This paper presents the synthesis, properties and potential applications of new polymers containing 1,3,4-oxadiazole rings, tacking into account the requirements of the modern technologies. Two classes of polymers containing oxadiazole rings were approached: polyamides and polyimides. All the polymers were characterized with respect to the identification of their chemical structure, solubility, molecular weights, film forming ability, thermal, dielectric and optical properties, and the behaviour of polyoxadiazole films upon irradiation with pulsed KrF laser. All the properties were discussed in correlation with their chemical structure and compared with those of related polymers.

Key words: polyoxadiazoles, thermostability, low dielectric constant, fluorescence, laser ablation.

1. INTRODUCTION

Engineering and high performance polymers cover a wide spectrum of materials from well-established plastics such as nylon to developing polymers such as polyimides, polyamides, poly(ether-ketone)s and liquid crystalline polymers. They are valued, amongst other properties, for their thermal stability, strength, dimensional stability and chemical resistance in several demanding applications. Engineering and high performance polymers experienced spectacular growth during the second half of the 1990s because of strong demand for IT/telecom products and automotive components. Product and applications development and substitution of traditional materials were also key drivers of growth. The eight end-markets that consume different kinds of high performance polymers for various applications are: aerospace and defence, automotive, computers and peripherals, consumer goods, electrical and electronic field, industrial and medical sectors and other application areas, e.g. coatings for building and construction [18,27].

Among high performance polymers, those containing 1,3,4-oxadiazole rings form an important class of heterocyclic polymers, which are of special interest for the
production of advanced materials due to their high thermal oxidative stability and certain specific properties which are determined by the nature of oxadiazole units. From the electronic and spectral points of view, the oxadiazole ring is similar to a para-phenylene structure and has a strong electron-withdrawing character. The following features motivated the introduction of 1,3,4-oxadiazole rings in the structural unit of macromolecular chains:

- 1,3,4-oxadiazole ring is free of hydrogen and, therefore, poly(1,3,4oxadiazole)s maintain their properties during heating, in air, better than other polymers;
- due to the similarity with para-phenylene unit, known as highly thermoresistent, the 1,3,4-oxadiazole ring is called pseudophenylene [24];
- conjugation between 1,3,4-oxadiazole and other aromatic rings in polymers is similar to that of polyphenylenes;
- 1,3,4-oxadiazole ring is free of tension;
- 1,3,4-oxadiazole cycle doesn't have any possibilities of rearrangement;
- 1,3,4-oxadiazole ring has a structural symmetry and it is thermally unreactive.

Poly(arylene-oxadiazole)s, like poly(p-phenylene)s and poly(p-phenylene-vinylenes) or polythiophenes, give easily redox reactions, chemically or electrochemically, and the resulting conducting materials are good candidates for electrochemical sensors or electroluminescent devices, to be used in data storage, telecommunications and other applications [25]. Besides their excellent thermal resistance, polyoxadiazoles exhibit a good hydrolytic stability, low dielectric constant and good mechanical properties that give them the position of high performance polymers. Some polyoxadiazoles have semiconducting properties, other can be electrochemically doped, thus becoming electroconductors, and other structures have liquid crystalline properties, which enlarge their potential applications in advanced technologies. They exhibit excellent fiber and film forming capabilities, thus being considered for use as heat-resistant reinforcing fibers for advanced composite materials, highly resistant fabrics for filtration of hot gases, special membranes for gas separation or reverse osmosis. Polyoxadiazoles could be precursors for highly oriented graphite fibers, films and blocks to be used in the construction of electronic instruments based on X-, neutron- or α-rays, or in the construction of nuclear reactor walls [21,25,29].
As compared with the first years (1960-1970) of the poly(1,3,4-oxadiazole)s research when they were studied for their high thermal stability, in the recent period, the electronic properties combined with their high heat resistance made them attractive for applications in microelectronics, optoelectronics, advanced telecommunications or other related fields.

Although fully aromatic polyoxadiazoles are known for their excellent thermal resistance and good hydrolytic stability, they have rigid molecules due to the delocalization of $\pi$-electrons, which makes them insoluble in organic solvents and infusible, and therefore their processing and practical use is very limited [25]. The most part of the recent research aims to obtain structurally modified poly(1,3,4-oxadiazole)s with good solubility in organic solvents and lower glass transition temperature, in order to allow their processing from solution, by casting or spin-coating, or from solid-state, by thermoforming technique, without affecting the properties that give them the status of high performance polymers. Such modifications are the introduction of certain substituents on aromatic rings, flexible bridges in the macromolecular chains, voluminous units pendent to the chain or, more recently, the oxadiazole ring forms a part of the side chain of other polymers [1,2,16,17,23].

