Influence of thermal treatment time on structural and physical properties of polyimide films at beginning of carbonization

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Abstract

Poly(4,4'-oxydiphenylene-oxydiphthalimide) (POO) was thermally treated at 773 K for 1, 15 and 60 minutes under argon atmosphere resulting in free-standing films with intermingled characteristics between polymer and carbon-rich derivatives. Degradative thermal analysis performed by pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) revealed CO₂ among the major products of thermal decomposition which according to electron paramagnetic resonance (EPR) passed through a radical process. X-ray diffraction (XRD) revealed thermal treated samples with semicrystalline organization that was attributed to the development of lamellae structure. Moreover, Atomic force microscopy (AFM) showed an increase in the roughness of the samples that acquired pronounced roughcast-like surface. Hence, there was an enhancement of

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mechanical strength and dielectric permittivity. From the data collected a mechanism of thermal decomposition was proposed.

Keywords: polyimide; carbon-rich derivatives; thermal degradation; structural rearrangement.

1. INTRODUCTION

A good understanding of the carbonization mechanism of polyimides (PI) is critical for the development of improved carbon materials for gas separation, and electrically conducting surfaces for microelectronics devices [1–3]. According to Lua and Su [4], the release of heteroatoms, most in form of CO and CO₂ from cleavage of the imide ring, and removing of aliphatic groups present in the PI chains up to 1023 K promote molecular rearrangements yielding chars. Such carbon-rich derivatives lead to graphite-like structures depending on the temperature and nature of the starting materials [4]. The structural rearrangement may also lead to formation of lamellae [5]. Important contributions concerning the carbonization of PI were made by Bourgerette and Oberlin [6] and Sazanov et al. [7]. Their studies revealed that carbonaceous materials are initially formed below 1273 K and basically composed of aromatic building blocks fused into planar 10-20 planar rings arranged in different configurations named basic structural units (BSU). Beyond 1273 K, after successive orientations and arrangements the BSU coalesce generating graphitic structures.

Aromatic PI [8–10] over the years have been used as suitable carbon precursors [11]. Shao et al. [12] observed pores after thermal treatment of 6FDA-based PI from degradation of the polymer chain and molecular rearrangements. That enhanced the

selectivity for H₂, He and CO₂ of the samples treated at 773 K with heating rate of 1 K min⁻¹. Partially carbonized PI films are also interesting for aerospace applications. The insulating nature of PI causes electrostatic accumulation and the carbonization process lead to thermally conductive surfaces avoiding local overheating and premature degradation. Heo and Chang [13] and Luong [14] et al. showed that is possible to enhance significantly the mechanical strength and the thermal and electrical conductivity of PI by the mere incorporation of up to 3 wt% of graphene sheets. However, the efficiency of any composite relies on the suitable dispersion of the additive into the matrix, hence, the PI-carbon compatibility could be improved if the graphene or graphene-like structures were generated *in situ*, providing a mixture at molecular level, as occurs in hybrid materials [15]. Thus, to get more insight regarding the carbonization process taking place at beginning of thermal decomposition, in this work we investigated the influence of thermal treatment time on poly(4,4'-oxydiphenylene-oxydiphthalimide), (POO) films treated at the very 773 K under argon atmosphere. The gases evolved during treatment and the changes on the molecular structure of POO and consequent changes on its physical properties were evaluated by thermoanalytical, spectroscopic and microscopy techniques.

2. MATERIALS AND METHODS

2.1 Materials

POO was synthesized from 4,4'-Oxydiphthalic anhydride (ODPA, Sigma-Aldrich, 97%) and 4,4'-oxydianiline (ODA, Sigma-Aldrich, 98 %), using N,N-Dimethylacetamide (DMAc, VETEC, 98 %) as solvent. DMAc was treated overnight with molecular sieves with 3Å pores, and under nitrogen (N₂, White Martins 99.99 %)

to provide inert atmosphere. Argon (Ar, White Martins, 99.99 %) was used in the thermal treatment.

