RHEOLOGICAL PROPERTIES OF SOME COMPLEX POLYMERS CONTAINING ALICYCLIC STRUCTURES

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ABSTRACT

Two polyimides obtained from an alicyclic and flexible dianhydride, namely 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride (DOCDA) and an aromatic diamines 4,4'-oxydianiline (ODA) or 4-(4-((4-(4-aminophenoxy) phenyl)sulfonyl)phenoxy (p-BAPS) were synthesized and analysed by rheological methods. The results were correlated with the chemical structure of polyimides and with other properties, such as flexibility, transparency, hydrophobicity and atomic force microscopy. It has been showed that the factors that contribute to the interactions in the polyimide systems can be controlled for improving the thermal, optical, and rheological properties, for subsequent microelectronic applications, in which relatively low permittivity and high thermal stability are required.

INTRODUCTION

Modern polyimide (PI) materials are the subject of great interest all over the world, due to their specific properties. These materials exhibit exceptional thermal and mechanical properties, are easily processable as thin films from soluble precursors, have desirable dielectric properties, high optical transparency, low refractive index, and high glass transition temperature [1,2]. From these reasons, they are some of the most popular of all high performance/high temperature polymers, useful as membranes [3], composite matrices, films, fibers, foams [4], coatings and adhesives in microelectronics [5], photoelectric industry [6]. In addition, polyimides are widely used in the microelectronic industry because of their relatively low relative permittivity values. Since the signal propagation speed and wiring density in multichip packaging are dependent on relative permittivity [7], considerable effort has been extended in the last decade to design and synthesize new polyimides with lower relative permittivity. In this context, two polyimides having a common monomer based on alicyclic and flexible dianhydride-5-(2,5-dioxotetrahydrofurfuryl)-3-

methyl-3-cyclohexene-1,2-dicarboxylic anhydride (DOCDA) and different aromatic diamines, 4,4'-oxydianiline (ODA) and 4-(4-((4-(4-aminophenoxy)phenyl)sulfonyl)phenoxy) (p-BAPS), respectively, were synthesized and investigated by rheological method in N-methyl-2-pyrrolidone, at different concentrations and temperatures. Incorporation of aliphatic and asymmetric DOCDA moieties and aromatic diamines with ether and sulfonic linkages in the molecular structure of polyimides, poly(DOCDA-ODA) and poly(DOCDA-p-BAPS), reduces differently electronic conjugation along the macromolecular chain. Therefore, using a flexible and aliphatic dianhydride as a co-monomer, *e.g.* DOCDA, seems to be reasonable to reduce the polyimide chain–chain interaction and to disrupt the interaction among the aromatic moieties of ODA or p-BAPS diamines. As a consequence, a good knowledge on these properties is important for their handling and formulation, and also for better understanding and controlling the process of polyimide coatings.

NOMENCLATURE

c	[g/dL]	Concentration of polymer solution
E_A	[kJ/mol]	Activation energy
f	[Hz]	Oscillation frequency
G'	[Pa]	Storage modulus
G''	[Pa]	Loss modulus
K	[$Pa \cdot s^n$]	Consistency index
n	[-]	Flow behaviour index
T	[K]	Temperature

Special characters

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δ	[°]	Phase angle
$\dot{\gamma}$	[1/s]	Shear rate
η	[$Pa \cdot s$]	Dynamic viscosity
λ	[nm]	Wavelength
σ	[Pa]	Shear stress

