	60	20	20.02	26.34	53.67	3.23	46.36
CPI 1-ch	36	58	18	21.18	25.17	4.19	0.67	46.36
CPI 2	85	42	58	35.52	1.08	4.28	0.07	35.60
CPI 2-p	37	59	24	20.77	23.93	49.9	2.87	44.70
CPI 2-ch	33	59	24	20.30	24.64	4.90	0.50	44.94

Biological systems are aqueous environment and therefore increasing the contact angle with water after surface modification leads to the conclusion that such material may have a good compatibility with blood. Increased wettability (determined based on the decrease of water contact angle) is not sufficient to assess whether or not a material is biocompatible. Another element that determines the biocompatibility is *surface free energy* - ΔGw which is a measure of balance between hydrophilic and hydrophobic behaviour of the material. According to literature [37, 38], if ΔGw is less than -113mJ/m, can be considered that the polymeric material is more hydrophilic, or more precisely, hydrophilic component is stronger than the hydrophobic component. According to the results from Table 2, the decreasing of interfacial tensions between polymer-blood, γ_{sb}, and the surface free energy, ΔGw, reveal that the studied polymers possess a higher hydrophilicity after surface treatment and implicitly a high wettability, property useful for biomedical applications.

Blood is a complex aqueous system and therefore not only the interactions of the polymer with water determine hemocompatibility but also the interaction of blood components with the polymer film surface. For a material to be considered blood compatible, it must prevent the absorption and fixation of blood components on the surface. Furthermore, the interfacial tension material/blood - γ_{sb} - must be between 1 - 3 mJ/m [39]. From Table 2 can be observed that all modified films, in plasma and chemically, qualify for blood compatibility applications.

Table 2

Work of spreading (mN/m) values of different blood components on pristine and modified samples

Sample	**Work of spreading for some blood components**						
	γ_{sb}	W_{fib}	W_{IgG}	W_{alb}	W_{RBC}	W_{plat}	ΔG_{w}
CPI 1	27.12	-1.01	-19.76	-45.21	6.56	-102.07	-80.22
CPI 1-p	2.07	-1.05	-6.84	-16.01	6.19	-86.13	-134.14
CPI 1-ch	2.64	0.08	-6.43	-16.65	7.39	-86.08	-131.72
CPI 2	32.08	-5.80	-24.50	-48.88	1.04	-101.09	-80.51
CPI 2-p	2.91	-1.55	-8.22	-18.38	5.62	-87.08	-130.52
CPI 2-ch	2.52	-2.56	-8.49	-17.51	4.43	-85.81	-133.68

γ_{sb} = solid - blood interfacial tension
W_{fib} = work of spreading for fibrinogen
W_{IgG} = work of spreading for immunoglobulin
W_{alb} = work of spreading for albumin
W_{RBC} = work of spreading for RBC
W_{plat} = work of spreading for platelet
ΔG_w = surface free energy (free energy of hydration)

To fully assess the blood compatibility of modified copolyimide films, interaction of polymeric material with blood components was investigated. The work of spreading the various blood components can be calculated by the difference between the work of adhesion and cohesion work done according to equation 4:

$$W_s = W_a - W_c = 2 \cdot \left[\left(\gamma_{sv}^{d} \cdot \gamma_{lv}^{d}\right)^{1/2} + \left(\gamma_{sv}^{+} \cdot \gamma_{lv}^{-}\right)^{1/2} + \left(\gamma_{sv}^{-} \cdot \gamma_{lv}^{+}\right)^{1/2} \right] - 2 \cdot \gamma_{lv} \qquad (4)$$

Introducing in equation 4 the surface tension parameters for the main blood components namely albumin [32, 33], red blood cells [29], fibrinogen [30], immunoglobulin IgG [31], and platelets [29], we can calculate the work of spreading of these components. If the work of cohesion is greater than the work of adhesion, respectively W_s is negative, blood component does not adhere to the material, thus preventing clotting and immune response onset. Is observed an increase of spreading mechanical work for RBC, which indicates an increased bioavailability compared with pristine copolyimide modified one. Low values for W_{plat} and W_{fib}, blood components responsible for the clot appearance, indicate that modified films preventing thrombus formation.

Given that the polymers investigated interaction with various blood components are within the limits imposed by the literature, one can conclude that these materials meet the conditions of compatibility with blood. These results suggest that modified polyimide films by plasma or chemical treatment can be used in devices that come into direct contact with blood.

6. Surface morphology

Changes of surface morphology after plasma and chemical treatments were investigated using atomic force microscopy techniques – AFM (Solver Pro-M – NT-MDT, Russia) (Fig. 2 and Fig. 3). It is well known that in order to ensure a laminar flow of the blood and prevent the formations of clots the roughness of the contact surface should be as small as possible.

Table 3

Average roughness of pristine and modified copolyimides films

	CPI 1	**CPI 1-p**	**CPI 1-ch**	**CPI 2**	**CPI 2-p**	**CPI 2-ch**
S_a (nm)	0.760	1.173	0.329	2.839	21.281	0.383

Following the AFM scans has been noticed that the untreated polyimides films surfaces are uniform, without defects, revealing a low roughness –Table 3. Vertical formations observed at the surface of CPI 2 film (Fig. 3 a) can be related with higher backbone flexibility of this polyimide, due to the presence of DCHM moieties into the structure.