2.2 Synthesis and carbonization procedure

In a flask, 1.5 mmol of ODA were dissolved with 8 mL of DMAc under stirring followed by addition of 1.5 mmol of ODPA. The system was sealed, put under N₂ atmosphere and allowed to react for 130 min. Then additional 2 mL of DMAc were added and the reaction proceeded for another 20 min, when the stirring was turned off. The reaction produced poly(amic acid), here named OO, which is the PI precursor. The viscous yellow solution was dropped onto clean Teflon® molds, each one filled with 3 mL of solution and taken to a pre-heated oven at 333 K/15 h in air to evaporate most of the solvent. The OO films obtained were then thermally converted into PI, hereafter named POO, in tubular furnace under argon atmosphere according to the following routine: T_{ambient} → 373 K/60 min → 473 K/60 min → 573 K/60 min, 3 K min⁻¹ rate flow.

POO films were cut in pieces, supported on alumina plates and thermally treated in different times from room temperature to 773 K in tubular furnace under argon atmosphere. The heating rate applied was of 3 K min⁻¹. The pre-determined time used and the respective code of the thermally treated POO samples are shown in Table 1.

Table 1. Thermal treatment time and respective code of thermally treated POO samples.

Time (min)	Code
1	PI-1
15	PI-15
60	PI-60

2.3 Characterization

2.3.1 *Fourier transform middle infrared in attenuated total reflectance mode (ATR-FTMIR)* was carried out in a SHIMADZU spectrophotometer model IRAffinity-1, in the range of 4000 to 650 cm^{-1} with spectral resolution of 4 cm^{-1} .

2.3.2 *Thermal analysis (TGA)* was carried out in a SHIMADZU instrument, model TG-50A in the range of 298 to 1253 K, heating rate of 10 K min^{-1} , under argon atmosphere, using a platinum pan with ca. 8 mg of sample mass.

2.3.3 *Pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS)* using a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 gas chromatograph (GC) with an Agilent 5973N quadrupole mass spectrometer (MS) for detection of analytes. The samples (ca. 0.5 mg) were measured into quartz sample tubes loaded into the Pt filament coil of the pyro-probe apparatus for pyrolysis. For the determination of the products of degradation, the sample was held at an initial temperature of 333 K for 0.5 min, and then pyrolyzed at a ballistic heating rate from 333 to 1273 K under a purge flow of helium (He) gas for a total pyrolysis time of 2.0 min. The degradation products were continually transferred from the pyro-probe apparatus to the GC inlet using an inert transfer line (both at 573 K) with a 10:1 split flow for the total pyrolysis runtime. An Agilent DB-1 (30 m x 0.25 mm i.d., 0.25 μm) analytical column under constant flow of 2.0 ml min^{-1} with He used as carrier gas. The initial GC oven temperature was set at 313 K for 2.0 min and then ramped at 10 K min^{-1} to 573 K and held for 10 min at the final temperature for a total analysis time of 38.0 min. The MS ion source and quadrupole temperatures were 503 K and 423 K, respectively. Total ion chromatograms (TIC) of the pyrolysis products were collected for each run, disposed in TIC plots, normalized to sample mass, baselined and individual identified product peaks were integrated to yield a relative assessment of the abundance of degradation products.

2.3.4 *X-ray diffraction (XRD)* experiments were performed on a Rigaku diffractometer, model Rotaflex RU-200, with K_{α} radiation from copper ($\text{Cu } K_{\alpha}$ 1.54 Å) in the range of 3° to 60° and acquisition rate $0.03^{\circ} \text{ min}^{-1}$, operating in grazing mode. Wide-angle x-ray scattering (WAXS) was performed in the National Laboratory of Synchrotron Light (LNLS) at Campinas, SP, Brazil, in a machine bench of rotating anode operating at 0° with the normal, with $\text{Cu } K_{\alpha}$ 1.54 Å, detector of Si(Li) at 150 mm from the samples and collection time of 120 s. The obtained images were processed using the calibration algorithm of FIT2D software.