EXPERIMENTAL

Polymer synthesis

High purity chemicals, Epiclon (5-(2,5-dioxotetrahydro-furfuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid anhydride) (DOCDA, Merk, 98% purity), 4,4'-oxydianiline (ODA, Aldrich, 99% purity), and 4-(4-((4-(4-aminophenoxy) phenyl)sulfonyl)phenoxy (p-BAPS, Aldrich 99.9% purity), were used in synthesis process. Pure polyimides were prepared by a conventional two-stage thermal imidization process [8]. In the former stage, two poly(amic acid)s (PAADOCDA-ODA and PAADOCDA-p-BAPS) were prepared by addition of stoichiometric amounts of solid dianhydrides to the stirring solutions of the respective diamines, by keeping a 20 wt% solid content in a N-methyl-pyrrolidone (NMP) solvent [9]. The polymerization reactions were carried out at temperatures around 15-20°C, under completely anhydrous conditions, for different time periods.
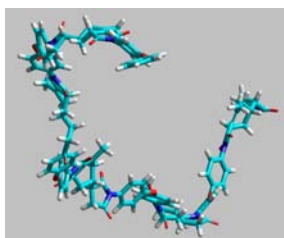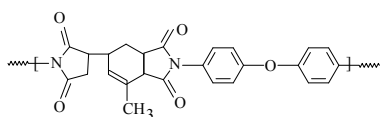
Figure 1 General chemical and conformational structures of poly(DOCDA-ODA)
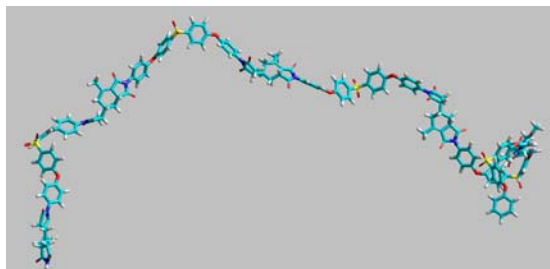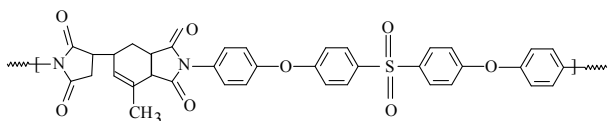
Figure 2 General chemical and conformational structures of poly(DOCDA-p-BAPS)

Figures 1 and 2 present the chemical structures and a generalized view of the chemical conformations of four

repeating units, performed with the HyperChem 8.07 professional program (Demo version, using molecular mechanics MM+ force field approximation method) [10], suggesting the flexibility degree of the studied polyimides. Therefore, an optimized characteristic adjusting rigidity and a lower flexibility could be achieved by blending of these polyimides.

Rheologycal measurements

For rheological measurements, a standard procedure for preparing polyimide solutions in N-methyl-2-pyrrolidone (NMP) from poly(DOCDA-ODA) and poly(DOCDA-p-BAPS) was applied. The concentrations were around 24, 26 and 27 g/dL for all of polymer solutions. The flow properties were determined on a Bohlin CS50 rheometer, manufactured by Malvern Instruments. The measuring system presents a cone-plate geometry with a cone angle of 4° and a diameter of 40 mm. Shear viscosities were registered over the 0.5–1000 1/s shear rate domain, at several temperatures (25–40°C). According to the amplitude sweep test at a frequency of 1 Hz, realized in the linear viscoelastic regime for shear stresses between 0.5 and 20 Pa, a shear stress of 1 Pa was selected for all samples. During oscillatory shear tests, frequency was varied between 0.1–60 Hz.

Films preparation

For obtaining polyimide films, using in transmission spectroscopy and atomic force microscopy analysis, polymer solutions of 10 wt% in N,N-dimethylacetamide (DMAc) were mixed and stirred in capped reagent bottles for 10 h at room temperature, being subsequently degassed and poured on glass substrates. The glass plates were heated first at 70°C for 8 h, after which the films were dried for 4 h in an air oven at 50°C to remove the residual solvent. Thickness of the resulting films was found to be around 40 μm.

Transmission spectra

The optical transparency of films was recorded at 200–1100 nm wavelengths, on a SPECORD 200 Analitik-Jena spectrophotometer.

Atomic force microscopy (AFM) measurements

AFM height imaging was performed in air, at room temperature (23°C), in tapping mode, using a scanning probe microscope Solver PRO-M with commercially available NSG10 rectangular-shaped silicon cantilever (NT-MDT, Zelenograd, Moscow, Russia). The cantilever's normal spring constant of 1.29 N/m was determined by Sader's method from data on the resonance peak (194 kHz) and the planar dimensions of the cantilever (length = 95±5 μm, width = 30±5 μm, thickness = 1.5-2.5 μm). For image acquisition and analysis Nova v.1.26.0.1443 for Solver software was used. The scan area was 1 x 1 μm^2 and 256 x 256 scan point size images were obtained for both samples. To evaluate the topography of the polymer film surfaces, the average height (*Ha*) and the root mean square roughness parameter (*Sq*) were determined. Also must be taken into consideration that the information obtained on surface topography by AFM technique is stored and

processed in digital form as a matrix $Z(N, M)$, where N is the number of points along of scan lines and M is the number of lines [11]. Therefore, these parameters are defined as follows. Average height (Ha) represents the first moment of the height distribution and can be described by the equation:

$$Ha = \frac{1}{MN} \sum_{k=o}^{M-1} \sum_{l=0}^{N-1} z(x_k, y_l)$$ (1)

where z is the height of each point of coordinates x_k și y_l.