Because of their special properties and large number of high performance applications since their discovery up to now, which permanently responded to the contemporary requests, polymers based on 1,3,4-oxadiazole have received our attention. Thus, in this article we present a review of the recent results obtained by our group with respect to the synthesis, properties and potential applications of new polymers containing 1,3,4-oxadiazole rings, tacking into account the requirements of the modern technologies. We approached two classes of polymers containing oxadiazole rings: polyamides and polyimides.

2. SYNTHESIS

2.1. MONOMERS

The monomers used in the preparation of the polymers were aromatic diamines containing preformed oxadiazole rings, diacid chlorides containing diphenylsilyl or hexafluoroisopropylidene groups, and five- or six-member carboxylic acid dianhydrides. The structures of the monomers are shown in Scheme 1.
Diamines

1a

1b

1c

1d

Diacid chlorides

2a

2b

Dianhydrides

3a

3b

3c

Scheme 1. Structure of monomers.

2.2. POLYMERS

Oxadiazole-containing polyamides I and II and copolyamides III (scheme 2) were obtained by polycondensation reaction of equimolar amounts of a diamino-oxadiazole or a mixture of a diamino-oxadiazole and fluorene-containing diamine with a diacid chloride, using N-methylpyrrolidinone (NMP) as a solvent and with pyridine as an acid acceptor. Polycondensation reactions were run by adding the powdered diacid chloride
to the diamine(s) solution with stirring, under nitrogen, at -5°C. Solutions, after addition of the diacid chloride, had a concentration of 10-15%. After addition of diacid chloride, the reaction mixture was kept at -5°C for 30 min, then it was allowed to increase to room temperature by removing the cooling bath, and the solution was further stirred for 4 h. The polymer solution was diluted to about 5% by addition of more NMP and the polymer was precipitated by pouring into water. It was filtered, washed twice with water and once with ethanol, and dried under vacuum at 105°C for 2-3 h [5,19,20].

![Polyamide structures](image)

<table>
<thead>
<tr>
<th>Polyamide</th>
<th>Ia</th>
<th>Ib</th>
<th>Ic</th>
<th>IIa</th>
<th>IIb</th>
<th>IIc</th>
<th>IIIa</th>
<th>IIIb</th>
<th>IIIc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamine</td>
<td>1a</td>
<td>1b</td>
<td>1c</td>
<td>1a</td>
<td>1b</td>
<td>1c</td>
<td>1a; 1d</td>
<td>1b; 1d</td>
<td>1c; 1d</td>
</tr>
<tr>
<td>Dichloride</td>
<td>2a</td>
<td>2a</td>
<td>2b</td>
<td>2b</td>
<td>2b</td>
<td>2a</td>
<td>2a</td>
<td>2a</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 2. Oxadiazole-containing polyamides and copolyamides.

In order to obtain polyimides (IV, V) and copolyimides (VI) containing oxadiazole rings (scheme 3), the polycondensation was run with equimolar amounts of a dianhydride or a mixture of two dianhydrides and diamino-oxadiazoles, in NMP as solvent, at a concentration of 15% total solids and at room temperature for 1-2 h, followed by heating at 185-195°C for 3-4 h. A small part of the polyamidic acid solution resulting from the first step of reaction at room temperature was used to precipitate the soluble polymers which were further characterized, and another small part was poured onto glass plates to check the film-forming ability. The final polyimide
solution was also used to precipitate the resulting polymer and to test the characteristics of the corresponding thin films [4, 11, 22].

\[
\begin{align*}
&\text{IV} \\
&\text{V} \\
&\text{VI}
\end{align*}
\]

\[
\text{Ar}: \ a = \text{phenyl} \\
\text{b} = \text{phenyl-COH} \\
\text{c} = \text{p-anisyl} \\
\text{Z} = \text{Bz}
\]