2.3.5 *Scanning electron microscopy (SEM)* was performed in a JEOL microscope model JSM-6390 LV operating with electron beam of 10 kV. The samples were previously gold and palladium coated by sputtering using a BAL-TEC metallizer model 020 instrument (Balzers).

2.3.6 *Atomic force microscopy (AFM)* was acquired in a Bruker microscope, model Dimension Icon® in intermittent contact mode, in air, using a silicon probe, spring constant about 40N/m, oscillating frequency 320 kHz, and scan speed 1Hz. Roughness parameters [16–18] were used to analyze the surface of the films.

2.3.7 *Nanoindentation (NI)* was carried out in a MTS Instruments equipment, model Nanoindenter®XP. In the analysis, 10 loads of 0.05 N were applied using a diamond Berkovich tip from Micro Star of order of 50-100 nm in three-faced pyramid shape.

2.3.8 *Electrical permittivity measurements* were performed with a Solartron SI impedance analyzer, model 1260, coupled to a furnace. The samples were coated with gold electrodes, by sputtering, and analyzed in the range of frequency from 0.1 Hz to 1 MHz, with alternating voltage of 1 V, in temperature range of 298-423 K. The whole process was controlled by a computer using Smart software for data collection. To

avoid water interference in the results, previously to the experiments the samples were heated up until 423 K and cooled down until the room temperature around 298 K.

3. RESULTS AND DISCUSSIONS

3.1 PI conversion and thermal stability

The conversion of OO into POO was evaluated by ATR-FTMIR and the spectra are presented in Figure 1a. The bands assigned to the amide group at 1652 cm^{-1} (axial deformation of C–O bond), and in the range of $1560\text{--}1520\text{ cm}^{-1}$ assigned as angular deformation of C–N–H bonds were no longer observed after imidization. Instead, the characteristic absorption bands from the imide group emerged at 1778 and 1711 cm^{-1} assigned to the asymmetric and symmetric axial deformation of C–O bond from carbonyl groups, and at 1364 cm^{-1} assigned to the axial deformation of C–N bond from imide ring. Characteristic bands from aromatic rings in the range of $1520\text{--}1420\text{ cm}^{-1}$ and at 1596 cm^{-1} corresponding to the breathing mode vibration and the axial deformation of C=C bond, respectively, were also observed both in OO and POO. All of these assignments are consistent with previous detailed work [19]. Once the POO formation was confirmed, the thermal stability of the polymer was evaluated, Figure 1b. No significant mass lost was detected below 803 K, only 5 wt%. The largest weight loss in the analyzed range was detected at 830 K and at 1253 K significant residual mass still remained (ca. 50%).

Figure 1 – a) ATR-FTMIR spectra of OO and POO films and b) TGA (solid line) and derivative (dashed line) curves obtained for POO under argon atmosphere.

3.2 Carbonization process

After thermal treatment, most of the PI still remained, preserving the polymer properties such as flexibility, as already pointed out by Barsema et al. [20]. Detailed information regarding the thermal behavior of POO series was obtained by Py-GC/MS. Table 2 shows the relative abundances of the degradation products identified from POO to PI-60 samples. Note that there are significant changes in the relative distributions of all degradation products and the product yield and release of chemical compounds decrease from POO to PI-60 as a function of thermal treatment time. While the individual trends are quite complex to evaluate, due to multiple sources of products driven by the thermal energy provided, there is clearly a global trend described following.

Table 2 – Relative abundances for all significant identified degradation products in the thermally treated POO series.