Root mean square roughness (Sq), the most used parameter that describes the degree of surface roughness, is defined as the root mean square of the surface departures from the mean plane within the sampling area and can be expressed by the equation:

$$Sq = \sqrt{\frac{1}{MN} \sum_{k=o}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l) - Ha]^2}$$ (2)

RESULTS AND DISSCUSION

Optical properties

The optical transparency of films is shown in Figure 3. It is well known that the origin of coloration in aromatic polyimides is caused by inter- and intra- molecular charge transfer interactions between the five-membered ring of the imide group and the aromatic ring. It is known that a relatively high permittivity and low transparency, also arising from these interactions, is a demerit of the aromatic polyimides. Efforts to suppress the charge transfer interactions have included incorporation of atoms which minimize polarizability, such as aliphatic moieties. Therefore, using a flexible and aliphatic dianhydride as a co-monomer, *e.g.* DOCDA, seems to be reasonable to reduce the polyimide chain–chain interaction and to disrupt the interaction among the aromatic moieties of ODA or p-BAPS diamines, thus increasing transparency. In this context, values obtained for transmittances are generated by the presence of low polarizable groups in these polyimides, which reduce the probability of $\pi \rightarrow \pi^*$ transition of the π-electronic system delocalized along the backbone chain moieties.
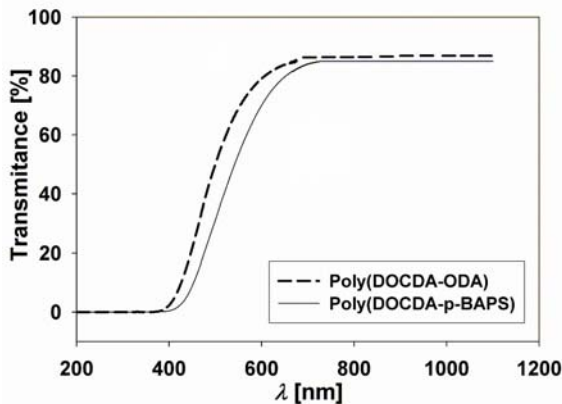

Figure 3 Typical overall transmission spectra of poly(DOCDA-ODA) and poly(DOCDS-p-BAPS)

Thus, it is observed that the transmittance of around 88 % for poly(DOCDA/ODA) polyimide film from the visible towards the UV region is higher as that corresponding to poly(DOCDA-p-BAPS) on 85 %. Consequently, presence of low polarizable groups in these polyimides leads not only to high transparency and implicitly, to low dielectric properties and higher flexibility, but also influences the solution properties.

Dynamic viscosity

The viscosity of polyimides is dependent on their chain packing efficiency, molecular weight, and intermolecular interactions which, in turn, are influenced by the rigidity, symmetry, and of the molecular backbone [12]. Because the molecular weights of the studied polymers have close values, the effect of molecular weight on dynamic viscosity was considered as minimum. On the other hand, the competition between flexible dianhydride and aromatic diamines - characterized by different steric hindrances, can prohibit close packing of chains, influencing the rheological parameters.
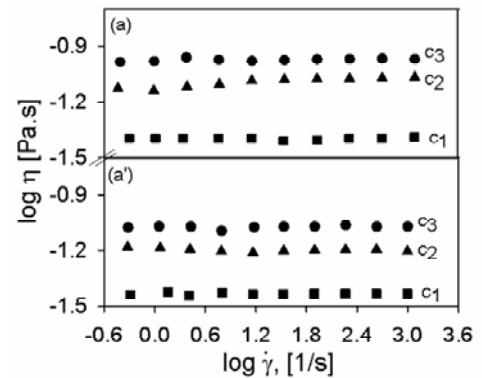
Figure 4 Double logarithmic plot of viscosity vs. shear rate for poly(DOCDA-ODA) (a), and poly(DOCDA/p-BAPS) (a'), in N-methyl-2-pyrrolidone at 25°C and different concentrations: (■) $c_1 = 24.1$ g/dL , (▲) $c_2 = 25.7$ g/dL , (●) $c_3 = 27.1$ g/dL

According to Figure 4, these two polyimides, having a common dianhidride, exhibit a Newtonian behaviour in N-methyl-2-pyrrolidone, with constant viscosity region over the entire shear rates range, at 25°C. Same dependencies, characterized by constant viscosity over the entire shear rates, were obtained for all studied temperatures.