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>IVa</th>
<th>IVb</th>
<th>IVc</th>
<th>Va</th>
<th>Vb</th>
<th>Vc</th>
<th>Vla</th>
<th>Vlb</th>
<th>Vlc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamine</td>
<td>1a</td>
<td>1b</td>
<td>1c</td>
<td>1a</td>
<td>1b</td>
<td>1c</td>
<td>1a</td>
<td>1b</td>
<td>1c</td>
</tr>
<tr>
<td>Dianhydride</td>
<td>3a</td>
<td>3a</td>
<td>3a</td>
<td>3b</td>
<td>3b</td>
<td>3b</td>
<td>3b; 3c</td>
<td>3b; 3c</td>
<td>3b; 3c</td>
</tr>
</tbody>
</table>

Scheme 3. Oxadiazole-containing polyimides and copolyimides.

2.3. FILMS

Films of the polymers (I-VI) were prepared by casting a solution of 8-12% concentration of polymers in NMP onto glass plates, followed by gradual heating from room temperature up to 200°C, and kept at 200°C for 1 h. Also, very diluted polymer solutions (1% concentration) in NMP were cast onto glass plates, followed by the same heating cycle, in order to obtain very thin coatings which were then investigated with regard to the quality of their surface. Transparent coatings resulted having strong adhesion to the glass support. In order to take these films off the plates it was necessary
to put them in hot water for 1-2 h. The resulting free-standing films of the polymers were flexible and were used afterwards for various measurements.

3. BASIC CHARACTERIZATION OF THE POLYMERS

The structures of the polyoxadiazoles were identified by infrared spectra (FTIR). The FTIR spectra of polyamides and copolyamides (I-III) showed the presence of amide groups by absorption peaks at 3400-3360 cm\(^{-1}\) due to NH and at 1675-1660 cm\(^{-1}\) due to C=O in amide groups. In the FTIR spectra of the polyimides and copolyimides (IV-VI) absorption peaks appeared at 1770-1780 cm\(^{-1}\), 1710-1720 cm\(^{-1}\) and 720-730 cm\(^{-1}\) which are characteristic for imide ring. The weak absorption peaks at 1025-1015 cm\(^{-1}\) and 965-950 cm\(^{-1}\) were attributed to the 1,3,4-oxadiazole rings; these absorption bands are also present in the spectra of the diamino-oxadiazole monomers. The absorption bands at 1420 cm\(^{-1}\), 1120 cm\(^{-1}\) and 700 cm\(^{-1}\) in the spectra of polymers IV are characteristic for phenyl-silicon bonds. The absorption peak at 1220 cm\(^{-1}\) in the spectra of polymers V was assigned to hexafluoroisopropylidene groups. Typical FTIR spectra of oxadiazole containing-polyamides and polyimides are shown in Figure 1.
Fig 1. FTIR spectra of a) copolyamide III and b) polyimide IV.

The molecular weights of polyoxadiazoles were measured by gel permeation chromatography, by using polystyrene standards of known molecular weights. The obtained molecular weight values are typical for polycondensation polymers. The polyamides II have $M_w$ in the range of 200000 to 300000, $M_n$ in the range of 100000 and polydispersity $M_w/M_n$ in the range of 2-2.5. The inherent viscosities of polyoxadiazoles, measured in NMP solution, were generally registered between 0.2 and 1.5, for the poly(oxadiazole-amide)s II being of 0.5 - 1.4 dl/g. The three-dimensional diagram showing molecular weight distribution for one of the fluorinated polyoxadiazole II is shown in Figure 2 [6].
Usually, fully aromatic polyoxadiazoles are only soluble in strong acids such as \( \text{H}_2\text{SO}_4 \) and methansulfonic acid, but our polymers containing oxadiazole rings and various flexible groups are soluble in polar solvents as NMP, DMF, DMAc or DMSO, and in some cases they became soluble even in less polar solvents as THF or chloroform. The shape of a macromolecule became far from a “rigid-rod”, and thus facilitates the diffusion of the small molecules of solvent. In this example, by introducing of ether and diphenylsilyl units in fully aromatic poly(oxadiazole-amide)s, the polymer chains became soluble in NMP and DMF, and by further introduction of voluminous fluorene units, the polymers became soluble in THF [9].

The polyoxadiazoles, especially those containing imide structures, have high thermal stability, over 440°C, and a glass transition in a moderate temperature range, from 150°C up to 250°C, and therefore can be used as high-temperature resistant materials, e.g. fireman cloths. There is a large interval between decomposition and glass
transition temperature that can be advantageous for their processing by a thermoformic technique. Representative TGA and DSC curves are shown in Figure 3.