Identification	Integrated peak area (10^4 counts s ⁻¹)			
	POO	PI-1	PI-15	PI-60
CO ₂ , H ₂ O, N ₂	33.78	19.97	37.29	2.77
Benzene	30.75	9.51	7.65	0
Aniline	13.46	14.74	12.86	0

Phenol	20.67	27.49	18.04	4.67
3-hydroxy benzonitrile	0	9.78	3.55	6.22
4-hydroxy benzonitrile	10.39	7.16	0	3.21
Naphthol[2,1-6]furan	12.35	16.12	18.81	0
4-phenoxy benzonitrile	10.23	5.50	7.97	0
Hydroxy/carboxyphenyl species	5.26	2.15	0.67	0.99

It can be observed that POO series share common degradation chemistry, such as depolymerization, pyrolytic reformation and progressive loss of organic functionality through radical scission (see EPR data in supplementary material). Thus, based on the experimental data and mainly on the mechanism proposed by Sazanov et al. [7] and Hatori et al. [21], a general mechanism of thermal decomposition under argon atmosphere at 773 K was proposed and is summarized in Figure 2. Basically, the thermal decomposition of POO undergoes successive homolytical and hydrolytic cleavages (due to absorbed water or hydroxyl ions), followed by hydrogen ablation, intermolecular coupling and molecular rearrangements. In Figure 3 is the pathway in which the BSU are likely to form. Both pathways lead mainly to CO₂ evolution.

Figure 3 – Scheme of BSU formation.

3.3 Crystallinity

The structural characteristics of the POO samples were evaluated by XRD, and their respective diffractograms are presented in Figure 4. Three broad peaks were

identified centered at $2\theta = 11.8^\circ$, 20.5° (22° for thermally treated films), and at 43.8° . Such a pattern found for POO-series revealed an ordered intermolecular packing typical of semi-crystalline polyimides indicating that the thermal treatment led to formation of lamellae structure [5,22]. The peaks are better evidenced by the experiments at grazing angle and became more prominent after longer time of thermal treatment (from POO to PI-60). Bragg's equation [23] was used to determine values of correlation length. Based on studies of Ojeda and Martin [22], the peak at 11.8° ($d = 7.5 \text{ \AA}$) can be assigned to the distance between adjacent lamellae. The peak at 20.5° ($d = 4.3 \text{ \AA}$) reflects the average distance between layers of a same lamellae, and its shift to 22° ($d = 4.1 \text{ \AA}$) indicated a narrowing in that distance after thermal treatment of POO. Finally, the peak centered at 43.8° ($d = 2.1 \text{ \AA}$) was assigned to the distance between polymeric chains in the lamellae. WAXS data also show peaks in the same region XRD and provide a better view of the peak around 45° . Additionally, XRD diffractograms in grazing configurations and WAXS in transmission configuration suggest that most of the lamellae structures are present at the surface since higher organization was found in this region. This also suggests a heterogeneous crystallization from the surface [24].

Figure 4 – a) XRD diffractograms obtained for POO-series samples; b) WAXS patterns obtained for POO and PI-15.

A representation of the molecular arrangements displayed by the polymeric chains in the POO series is shown in Figure 5. The possible formation of the BSU represented in Figure 3 was assumed to start in the ordered regions.

Figure 5 – Representation of the molecular arrangements of POO chains in the material.

3.4 Morphology

AFM images revealed that from POO (Figure 6a) to PI-60 (Figure 6d), the films acquired a roughcast-like appearance that became more pronounced as the time of thermal treatment increased. This is due to weight loss from gas evolution during thermal decomposition, causing the material to shrink and become wrinkled. From the evaluation of the roughness parameters, both the arithmetic average (R_a) and root mean square (R_q) average of height showed significant deviations from the mean line/plane between POO and its thermal treated samples, resulting in a decrease in the peak-to-

valley height difference. Additionally, theory of statistics shows a ratio $R_q/R_a \approx 1.25$ implying in a Gaussian distribution of the heights from the mean line [25]. Additionally, the positive Skewness ($R_{sk} > 0$) and the higher than 3 Kurtosis ($R_{ku} > 3$) showed that the surface of the scanned areas were predominantly constituted by sharp peaks spread throughout the surface. The data are presented in Table 3.