Moreover, this behavior is confirmed also by the values obtained for the flow behavior (n) and consistency indices (K), from dependence of shear stress, σ, on shear rate described by equation:

$$\sigma = K \cdot \dot{\gamma}^n$$ (3)

Thus, the results from Table 1 show that the flow behaviour index for both polyimide solutions is approx. equal to the unity, as expected for a Newtonian fluid.

Table 1 Flow behavior index, consistency index and activation energy for polyimides at different concentrations and 25°C

Sample	c	n	K	E_A
Poly(DOCDA-ODA)	24.01	1.05	0.03	22.48
	25.71	1.04	0.07	24.29
	27.01	1.01	0.09	24.98
Poly(DOCDA-p-BAPS)	24.10	1.04	0.04	23.01
	25.71	0.99	0.07	24.58
	27.01	1.05	0.08	25.72

The interactions among chain segments induce modifications of dynamic viscosity, generated by chemical structures and polyimides affinity for the used solvent. These modifications are reflected in the activation energy, evaluated from Arrhenius expression (equation 4, Figure 5):

$$ln\,\eta = ln\,\eta_0 + \frac{E_a}{RT} \qquad (4)$$

where $\eta_0 \propto e^{-\Delta S/R}$ [13] represent a pre-exponential constant, ΔS is the flow activation entropy, R is the universal gas constant and T is absolute temperature. The activation energy for relaxation in polymer solutions is directly related to the disengagement of the associated chain formation. In this context, the overall activation energy involves two processes:

$$E_a = E_{dis} + E_{ass} \qquad (5)$$

where E_{dis} is the positive contribution from disengagement and E_{ass} is a negative contribution from the associated formations.

In this context, the slopes from Figure 5 have positive values, which led to different values of the activation energy, depending on the type of polyimides, solution concentrations, and solvent. A lower value of E_a implies a lower energy barrier for the movement of an element in the fluid, and corresponds to higher flexibility of polymer chain. In the case of the polymeric solutions here under analysis, this barrier can be related to the interaction among chain segments, where the flexibility of the involved polyimides increases in the order: poly(DOCDA/p-BAPS) < poly(DOCDA-ODA). On the other hand, according to Table 1, the positive values of the activation energy for both polyimides are generated by the positive contribution of disengagement, which becomes preponderant, compared with the negative contribution from the associated formations, E_{ass}.

Moreover, one can mention that the rheological properties are influenced by the low hydrophilic characteristics, where the electron-donor interactions are higher than the electron-acceptor ones for both samples. Thus, contact angles of water on poly(DOCDA-ODA) and poly(DOCDA-p-BAPS) films are 68° and 59°, respectively.

Viscoelastic properties

The effect of the chemical structure of polyimides on the viscoelastic properties is reflected in the mobility of segments from the shear field, quantified by storage and loss moduli are plotted in Figures 6 and 7, as a function of frequency, for both polyimides in N-methyl-2-pyrrolidone, at three concentrations and 25°C.
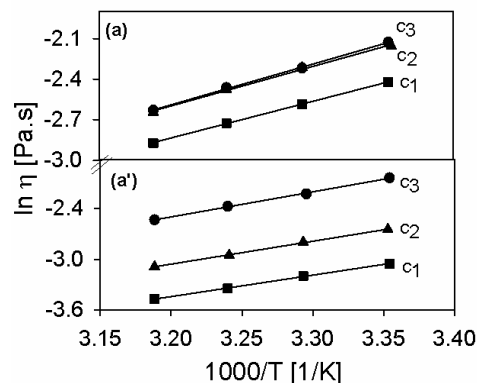

Figure 5 Arrhenius plot for poly(DOCDA-ODA) (a), and poly(DOCDA/p-BAPS) (a'), in N-methyl-2-pyrrolidone at 25°C and different concentrations: (■) $c_1 = 24.1\,g/dL$, (▲) $c_2 = 25.7\,g/dL$, (●) $c_3 = 27.1\,g/dL$
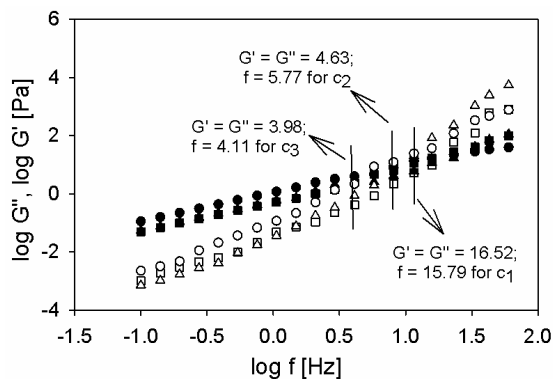
Figure 6 Double logarithmic plot of storage ((■) – for c_1, (▲) – for c_2, (●) – for c_3) and loss moduli ((□) – for c_1, (Δ) – for c_2, (○) – for c_3) as a function of frequency for poly(DOCDA-ODA) at 25°C