![TGA and DSC curves](image)

Fig. 3. TGA(a) and DSC (b) curves of a siloxane-containing poly(oxadiazole-imide) IV.

All the synthesized oxadiazole-containing polymers possess film-forming ability. The polymer solutions (10%) in NMP were processed into thin films by casting onto glass plates. The free-standing films having a thickness in the range of 10-30 μm were flexible, tough and creasable, and maintained their integrity after repeated bendings. Some representative images of one film made from a polyoxadiazole-amide containing diphenylsilane units (I) are shown in Figure 4.

![Film images](image)

Fig. 4. Images of the free-standing film prepared from a poly(oxadiazole-amide) I.

In order to be used as advanced materials, the films must have good mechanical properties. These films proved good mechanical resistance. Elastic modulus, tensile strength and elongation to break have been determined as averages of three drawing experiments. Usually, polyoxadiazoles showed the values of tensile strength in the range of 50-120 MPa, elastic modulus in the range of 1.5-3 GPa and elongation to break...
in the range of 2-9%, recommending the use of such polymers as flexible substrates in organic devices, e.g. organic field-effect transistors (OFETs).

Very thin films of polyoxadiazoles having the thickness in the nanometer range were deposited by spin-coating technique onto silicon wafer, by using diluted polymer solution (concentration of 1%). The quality of these films was studied by atomic force microscopy (AFM). These films showed a very good quality, without cracks or pinholes and with root mean square roughness in the range of 5-10 Å, close to that of the substrate. It means that the present polymer films are very smooth, practically defectless. A typical AFM image is shown in Figure 5.

![AFM images of the spin-coated film of a copolyimide VI](image)

**Fig. 5. AFM images of the spin-coated film of a copolyimide VI**
(left: top view, right: side view).

4. **SPECIAL PROPERTIES OF POLYOXADIAZOLES**

4.1. **PHOTO-OPTICAL PROPERTIES**

Since 1,3,4-oxadiazole ring is known as a light emissive unit, we performed the study of the UV absorption and photoluminescence properties of polyoxadiazoles. Polyoxadiazoles present one strong absorption peak around 300 nm due to diphenyl-1,3,4-oxadiazole unit. In the case that other chromophores are present in the macromolecular chain of polyoxadiazoles, additional shoulders or peaks at higher wavelengths could be detected. In films the maxima are shifted (to blue or red) with respect to the absorption of the isolated molecules that account for negligible intermolecular interactions of the conjugated segments of the polymer chains. The Kramers-Kronig analysis [15] applied to the reflectance spectra of polymer films VI (Fig. 6) yields the values of the refractive index, \( n \), between 1.63 and 1.92, and for extinction coefficient, \( k \), between 0.03 and 0.05, being typical for polymer films. The
energy gaps of the films, following the Tauc relation, are found to change from 2.77 eV to 3.04 eV, depending on the length of conjugated part of the polymer chain.

![Graph showing transmission and reflectivity spectra of the thin films of polyimides VI.](image1)

Fig. 6. Transmission and reflectivity spectra of the thin films of polyimides VI.

The UV-vis absorption spectroscopy has been used in order to monitor the changes in spectroscopic properties of polyimides during heating. The results indicated that the investigated polyimides have a very good optical stability in the temperature range below the glass transition temperatures (Fig. 7). All the data presented here are very important from the point of view of possible applications of polyoxadiazoles in photo-electronic devices [10].

![Graph showing UV absorption spectra of poly(oxadiazole-imide) VIc at different temperatures.](image2)

Fig. 7. UV absorption spectra of poly(oxadiazole-imide) VIc at different temperatures.
It was found that polymers VI show three strong UV absorption peaks at 300-310 nm, 360-361 nm and 380-381 nm, in DMAc solutions. The absorption maxima at 300-310 nm of these polymers are mainly determined by the diphenyl-1,3,4-oxadiazole unit, because the unsubstituted diphenyl-1,3,4-oxadiazole in hexane shows its absorption maximum at 284 nm. The absorption peaks at 360-361 nm and 380-381 nm are due to the chain segments containing naphthylimide unit.