Figure 6 – AFM images obtained for a) POO, b) PI-1, c) PI-15 and d) PI-60.

Table 3 – Roughness parameters obtained for POO series.

Samples	R_a	R_q	R_q/R_a	R_{Sk}	R_{Ku}
POO	0.433	0.548	1.27	0.214	3.44
PI-1	0.172	0.218	1.27	0.00930	2.99
PI-15	0.189	0.238	1.26	-0.101	3.09
PI-60	0.218	0.277	1.27	0.242	3.60

Further morphological information was obtained by SEM analysis, Figure 7. Despite the gas evolution, no significant differences were detected on the cross-section surface of the materials, so that even after 60 minutes of thermal treatment no pores were observed. Thus, the samples remained fairly dense, suggesting that any eventual change occurred on a much smaller scale.

Figure 7 – Cross-section SEM images of a) POO, b) PI-1, c) PI-15, d) PI-60.

3.5 Nanoindentation

The influence of the thermal treatment on the mechanical properties of the POO series was evaluated by measuring the hardness (Figure 8 Left) and Young's modulus (Figure 8 Right) via nanoindentation measurements. Both hardness and Young's modulus displayed similar behavior, the deeper the penetration, the lower the values obtained suggesting a stiffer surface and softer interior. Such behavior was in agreement with the XRD data that revealed ordered, thus stiffer, molecular arrangements on the surface from the development of lamellae structure and carbon-rich products such as graphene precursors. At 4500 nm penetration, the difference in hardness between POO and PI-60 was about 70 MPa, which corresponds to 50% enhancement comparable to polymer-graphene nanocomposites [13,14,26].

Figure 8 – Hardness (Left) and Young's modulus (Right) versus the indentation depth measured for POO and its thermally treated films.

3.6 Electrical characterization

Electrical measurements as a function of frequency and temperature also revealed significant increase of permittivity of the materials with the time of thermal treatment, Figure 9; which make the POO-series as potential materials for the production of dielectric components. The enhancement was attributed to the formation of free radicals and polar groups trapped in the samples after the treatment. Moreover, the possible formation of BSU works as significant unsaturated regions enabling overlapping of π -orbitals increasing locally the electronic density, but not to the point of cause electronic conduction [21,27,28]. Additionally, in contrast with POO, PI-15 and PI-60 displayed a decrease in permittivity with temperature up to 333 K, from which became constant. According to Li et al [28], this behavior results from relaxation processes that occurs in the PI's structure as well as rearrangement of the carbon-rich derivatives.

Figure 9 – Relative dielectric permittivity obtained in function of frequency and temperature for POO and its partially carbonized products.

4. CONCLUSIONS

POO was successfully synthesized by polycondensation reactions and thermal imidization, as confirmed by FTIR. TGA under Ar atmosphere revealed higher thermal stability with residual mass yield about 50 wt% at 1253 K. Complementary, Py/MS-GC showed CO₂ among the major product of thermal decomposition. The data helped to set a model to describe the thermal decomposition process of POO, which included the possible formation of BSU. The evaluation of the physical properties showed that even at the onset temperature of thermal decomposition (773 K) was enough to increase not only the hardness of the material up to 50%, but also the dielectric permittivity (60%). Such enhancements were correlated with structural changes that took place in the material. This study presents the viability to produce PI-carbon rich materials with improved compatibility between the organic (PI) and inorganic (carbon) parts, mixed at molecular level, with properties that can be tuned by the time of thermal treatment. Moreover, the PI treated at 773 K afford suitable materials, for instance, to the

development of flexible and mechanically strength membranes for purification of gases (e.g. hydrogen), as well as dielectric films and coatings for electronic devices.

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