Typically, at lower frequencies, the values of G'' exceed those of G' and also the storage modulus, G', and the loss modulus, G'', is proportional to f^2 and f^1, respectively.
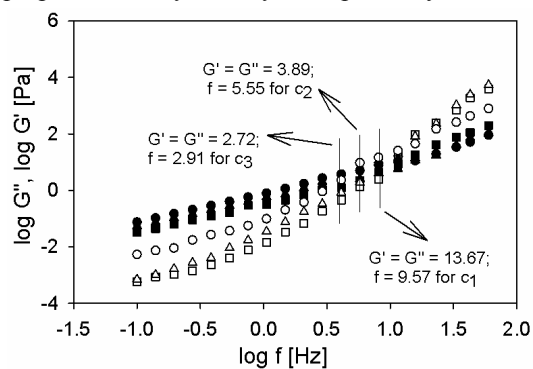

Figure 7 Double logarithmic plot of storage ((■) – for c_1, (▲) – for c_2, (●) – for c_3) and loss moduli ((□) – for c_1, (Δ) – for c_2, (○) – for c_3) as a function of frequency for poly(DOCDA-p-BAPS) at 25°C

Moduli variation with frequency is typical for viscoelastic Maxwellian fluids. At higher values of frequency, G' becomes higher than G'', and the frequency corresponding to their overlapping increases with decreasing concentration.

In addition, these figures show the influence of the chemical structures of polyimides and of the used solvent. The frequencies corresponding to the crossover point, which delimit the viscous flow from the elastic one, and for which $G' = G''$, exhibit lower values for the poly(DOCDA-p-BAPS)); also these frequencies exhibit lower values for higher concentration, for both polyimides. On the other hand, the magnitude of phase angle tangent, $tan\delta$, indicates the relative amount of energy dissipated by the material during cyclic stress in oscillatory testing. This energy, represented by $tan\delta$, showed that the favourable interactions among the chains, responsible for the decrease in free volume, appears for poly(DOCDA-ODA), so that its behaviour becomes more elastic compared to poly(DOCDA-p-BAPS).

Surface morphology of polyimides

In order to investigate the effect of surface morphology of polyimides blends consisting of the partially aliphatic polyimides with different flexibilities, the atomic force microscopy was used. Figures 8 and 9 show bi- and three-dimensional atomic force microscopy images, the profiles and histograms of the surfaces of poly(DOCDA-ODA) and poly(DOCDA-p-BAPS) films.
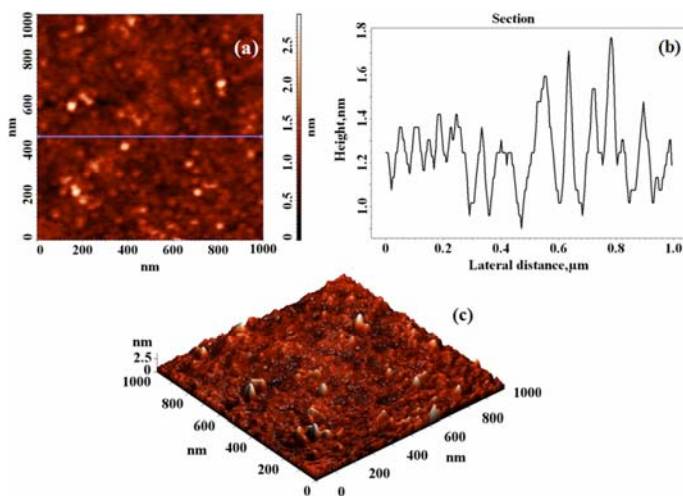
Figure 8 Two-dimensional (a) and three-dimensional (c) height AFM images and cross-section profile taken along the straight line in the 2D image (b), obtained for the poly(DOCDA-ODA) film