There is currently much interest in polymeric electroluminescent materials, particularly in those which are able to emit blue light which is difficult to attain from the already known inorganic ones [26]. In addition, the use of electroluminescent thin films made from highly thermostable polymers would avoid thermal degradation in the final device while in service at elevated temperatures. The light emitting ability of copolymers III containing both oxadiazole and fluorene cromophores was assessed on the basis of the photoluminescence spectra which were recorded for polymer films cast from THF solutions, after irradiation with UV light. These polymers were spin coated on glass at different spin velocities in order to check the optimal layer thickness for the future use of these materials in OLED structures. The UV absorption spectra of the films of different thicknesses showed similar aspect with strong absorption maxima around 300 nm. The absorption intensity of the polymer films increases with the thickness of the layers. The layer thickness over spin velocity diagram was used to establish that a spin velocity of 500-600 rpm is optimal for a layer thickness of about 80 nm for OLED structures. The PL spectra were recorded at three different excitation wavelengths: 360, 254 nm and 300 nm. When excited with UV light peaking at 300 nm, the emission maxima were centred at 445 nm and 455 nm. The PL intensity increased upon increasing the layer thickness, for both polymers (Fig. 8a). The PL maxima were equivalent to those occurring at a 254 nm excitation. When excited with UV light peaking at 360 nm, both polymers gave plots having similar behaviours: no PL activity in most part of the visible spectral range, a steady PL increase in the range of 600 nm to 450 nm, and a marked clear maximum at 410-420 nm afterwards, which is almost invisible to the normal human eye (Fig. 8b). The photoluminescence (PL) spectra at different excitation wavelengths and similar layer thicknesses, in the logarithmic scale showed that the blue emission occurring after excitation at different wavelengths is caused by different emitters which can be oxadiazole, fluorene or longer segments.
containing such cromophores. Applications of these polymers in blue light-emitting devices are foreseen [7].

Fig. 8. PL spectra of an oxadiazole-containing copolyamide II, by excitation with UV light peaking at 300 nm (a) and 360 nm (b).

4.2. MOLECULAR RELAXATIONS

Dynamic mechanical and dielectric relaxation techniques have been widely applied to establish transition temperatures, relative relaxation intensity, and the time-temperature characteristics of the motional transitions encountered in the polymer films. Typically, three relaxation processes are observed with increasing temperature, designated \( \gamma \), \( \beta \) and \( \alpha \), respectively, with a corresponding to the glass–rubber relaxation. For Matrimid polyimide the peak temperatures corresponding to these relaxations are \(-112°C (T_{\gamma})\), \(80°C (T_{\beta})\) and \(313°C (T_{\alpha})\) [3]. The dynamo-mechanical relaxation properties of the siloxane-containing poly(oxadiazole-imide)s IV, in comparison with that of Kapton, one of the most used polyimide in electronic applications, were studied. At very low temperatures (Fig. 9, left), inferior to \(-125°C\), IVa and Kapton HN present high storage modulus values, over \(10^9\) Pa, typically for glassy polymers and display secondary (\( \beta \)) relaxations while in the case of IVb, a more flexible polymer, a distinctive upturn in the \( E' \) modulus is displayed around \(-100°C\), which can be consistent solely with the evolution of a crystallization process. Similar feature was observed in other polyimide-polydimethylsiloxane copolymers but no comments were made on it. Further dielectric spectroscopy investigations show that the crystallization process is overlapping on the gamma relaxation. The behaviour of IVa and Kapton films in the high temperature
range (Fig. 9, right) can be described comparatively. The tanδ peak, which is taken as the glass transition temperature, was found at 198°C for IVa and approx 420°C for Kapton. Kapton presented a broad peak with an extremely low value of the peak amplitude (0.056), as opposed to the sharp and high peak (2.24) of IVa. The broadening of the transition is a sign for a large distribution of the relaxation times for Kapton, which means a heterogeneous structure, whereas the amplitude of tanδ peak is related to the mobility of the polyimide backbone characteristic for siloxane-containing poly(oxadiazole-imide) [8].

Fig. 9. The dynamical relaxations of IVa, IVb and Kapton HN.