After plasma treatment the roughness of the polymers film surface has been increased substantially. This increase can be explained by the breaking of some chemical bonds of the polymeric chains at the surface and the emergence of new functional groups. Changing of roughness is greater for CPI 2 precisely because of those vertical formations that determine a higher specific contact area surface. In additions, the higher flexibility of emerging chain segments facilitates the reorganization of functional groups at the surface.

For CPI 1 polyimide film increased of roughness has not been so intense. Also for this film some vertical formations have been observed, due to the emerging of new functional moieties at the surface –Fig. 2 b.

The chemical treatment, instead, led to a dramatic decrease of surface roughness. The chemical attack of diaminobenzoic acid has the effect of formation of new chemical bonds intra- and inter-chain, leading to a levelling of the surface. Including this case, the changes of surface roughness are more pronounced for CPI 2 film.

The similar morphology and comparable roughness observed for the chemical treatment films lead to the conclusion that it is mainly determined by the presences at the surface of a superficial layer of diaminobenzoic acid moieties, suggesting the formation of a relatively uniform coating.

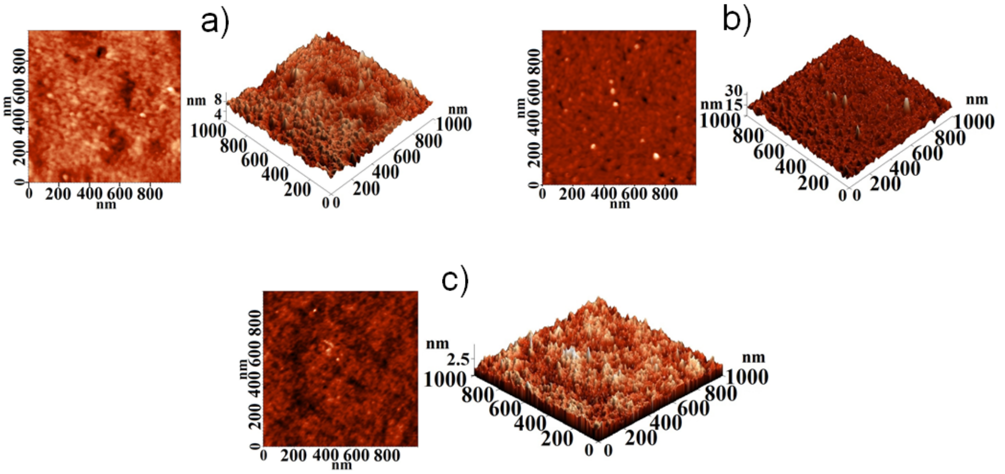


Fig. 2. AFM Image for CPI 1 – a) pristine; b) Plasma modified; c) chemical modified

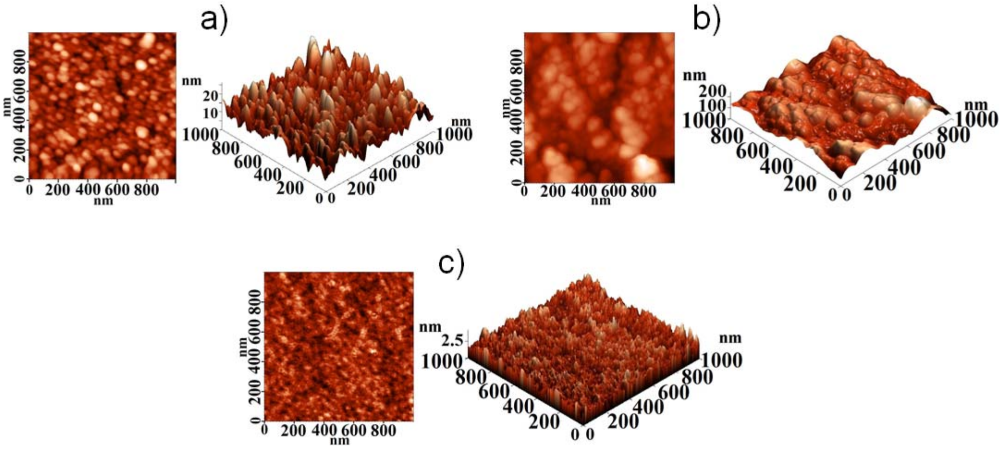


Fig. 3. AFM Image for CPI 2 – a) pristine; b) Plasma modified; c) chemical modified

7. Conclusions

To increase bio- and hemo-compatibility of two partially aliphatic copolyimides films two modifications techniques of the surfaces were adopted:

the treatment in radiofrequency He plasma and chemical modification with an alcoholic solution of acid diaminobenzoic. The changes that occur at the surface were investigated by infrared spectroscopy, confirming the appearance of functional groups.

Bio- and hemocompatibility properties were determined indirectly using the theory of interfacial tensions. For that the contact angles between the surface of polyimide films (pristine and modified) with three test fluids - water, ethyleneglycol and methylene iodine - was determined. The surface tension components were calculated using van Oss, Good, and Chaudhury equations. All modified films showed an improvement in the biological and hemolytic response, the calculated values for surface tension and work of spreading for the main components of blood hovering in the interest range.

The surface of the polyimide film, analysed by AFM, showed an increase in the roughness of the films after the plasma treatment and a decrease in surface roughness after chemical treatment.

All these results lead to the conclusion that the techniques of surface modification of polyimide films by plasma treatment and chemical modification lead to an improvement of hemo-, and biocompatibility. The chemical treatment technique with alcoholic solution of diaminobenzoic acid is highlighted, on the one hand due to the simplicity of implementation and low cost of treatment and on the other hand by levelling of films surface with significant decreases of roughness.

Acknowledgments

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