The 2D and 3D AFM images of the poly(DOCDA-ODA) film shows a uniform and smooth surface with a root mean square roughness of about 0.3 nm. The height profile analysis (Figure 8 (b)), characterizing the topology of the surface, indicates an average height of 1.2 nm. On the other hand, the poly(DOCDA-p-BAPS) film shows a slightly higher root mean square roughness and average height (Figures 9 (a) and 9 (c)) of 0.4 nm and 1.4 nm, respectively, over the same scan area.
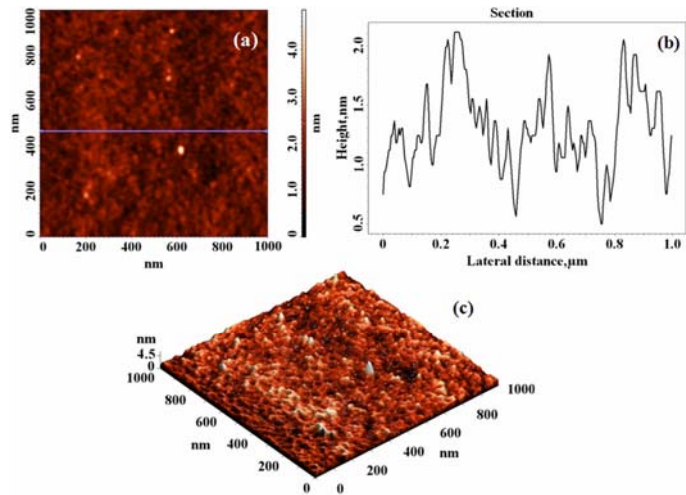
Figure 9 Two-dimensional (a) and three-dimensional (c) height AFM images and cross-section profile taken along the straight line in the 2D image (b), obtained for the poly(DOCDA-p-BAPS) film

Additionally, the surface morphology, derived mainly from the characteristics of the polymer chains that governs aggregation and molecular ordering, occurring during drying and thermal imidization processes [14], revealing the rough granular structures. Grains with mean diameter of 43±4 nm for poly(DOCDA-ODA) and 25±2 nm for poly(DOCDA-p-BAPS), calculated by averaging the diameters of 20 grains for each sample, were obtained. Roughness and size differences between these two samples were generated by introducing different diamine structures in the synthesis of the polyimides.

In addition, a general affirmation was that surface roughness and average heights increase and grain diameters decrease, while hydrophobicity decreases for more rigid polyimides. Moreover, these results are consistent with the rheological properties, reflecting flexibility, transparency, or hydrophobic characteristics of studied partial aliphatic polyimides.

CONCLUSIONS

Partially aliphatic polyimides with different flexibilities, poly(DOCDA-ODA) and poly(DOCDA-p-BAPS), were studied by some methods. These investigations indicate:

- higher transparency by the utilization of a flexible and aliphatic dianhydride, DOCDA, which reduce more the chain–chain interaction and disrupt the charge transfer interaction among aromatic diamine 4,4'-oxydianiline (ODA) moieties than among aromatic diamine 4-(4-((4-(4-aminophenoxy) phenyl)sulfonyl) phenoxy) (p-BAPS);
- a Newtonian behaviour of dynamic viscosity *versus* shear rate dependencies;
- increasing of the rigid component amount of poly(DOCDA-p-BAPS) induces stronger polymer entanglements and interactions among the chain segments, as revealed by the higher flow activation energy values, compared with poly(DOCDA-ODA);

- shear moduli dependence on frequency follows a power law, where exponents are characteristic of viscoelastic fluids;
- the frequencies corresponding to the crossover point, which delimit the viscous flow from the elastic one, and for which $G' = G''$, exhibit lower values for the poly(DOCDA-p-BAPS)) with lower flexibility; also these frequencies exhibit lower values for higher concentration, for both polyimides.

On the other hand, the AFM images showed that surface morphology is characterized by roughness and rough granular formations, depending on the composition of polyimides and in relation with their flexibility and surface properties. Thus, surface roughness and average heights increase and grain diameters decrease, while hydrophobicity decreases for more rigid polyimides. In conclusion, these results are in agreement with the rheological properties, reflecting flexibility, transparency, or hydrophobic characteristics of studied partial aliphatic polyimides.

In conclusions, depending on the molecular chains characteristics of individual polyimides, the factors that contribute to the interactions in the polyimide system can be optimized for improving the thermal, optical, dielectric and rheological properties, for subsequent microelectronic applications, in which relatively low permittivity and high thermal stability are required. References

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