4.3. DIELECTRIC PROPERTIES

Electrical insulating properties of the polymer films IVa and IVb were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency at various temperatures. Figure 10 presents the dependence of real part of complex permittivity, which is the dielectric constant $\varepsilon'$ value, and the imaginary part of complex permittivity, which is the dielectric loss $\varepsilon''$ value, on frequency, at -100°C; -50°C, 0°C, +50°C and +100°C, for one representative polymer. At very low and moderate
temperatures the dielectric constant increases very slowly, linearly, with decreasing of frequency, taking low values even at very low frequency. In the same time at high temperatures (100°C), these polymers present slightly higher values of dielectric constant, due to the mobility of charge carrier at these temperatures. Poly(oxadiazole-imide) IVa showed peaks on dielectric loss versus frequency dependence in the entire interval of the measured temperatures, due to the presence of $\gamma$ and $\beta$ relaxations in this polyimide. However, the dielectric loss of this polyimide varies with frequency and temperature in a small range between 0.001 and 0.02. As for the dielectric loss ($\varepsilon''$) of polymer IVb, at low (-100°C), moderate (50°C) and high temperature (100°C) the dielectric loss is invariable in the range of 1 Hz-10^6 Hz, and increases sharply at very low frequencies (1 Hz-10^{-1} Hz) and high temperature, due to the mobility of charge carriers.

![Graph](https://via.placeholder.com/150)

Fig. 10. Dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) versus frequency for IVb.

The dielectric constants and the dielectric loss of the films made from polymers I and II at 10 Hz, 1 kHz and 1 MHz, at 20°C, as were read from the dielectric constant and the dielectric loss vs. frequency curves, are presented in Table 1. The dielectric constant values at 20°C and in the frequency range of 10 Hz-1 MHz are in the range of 2.70-2.78, which are significantly lower in comparison with that of a conventional polyimide film (Kapton) which is 3.5 [28]. The low dielectric constant values might be due to the presence of flexible tetramethylsiloxane group in the polymer chain which decreased the chain packing and increased the free volume. The values of the dielectric
loss are comparable with that of the Kapton HN film measured in the same conditions (at 10 Hz and 20°C: IVa-0.0040, Kapton film-0.0044). Low values of the dielectric loss are indicative of minimal conversion of electrical energy to heat in the dielectric material. It is advantageous to have low values for both dielectric constant and dielectric loss because electrical signals loss will be lower in the dielectric medium [12].

Table 1
Dielectric constant and dielectric loss of poly(oxadiazole-imide)s at selected frequencies, at 20°C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dielectric constant at 10 Hz</th>
<th>Dielectric constant at 1 kHz</th>
<th>Dielectric constant at 1 MHz</th>
<th>Dielectric loss at 10 Hz</th>
<th>Dielectric loss at 1 kHz</th>
<th>Dielectric loss at 1 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVa</td>
<td>2.74</td>
<td>2.72</td>
<td>2.70</td>
<td>0.0069</td>
<td>0.0038</td>
<td>0.0036</td>
</tr>
<tr>
<td>IVb</td>
<td>2.78</td>
<td>2.77</td>
<td>2.75</td>
<td>0.0068</td>
<td>0.0048</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

4.4. LASER ABLATION BEHAVIOR

For aerospace applications polyimides resistant to laser ablation are much desired. On the other hand, the use of an excimer laser for the ablation of polyimides to produce hole-patterns has attracted considerable attention in recent years because polyimide films are widely used in electronics. These two applications depend by the laser fluence. Therefore, the film of a polynaphthylimide VI has been subjected to UV laser ablation at two fluences. After 30 laser pulses at 57 mJ/cm² (slightly higher than the ablation threshold), the surface topography changed from an original smooth surface, with some irregular protuberances, to a surface characterized by the appearance of cone-like structures with closely packed cones that, at a certain level, lead to the formation of long periodic structures. When the laser fluence was increased to 240 mJ/cm² (Fig. 11), higher cones could be observed. This behaviour can be ascribed to shielding by opaque impurities being present in the polymer. During irradiation, the impurity particles are not ablated, while the surrounding polyimide is removed. Moreover, self-organization of polyimide molecules and clusters under UV laser irradiation at the fluence above the ablation threshold can be considered responsible for the formation of long periodic structures.
From XPS measurements, carbon, nitrogen, oxygen, fluorine, silicon, sodium, calcium and sulphur atoms were detected at the surfaces of polyimide film VI irradiated with laser fluence of 240 mJ/cm². The compositions (± 2.0%) obtained from curve fitting for each core-level spectrum of the original and ablated polyimide film VI are summarized in Table 2.
The compositions (± 2.0%) obtained from curve fitting for each core-level spectrum of the original and ablated polyimide film VI, at laser fluence of 240 mJ/cm²

<table>
<thead>
<tr>
<th>Original polyimide I film</th>
<th>Ablated polyimide I film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Atom %</td>
</tr>
<tr>
<td>C 1s</td>
<td>76.3</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Si 2p</td>
<td>4.7</td>
</tr>
<tr>
<td>N 1s</td>
<td>1.6</td>
</tr>
<tr>
<td>F 1s</td>
<td>0.4</td>
</tr>
<tr>
<td>Na 1s</td>
<td>0.4</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>0.3</td>
</tr>
<tr>
<td>S 2p</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The observed XPS spectra for the surface irradiated at 240 mJ/cm² shows that modified bonding environments are produced at ablated surface. The C spectrum is tentatively curve-fitted to five components as compared with the C spectrum of the original polyimide VI film surface that can be assigned to carbon atom which suggest the formation of carbon-rich surfaces observed after the irradiation, probably resulting from the preferential removal of imide groups in polyimide molecules, followed by chemical bond formation processes such as rearrangement and recombination. Thus, this carbon substrate acts as a barrier for laser radiation protecting the polyimide. When the laser fluence was 58 mJ/cm² similar features have been observed, except the formation of a very low carbon-rich surface. At this fluence even the impurities are ablated, because of the absence of the C layer. Overlay views of the unmodified and ablated regions of the polyimide film shows that the ablation increases the overall levels of carbon and nitrogen, and decreases the amount of oxygen. The contribution of the
reaction similar to combustion followed by leaving incompletely combusted hydrocarbons is suggested. Also, the contributions of redeposition and surface oxidation are suggested.

Contact angle values on unprocessed and processed polyimide films with 30 pulses at 57 and 240 mJ/cm² were measured. It is clearly evident that laser processing induces a remarkable change in the wettability of polyimides. The corresponding contact angle of the pristine polyimide film is 87° (Fig. 12a). After laser processing at 57 mJ/cm², the contact angle increases at about 120° (Fig. 12b) and after processing at 240 mJ/cm², the contact angle is 139° (Fig. 12c), an increase of 52° with respect to the pristine surface. So we can point out that modification of polyimide wettability can be achieved by KrF pulsed laser ablation, this technique being a powerful and promising tool for the preparation of superhydrophobic surfaces in different materials [13, 14]

Fig. 12. Photographs of water droplets on untreated (a) and laser treated polyimide surface: b- treated with 57 mJ/cm²; c- treated with 240 mJ/cm²

5. CONCLUSIONS

New polymers containing 1,3,4-oxadiazole rings, specially designed for use as advanced materials in electronics and optoelectronics, have been synthesized. These polymers displayed high molecular weight values and quite narrow polydispersities, and were easy soluble in polar amidic solvents such N-methylpyrrolidinone and dimethylformamide, and even in less polar solvents such as THF and CHCl₃. Due to their good solubility, the oxadiazole-containing polymers were processed into thin flexible films having good mechanical properties. The very thin films deposited on glass plates by spin-coating with thickness in the range of nanometers are of a very good
quality, without pinholes and cracks, presenting a very neat surface. Polyoxadiazoles exhibited high thermal stability, their decomposition beginning above 400°C, and reasonable glass transition temperature. The main absorption maximum of oxadiazole-containing polymers is centred at 300 nm, and their photoluminescence upon irradiation with UV light occurred in the blue spectral range. Polyimides containing oxadiazole rings displayed γ and β secondary relaxations and low dielectric constant values, lower or comparable with that of the conventional polyimide film (Kapton). The pulsed KrF laser irradiation of the poly(oxadiazole-imide) films produced carbon substrate on the top of the polyimide film surface that acts as a barrier for laser radiation protecting the polyimide material. Such properties make the present polyimides attractive for applications in advanced electronics, opto-electronics, aerospace and other related fields.

**Authors’ contributions:** M.D Dămăceanu and M. Brumă designed the experiments and the methodology; R.D. Rusu conducted experiments; M.D. Dămăceanu and R.D. Rusu analyzed data; M.D. Dămăceanu, R.D. Rusu and M. Brumă wrote the paper.

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